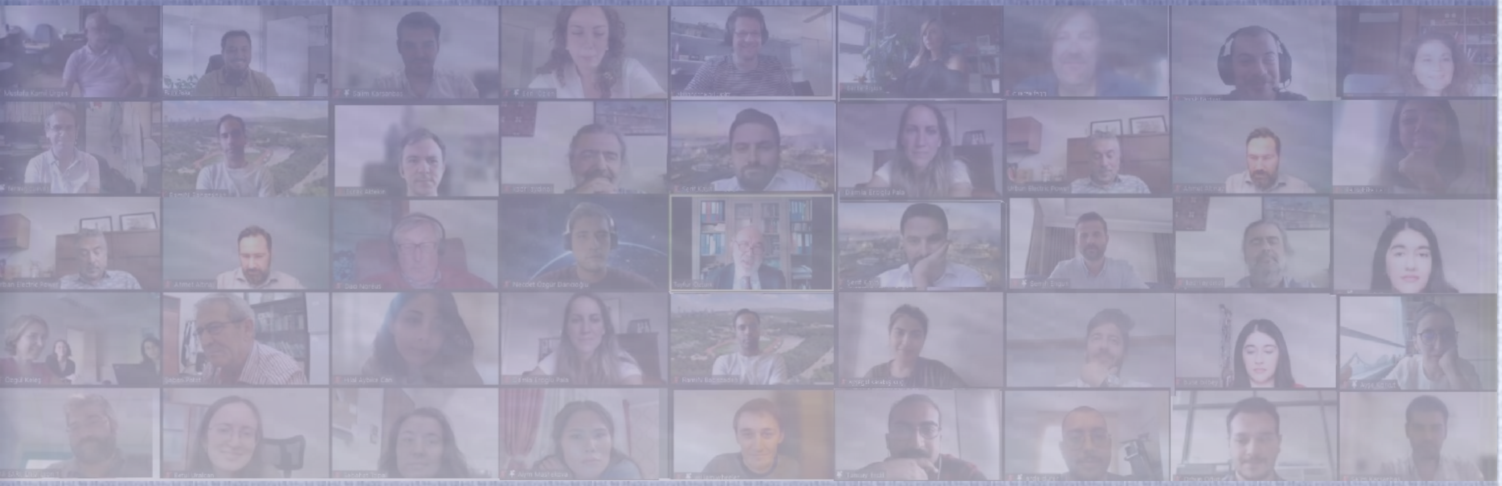
5th International Symposium on Materials for Energy Storage and Conversion

14-17 September 2021, Virtual Meeting

Book of Abstracts/Proceedings



book of abstracts/proceedings
ISBN 978-625-00-0478-4

mesc-is.org

mESC-IS 2021

The Fifth International Symposium on Materials for Energy Storage and Conversion

Edited by
Ezgi Onur Şahin and Fatih Pişkin

14-17 September 2021, Virtual Meeting

ISBN 978-625-00-0478-4

Welcome Address and Preface

I welcome you all to the 5th International Symposium on Materials for Energy Storage and Conversion. I remember the welcome address I have given in 2019 in Akyaka, I also remember few words I said in Belgrade in mESC-IS 2018. I was confident about what I said then.

Today the picture is quite different.

My feeling is like that of someone who has worked very hard, made preparation for all, just to realize that missed the big event.

We are confident as to what we can do as mankind. We altered the surface of the world, we have opened agricultural fields in the land, built dams on rivers. The picture of the world from space, cities shinning with brightness perhaps summarizes what I am trying to say.

It is true that whatever we have achieved, we achieved in the last 10,000 years., i.e. in a period of global warming. Whatever we have achieved is confined to a thin layer of the earth's crust and no more. We talk about colonising Moon and Mars. But at the same time we feel helpless against wildfires and floods losing hundreds of lives and millions of trees.

We never looked at the problem of controlling the thin layer of atmosphere that wrapped us all around. We have to find a way of draining rains from clouds before they are overloaded with too much humidity causing floods. Similarly we have to find a way of enriching atmosphere with humidity before it becomes too dry to cause wildfires.

So far we looked at our energy needs as a way of maintaining our lives on earth. But I guess we have to change this and relook at the energy needs as a way of "colonizing" the world. This means lots of green energy and seasonal storage.

Returning to mESC-IS, the agenda is quite clear. We have made considerable progress with regard to mobility. Electric vehicles are going to replace the existing fleet based on internal combustion engines. I am happy to say that many of the papers in this symposium, including the first session this morning, have this at their background.

Also we will have a fast progress with renewable energy. There is a challenge there whether to store the renewable energy in batteries or generate hydrogen via electrolysers feeding it to a gas network or perhaps storing it underground. If the former is to be the case, there ought to be a drastic reduction in the cost of batteries. Again I am happy to say that this is an area also addressed in this symposium.

It is true that storing gas is easier than storing electrons. It appears that initially renewable energy-hydrogen route, i.e. the so called renewable hydrogen will dominate. As a result, we shall see the integration of electricity grid with a gas grid opening up a vast area for reversible cells, i.e. cells acting as electrolysers to produce hydrogen and when needed acting as fuel cell generating electricity.

Finally, I guess we reach a stage where hydrogen would be as accessible as the electricity is today. There will, then, be a real challenge, as to whether it will be the batteries – electric car which seems to be prevailing path now will continue their dominance thereafter or it will be hydrogen-fuel cell which will work their way in, perhaps become equally or even more attractive. Till we reach this point we will live through an incubation period where each line of activity serving its own purpose, complimenting one another in certain ways.

We are holding this symposium online due to COVİD-19 Pandemic which has been affecting us all in the last one and half year or so . Still I am quite happy with the spectrum of papers to be presented in this symposium. We seem to be addressing all important issues. I am also quite happy about the partcipants, i.e. new comers, both in summer school and symposium whom make us feel confident about the future. I am sure that the sessions we will have throughout this 4-day period will be both fruitful and enjoyable, continuing the tradition of previous mESC-IS symposia.

In organizing this event, we, as members of International Steering Committee and Local Organising Committee are grateful to the support we have had from a number of institutions and the sponsors. We would like acknowledge our respective Universities/Institutions. I would like to thank Middle East Technical University, in particular my colleague, Yunus Eren Kalay, for his help in various aspect of this organization. I would like also to thank Fermin Cuevas for his contributions in structuring this symposium. The summer school which preceeded the symposium was supported via TUBITAK BİDEB 2237-A program which we gratefully acknowledge. Similarly the symposium was supported TUBITAK BİDEB 2223-B program.

As before we will continue the tradition of holding this symposium in Akyaka in odd years and we will move to one of the participating countries, in even years. Accordingly mESC-IS 2022 will take place in Bol, Island of Brac in Croatia . In 2023 we will be back to Akyaka for a regular symposium.

Tayfur Öztürk
Symposium Chair
14/09/2021

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mESC-IS 2021
5th Int. Symp on Materials for Energy Storage and Conversion

	September 14th Tuesday 2021
08:30 17:30	Registration
08:30 09:00	Opening Addresses
	Chair: Dag Noréus
09:00 09:30	Prospects for lithium-ion batteries and beyond Mihri Ozkan
09:30 10:00	Material aspects of alternative energy stores: sodium-ion and solid-state batteries Philipp Adelhelm
10:00 10:30	Ultra fast charging high energy lithium-ion batteries utilizing borophene/h-BN aerogel layers Onur Ergen
	Coffee Break

	Chair: Marie Guignard	**Chair: Duncan Paul Fagg**
	Li-ion Battery (Cathode)	**Advances in Fuel Cells**
11:00 11:20	Study of the structural and lithium storage properties of the rock-salt structured (MgCoNiMnLiX)O (X=Cr, Fe, Al) high entropy oxides Ersu Lökçü, Meltem Çayırlı and Mustafa Anık	Synthesis of Thermally Reduced Graphene Oxide Welded Graphene Aerogel Support Material for PEM fuel cells Meryem Samancı and Ayşe Bayrakçeken Yurtcan
11:20 11:40	Supercritical CO2-Approach to Prepare Lithium-rich Layered Metal Oxide Material for Li-ion Batteries Ali Yalçin, Müslüm Demir, Solmaz Khankeshizadeh, Mehmet N. Ates, Mehmet Gönen and Mesut Akgün	Enhancing the electrochemical performance of misfit calcium cobaltite electrodes for reversible solid oxide cells Francisco Loureiro, Allan Araújo, Laura Holz, Vanessa Graça, João Grilo, Daniel Macedo, Carlos Paskocimas and Duncan Fagg
11:40 12:00	Sodium and Niobium Co-doped Lithium Titanate as a High Rate Anode for Lithium Ion Batteries Şaban Patat, Sunardi Rahman and Ahmet Ülgen	Optimization of the flow-field for solid oxide fuel cell thin sheet interconnectors Bora Timurkutluk and Emre Ucar
12:00 12:20	Electrochemical properties of Ni-rich NMC cathodes for Li-ion batteries Ahmed M. Faris, Tuğrul Çetinkaya, Mahmud Tokur and Hatem Akbulut	Combinatorial Development of LSC Based Cathode Material for IT-SOFC Ramin Babazadeh Dizaj and Tayfur Öztürk
	Lunch Break	
	September 14th Tuesday 2021 (Afternoon)	
	Chair: Branimir Banov	**Chair: Ümit B Demirci**
	Li-ion Batteries (Anode)	**Electrolysers and Renewable Hydrogen**
13:30 13:50	Spinel-structured type high entropy oxides as anodes for lithium-ion batteries Deniz Okan Bayraktar, Ersu Lökçü and Cigdem Toparli	Enhanced CO_2 stability of nickel doped $BaCe_{0.9}Y_{0.1}O_{3-d}$ (BCY10) Vanessa Graça, Francisco Loureiro, Laura Holz, Sergey Mikhalev and Duncan Fagg
13:50 14:10	Investigation of Electrochemical Processes of Metallic Li Batteries using Temperature Dependent Electrochemical Impedance Spectroscopy Mohammed Ahmed Zabara and Burak Ulgut	Effect of Dual Perovskites on Hydrogen Production by Thermochemical Water Splitting Seyfettin Berk Şanlı, İhsan Emre Yiğiter, Gülhan Çakmak, Fatih Pişkin and Berke Piskin

14:10 14:30	Anodes for Li-ion batteries based on silicon monoxide carbonized with fluorocarbon Darina Lozhkina, Ekaterina Astrova, Alexander Rumyantsev and Alesya Parfeneva	Combinatorial Development of LSF Based Cathode Material for IT-SOFC Fahrettin Kılıç, Havva Eda Aysal and Tayfur Öztürk
14:30 14:50	Nano Silicon Powder Reinforced Carbon Anodes for High Capacity Lithium Ion Battery Salman Ahmad, Tugrul Cetinkaya, Mahmud Tokur and Hatem Akbulut	Sr doped $LaMn_{0.6}Al_{0.4}O_{3-\delta}$ for H_2 production based two-step thermochemical water splitting İhsan Emre Yiğiter, Seyfettin Berk Şanlı, Gülhan Çakmak, Berke Piskin and Fatih Pişkin
	Coffee Break	
	Chair: Hatem Akbulut	
15:30 16:00	Nano Designs for Lithium Battery Anodes Mahmud Tokur and Hatem Akbulut	
16:00 16:20	New lithium-rich layered oxides as positive electrode materials for lithium-ion batteries Marie Guignard	
16:20 16:40	High Performance Electrospun Anatase/Poly(3,4-Ethylenedioxythiophene) Polystyrene Sulfonate-based Anodes for Li-ion Battery Begüm Yarar Kaplan, Vahid Charkhesht, Alp Yürüm and Selmiye Alkan Gürsel	
16:40 17:00	Inspection on Capacity Fade Challenge for $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Tayfun Kocak, Zhang Xiaogang, Muharrem Kunduraci and Servet Turan	
17:00 17:20	Electrochemical performance of highly concentrated LiFSI-EC electrolytes in Silicon/Graphite - NMC111 Li-ion batteries Burak Aktekin, Guiomar Hernández, Reza Younesi, Daniel Brandell and Kristina Edström	

	September 15th Wednesday 2021 (Morning)	
	Chair: Philipp Adelhelm	
09:00 09:30	Advanced aqueous alkaline batteries based on hydrogen Dag Noréus	
09:30 10:00	Multivalent-ions Rechargeable Batteries in Aqueous Medium Rezan Demir Çakan	
10:00 10:30	A Novel Air-Stable O_3-Type Layered Oxide Cathode Material with Low Ni Content for Sodium-Ion Batteries Şaban Patat, Ayşe Şahin, Yusuf Taş, Ferhat Şanlı, Yakup Yılmaz and Tayfur Öztürk	
	Coffee Break	
	Chair: Servet Turan	**Chair: Akif Aliyev**
	Li-ion Batteries (Solid Electrolyte)	**Electrolysers and Renewable Hydrogen**
11:00 11:20	Study of the Solid Electrolyte Thin Films with Li Loss Compensation Aiym Mashekova, Mukagali Yegamkulov, Aliya Mukanova and Ivan Trussov	A two-step thermochemical water splitting by doped perovskite structures Seyfettin Berk Sanli, İhsan Emre Yigiter, Berke Piskin, Fatih Piskin and Gülhan Cakmak
11:20 11:40	A Long Cycle Life and High Ionic Conductivity, Hybrid LATP/PEO Solid Electrolyte for Lithium-Ion Batteries Samet Usta, Mustafa Çelik, Tuğrul Çetinkaya and Hatem Akbulut	Electrochemical promotion of N_2O reduction on LSCF catalyst Laura Holz, Francisco Loureiro, Allan Araújo, Vanessa Graça, Diogo Mendes, Adélio Mendes and Duncan Fagg

11:40 12:00	Crystallization of $Li_7P_3S_{11}$ Solid Electrolytes for Solid Lithium Sulfur Batteries Seda Eğri and Mahmud Tokur	Improved hydrogen production by the substitution of $LaMnO_3$ based perovskite oxides for thermochemical water splitting Cagla Unal and Berke Piskin
12:00 12:20	The Effect of Sulfur Load on Graphene-Sulfur Cathodes Synthesized by Sulfur-Amine Chemistry for All-Solid-State Batteries Çağrı Gökhan Türk and Mahmud Tokur	Electrochemical performance of calcium cobaltite as oxygen electrode for solid oxide cells with Pr-doped ceria active layer Allan Araújo, Francisco Loureiro, Laura Holz, Vanessa Graça, João Grilo, Daniel Macedo, Carlos Paskocimas and Duncan Fagg
	Lunch Break	

	September 15th Wednesday 2021 (Afternoon)	
	Chair: Saban Patat	**Chair: Mustafa Urgen**
	Na-ion Batteries	**Supercapacitors-I**
13:30 13:50	Salt-templated N-doped porous carbon anode materials for sodium ion batteries Emrah Demir	Organic Electrochromic-Energy Storage Application Based on Dithienothiophene, Triphenyamine and 3,4-ethylenedioxythiophene Sebahat Topal, Esma Sezer, Belkis Ustamehmetoglu and Turan Ozturk
13:50 14:10	Tin Selenide Anode Material in SIB Synthesized via High Energy Ball Milling Meral Aydin and Rezan Demir Çakan	Capacitive performance of chemically modified Fe/O co-doped graphene Neriman Sinan Tatli and Ece Unur Yilmaz
14:10 14:30	Investigation the effect of the binder and the electrolyte salt anion for optimizing the sodium-selenium battery system Zeynep Erdöl, Ali Ata and Rezan Demir-Cakan	Induced bifunctionality in dual-doped lanthanum cobalt-based perovskite for zinc-air batteries Mohamed Elhousseini Hilal, Seyfettin Berk Şanlı, Francis Verpoort and Berke Piskin
14:30 14:50	Analysis of the effect of sulfur loading on the performance of lithium-sulfur batteries H. Merve Bilal and Damla Eroğlu	Advances in Harvesting Triboelectric Nano Energy within ZnO/Ag/Si(100) Gizem Durak Yüzüak, Seray Özkan and Ercüment Yüzüak
	Coffee Break	
	Chair: Sanjoy Banerjee	
15:30 15:50	First Principles Investigation of Anion Intercalation into Graphitic Carbon Cathode Taner Akbay and Tatsumi Ishihara	
15:50 16:10	Assessment of Ionic Liquid Electrolytes for High Performance Li-S Batteries Using Machine Learning Aysegul Kilic, Ramazan Yildirim and Damla Eroglu	
16:10 16:30	Preparation of an MXene/CNT composite electrode for high-performance supercapacitor Muslum Demir, Murat Yılmaz and Omer Sadak	
16:30 16:50	Elucidation of Efficient Charge/Discharge Mechanisms in Electrical Double Layer Capacitors Betul Uralcan and Ayse Korkut	
16:50 17:20	Advancing the Promise of Low-Temperature Molten Sodium Batteries Erik D. Spoerke	
17:20 17:40	Materials technology gaps for low cost grid energy Babu Chalamala	

September 16th Thursday 2021 (Morning)

	Chair: Selmiye Alkan Gürsel	
09:00 09:30	Enabling the success of the hydrogen-energy chain through international cooperation Fermin Cuevas, François Aguey-Zinsou, Junxian Zhang and Michel Latroche	
09:30 10:00	Materials development for proton ceramic cells Olivier Joubert	
10:00 10:30	Nitride materials as possible electrodes for NH_3 reversible fuel cells Duncan Paul Fagg	
	Coffee Break	
	Chair: Rezan Demir-Çakan	**Chair: Semen Klyamkin**
	Aqueous Batteries	**Hydrogen Storage and Separation-I**
11:00 11:20	Development of Energy Storage Systems Based on Aluminum-Ion in Aqueous Medium Burcu Ünal, Sevde Nazlı Dambasan, Selin Sarıyer and Rezan Demir Cakan	Hydrogen absorption kinetics comparison of the $LaNi_{4.4}Al_{0.3}Fe_{0.3}$-alloy based compact and the free powder bed Ivan Romanov, Vasily Borzenko and Alexey Kazakov
11:20 11:40	Search for New Compositions for Cathode Materials In MnO2 Secondary Alkaline Batteries Necdet Özgür Darıcıoğlu, Yiğit Akbaş and Tayfur Ozturk	Uncovering the influence of the surface oxidation on hydrogen absorption/desorption process of magnesium ultra-thin films M. Blanco, C. Morales, F. Leardini, J. I. Flege, J-F Fernández, I. J. Ferrer and J-R Ares
11:40 12:00	The effect of crosslinked binders on electrochemical performance of MnO2 cathode in zinc-ion aqueous electrolyte Selin Sariyer and Rezan Demir-Cakan	Developing Hydrogen Separation Dense Metallic Membrane Based on Pd-Mn-Ag Ternary alloy Mehmet Mert Köse, Hilal Aybike Can, Fatih Piskin and Tayfur Öztürk
12:00 12:20	New Cathode Compositions for Mildly Acidic Zn/MnO_2 Batteries Yiğit Akbaş, Necdet Özgür Darıcıoğlu and Tayfur Öztürk	High pressure hydrogen storage performance of Basolite® MOFs Sergey Chuvikov and Semen Klyamkin
	Lunch Break	

September 16th Thursday 2021 (Afternoon)

	Chair: Önder Metin	**Chair: Mykhaylo Lototskyy**
	Metal Air Batteries	**Hydrogen Storage and Separation-II**
13:30 13:50	Bifunctional gas-diffusion electrodes based on carbon free materials Emiliya Mladenova, Miglena Slavova, Borislav Abrashev, Valentin Terziev, Blagoy Burdin and Gergana Raikova	Experimental Research of Metal Hydride-Based Heat Storage System Processes Alexander Bezdudny, Dmitri Blinov and Vasiliy Borzenko 61
13:50 14:10	Lithium and Oxygen Adsorption at the α-MnO2 surface Doaa A. Ahmed, Tuğrul ÇetΙnkaya, Abdulkadir Kizilaslan and Hatem Akbulut	Effect of Heterointerfaces on the Electrical Conductivity of $BaZr_{0.80}Y_{0.20}O_{3-\delta}$ - $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ Composite Thin Films Taner Özdal, Gülhan Çakmak, Berke Pişkin and Fatih Pişkin60
14:10 14:30	Analysis of key materials and cell design parameters for high capacity lithium-oxygen batteries using machine learning Aysegul Kilic, Damla Eroglu and Ramazan Yildirim	Electrochemical performance of AB_5 type metal hydride electrodes with carbon nanotubes Alexey Kazakov, Dmitry Blinov, Natalia Zaytseva and Alexey Volodin
14:30 14:50	Enhancement of the Stability and Ionic Conductivity of Quasi Solid Li-O2 Batteries Using Double Layer Gel Polymer Electrolytes Mustafa Çelik, Samet Usta, Tuğrul Çetinkaya and Hatem Akbulut	Structure investigation of multi-base-component alloys and their hydrides Artem Korol, Vladislav Zadorozhnyy, Elena Berdonosova, Mikhail Zadoroznhyy, Semen Klyamkin and Polina Borisova

	Chair: Fermin Cuevas
15:00 15:30	How to increase the catalytic efficacy of platinum-based nanocatalysts for hydrogen generation from the hydrolysis of ammonia borane Saim Özkar
15:30 16:00	Photoelectrochemical Water Oxidation using BiVO4 Photoanodes Sarp Kaya
16:00 16:30	How A-site doping strategy influences the OER activity on La-based parent perovskite oxides through oxidation state and lattice distortion Cigdem Toparli
16:30 17:00	From model-type thin film electrodes to 3D porous cermets and beyond Alexander Opitz
17:00 17:30	Energy-Efficient Hardware and Intelligent Materials for Brain-inspired Computing: Artificial Synapses Based on Proton and Oxygen Motion Bilge Yıldız
	Break
18:30 20:00	**September 16th Thursday 2021 (Evening)**
	Poster Session
September 16th Thursday 2021 (Evening) Poster Session	**Chairs: Akif Aliyev, Şaban Patat**
	Development of Borides/Borates for Energy Storage Devıces Doruk Bahtiyar and Mehmet Kadri Aydınol
	Synthesis and Performance of Mixed Metal Sulfides as Electrode Materials for Lithium-based Battery Systems Cansu Savaş Uygur and Mehmet Kadri Aydınol
	LFP battery aging study: selecting batteries for reuse in a second life William Wheeler, Ali Sari, Pascal Venet, Yann Bultel, Elie Rivière and Frédéric Meniere
	Effect of micro-fluidization on the crystal structure and electrochemical performance of layered-oxide cathodes Semih Engün, K. Burak Dermenci, Umut Savacı and Servet Turan
	Development of Cathode Materials for Li-Ion Batteries by Magnetron Sputter Deposition Erdem Erkin Erdoğan, M. Kadri Aydınol and Tayfur Öztürk
	Ni-Rich $LiNi_xMn_yCo_zO_2$ (x>0.6) Cathode Material Development for Li-Ion Battery via Sol-Gel Method Mustafa Alp Yildirim
	Production of high C-rate LiFePO4 cathode boosting with Graphene for Li-ion Batteries Ali Jamal Abdulkareem, Tuğrul Çetinkaya, Mahmud Tokur and Hatem Akbulut
	Ni-rich $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ nanoparticles / graphene aerogel cathode material for lithium ion batteries Deniz Kuruahmet, Sıdıka Yıldırım, Hatice Güngör, Aslıhan Güler, Mehmet Oğuz Güler and Hatem Akbulut
	Cobalt-free, high-nickel $LiNi_{0.8}Mn_{0.15}Al_{0.05}O_2$ /graphene aerogel composites as cathode materials for lithium-ion batteries Deniz Kuruahmet, Sıdıka Yıldırım, Hatice Güngör, Aslıhan Güler, Mehmet Oğuz Güler and Hatem Akbulut
	Effect of storage on the elctrochemical performanse of LiMnO2 Krum Banov, Iliyan Popov, Dimka Ivanova and Branimir Banov

September 16th Thursday 2021 (Evening) Poster Session	Peach stone supported Fe_3O_4 particles for environmental friendly anode for Lithium – ion batteries Krum Banov, Iliyan Popov, Simeon Stankov, Ofeliya Kostadinova and Branimir Banov
	Silicon/Lithium Alloy Anode Material for Lithium Sulfur Batteries Muhammed Osman Numan Oğuz, Hatem Akbulut and Mahmud Tokur
	Photovoltaic Industry Waste as a Sustainable Source of High Capacity Li-ion Battery Anodes Mehmet Nevzat Duman and Mehmet Kadri Aydınol
	N and B Co-Doping Hierarchical Porous Carbon Anode for Li-ion Battery Hatice Gungor, Deniz Kuruahmet, Sıdıka Yildirim, Aslıhan Guler, Mehmet Oğuz Guler and Hatem Akbulut
	Composite anode based on red phosphorus for lithium-ion batteries Zarina Yelemessova, Assemay Nauryzbayeva, Aiym Mashekova, Aliya Mukanova and Zhumabay Bakenov
	Investigation of the Calendering Parameters for High Energy Density Lithium Ion Battery Electrodes Muhammet Barış Ekici, Mahmud Tokur and Mustafa Akçil
	Coprecipitating Ni^{2+}, Mn^{2+} and Co^{2+} By Using Ammonium Oxalate as Precipitant for Ni-Rich Li-ion Batteries Cathode Fırat Tekmanlı and Kadri Aydınol
	Synthesis of carbon encapsulated tin nanoparticles by induction thermal plasma as anode for Na-ion batteries Aylin Elçi and Tayfur Öztürk
	Synthesis and research of $Zn_2[EDTA(H_2O)]$ metal-organic framework (MOF) for application as anode material in sodium-ion batteries Radmira Shiyanova, Alena Rubanova and Ivan Trusov
	Effective Cathode Slurry Preparation for Ni-MH Batteries Necdet Özgür Darıcıoğlu, Yiğit AkbaŞ and Tayfur Ozturk
	P[Th_3CNTT-TPA] based electrode material for supercapacitors Sema Topal, Sebahat Topal, Garen Suna, Belkıs Ustamehmetoğlu, Turan Öztürk and Esma Sezer
	Modeling the distribution of ions in a electrolytic capacitor Jami Torki, Ali Sari and Charles Joubert
	Ultrasonic Spray Deposition of Cobalt Based Metal Organic Frameworks for Textile-Based Supercapacitor Electrodes Mete Batuhan Durukan, Asude Cetin, Tufan Bolukbasi and Husnu Emrah Unalan
	Supercapacitor Based on Functionalized Carbon Materials and Room Temperature Ionic Liquid Ayse Korkut and Betul Uralcan
	Optimization of energy density in supercapacitors by utilizing a Hybrid Artificial Neural Network-Genetic Algorithm Betül Uralcan and Duygu Kaya
	Enhancing the OER activity of benchmark BaSrCoFeO6 electrocatalyts through A-site doping strategy Tuncay Erdil, Ersu Lökçü and Çiğdem Toparlı
	Effect of Fe Alloying On The Electrochemical Performance and Long-Term Stability of Ni Thin Film Electrodes Mustafa Ünsal Ünver and Aligül Büyükaksoy
	High Performance LSF based fuel electrodes for Solid Oxide Fuel Cells Buse Bilbey and Aligül Büyükaksoy

	Sulfonated Silica-Based Proton Conductive Hybrid Electrospun Membranes for Low Humidity Operation of PEM Fuel Cells Naeimeh Rajabalizadeh Mojarrad, Ahmet Can Kırlıoğlu, Selmiye Alkan Gürsel and Begüm Yarar Kaplan
	Synthesis and characterization of carbon supported PdCu for direct glycerol fuel cells Kübranur Ağtoprak
	Anion Exchange Membrane Development for Direct Glycerol Fuel Cell Ceyda Elif Meydan
	Characterization of CdS thin films electrodeposited on conductive glass for application in solar cells Shikhamir Eminov, Akif Aliyev, Jafar Guliyev, Khuraman Jalilova and Vusala Majidzade
	Artificial Neural Network (ANN) for Pressure- Concentration- Temperature (P-C-T) curves of metal hydrides. Ziphezinhle Khethiwe Simelane
	Effect of B-site dopant on the structural properties of $La_{0.2}Na_{0.8}Al_{0.3}M_{0.7}O_3$ (M=Mn and Mg) perovskite oxides Müzeyyen Özdemir and Berke Piskin

	Posters: Entry level Design Exhibition
September 16th Thursday 2021 **(Evening) Entry Level Design Exhibition**	Design Requirements and Materials Selections for Battery Packs in Electric Vehicles Salih Alçın, Sebnem Temel, Hande Ozturk, Cahit Günes and Gurkan Pekoz
	Design Requirements and Roadmaps for Cathodes Used in Electric Vehicles, Yiğit Hamza Yıldız, Selahattin Cat, Fatih Kaan Gullu and Sertac Celik
	A Comparative Study of Comparison of Recycling Methods for Lithium-Ion Batteries Orhun Oguz, Oytun Berkman, Yunus Emre Gul, Ahmet Suat Gursoy, Emre Bayboga, Ozgul Keles and Sebahattin Gurmen
	Anode Design Requirements and Materials Selection for Electric Vehicles, Arda Durer, Elif Sarikas, Yagiz Arslan, Melike Korkman, Anil Savran, Ozgul Keles and Sebahattin Gurmen
	Design of 1 MW Energy Storage System for Renewable Energy- Li-ion Batteries Berkhan Karadede, Özge Karataş, İbrahim Dereli, Cansu Şimşek, Aykut Şahbazoğlu, Eren Sefer
	Design of 1MW Energy Storage System for Renewable Energy- Flow Batteries Ali Ataberk Ergün, Mustafa Itri Gerçek, Beril Özlen, Gözde Öztürk
	Design of Solar Battery Storage System for A Residential Home Salim Karsanbaş

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September 17th Friday 2021 (Morning)

	Chair: İbrahim Pamuk
09:00 09:25	Thermallydriven hydrogen compression utilizing metal hydrides Mykhaylo Lototskyy
09:25 9:50	Composition design, preparation techniques and hydrogen storage properties of high entropy alloys Semen Klyamkin, Vladislav Zadorozhnyy, Elena Berdonosova, Mikhail Zadorozhnyy, Artem Korol and Ivan Savvotin
09:50 10:15	Feasibility study of fuel cell powered forklift truck Gojmir Radica, Ivan Tolj, Michael Lototskyy and Sivakumar Pasupathi
10:15 10:40	Transient CFD Analysis of 1 kW Air-Cooled PEM Fuel Cell Stack During Startup Ivan Tolj, Gojmir Radica and Željko Penga
	Coffee Break

	Chair: Damla Eroğlu Pala	Chair: Saim Özkar	Chair: H. Emrah Unalan
	Flow Batteries	**Catalyst and Active Material Synthesis**	**Supercapacitors-II**
11:00 11:20	The effects of heat treatment on the felt electrodes in Vanadium Redox Flow Battery Mert Taş and Gülşah Elden	Structure evolution of Ti_xO_y photocatalysts from the molecular form to the amorphous state: post-ultraviolet illumination effects E O Şahin, Y Dai, C. K. Chan, H.Tüysüz, W. Schmidt, J. L., Siyuan Zhang, C. Scheu and C. Weidenthaler	Synthesis of Biomass-derived hierarchical porous carbon for supercapacitor electrode material Murat Yılmaz and Müslüm Demir
11:20 11:40	A Numerical Analysis on Vanadium Redox Flow Battery Based on Different Nafion Membranes Phil Jacques Alphonse and Gülşah Elden	Effect of lateritic Ni ores on the crystal structure and electrochemical properties of NMC cathodes Semih Engün, Burak Dermenci and Servet Turan	Development of Activated Carbon / Bimetallic Transition Metal Phosphide Composite Materials for Electrochemical Capacitors and OER Catalysis Kadir Özgün Köse and Kadri Aydınol
11:40 12:00	Investigation of electrocatalysts containing single, binary, ternary, and quaternary metal ions deposited on graphite electrode for vanadium redox battery Niyazi Özçelik, Zeliha Ertekin, Nuran Özçiçek Pekmez and Kadir Pekmez	Recovery of Li,Ni,Co and Mn From Spent Lithium-ion Batteries Fırat Tekmanlı and Kadri Aydınol	Ti_3C_2 MXene Supercapacitor with Thin Film h-BN Separator Alptekin Aydinli, Xuehang Wang, Husnu Emrah Unalan and Yury Gogotsi
12:00 12:20	Nanoporous Ni Surface Modification by Electrochemical Dealloying Taner Özdal and Fatih Pişkin	Effect of carbon support type on anode electrocatalyst for EOR performance E S Kazan, M Bayramoğlu and C. Arslan	Double layered hydroxide (Ni-Co)OOH for energy storage application Nourhan Mohamed, Ozden Gunes Yildiz and Mustafa Urgen
	Lunch Break		

September 17th Friday 2021 (Afternoon)

	Chair: Olivier Joubert
13:30 13:50	Hydrogen generation by PEM electrolysis - a numerical investigation Elena Carcadea, Mihai Varlam, Daniela Ion-Ebrasu, Konstantin Petrov, Catalin Jianu, Laurentiu Patularu and Dorin Schitea
13:50 14:10	Effect of Boron Doping on the Layered Iron Nickel Sulphide Nanosheets for Electrochemical Hydrogen Evolution Reaction Esaam Jamil, Begüm Yarar Kaplan, Selmiye Alkan Gürsel and Alp Yürüm
14:10 14:30	Impact of Anode Loading on the CO Tolerance of $Ti_{0,8}Mo_{0,5}O_2$-C supported Pt Electrocatalyst Ceyhun Yildirim, Emine Sena Kazan, Osman Ozturk, Irina Borbath, Andras Tompos and Mehmet Suha Yazici
14:30 14:50	High Performance electrospun Pt/C/Sulfonated Silica/P(VDF-TrFE) fibrous cathodes for PEM fuel cells Bilal Iskandarani, Selmiye Alkan Gürsel and Begüm Yarar Kaplan
14:50 15:10	Heterogeneous A-site Deficient / Stoichiometric (La, Ca)CoO3 Electrodes for Solid Oxide Cells Mehmet Sezer, Ali Şems Ahsen and Aligül Büyükaksoy

15:10	Coffee Break
	September 17th Friday 2021 (Late Afternoon)
	Chair: Kadri Aydınol
15:30 16:00	Replacement of Cobalt with Copper in NCA Cathode Materials Ozgul Keles and Dila Sivlin
16:00 16:30	Refinement of Metal Sulphates and Synthesis of NMC Cathode for Li-ion Batteries from Gördes Ni-Co Deposits. Serif Kaya
16:30 17:00	Development of rechargeable zinc manganese dioxide batteries from concept through product to market Sanjoy Banerjee
17:00 17:30	Current Status and Future Prospect of Li-Ion Battery Technology in Turkey Ahmet Altınay
	Short Break
17:40 18:00	**Closing session (Awards)**

TABLE OF CONTENTS

GENERAL - CHARACTERIZATION TECHNIQUES

BATTERIES

SUPERCAPACITORS

RENEWABLE HYDROGEN

HYDROGEN STORAGE AND SEPARATION

FUEL CELLS AND ELECTROLYSERS

CATALYST AND ACTIVE MATERIAL SYNTHESIS

SYTEMS AND APPLICATIONS

Appendix: POSTERS AT ENTRY LEVEL DESIGN EXHIBITION

GENERAL- CHARACTERIZATION TECHNIQUES

Energy-Efficient Hardware and Intelligent Materials for Brain-inspired Computing: Artificial Synapses Based on Proton and Oxygen Motion

Bilge Yıldız

Nuclear Science and Engineering and the Materials Science and Engineering Departments
Massachusetts Institute of Technology (MIT)

The Deep learning is a hugely successful and powerful algorithm for machine learning applications such as computer vision and natural language processing. However, the training of these neural networks is limited by the traditional von Neumann architecture of our current CPUs and GPUs. Shuttling data back and forth between the separate memory and computation units in such architecture results in significant energy consumption; many orders of magnitude greater than the energy consumption in human brain. Our projects focus on designing materials and hardware that can instead perform data storage and computation in a single architecture using ions, inspired by the human brain. In one project, we have designed a protonic electrochemical synapse that changes conductivity deterministically by current-controlled shuffling of dopant protons across the active device layer; resulting in energy consumption on par with biological synapses in the brain. In our second project, we demonstrate controlled conducting oxygen vacancy filament formation in resistive memory devices via dopant and microstructure engineering. These strategies provide pathways towards neuromorphic hardware that has high yield and consistency, performs data storage and computation in a single device, and uses significantly lesser energy as compared to current computing architectures.

Bilge Yildiz is a professor in the Nuclear Science and Engineering and the Materials Science and Engineering Departments at Massachusetts Institute of Technology (MIT), where she leads the Laboratory for Electrochemical Interfaces. She received her PhD at MIT in 2003 and her BSc from Hacettepe University in 1999. After working at Argonne National Laboratory as a research scientist, she returned to MIT as an assistant professor in 2007. Yildiz's research focuses on laying the scientific groundwork to enable next generation electrochemical devices for energy conversion and information processing. The scientific insights derived from her research guide the design of novel materials and interfaces for efficient and durable solid oxide fuel cells, electrolytic water splitting, brain-inspired computing, and solid state batteries. Her laboratory has made significant contributions in advancing the molecular-level understanding of oxygen reduction, water splitting, ion diffusion, and charge transfer on mixed ionic-electronic conducting oxides. Her research has uncovered the effects of surface chemistry, elastic strain, dislocations, and strong electric fields on the reactivity, efficiency, and degradation in these applications. Her approach combines computational and experimental analyses of electronic structure, defect mobility and composition, using *in situ* scanning tunneling and X-ray spectroscopy together with first-principles calculations and novel atomistic simulations. Her teaching and research efforts have been recognized by the Argonne Pace Setter (2016), ANS Outstanding Teaching (2008), NSF CAREER (2011), IU-MRS Somiya (2012), the ECS Charles Tobias Young Investigator (2012), the ACerS Ross Coffin Purdy (2018), and the LG Chem Global Innovation Contest (2020) awards.

From model-type thin film electrodes to 3D porous cermets

Alexander Opitz
TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria

To fight global warming, a highly efficient utilisation of fuels and storage of renewably produced energy is of utmost importance. Solid oxide fuel and electrolysis cells (SOFCs and SOECs) are a promising technology that can make an important contribution to the energy transition, since they allow conversion of chemically stored energy into electricity as well as electrolysis of H_2O or CO_2 to store electricity in a persistent form – both with highest efficiencies. For these cells, gadolinia-doped ceria (GDC) based materials such as Ni/GDC are the currently most promising fuel electrodes. For a targeted optimisation of real porous Ni/GDC cermet electrodes, a detailed insight into the role of the material properties for the electrochemical polarisation resistance is crucial.

Here, model-type GDC thin film electrodes grown by pulsed laser deposition were used for basic characterization of the material's electrochemical elementary parameters such as surface reaction resistance and chemical capacitance. These parameters and their physically correct relationship on Ni/GDC cermet structures were used to interpret of the impedance of real 3D porous electrodes. Accordingly, an analytical transmission line circuit is derived. Fitting the electrode impedance to this circuit, allows separation and quantification of the individual contributions to the electrode polarisation resistance, such as oxygen ion transport across the electrolyte/GDC interface, ionic conductivity of the ceramic phase, and electrochemical reaction at the GDC surface. Comparison with our model studies yields very good quantitative agreement. With these detailed insights, we can quantitatively explain the polarisation resistance of real porous Ni/GDC fuel electrodes. Moreover, we can demonstrate that fuel electrode functional layers consisting entirely of GDC (i.e. without any metallic phase) can even surpass the performance of cermet electrodes, if the functional layer is sufficiently thin and good contact to a current collecting layer is established.

Alexander K. Opitz is the head of the research group Electrochemical Energy Conversion at TU Wien(Vienna, Austria). There he also received his PhD in 2011. He was a visiting scientist at MIT in 2017 and returned to a tenure track position at TU Wien, where he is now an Assistant Professor in the research division of Technical Electrochemistry. He is doing research in the fields of Solid State Ionics (electrode kinetics, current pathways, and electrochemically active zones of solid state electrochemical systems), heterogeneous catalysis (in-situ spectroscopic and analytic studies on the surface chemistry and catalytic activity of electrodes), and materials chemistry (synthesis and characterization of novel, alternative materials for solid oxide cells).

Structure evolution of Ti_xO_y photocatalysts from the molecular form to the amorphous state: post-ultraviolet illumination effects

Ezgi Onur Şahin[1], Yitao Dai[1], Candace K. Chan[2], Harun Tüysüz[1], Wolfgang Schmidt[1], Joohyun Lim[3,4], Siyuan Zhang[3], Christina Scheu[3] and Claudia Weidenthaler[1]

[1]Max-Planck-Institute für Kohlenforschung, Heterogeneous Catalysis, Mülheim an der Ruhr, Germany

[2]Arizona State University, Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Tempe, USA

[3]Max-Planck-Institut für Eisenforschung GmbH, Nanoanalytics and Interfaces, Düsseldorf, Germany

[4] Kangwon National University, Department of Chemistry, Chuncheon, Republic of Korea

Since the discovery of splitting water at semiconductor electrodes, titanium oxide has been investigated as a photocatalyst for light-induced water splitting. It is still considered as an environmentally friendly catalyst or catalyst support. While crystalline titanium oxides have been studied extensively due to lower probability of recombination centres for the charge carriers, amorphous titanium oxides are also considered as promising photocatalysts. Titanium oxides synthesized via the direct injection of the titanium alkoxide precursor into the reaction solution were reported to exhibit higher photocatalytic activity for H_2 generation compared to the crystalline TiO_2 benchmark catalyst P25.[1] X-ray diffraction showed that the materials prepared by the direct injection method are lacking long-range order.

Understanding the reasons for high activities reported for the amorphous catalysts necessitates to determine the structure-property relationship. This has been a challenge due to the complications of structure investigations of amorphous materials. Local structures of non-crystalline materials are not accessible by conventional X-ray diffraction methods. Therefore, local probes such as the analysis of the total scattering data and the subsequent pair distribution functions (PDF),[2] which provide information at the atomic scale, are required.

In this study, the evolution of the local structure from the molecular precursor to the amorphous solid and later the effects of short and long term photocatalytic process were investigated mainly by the analysis of the PDFs obtained from X-ray total scattering data. Additionally, scanning transmission electron microscopy (STEM)- electron energy loss spectroscopy (EELS) techniques were used to shed light on the effects of post-UV illumination on the coordination environment.

PDF analysis reveals that the formed titanium oxide photocatalysts exhibit ordered domains with anatase-like arrangement of less than 7 Å in size. During photocatalytic process, the reaction suspension is illuminated under ultraviolet (UV) light. This induces the change of the colour of the suspension from white to dark blue as an indication of the formation of reduced Ti centres (Ti^{3+}).[3] The catalytic process takes 2 hours, whereas it was extended to 24 hours in order to examine the effects of longer periods of UV illumination. The products of the suspensions which were exposed to 2 and 24 hours of UV light was examined by PDF analysis and spatially resolved EELS.

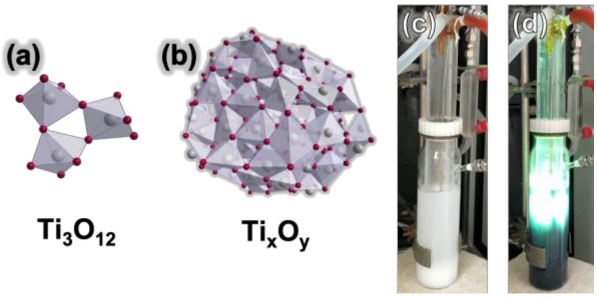

Figure 1. Injection of the trimeric precursor (a) into the solution mixture yields the formation of Ti_xO_y units (b). Upon UV illumination, the reaction suspension changes colour (c and d) indicating the formation of reduced species.

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Acknowledgements

E. O. S. acknowledges the International Max Planck Research School for Interface Controlled Materials for Energy Conversion (IMPRS-SurMat) for funding. C. K. C. and J. L. would like to thank the Alexander von Humboldt Foundation for support of this work through a Humboldt Research Fellowship. C. W., Y. D., and H. T. thank the Max Planck Society for basic funding. We acknowledge Diamond Light Source (proposal EE12102-1) and Deutsches Elektronen-Synchrotron (proposal I-20190175) for beamtime.

Ezgi Onur Şahin is a graduate of Middle East Technical University Department of Metallurgical and Materials Engineering. She obtained her M.Sc. from the same department. She worked as a doctoral research fellow at the Max-Planck-Institute für Kohlenforschung while she attended International Max Planck Research School for Interface Controlled Materials for Energy Conversion. She obtained her Ph.D. from University of Duisburg-Essen Faculty of Chemistry. Her research interests include local structure analysis by X-ray total scattering methods, photocatalysis, amorphous ceramics and crystallisation.

Presenting author: Ezgi Onur Şahin, onur@mpi-muelheim.mpg.de

Investigation of Electrochemical Processes of Metallic Li Batteries using Temperature Dependent Electrochemical Impedance Spectroscopy

Mohammed Ahmed Zabara, Burak Ulgut
Department of Chemistry, Bilkent University, Ankara, Turkey

The utilization of metallic Li anodes provides high gravimetric and volumetric energy densities for next generation Li batteries. The limitation of its utilization presents in the unwanted interfacial processes taking place such as Li plating and dendrites formation. In any Li battery chemistry, Li is protected by a passive layer which prevent it from reacting with the electrolyte. This layer is called the Solid Electrolyte Interface (SEI) and has important role in the battery operation by allowing Li-ions to transport with the prevention of electron leakage [1]. Understanding the underlining Li-ion transport mechanisms through such interfaces is crucial for the utilization of metallic Li and in preventing the accompanying unwanted processes.

For this aim, we use temperature dependent Electrochemical Impedance Spectroscopy technique. The linear and accurate Electrochemical Impedance technique is shown to clarify various processes of the Li based batteries [2]. The obtained data show a drastic change in the electrochemical impedance of the high frequency response by varying the temperature which can be seen in Figure 1.

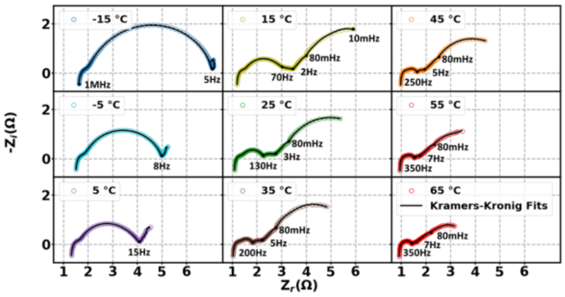

Figure 1. Nyquist plots for Li/$SOCl_2$ battery from -15 ºC to 65 ºC.

Analysis of this data is achieved by Equivalent Circuit models. The models show the existence of two-layer structure for the SEI with larger variations in the second layer. Kinetic parameters are studies using the resistance values obtained for the two layers. The transport of Li-ion through the second layer is showing Arrhenius behavior at low temperatures and non-Arrhenius behavior at high temperatures as shown in Figure 2. The two behavior temperature dependency is indicating the existence of more than one mechanism for the Li-ion transport in the anode. The calculated activation energy obtained from the linear regions shows values around 30 kJ/mol for Lithium Thionyl Chloride and 50 kJ/mol for Lithium Manganse Dioxide which highlights the effect of the different SEI structures on the activation energies of the Li-ion transport process.

We will show temperature dependent investigations for various chemistries of metallic Li based batteries such as Lithium Thionyl Chloride, Lithium Manganese Dioxide and Lithium Polycarbon Monofluoride chemistries which all illustrate the high temperature dependency of the different electrochemical processes.

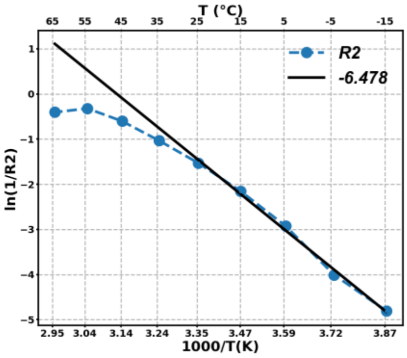

Figure 2. Arrhenius plot obtained from the resistance for the Li-ion transport process (R2).

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Mohammed A. Zabara is a PhD. candidate at chemistry departement, Bilkent University. He obtained his B.S. and Msc. in chemistry from Middle East Technical University. Under the supervision of Ass. Prof. Burak Ulgut he is working on the electrochemical characterization and modeling of various energy storage systems utilizing Electrochemical Impedance Spectroscopy technique.

Presentating author: Mohammed Ahmed Zabara, e-mail: mohammed.zabara@bilkent.edu.tr

BATTERIES

Material aspects of alternative energy stores: sodium-ion and solid-state batteries

Philip Adelhelm

Helmholtz-Zentrum Berlin (HZB) and Humboldt-University Berlin

The rising demand of rechargeable batteries for electric vehicles and grid storage applications sparks a lot of interest on alternatives to “standard Li-ion battery technology”. The size of these markets is so large that great efforts are currently undertaken towards using more cost-effective materials that will not run into supply and/or resource constraints. Here, sodium-ion batteries are one important option that primarily aim at realizing high energy batteries based on sodium and other abundant elements such as carbon, iron or manganese. On the other hand, solid-state batteries (SSBs) are considered as promising option for electric vehicles. In these types of batteries, a solid electrolyte replaces the flammable organic liquid electrolyte, which improves safety. At the same time, SSBs might enable energy densities exceeding conventional lithium-ion technology.

This talk gives an overview on materials aspects on sodium-ion and solid-state batteries and how they compare to lithium-ion batteries. Specific examples on inorganic materials will be discussed, including high capacity metal/carbon negative electrodes[1], layered oxides of the type $Na[Mn_xFe_yTM_z]O_2$[2], solvent co-intercalation reactions (graphite)[3] and metal sulfides (CuS, Cu_3PS_4, $NaTi_xTM_yS_2$)[4] (TM = transition metal).

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Philipp Adelhelm is a materials scientist and graduated from the University of Stuttgart. He received his PhD degree in 2007 for his work on carbon materials for energy storage at the Max-Planck-Institute of Colloids and Interfaces in Potsdam (Antonietti group). From 2007-2009, he was postdoc at the Debye Institute of Nanomaterials Science in Utrecht, The Netherlands (de Jongh group) studying hydrogen storage materials. Between 2009-2015, he was group leader at the Justus-Liebig-University Giessen (Janek group), with the main interest in exploring the cell chemistry of sodium based batteries. From 2015-2019 he was professor at the Friedrich-Schiller-University Jena.Since 2019 he is professor at Humboldt-University Berlin (Physical chemistry of materials / electrochemistry) and heads a joint research group on “operando battery analysis” between Helmholtz-Zentrum Berlin (HZB) and Humboldt-University Berlin.

Ultra fast charging high energy lithium-ion batteries utilizing borophene/h-BN aerogel layers

Onur Ergen[1]
[1] *Electrical and Electronics Engineering Faculty, Istanbul Technical University, Istanbul/ Turkey*

Even though, development of lithium ion batteries has progressed tremendously over the last few decades in energy density, efficiency, and reliability, battery capacity still cannot keep up and sustain the increasing demands of fast charging and energy density.[1] Especially, to allow ultra-fast charging (80% recharged in less than 5 minutes), it is necessary to increase the battery charging rate to 10C, 10 times to rated current. At this high current rate, conventional LIBs exhibit poor performance, low energy density, and degradation, but most importantly, become unstable and more prone to catastrophic failure (fire or explosion).[2,3] Recent innovations in battery technology have focused on incremental improvements in battery chemistry, addressing ion acceptance and energy density but ignoring key problems, such as safety, high internal resistance, and thermal runaway.

Moreover, the most common conventional graphite anodes are not suitable for ultra fast charging and exhibit severe capacity loss due to poor Li^+ intercalation kinetics. Specifically, Li dendrite formation on the graphite anodes is very common at high current rates due to high polarizaiton. [4]Due to these limitations of conventional graphite, aternatively, silicon anodes are widely studied and partially commercialized. Silicon provides a higher gravimetric capacity and better Li^+ intercalation kinetics than graphite. However, silicon has its own drawbacks including high charge transfer resistance, extreme volume changes, and poor electrical conductivity. Besides, the silicon approach still cannot fully address the fast charging and enegy density demand.[4]

Thus, new battery anode chemistries are necessary to meet the fast charging demand along with safety. At this point, a new material, borophene, is emerging. Borophene's high adsorption energy and low barrier for ion diffusion makes it an excellent candidate for a next generation anode that can provide high capacity and fast charging.[5]

Here, we demostrate a new anode material utilizing borophene/h-BN aerogels. In this study, borophene/h-BN aerogels were directly synthesized from graphite as indicated from our previous research.[6,7] The resultant battery cells exhibit excellent properties in relation to fast charging and performance (Fig. 1). Moreover, the advantages in chemical inertness and thermal stability of h-BN truly elevate borophene's performance. We believe architectures with borophene/h-BN aerogel implementation not only enable ultra fast charging batteries but enable new anode geometries.

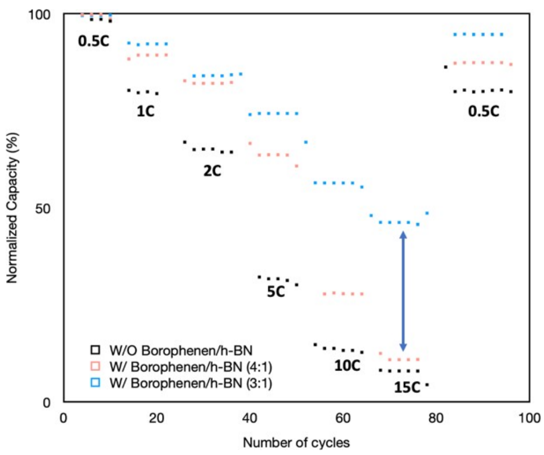

Figure 1. Rate performance of battery cells with and without borophene/h-BN aerogel implementation. borophene/h-BN (3:1) exhibits superior battery performances at high charging rates.

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Dr. Onur Ergen holds MS, MA, and Ph.D. degrees, in Electrical Engineering and Physics, all from the University of California Berkeley. He recently joined the faculty of the Istanbul Technical University where he is currently an assistant professor of Electrical and Electronics Engineering. Previously, Onur worked on developing new semiconductor technologies at Intel Corp., was responsible for developing automated systems and AI interfaces at Apple Inc. and worked on R&D research and development activities at Solo Power Inc. He developed various new concepts and device architectures from wearable electronics to lithium-ion batteries, etc. Onur has a strong academic foundation in energy and novel device architectures and has over 22 publications and 12 patents.

Presentating author: Onur Ergen, e-mail:oergen@itu.edu.tr tel: +90 (212) 285 3613

New lithium-rich layered oxides as positive electrode materials for lithium-ion batteries

Marie Guignard[1], Valentin Saïbi[1] and Claude Delmas[1]

[1] CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

Lithium-rich layered transition metal oxides of the general formula $Li_{1+x}M_{1-x}O_2$ (where $0 < x < 1/3$, and M is usually a mix of manganese, nickel and cobalt) have been intensively studied for use as positive electrode materials in lithium-ion batteries due to their high lithium intercalation and deintercalation rate. However, lithium-rich layered oxides also present some serious drawbacks. For instance, the batteries made with these materials at the positive electrode show an important voltage drop upon cycling that involves a decrease of the energy density. One possible origin of this voltage drop is the migration of manganese ions within the lithium layers and the formation of a spinel-like structure at the surface of the particles.

To overcome this problem, we decided to synthesize new lithium-rich layered oxides with the general formula $Li_xNi_yMn_zO_2$ (with $1 < x < 1.25$) with a different oxygen stacking that would make the migration of manganese ions unfavourable thanks to a stronger coulombic repulsion between the layers (alternative of face- and edge-sharing octahedra).

Two samples with these two different structure types (O2- and O3-type) have been synthesized in our laboratory. The O2-type structure compound has been obtained by ion exchange at moderate temperature (below 300°C) from the sodium layered oxide $Na_{0.7}Li_{0.14}Ni_{0.14}Mn_{0.72}O_2$. The O3-type structure one has been obtained after a heat treatment of the O2-type structure compound at 450 °C in a sealed tube. The synthesis of the O3-type oxide from the O2-type one allowed the two compounds to have the same general chemical formula, $Li_{0.85}Ni_{0.14}Mn_{0.72}O_2$. Moreover, we expect that their particles have the same morphology.

Moreover, whereas the first charge capacities recorded for both materials are very similar (approximately 250 mAh/g), the irreversible capacity after the second discharge (which corresponds to the first full discharge) is much more important for the battery made with the O3-type structure oxide (55 mAh/g) than the one made with the O2-type structure oxide (33 mAh/g).

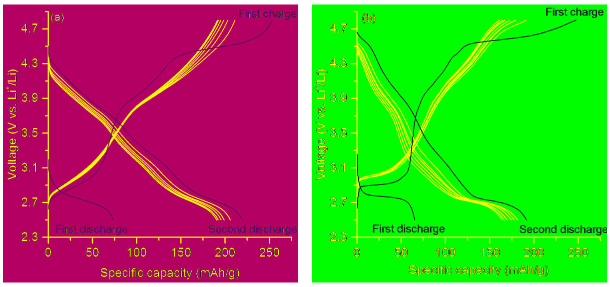

Figure 1: Galvonostatic cycling curves at C/20 rate in the voltage range 2.5-4.8 V for lithium batteries made with (a) O2-$Li_{0.85}Ni_{0.14}Mn_{0.72}O_2$ and (b) O3-$Li_{0.85}Ni_{0.14}Mn_{0.72}O_2$ as positive electrode materials.

Marie Guignard is a CNRS researcher and has expertise in solid state chemistry. She joined the Institute of Condensed Matter of Bordeaux (ICMCB) in 2009. Her main interest is the structural studies of inorganic materials. For the last ten years, she has been working on sodium layered oxides as positive electrode for sodium-ion batteries. More specifically, she has performed *operando* powder X-ray diffraction and pair distribution function (PDF) experiments to understand structural mechanisms occurring both at the long- and the short-range order in these materials upon cycling

Presentating author: Marie Guignard, e-mail: marie.guignard@icmcb.cnrs.fr tel: +33 5 40 00 63 30

Electrochemical performance of highly concentrated LiFSI-EC electrolytes in Silicon/Graphite - NMC111 Li-ion batteries

Burak Aktekin[1*], Guiomar Hernández[1], Reza Younesi[1], Daniel Brandell[1], Kristina Edström[1]
[1]Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-75121, Uppsala, Sweden

The development of advanced lithium-ion batteries (LiBs) is still of highest priority for the fast-growing energy storage applications such as electric vehicles. Preferably, electrode materials in a LiB should have high specific charge capacities and also result with a high cell voltage. Unfortunately, this requirement also brings significant (electro)chemical instability issues in conventional battery systems which mainly consist of $LiPF_6$ salt dissolved in organic carbonate solvents as the electrolyte due to their rather limited electrochemical stability window.[1] As a result of this, electrolyte reduction and oxidation reactions occur on anode and cathode, respectively. In the case of low voltage anodes, Li dendrite formation poses another problem. Unfortunately, $LiPF_6$ salt also has a relatively low thermal stability and carbonate-based solvents are volatile and flammable. All of these issues bring a negative impact on the battery cycle life and safety.

One promising direction to overcome these problems is to increase the Li salt concentration in the electrolyte to high levels. In recent years, the realization of unusual physical and chemical properties of electrolytes with excessive salt contents has resulted with a significant interest in highly concentrated electrolytes, especially for their application in batteries with lithium metal and graphite negative electrodes.[2] Here, we report the electrochemical cycling results of a simple binary electrolyte system, consisting of lithium bis(fluorosulfonyl)imide (LiFSI) salt and ethylene carbonate (EC) solvent. This electrolyte system was tested in different cell configurations with a focus on the Si/Graphite – NMC111 full cell configuration. Li-metal - Si/Graphite cells with the LiFSI:EC electrolyte outperformed its LiTFSI-counterpart as well as the conventional LP40 electrolyte, however, very high concentrations larger than 1:4 salt:solvent ratio need to be avoided due to negative impact on the Li-metal performance. In the absence of Li-metal electrode, it was possible to use higher concentration electrolytes (e.g. as high as 1:2 salt:solvent).

A considerable improvement on the electrochemical performance of NMC111 – Si/Graphite cells was achieved with the LiFSI:EC 1:2 electrolyte and LiFSI:EC 1:3 electrolyte (see Figure 1) at elevated temperature.

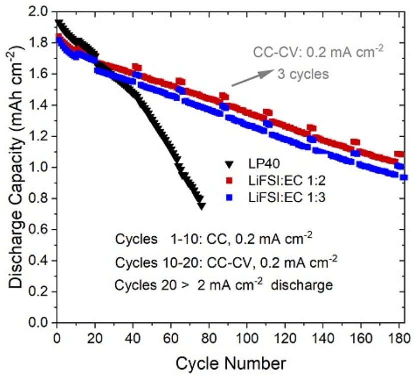

Figure 1. Elevated temperature electrochemical cycling results of NMC111 – Si/Graphite full cells. The nominal capacity of NCM111 electrodes are 2 mAh cm^{-2}.

Surface characterization with SEM and XPS showed that thicker surface films are deposited on both NMC111 and Si/Graphite electrodes after cycling with the LiFSI-based electrolyte as compared to LP40. This difference is more pronounced in Si/Graphite electrodes and the results show that the LiFSI promote the formation of a thicker SEI film rich in oxygenated species but relatively deficient in fluorinated components (e.g. LiF) and cathode-originated Ni ions. It is understood that such surface films are beneficial to cycling stability during longer term cycling since the LiFSI-based electrolyte considerably improved the capacity retention behaviour of both full and half cells.

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Burak Aktekin is currently working as a postdoc associate on all solid state batteries at the Justus Liebig University Giessen, Germany. He obtained his PhD degree from Uppsala University – Chemistry department (Sweden) with his work on high voltage spinel positive electrodes for lithium ion batteries. He also worked as a postdoc associate at the Angstrom Advanced Battery Centre for a short term after his PhD. He obtained his BS and MSc degrees in Metallurgical and Materials Engineering from Middle East Technical University, Ankara, Turkey.

*Presenting author: Burak Aktekin, e-mail: burakaktekin@gmail.com, tel: +49 (0) 641-9934510

Inspection on Capacity Fade Challenge for $LiNi_{0.5}Mn_{1.5}O_4$ Cathode

Tayfun Kocak[a], Muharrem Kunduraci[b], Servet Turan[c], Xiaogang Zhang[a]
[a]Jiangsu Key Laboratory of Electrochemical Energy Storage Technologies, College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China
[b]Tarsus University, Aerospace Engineering Department, Mersin 33400, Turkey
[c]Eskisehir Technical University, Department of Materials Science and Engineering, Eskisehir 26000, Turkey

Lithium-ion batteries are widely used in electric vehicles (EV) and mobile devices. The cycle life is one of the most important features of the battery in an EV [1]. The affordability of battery energy storage critically depends on low cost and long cycle life [2]. Current state-of-the-art lithium-ion battery cathodes rely too much on expensive Co and Ni elements, creating a potential cost problem in the future. On the other hand, Mn-based $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO) has attracted much attention in the last decade due to its low cost, natural abundance of manganese ores, and high theoretical capacity (147 mAh/g) of this spinel cathode. Also, its high operating voltage of 4.7 V makes its energy density 20-30% higher than that of commercially available $LiCoO_2$ and $LiFePO_4$ cathodes. According to the EU Technology report, LMNO was named as a generation 3b cathode with a potential market deployment around 2025 [3]. The main obstacle towards commercialization is rapid capacity fade resulting from electrolyte decomposition at high voltage (~4.7V). To overcome this obstacle, engineering the surface chemistry of spinel powders and use of dopants into spinel lattice doping methods are two main trends to prevent capacity degradation during extended cycling. The doping or surface coating methods independently suppresses capacity fade and improves the high-temperature stability of LMNO. The acidic HF environment causes surface degradation and how doping or surface coating protects the electrolyte degradation need to be explored more.

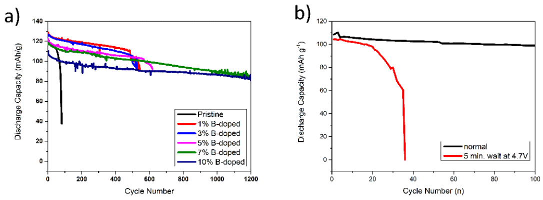

Fig. 1 a) Cycle performance of pristine, 1 %B-doped, 3 %B-doped, 5 %B-doped, 7 %B-doped and 10 % B-doped LMNO half-cells at 50 °C and 1C-rate until 1200 cycles b) Comparison of 5 minutes additional duration at 4.7 V charging to each step for 10% B-doped LMNO half-cells cycling performance at 50 °C and 1C rate.

Wang et al. studied the surface coating of LMNO with V_2O_5 and 5 wt. % V_2O_5 was found to be optimal [4]. However, 10 wt. % V_2O_5 coated LMNO (97.8%) exhibits better capacity retention than 5 wt. % V_2O_5 (92.2%) after 100 cycles. Similarly, we applied boron doping to the LMNO. High amount boron doping (10 wt. %) apparently decreases first discharge capacity but exhibits highest capacity retention after 1200 cycles at 1C-rate and 50 °C. Researchers mostly focus on higher first discharge capacity or first 100 cycles performance. However, batteries must be stable >2000 cycles for practical applications. Operando DEMS equipment reveals that H_2 and CO_2 gases emission increases at ~4.7 V for LMNO half-cell cathode due to electrolyte decomposition. At this point, duration at high voltage (~4.7 V) is the deterministic parameter of capacity retention of LMNO. Fig.1a shows the comparison of 7 % and 10 % boron-doped LMNO half-cells at 1C rate and 50 °C until 1200 cycles. In the beginning, 7 % B-doped LMNO has higher discharge capacity, but higher capacity fade after 1200 cycles. Therefore, to understand of real benefits of doping or surface coating, an extended cycle life test must be applied for LMNO. Additional duration (~5 minutes for each charging step) at ~4.7 V can reveal practical benefits of doping or surface coating with lower cycle number due to rapid decomposition at high voltages (Fig. 1 b). Detailed surface coating and doping amount comparison on capacity retention will be discussed at the presentation.

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First Principles Investigation of Anion Intercalation into Graphitic Carbon Cathode

Taner Akbay[1] and Tatsumi Ishihara[2,3]
[1]Department of Materials Science and Nanotechnology Engineering, Yeditepe University, Istanbul, Turkey
[2]Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan
[3]International Institute for Carbon-neutral Energy Research (WPI-I^{2}CNER), Kyushu University, Fukuoka, Japan

Dual carbon battery (DCB) is a promising alternative for lithium ion batteries (LIBs) because of the long cycle life, high discharge potential and lower cost. Although intercalation of various anions into graphitic carbon have been reported, their electronic structures have not been studied in detail. Recently, our group investigated the fast diffusivity of PF6$^-$ and reported the graphite gallery height expansion and activation energy barrier values as about 7.3 Å and 0.26 eV respectively. Placke et al. presented promising results using bis(trifluoromethanesulfonyl)imide (TFSI$^-$) ionic liquid anion for cathode intercalation [1]. In this work, we employed *ab-initio* electronic structure calculations in the density functional theory (DFT) formalism for investigating the intercalation structures of a series of anions into the graphitic carbon cathode and their interlayer filling geometries.

In this work, DFT calculations were carried out in order to shed light on the electronic structures of the GICs of a group of anions. Separate computational approaches were adopted for analysing the anion conformations and the stage-I structures of the GICs. As for the first set of computations, minimum energy conformations and the corresponding self-consistent field energy values for the GICs as well as their transport properties were calculated by using the localised molecular orbital basis sets and the coupled cluster approximation as implemented in the TURBOMOLE package. The second set of computations, on the other hand, consisted of detailed electronic structure analyses for the stage-I GIC structures and corresponding theoretical capacity estimations by using the DFT methodology as implemented in the Vienna Ab initio Simulation (VASP) package. The dispersion effect was also included using the Grimme method in both approaches. geometries.

The stability study was performed for the stage-I GICs of each anion and the most preferential interlayer filling geometries. Figure 1, shows the most stable GIC structure for each anion for half-filled supercells with the estimated gallery height values of 8.0, 7.4 and 6.9 Å for TFSI$^-$, PF6$^-$, and BF4$^-$ respectively, the models built correspond to the theoretical capacity values of 69.8 mAh/g in the case of TFSI$^-$, and 139.6 mAh/g in the case of PF6$^-$, and BF4$^-$. From the molecular orbital analysis, we found that HOMO is mainly formed by the most electronegative atoms, N 2p and O 2p in the case of TFSI$^-$ and F 2p in the case of PF6$^-$, and BF4$^-$. Therefore, it is expected that charge gets transferred from nitrogen or oxygen and fluorine to carbon when the anion electrochemically intercalated into the graphitic carbon. Binding energy values were also calculated for each anion, finding out that the maximum interaction between anions and graphite takes place when the interlayer space is half filled.

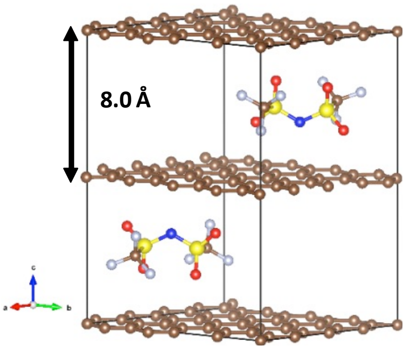

Figure 1. Optimised structure for GIC of TFSI$^-$ anion with the corresponding gallery height.

Activation energies for the diffusion of anions in graphite were also estimated as 0.12, 0.24 and 0.13 eV for TFSI$^-$, PF6$^-$, and BF4$^-$ respectively. Although the TFSI$^-$ anion has the largest molecular size, high diffusivity was estimated due particularly to charge partitioning.

Acknowledgements

TA acknowledges the support of the Scientific and Technological Research Council of Turkey (TUBITAK 2232 Programme). Authors also acknowledge the New Energy and Industrial Technology Development Organization (NEDO) Japan.

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Dr. Taner Akbay is affiliated with the Department of Materials Science and Nanotechnology Engineering at Yeditepe University. After receiving his BSc and MSc degrees in Metallurgical Engineering from Middle East Technical University in 1986 and 1989 respectively, Dr. Akbay obtained his PhD degree in Materials Engineering from Imperial College London in 1993. His research interests cover the broad area of energy conversion and storage applications namely dual-carbon, dual-ion batteries, solid oxide fuel/electrolyser cells.

Presentating author: Taner Akbay, e-mail: taner.akbay@yeditepe.edu.tr tel: +90-216-578-0403

Study of the structural and lithium storage properties of the rock-salt structured (MgCoNiMnLi*X*)O (*X*=Cr, Fe, Al) high entropy oxides

Ersu Lökçü[1], Meltem Çayırlı[1] and Mustafa Anik[1]

[1] Department of Metallurgical and Materials Engineering, Eskisehir Osmangazi University ,26040, Eskisehir, Turkey

The increasing demand for the clean and renewable energy makes the development of high capacity energy storage systems inevitable [1]. Lithium-ion batteries (LIBs) have become the main power source for the portable electronic devices, since the day they were discovered. In the short term, they are also the most promising systems for the applications require high capacities (such as electric vehicles). Therefore, the tremendous efforts have been devoted to the development of new electrode materials with high capacity as well as superior cycling and rate performance for LIBs [1, 2].

High entropy oxides (HEOs) are the new class of materials attracted great attention in the recent years due to their superior lithium storage properties and electrochemical performances [3, 4]. Sarkar et al. reported the first rock-salt structured $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ HEO anode, which has reversible capacity of 590 mA h g^{-1} after 500 cycles at 200 mA g^{-1} [4]. Chen et al. synthesized a spinel structured $(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$, which retains a discharge capacity of 504 mA h g^{-1} after 300 cycles at 200 mA g^{-1} [5]. Owing to the entropy-driven stability, HEOs show better cycling and rate performance with respect to their corresponding single transition metal oxides [4, 5].

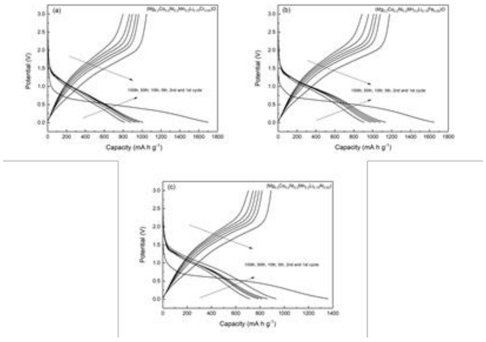

Figure 1. Discharge−charge curves of (a) HEOCr5, (b) HEOFe5, (c) HEOAl5 anodes for selected cycles.

In this work (MgCoNiMnLi*X*)O (*X*=Cr, Fe, Al) high entropy oxides were synthesized using conventional solid state method and their electrochemical properties were examined in the lithium-ion coin cell as the anode material. The charge-discharge tests were performed galvanostatically in a potential range change between 0.01 V and 3.00 V (vs. Li$^+$/Li) at 100 mA g^{-1} current density. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 0.1 to 100000 Hz with an amplitude of 5 mV. The HEOs, which have single phase rock-salt crystal structure, have been characterized structurally by using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The galvanostatically measured discharge (reduction)−charge (oxidation) curves of the anodes are given in Figure 1. The initial charge capacities of HEOCr5, HEOFe5 and HEOAl5 are 1046, 1178 and 891 mA h g^{-1}, respectively. The charge capacities of the HEOCr5, HEOFe5 and HEOAl5 anodes are 800, 886 and 702 mA h g^{-1}, respectively at the end of 100th cycle. These results indicate that the electrochemical performances of HEO based anodes can be improved simply by tuning their cation contents.

Acknowledgements

This research was supported by the Scientific and Technological Research Council of Turkey under the project number 219M269.

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Dr. Ersu Lökçü is with the Department of Metallurgical and Materials Engineering, Eskisehir Osmangazi University. Having graduated from Istanbul Technical University in 2012, Ersu Lökçü obtained his Ph.D. in 2020, from Eskisehir Osmangazi University. His research interest covers electrochemical energy storage, nanostructured materials and high entropy materials.

Presentating author: Ersu Lökçü, e-mail: elokcu@ogu.edu.tr tel: 0(222) 239 37 50 - 3705

Supercritical CO_2-Approach to Prepare Lithium-rich Layered Metal Oxide Material for Li-ion Batteries

Ali YALÇIN[1,2*], Muslum DEMIR[3], Solmaz KHANKESHIZADEH[4], Mehmet N. ATES[4], Mehmet GÖNEN[2] and Mesut AKGÜN[1]

[1]Department of Chemical Engineering, Faculty of Chemical and Metallurgical, Yıldız Technical University, İstanbul-TURKEY
[2]Department of Chemical Engineering, Faculty of Engineering, Süleyman Demirel University, Isparta-TURKEY
[3]Department of Chemical Engineering, Faculty of Engineering, Osmaniye Korkut Ata University, Osmaniye-TURKEY
[4]Scientific and Technological Research Council of Turkey (TÜBİTAK), Rail Transport Technologies Institute (RTTI), Energy Storage Division, Kocaeli-TURKEY

Li-rich layered metal oxides (Li-NMC) are widely preferred in applications requiring high voltage and high energy density due to their high electrochemical properties [1]. These materials are used as the cathode electrode in the lithium-ion battery and they are the most expensive part of the battery. Li-NMC materials have been produced by traditional methods such as the co-precipitation method, sol-gel method, ion exchange method and combustion synthesis method. The disadvantages of these methods are the high calcination temperatures and longer calcination times [2]. Other disadvantages are the use of organic chemicals, such as oxalic acid, sodium carbonate, citric acid, ethylene glycol, ethanol and ammonia, etc. utilized during the production of these cathode materials [2]. In this study, the supercritical CO_2-assisted method was investigated for the synthesis of $Li_{1.2}Mn_{0.52}Ni_{0.20}Co_{0.08}O_2$. This method has enabled to decrease in the thermal decomposition temperature of lithium, nickel, manganese and cobalt nitrate salts [3]. Li-rich layered cathode materials synthesized in this study were characterized by using XRD, SEM, EDS and ICP. The electrochemical characterizations were carried out using CR2032 coin cells at room temperature.

Experimental Methods

The $Li_{1.2}Mn_{0.52}Ni_{0.20}Co_{0.08}O_2$ as a cathode material was prepared by using the supercritical CO_2-assisted method. First, a stoichiometric amounts lithium nitrate ($LiNO_3$, +98% wt, Merck), $Mn(NO_3)_2.4H_2O$ (manganese nitrate tetrahydrate) 98.5% wt, Merck, $Ni(NO_3)_2.6H_2O$ (nickel nitrate hexahydrate) 19.7% of nickel assay in mass, Kimetsan) and cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 99.1% wt, Kimetsan) were dissolved and well-mixed with 90 mL of distilled water, subsequently transferred to an autoclave reactor (190 mL). Secondly, CO_2 gas was transferred to the reactor, which was placed in a temperature-controlled water bath on a hot plate equipped with a magnetic stirrer (Wise Stir MSH-20D). Thirdly, the mixture was heated at 80°C, 2 hours with a stirring rate of 300 rpm and the reactor pressure was controlled by the CO_2 tank which was set to 77 bars. The black precipitates were remained after removing the water at elevated temperature [3]. Then, the black precipitates were calcined in an oven (Protherm, PLF 120/5) at a temperature range from 600 to 900°C for 5 hours in an air atmosphere.

Preliminary Results

$Li_{1.2}Mn_{0.52}Ni_{0.20}Co_{0.08}O_2$ material was successfully produced using the supercritical CO_2-assisted method. The charge/discharge performances of LiNMC-900 and B-LiNMC-900 (blind sample without $scCO_2$ utilization) synthesized at the same calcination conditions (900°C, for 5 hours) were shown in Fig. 1. The reversible discharge capacity of LiNMC-900 remains around 221 $mAh.g^{-1}$ at C/10 and around 130 $mAh.g^{-1}$ at 3C, as depicted in Fig. 1. On the other hand, the reversible capacity of the blind sample (B-LiNMC-900), rapidly drops to 210 $mAh.g^{-1}$ at C/10 and to 21 $mAh.g^{-1}$ at 3C. These rate capability results demonstrate that the B-LiNMC-900 exhibits capacity retention of approximately 10.00% while LiNMC-900 shows capacity retention of around 58.82% when increasing from C/10 to 3C. The prelimanry result proves that the SC-CO_2 assisted method has produced better results when compared to the other methods in the preparation of Li-rich layered metal oxides (Li-NMC).

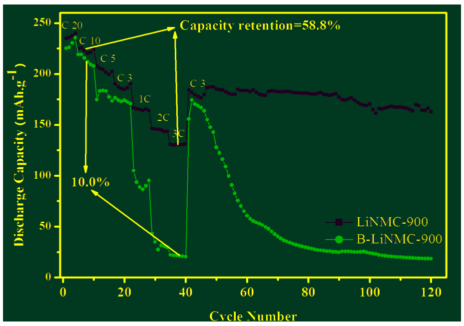

Figure 1. Rate capabilities of B-LiNMC-900 and LiNMC-900.

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The presenting author has worked as a research assistant at the Department of Chemical Engineering at Süleyman Demirel University. He is also a PhD student at the Department of Chemical Engineering at Yıldız Technical University. He has been researching lithium-rich NMC cathode material and investigating of its electrochemical properties.Presentating author: Ali YALÇIN, e-mail: aliyalcin@sdu.edu.tr

Sodium and Niobium co-doped Lithium Titanate as a High Rate Anode for Lithium Ion Batteries

Patat, S[1,2]., Rahman, S[1] and Ülgen, A[1]
[1]Chemistry Department, School of Natural and Applied Science, Erciyes University, Kayseri, Turkey
[2]ERNAM, Erciyes University, Kayseri, Turkey

Graphite has been selected as a commercial anode material for lithium ion batteries. The major problems of graphite are found that the anode requires high current density and incur metallic ion deposition on the surface [1]. Although the other anodes, such as lithium metal and silicon, perform high specific capacity and energy density, the materials react easily with electrolyte, resulting in the unstable surface-electrolyte interphase (SEI). Reactivity between an electrolyte and the anodes originates lithium dendrite. Therefore, the occurance substantially reduces the cycling capability of batteries. To overcome the major drawbacks of the anodes, $Li_4Ti_5O_{12}$(LTO) performs futuristic electrochemical performance such as excellent reversible capacity, good thermal and structural stability providing long durability for insertion and extraction of Li^+ due to zero-strain material or insignificant volume change (~0.2%). In addition, flat charge-discharge potential plateau of LTO at 1.5 V (Li^+/Li) avoids solid electrolyte interphases (SEI) layers and possible lithium dendrit. However, LTO exhibits the low electronic conductivity (10^{-13} S cm^{-1}), caused by lack of electron in 3d orbital [1]. Additionally, the low charge-discharge rate of LTO results from the low lithium diffusion coefficient (10^{-9}-10^{-13} cm^2 s^{-1}), restricting initial columbic efficiency and rate performance. In order to improve the rate capability of LTO materials, some methods such as ionic doping, nanostructuring, and surface coating, have been demonstrated to be an efficient method.

In this study, Na^+ and Nb^{5+} co-doped LTO was synthesized through a simple solid state method. Na^+ is introduced into the main structure to expand the lattice, while Nb^{5+} increases the electronic conductivity during the discharge-charge process. Electric conductivity measurements reveal that the Na^+ and Nb^{5+} co-doped $Li_{3.98}Na_{0.02}Ti_{4.98}Nb_{0.02}O_{12}$ exhibits a higher electronic conductivity than the $Li_4Ti_5O_{12}$, Na^+ doped $Li_{3.98}Na_{0.02}Ti_5O_{12}$ and Nb^{5+} doped $Li_4Ti_{4.98}Nb_{0.02}O_{12}$It is found that the discharge capacity of $Li_{3.98}Na_{0.02}Ti_{4.98}Nb_{0.02}O_{12}$ is higher than those of the un-doped $Li_4Ti_5O_{12}$, Na^+ doped $Li_{3.98}Na_{0.02}Ti_5O_{12}$, and Nb^{5+} doped $Li_4Ti_{4.98}Nb_{0.02}O_{12}$ which indicates the significant synergic effect of Nb^{5+} and Na^+ co-doping on the improvement of the electrochemical performances of $Li_4Ti_5O_{12}$.

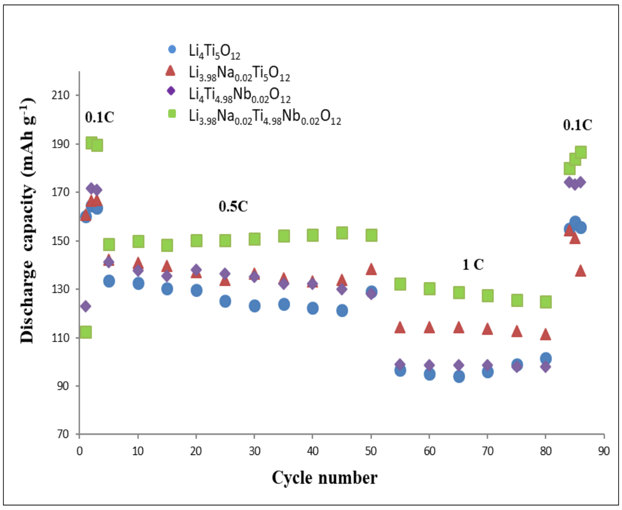

Figure 1. Cycling performances and rate capabilities of the pristine $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_4Ti_{4.98}Nb_{0.02}O_{12}$, and $Li_{3.98}Na_{0.02}Ti_{4.98}Nb_{0.02}O_{12}$ at different charge/discharge rates in CR2032 coin-type half cells (the charge and discharge rate were the same).

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*Şaban Patat is a Professor in the Department of Chemistry at Erciyes University. He received B.Sc degree in Chemistry from Black Sea Technical University in 1982, Master's degree in Inorganic Chemistry from Erciyes University in 1985, and Ph.D. in Solid State Science from Oxford University 1992. He is interested in Li-ion and Na-ion batteries and supercapacitors
Corresponding author: Şaban Patat e-mail: patat@erciyes.edu.tr tel: +90 3522076666 ext: 33162

Electrochemical properties of Ni-rich NMC cathodes for Li-ion batteries

Ahmed M. Faris [1,2], Tuğrul Çetinkaya [2,3,4], Mahmud Tokur [2,3,4] and Hatem Akbulut [2,3,4]
[1]Sakarya University, Institute of Natural Sciences, Nanoscience and Nanoengineering Department, Esentepe Campus, 54187, Sakarya, Turkey
[2]Sakarya University Research, Development and Application Center (SARGEM), Esentepe Campus, 54187, Sakarya, Turkey
[3]Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187, Sakarya, Turkey
[4]NESSTEC Energy & Surface Technology A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Lithium-ion batteries (LIBs) are currently considered to be the most promising candidates to facilitate the shift from internal combustion engines to electric motors due to their high energy and power densities and long cycle life [1]. The specific capacity of LIBs is dependent on the cathode materials used as they control the overall capacity of the cell. $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) materials have become a popular cathode family, and are based on a variety of molar ratios of various oxides of transition metals (TMs). Almost all LIBs today use cobalt a toxic, scarce, and expensive element that harms the environment. For that reason low-cobalt, Ni-rich cathodes are now being developed [2]. NMC811 is a cathode composition with 80% nickel, 10% manganese, and 10% cobalt. It's an improvement of what's on the market already, rather than distinct, novel chemistry [3]. It has a theoretical capacity of 275 (mAh/g) and a practical capacity of approximately 200 (mAh/g) almost 45% higher than the conventional NMC111. However, previous studies have shown that NMC811 is significantly more sensitive chemistry than NMC111 and the production of this material requires not only improved synthetic processes but also additional post-processing steps which increases the manufacturing costs, the reason for this is attributed to the high nickel content [4].

When conducting this study an electrode with 80% NMC811, 10% Carbon black (Super P), and 10% PVDF binder dissolved in NMP was cast onto a pure Al-foil using a doctor blade. The electrode was then dried in a vacuum oven at 80°C overnight. Circular-shaped samples were cut and stored in different conditions for one week before assembling the half-cells for electrochemical testings. The study has shown that NMC811 cathodes tend to be unstable and reactive when left exposed to ambient air with high levels of humidity. And the electrochemical properties were far inferior when compared to samples stored under an inert gas (Argon) as shown in Figure 1. The reason for this loss in capacity is attributed to the formation of impurity species with CO_2 and H_2O when stored in ambient air which leads to the generation of undesirable Li_2CO_3 and LiOH on the surface of NMC811. In this study, we are implementing the use of advanced 2D membrane as a possible solution for this problem by coating the surface of the electrode with materials such as reduced graphene oxide and MoS2 that will play the role of a barrier that protects the electrode from further reacting with the air and enhance the performance of NMC811 batteries.

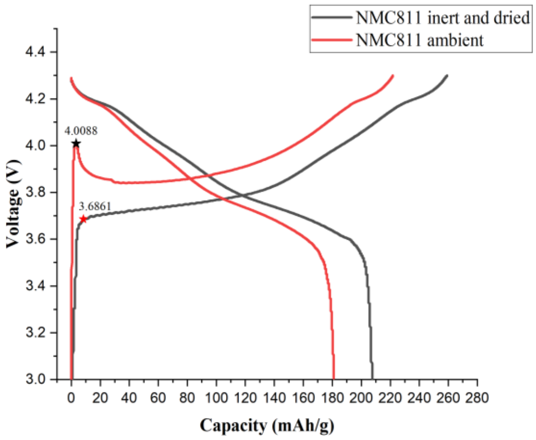

Figure 1. First cycle capacity for two half-cells one stored in Argon-filled glovebox and the other left exposed to ambient air, the test was carried out at a current rate of C/10.

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Ahmed M. Faris is a master's degree student at Sakarya University in Turkey, where he researches and does his experimental studies at the University's laboratories. He graduated with a bachelor's degree in materials science and engineering form the University of Al-Mustansiriyah / Iraq in 2017. His recent works foucs on energy storage systems namely Lithium-ion and Lithium-sulfur battery systems. Over the past two years he has been living in Turkey and he is currently involved in a project that aims to commercialize the use of Lithium sulfer batteries in stationary applications.

Presentating author: Ahmed A. Faris, e-mail: ahmed.faris@ogr.sakarya.edu.tr tel: +905386817197

Synthesis and Performance of Mixed Metal Sulfides as Electrode Materials for Lithium-based Battery Systems

Cansu Savaş Uygur[1,2*] and M. Kadri Aydınol[1,2]
[1] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey
[2] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, Turkey

Acceleration of demand for portable electronics and power electric vehicles increased the studies in rechargeable batteries parallel with the researches to find novel energy storage materials. In this manner, other than oxide-based materials, sulfide-based electrodes have found a place in energy storage materials due to their chemical nature to provide higher capacity for Li-ion batteries. The reason behind the possibility to achieve higher specific capacity from sulfides is their Li-storage mechanism. Unlike many oxides, many sulfide-based materials undergo both intercalation and conversion reactions providing more than one lithium atom storage per chemical formula which increases the specific capacity of a battery. However, there are also some common problems to be solved for sulfides which are their lower conductivity, unwanted interactions with the electrolyte and extensive volume change and voltage hysteresis during charging/discharging [1]. These problems can be solved by coating the active materials, using additives (sulfide additives and other chemistries) and also choosing proper stoichiometries to be avoided from the as-mentioned problems [2].

In the scope of this research, AB_2S_4 type of mixed transition metal sulfides were studied as electrode materials for Li-based batteries. Metal sulfides were synthesized via the microwave-assisted hyrdo-/solvothermal method from nitrate salts of the transition metals and thiourea was used as a sulfur source. Ethylene glycol-pure water mixture was used as solvents and degassing of the solvent with N_2 gas was carried out prior to the hydrothermal process. Synthesized powders were washed with distilled water, absolute alcohol, dried under vacuum at 80 °C and heat-treated at 450 °C for 1 h under N_2 atmosphere.

Phase analysis was carried out by X-ray diffraction (XRD) (Bruker D8 Advance, CuKα radiation, 2θ range of 10-90°, 0.05 step size, 2°/min data collection time). XRD spectrums of as-synthesized and heat-treated $NiCr_2S_4$ powders were given in Figure 1. As can be seen in this figure that as-synthesized powders showed poor crystalline behavior. Although small peaks appeared in the spectrum, complete crystalization was achieved after heat treatment. All peaks of heat-treated $NiCr_2S_4$-ht sample belong to $NiCr_2S_4$ phase with hexagonal ordering (space group P63/mmc, no:194, ICSD collection code 43562).

Elemental analysis was carried out by energy dispersive spectroscopy (EDS) and stoichiometry of the powders stayed unchanged after heat-treatment as expected.

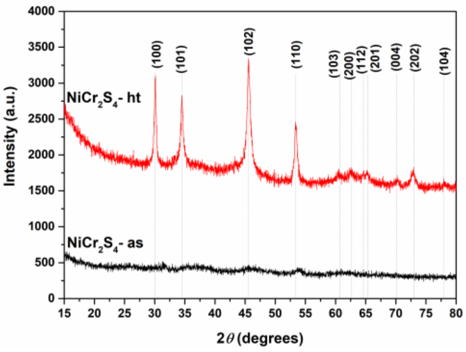

Figure 1. XRD Spectrums of (a) as-synthesized and (b) heat-treated $NiCr_2S_4$ powders.

EDS-mapping was also carried out for both samples and EDS-mapping images were given in Figure 2. As can be seen in Figure 2 that all elements were distributed homogeneously throughout the samples for both as-synthesized and heat-treated powders.

Synthesized powders will be tested as electrodes for Li-based batteries.

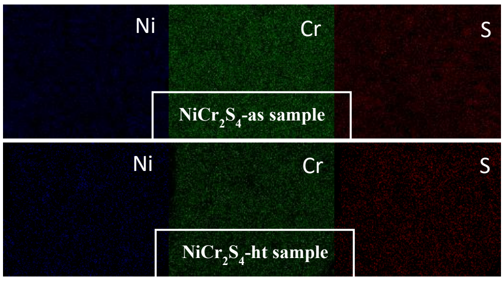

Figure 2. EDS-mapping images of as-synthesized and heat-treated $NiCr_2S_4$ powders.

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Cansu Savaş Uygur

Cansu Savaş received bachelor's and M.S. degrees (Dept. of Metallurgical and Materials Engineering) from Middle East Technical University in 2014 and 2017, respectively. She is now a Ph.D. candidate in the same department and university. She also has been a researcher in ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University since 2016 November. Her research topic mainly covers the structure and electrochemistry of lithium-ion batteries.

Corresponding author: Cansu Savaş Uygur, e-mail: scansu@metu.edu.tr tel: +90 312 210 58 31

Effect of micro-fluidization on the crystal structure and electrochemical performance of layered-oxide cathodes

Semih Engün[1,2], K. Burak Dermenci[1], Umut Savacı[1] and Servet Turan [1,]
[1]Dept. of Materials Science and Engineering, Eskisehir Technical University, 26555, Eskisehir, TURKEY
[2]Dept. of Metallurgical and Materials Engineering, Zonguldak Bulent Ecevit University, Zonguldak, 67100, TURKEY

Layered oxide structured cathode materials have attracted the most attention for the high energy density Li-ion batteries. Li-ions can easily intercalate and de-intercalate into the host atoms thanks to the two-dimensional spaces of the layered structures. Layered cathode materials such as $LiCoO_2$ (LCO), $LiNi_{0.33}Mn_{0.33}Co_{0.33}$ (NMC) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) are used commercially in the Li-ion battery market. However, there are still some limitations that affect the cyclic performance of these materials. In particular, the high rate performance of batteries related to Li-ion diffusion still needs to be further improved. The micro-fluidization process, which is based on passing the material through microchannels at high pressure, is a convenient way for dispersion of nanoparticles and producing nanosheet materials such as graphene and hexagonal nitride boron nanosheets [2–5]. Unlike other techniques, the method also can selectively reduce particle size and allow an oriented structure with a top-down approach. In the present study, we first time subjected the widely used layered oxide cathodes into the micro-fluidization process and obtained an oriented structure. Improving high-rate capacity retention by the size reduction along the c-axis was targeted within this study as Li-ion diffusion occurs along c-direction in layered structured cathodes [1]. The overall micro-fluidization process was described in Figure 1.

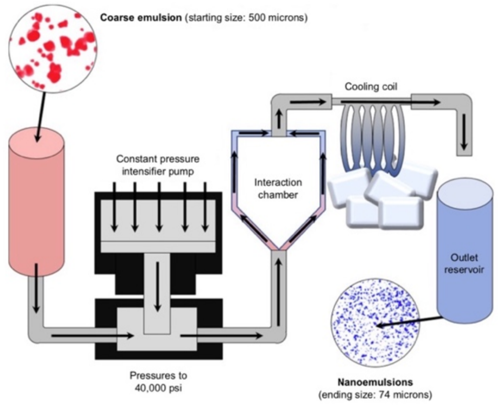

Figure 1. Schematic representation and working principle of the micro-fluidization process.

Commercial LCO, NMC and NCA powders were passed into the micro-fluidizer (Microfluidics Corp.) at constant pressure (207 MPa) for several times. The crystal structure of pristine and micro-fluidized powders was characterized by X-ray diffraction (Rigaku, Miniflex 600). Structural parameters were analyzed by Rietveld refinement (MAUD Software [6]). It was seen that the peak intensity of (003) planes increased of all micro-fluidized cathode powders resulting in the c-axis oriented powders were achieved.

Galvanostatic charge/discharge tests were performed to see the long-term stability and rate capability of pristine and micro-fluidized powders. While micro-fluidization does not help the first-discharge capacity and rate capability of NMC and NCA powders, remarkable improvement was observed for micro-fluidized LCO material. To further explain the reasons behind the improvements, scanning electron microscope (SEM), transmission electron microscope (TEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis were carried out.

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Acknowledgments

Authors acknowledge support from the Eskişehir Technical University Scientific Research Projects Unit with the grant number of 1803F057. Thanks are also to Prof. Dr. A. Tuğrul Seyhan for the use of micro-fluidization equipment.

Semih Engün is a Research Assistant of Metallurgical and Materials Engineering at the Zonguldak Bülent Ecevit University. He received B.Sc. in 2012 and M.Sc in 2016 in the Department of Materials Science and Engineering from Anadolu University in Eskisehir. He is a PhD candidate in the Department of Materials Science and Engineering at Eskisehir Technical University. His research interests include Lithium-ion batteries, solid-state batteries and electron backscattered diffraction (EBSD) techniques.

Corresponding author: Semih Engün, e-mail: semihengun@beun.edu.tr, tel: +90 372 291 19 73.

Ni-Rich $LiNi_xMn_yCo_zO_2$ (x>0.6) Cathode Material Development for Li-Ion Battery via Sol-Gel Method

Mustafa Alp YILDIRIM[1,2] and Kadri AYDINOL[1,2]
[1]Dept. of Metallurgical and Materials Engineering, Middle East Technical University, 06531 Ankara, Turkey
[2]ENDAM, Middle East Technical University, 06800 Ankara, Turkey

Lithium-Ion Battery is one of the most prominent energy storage alternatives for the specific mobile applications like mobile phones and electric vehicles. $LiNi_xMn_yCo_zO_2$ (NMC, x+y+z=1) has been considered as an appealing cathode material among other candidates in terms of its improved stability and electrochemical performance as well as environmental friendliness. In NMC, only Ni and Co are electroactive, while Mn generally functions as a structural stabilizer. The specific capacity of the compound is very much dependent on the Ni content, which adversely affects the structural stability.

The aim of this study is to increase the capacity of NMC cathode active material by increasing the amount of Ni, without much decrease in stability. In that regard, produce NMC with different amounts of Ni, all of which to be considered as a Ni rich composition, i.e, x>0.6.

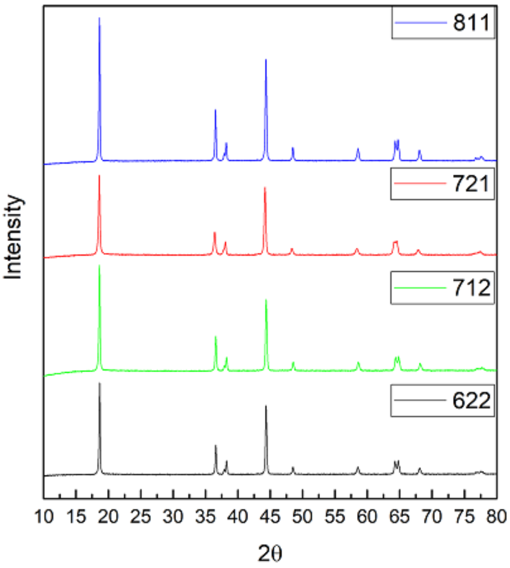

Figure 1. XRD results of NMC 622, 712, 721 and 811.

NMC powders which have ratio of 622, 712, 721 and 811 were synthesized citric acid assisted Sol-Gel method.[1] Nitrate compounds of Lithium, Nickel, Cobalt, and Manganese were used for the precursors. Precalcination process of the powders performed 6 hours at 450 °C. Calcination process performed 24 hours at 850 °C for 622 and 800 °C for 712, 721, 811.

NMC	I_{003}/I_{104}
622	1.244
712	1.360
721	1.142
811	1.346

Table 1. I_{003}/I_{104} ratio of XRD results.

The XRD results of the produced samples which correspond to the NMC structure in the literature have been shown in figure 1. Cation Mixing phenomena which affect to capacity retention can be understanding from I_{003}/I_{104} ratio. According to literature I_{003}/I_{104} ratio must be bigger than **1.2**.

Electrochemical measurements of the cathodes will be done by galvanostatic charge-discharge tests and cyclic voltammetry (CV) to focus on capacity, cycle life, safety and rate capability properties of the active materials. As expected in Table 1, capacity increase with Ni content if $I_{003}/I_{104}>1.2$. On the other hand, 721 capacity was faded.

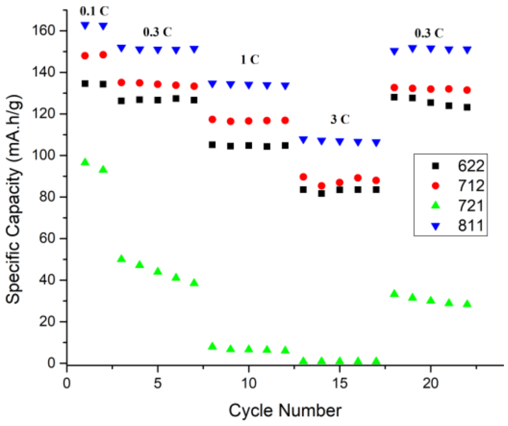

Figure 2. The Graph shows the capacity of NMC 622, 712, 721 and 811.

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Mustafa Alp YILDIRIM is M.S. student in the Department of Metallurgical and Materials Engineering, Middle East Technical University. He has been working as a R&D Engineer at Meta Nikel Co. since 2020. He obtained his BS Degree from TOBB Economy and Technology University, Department of Material Science and Nanotechnology Engineering, in 2017.

Presentating Author: Mustafa Alp YILDIRIM, e-mail: mustafalp.yil@gmail.com, Phone: +905558810528

Production of high C-rate LiFePO4 cathode boosting with Graphene for Li-ion Batteries

Ali Jamal Abdulkareem[1,2], Tuğrul ÇETİNKAYA [1, 2, 3, 4], Mahmud TOKUR [1, 2, 3, 4] and Hatem AKBULUT [1, 2, 3, 4]

[1]Sakarya University, Institute of Natural Sciences, Nanoscience and Nanoengineering Department, Esentepe Campus 54187, Sakarya, Turkey

[2]Sakarya University Research, Development, and Application Center (SARGEM), Esentepe Campus, 54187 Sakarya, Turkey

[3]Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

[4]NESSTEC Energy & Surface Technology A.S., Technology Development Zones, Sakarya University, 54050, Sakarya, Turkey

Wide-spread and extended applications of Li-ion secondary batteries necessitate the development of advanced electrode materials with exceptional electrochemical performances, which mostly depends on the cathode materials [1]. LiFePO4 (LFP) has been extensively considered as promising cathode materials due to its high stability, abundance and environmentally friendliness. Herein, a simple solution combustion technique is developed to prepare single phase LFP material with submicron particles based on the glycine–nitrate process with inexpensive iron (III) as the raw material is introduced. Pure phase LiFePO4 was obtained at an optimal glycine to LiFePO4 ratio of 4:1 [2]. And also it is important to mention that to obtain phase-pure LiFePO4, oxidation of Fe2+ to Fe3+ during the synthesis must be avoided by using inert gas during the pyrolysis process. As revealed in XRD, single phase LiFePO4 is obtained in glycine assisted combustion (G-LFP) and it delivers 102 mA h/g discharge capacity.

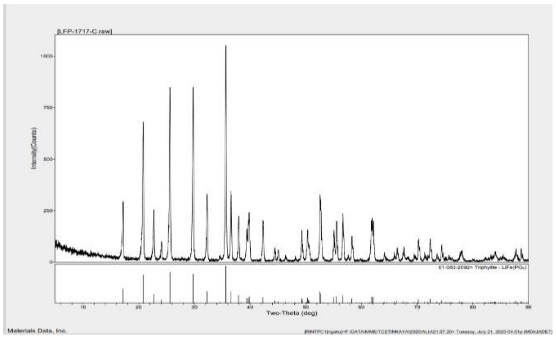

Figure 1. XRD result of pure phase LiFePO4 powder.

LiFePO4 's electrochemical performance is restricted by low electronic and ionic conductivities. This problem can be alleviated by metal ion doping, carbon coating and size reduction. Recently, graphene has become the spotlight in lithium ion battery research because it owns several desirable features, including high surface area and excellent electronic conductivity, for improving the electrochemical performance of LFP.

The presence of graphene oxide (GO), in LFP/GO composite, control the growth and agglomeration, and helps to enhance the electron transport rate in cathodes of LiFePO4, and therefore the capacity increased [3].

The excess capacity is attributed to the reversible reduction–oxidation reaction between the lithium ions of the electrolyte and the exfoliated graphene flakes. The highly conductive graphene flakes wrapping around carbon coated lithium iron phosphate also assist the electron migration during the charge/discharge processes.

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Ali Jamal Abdulkareem is a Master student in Nanoscience and Nanoengineering at Sakarya University / Turkey. he graduated from the Department of Materials Engineering, AL-MUSTANSIRIAYAh University / Iraq in 2016)

Ali Jamal Abdulkareem, e-mail: ali.abdulkareem@ogr.sakarya.edu.tr, tel: +905394642354

Ni-rich $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ nanoparticles / graphene aerogel cathode material for lithium ion batteries

Deniz Kuruahmet, Sıdıka Yıldırım, Hatice Güngör, Aslihan Güler, Mehmet Oğuz Güler, Hatem Akbulut
Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering,
Esentepe Campus, 54187, Sakarya/Turkey

Lithium ion battery (LIB) has many advantages, such as high output voltage, high practical capacity high energy density, long cycle life and low environmental pollution. NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) is a cathode electrode which is made up of $LiNiO_2$ combined with aluminum and cobalt for Li-ion batteries [1]. Co reduces the Li^+/Ni^{2+} cation mixing along with enhancing the structural stability, and, Al effectively improves the structural stability as well as conductivity of Ni-rich layered structure. Despite such improvement, NCA still has the shortcoming of capacity fade during charge-discharge cycling. One of the effective ways to enhance the cycling performance of $LiNiO_2$ based materials have been applied by using graphene. Due to the high electronic conductivity, large specific surface area and excellent structural stability, graphene have been used as conductive nanostructured carbon matrices to improve the electronic conductivity, specific capacity, rate capability and cycling stability of the NCA [2,3].

Thanks to its excellent electron transport properties and high specific surface area, graphene is also of great interest in electrochemical analysis [4]. Three-dimensional (3D) nanoarchitectures can improve the performance of electrical energy storage systems [5]. Ultra-low density and highly porous 3D graphene aerogels (GA) preserve the essential properties of graphene sheets and also prevent re-stacking of individual sheets.

In the present work, we comparatively study the electrochemical characteristics of nanoparticles NCA and NCA/GA. NCA nanoparticles were synthesized by the sol-gel method. The Graphene oxide (GO) solution was initially prepared using a modified Hummers method, followed by reduction with ascorbic acid to form reduction GO layers. Then prepared NCA, into GO solution was dispersed with ultrasonication for 1 h. The resulting hydrogel was first purified in copious distilled water to remove soluble species and then freeze-dried to obtain the graphene aerogel. NCA nanoparticles dispersed in 3D graphene aerogel were successfully synthesized.

The morphologies of the NCA and NCA/GA were imaged by FE-SEM and are illusrated in **Fig. 1** (a), (b). It can be seen that the GA has interconnected three-dimensional porous structures. to investigate structures of nca and NCA/GA, X-ray diffraction (XRD) technique was used and Fig. 1 (c) shows these XRD pattern. The NCA cathodes were investigated by cyclic voltammetric (Fig 1(d)).

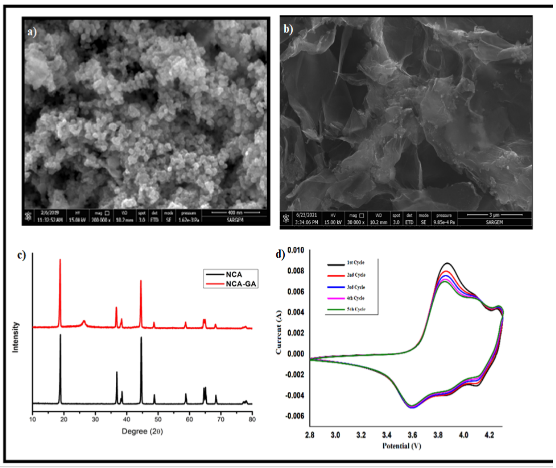

Fig1: (a) FE-SEM image of NCA (b) FE-SEM image of NCA-GA (c)XRD spectra of NCA and NCA-GA d) CV curves of pristine NCA

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Deniz Kuruahmet was born in Istanbul. She graduated from Sakarya University in physics department in 2013. In the same year, she started to study master of science in deperment of metallurgical and materials engineering in Sakarya University and completed her master’s thesis focus on Li-ion batteries in 2017. She is currently a PhD student in Sakarya University. Her research interests are lithium ion batteries and energy storage devices.

Presentating author: Deniz Kuruahmet, e-mail: deniz_nalci@hotmail.com tel: +90 551 234 06 98

Cobalt-free, high-nickel $LiNi_{0.8}Mn_{0.15}Al_{0.05}O_2$ /graphene aerogel composites as cathode materials for lithium-ion batteries

Deniz Kuruahmet, Sıdıka Yıldırım, Hatice Güngör, Aslıhan Güler, Mehmet Oğuz Güler , Hatem Akbulut
Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187, Sakarya/Turkey

Lithium-ion batteries (LIBs) have cornered the energy storage market for portable electronics and electric vehicles (EVs) because of their high energy density for decades [1]. LIB used in electric vehicle applications rely on two main cathode compositions transition metal (TM), layered $LiNi_{1-x-y}Co_xAl_yO_2$, $(x + y <0.2)$ (NCA) and $LiNi_xMn_yCo_zO_2$, $(x + y + z = 1)$ (NMC) [2]. Both NMC and NCA contain cobalt, an expensive and scarce metal generally believed to be essential for their electrochemical performance[3]. Leading battery manufacturers are trying to further reduce their production costs by eliminating cobalt dependence in their cathode materials[1]. Rapidly reducing global cobalt reserves have also fueled a supply chain constraint that is slowly starting to threaten future projections of the electric vehicle market [4]. Thus, it is necessary to develop a stable and high energy density Co-free high-Ni layered oxides through doping and substitution of various elements with a proper amount.

Owing to the superior mechanical property and electrochemical performance, graphene is intensively studied as energy-storage material. However, graphene, stacking by a single layer or more of sp2 hexagonal carbon atoms, exhibits an extremely lower electrochemical capacitance than the anticipated value. To overcome this, one solution is to engineer two-dimensional graphene sheets to three-dimensional (3D) structure [5]. Ultra-low density and highly porous 3D graphene aerogels preserve the essential properties of graphene sheets and also prevent re-stacking of individual sheets.

In this study, $LiNi_{0.8}Mn_{0.15}Al_{0.05}$ (NMA), which is stable in terms of materials science and electrochemistry, does not contain cobalt and has a cheap high Ni ratio, was produced. Nma nanoparticles were synthesised via sol-gel method as a cathode active material. Graphene oxide was synthesized via modified Hummers method. A solution with a solid content of 3 mg mL was prepared by the method. Graphene was prepared using ascorbic acid as the reducing agent. Then synthesized NMA powders were dispersed with ultrasonication. A 3D porous conductive graphene aerogel wrapped $LiNi_{0.8}Mn_{0.15}Al_{0.05}$ nanoparticle composite has been successfully prepared. The designed porous conductive network not only offers plenty of pores to store electrolytes and increase the electrode/electrolyte contact area, but also improves the conductivity of the whole composite, which facilitates rapid diffusion of both Li^+ and electrons and accommodates well the volumetric change during the Li+ insertion/deinsertion process.

The morphologies of the NMA and NMA/GA were imaged by FE-SEM and are illusrated in **Fig. 1** (a),(b). It can be seen that GA has three-dimensional porous structures. **Fig 1**(c) shows EDS EDS Spectra of NMA/ GA/ To investigate structures of nca and NMA/GA, X-ray diffraction (XRD) technique was used and **Fig. 1** (d) shows these XRD pattern.

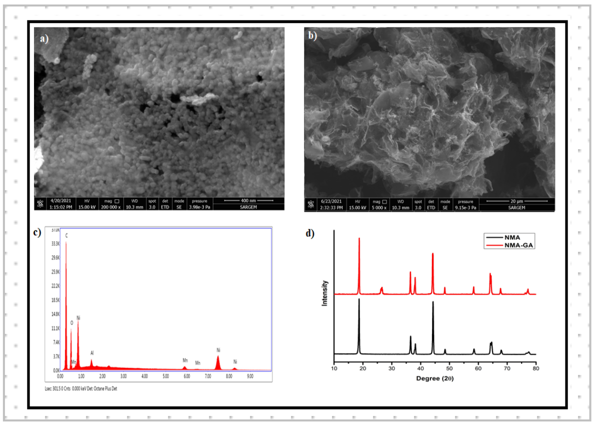

Fig1: (a) FE-SEM image of NMA (b) FE-SEM image of NMA-GA c) Eds pattern of NMA-GA (d)XRD spectra of NMA and NMA-GA.

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Presentating author: Deniz Kuruahmet, e-mail: deniz_nalci@hotmail.com tel: +90 551 234 06 98

Effect of storage on the elctrochemical performanse of $LiMnO_2$

Krum Banov [1,2], , Iliyan Popov [1], Dimka Ivanova [2] and Branimir Banov [1,3]
[1] Institute of Electrochemistry and Energy Systems, IEES, “Acad. E. Budevski”, 1“Acad. G. Bonchev” str. BL10, 1113 Sofia
[2] University of Chemical Technology and Metallurgy – UCTM, bul. “Kl. Ohridski” N:8, 1756 Sofia
[3] European Polytechnical University, EPU, “Ciril and Methodius” str. N:23, 2300 Pernik

The rechargable lithium ion batteries are biggest power supply kind of portable consumer electronics like smartphones and laptops. With the increased demand on more environmentally friendly transport, the usage of electric cars, respectively of lithium ion batteries increase. The performance, price and safty of the lithium ion batteries rely mostly on the cathodes materials. Considerable attention has been paid to the research and development of high capacity, cheap and safe cathode materials for lithium ion batteries. The major breakthrough was made with the patenting of LiCoO2.However, the rising prices of Cobalt and the toxicity, driven the research group in pursuit of alternative materials. The LiMn2O4 and LiMnO2 are promising materials, because they are cheap,have good electrochemistry and enhanced safety. The LiMn2O4 is widely studied material and suffers with capacity loss in the voltage window 3.0V – 4.0V. On the other hand , the has stabile voltage window between 2.0V – 4.5V. [1] with theoretical capacity is 285 mAh/g

The aim of this work is to synthesis $LiMnO_2$ and then to evaluate the influence of the storage on the electrochemical performance on the material. For the synthesis was used sol-gel method. Stoichiometric amounts of $Li(CH_3COO.2H_2O)$ and $Mn(CH_3COO)_2.4H_2O$ and 1:4 molar amount of citric acid were dissolved in water. The mixture was stirred at 80°C until viscous solution is created. Then solution was transferred in furnance and heated at 750°C for 18 h. For the increasing rate of storage of the material, the half of the so synthesized material was put in a glass tube filled with oxygen and put in furnance at 80°C for 6 moths, which could stimulate storage of the material for normal storage of 2 years. For determining the morphology and crystallinity of the pristine and aged samples was used SEM,EDX and XRD. For the estimation of the electrochemical properties of the material, standart electrolyte 1.0M $LiPF_6$ in EC:DMC and 3 electrode cell was used. The galvanostatic and potentiostatic test were carried out in the voltage window of 2.0 V – 4.5V. The electrode fabrication was used the normal doctor blade with cathodic loading of 0,5 mg cm-1. On Fig.1 is shown comparisment between pristine (solid line) and “aged” (dashed) line. The latence parameters of the pristine are A=3,18 Å B=5,31 Å C=5,44 Å and represents C2/m (JCPDS 871255). On the othere hand, the “aged” sample has A=5,32 Å B=5,2 Å C=2,9 Å and represents Pmnm (JCPDS 88034). This structural change could be caused due to unstability of the monoclinic structure [2] or due to storage mechanisum of the material, which is not a part of this study.

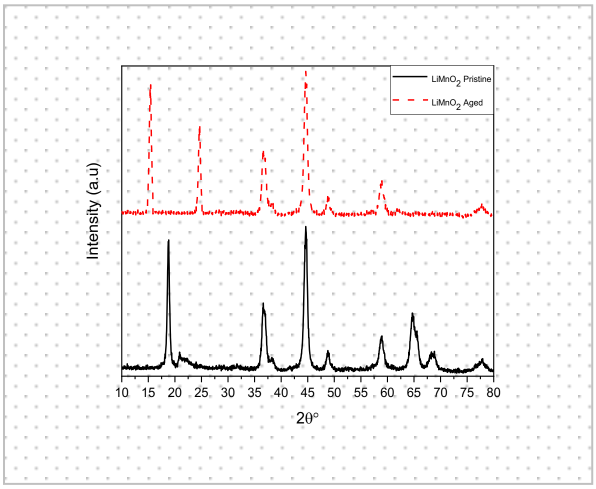

Figure 1. XRD comparisment between pristine and stored (aged)

From the electrochemical point of view both materials have good performance. The pristine material is characterized by higher initial discharge capacity due to its monocline structure. The orthorhombic structure has less capacity fade compared to the monoclin structure. Both materials have enhanced discharge rate capabity compared to other materials contatring Nickel and Cobalt in their structure. [3]

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Krum Banov, MS of Chemical Engineering graduated at University of Chemical Technology and Metallurgy UCTM Sofia on German language, MS of Chemical Engineering of Technischen Universitat Hamburg-Harburg TUHH, assistant at Institute of Electrochemistry and Energy Systems IEES, of Bulgarian Academy of Sciences, PhD student at department of “Inorganic and Electrochemical Products” at UCTM. Involved in R&D and electrochemistry of active electrode materials and catalysts for advanced lithium ion batteries. Presentating author: Krum Banov , e-mail: k.banov@iees.bas.bg tel:+359897803368

Nano Designs for Lithium Battery Anodes

Mahmud Tokur

Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey
Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey
NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Abstract

The increasing use of electronics requires highly effective, flexible, sustainable, and safe energy supply systems. Lithium-based batteries are the most-used energy storage devices due to the larger amounts of energy stored in. However, the energy and power density balances of existing battery systems are still not satisfactory. Electronic conductivity and ionic transport are crucial in enhancing the battery performance. Several approaches have been investigated to modify or replace the electrode materials to enhanced aforementioned properties. Nanomaterials offer great features to overcome widely known problems by enabling the occupation of all intercalation sites available the particle volume. Although these features lead to tolerate high currents and promising solution for high-energy and power density, the nature of the electrode materials allow limited supply for greatly developed electronics.

Here in this review, it will be discussed the nano designs from conventional anodes to next generation anodes for lithium-based batteries.

1.Introduction

Supported by modern battery engineering, the conventional Li-ion battery chemistries are close to their theoretical limits. At the same time, new approaches on the battery systems have also been developing to exceed these limits.

Positive electrodes, also known as cathode, are usually the main contractor in increasing capacity in a battery. Besides, the negative electrode sides, called as anode, are mostly vital in contributing energy density and stability. Synergistic effect of the electrochemical reactions between anode and cathode cannot be ignored either [1].

Recently, cathode architectures have been evolving from metal oxide-based electrodes to sulfur-based electrodes to obtain higher capacity and lower cost. Whereas the anode architectures seem to have not found its course exactly yet. Although, the story of the negative electrode has started with lithium metal at the beginning, however, it has continued on graphite for a long time due to many important safety concerns. Despite all the challenges, indispensable charm of lithium metal has been continuing to keep it on the agenda. At the same time, the attraction of anodes such as silicon, which provides high capacity but have many challenges, extends the alternatives [2].

2. Historical Change of Lithium Ion Battery

Lithium-ion batteries have been commercialized by Sony in 1991 with the combination of $LiCoO_2$ cathode and Graphite anode materials [3].

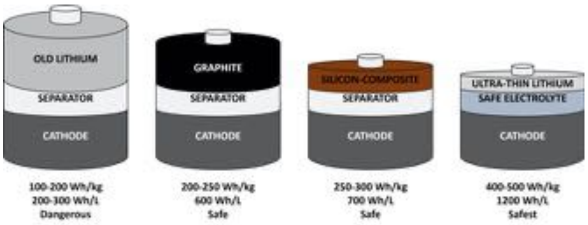

Figure 1. Evoulation of Lithium Ion Battery Concepts

Actually, there were a lot of efforts to commercialize lithium metal before graphite. Because, without any doubt, lithium metal is one of the most attractive candidates as an anode material for lithium ion batteries due to its high theoretical specific capacity (more than 3000 mAh/g) and lightest weight, and great conductivity. However, the practical application of lithium metal was seriously hindered by some safety concerns and left as experimental laboratory studies before 1991. Historical changes of the anode materials of the current lithium ion battery technology is given in Figure 1. With the continuously increasing environmental concern, graphite based lithium-ion batteries with high-energy density and long cycle life have become a key enabling technology for sustainable, clean, and efficient energy supply [4]. Graphite is the most densely used commercialized anode material with 372 mAh/g theoretical specific capacity in lithium-ion batteries [5]. Because, it has many advantages such as a flat and low voltage range

Mahmud Tokur

Mahmud TOKUR was born in Istanbul, Turkey. He received his B.S, M.S and PhD degree in Metallurgical and Materials Engineering Department from Sakarya University in Turkey. He has worked as a visiting researcher at Brown University, USA, in 2018. His academic carrier is carrying on as an Assist. Prof. Dr. in Sakarya University. Besides, he is one of the Co-Founder of NESSTEC Energy and Surface Technologies AS since 2020. His current researches focused on new architectured electrode and novel electrolyte materials on Li-ion, Li-air and Li-S batteries.

Corresponding author: Mahmud TOKUR, e-mail:mtokur@sakarya.edu.tr tel: +90 539 967 62 65

with high reversibility and natural abundance and low cost [6]. However, this very limited capacity of graphite cannot meet high and increasing energy demands of new technology market including advanced portable electronic devices and electric vehicles. Therefore, it is urgent to find alternative electrode materials that are the central components of lithium-ion batteries and largely dictate their ultimate performance [7]. Thus, alternative strategies have been developed to catch up with the progress in the market. Researchers have been working on new and nanostructured materials with higher lithium accommodation (that means higher specific capacity) capability such as Aluminum (Al) [8], Germanium (Ge), Antimony (Sb) [9], Tin (Sn) [10], and Silicon (Si) [11] to replacing the graphite anode. Among them, silicon is the most attractive and promising candidate electrode material for lithium ion batteries owing to its highest known theoretical specific capacity of~3579 mAh/g (almost ten times higher than that of commercialized graphite) and its natural abundance on earth crust. But the practical application of using silicon anode is not so easy because of huge volume changes (~300%) due to the increasing accommodation of Li+ upon lithiation. This problem leads to rapid capacity fading and loss of electrical contact in the electrode [3]. The common problems of the silicon anode related with volume change has summarized in Figure 2.

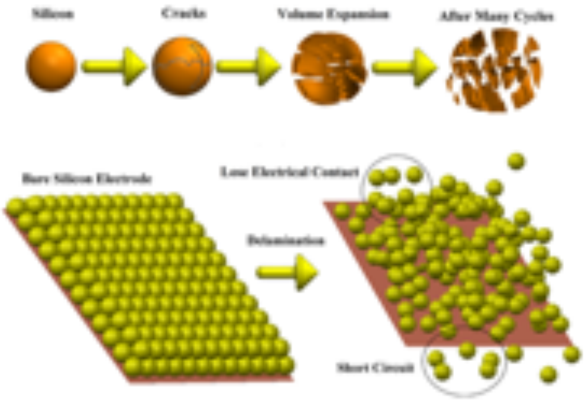

Figure 2. Relation of Silicon Anode and Lithiation Reactions [3]

3. Overview of Nanomaterials Platform

Nanomaterials with special structures can change the paradigm for energy storage with the help of large electrochemically active surfaces that occur orders of magnitude faster and allow a greatly improved power and cycle life. In other words, sizes, morphologies, and structures are strongly affect to the electrochemical performances of the electrode materials. Thus, many efforts have been devoted to designing novel nanostructured electrode materials. This can not only offer high electronic and ionic conductivity but also provide good structural and mechanical integrity [1].

In this context, carbonaceous materials, such as carbon nanotubes, carbon nanofibers, amorphous carbons, and graphenes have been used widely to tackle the aforementioned issues even in using nanomaterials structures.

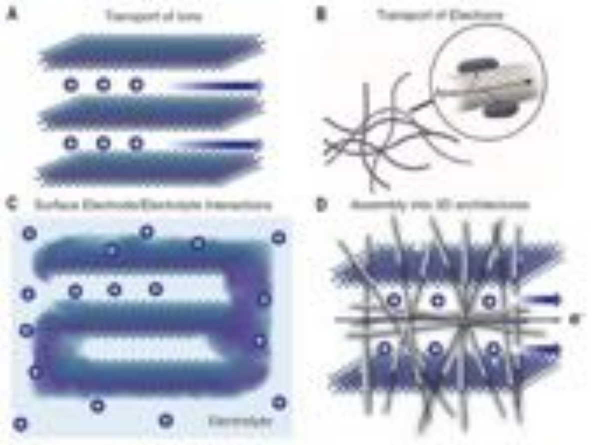

Figure 3. Fundamental properties governing the performance of nanostructured materials for energy storage application. (A) Transport of ions. (B) Transport of electrons. (C) SEI formation and parasitic reactions between electrode and electrolyte. Blurry areas represent reaction products, such as SEI. (D) Connectivity and transport in 3D space [1].

Pomerantseva et all. [1] have illustrated the hybridization of dissimilar nanomaterials with the combination of oxide nanoparticles and carbons that maximizes heterointerfaces and shown in Figure 3. They also stated that different work functions of carbons and oxide nanoparticles led electrons to be injected from the carbon into the oxide, increasing the electrical conductivity of the latter.

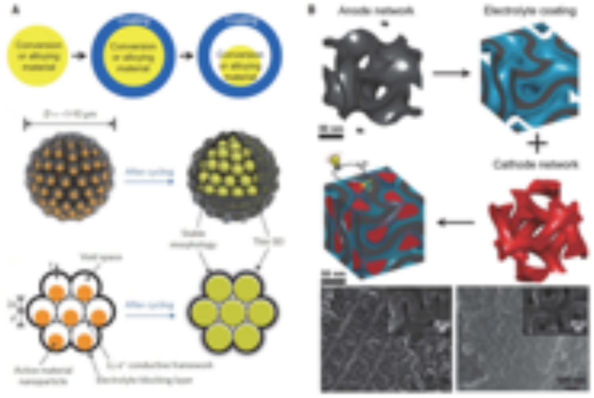

Figure 4. Strategies developed to overcome performance limitations of nanomaterials in energy storage applications. (A) Nanoscale coatings on the surface of conversion and alloying electrode materials need to avoid mechanical instability caused by large-volume change and loss of the surface area as a result of agglomeration [12]. D, diameter of pomegranate microparticle; t, thickness of the conducting framework; 2a, void dimension; d, diameter of the active material primary particles. (B) Nanostructured 3D electrode architecture can be realized through a scalable block-copolymer self-assembly process [13, 1].

Therefore, the synergistic effects between different nanomaterials are reported to be achieved by combining materials with different properties. This effect is shown in Figure 4. According to the presented study, core-shell, and new architectured yolk-shell structures can help to improve the battery performance by acting as a buffer layer via protecting the mechanical integrity and reducing the internal stress. In addition, the strong and flexible 3D network can assists the charge transfer and contribute the electrochemical performance. Finally, it can block the ultra electrolyte diffusion to control the SEI formation on the surface of electrode.

4. Future Prospect of Lithium-Based Batteries

After 30 years left of commercializing lithium-ion batteries, researchers are still considered using lithium metal as the most attractive approach to develop advanced Li-metal batteries due to possessing an extremely high theoretical specific capacity (3860 mAh/g) and the most negative electrochemical potential (−3.04 V vs the standard hydrogen electrode) [14]. Some new strategies have been developed to overcome the still ongoing problems such as liquid electrolyte engineering, solid electrolytes, Li-metal hosts, and artificial SEIs (ASEIs) which can be finely designed and tuned to address the above-mentioned drawbacks as favorable Li morphology for safe, energy-dense, and long-cycling Li-metal batteries.

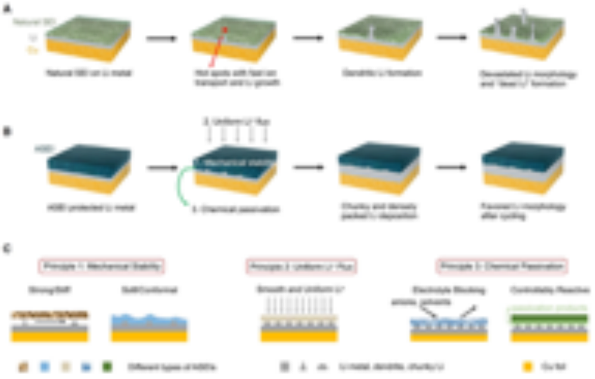

Figure 5. Conceptual Schemes of Design Principles for ASEIs (A and B) Scheme of the Li-metal morphological evolution with cycling under natural SEI (A) and ASEI (B). (C) Conceptual scheme showing 3 key properties of ASEIs and the corresponding approaches for each point. Principle 1: mechanically strong ASEIs suppress dendrites with high modulus, while soft coatings conformally adapt the surface fluctuation during cycling. Principle 2: uniform and fast Li+ flux across the ASEIs enables non-dendritic growth. Principle 3: completely blocking the electrolyte from contacting Li reduces the side reactions, while controllable reactions between coatings and Li generate a favorable interfacial layer to mitigate further Li corrosion [15].

Yu et all. [15] have developed SEI designs and they categorized and elaborated in their rewiev in Figure 5. It has well reported that these structures can suppress dendrites with high modulus, while soft coatings conformally adapt the surface fluctuation during cycling (Principle 1). They also presented uniform and fast Li^+ flux across the ASEIs enables non-dendritic growth (Principle 2). Finally, it is observed completely blocking the electrolyte from contacting Li reduces the side reactions, while controllable reactions between coatings and Li generate a favorable interfacial layer to mitigate further Li corrosion (Principle 3).

Zhai et all. [14] designed diffent strategy to achieve superior performance with containing lithium metal electrode. They have developed a 3D architecture is constructed with g-C_3N_4/graphene/g-C_3N_4 insulator–metal–insulator sandwiched nanosheets to guide uniform Li plating/stripping in the van der Waals gap between the graphene and the g-C_3N_4, and the function of which can be regarded as a 3D artificial SEI. Figure 6 shows their unique design for future lithium ion batteries.

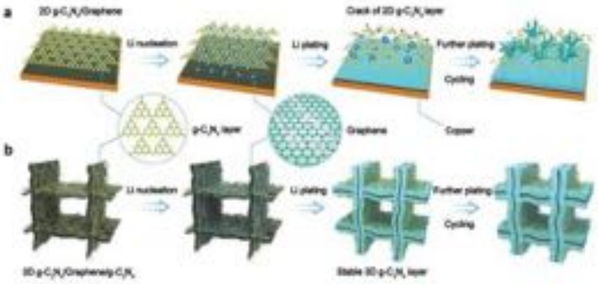

Figure 6. Illustration of Li deposition in the van der Waals gap between graphene and g-C_3N_4. a) Li deposition on the 2D g-C_3N_4/Graphene electrode. As a result of large volume change and high local current density, the 2D artificial C_3N_4 layer tends to crack during cycling, which therefore exposes Li to electrolyte and induces Li dendrites formation. b) Li deposition on the 3D g-C_3N_4/G/g-C_3N_4 electrode. 3D structure effectively accommodates the volume change and reduces the local current density. The 3D artificial g-C_3N_4 layer with a high homogeneity modulates conformal Li deposition in the van der Waals gap between g-C_3N_4 and graphene [14].

According to their results, high Coulombic efficiency for Li metal anodes without dendrite growth was achieved. They have reported that this design takes advantages of the high homogeneity and good stability of artificial SEI and the low local current density and good adaptability of the volume change of 3D host, promising for practical application of Li metal-based batteries.

5. Conclusion

After commercialized the lithium ion batteries, numerous efforts have been taken in both academia and industry to obtain high capacity, high energy density, high safety and high cycleability. While the use of nanomaterials in commercial devices is very attractive, it also presents many challenges. Several nanostructuring examples have been demonstrated in this review which led to breakthroughs in performance.

According to the presented results in this study, it is believed that nanostructured materials can provide solutions to create high-energy, high-power, and long-lasting energy storage devices.

Acknowledgement

This work is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the contract number 120N492. The authors thank the TUBITAK workers for their financial support.
The authors also thank to TUBITAK TEYDEB-BIGG-1512 program for their financial support under the contract number 2190317.
This work is also supported by Research Fund of the Sakarya University under the project no: 2019-6-22-251 and 2019-5-19-265.
This work also receives funding from the European Union´s Horizon 2020 research and innovation program (under the grant agreements no. 100825) under the scope of Joint Programming Platform Smart Energy Systems (MICall19).

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High Performance Electrospun Anatase/Poly(3,4-Ethylenedioxythiophene) Polystyrene Sulfonate-based Anodes for Li-ion Battery

Vahid Charkhesht[1], Alp Yürüm[2], Selmiye Alkan Gürsel[1,2] and Begüm Yarar Kaplan[2]

[1] Sabancı University, Faculty of Engineering and Natural Sciences, 34956, Istanbul, Turkey
[2] Sabancı University Nanotechnology Research and Application Center (SUNUM), 34956, Istanbul, Turkey

Among the other type of rechargable batteries, Li-ion batteries (LIBs) as one of the pioneers has become an intrinsic part of almost all the electronic devices. Recently, the demand for LIBs with high energy and power densities has been gradually increased. To achieve the demands of current technology, novel electrodes with higher capacities, and longer working life must be developed [1].

In recent years, electrospinning is frequently used to produce nanomaterials especially in the field of energy including solar cells, fuel cells, lithium-ion batteries, lithium sulfur batteries, supercapacitors, etc. [2]. Electrospinning is also a promising technique for creating nanostructured 3D nanofiber based electrodes with high gravimetric, areal, and volumetric capacities [3]. By means of nanofiber based materials, the electrochemical performance of electrodes can be improved thanks to the enhancement of connection of the electrolyte with active material by increasing voids to facilitate the Li^+ transference. This technique has lots of advantages to build up the nanofiber based electrodes used in LIBs for instance; simple, scalable, and cost-effective as well.

In this work, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS):poly(ethylene oxide) (PEO) polymer mixture used as carrier of electrospun TiO_2/CB-based anode. Due to the low viscosity of PEDOT:PSS solution, another carrier polymer with high molecular weight, PEO, was added to electrospinning ink to increase the viscosity and make the electrospinning process viable. A systematic optimization was performed to achieve the homogeneous ink composition and finally nanofibers with homogeneous particle distribution. The parameters include, PEO/PEDOT:PSS ratio, content, solvent type, and PEO molecular weight besides the operational parameters like operational voltage, needle to collector distant, polymer feeding rate and relative humidity. XRD, RAMAN, FTIR, TEM and FE-SEM techniques were used to characterize the electrodes. Figure 1a shows the typical morphology of electrospun fibers, and TEM images confirms homogeneous particle (TiO_2 and CB) distribution along the fiber (Figure 1b).

After electrode fabrication, electrochemical tests including galvanostatic charge/discharge, cyclic voltammetry, and electrochemical impedance spectroscopy were performed.

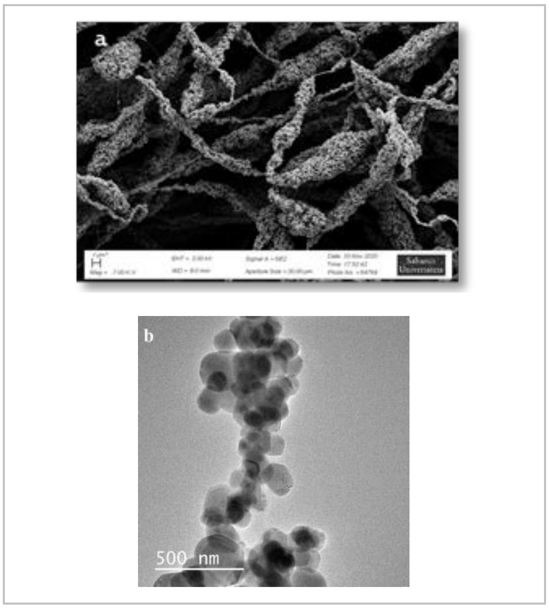

Figure 1. a) SEM micrograph and b) TEM image of TiO_2/CB/(PEDOT:PSS):PEO nanofibers.

Presence of PEDOT:PSS assists the anode performance by: i) improved conductivity and ii) increased capacity due to the electrochemical activity of the binder/carrier polymer. Not only the achieved areal capacity (1.67 $mAh.cm^{-2}$) was comparable to the other studies, but also the gravimetric capacity (300 $mAh.g^{-1}$) was much higher than similar studies. These results are very promising for the next generation electrospun LIB anodes fabricated using PEDOT: PSS as a binder/carrier.

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Begüm Yarar Kaplan is currently researcher at Sabancı University Nanotechnology Research and Application Center (SUNUM). She earned her bachelor degree at Hacettepe University, Chemistry Department in 2010, master degree at Polymer Chemistry in 2013, and PhD in Materials Science and Engineering Department from the Sabancı University in 2017. During her PhD, she conducted research on electrospun electrodes for PEM fuel cells at Vanderbilt University, USA (2016). Her current research interests are electrospun membranes and electrodes for energy conversion and storage systems.

Presentating author: Begüm Yarar Kaplan, e-mail:begumyarar@sabanciuniv.edu

Spinel-structured type high entropy oxides as anodes for lithium-ion batteries

Deniz Okan Bayraktar [1], Ersu Lökçü[3], Çiğdem Toparlı[1,2]
[1]Middle East Technical University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Ankara, Turkey
[2] ENDAM, Center for Energy Materials and Storage Devices, Middle East Technical University, Ankara, Turkey
[3] Eskisehir Osmangazi University, Department of Metallurgical and Materials Engineering, Eskisehir, Turkey

Amongst the various anode candidates for Li-ion batteries, the conversion-type transition metal oxide anodes attract great attention due to their promising capacities between 500 and 1000 mA h g^{-1}. Therefore, many studies in the literature have been focused on the adjusting the structural properties such as morphology, size, and defect formation of these transition metal oxides in order to solve their fundamental problems which are low Coulombic efficiency (CE), unstable solid electrolyte interface (SEI) film formation, large potential hysteresis, and poor cycling and rate capability. A recent important development in this field has been the realization of potential utilization of high entropy oxides as anode materials for Li-ion batteries. High entropy oxides possess unprecedented structural characteristics, tailorable chemical composition and thus tunable functional properties which draw tremendous interest in the fields of environmental science and renewable energy technology. For instances, rock-salt-structured type of high entropy oxide $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ material has been investigated and higher specific capacities compared to graphite have been reported[1-5]. Motivated by these results, various type of high entropy oxides has been investigated in more detail as anode materials for Li-ion batteries. Among these diverse crystal structures in high entropy oxides, spinel structure allows 3-D pathway for lithium transport, while rock-salt-structured type of high entropy oxides would allow 2-D pathway for ionic lithium transport. It is known that 3-D pathway for ionic lithium transport would foster the Li-ion migration and thus high cycling and rate performance [6,7].

In this work, we have investigated the spinel-structured type of new $(Fe_{0.2}Co_{0.2}Mn_{0.2}Cr_{0.2}Zn_{0.2})_3O_4$ high entropy oxide (S-HEO) as anode materials for Li-ion batteries. The S-HEO was synthesized through co-precipitation method. Structural and morphological characterizations of S-HEO were performed through X-ray diffraction (XRD) and scanning electron microscopy (SEM). Cyclic voltametry, electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) were applied in order to evaluate the Li diffusion kinetic. Results show that the Li diffusion kinetic of S-HEO is enhanced when comparing to it's corresponding single transition metal oxides due to high-entropy stabilization chemistry.

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Deniz Okan Bayraktar obtained his B.S degree in Chemical Engineering at Middle East Technical University in 2021. He is currently pursuing M.S. degree in Metallurgical and Materials Engineering at Middle East Technical University in the Laboratory for Electrochemical Energy Materials. His research focusses on designing next-generation materials for electrochemical energy storage and cell design for lithium-ion batteries.

Presentating author: Deniz Okan Bayraktar, e-mail: bayraktar.okan@metu.edu.tr, tel: +90 546 929 0919

Anodes for Li-ion batteries based on silicon monoxide carbonized with fluorocarbon

Darina Lozhkina, Ekaterina Astrova, Alexander Rumyantsev and Alesya Parfeneva
Ioffe Institute, 194021, Russia, St. Petersburg, Polytechnicheskaya street 26

The recently proposed new simple method for carbonization of nanosilicon by reacting it with polymer carbon monofluoride $(\mathrm{CF}_x)_n$ [1] was used to form carbon composites based on silicon monoxide SiO/C. A mixture of SiO and $\mathrm{CF}_{0.8}$ powders was subjected to compression and subsequent annealing of the resulting tablets in an inert atmosphere at T = 800-1150 °C for 1 hour.

$$\mathrm{SiO} + 5\mathrm{CF}_{0.8} = \mathrm{SiF}_4\uparrow + 4\mathrm{C} + \mathrm{CO}\uparrow \tag{1}$$

With an excess of SiO, a porous composite with a carbon shell and an electrically conductive framework is formed. Under the annealing at T>1000°C simultaneously with the carbonization occurs disproportionation of silicon monoxide:

$$2\mathrm{SiO} = \mathrm{Si} + \mathrm{SiO}_2 \tag{2}$$

It results in formation of silicon precipitates and a change in the composition of the SiO_x matrix (d-SiO) [2]. At higher temperatures T>1150°C, silicon carbide is sintesized, including in the form of whiskers [3].

$$3\mathrm{SiO} + 5\mathrm{CF}_{0.8} = 2\mathrm{SiC} + \mathrm{SiF}_4\uparrow + 3\mathrm{CO}\uparrow \tag{3}$$

In the presented work, the electrochemical performance of anodes based on composite SiO/C material were investigated depending on the composition of the initial mixture and the annealing temperature. Galvanostatic incorporation of lithium into SiO/C electrodes (charge semi cycle) was limited to a voltage of 10 mV, extraction (discharge) with a voltage of 2 V. The optimal concentration for stable SiO/C electrodes was found to be 40-50 *wt* % SiO. The specific capacity of these electrodes is 600-700 mAh/g at a current density of 10 mA/g. It was revealed that an increase in the annealing temperature up to 1050°C leads to an increase in the discharge capacity from 450 to 790 mAh/g due to formation of d-SiO. It is followed by increase of the charge/discharge rate (Fig. 1) and the coulumbic efficiency of the first cycle.

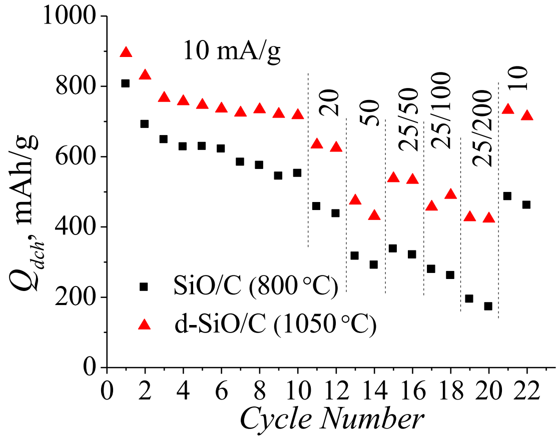

Fig. 1 Discharge capacity of SiO/C (800°C) and d-SiO/C (1050°C) anodes at different charge/discharge currents for 40 *wt*% SiO

For annealing temperatures T≥1100 °C at the first charge, the voltage quickly drops to the set limit of 10 mV, and the electrode does not gain capacity. It was found that the electrodes can be charged by decreasing the charging current in the first cycle. Then, on subsequent cycles, they are able to operate at higher values of j.

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Darina Lozhkina received her master's degree from the Department of Chemistry of Substances and Materials, Saint-Petersburg Institute of Technology. Now she is a PhD student at the Ioffe Institute. Her research interests are focused on silicon-based nanomaterials for application in lithium-ion batteries.
Presentating author: Darina Lozhkina, e-mail:darina.lozhka94@gmail.com

Nano Silicon Powder Reinforced Carbon Anodes for High Capacity Lithium Ion Battery

Salman Ahmad[1], Mahmud Tokur[2], Tugrul Cetinkaya[3], Hatem Akbulut[4]

[1]Sakarya University, Institute of Natural Sciences, Nanoscience and Nanoengineering Department, Esentepe Campus 54187, Sakarya, Turkey
[2]Sakarya University Research, Development, and Application Center (SARGEM), Esentepe Campus, 54187 Sakarya, Turkey
[3]Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey
[4]NESSTEC Energy & Surface Technology A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Abstract: Storage devices are the best alternatives to the increased energy demand around the world. The potential usage of Li-ion batteries in electric vehicles, Solar panels, cellular phones, laptops and many other electronic devices are inspiring but lacks improved power and energy density in high power applications. In this regard, the choice of electrode material greatly effects the performance of the battery. Typically, graphite is considered as a preferred anode candidate, but its low specific capacity limits its uses and alternatively, Silicon (Si) may offer the best theoretical capacity. The current study aims to attain a Nanocomposite anode material by adding different quantities of nano silicon powder into a graphite slurry to increase the specific capacity of graphite. The optimized Nanocomposite anode has utilized as an anode material against lithium to determine the capacity in a half cell system. Furthermore, using an 8-channel Battery Testing System and Data Analysis (BTSDA), the electrochemical characterization for different current rates (C/10, C/5, C, 2C) is performed. Our analysis revealed that by increasing Si content [5%, 10%, and 15%], the discharge capacity increased and remained stable with different iterations. On the other hand, higher current rates causes instability and quick capacity decline. Conclusively, the addition of Si into a graphite has shown an enhanced capacity compare to bare graphite. Furthermore, examining the optimal current value and voltage window of anode material needs to be investigated to determine its potential use for different purposes.

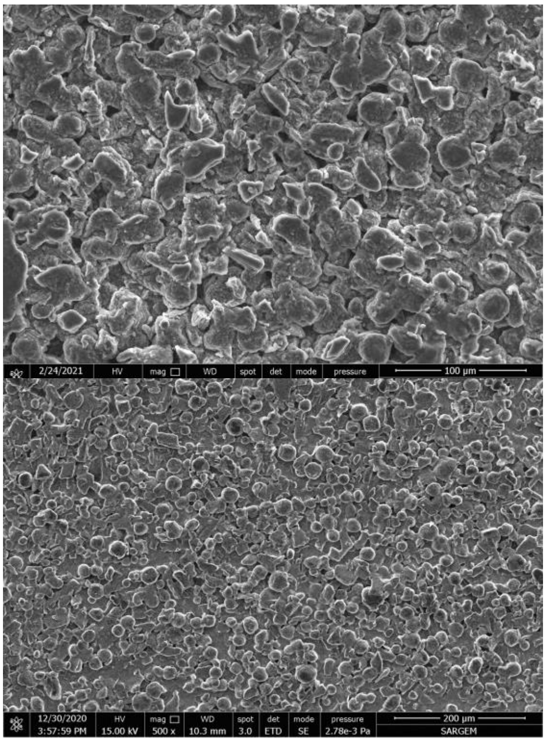

Figure-1 SEM images before and after electrochemical testing

Mr. Salman Ahmad, is a Master degree student at the Department of Nanoscience & Nanoengineering, Institute of Natural Sciences, Sakarya University, Turkey. His research interests include developing electrode materials for Li-ion batteries. Currently, he is working on producing high capacity Nano composite anode material.

Presentating author: Salman Ahmad, e-mail: salman.ahmad@ogr.sakarya.edu.tr, tel: +905388968248

Peach stone supported Fe_3O_4 particles for environmental friendly anode for Lithium – ion batteries

Krum Banov [1,2] , Iliyan Popov [1], Simeon Stankov [1], Ofeliya Kostadinova [1] and Branimir Banov [1,3]
[1] Institute of Electrochemistry and Energy Systems, IEES, “Acad. E. Budevski”, 1“Acad. G. Bonchev” str. BL10, 1113 Sofia
[2] University of Chemical Technology and Metallurgy – UCTM, bul. “Kl. Ohridski” N:8, 1756 Sofia
[3] European Polytechnical University, EPU, “Ciril and Methodius” str. N:23, 2300 Pernik

Lithium ion batteries are the dominating electrochemical system for energy storage, as well as their usage in portable electronic devices. In the recent years, their usage in electric cars increased due to companies like Tesla. The majority of the lithium batteries, are using anode materials based on one exchange electron reaction, which could not not bring the neccesary discharge capacity and volumetric density for the next generation batteries. New class of anode materials with increased electron exchange reaction attracks more attention. A typical example is Fe_3O_4, which is cheap,abundant and environmental friendly. With its electrochemical reaction

$$Fe_3O_4 + 8Li^+ + 8e^- \rightleftharpoons 3Fe^0 + 4Li_2O \qquad (1),$$

which leads to theoretical capacity of 924 mAh/g [1] . Unfortunately the pure Fe_3O_4 suffers from poor cyclability, which leads to different strategies for increasing it. One the most common is the introduction of carbon as a carrier for the Fe_3O_4 particles[2] .

The aim of the current work is to synthesis Fe_3O_4 supported by carbon carrier, which synthesized from peach stones. Peach stones were collected from locally bought peaches and subsequently dried for three days in ambient air. The dry peach stones were milled down to size of 100 µm , transferred into an alumina boat and calcinated in a tube furnace at 700 °C for 8 hours under argon atmosphere with a heating rate of 5 °C min^{-1}. Impurities were removed by washing the obtained black powder three times with copious amount of aqueous hydrochloric acid ($HCl:H_2O$ = 1:1). Afterwards, the powder was soaked for 4 h with an aqueous solution (25 wt.%) of the iron precursor, iron chloride ($FeCl_3$, 99.9%, Sigma Aldrich) and then dried for 2 h. The soaking and drying was repeated once again prior to another calcination step under oxygen, directly pumped into the tube furnace for reduction of the carbon quantity performed at 700 °C for 3 hours. The obtained catalyst Fe_3O_4/C was rinsed with deionized water and dried for 6 h at 120 °C. Brunauer–Emmett–Teller, XRD, SEM and EDX were carried out for determinatiung the pore distribution, morphology and crystalinaty. For the estimation of the electrochemical properties of the material, standart electrolyte 1.0M $LiPF_6$ in EC:DMC and 3 electrode cell was used. The electrode fabrication was used the normal doctor blade with cathodic loading of 1,6 mg cm^{-1} The galvasnostatic and potentiostatic test were carried out in the voltage window of 0,05V – 3.0V. Fig .1 shows the cycling voltammetry, which presents good overlapping of the cycles after creation of stable SEI film in the first cycle.

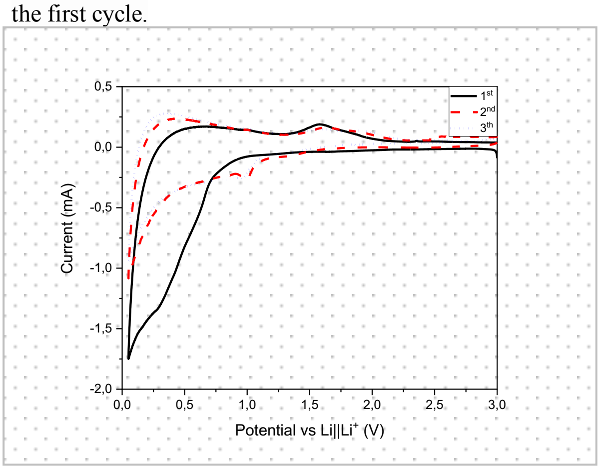

Figure 1. CV Diagram of Fe_3O_4/C

The galvanostatic measurements show discharge capacity of 1400 mAh/g during cycle and 800 mAh/g retained capacity during the cycling. The material shows good discharge capacity by different discharge rates, which indicates for the supportive function of the carbon carrier. The efficiency and the capacity retention are sufficient, which is another evidence for the enhanced electrochemical performance of the material. By lower discharge rates (1 A/g), the material shows good cycling stability and enhanced efficiency, proof for it’s performance. Thanks to its cheap price, abundant and environmental friendly composition, the material could ensure alternative to the conventional cathode materials.

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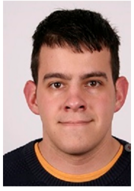

Krum Banov, MS of Chemical Engineering graduated at University of Chemical Technology and Metallurgy UCTM Sofia on German language, MS of Chemical Engineering of Technischen Universitat Hamburg-Harburg TUHH, assistant at Institute of Electrochemistry and Energy Systems IEES, of Bulgarian Academy of Sciences, PhD student at department of “Inorganic and Electrochemical Products” at UCTM. Involved in R&D and electrochemistry of active electrode materials and catalysts for advanced lithium ion batteries. Presentating author: Krum Banov , e-mail: k.banov@iees.bas.bg tel:+359897803368

Silicon/Lithium Alloy Anode Material for Lithium Sulfur Batteries

Muhammed Osman Numan Oğuz,[1,2] Hatem Akbulut,[1,2,3] Mahmud TOKUR[1,2,3]

[1]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey
[2]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey
[3] NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Lithium ion batteries has high capacity, high energy density and long cycle life. However, current lithium ion batteries have not meet the demand of constantly evolving technology. The main reason for this is that the limited capacity of transition metal oxides and graphite, which are mostly using in state of the art lithium ion batteries. Without any doubt, lithium metal is one of the most attractive anode material for lithium ion batteries. Nevertheless, lithium metal is very sensitive to air or water and causes swelling and explosion in lithium-ion batteries. Therefore, researchers make great effort to commercialize the Lithium-Sulfur technology, which has a much higher theoretical capacity (~10 times) and energy density (~5 times) than lithium ion technology.

Lithium sulfur batteries have a promising future beyond lithium-ion battery technology due to their high theoretical specific capacity (1,675 mAh/g), high energy density (2567 Wh/kg), long cycle life ,low cost and environmentally friendly nature due to non-toxicity of the sulfur cathode material. In a main lithium sulfur battery, Lithium metal at the anode consists of sulfur, carbon, binder, organic electrolyte and a porous separator at the cathode. Both Lithium and sulfur have high theoretical specific capacities of 3860 mAh/g and 1675 mAh/g, respectively. is another expression of longer-lasting energy use than lithium-ion batteries.

Although there are many advantages in lithium sulfur batteries, there are many challenges such as the precipitation of reaction materials on the cathode surface, the shuttle effect due to the migration of polysulfides formed during charging to the anode, and finally the volume change of sulfur based cathodes. All these mentioned problems further decrease already low electronic conductivity of the cell and rapid decrease in capacity.

In this study, in order to decrease the several problems of lithium metal, Lithium/Silicon based alloy anode materials will be produced. The surface morphology of the produced electrodes will characterized using Field-emission scanning electron microscopy (FESEM), and Energy dispersive spectroscopy (EDS) in order to understand the elemental surface composition of composites. The structures of the composites will characterized using X-ray diffraction (XRD) patterns and Raman spectroscopy. The electrochemical performance of the produced Si-Li electrodes will investigated by charge/discharge and cyclic voltammetry tests from in CR2016 test cells. The resistances of the cells will investigated using ac impedance technique (EIS). This study could contribute to improvements in Li-S battery technology.

Keywords : Energy Storage, Lithium Sulfur Battery, Lithium/Silicon Anode

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Acknowledgements

This work is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the contract number 120N492. The authors thank the TUBITAK workers for their financial support.

This work also receives funding from the European Union´s Horizon 2020 research and innovation program (under the grant agreements no. 100825) under the scope of Joint Programming Platform Smart Energy Systems (MICall19).

Muhammed Osman Numan OĞUZ was born in Tekirdag,Turkey.He is studying Metallurgical and Materials Engineering in Sakarya University, Turkey. He had his intersnhip in Department of Production in Kardemir Inc., Karabuk, Turkey. He is currenlty working on a project of TUBITAK 2247-C 2247 - C Trainee Researcher Fellowship Program (STAR): Silicon/Lithium Alloy Anode Material for Lithium Sulfur Batteries.

Presentating author: Muhammed Osman Numan Oğuz, e-mail: osmanoguz554@icloud.com
tel: +90 5305580296

Photovoltaic Industry Waste as a Sustainable Source of High Capacity Li-ion Battery Anodes

M. Nevzat Duman[1,2], M. Kadri Aydınol[1,2]
[1]Dept. of Metallurgical and Materials Engineering, Middle East Technical University, 06800, Ankara, Turkey
[2]Center for Energy Materials and Storage Devices, Middle East Technical University, 06800, Ankara, Turkey

Energy storage is essential for maintaining greener energy operations that include the generation and the use of renewable energy. By means of its high energy density, lithium-ion batteries play a key role in a variety of energy storage systems. Lithium-ion batteries have come a long way since they were invented, and thanks to this technology, portable electronic devices and electric vehicles have become widespread. Nonetheless, currently used electrode materials have approached their limits and active materials with higher energy density are needed, especially for the future of electric vehicles. On the anode side, silicon is considered as a promising alternative, since it has ten times higher theoretical capacity compared to graphite, the existing anode material [1]. However, the commercialization of Si is hampered by the high cost of battery grade Si and pulverization of the electrode due to substantial volume fluctuations (300 %), resulting in poor cycle stability during discharge and charge.

In this work, usability of photovoltaic industry waste derived silicon is investigated as a cheap and advanced anode active material for Li-ion batteries. By this way, it is possible to increase industrial efficiency of sources through the well-integrated production of two relevant technologies: solar cells and rechargeable batteries. Indeed, silicon wafers of photovoltaic cells are produced by sawing a silicon ingot into extremely thin slices with the help of a diamond wire. During this process, almost half of the material is lost as micro-chips of silicon, flushed by a sawing liquid. The discarded sludge is composed of the saw dust and polyethylene glycol (PEG) as sawing liquid. The waste sediment (i.e. kerf) is pretreated with acetone and sulfuric acid to remove impurities. Resultant powder is mildly grinded with ball-mill and then characterized via various techniques including X-Ray Diffraction (XRD), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Laser Diffraction. XRD **(Figure 1)** and ICP analysis confirmed that the resultant powder is crystalline, battery grade Si. Average particle size of the product is also determined by Laser Diffraction analysis, as 0.176 µm **(Figure 2)**.

The successor study is currently being conducted to overcome the other drawback of the Si anode material: poor cycling stability. Perpetual and large volume variations do not only pulverize the active material, but also forms new surfaces on which SEI will form. As a consequence, continuous SEI formation irreversibly consumes the lithium in the cell and causes the capacity to decline [2]. Facile pre-lithiation strategy is applied to the Si active material to resolve aforementioned issues. The strategy involves air oxidation of Si to form Si@SiO_x core-shell structure and further selective lithiation of the surface oxide layer to form Si@Li_2SiO_3 composite within Li_3PO_4 matrix.

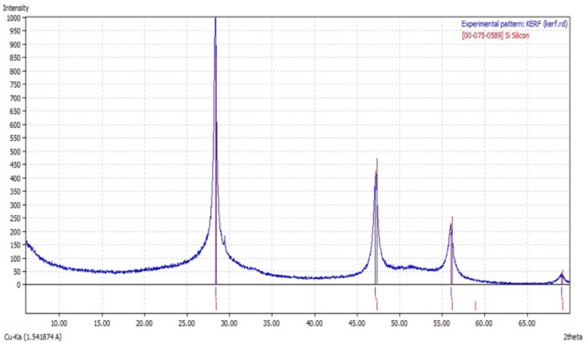

Figure 1: XRD spectrums of the treated kerf and c-Si.

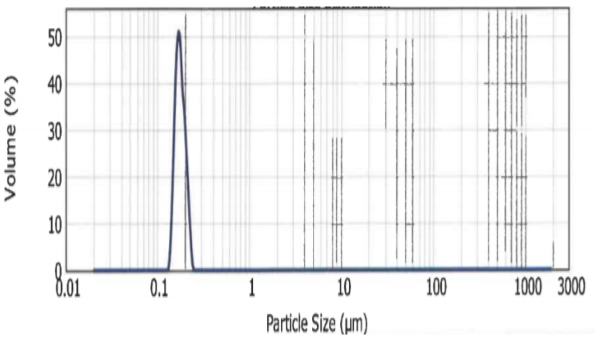

Figure 2: Particle size distribution of the produced active material.

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Mehmet Nevzat Duman received his B.S. degree in Chemical Engineering from Middle East Technical University in 2021. He joined Prof. Mehmet Kadri Aydınol's group at Middle East Technical University in 2020 and he is currently pursuing his M.S. degree. His research interests include lithium batteries and corrosion.

Corresponding author: Mehmet Nevzat Duman, e-mail: nevzat.duman@metu.edu.tr

N and B Co-Doping Hierarchical Porous Carbon Anode for Li-ion Battery

Hatice Güngör[1], Deniz Kuruahmet[2], Sıdıka Yıldırım[3] and Aslıhan Güler[4], Mehmet Oguz Guler[5] and Hatem Akbulut[6]

[1]Sakarya University, Engineering Faculty, Dept. of Metallurgical & Materials Engineering,
54187, Sakarya/TURKEY
[2]Sakarya University, Research, Application and Application Center, 54187, Sakarya/TURKEY

In several decades, porous carbon is examined as an anode electrode for Li-ion batteries [1]. Hierarchical porous carbon has a high specific area and numerous pores of various sizes, which make shorter the transport way of Li^+ ions as well as offer a large between electrode and electrolyte interface for charge-transfer reactions with a sustained electron pathway [2].

Hierarchical porous carbon shows excellent electrochemical performance, especially at high capacity, which passed graphite's theoretical capacity (372 mAh g^{-1}) [3]. Heteroatom (O, N, B, S, P, etc.) doping is established in more active sites and reduces charge transfer resistance, and thus can improve the electrochemical performances of porous carbon [4].

This study was applied for hierarchical porous carbon synthesis with the NaCl hard template method without acidic or basic treatment. The citric acid ($C_6H_8O_7$) was used as carbon source, NaCl crystals as hard template, boric acid (H_3BO_3) as B source and urea (CH_4N_2O) as N source. The process consists of solution preparation, freeze-drying, calcination and template removal.

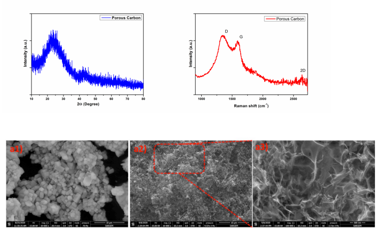

Figure 1. Xrd pattern, Raman shift and FESEM image of hierarchical porous carbon (a1: before NaCl template removal, a2 and a3: after template removal)

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Hatice Güngör graduated from Department of Metallurgical & Materials Engineering Sakarya University in 2015. She started to study Master of Science in department of Manufacturing Engineering in Sakarya University and completed her master's thesis focus on Li-ion batteries in 2018. She is currently a PhD student in Sakarya University. Her research interests are lithium-ion batteries and energy storage devices.

Presentating author: Hatice Güngör, e-mail: g.hatice.19@hotmail.com tel: +90 507 936 64 69

Composite anode based on red phosphorus for lithium-ion batteries

Z.Yelemessova, A.Nauryzbaeva, A. Mashekova, A. Mukanova, Z. Bakenov
"Institute of batteries" LLC, 53 Kabanbay Batyr Ave., Nur-Sultan, Kazakhstan

Lithium ion batteries (LIBs) have been intensively used in portable electronic devices and electrical vehicles as one of the most important energy storage devices. Commercial LIBs are generally restricted by the limited theoretical capacities of electrodes and unsatisfactory rate performances, which cannot satisfy the demand for increasing energy and power densities [1-3]. Therefore, it is of urgent need to develop novel materials with a large capacity, high cycling stability and excellent rate capability. Recently, intensive research efforts have been focused on elemental phosphorus as an anode material [4] with a high theoretical specific capacity of 2596 mAh/g, low potentials of lithiation/delithiation, and abundance. The disadvantages of phosphorus are low electric conductivity and volume change during lithiation (up to 300%).

Herein, the work focuses on new composite anodes based on red phosphorus for creating next generation LIBs with high performance and long service life. The particle size of 2 – 4 µm was achieved by grinding commercial red phosphorus in a ball-milling machine during 14 h. The TiO_2 doping impurity was added to enhance the electric conductivity using liquid phase method. X-ray diffractometry and Raman spectroscopy was used to confirm amorphous structure of RP and bonding TiO_2 with RP. The coin cell CR2032 were assembled with LPF6 in EC:EMC:DEC (1:1:1) electrolyte, Celgard 2400 separator and lithium metal as a reference and opposite electrode. Electrochemical cycling showed that the cell assembled with RP-based anode (mass loading 2,5 µg) shows the initial reversible capacity around 550 mAh/g with a gradual capacity grade, while the doping TiO_2 improves the capacity and cycling performance. The characterization details as well as electrochemical test results will be presented at the conference.

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This research was supported by the research grants AP09260012 "Development of composite anodes based on red phosphorus for the next generation of lithium-ion and sodium-ion batteries" (2021-2023) from the ministry of Education and Science of Republic of Kazakhstan.

Ms. Aiym Mashekova is a holder of BSc and MSc degrees in Materials science from National University of Science and Technology "MISIS", Moscow. Her research was based on studying the physico-chemical processes in metal-carbon nanopowders via different methods. She has about 2 years experience as reseaech assistant at Nazarbayev University and specalized in application of solid-state electrolyte in lithium-ion batteries.

Presentating author: Aiym Mashekova, e-mail: aiym.mashekova@nu.edu.kz tel:+7(702)-100-16-16

Salt-templated N-doped porous carbon anode materials for sodium ion batteries

Emrah Demir[1,2*]
[1] Institute of Nanotechnology, Gebze Technical University, 41400, Gebze, Kocaeli, Turkey
[2] Department of Electrical and Electronics Engineering, Gazi University, 06570, Cankaya, Ankara, Turkey

Lithium ion batteries (LIBs) are known as one of the most favoured energy storage technology compared to others due to their excellent cycling performance as well as good energy density[1]. These features trigger their intensive usage from electric cars to portable electronic devices. However, lithium resources are limited in nature and inversely expensive which require to focus on and develop alternative energy technologies. By exhibiting similar physicochemical properties with lithium as well as wide abundance and low production cost of sodium, sodium ion batteries (SIBs) have emerged as a new and suitable technology[2]. Since the size of the sodium ions is larger than lithium ions, the graphite anode which is the most common anode material for LIBs can not be used for SIBs[3]. Therefore, it is necessary to search for convenient anode materials which will be able to host sodium ions sufficiently.

Among the carbon anode materials, usage of hard carbons derived from biomass resources are considered as cheap and sustainable aproach since these biowastes are abundant and enable easy and sustainable conversion process into carbon structures[4]. However, electrochemical properties such as rate capability and cycling performance of hard carbons need to be improved and introducing porous structures into carbon structures are considered as suitable strategy to gain further improvement in terms of those properties. By introducing porosity within carbon structure, larger specific surface area, shorter diffusion pathways with higher diffusion coefficient values, controllable pore size distribution as well as enhanced contact area of electrode/electrolyte interface for more favourable sodium ion transportation are achieved. In order to get even further improvement in terms of electrochemical performance, porous carbons are doped by heteratoms especially with nitrogen to provide extra active sites for sodium ion storage[5]. One of the most sustainable porous carbon preparation approach is called "salt templating" in which carbon precursors are mixed with non-carbonizable salt or salt mixtures[6,7].

Herein, the preparation of N-doped porous carbon structure (donated as GA-ST-800) via salt templating method by mixing the $LiCl/ZnCl_2$ inorganic salt mixture as template and glucosamine as carbon precursor with subsequent pyrolysis treatment at 800 °C is presented. Apart from that, hard carbon (donated as GA-P-800) derived via direct pyrolysis of glucosamine at 800 °C is also introduced in order to observe the contribution of salt templating procedure on structural, morphological and electrochemical properties of anode materials.

All in all, GA-ST-800 anode material displays improved electrochemical properties compared to the GA-P-800 by exhibiting superior cycling stability with a discharge capacity of 202 mAh/g at a current density of C/10 after 350 cycles as presented in Figure 1.

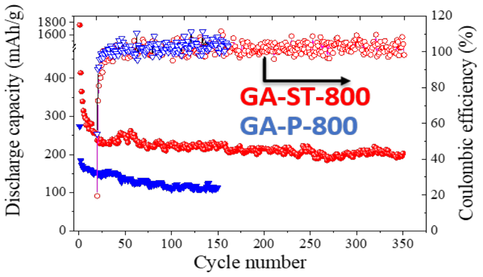

Figure 1. Cycle performances of salt-templated porous carbon and hard carbon anode material treated at 800 °C

Acknowledgements

E.D. would like to thank for The Scientific and Technological Research Council of Turkey (TUBITAK) 2218 postdoctoral research scholarship. Rezan Demir-Cakan was thanked for fruitful discussion.

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Emrah Demir obtained his PhD in Polymer Chemistry at Dresden University of Technology in Germany in 2015. Later on, he worked as a postdoctoral fellow in the fields of Rechargeable Battery Technologies at Gebze Technical University and subsequently worked as a researcher at TENMAK Boron Research Institute in Ankara. Currently, he works as an Assistant Professor at the department of Electrical and Electronics Engineering at Gazi University in Ankara, Turkey.
Presentating and corresponding author: Emrah Demir, e-mail: emrahdemir@gazi.edu.tr

Synthesis of carbon encapsulated tin nanoparticles by induction thermal plasma as anode for Na-ion batteries

Aylin Elçi[1,2], Emren Nalbant Esentürk[1,2,3], Tayfur Öztürk [1,2,4]
[1]ENDAM, Center for Energy Materials and Storage Devices, Middle East Technical University, 06800 Ankara, Turkey
[2]Micro and Nanotechnology Program, Middle East Technical University, 06800 Ankara, Turkey
[3]Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey
[4]Department of Metallurgical and Materials Engineering, Middle East Technical University, 06800 Ankara, Turkey

Recently, ambient temperature sodium-ion batteries start to gain attention as a promising alternative to lithium-ion batteries mainly because of the high abundance and low cost of sodium resources. Hence, sodium-ion batteries are promising alternative to lithium-ion batteries. However, current sodium-ion batteries face the challenges of low energy density and inadequate cycling stability, and they still cannot be used in practical applications. As a result, it is critically important to develop new sodium-ion battery materials with increased capacity and improved cycling stability for smart electric grids and stationary energy storage that will potentially use sodium-ion batteries as the power source. Materials capable of alloying with sodium have received great interest in the search for anodes with high density for SIBs. In fact, many metals and nonmetals of Group IVA and VA of the periodic table such as Sn, Sb, Bi, Si, Ge and P provide high theoretical capacity values due to the multiple electron exchange related to the alloying process at an average operating voltage below 1.0 V. However, they have serious issue about structural changes based on cycling related to large volume expansion and consequent electrode disintegration, loss of electrical contact and capacity fading. The large volume changes of these materials create critical problems in their applications in SIBs.[1],[2],[3]

Among them, metallic Sn has high theoretical specific capacity of 847 mAh/g from the alloying reaction ($4Sn + 15Na \rightarrow Na_{15}Sn_4$), one of the most promising anode materials. Also, being low cost and environmentally friendly make Sn quite advantageous as anode material. However, this theoretical capacity obtained from the phase transformations ($NaSn_5$, NaSn, Na_3Sn and $Na_{15}Sn_4$) with the huge volume expansion of 420% during alloying reaction leads to particle pulverization/exfoliation and hence detrimentally damaged electrode structure and rapid capacity fading of these materials. In addition, the unstable SEI is formed while Na^+ insertion/extraction. Currently, in order to overcome these problems, using the nanoscaled active materials and combining them with carbon structures are two most studied approaches for alleviating the volume expansion problem, which adopts to the large volume change and increase the interfacial area of contact between electrodes with electrolyte, and provides enormous conductivity by means of carbon matrix. [4],[5]

The current study includes development of carbon encapsulated Sn nanoparticles as anode materials for NIBs produced by RF thermal plasma in which carbon coating was achieved by co-feeding Sn powder and different amounts of acetylene gas into the thermal plasma reactor. Here, the constant 5 g/min of flow rate of Sn powder was fed to the reactor with Ar as carrier gas. Acetylene was fed to the carrier gas at the 0.2, 0.4, 0.6 and 0.8 slpm flow rates.

Particles were characterized structurally by X-ray diffraction (XRD). Also, they examined using field emission scanning electron microscope (SEM) for morphological observations.

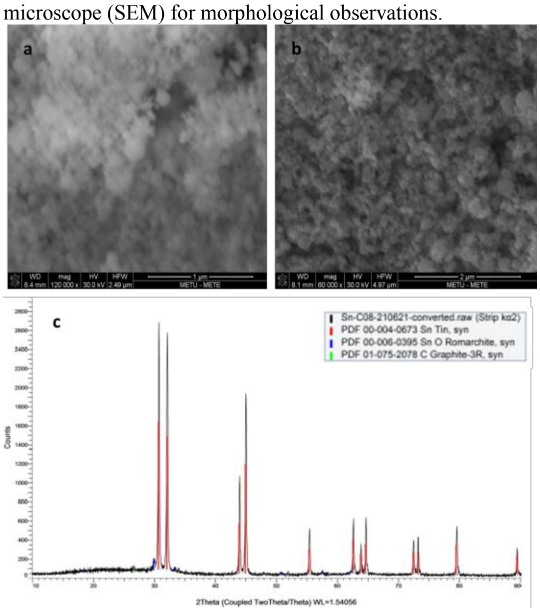

Figure 1. (a), (b) SEM image and (c) XRD pattern of carbon coated Sn nanoparticles with 0.8 slpm flow rate of acetylene.

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Aylin Elçi is currently PhD student in Micro and Nanotechnology Program. She obtained BS degree in 2014 and MSc degree in 2017 from Chemistry department, Middle East Technical University. Her research interest covers development of high energy density anode materials for Na-ion batteries.

Corresponding author: Aylin Elçi e-mail: e165246@metu.edu.tr tel: +90 312105919

Synthesis and research of $Zn_2[EDTA(H_2O)]$ metal-organic framework (MOF) for application as anode material in sodium-ion batteries

Shiyanova Radmira, Rubanova Alena and Trusov Ivan
Center of Physico-Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University, Almaty, Kazakhstan

Nowadays, metal-ion batteries are leading in energy supply for electronic devices and electric cars. The most common are lithium-ion batteries. However, the scarcity of its resources, causing an increase in the cost of raw materials, creates the prerequisites for replacing lithium. Sodium, which is also widespread in the Earth's crust, is next element in terms of atomic size and electronegativity after lithium. Therefore, the development of sodium-ion batteries has great perspectives. A disadvantage of such systems is the ionic diameter of sodium, wich is larger than that of lithium. This leads to accelerated degradation of electrode materials during intercalation-deintercalation process. A large problem is inability of Na to intercalate into graphite. Lots of research is done on how to apply Hard Carbon as an anode for Na-ion batteries, however there still some problems remain. Another family of materials such as metal-organic frameworks (MOF) may bring a new wave into Na-ion research members of this family usually have large tunnel capable for Na transport. However, representatives of this class of substances have low electrical conductivity, universal synthesis method is absent, the mechanism of structure formation has not been studied, and an individual modification method/creation of electrode composite for each compound is required [1, 2].

The object of the study is MOF $Zn_2[EDTA(H_2O)]$, that was chosen based on the characteristics of it's structure and the economic profitability of using precursors. In this study, synthesis method of $Zn_2[EDTA(H_2O)]$ is optimized, that makes it possible to obtain up to 90% yield of the target product. Also, method of obtaining stable electrically conductive anode mass to use in aqueous and non-aqueous electrolytes is proposed. The results were confirmed by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Cyclic Voltammetry (CV, Figure 1) analyzes .

The synthesis of the material was carried out by the hydrothermal method at various temperatures, concentrations of initial solution, pH values and time. Influence of each factor on the synthesis process flow, yield and the formation of by-products was determined. According to this, the synthesis procedure was optimized and mechanism of the formation of crystals was proposed.

The anode mass was made using carbon black as an electrically conductive additive, polyvinylidene fluoride and sodium alginate as binders for use in aqueous and organic media respectively. The optimal ratio of components, time and method of drying were determined to obtain mechanically strong, stable in liquid media material, with the possibility of it's use without a conductive substrate.

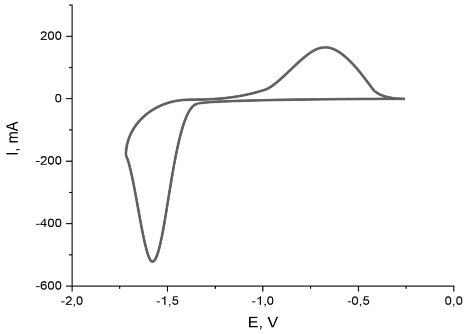

Figure 1. Cyclic voltamperogram of $Zn_2[EDTA(H_2O)]$ based electrode

Achieved results prove that further studies of $Zn_2[EDTA(H_2O)]$ are promising in order to create a composite anode material based on it to increase the specific capacity and life cycle of sodium-ion batteries, in which this material will find application.

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Acknowledgements

Authors acknowledge support from the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan. This work was carried out within the grant IRN AP09058322.

Radmira Shiyanova graduated from Al-Farabi Kazakh National University in 2021. Her research interest covers electrode materials for metal-ion batteries, metal-organic frameworks.

Corresponding author: Shiyanova Radmira, e-mail: radmira.shiya@gmail.com tel: +7 775 128 19 52

Advanced aqueous alkaline batteries based on hydrogen

Dag Noréus
Department of Materials and Environmental Chemistry, Stockholm University

Aqueous batteries, based on water which is environmentally benign are promising for safe, cost-effective energy storage. Aqueous electrolytes with fast diffusion rates promoted by the Grotthuss mechanism enable high power density and tolerance against mishandling. This also simplifies the construction as thicker electrodes can be used reducing manufacturing costs. The promising combination of safety, low cost of raw materials and manufacturing, and environmental benignity should allow aqueous batteries to become good candidates for energy storage solutions. To date, considerable progress on aqueous batteries has been achieved. We have witnessed an explosive growth of publications regarding advanced aqueous batteries.

Grid-scale applications have, however, been impeded by two issues, limited energy density and unsatisfactory cycle-life.

Fundamentally, water has an inherent thermodynamic oxidation potential [oxygen evolution reaction (OER)] and a reduction potential [hydrogen evolution reaction (HER)], which differ by a narrow voltage window of 1.23 V. This narrow electrochemical stability window puts a limit to the operating voltage, leading to a low energy density of water-based battery chemistries.

Hydrogen, as charge carrier, is found in a number of rechargeable aqueous battery chemistries.

In the nickel-hydrogen battery (NiH_2), hydrogen gas is directly the active materiel.[1] A NiH_2 battery combines a reasonable specific energy of 55–60 Wh/kg with a very long cycle life (40,000 cycles at 40% Depth Of Discharge) and operating life (>15 years).[2] The cells can tolerate overcharging and accidental polarity reversal. The NiH_2-battery is thus a good choice for long lasting space missions. Especially in low orbit missions where the number of cycles soon becomes very significant. NiH_2 batteries have orbited the earth as well as Mercury (Messenger) and Mars (Odyssey and Global Survivor). When the NiH2 batteries in the Hubble Space Telescope were replaced after 19 years, they had reached the highest number of charge/discharge cycle ever.[3] As the hydrogen is stored in pressurized gas tanks, the volumetric energy density is low, which limits their practical use, even if the cycle-life is very good.

In the Hydride battery (NiMH) hydrogen is stored in the solid state as a metal hydride (MH), that also is the main part of the MH-electrode. The volumetric storage capacity in the alloy corresponds to about twice of that in liquified hydrogen, leading to a high volumetric energy storage density, at par with Li-batteries, even if the gravimetric energy density is lower. In aqueous chemistries gas reactions including oxygen and hydrogen can further be used to increase cycle-life. This makes it possible to increase the total energy throughput, (= capacity times cycle-life), to be better than in Li-chemistries.[3] When hydrogen corrodes, it forms water, when lithium corrodes it forms insolvable oxides.

Somewhat more complex chemistries are found in NiFe-, NiZn- and NiCd-batteries where hydrogen is produced by the corrosion of Fe, Zn and Cd by the electrolyte during discharge and intercalated in the Ni-electrode where Ni(III)OOH is transformed to $Ni(II)(OH)_2$. MnO_2, MnOOH and Mn^{2+} ions are also interesting in corresponding cathodes to increase electrode capacity by allowing for more electrons to be transferred. Chemistries based on hydrogen thus offers new paths for development.

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Dag Noréus is a professor in the Department of Materials and Environmental Chemistry at Stockholm University. He earned his PhD degree in reactor physics in 1982 at the Royal Institute of Technology, Stockholm, Sweden, and completed his postdoc at Daimler-Benz, Metal Hydride Laboratory, Stuttgart, Germany, in 1983. Noréus became a researcher in 1984 and a professor in 2000 in the Department of Structural Chemistry, Stockholm University. His research interests include x-ray diffraction, elastic and inelastic neutron scattering, and electrochemistry focusing on the understanding of metal-hydrogen interaction in metal hydrides and electrodes. http://www.h2fc-fair.com/hm14/exhibitors/nilar.html

Presentating author: Dag Noréus dag@mmk.su.se

Multivalent-ions Rechargable Batteries in Aqueous Medium

Rezan Demir-Cakan[1]*, Selin Sariyer[1], Elif Canbaz[1], Burcu Unal[1], Sevde Nazli Dambasan[1], Nazmiye Kilic[2], Serkan Yesilot[2], Ozlem Sel[3]

[1] Gebze Technical University, Department of Chemical Engineering, 41400 Gebze, Kocaeli, Turkey
[2] Gebze Technical University, Department of Chemistry, 41400 Gebze, Kocaeli, Turkey
[3] Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE, 75005 Paris, France

Among energy storage options, lithium-ion batteries are one of the most attractive candidates due to their high energy density. However, factors such as high costs, safety and lifetime prevent these systems from operating on a large scale. Additionally, organic electrolytes which constitute the main axis of cost and security vulnerability prevent Li-ion batteries from working on a large scale. In this context, the development of batteries containing aqueous electrolytes has gained significant importance [1].

Thus, we aim to create a new generation, low-cost and high-security aqueous electrolyte Zn/Al-ion energy storage system that can provide an alternative to existing Li-ion, lead acid or nickel-metal hybrid battery technologies and to improve their performance. In this context, both inorganic and organic compounds are subjected and EQCM (electrochemical quartz crystal microbalance) and the novel ac-electrogravimerty methodology and are employed to investigate the Zn/Al-ion transfer and transport properties in electrode materials.

Acknowledgements
The authors thank the Bilateral Cooperation Programs between Turkey and France. TUBITAK is acknowledged for the financial supports (project no: 119N054).

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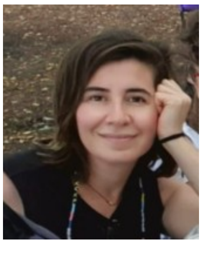

Rezan Demir-Cakan completed her bachelor and master degree from Yildiz Technical University at the Chemical Engineering Department. She received her Ph.D. degree at the Max Planck Institute of Colloids and Interfaces Interfaces, in Germany (2009), under the supervison of Markus Antonietti working on the synthesis, characterization and applications of hydrothermal carbon materials. Then she moved to France, the group of Jean-Marie-Tarascon, focusing on the rechargeable lithium batteries, more specifically on lithium-sulphur batteries between 2009-2012. Currently she has been working as an Associate Professor at the Chemical Engineering Department of Gebze Technical University. Her research interests include the synthesis of nanostructured energy materials and their application in the field of rechargable batteries.

Presentating and author corresponding: R. Demir-Cakan e-mail: demir-cakan@gtu.edu.tr tel: +902626051765

A Novel Air-Stable O_3-Type Layered Oxide Cathode Material With Low Ni Content for Sodium-Ion Batteries

Şaban Patat[1,2,3], Ayşe Şahin[2,3], Yusuf Taş[2,3], Ferhat Şanlı[2,3], Yakup Yılmaz[2,3] and Tayfur Öztürk
[1]Erciyes University, Faculty of Science, Department of Chemistry, Kayseri, Turkey
[2]ERNAM, Erciyes University, Kayseri, Turkey

Sodium-ion batteries (SIBs) based on cost-effective and naturally abundant sodium cation have become potential candidates for low cost and sustainable EESs [1]. The cathode active materials plays a key role in overall performance of SIBs. Among the cathode active materials, sodium-based layered transition metal oxides Na_xMeO_2 ($x \leq 1.0$, Me=Ti, Cr, Mn, Fe, Co, Ni etc.) have been considered as one of the most promising cathode materials for sodium ion batteries because of high specific capacity, low cost and facile preparation methods. However, sodium layered transition-metal oxides exhibit i)poor air stability, ii)phase transition during charge/discharge, iii)low conductivity, leading to rapid capacity decline and deteriorated rate capability and iv)contain toxic and expensive Co and Ni elements[1]. In order to enhance water resistant and conductivity and suppress the phase transitions of Na-layered metal oxides over a wide compositional range, some methods such as metal ion doping, a metal oxide (or carbon) coating on the surface, special structure/composition design and size reduction have been demonstrated to be an efficient method. Aiming to address these issues, herein, for the first time, we report a novel, low Ni content and Co free O3-type layered oxide cathode material, O3-$NaMn_{0.42}Fe_{0.42}Ni_{0.17}O_2$, for SIBs. Ni^{2+}, Cu^{2+} and Ca^{2+} substitution for Mn^{4+} and Fe^{3+} is carried out to obtain air-satable O3-type layered oxide cathode material**.** This material can show a reversible capacity of about 120 mAh g^{-1} at 0.1C (1C=160 mAh/g) at an average voltage of 3.2 V. When coupled with hard carbon anode, a full cell gives an energy density of 220 Wh kg^{-1} based on the total mass of cathode and anode, high Coulombic efficiency of 99.9%, and long cycle life. These desired performances of O3-$NaMn_{0.33}Fe_{0.33}Ni_{0.21}Cu_{0.08}Ca_{0.04}O_2$ make it a promising material for practical applications in SIBs O3-$NaMn_{0.33}Fe_{0.33}Ni_{0.21}Cu_{0.08}Ca_{0.04}O_2$

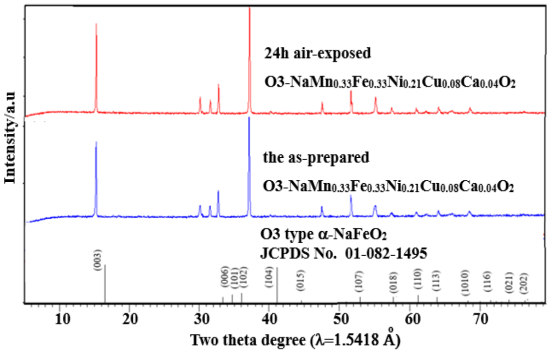

Figure 1. Powder XRD pattern of the as-prepared and 24h air-exposed O3-$NaMn_{0.33}Fe_{0.33}Ni_{0.21}Cu_{0.08}Ca_{0.04}O_2$ samples

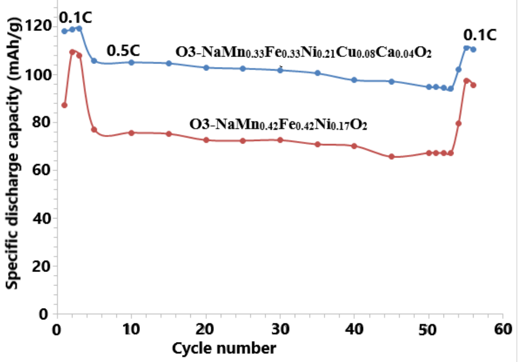

Figure 2. Cycling performance of the O3-$NaMn_{0.42}Fe_{0.42}Ni_{0.17}O_2$ and O3-$NaMn_{0.33}Fe_{0.33}Ni_{0.21}Cu_{0.08}Ca_{0.04}O_2$ in the voltage range of 1.5−4.05 V versus Na^+/Na at the current density of 80 mA g^{-1} (1C=160 mAh/g

Acknowledgements: This work was supported by the The Scientific and Technological Research Council of Turkey (TUBİTAK) with Project Number 118M077

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*Şaban Patat is a Professor in the Department of Chemistry at Erciyes University. He received B.Sc degree in Chemistry from Black Sea Technical University in 1982, Master's degree in Inorganic Chemistry from Erciyes University in 1985, and Ph.D. in Solid State Science from Oxford University 1992. He is interested
in Li-ion and Na-ion batteries and supercapacitors

Corresponding author: Şaban Patat e-mail: patat@erciyes.edu.tr tel: +90 3522076666 ext: 33162

The Effect of Synthesis Method on Electrochemical Performance of O3- $Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$ Cathode Material for Sodium-Ion Batteries

Yakup Yılmaz[2,3*] , Şaban Patat [1,2,3] and Tayfur Öztürk [3]
[1] Erciyes University, Faculty of Science, Department of Chemistry, Kayseri, Turkey
[2] ERNAM, Erciyes University, Kayseri, Turkey
[3] ENDAM, Middle East Technical University, Ankara, Turkey

Sodium-ion batteries (SIBs) based on cost-effective and naturally abundant sodium cation have become potential candidates for low cost and sustainable EESs [1]. The cathode active materials plays a key role in overall performance of SIBs. Among the cathode active materials, sodium-based layered transition metal oxides Na_xMeO_2 ($x \leq 1.0$, Me=Ti, Cr, Mn, Fe, Co, Ni etc.) have been considered as one of the most promising cathode materials for sodium ion batteries because of high specific capacity, low cost and facile preparation methods. O3-$Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$ is Co/Ni-free metal oxide cathode material among O3 type layered transition metal oxide cathodes [2]. This material shows low reversible capacity of about 96 mAh g^{-1} at 10 mAh/g current density with an average voltage of 3.2 V. In this study, to investigate the effects of the synthesis method on the electrochemical performance of the cathode material, O3-$Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$, it was synthesized by solid state reaction method and co-precipitation with carbonate followed by heating at 850°C and characterized by X-ray powder diffraction (XRD) and scanning electron microscope (SEM) methods. As can be seen in the figure 1, the XRD powder pattern of the cathode material, synthesized by co-precipitation method is nearly identical to that of the one synthesized by solid state method. According to the SEM images given in Figure 2, while the cathode material synthesized by the solid state method consists of shapeless crystals, the substance synthesized by the solid state method consists of smooth crystals.

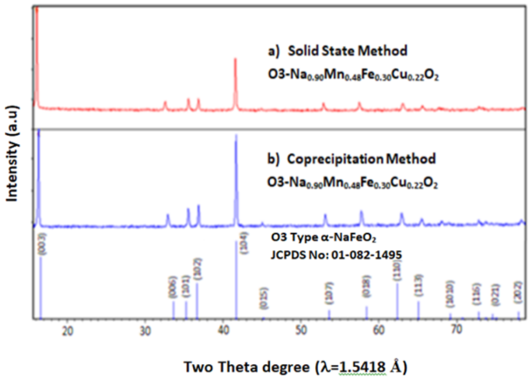

Figure 1. Powder XRD patterns of O3-$Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$ synthesized by **a)** solid state reaction method and **b)** co-precipitation with carbonate followed by heating at 850°C

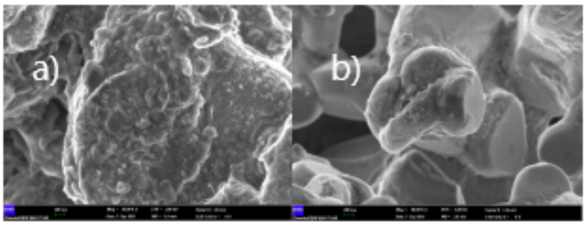

Figure 2. SEM images of O3-$Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$ synthesized by **a)** solid state reaction method and **b)** co-precipitation with carbonate followed by heating at 850°C

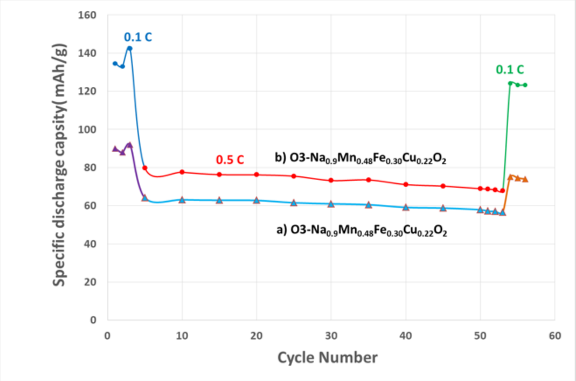

Figure 3. Cycling performance of O3-$Na_{0.9}Mn_{0.48}Fe_{0.30}Cu_{0.22}O_2$ synthesized by **a)** solid state reaction and **b)** co-precipitation with carbonate followed by heating at 850°C in the voltage range of 1.5−4.05 V versus Na^+ /Na at the current density of 80 mA g^{-1} (1C=160 mAh/g)

Acknowledgements: This work was supported by the Research Foundation of Erciyes University (Project Number FDK-2021-11102). The authors thank I. Akşit, K. Gürmen and A. Boyraz (TAUM, Erciyes University) for the XRD and SEM measurements.

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* Yakup Yılmaz is a PhD student in the Department of Chemistry at Erciyes University. He received B.Sc degree in Chemistry from Erciyes University in 2011 and Master's degree in Analytical Chemistry from Erciyes University in 2014, He is interested Na-ion batteries Corresponding author: Yakup Yılmaz e-mail: yakup_ylmz38@hotmail.com tel: +90 3522076666 ext: 33349

Study of the Solid Electrolyte Thin Films with Li Loss Compensation

A. Mashekova[1,2], M. Yegamkulov[1,2], A. Mukanova[1,2], I. Trussov[1]
[1]Institute of Batteries, 53, Kabanbay Batyr Avenue, Z05P4X0 Nur-Sultan, Kazakhstan
[2]School of Engineering and Digital Science, Nazarbayev University, 53, Kabanbay Batyr Avenue, Z05P4X0 Nur-Sultan, Kazakhstan

The increasing number of microelectronics and autonomous wireless devices urges the development of micro power sources. The solid-state thin film cells are a promising candidate for a variety of microscale applications due to their shape, versatility, flexibility and lightness, as well as the high volumetric and gravimetric power density. As the electrolyte is one of the crucial components in a cell structure, there is a need to develop high-quality materials for integration in the microcells. Crystalline electrolytes with the ability to reach high ionic conductivity and thermal stability are promising candidates for a solid state microbattery. The NASICON-type solid-state electrolyte $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) phase has the conductivity of more than 10^{-3} $S\cdot cm^{-1}$. However, in most cases the studies show the deposited electrolyte thin films are lithium deficient, and therefore have lower conductivity than pristine phase. In this work we report our findings on deposition of thin films of LATP in various modifications. We performed a magnetron sputtering of LATP doped with Zr, Hf, Ca, Mg, and Sr and studied their crystalline structure, morphology, and electrochemical properties. We found that addition of Li source has a positive effect on the Li content and electrochemical properties of obtained thin films. Furthermore, the use of radio frequency magnetron sputtering technology allows not only the synthesis of thin-films, but also offers a number of advantages, such as control of the orientation of synthesized materials, crystallinity and deformation to create powerful lithium batteries. The parallel evaporation of the lithium oxide and doped LATP allows to compensate the loss of the lithium. The results of the study will be presented at the conference in detail.

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Acknowledgements

This research was supported by the research grants №AP08052231 “Development of solid electrolytes with high ionic conductivity for next generation lithium ion batteries” from the Ministry of Education and Science of the Republic of Kazakhstan for 2020-2022.

Ms. Aiym Mashekova is a holder of BSc and MSc degrees in Materials science from National University of Science and Technology "MISIS", Moscow. Her research was based on studying the physico-chemical processes in metal-carbon nanopowders via different methods. She has about 2 years experience as reseaech assistant at Nazarbayev University and specalized in application of solid-state electrolyte in lithium-ion batteries.

Presentating author: Aiym Mashekova, e-mail: aiym.mashekova@nu.edu.kz tel: +7(702)100-16-16

A Long Cycle Life and High Ionic Conductivity, Hybrid LATP/PEO Solid Electrolyte for Lithium-Ion Batteries

Samet USTA[1], Mustafa ÇELİK[1], Tuğrul ÇETİNKAYA[1,2,3] and Hatem AKBULUT[1,2,3]
[1] Sakarya University, Research, Development and Application Center, Esentepe Campus, 54187 Sakarya, Turkey
[2] Sakarya University Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187, Sakarya, Turkey
[3] NESSTEC Energy and Surface Technology A.S., Technology Development Zones, Sakarya University, 54050 Sakarya, Turkey

The commercialized li-ion battery electrode and electrolyte materials used in li-ion battery (LIB) technology, which has been developing for 35 years, and currently they have achieved great success in powering mobile electronic devices and electric vehicles. However, there is increasing concern on the safety issues of current LIBs based on organic liquid electrolytes, which are volatile and flammable [1].

After the rapid transition from internal combustion engines to electric vehicles with the effect of Li-ion battery technology developments, the issue of how safe the batteries are was also discussed and it was observed that solid electrolytes are safer than liquid electrolyte [2]. Producing new generation batteries which will meet demands with high energy density and stability; depends on developing novel electrolytes that are chemically and physically more stable and have no safety risk instead of conventional liquid electrolytes. Although solid-state electrolytes show promise for safety, they show lower ionic conductivity than liquid electrolytes. Recently one of the most commonly used solid electrolytes, NASICON type superionic conductors have attracted attention due to their superior diffusion properties. Besides their mechanical and chemical stability, NASICON-type solid electrolytes such as $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) have low cost and high ionic conductivity. Although satisfying properties, the inflexible and rigid structure of LATP leads to inferior interface contact performance, and as a result, the interfacial resistance of the electrode materials gradually increased.

Recent studies have been focused, ceramic reinforced polymer hybrid solid electrolytes because of their ability to easily form films and their wettability. Although low ionic conductivity of polymer electrolytes at room temperature, adding ceramic additives such as LATP provide enhanced ionic conductivity by increasing the amorphous phase and chain mobility. In this research, a polymer will be introduced to enhance the solid electrolyte performance. Polyethylene oxide (PEO), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyvinylidene fluoride hexa fluoropropylene (PVDF-HFP) and poly-methylmethacrylate (PMMA) are the most common polymer electrolyte candidates, studied in the literature.

In this study, hybrid solid electrolytes were prepared with LATP ceramic and PEO polymer electrolytes by following different methods to find out the optimal hybrid electrolyte preparation method for solid-state lithium-ion batteries. Sandwiched type PEO/LATP/PEO, polymer in ceramic and ceramic in polymer types of solid electrolyte was produced to increase the ionic conductivity, decrease the interface resistance and prevent LATP decomposition.

LATP solid electrolytes were synthesized by sol-gel method and crystallized at an appropriate temperature which is performed at different temperatures and optimized to obtain the highest ionic conductivity value. For synthesizing the polymer electrolyte, PEO and LiTFSI salt were dissolved in acetonitrile in the appropriate stoichiometry to form a gel. Then different amounts of LATP were added to the gel to find out the effect on the electrochemical performance of ceramic filler. As a reverse strategy, different amounts of PEO were added to the LATP ceramic powder to find out the effect on electrochemical performance. Further, to prepare PEO film-coated sandwiched type electrolytes, LATP solid electrolytes were pelleted and sintered at optimized temperature. Electrochemical tests were performed in all different types of hybrid solid electrolytes.

The current study will shed light on the development of unique batteries by overcoming the main problems and concerns on safety issues of the Li-ion batteries and new generation batteries that provide high energy densities. Thus, it will be provided the development of much more efficient and safe grid energy storage systems and the development of much longer-range electric vehicles.

Acknowledgments

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Samet USTA graduated from Sakarya University in Physics department in 2014. He received his master's degree with a focus on Na-ion batteries in 2019 from department of Metallurgical and Materials Engineering at Sakarya University. He is currently a PhD student at Sakarya University. His research interests are nanomaterials for energy storage, new generation battery technologies for electric vehicles and renewable energy systems.

Corresponding author: Samet USTA, e-mail: sametusta@sakarya.edu.tr tel: +90 554 574 18 98

Crystallization of $Li_7P_3S_{11}$ Solid Electrolytes for Solid Lithium Sulfur Batteries

Seda EĞRİ[1,2], Mustafa Çelik[1,2], Abdulkadir Kızılaslan[1,2], Hatem Akbulut[1,2,3], Mahmud TOKUR[1,2,3]

[1]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey
[2]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey
[3] NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Energy is needed in all areas of life. For this, it is very important to convert the electrical energy of the batteries into electrochemical energy. If desired stored energy can be used as electric energy. Lithium batteries are very popular because they have long-life high-capacity and high energy density. Nevertheless , li-ion batteries cannot meet the demand of electric vehicles and smart grid systems.

Lithium-Sulfur (Li-S) batteries are considered the most suitable candidate with their high energy density (2500 Wh / kg). However, despite the advantages of Li–S batteries, they exhibit ignitability, toxicity, liquid leakage, and volatilization because of their organic liquid electrolyte components. Moreover, Li dendrites form during cycling, resulting in internal short circuit that leads to combustion and even cell explosion. In Li–S cells, various soluble polysulfide (Li_2Sx, $4 \leq x \leq 8$) intermediates formed on the cathodes can dissolve into and diffuse through the organic electrolyte and to the Li metal anode, where they are reduced to insoluble Li_2S and Li_2S_2, which then accumulate on the Li surface. The insoluble Li_2S and Li_2S_2 compounds eventually form lower polysulfide compounds, which then transfer to the cathode where they are reoxidized before they finally return to the anode.The iterative parasitic process generates a undesired “shuttle effect.” These problems result in poor cycle and rate performance, preventing the practical application of Li–S batteries. One of the optimal methods to offset these disadvantages is developing solid-state Li–S batteries and replacing conventional organic electrolytes with solid electrolytes, such as inorganic and polymer ones.Overall, solid-state Li–S batteries present many attractive advantages.[1]

Solid state batteries eliminate the mentioned problems caused by liquid leakage and volatilization. Furthermore solid electrolytes prevent the risk of combustion and explosion of organic compounds. When adopted in Li–S batteries, solid electrolyte layers can effectively prevent the “shuttle effect” because soluble polysulfide compounds cannot permeate the solid electrolytes.

Therefore, using solid electrolytes in solid-state Li–S batteries can fundamentally solve some inherent problems and thus may greatly contribute to the development of Li–S batteries.

The ideal solid-state electrolyte must have exceptional chemical and electrochemical stability, lower interfacial resistance ,high ionic conductivity, and high active material utilization. $Li_7P_3S_{11}$ (LPS) solid electrolytes have significant advantages, such as high lithium-ion conductivity, and can easily fabricate to make bulk-type all-solid-state lithium batteries. [2] However, LPS has a disadvantage because of large interfacial resistance with lithium, which give a limitation for all-solid-state battery. Therefore, in this study the crystallization temperature of $Li_7P_3S_{11}$ has been compared to obtain desired ionic conductivity.

Five different temperatures (230°C ,240°C , 250°C ,260°C 270°C) and 3 different times (2h, 3h, 4h) were used in the production of $Li_7P_3S_{11}$. Electrochemical tests of the product at every temperature value was performed.. Our ionic conductivity results are measured in the range of $1x10^{-3}$ $S.cm^{-1}$ to $4x10^{-3}$ $S.cm^{-1}$. As a result, we determined the optimum crystallization temperature and time. And we synthesized solid electrolytes with good electrochemical performance for solid lithium sulfide batteries.

Acknowledgements

This work is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the contract number 120N492. The authors thank the TUBITAK workers for their financial support.

This work also receives funding from the European Union´s Horizon 2020 research and innovation program (under the grant agreements no. 100825) under the scope of Joint Programming Platform Smart Energy Systems (MICall19).

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Seda EĞRİ graduated from Sakarya University, Department of Metallurgical and Materials Engineering in 2020. She studies focused on the development of Lithium sulfur battery systems.

Presentating author: Seda EĞRİ, e-mail: seda.egri@ogr.sakarya.edu.tr tel: +90 5310249672

The Effect of Sulfur Load on Graphene-Sulfur Cathodes Synthesized by Sulfur-Amine Chemistry for All-Solid-State Batteries

Çağrı Gökhan Türk[1,2], Abdulkadir Kızılaslan[1,2], Hatem Akbulut[1,2,3], Mahmud Tokur[1,2,3]

[1]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey

[2]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey

[3]NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

All-solid-state lithium ion(sulfur) batteries are considered as the next generation battery systems to be utilized in electrochemical energy storage devices. With the development of highly ionic conductive solid electrolytes the bottleneck of these systems reside on the cathode side which is more complex compared to the traditional battery systems using liquid electrolyes.[1] Hence, the optimization of the cathode components is of great importance. In this study we focused on the effect of sulfur load in graphene-sulfur cathodes synthesized through solution-based techniques namely sulfur-ethylene diamine chemistry. Graphene was obtained by the reduction from Graphene Oxide with ethylene diamine and the sulfur source was selecetd as $Na_2S_2O_3$. Sulfur load in the composite was changed by utilizing different amount of $Na_2S_2O_3$. [2]Total sulfur load in the composite was ranged between 30-50% with the increment of 5 % wt. Our results revealed the strong correlation between the sulfur load and the electrochemical performance of the cells which was attributed to the optimum triple contact between the active material and ionic-electronic conductive agents. With the aid of different characterization techniques utilized in this study, we have determined the optimized active mass load on cathode as 35-40 % wt. Our results put forward the significance of the ratio between cathode components and are expected to put new insights into new cathode chemistries.

Acknowledgements

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Çağrı Gökhan Türk, I graduated from Gazi University Metallurgical and Materials Engineering Department in 2020 and my scientific study on capacitors has been published. Currently, I am continuing my master's degree at Sakarya University and I am interested in the cathode parts of Li-S batteries.
Presentating author: Çağrı Gökhan Türk e-mail: turkcagrigokhan@gmail.com tel:+905367015527

Tin Selenide Anode Material in SIB Synthesized via High Energy Ball Milling

Meral Aydin[1,2] and Rezan Demir-Çakan [1,2*]
[1] Gebze Technical University, Department of Chemical Engineering, 41400 Gebze, Kocaeli, Turkey
[2] Gebze Technical University, Institute of Nanotechnology, 41400 Gebze, Kocaeli, Turkey

Sodium ion battery (SIB) systems are very crucial alternatives for lithium ion batteries. Nonetheless, SIBs have some obstacles that need to solve for large-scale applications. For instance, effective anode material, which can host large sodium ion, is essential to progress [1].

Carbonaceous materials, metal oxides, metal sulfides and metal selenides are commonly studied as anode materials for sodium ion batteries [2-4]. Bond between metal and calcogenide is weaker in M-Se than M-S, for this reason metal selenides are more convenient to reversible reactions during charge/discharge process. And also, metal selenides has higher electrical conductivity than metal sulfides [5].

The main problem of metal selenide is volume expansion caused by the introduction of more than one sodium ion into the structure. The volume expansion causes the structure to deteriorate and collapse, thus rapidly reducing the cycle capability. As a solution to this problem, synthesis of nanostructured metal selenide, carbon modification method, control of the cut-off voltage, and determination of the appropriate electrolyte have been reported in the literature [6].

Herein, tin selenide (SnSe has high theoretical capacity as 780 mAh/g) was synthesized via high energy ball milling (HEMB) method which is not only low cost but also environmental friendly. Initially, synthesis conditions were optimized then electrochemical test were made in SIB half cell systems. Tin Selenide was prepared as an electrode material by adding sodium alginat binder and carbon super P conductive agent with ratio of 8:1:1, respectively. 1 M $NaClO_4$ dissolved in EC/PC solution (1:1 v/v) with addition of 5% FEC. Surface morphologies and elemental analysis were made by SEM and EDX, respectively.

Figure 1 a) shows XRD patterns of SnSe synthesized at 25 Hz and different times. First charge/discharge capacities are shown in Figure 1 b). 2 hours synthesis time was sufficient to obtain orthorhombic phase of SnSe and it had the best charge/discharge capacity of 611 mAh/g at first cycling performance. Then, the electrode performances were optimized with investigation of the binder, electrolye and conductive additives.

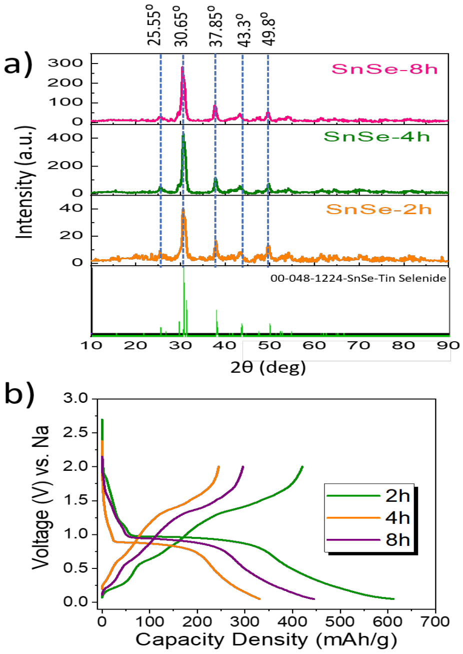

Figure 1. a) XRD pattern and b) 1st galvanostatic cycle of SnSe anode synthesized via HEBM (current density is 0.027 A/g and voltage range of 0.05-2 V).

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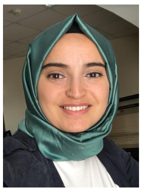

Meral Aydin graduated from Chemical Engineering Department of İzmir Institute of Technology in 2012. She completed her Msc. in Gebze Technical University and has continued her PhD degree under the supervision of Associate Professor Rezan Demir-Çakan.

Presentating author: Meral Aydin, e-mail: meralaydin@gtu.edu.tr tel: +90 553 380 33 11
Corresponding author: R. Demir-Cakan e-mail: demir-cakan@gtu.edu.tr

Investigation the effect of the binder and the electrolyte salt anion for optimizing the sodium-selenium battery system

Zeynep Erdol[1,2], Ali Ata[2], Rezan Demir-Cakan[3]

[1] Turkish-German University, Material Science and Technology, 34820 İstanbul, Turkey
[2] Gebze Technical University, Department of Materials Science and Engineering, 41400 Kocaeli, Turkey
[3] Gebze Technical University, Department of Chemical Engineering, 41400 Kocaeli, Turkey

In SOFC system, the interconnector component that ensures Compared to lithium, sodium is one of the most abundant elements on Earth, and correspondingly, sodium resources are everywhere. Therefore, sodium-based batteries have increasing attention as promising alternative to lithium-based batteries [1]. In recent years, studies are focused on sulfur as a cathode material, because of its high specific capacity and abundance. However, S has some crucial problems, which are not solved yet such as the sluggish kinetics of the formation and decomposition of different polysulfide species [2]. Selenium is a 6A group element and has similar properties with S. On the other hand, due to its larger volumetric capacity and electronic conductivity than sulfur, Se is one of the most promising cathode material for Na metal batteries [3].

In this study, to optimize Na-Se batteries, we focused on the effect of the binder and the electrolyte salt anion on the electrochemical performance. To do so, poly(vinylidene fluoride) (PVDF), sodium alginate (Alg.), the mix of carboxymethyl cellulose (CMC) and styrene butadiene (SBR) were compared in which CMC-SBR binder performed much better performance and less capacity fading. Furthermore, to investigate different electrolyte salt anion effects, we used various electrolytes based on sodium hexafluorophosphate (NaPF6), sodium perchlorate (NaClO4), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) and sodium trifluoromethanesulfanote (NaOTF) as a salt in the same solvent mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 by wt.). In comparison with other salt, NaPF6 in EC:DMC possess high cycling stability and superior specific capacity. In order to increase Se cathode utilization, electrocatalyst concept was applied different types of metal oxides such as NiCo2O4 and Co3O4. Composite with metal oxide electrocatalyst displayed higher specific capacity and stable cycling performance than without metal oxide. Figure 1 demonstrates the initial charge-discharge profiles of composite with/without Co3O4 electrocatalyst.

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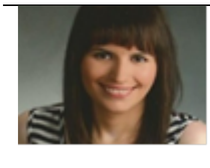

Zeynep Erdöl studied Chemical Engineering at Gazi University and graduated in 2012. She obtained her M.S. degree in 2016 from Gebze Technical University (GTU). She is currently a Ph.D. candidate at GTU in the Material Science and Engineering.
Presentating author: Zeynep Erdöl, e-mail: erdol@tau.edu.tr tel:5516000621

Analysis of the effect of sulfur loading on the performance of lithium-sulfur batteries

H. Merve Bilal[1] and Damla Eroglu[1]

[1]Bogazici University, Department of Chemical Engineering, Istanbul 34342, Turkey

Rechargeable batteries comprising the lithium-sulfur (Li-S) chemistry are esteemed to be one of the most promising candidates for next generation battery systems owing to their high theoretical energy density, specific capacity and low cost. Cell design plays an important role on the performance of Li-S batteries; there is a strong relation between key design factors such as electrolyte-to-sulfur (E/S) ratio, carbon-to-sulfur (C/S) ratio, and sulfur loading and the cell- and system- level battery performance. Consequently, these design factors must be carefully selected [1].

Sulfur loading is one of the key design parameters that has a significant impact on the Li-S battery performance. Li-S batteries are expected to excel the energy density of Li-ion batteries only at high of sulfur loadings [2]. Areal sulfur loading in the cell can be increased by increasing the cathode thickness at a constant C/S ratio, yet, at high electrode thicknesses mass transport becomes more challenging hindering the diffusion and the reaction kinetics and thus worsening the performance of the cell [3]. Therefore, sulfur loading should be optimized to achieve high performance Li-S batteries.

In this work, the effect of sulfur loading on the electrochemical, cell- and system-level performance of Li-S batteries was characterized by integrating electrochemical characterization and modeling techniques. Li-S cathode was produced by mixing carbon, sulfur and binder at a C/S ratio of 0.5 as described elsewhere [1]. Cathode thickness was set to 500, 700 and 800 μm with a doctor blade corresponding approximately to sulfur loadings of 1.6, 2.4 and 3.4 mg cm^{-2}, respectively. Electrochemical performance was examined by galvanostatic cycling and the discharge capacities and the cycling performance of Li-S cells with varying S loadings were obtained.

Figure 1 illustrates the cycling behavior of Li-S batteries with different sulfur loadings. As the sulfur loading increases, the initial discharge capacity of the Li-S cell decreases. Li-S cell with a sulfur loading of 1.6 mg cm^{-2} provides the highest initial discharge capacity of 1016 mAh g^{-1} S. Low electronic conductivity at higher S loadings may hinder the reaction kinetics, this may create the difference in the initial discharge capacities. However, better capacity retention is achieved with higher sulfur loadings; after 30 cycles all cells show a similar cycling performance.

Figure 1. Cycling performance and Coulombic efficiency of Li-S cells with different sulfur loadings at an E/S ratio of 35 μL mg^{-1} at 0.1C.

Cell- and system-level energy densities of Li-S batteries with varying sulfur loadings are also projected in this study by developing performance models, which are fed by the experimentally achieved discharge capacities. System-level performance was modeled by altering the publicly available design and cost model, Battery Performance and Cost (BatPaC). An one-dimensional electrochemical model was developed as a part of the system-level performance model to calculate the area specific impedance (ASI) and overpotential for each cell component and thus to predict the current-voltage relationship.

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Acknowledgements

This work was supported by the Bogazici University Research Fund, Grant No: BAP-14443SUP.

H. Merve Bilal is a PhD candidate in the Department of Chemical Engineering at Boğaziçi University. She got her B.Sc. at Izmir Institute of Technology in 2013. H. Merve Bilal received her M.Sc. in Fuel and Energy Technologies in 2015 and in Chemical Engineering in 2016 at Boğaziçi University. Her research interests are lithium-sulfur batteries, electrochemical characterization and modeling of rechargeable batteries.

Corresponding author: H. Merve Bilal, e-mail:merve.can1@boun.edu.tr, tel: +90 212 359 64 71

Assessment of Ionic Liquid Electrolytes for High Performance Li-S Batteries Using Machine Learning

Aysegul Kilic, Ramazan Yıldırım[1] Damla Eroglu[1]
[1] Bogazici University, Department of Chemical Engineering, Turkey 34342

Lithium-sulfur (Li-S) batteries are one of the most promising battery chemistries that can replace Li-ion batteries with their high specific capacity of 1675 mAh g^{-1}. However, their commercialization is hindered by severe problems such as the insulating nature of sulfur and the discharge product, high reactivity of the anode, polysulfide shuttle mechanism and the cathode volume change during discharge/charge. These phenomena increase the cell resistance and significantly reduce the specific capacity and cycle life of a Li-S battery. Consequently, there has been a great research effort on maximizing the discharge capacity and cycle life of Li-S batteries. Yet, the system-level energy density and specific energy should also be determined to compare the performance of the Li-S batteries with the Li-ion batteries. In order to increase the system-level energy density of a Li-S battery, inactive materials mass in the battery pack should be minimized. Electrolyte constitutes a big portion of the inactive materials mass [1]. Hence, the selection of electrolyte materials that work in lean electrolyte conditions can lead to high performing batteries. In this respect, ionic liquids have gained significant attention recently as promising electrolyte solvents that can increase the specific capacity of the Li-S cells [2]. However, the amount of data reporting the system-level performance of Li-S batteries using ionic liquid electrolytes is very limited.

In this work, we reviewed most of the Li-S literature to extract the articles that utilize ionic liquids as liquid electrolytes in their cells. A dataset including widely reported materials and design parameters as well as their reported specific capacities was constructed for Li-S cells with ionic liquid electrolytes. Then, we developed a system-level performance model (based on BatPaC model [1]) that can predict the system-level energy density and specific energy of these cells. Finally, machine learning methods were used to determine the most critical ionic liquid properties and materials and cell design factors that can result in high Li-S battery performance.

First, association rule mining (ARM) was applied to the dataset to determine factors leading to high specific capacities. ARM provides single factor effects and can show the promising categories of a variable [3]. The results are compared through the lift value. Lift value indicates the ratio of the fraction of a category in high performing cells to the fraction of that factor in the total data. Hence, lift values greater than 1 shows that this category will provide high specific capacity with high probability. In the dataset, 93% of the ionic liquids contains TFSI as the anionic part. On the other hand, 20 different cationic groups are investigated in the literature. The ARM results of the top 15 ones are given in Figure 1. As can be seen in the figure, these ionic liquids have similar lifts when high capacity class is defined for the specific capacities higher than or equal to 800 mAh g^{-1}. However, this is just the half of the theoretical specific capacity of a Li-S cell and not enough for the future energy needs. Hence, higher capacity limits are defined. When the limit of the high capacity class is further increased to 1000 mAh g^{-1} and to 1200 mAh g^{-1}, the promising cationic groups become more apparent. Having the highest lift values at high specific capacities, n-methyl-n-allyl-pyrrolidinium (P1A3), n-methyl-n-propyl-pyrrolidinium (MPP), n-methyl-n-butyl-piperidinium (PP14) and 1-ethyl-3-methyl-imidazolium (EMI) are shown to be promising for high specific capacities.

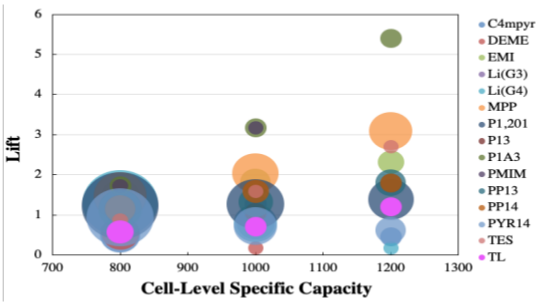

Figure 1. The change of lift values with respect to specific capacity (mAh g^{-1}) for cations of the ionic liquids.

Similar ARM analyses were conducted in the second part of the work; this dataset was fed to the system-level performance model to assess the effect of ionic liquid type and properties on the system-level energy density of the Li-S battery. In addition, the effect of critical design parameters such as electrolye-to-sulfur ratio and ionic liquid to organic solvent ratio on the energy density are also investigated.

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Damla Eroglu Pala is an associate professor in Chemical Engineering Department at Bogazici University. She worked as a postdoctoral researcher at Argonne National Laboratory as a part of the Joint Center for Energy Storage. She received her Ph.D. in Chemical Engineering from Columbia University in May 2013. Prior to her Ph.D., she earned her M.Sc. and B.Sc. degrees in Chemical Engineering from Middle East Technical University in 2008 and 2006, respectively. Her expertise is in electrochemical characterization and modeling in complex electrochemical systems such as lithium-sulfur batteries.

Presenting author: Damla Eroglu Pala, E-mail: eroglud@boun.edu.tr. Phone: 90 212 359 6866

Development of Energy Storage Systems Based on Aluminum-Ion in Aqueous Medium

Burcu Unal [1,2], Sevde Nazlı Dambasan [1], Selin Sarıyer [1,2] and Rezan Demir-Cakan [1,2*]

[1] Gebze Technical University, Department of Chemical Engineering, 41400, Gebze, Turkey
[2] Gebze Technical University, Nanotechnology Institute, 41400, Gebze/Turkey

The 21st century has seen significant advances in Li-ion battery (LIB) technologies due to the increasing use of portable devices and large-scale energy storage systems. While these developments are still ongoing, LIB technology has the potential to create serious environmental problems as it contains toxic electrolytes, heavy metals and also increased LIB production has caused to higher raw material prices. High energy density and high discharge capacities have led to the intensive use of Li-ion batteries for energy storage. The threat of future extinction of lithium reserves and safety concerns have been the driving force for research of other energy storage systems [1].

As an alternative to lithium metal, aluminum offers the potential to rival LIBs, which has relatively low cost, safety, and ability to transfer trivalent ions theoretically [2]. At the same time, aluminum is one of the most abundant metals in the world and its gravimetric and volumetric energy density is comparable to Li (gravimetric energy density 2.98 Ah/g, volumetric energy density 8.04 Ah/cm^3) [3]. Since Al^{3+} cation (53.5 pm) in the electrolyte has a smaller radius than the Li$^+$ cation (76 pm), this chemistry offers promising option for the intercalation/deintercalation mechanism [4]. Since ALIB cells operate in lower voltage ranges compared to Li-ion cells, improvements are needed for the development of electrodes to reach higher energy densities in aqueous electrolytes [5].

In this study, different ratio of carbon nanotubes (CNT) doped-TiO_2 was investigated as an alternative anode materials in $AlCl_3$ aqueous electrolyte for rechargeable aluminum ion batteries. The characterizations of CNTs doped-TiO_2 were supported by SEM, XRD and TGA. Electrochemical cyclic voltammetry (CV) and galvanostatic charge-discharge tests were performed in 1.0 M $AgCl_3$ aqueous electrolyte at (-1.4-0) V voltage range and different current densities, against to Ag/AgCl reference electrode with a 3-configuration test cell and they were compared with bare TiO_2 electrode.

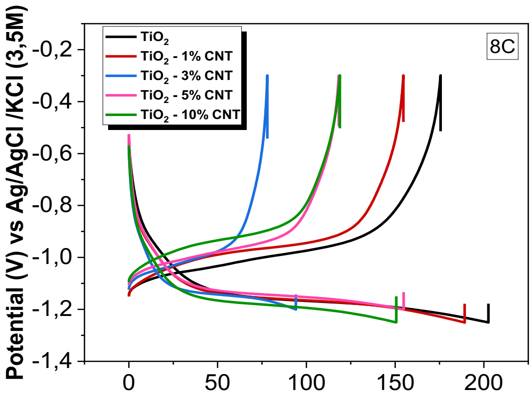

Figure 1. Specific capacities of different ratio of (w/w) CNT doped-TiO_2

TiO_2 and CNTs doped-TiO_2 electrodes that can be used instead of aluminum metal as an anode materials have reached high capacity values in the aqueous electrolyte medium and this study shows that they can be used as promising anode electrodes in Al-ion energy storage systems.

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Burcu Unal gratuated from Gazi University at Chemical Engineering Department. She received her Msc. Degree at Gebze Technical University in 2019. Currently she has been continuing PhD under the supervision of Associate Professor Rezan Demir-Cakan at Gebze Technical University Chemical Engineering Department. Her research interests based on the rechargeable aqueous electrolyte Na-ion/Al-ion batteries.

Presentating author: Burcu Unal, e-mail: bunal@gtu.edu.tr

Effective Cathode Slurry Preparation for Ni-MH Batteries

Necdet Özgür Darıcıoğlu[1, 2], Yigit Akbaş[1, 2] and Tayfur Öztürk[1, 2]

[1] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, TURKEY
[2] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, TURKEY

$Ni(OH)_2$/NiOOH is a redox couple which is widely used in battery industry due to excellent reversibility of the active material. Many battery technologies employ this material as the positive electrode active material including Ni-MH batteries. However, obtaining a fully functional positive electrode is quite a challenge. Due to the fact that, this material is an insulator with a band gab of 3.0-3.5 eV [1]. In order to overcome this problem Co based compounds are used as conductive additives. Co based compounds have a dissolution and reprecipitation formation mechanism and therefore, they form a continuous and homogenous conductive network on the surface of the $Ni(OH)_2$ powders [2]. Although, this conducive network works very well due to being continuous and homogenous, price of this materials are unstable and high [3]. Many carbon derivatives are studied as a replacement to Co [3,4]. Although, this replacement achieved some success, carbon based technology haven't been commercialized yet. Carbon, having low density and being hydrophobic is difficulty to blend with $Ni(OH)_2$ in a homogenous manner with conventional slurry preparation steps which reflects badly on the electrochemical properties and the reproducibility of the batteries [5].

This study aims to increase the reproducibility of the cathode by addition of ethanol to the slurry mixture, ball milling the powders before slurry preparation and using right amount of carbon black. 6 experiments were conducted and investigated in terms of maximum capacity attained (mAh/g), percent capacity loss in 5 cycles after the maximum capacity has attained and the percent standard deviations of those 2 data. Each experiment is performed 4-6 times to obtain the average values and standard deviations. Data is provided in table 1.

It is seen that addition of ethanol during slurry preparation, employing ballmilling and carbon black amount have drastic effects on the electrochemical properties and reproducibility of the data.

Table 1. Results of the study.

Sample	Max Capacity (avg.)(mAh/g)	%St.Dev.	%Capacity loss in 5 cycles	%St.Dev.
Water-10%CB	151,95	4,15	15,04	18,82
Ethenol-10%CB	177,35	3,28	13,45	7,26
Ethenol-5%CB	164,9	2,59	19,03	8,03
BallMill-Ethenol-10%CB	68,37	3,36	1,91	51,01
BallMill-Ethenol-5%CB	99,6	3,52	1,24	29,68
BallMill-Ethenol-2,5%CB	102,53	10,94	2,26	18,99

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Necdet Özgür Darıcıoğlu graduated from the Departement of Metalurgical and Materials Engineering in Middle East Technical University in 2017. He is now a research assistant and a PhD student in the same department. His research interest covers the development of positive electrode in Ni-MH and MnO_2 rechargable batteries.

*Corresponding author: N. Özgür Darıcıoğlu, e-mail: ozgurd@metu.edu.tr tel: +90 505 946 9128

Search for New Compositions for Cathode Materials In MnO_2 Secondary Alkaline Batteries

Necdet Özgür Darıcıoğlu[1, 2], Yigit Akbaş[1, 2] and Tayfur Öztürk[1, 2]

[1] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, TURKEY
[2] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, TURKEY

MnO_2 is a battery active material used in vast number of battery technologies. Having high defect density and structural disorder such as low crystallinity, small crystallite size, unoccupied lattice sites and foreign cations and molecules within the structure, these material is suitable for electrochemical applications [1]. Also being highly abundant in nature this material is quite cheap with respect to other battery active materials.

Although MnO_2 is used extensively in primary battery technologies, using these material in secondary batteries is a hot topic. The main problems of MnO_2 based secondary batteries are reversibility and cycle life due to irreversible reactions taking place [2]. Vast number of elements and compounds have been tried to remedy this problem, however only Bi is found to have sufficient effects [2,3]. Yadav et. al. were able to reach 80-95 % of the full 2 electron capacity (617 mAh/g) at high loadings and areal capacities for thousands of cycles (>6000 cycle) with Cu-intercalated Bi-birnessite (layered) MnO_2 [4,5]. However, the operating voltage of the battery was too low especially for the second electron process, yielding a low energy density.

Aim of this work is to produce layered δ- MnO_2 with various compositions using combinatorial approach to find new composition that can deliver full two electron capacity at a proper voltage value with high cyclic stability. The samples are produced using magnetron sputtering with the targets of $NaMnO_2$, NiO, Bi_2O_3 and MnO_2. Compositional range of the samples are given in figure1. The thick film cathodes (2-3 μm) are characterized with cyclic voltammetry and galvanostatic cycling as well as SEM and XRD.

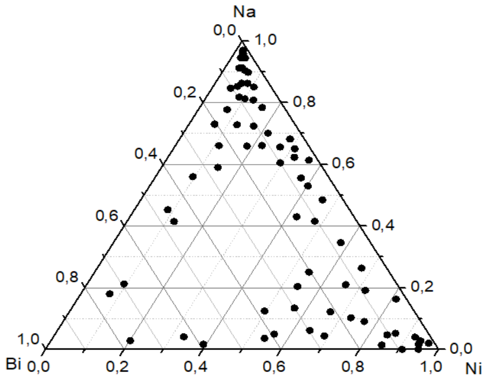

Figure 1. Composition variations of the samples.

Different behavior of the samples is observed such as; high nickel content regions were giving excellent cyclic stability but low capacity and voltage value. On the other hand, high Bismuth content regions showed high capacity but they behaved as primary battery.

Structural characterization of the samples showed that layered δ- MnO_2 was successfully produced for all compositions. However, SEM images revealed a lot of peeling offs and cracks after the galvanostatic cycling experiments which can explain the constant capacity decrease in the samples.

Prominent samples are chosen for prototyping with conventional methods.

Acknowledgements: This work is supported by TUBITAK 1001 (Project No: 118M076).

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*Corresponding author: N. Özgür Darıcıoğlu, e-mail: ozgurd@metu.edu.tr tel: +90 505 946 9128

The effect of crosslinked binders on electrochemical performance of MnO_2 cathode in zinc-ion aqueous electrolyte

Selin SARIYER[1], Rezan DEMIR-CAKAN[1]
[1]Chemical Engineering, Gebze Technical University, Kocaeli 41400, Turkey

Zinc ion aqueous batteries (ARZIB) containing aqueous electrolyte have attracted incereasing attention due to high abundance of zinc metal in the earth's crust (79 ppm), large scale production, easy processing, low cost (0.5-1.5 $/lb), high volumetric energy density (5851 mAh cm^{-3}) and high theoretical capacity (820 mA h g^{-1}) with two-electron redox reaction, stability and compatibility with aqueous environment (standard reduction potential -0.76 V vs. Standard Hydrogen Electrode (SHE)). Therefore, ARZIB alternative battery systems are composed of zinc metal used as anode, cathode in which zinc ions can be intercalated, and an aqueous electrolyte containing zinc salt. In addition, aqueous electrolytes have higher ionic conductivity compared to organic electrolytes and are not flammable [1].

Manganese oxides (MnO_2) are promising cathode materials for ARZIB owing to their different crystallographic polymorphs exhibiting various electrochemical behaviors and high theoretical capacity (308 mAh g^{-1}), low cost, and abundance in the earth [2]. One of the main challenging factor of Mn-based cathode materials is the dissolution of manganese ions (Mn^{2+}) in the aqueous electrolyte according to the Jahn-Teller effect during charge/discharge process. In order to suppress manganese dissolution into electrolyte, the most commonly used method is the pre-addition of manganese sulfate in the electrolyte [3].

Herein, MnO_2 was synthesized by the hydrothermal method. The obtained active material was characterized using X-Ray Diffraction and Scanning Electron Microscopy (SEM-EDX). The positive electrode was prepared using crosslinked binder such as polyacrylic acid (PAA)-xanthan gum (XG), xanthan gum (XG)-citric acid (CA), agar- 3- glycidoxypropyl trimethoxysilane (GPTMS). In addition, the functional groups of of cross-linked films was performed by FTIR. Electrochemical performance of MnO_2 was tested in two different electrolytes ($ZnSO_4$ and $Zn(CF_3SO_3)_2$ and the the influence of commonly used PVdF binder and cross-linked binders on electrochemical performance were compared.

As shown in the Figure 1, $Zn(CF_3SO_3)_2$ electrolyte exhibited better electrochemical performance than $ZnSO_4$ electrolyte. Furthermore, compared to the MnO_2 electrode containing PVdF binder, XG-CA, PAA-XG and Agar-GPTMS binders demonstrated more stability and higher capacity (Figure 1).

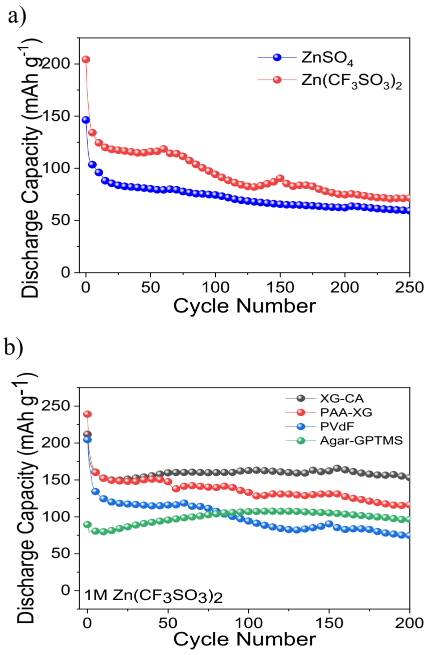

Figure 1. a) The effect of different electrolyte in electrochemical performance b) The comparision of various crosslinked binder at 1C.

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Acknowledgements

This work is supported financially by TUBITAK 1001 project (project no: 119N054).

Selin Sariyer has been working as a research assistant at Gebze Technical University, Chemical Engineering Department. She received her BSc and Msc degrees in chemical engineering from Yıldız Technical University. She is currently pursuing her PhD at Gebze Technical University. Her PhD subject is about aqueous electrolyte zinc-ion batteries.

Presenting author: Selin Sarıyer, e-mail: selinsariyer@gtu.edu.tr tel: 05069415526
Corresponding author: Rezan Demir-Cakan, e-mail: demir-cakan@gtu.edu.tr

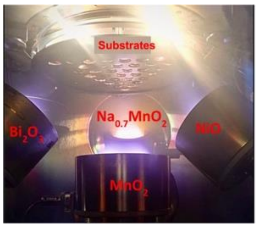
New Cathode Compositions for Mildly Acidic Zn-MnO_2 Batteries

Yigit AKBAS[1,2], Necdet Özgür DARICIOĞLU [1,2] and Tayfur ÖZTÜRK [1,2]
[1]Middle East Technical University, Department of Metallurgical and Materials, Ankara, TURKEY
[2]ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, Turkey

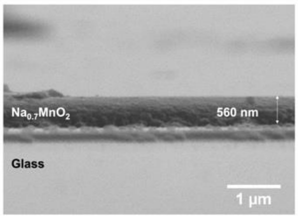
Zn-MnO_2 is normally a low cost primary battery but can be made rechargeable provided that depth of discharge is not more than 5-10%. There is considerable interest in making this battery truely rechargeable, i.e. with the customary level of DoD. Recent effort on alkaline Zn-MnO_2 has concentrated on two electron exchange aiming for a discharge capacity close to 616 mAh/g. However there are severe problems associated with this approach; namely low voltage profile at the second electron exchange and capacity decay due to zinc poisining [1].

An alternative approach would be to aim for a more modest discharge capacity using mildly acidic electrolyte. In fact discharge capacity in the order of 220 mAh/g was already reported by Chamoun et al. A number of studies were conducted (e.g. $Zn(CF_3SO_3)_2$, H_2SO_4, TBA_2SO_4) for the choice of acidic electrolytes. The use of $ZnSO_4$ especially when dilute yielded a capacity in the order of 140 mAh/g, but the best results were obtained with an elctrolyte of 2 M $ZnSO_4$ and 0.1 M $MnSO_4$ [2]

The current work, makes use of above electrolyte, concentrates on cathode chemistry to identify improved composition by modifying the γ-MnO2. So as to obtain modifed chemistry, cathodes were sputter deposited with combinatorial approach [3].



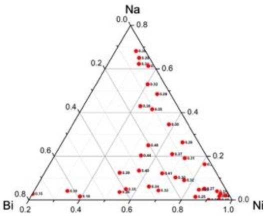
Photograph of sputter deposition of cathodes with combinatorial approach



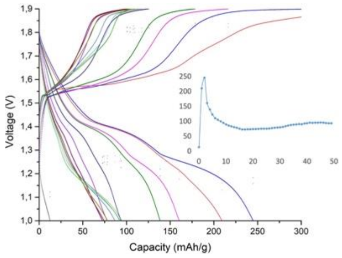
SEM image of $Na_{0.7}MnO_2$ coatings obtained on a glass substrate for tooling purposes. Cathodes deposited were typically 3 µm.

For sputter deposition, four sputter targets, namely Bi_2O_3, $Na_{0.7}MnO_2$, NiO and MnO_2 were prepared. Active materials procured as nitrates which were calcined at selected temperature yielding the oxides. These were then pressed with deformable die and sintered at selected temperatures. In the case of $Na_{0.7}MnO_2$, first Mn_2O_3 powder was obtained and then this was ball milled with Na_2CO_3 and calcined again.

A total of 36 cathodes were deposited in a single experiment, each with a different composition. So as to make samples comparable to each other, the sputter targets were adjusted carefully so that each target when operated on its own yielded one third of the thickness at the center as compared to the nearest corner on substrate plane. Power loading was adjusted on each gun so that they yielded coating of nearly the same thickness (~ 3µm.) Two sets of cathodes were deposited, one set on aluminum and the other on nickel foil.



Distribution of cathode compositions in ternary field



Charge and discharge curves for $Bi_{0.06}Na_{0.26}Ni_{0.43}Mn_{0.26}O_x$ cathode up to 50 cycles

The cathodes deposited on Al was characterized witth EDS from which their chemical composition were determined. Most of the samples were close to Na-Ni line and Mn content varied though in no case it was more than 32 at%. Curently the work is in progress to evaluate the electrochemical performans of the cathodes. The figure above refers to charge–discharge curves of $Bi_{0.06}Na_{0.26}Ni_{0.43}Mn_{0.26}O_x$ cathode. The initial capacity is 245 mAh/g but it reduces to 80 mAh/g after 10 cycles.

Having characterized all samples, we are planning to deposit a new set of samples with a more homogeneous distribution of cathodes within the ternary field and with significantly higher Mn content.

Acknowledgement

The work was supported by TUBİTAK with project number 118M076, which the authors gratefully acknowledge.

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Yiğit Akbaş is a MSc student at the Department of Metallurgical and Materials Engineering at Middle East Technical University. He obtained his bacholors degree from Materials Science and Enigeering Dept , Anadolu University in 2018. While as undergraduate student, he worked on the synthesis and characterization Li-ion battery cathode (Li_2FeSiO_4). He was on two Erasmus Internship, during which he worked on recyling LCD at Chalmers University of Technology, and on electrodeposition of solid-state electrolyte (LLZO) for Li-ion batteries at Aalto University. He is currently working on Mildly Acidic Zn/MnO2 Battery Cathodes supported by TUBİTAK.

Presenting author: Yiğit AKBAŞ, e-mail: yigitakbas@gmail.com tel: +90 546 835 35 26

Lithium and Oxygen Adsorption at the MnO_2 surface

Doaa A. AHMED[1,2], Abdulkadir KIZILASLAN[2,3], Tugrul CETINKAYA[2,3,4] and Hatem AKBULUT[2,3,4]

[1]Sakarya University, Institute of Natural Sciences, Nanoscience and Nanoengineering Department, Esentepe Campus 54187, Sakarya, Turkey

[2]Sakarya University Research, Development, and Application Center (SARGEM), Esentepe Campus, 54187 Sakarya, Turkey

[3]Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

[4]NESSTEC Energy & Surface Technology A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Rechargeable Li-air (Li-O_2) batteries, which have a theoretical energy density almost ten times higher than their Li-ion counterparts, are bearing the hope in development of high-performance power sources.[1] In this battery the cathode reaction is not the formation of an intercalation compound but the reduction of oxygen gas in the presence of Li^+ ions forming lithium peroxide Li_2O_2.[2] Among different cathode catalysts, transition metal oxides are generally utilized as an air cathode for lithium-air (Li-air) batteries.[3] Manganese dioxide (MnO_2) has been widely investigated as a cathode material in Li batteries, due to their Li intercalation capacity (forming Li_xMnO_2 phases), low toxicity, and relative low cost compared to oxides of other metals like Co or Ni. In Li-O_2, MnO_2 also play an important role, it has been shown that nanostructured MnO_2 in different polymorphic states are able to catalyze Li^+ and O^- for the formation and decomposition of Li_2O_2, which effects the overpotentials and operation of the Li–air cell. Therefore, the surface of the manganese oxide controls the function of the cathode.[2]

Understanding the behavior of the cathode catalysts is the key for improving the function of Li–air batteries. In this study, we have investigated the adsorption of lithium and oxygen at the surface of α-MnO_2 using Vienna Ab-initio Simulation Package (VASP). The DFT+U calculation was used to improve the accuracy of the electronic property prediction for transitional metal oxides. The cutoff of the plane-wave kinetic energy was 520 eV. 4 × 4 × 1 Monkhorst k-point was used for the geometry optimization of bulk system.

To define the stability of surface, plane surface energy (211) was calculated using the below formula.

$$E_{surface} = [E_{slab} - E_{bulk}]/2A$$

The adsorption energies of Li and O atoms were calculated by the following formula

$$E_{ads} = -[E_{system} - E_{adsorbent} - E_{adsorbate}]$$

The preferred site for the lithium and oxygen atoms and adsorbs site was investigated as shown in Figure 1. The result shows that, Li atoms are preferred for adsorption on (211) α-MnO_2 plane.

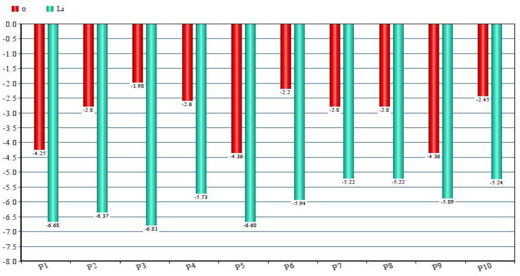

Figure 1. The value of adsorption energy for Li and O on α-MnO_2 (211).

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This work is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under contract number 217M979.

All calculations are done by Turkish Science e-Infrastructure (TRUBA).

Doaa A. Ahmed is a PhD student in Nanoscience and Nanoengineering at Sakarya University / Turkey. She graduated from the Department of Physics, University of Baghdad / Iraq in 2014. obtained a master's degree in the Physics Department from Sakarya University in 2019.

Doaa A. Ahmed, e-mail: aasef.ahmed@ogr.sakarya.edu.tr, tel:+905511498108

Bifunctional gas-diffusion electrodes based on carbon free materials

Emiliya Mladenova[1], Miglena Slavova[1,2], Borislav Abrashev[1], Valentin Terziev[1], Blagoy Burdin[1] and Gergana Raikova[1]

[1] Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, Sofia 1113, Bulgaria

[2] Department Machine Elements and Chemistry, Faculty of Transport Management, Todor Kableshkov University of Transport, Sofia, 158 Geo Milev Str., Sofia, Bulgaria

Secondary metal air batteries are emerging as a suitable technology for storing energy obtained from renewable energy sources. Energy density of zinc air battery are attractive for that purpose and bacause the Zn is cheap, non-toxic, works in humid environment and in water electrolytes, has a low self-discharge and ofers recyclable, the Zn-Air battery technology advantages over lithium–air batteries, and thus it is one of the most promising candidates. The main problem with their commercialization is the lifetime, which is related to the degradation of the electrodes during cycling. Traditionally, the gas diffusion electrode (GDE) consists of gas diffusion layer which ensures the needed oxygen and catalytic layer where the oxygen reduction/evolution takes place. The catalytic layer containing a bifunctional catalyst, usually comprising expensive precious metals, e.g. Pt, Ir or Ag. The classical gas diffusion layer containing carbon black, which is oxidized during charging [1] . This leads to the destruction of the electrodes and is a limiting factor for the life of the secondary metal-air batteries. The problem solving approach is the replacement of carbon with non-carbon material [1].

In this work we propose an innovative concept for a monolithic gas diffusion electrode, in which the gas diffusion and catalytic layers are combined in a so-called monolithic gas diffusion electrode. It is based on non-noble metal oxides such as Co_2O_4, $NiCo_2O_4$ and produced by hot pressing of a mixture with most commonly applied hydrophobic bonding material, polytetrafluoroethylene (PTFE). Additianally, to enhanced electrical conductivities and thus to increase OER performances, up to 30 wt % Nickel powder was included.

The prodused monolithic gas diffusion electrodes were tested in a half-cell configuration with 6 M KOH electrolyte with stainless steel as counter electrode and hydrogen reference electrode (HRE, Gascatel) at room temperature. The results were compared with the so called Baseline (BL) carbon electrode [1] fabricated by gas-diffusion layer (GDL): Vulcan XC-72(Cabot corp.), modified by PTFE (Teflon emulsion, Sigma Aldrich) and active layer (AL): mixture of Ag (70 wt.%), Co_3O_4 (20 wt.%) and PTFE powder (10 wt.%).

The electrochemical behavior of the electrodes was examined as steady state measurements and charge/discharge tests. Steady state curves were recorded using a Solartron Schumberger 1820 potentiostat and Tacussel (Bi-PAD) supplied with commercial software. Charge/discharge tests were performed using an eight channel Galvanostate 54 (PMC) working in the potential range -1,0 V to +2 V in the exploitation conditions: charged (OER) for 45 min and discharged (ORR) for 30 min

The electrochemical behavior of the new type of monolithic gas-diffusion electrodes is presented on Fig.1. It is comparable to that of the classical BL carbon-based gas-diffusion electrodes. Monolithic electrodes containing $Ni:NiCo_2O_4$ have better characteristics: during discharge they reach a current density of 45 mA/cm^2, in contrast to those containing $Ni:Co_3O_4$, reaching a current density of 12 mA/cm^2.

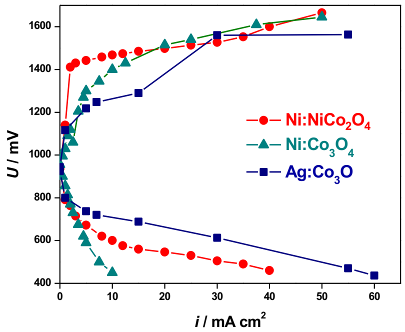

Figure1. Volt-ampere characteristics on monolithic gas diffusion electrodes during discharge and charge compared with the BL carbon based gas diffusion electrode.

Better mechanical and chemical stability of Ni: $Ni:NiCo_2O_4$ electrodes is also registered by charge/discharge cycles, it is stable without significant changes for more than 150 cycles.

The proposed carbon free gas diffusion electrodes based on Nickel- and Co-based bifunctional electrocatalysts show acceptable overpotentials for both O_2 reduction and evolution.

Acknowledgments
This work was supported by the National Science Found Project: Innovative Rechargeable Carbon-free Zinc-Air Cells (INOVI) under GA KP-06-N27-15/14.12.18.

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Dr. Miglena Slavova is a Senior Assistant at the Institute of Electrochemistry and Energy Systems and at the University of Transport, both in Sofia, Bulgaria. After graduating with a master's degree from Sofia University in 2002, Miglena Slavova received her doctorate in 2017 from the University of Shumen. Her research interests include zinc air batteries and solid oxide fuel cells/ electrolyzers.

Presentating author: Miglena Slavova, e-mail: mslavova@iees.bas.bg tel: +359/89735266

Analysis of key materials and cell design parameters for high capacity lithium-oxygen batteries using machine learning

Aysegul Kilic[1], Damla Eroglu[1], Ramazan Yildirim[1]
[1] Bogazici University, Department of Chemical Engineering, Turkey 34342

Due to the ever-increasing demand for high capacity energy storage systems, beyond lithium-ion (Li-ion) batteries have gained significant attention. Among these chemistries, the theoretical specific capacity of a lithium-oxygen (Li-O_2) battery is 3-4 times higher than that of a Li-ion battery [1]. However, practical capacities of Li-O_2 batteries are much lower than their theoretical capacities and their cycle lives and round-trip efficiencies are very limited. These can be attributed to various side reactions taking place inside the cell as well as inadequate materials and cell design [2]. Hence, it is very critical to determine key cell design factors and effective materials that should be utilized in a Li-O_2 cell. Since there are many variables that can affect the Li-O_2 cell performance, it is not straightforward to determine the relation between materials and cell design with the battery performance and select the promising ones among these factors. In this respect, machine learning is a powerful tool to reveal the complex variables leading to high battery performance [3]. In this work, two machine learning techniques, association rule mining (ARM) and decision tree (DT) are used to determine the promising materials and design factors in Li-O_2 batteries that lead to high peak discharge capacities (PDC) and cell voltages.

To apply machine learning techniques, a dataset is collected using the Web of Science platform. Experimental articles published after 2010 are sorted according to the relevance and 157 papers are collected from the top. 774 of data points provide constant-current discharge capacities and these data are labeled as the *capacity testing* group. On the other hand, 242 data points report the cut-off voltages obtained at a specified capacity and they constitute the *voltage testing* group. The analyses are performed separately for discharge specific capacity and cut-off voltage as the desired output for the capacity and voltage testing groups, respectively. 13 variables that are widely reported in the literature are determined as the inputs to the analyses. Since the amount of cycling data is limited in the literature, cycle life analysis is not included. ARM analyses are used to reveal the single factor effects on high PDCs and voltages by comparing the lift values of the individual categories of a variable. Lift value indicates the ratio of the fraction of a category in high PDC cells to the fraction of that category in the total data. Apparently, for a category to be promising it should have lift values higher than 1. Finally, DT analysis is used to study the multi-factor effect that can give rules to get high PDCs. To do that, the dataset is divided into training and testing groups, which constitute 75% and 25% of the total capacity testing group, respectively. 5-fold cross-validation is used in the training set to determine the most successful DT model and this model is tested with the testing group.

Figure 1 shows a bubble graph where bubble size indicates the number of data points obeying the rule. It represents the change of lift values with respect to PDCs ranging from 3000 to 10000 mAh g^{-1} for different cathode materials. As can be seen in the figure, N-doped carbons, graphene, graphene oxide and porous carbons are proposed to be promising for high PDCs with increasing lift trends.

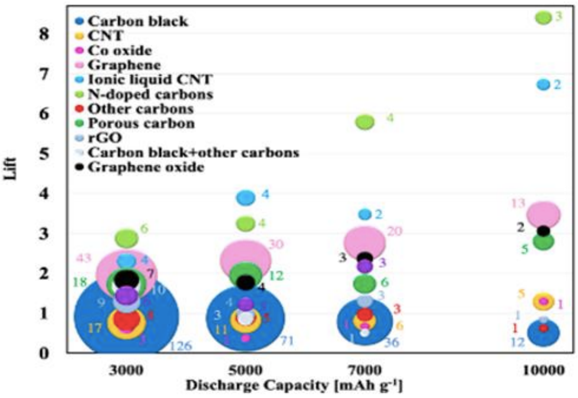

Figure 1. Lift vs PDC for the cathode material type in a Li-O_2 battery

ARM and DT analyses show similar results for high performance Li-O_2 batteries. Cathode materials, cathode ingredients and electrolyte solvents are found to be the most critical variables. LaFe oxides, Ni oxides and Ru are suggested to be used as cathode ingredients, whereas DME, DMSO, triglyme and tetraglyme without a salt or with $LiClO_4$ salt are suggested as promising electrolytes for Li-O_2 batteries.

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Aysegul Kilic is currently a PhD student in the Department of Chemical Engineering at Bogazici University. She received her MSc and BSc degrees from Bogazici University Chemical Engineering Department in 2019 and 2016, respectively. After a short period of a pharmaceutical industry experience, she started to work as a Graduate Assistant in the same department. Her PhD thesis is material-to-system level analysis of the lithium-sulfur battery.

Presenting author: Aysegul Kilic, e-mail:aysegul.karakus@boun.edu.tr

Enhancement of the Stability and Ionic Conductivity of Quasi Solid Li-O2 Batteries Using Double Layer Gel Polymer Electrolytes

Mustafa ÇELİK[1], Samet USTA[1], Tuğrul ÇETİNKAYA[1,2,3] and Hatem Akbulut[1,2,3]
[1] Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187, Serdivan, Sakarya
[2] Sakarya University Research, Development and Application Center (SARGEM), Esentepe Campus, 54187 Sakarya, Turkey
[3] NESSTEC Energy & Surface Technology A.S., Technology Development Zones, Sakarya University, 54050 Sakarya, Turkey

Among rechargeable energy storage systems, lithium-oxygen batteries (LOBs) offer one of the highest theoretical energy densities (around 11.5 kWh / kg). Conventional non-aqueous refillable LOB systems consist of a lithium metal anode, a porous cathode, and a lithium-ion conductive liquid electrolyte. Various concerns arising from the use of liquid electrolytes prevent their use in LOBs, ie low volatility temperature, passivation of the metal anode surface, dissociation at potentials above 4V [1].

This work covers the synthesis of PVDF-HFP based gel-polymer electrolytes to replace liquid electrolytes to eliminate the aforementioned concerns. Although gel-polymer electrolytes are free from the basic problems encountered in their liquid counterparts, they suffer from low ionic conductivities due to the occurrence of crystalline phases. Most efforts to increase the ionic conductivity of polymer electrolytes have been devoted to introducing ceramic fillers such as Al_2O_3, SiO_2, and TiO_2 into the polymer matrix [2]. Another method is to include low lattice energy lithium salts and bulky anions such as LiTFSI to delay crystallization kinetics.

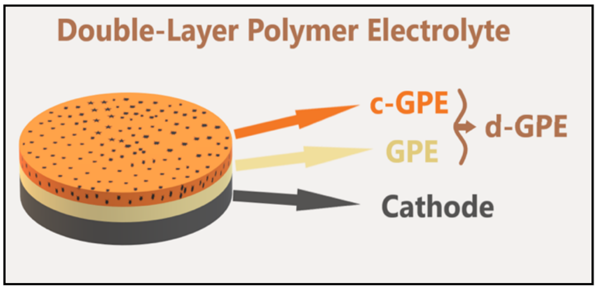

Figure 1. Double-layer gel polymer electrolytes are composed of GPE's and c-GPE's.

In this study, we synthesized Li1.3Al0.3Ti1.7(PO4)3 (LATP) dispersed PVDF-HFP gel electrolyte containing LiTFSI salts to increase ionic conductivity and stability of the quasi solid electrolyte for Li-O_2 batteries. The obtained gel polymer electrolytes was utilized with two different methods. In first the manufactured PVDF-HFP / LiTFSI / LATP (c-GPE) was directly applied on the surface of oxygen cathode. In the second method double layer gel polymer electrolyte was used, in the first layer PVDF-HFP/LiTFSI was coated on the oxygen cathode and then PVDF-HFP/LiTFSI/LATP composite gel polymer electrolyte was coated on it as second layer to design an optimal high ionic conductive polymer gel electrolyte (d-GPE) for Li-O2 batteries.PVDF-HFP / LiTFSI gel We compared the electrochemical properties of as-produced GPEs and c-GPEs and d-GPE . The gel polymer electrolytes were prepared by dissolving the PVDF-HFP polymer in acetone and DMF, and the ceramic filler to be applied here was dispersed. As shown in Figure 1, Double-layer gel polymer electrolytes are composed of different thickness GPE's and c-GPE's.

Electrochemical performance of GPEs, c-GPEs and d-GPE electrolytes was tested with ECC-air test cell using lithium foil, gas diffusion layer (GDL, Sigracet 24BC) and gel polymer as an anode, cathode and electrolyte respectively . The ionic conductivity and activation energy of GPEs were calculated using Electrochemical Impedance Spectroscopy (EIS) technique. The reaction potentials of the cell were determined by the Cyclic Voltammetry test. Galvanostatic charge-discharge tests were carried out between 2V and 4.5V at a constant current density of 0.1 mA / cm2.

Our results show that the inclusion of ceramic fillers in gel-polymer electrolytes increases ionic conductivity but negatively affects cycle performance. However the such issue was overcome with double layer gel polymer electrolyte. It concluded that the double layer gel polymer electrolyte is a solution for high performance quasi solid state Li-O2 batteries.

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Mustafa ÇELİK graduated from Sakarya University, Department of Metallurgical and Materials Engineering in 2017. He has been pursuing his studies in the same department since 2018. His studies focused on the development of gel-polymer electrolytes to replace liquid counterparts to enhance the electrochemical performance of lithium-air battery systems.

Presentating author: Mustafa Çelik, e-mail: mustafacelik@sakarya.edu.tr tel: +90 530 326 54 08

The effects of heat treatment on the felt electrodes in Vanadium Redox Flow Battery

Mert Taş [1] and Gülşah Elden [1,2]
[1]Erciyes University, Department of Energy Systems Engineering, Melikgazi, 38039 Kayseri, Turkey
[2]Erciyes University, Energy Conversions Research and Application Center, Melikgazi, 38039 Kayseri, Turkey

Renewable energy costs gradually compete with conventional energy sources. However, renewable energy resources have challenges due to fluctuations and the need for storage of the produced electricity. Vanadium Redox Flow Battery (VRFB) is one of the biggest candidates to solve this problem with its long life, scalability and large-scale energy storage. VRFB mainly consists of electrolyte, membrane and electrode. The redox reactions of vanadium species during charge and discharge of electrical energy occur at the electrode-electrolyte interface. Therefore, electrochemical properties, functional groups, electrolyte accessibility and electrochemical surface area of the electrode are important for energy efficiency and capacity of the battery.

Thermal [1,2], chemical [3] and electrochemical treatments [4] were performed to improve these properties of bare graphite and carbon felt electrodes. Kabtamu et al indicated that applying thermal treatment on the commercial electrode decreased contact angle from 136 ° to 110 ° and provided to obtain pure XRD peaks [5]. Also, this treatment reduced the overpotentials occurred in the electrode.

The aim of the study is to investigate the effects of thermal treatment on the electrolyte accessibility and fiber morphology of commercial electrodes of VRFB. To achieve this aim, four commercial electrodes in dimension 20x20 mm^2 (Sigracell KFD 2.5, Sigracell GFD 2.5, Sigracell GFD 4.6 and Sigracell GFA 6) are treated thermally in three different temperatures (200 °C, 400 °C and 600 °C) for 12 hours. The surface morphology of fibers is examined with SEM analysis. XRD peaks are conducted to bring out the alteration of peaks. And also, contact angle measurements are analyzed to compare the electrolyte accessibility of pristine and treated electrodes.

The fiber structures of the bare four electrodes are given in Figure 1. Some impurities on the fibers are marked in red. When these impurities are not eliminated from the fiber surface during the redox reactions of vanadium species, they mix into the electrolyte. It leads to the contamination of electrolyte. Also, these impurities which keep holding on the fiber surface can affect the charge-discharge reactions. Therefore, these undesirable particles reduce the performance, capacity and cycle life of the vanadium redox flow battery.

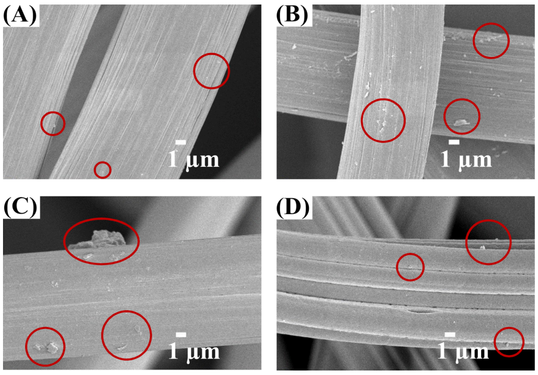

Figure 1. SEM images of four commercial electrodes (A): KFD 2.5; (B): GFD 2.5; (C): GFD 4.6; (D): GFA 6 (Impurities are marked in red)

As it can be seen from Figure 1, there are many particles are on the fibers of four commercial electrodes. The heat treatments are applied to these commercial electrodes for the removal of these impurities and the increasing of the electrode surface properties.

Acknowledgments

The authors would like to thank the Scientific Research Projects Unit of Erciyes University for funding and supporting the projects under the contract no: FDK-2020-10376.

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Mert TAŞ received his Bachelor's and Master degrees in Energy Systems Engineering from Erciyes University. He is currently pursuing his PhD degree in Energy Systems engineering at same department. His current research interests focus on experimental and computational studies about Vanadium Redox Flow Batteries, electrodes and electrocatalysts and PEM fuel cell.

Presentating author: Mert Taş, e-mail: merttas@erciyes.edu.tr tel: +90 352 207 66 66
Corresponding author: Gülşah Elden, e-mail: gulsah@erciyes.edu.tr

A Numerical Analysis on Vanadium Redox Flow Battery Based on Different Nafion Membranes

Phil Jacques ALPHONSE[1], Gülşah ELDEN[1]

[1]Dept. of Energy Systems Engineering, Erciyes University, Kayseri, Turkey

Nowadays, the demand for energy storage systems is increasing with the increase in the use of clean and renewable energy sources. Therefore, the research, development and innovations related with the energy storage systems have been performed over the past decade. A vanadium redox flow battery (VRFB) having many advantages (high energy efficiency, large scale energy storage and unlimited energy capacity etc.) is one of the energy storage systems.

The VRFB store chemical energy and generate electricity by a redox reaction between vanadium ions (V5, V4, V3 and V2) dissolved in sulfuric acid (H2SO4). The main components of VRFB are positive and negative porous electrodes, membrane, current collectors, electrolyte tanks, and pumps. The membrane plays a very important role in a VRFB system. The membrane in VRFB is used to separate two porous electrodes and to transfer hydrogen protons. Several parameters are employed to describe the membrane in the VRFB applications, such as conductivity, water transfer and permeability [1]. The conductivity denotes the ability of a membrane to transport protons. The water transfer represents the ability of a membrane to absorb water. The permeability impacts the water flux passing through the membrane. Many types of membrane materials are available on the industrial market. Generally, Nafion membrane is used for a VRFB systems, since it is high ionic conductivity and a good chemical stability.

The objective of this study is to investigate the performance of VRFB for the different Nafion membrane properties. In this study, the most used Nafion membranes in the VRFBs are chosen, such as N105, N112, N115, and N117 [2].To achieve this objective, a two-dimensional numerical model for four different types of Nafion membrane is studied. The effect of the thickness and ionic conductivity of Nafion membrane are examined. The models are developed with COMSOL Multiphysics 5.5.

Figure 1 shows the variations of cell voltage with SOC for different Nafion membranes of N105, N112, N115 and N117 during discharge processes at the applied current density I=40mA/m^2. It is seen that the Nafion membrane N105 has higher performance compared to those other Nafion membrane types due to the highest ionic conductivity of Nafion membrane N105. It is concluded that the membrane ionic conductivity affects more impact on the performance of VRFB rather than thickness.

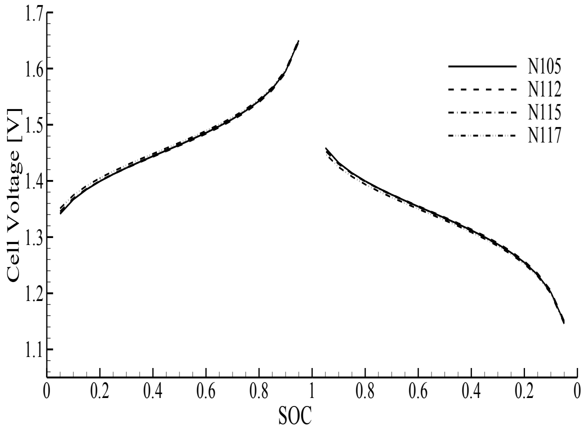

Figure 1. Cell voltage comparison of Nafion membrane N105, N112, N115, and N117.

For a good performance of VRFB, the membrane must have a high ionic conductivity. Generally, higher ionic conductivity in the membrane is provided with a good water transport mechanism [3].

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Acknowledgements

The authors would like to thank the Scientific Research Projects Unit of Erciyes University for funding supported by project coded FDK-2019-9340.

Phil Jacques Alphonse is a Ph.D student in the Department of Energy Systems Engineering Erciyes University, Kayseri, Turkey . His research interest includes key materials of vanadium redox flow battery, energy storage systems, renewable energy systems.

e-mail: aphilacques@gmail.com
tel: +90 538 075 88 46

Investigation of electrocatalysts containing single, binary, ternary, and quaternary metal ions deposited on graphite electrode for vanadium redox battery

Niyazi Özçelik, Zeliha Ertekin, Nuran Özçiçek Pekmez and Kadir Pekmez
Dept. of Chemistry, Hacettepe University, Ankara 06800, Turkey

According to the European Commission in the recently launched Green Deal, there is a need for safe, efficient, affordable, and large-scale energy storage applications [1]. To sustain energy needs, scientists have developed energy storage devices such as lead-acid batteries, lithium-ion batteries, sodium-sulfur batteries, Ni-MH batteries, and redox flow batteries [2]. Among these batteries, vanadium redox flow battery (VRAB) is one of the most promising technology for electrochemical energy storage devices. Different oxidation steps of vanadium ions (V^{2+}, V^{3+}, VO^{2+}, and VO_2^{+}) are used in both cathode and anode reactions. In the cathodic reaction, V^{3+} ion reduces to V^{2+} ion, which is a slow reaction step. Various methods have been used to accelerate this step, such as modifying the electrodes with a metal or metal oxide electrocatalyst. [3,4]. There are several techniques for modification of electrodes with the metal electrocatalyst, such as electrodeposition, impregnation/ drying, or direct addition of the metal ions into the battery electrolyte. The advantage of the electrodeposition method is that it provides the opportunity to control the grain size, mass, and thickness of the deposited metal on the electrode surface by changing the applied potential, deposition time, and electrolyte composition.

In this study, electrocatalyst alloys containing binary, ternary, and quaternary metals of Sb, Bi, Cu, and Sn are deposited for the first time on the graphite electrode to catalyze the reaction of the V^{3+}/V^{2+} redox couple. To determine electrochemical performance of $VOSO_4$ in H_2SO_4 solution, cyclic voltammetry (CV) is taken from 0.4 V to -1.0 V in H_2SO_4 solution containing $VOSO_4$ and the single (Sb^{3+},Bi^{3+},Cu^{2+},Sn^{2+}) binary (Bi^{3+}/Cu^{2+}, Bi^{3+}/Sb^{3+}, Bi^{3+}/Sn^{2+}, Cu^{2+}/Sb^{3+}, Cu^{2+}/Sn^{2+}, and Sb^{3+}/Sn^{2+}), ternary ($Cu^{2+}/Sb^{3+}/Sn^{2+}$, $Bi^{3+}/Cu^{2+}/Sb^{3+}$, $Bi^{3+}/Sb^{3+}/Sn^{2+}$, and $Bi^{3+}/Cu^{2+}/Sn^{2+}$), and quaternary ($Bi^{3+}/Cu^{2+}/Sb^{3+}/Sn^{2+}$) ions. Before the reduction of V^{+3} to V^{+2} (-0.62 V), other metals can be deposited at more positive potential (Sb^{3+} : 0.02 V, Bi^{3+} : -0.11 V ,Cu^{2+} : -0.38 V, Sn^{2+} : -0.58 V) on the electrode surface in this solution. The CV results reveal that adding binary metal ions to the electrolyte and Cu^{2+}/Sb^{3+} or Cu^{2+}/Sn^{2+} among the ions advance peak separation and increase in I_{pa}/I_{pc}.

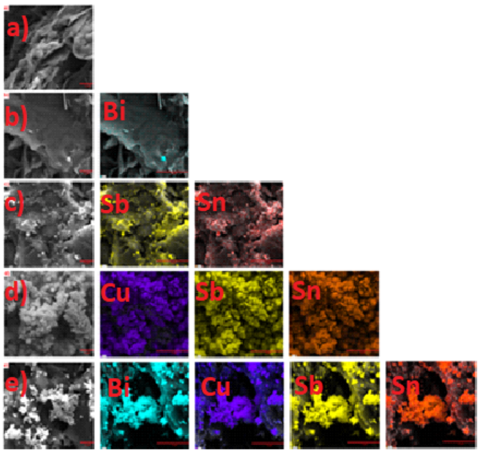

Figure 1. SEM image of a) bare electrode and b) Bi^{3+}, c) Sb^{3+}/Sn^{2+} , d) $Cu^{2+}/Sb^{3+}/Sn^{2+}$, e) $Bi^{3+}/Cu^{2+}/Sb^{3+}/Sn^{2+}$ electrodeposited on graphite electrode and their elemental mapping

The prepared electrodes via bulk electrolysis at appropriate potentials are characterized by scanning electron microscopy (SEM), energy dispersive X-Ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS). SEM-EDX mapping analyses show that target metals homogeneously distribute on the electrode surface, as observed in Fig.1. Also, they are deposited as nanoparticles in the range between 50 and 100 nm. It is also verified by XPS and EDX methods that all metals are deposited on the electrode surface. From EIS results, the charge transfer resistance (R_{ct}) decreased at all combinations of metal ions. As a result, the present study indicates that rapid and simple preparation of electrocatalysts has potential use for vanadium redox batteries.

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Niyazi ÖZÇELİK received his BS degree from Atatürk University in 2013 and MS degree from Hacettepe University in 2021. He has been working as Research Assistant in Chemistry Department of Hacettepe University since 2018. He is currently Ph.D. candidate in the same department.

Presentating author: Niyazi ÖZÇELİK, e-mail: niyaziozcelik@hacettepe.edu.tr tel: +90312 297 79 69

Nanoporous Ni Surface Modification by Electrochemical Dealloying

Taner Özdal[1] and Fatih Pişkin[1,2]
[1]Energy Materials Laboratory, Muğla Sıtkı Koçman University, Turkey
[2]Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University, Turkey

INTRODUCTION

316L porous stainless steel (PSS) is a suitable support material for thin-film Pd-based membranes due to its high thermal, oxidation resistance and having a similar thermal expansion coefficient with Pd[1,2]. However, commercially available PSS have often very large surface pores (>20µm) that affect the final thickness of the membrane deposited on it[3]. That's why the membrane thickness deposited on the PSS can reach several tens of microns in order to create a porous-free membrane.

There are several studies that focus on applying an interlayer between PSS and thin-film membrane so as to reduce the size of pores at the PSS surface[4,5], and thus reduce the thickness of the membrane. However, it is often not easy to control the size of surface pores and keep their size under a threshold. Any remaining large pore at the surface of support material causes the formation of pin-holes in the membrane and this might result in a reduction in hydrogen selectivity. That's why modification of PSS surface has to be employed in a controlled manner and should be reproducible.

The current study concentrates on surface modification of PSS as a support material in order to enable thin-film membrane (<1µm) deposition on PSS. In this respect, 316L foil was used as a model system to determine the application parameters for the formation of a nanoporous Ni surface layer on the PSS. 316L foils were initially electroplated by Ni-Cu alloys using plating solutions with different Ni:Cu concentrations. Subsequently, the Ni-Cu surface layers on 316L foils were subjected to an electrochemical dealloying process in order to dissolve Cu back into the plating solution and remain a nanoporous Ni layer.

EXPERIMENTAL

Electroplating and electrochemical dealloying processes were performed under ambient conditions in a three-electrode cell. Ni_xCu_{1-x} alloys were electroplated on 50µm 316L foils. Ni seeding layer was initially electroplated on all 316L foils in the study using 0.8M $NiSO_4.7H_2O$ solution for 5 min at -1.0V. Electroplating of Ni_xCu_{1-x} alloys was performed at the same potential in plating solutions composed of $NiSO_4.7H_2O$ and $CuSO_4.5H_2O$ for up to 30min. The concentration of $NiSO_4.7H_2O$ was kept constant at 0.8M while $CuSO_4.5H_2O$ ranged from 0.01M to 0.1M in the plating solutions in order to obtain different $NiSO_4.7H_2O$-$CuSO_4.5H_2O$ ratios, so the different Ni_xCu_{1-x} alloys. The alloys were then subjected to electrochemical dealloying in their respective plating solutions at +0.5V up to 15min.

RESULTS AND DISCUSSION

The methodology described resulted in a Ni layer having pores less than 100nm in diameter on a 316L foil surface. The porous Ni surface obtained via Ni-Cu electroplating and subsequent electrochemical dealloying of Cu was investigated by SEM, Fig. 1.

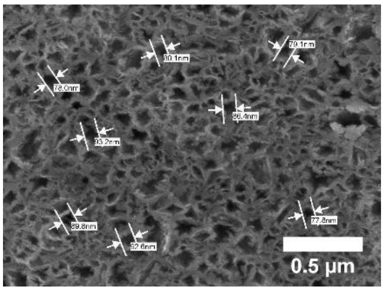

Fig. 1. Nanoporous Ni layer deposited on 316L foil.

CONCLUSION

In the current work, a sequential Ni-Cu electroplating and electrochemical dealloying process were applied to obtain a nanoporous Ni surface layer on 316L foil. In this respect, several plating solutions with different Ni:Cu concentrations were prepared. The electrochemical dealloying of Cu was performed on each Ni-Cu alloy deposited by different plating solutions and the ideal conditions were identified so as to obtain a porous Ni surface layer having pores less than 100nm in diameter on 316L foil.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of this research from the Scientific and Technological Research Council of Turkey (TUBITAK) with project number 119M636.

Taner ÖZDAL is a materials engineer and received his bachelor degree in Metallurgical and Materials Engineering department from Muğla Sıtkı Koçman University (MSKU). He is currently a researcher in Energy Materials Laboratory, MSKU, and is studying perovskite-type oxide composites for hydrogen separation membranes. He is also interested in cathode materials for Li-ion batteries, Na-ion batteries, and solid oxide fuel cells.

Presentating author: Taner ÖZDAL, e-mail: tanerodal74@gmail.com, tel: +90 545 738 43 93

Investigation of the Calendering Parameters for High Energy Density Lithium Ion Battery Electrodes

Muhammet Barış Ekici[1], Mahmud Tokur[2,3,4], Mustafa Akçil[1]

[1]Sakarya University of Applied Sciences, Technology Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

[2]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey

[3]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey

[4]NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Lithium-ion batteries have a wide range of uses, from transportation to defense industry, from daily use to space applications. The widespread use of consumer electronics day by day increases the need for this technology. In short, these energy sources, which allow us to live in almost every point of our lives without the need for binding factors such as cables, have become the most important part of our lives. For this reason, energy storage technologies are now extremely important strategic topics. Of course, this technology, which dominates our lives so much, has many limitations that need to be overcome. Low cycle life due to poor electrochemical efficiency of electrode materials is one of these limitations. At the same time, energy density constraints are also an obstacle to many technological developments. Therefore, it has become inevitable to find materials with higher capacity and higher cycle life and to develop production techniques in order to meet the demands. There are many strategies to improve these parameters. The main ones are to use active materials with high capacity and to develop production techniques to increase energy density.

Within the scope of this study, NMC cathode chemistry has been selected. As the anode, graphite-based anode material, which has not yet a commercial alternative, has been chosen. Capacity, energy density and cycle life values that will emerge after a standard production process will be improved. In order to increase the efficiency of the battery, much more effective contributions will be provided in a much cheaper and simpler way by manipulating the simple parameters in the production processes instead of changing the chemistry. Surface differences, non-homogeneous distribution and high or low thickness values that occur during the production of electrodes directly affect the performance of the battery. Because the application method is to be dispersed in liquid solution and covered and dried, it becomes difficult to control the surface properties during each wetting and drying. For this reason, it is very important to interfere with the surface after coating.

Commercial NMC cathodes and graphite anodes will be prepared for pouch cell sizes and physical and electrochemical characterizations will be carried out before and after calendaring. The electrodes will be prepared in certain thicknesses and calendered at 15%, 30%, 45% rates. Thickness changes, surface tensions and porosity changes will be compared. The surface morphology of the produced electrodes was characterized using Field-emission scanning electron microscopy (FESEM), and Energy dispersive spectroscopy (EDS) was conducted to understand the elemental surface composition of composites. The structures of the composites were characterized using X-ray diffraction (XRD) patterns and Raman spectroscopy. The electrochemical performance of the full cell was investigated by charge/discharge and cyclic voltammetry tests from 2.7V to 4.3V in pouch cells.

Keywords: Lithium ion battery, NMC cathode, Calendering, Pouch Cell.

Acknowledgments

The authors also thank to TUBITAK TEYDEB-BIGG-1512 program for their financial support under the contract number 2190317.

This work is also supported by Research Fund of the Sakarya University under the project no: 2019-6-22-251 and 2019-5-19-265.

This work is also supported by Research Fund of the Sakarya University of Applied Sciences under the project no: 2021-16.

Muhammet Barış EKİCİ was born in Sakarya, Turkey. He received his B.S degree both in Metallurgical and Materials Engineering from Sakarya University in Turkey. He has been pursuing his M.S degree in Sakarya University of Applied Sciences which are Metallurgical and Materials Engineering since 2019. His current research is on calendering parameters for high energy density battery electrodes in Li-ion batteries.

Corresponding author: Muhammet Barış EKİCİ, e-mail:m.baris.ekici@gmail.com tel: +90 543 778 09 88

LFP battery aging study: selecting batteries for reuse in a second life

William Wheeler[1,3], Ali Sari[1], Pascal Venet[1], Yann Bultel[2], Elie Rivière[3], Frédéric Meniere[3]
[1]Univ Lyon, Université Claude Bernard Lyon 1, INSA Lyon, Ecole Centrale de Lyon, CNRS, Ampère, UMR5005, 69622 Villeurbanne, France
[2]Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, F-38000 Grenoble, France
[3]EVE System, 69440 Taluyers, France

At the end of the first use of batteries in industrial electric vehicles (EV), the remaining capacity is expected to be around 80-70% of its initial capacity. Therefore, autonomy becomes insufficient for the original application, although these batteries could be reused for less demanding applications. The management of recycling is the responsibility of the manufacturer, and its cost is substantial for lithium-ion and in particular for lithium iron phosphate (LFP) batteries. Indeed, second life applications for lithium-ion batteries are an opportunity for the industry to postpone recycling costs, to improve lithium-ion batteries' economic value, and to reduce environmental impact.

Capacity and power limitations need to be predictable to meet required specifications throughout the second life. The purpose of this work is to identify the necessary parameters to sort battery modules in view of a second life application. To this aim, it is necessary to assess capacity decrease, resistance increase, and other events in the whole lifetime of the battery in order to allow second-life-battery manufacturers to certify that any battery pack it sells can fulfil second life requirements. The sorting process is considered at the module level because cells are assembled with the Battery Management System (BMS) and this helps modularity in reassembly for a second use unlike a battery pack. Moreover, the sorting process at the module level is expected to be faster, cheaper and easier than at the single cell level.

This work presents an aging study that intends to continue cell aging over the end of the first life. In this context, changing behaviour or unexpected events may appear: there is no certainty that cell aging will follow the same trend during the second life. The test conditions are determined according to different possible uses of industrial EV: medium or fast charge and discharge current, or high depth of discharge. Those different parameters of use are suspected to imply a sudden shift in cell aging: acceleration of capacity fade or resistance increase. By the way, some conditions can improve battery aging. Loss of lithium inventory is commonly reported in the literature as the main aging cause in first life, but loss of active material may accelerate cell aging. The predictability of those aging process is required to set a sorting process for lithium-ion batteries in order to guarantee their use in second life. This work aims at shedding light on harmful phenomena in some normal battery use, and collect data related to their appearance. In a long-term research, this experiment data will establish a diagnosis model to estimate remaining cell capacity and a specific aging process that may lead to sudden capacity fade. Then, the prognosis of the remaining useful life will decide potential reuse in a second life application.

Cell reference	DoD (%)	Charge type	Charge cut-off voltage	Charge C-rate	Discharge condition
prismatic cell 1	70	CC	3.65V	C/3	WLTP
prismatic cell 2	70	CC-CV	3.65V	C/3	WLTP
prismatic cell 3	70	CC-CV	3.55V	C/3	WLTP
18650 cells 4, 5	70	CC	3.65V	C/3	WLTP
18650 cells 6, 7, 8	100	CC	3.65V	C/3	WLTP
18650 cells 9, 10, 11	70	CC-CV	3.55V	C/3	WLTP
18650 cells 12, 13, 14	70	CC-CV	3.65V	2C	WLTP
18650 cells 15, 16, 17	70	CC-CV	3.55V	2C	WLTP
18650 cells 18, 19, 20	70	CC-CV	3.65V	2C	CC (2C)

Table 1. Aging conditions for each cell.

Tests are being carried out in two laboratories with four test benches on new industrial cells. Three LFP industrial-electric-vehicle 72Ah high capacity prismatic cells and twenty 18650 1.1Ah cells are cyclied on different test benches. All experiments are conducted under accelerated aging at a temperature of 50°C. An electric-vehicle-type discharged profile is calculated from the Worldwide harmonized Light vehicles Test Procedures (WLTP) standard. The cycle is used to approximate a typical operation of an electric vehicle during the aging study, with a C-rate peak of 2.7C in discharge and regenerative mode. The WLTP average discharge C-rate is C/3. Table 1 summarizes aging conditions for all 23 cells. The variations depend on Depth of Discharge (DoD), charge type, Charge cut-off voltage, Charge C-rate, or discharge scenario. The change in aging rate is reported as being due to a change in aging mode. For each cell, a characterization procedure is carried out on fresh cells and every 100 cycles at 50°C. Then, the characterization procedure is repeated every 100 aging cycles to follow parameters evolution. The characterization process consists of two tests: a C/3 CCCV charge and discharge from 0 to 100% State of Charge (SoC), and a C/25 charge and discharge for pseudo-open circuit voltage measurement. The first test allow calculating the battery's remaining capacity, and the second one electrodes capacity.

Born in 1995 in France, William Wheeler gets his engineering degree in mechatronics from Université de Technologie de Compiègne in 2018. Its experimental project on the topic of electric vehicles is a stepping stone to begin a Ph.D. thesis in the field of electric vehicles batteries. He currently works at the University Claude Bernard Lyon 1 and EVE System. He focuses his research on electric vehicles batteries, aging study and reuse in a second life.

Presentating author: William Wheeler, e-mail: william.wheeler@univ-lyon1.fr tel: +33761365228

SUPERCAPACITORS

Preparation of an MXene/CNT composite electrode for high-performance supercapacitor

Murat Yılmaz[1], Omer Sadak[2] and Muslum Demir[1]*

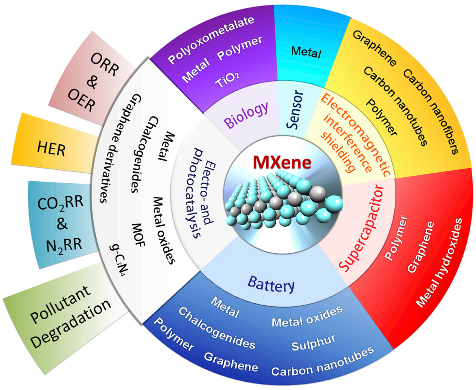
[1]Department of Chemical Engineering, Osmaniye Korkut Ata University, Osmaniye , Turkey
2[1]Department of Electrical and Electronical Engineering, Ardahan University, Ardahan , Turkey

The new family of 2D transition metal carbides, carbonitrides and nitrides (collectively named as MXenes) has extended rapidly in the past several years after the discovery of Ti2C. The materials have unique properties including surface terminations, such as hydroxyl, oxygen, or fluorine, which inform hydrophilicity to their surfaces. Since 2011, more than 22 different MXenes have been synthesized by selective etching of many atomic layers from their layered precursors' MAX phases. The availability of solid solutions, the control of surface terminations and a recent discovery of multi-transition-metal layered MXenes suggest the potential for synthesis of certain new structures. The adaptable chemistry of MXenes leads the tuning of properties for applications including energy storage technology, hydrogen storage technology, adsorptive environmental application, electromagnetic interference shielding, water treatment, gas- and biosensors, and chemical catalysis. In this talk, we present the synthesis, structure and physical and chemical properties of MXene/CNT composite. Additionally, energy storage applications including supercapacitors and an outlook for future research will be given.

Introduction

Recently, energy has become a very popular topic in nature. Due to the limitation of fossil fuel resources, renewable energy such as solar and wind energy attract great attention. However, wind and solar energies are suffered from sustainability because the energy supply is based on environment and weather conditions. Thus, Electrochemical energy storage technology including Li-ion batteries (LIBs), Li-S batteries (LISs) and supercapacitors are reflected to be alternative methods to store renewable energy supply. However, today’s battery performance could not meet the developing demand for scale-up energy storage. To overcome the abovementioned issue, scientists and industry specialist are seeking novel materials with advanced performance in energy storage technology. Since the discovery of single layer of graphite called two-dimensional (2D) graphene in 2004 [1], many 2D materials have been intensively investigated in detail because they have unique physical, chemical, mechanical and electrochemical properties. Examples of 2D materials are hexagonal BN1,2 silicene 3 germanane 4 transition metal dichalcogenides (TMDs) 5 and phosphorene were also successfully produced in laboratories. Especially, the high surface area to volume ratio and actual surface areas of 2D materials results in high energy density and large mobility ensuring making very strong candidates for ESD.

In this paper, Ti3C2 and Carbon nanotube (CNT) were mixed to obtain MXene\CNT composites by a facile method, which are subsequently coated on carbon nanotube fibers (CNTs). By controlling on morphology, the resulting MXene/CNT electrode exhibits a high specific capacitance and capacitance retention as well as superb flexibility, i.e., neglected capacitance loss at a bending angles . The as-prepared composite film opens a new door for transition metal carbides and transition metal oxides with great potential in flexible electronics.



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Muslum Demir is an assistant professor at Osmaniye Korkutata University, Osmaniye, Turkey. He was received his Ph.D. in Prof. Ram Gupta's lab at Virginia Commonwealth University (Virginia, USA) 2017. He received his M.S. in Chemistry from Rutgers University (USA) in 2013 and his B.S. from Cukurova University (Turkey) in 2008. His research focused on the development of biomass-derived carbon materials for energy storage and conversion applications. He has published more than 13 peer-reviewed papers and attended prestigious conferences such as ACS, AICHE and ECS meetings.

Corresponding author: Muslum Demir, muslumdemir@osmaniye.edu.tr tel:+90328 825 1818

Elucidation of Efficient Charge/Discharge Mechanisms in Electrical Double Layer Capacitors

Betul Uralcan[1]

[1] Bogazici University, Department of Chemical Engineering, Turkey 34342

Electrical double layer capacitors (EDLCs) store energy in the form of electrical charges at the interface between an electrolyte and a high surface area electrode. As their energy storage mechanism relies on physical interactions, EDLCs possess many advantages over conventional electrochemical energy storage technologies, including efficient operation at high power density, extended cycle life, and improved safety. Nevertheless, they suffer from low energy density [1]. The goal of this study is to rationally identify electrode/electrolyte combinations with optimized properties and incorporate them into EDLCs.

Room temperature ionic liquids (RTILs) possess unique properties (high charge density, electrochemical stability, low/negligible volatility, tunable polarity, etc.) that offer an attractive alternative to conventional electrolytes. RTILs' incorporation into EDLCs has been hindered, for the most part, due to the lack of fundamental knowledge on their structural and capacitive properties at the electrical double layer which differs markedly from that of conventional dilute electrolytes. In recent years, interfacial properties of pure RTILs have begun to be unraveled using experimental, simulation and analytical techniques [1-3]. Nevertheless, these studies have been limited to a narrow range of pure RTILs. Given the large number of RTIL ions and "coctails", there are practically an infinite number of solvent-free or solvent-enriched RTIL-based electrolytes with tunable properties. That, combined with numerous carbon-based electrode materials, makes choosing an optimum RTIL/electrode combination for any given application highly nontrivial, leaving the experimentalists with the only option of using heuristics [1].

In order to enable efficient screening and rational design of electrolyte/ electrode combinations, we designed a computational framework to systematically study how molecular features such as electrolyte polarity, size, and shape, and electrode properties such as pore structure affect energy storage capability [4-5]. We demonstrated the validity of this framework by unravelling the effect of electrolyte composition on capacitive response in realistically modeled electrodes (Figure 1), and confirmed our findings with experiments. These results provide insights into the microscopic mechanisms that determine electronic properties of the interface and enable means to rationally identify electrode/electrolyte combinations with optimized properties.

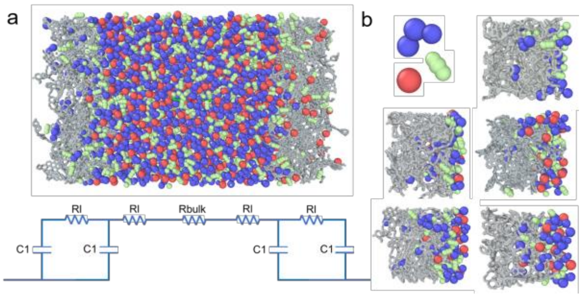

Figure 1. Simulated electrical double layer capacitor (EDLC). (a) EDLC is composed of an electrolyte between two porous electrodes (electrode carbon atoms (grey), cation (blue), anion (red), solvent (green)) with the equivalent circuit model (below), (b) Coarse-grained models for electrolyte molecules and electrode /electrolyte interfaces for five different electrodes with electrolyte ion fraction ρ= 47.

Acknowledgments

This study is funded by the Scientific and Technological Research Council of Turkey (TUBITAK), Grant No: T118C220.

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Betul Uralcan is an Assistant Professor in the Department of Chemical Engineering at Princeton University and a Fellow of Polymer Research Institute. She received her B.S. in chemical engineering in 2013 from Bogazici University, and her Ph.D. in chemical engineering from Princeton University, USA in 2018 under the supervision of Pablo G. Debenedetti. Betul continued her postdoctoral studies at Princeton until she joined Bogazici University. In 2019, she received the TUBITAK 2232 International Felloship for Outstanding Researchers.

Presentating author: Betul Uralcan, Current address: Boğaziçi University, Chemical Engineering Department, Istanbul, Turkey. E-mail: betul.uralcan@boun.edu.tr

Organic Electrochromic-Energy Storage Application Based on Dithienothiophene, Triphenyamine and 3,4-ethylenedioxythiophene

Sebahat Topal[1], Esma Sezer[1], Belkis Ustamehmetoglu[1], Turan Ozturk[1,2]

[1] Istanbul Technical University, Department of Chemistry, 34469 Maslak İstanbul.
[2] TUBITAK-UME, Chemistry Group Laboratories, PO Box 54, 41471, Gebze, Kocaeli, Turkey.

With the development of technology, electrochemical energy storage systems have attracted to create low weight, low cost, flexible and environmentally sustainable energy storage devices [1-3]. Many studies focus on a still challenge to improve energy for supercapacitor or improve power for batteries by using hybrid energy storage mechanism [4]. The skeleton idea of the hybrid devices is to combine supercapacitor-type electrode materials with the battery type electrode materials [5]. For this purpose, designing the new hybrid electrode materials have gained importance.

Organic electrode materials have received attention due to the relative abundance of their constituent, facile synthetic processes, and their flexible features [6,7]. With the improving the micro/nano materials, conjugated microporous polymers (CMP) have attracted to enhance the electrochemical energy storage system because of their high specific surface area to do suitable for pseudocapacitors and batteries [8]. CMPs material exhibit high capacitance and long cycle life due to π-conjugation and porosity [9]. However, these CMP compounds could be used only powder form and obtaining film state CMP is very rarely due to their low solubility with rigid and cross-linked structure. This problem could be solved with the directly CMP film forming on electrode surface by electrochemical deposition in one step [10]. This way provides to control film thickness by monitoring the polymerization condition and create flexible multifunctional applications [11].

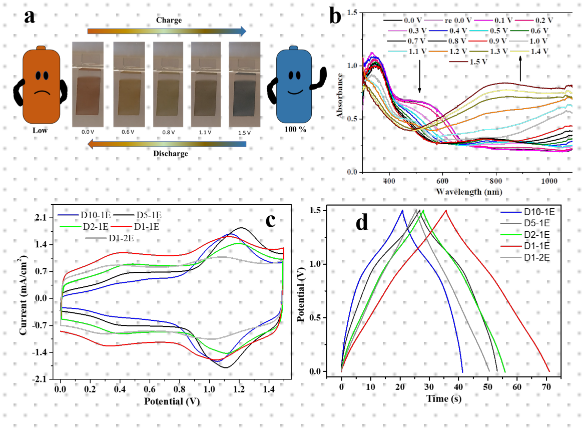

Figure 1. Electrochromic images of polymer film D5-1E (a), UV-vis spectra of the film at different potentials(b), CV of the different copolymer films at 50 mV/s and GCDs of these films at 0.5 mA/cm^2.

Additionally, organic electrode material could be used in electrochromic devices due to their coloration under different potential [12]. Nowadays, multifunctional applications have great attention and electrochromic-energy storage system is most popular area for future technologies.

In this study, we demonstrate that new organic electrode materials obtained electrochemical deposition with triphenylamine and dithienothiophene based monomer (D) and ethylenedioxythiophene (E) on ITO. The polymer films were prepared with different molar ratio of monomers (D/E) : 10/1; 5/1; 5/2; 1/1 and 1/2). The new copolymers indicate color changing between charge and discharge states (Figure 1). The concept of electrochromic and polymer films offers promising opportunities for the future multifunctional technologies and next generation energy storge applications.

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Sebahat Topal completed her MSc in chemistry from Istanbul Technical University in 2017 and her PhD study currently continue under the supervisor of Prof Turan Ozturk with a project. Her fields of interest include synthesis and characterization of organic compounds, polymers, nanomaterials, optoelectronics, and energy storage system. Her thesis is supported by government grants (Council of Higher Education YOK 100/2000 and The Scientific and Technological Research Council of Turkey TUBITAK 2211A) on ''Energy and Energy Storage''.

Presentating author: Sebahat Topal, e-mail:topalse@itu.edu.tr

Capacitive performance of chemically modified Fe/O co-doped graphene

Neriman Sinan Tatli, Ece Unur Yilmaz

Department of Chemistry, Bursa Technical University, Yildirim 16310, Bursa, Turkey

Advanced energy storage systems with both high energy and high power capabilities are urgently required for more efficient use of renewable energy sources to mitigate the adverse effects of climate change. Owing to their high energy density, batteries have become the most popular candidates for various applications. Supercapacitors, on the other hand, are more beneficial for high power applications as they can be charged/discharged in seconds and can withstand frequent charge-discharge cycles at high currents. However, the low energy density of supercapacitors needs to be overcome for commercial exploitation.

Tremendous efforts have been directed toward the production of efficient, highly capacitive electrode materials with larger specific surface areas, appropriate pore structure, and enhanced electrical conductivity. Owing to large theoretical surface area (2675 m^2 g^{-1}), high electrical conductivity ($2x10^3$ S cm^{-1}), and high mechanical stability, graphene-based nanomaterials are promising to enhance the effect of electric double layer (EDL), and thus to achieve higher gravimetric capacitance. However, the graphene sheets are prone to restack, leading to low specific capacitance. Recent studies have shown that the design of different graphene morphologies (e.g., porous 3D structures, hydrogels, and aerogels) and the doping of heteroatoms (e.g., nitrogen, oxygen, boron, and fluorine) can efficiently increase the specific capacitance up to 500 F g^{-1} [1]. The heteroatoms not only provide additional pseudocapacitance but also increase the surface wettability and the electrical conductivity, enhancing the overall electrochemical performance.

Generally, external templates such as ordered silica and toxic heteroatom precursors (e.g., NH_3) are used to prepare heteroatom doped 3D graphene structures [2][3]. This work presents a straightforward self-template approach for the synthesis of 3D Fe/O co-doped graphene. Interfacial tension between O atoms and Fe^{3+} ions (released from acid etched Fe_2O_3 particles) during hydrothermal reaction is responsible for the self-templating process. With the synergistic influence of pseudo-capacitive Fe-O moieties and EDL-capacitive graphene, 3D Fe/O co-doped graphene exhibited excellent capacitive properties, including a high specific capacitance (425 F g^{-1} at 0.25 A g^{-1}), high rate capability (71% retention at 20 A g^{-1}), and high cycling stability (5000 charge-discharge cycles at 10 A g^{-1}) using 1M H_2SO_4 electrolyte in a three-electrode system.

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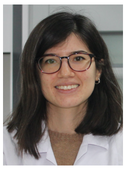

Neriman Sinan Tatli is a research assistant at Bursa Technical University, Department of Chemistry. She received her B.S. in Mechanical Engineering from Uludag University in 2014 and M.S. degree in Materials Science and Engineering from Bursa Technical University in 2016. Now, she is pursuing a PhD degree in the same program under the supervision of Prof. Dr. Ece Unur Yilmaz. Her research interests focus on energy storage materials and their applications.

Presenting author: Neriman Sinan Tatli, e-mail: neriman.tatli@btu.edu.tr tel: +90 224 808 10 59

Induced bifunctionality in dual-doped lanthanum cobalt-based perovskite for zinc-air batteries

Mohamed Elhousseini Hilal,[1, 2] Seyfettin Berk Şanlı,[2] Francis Verpoort,[1] and Berke Pişkin[2*]
[2] Wuhan University of technology, State key laboratory of advanced technology for materials synthesis, LOCOM, Wuhan, China
[1] Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey

For the last decades, multiple energy storage and conversion technologies were either uncovered for the first time or revived and further upgraded relying on the state-of-knowledge. Zinc-air batteries (ZAB), for instance, are traced back to the early nineteenth century, without any noticeable impact on the electrical energy storage market. Until 1997 that it re-emerged as a rechargeable risk-free strong potential alternative of Li-ion batteries, relying on the affordable cost of zinc metal and the intrinsically high theoretical energy density (~1300 Wh kg^{-1}).[1] The early-stage research on ZABs still needs extensive corroboration at the level of all three compartments: Anode, electrolyte and air-cathode. In our works, we concentrate on designing multifunctional materials to secure the well-functioning of the cathode's sluggish electrocatalytic reactions: oxygen evolution (OER) and reduction reaction (ORR). Nevertheless, engineering rational nano-sized materials and achieving the required synergism remain a major challenge.

Perovskite oxides-based electrocatalysts having ABO_3 type structure were comprehensively investigated to replace noble metals for oxygen reactions, making prove of interesting catalytic activities.[2] The mixed-oxide nature of perovskites enables tuning their properties by selecting various combinations of rare earth and transition metals for A and B sites, respectively. In this study, lanthanum-cobaltite ($LaCoO_3$) was selected on account of its renowned activity toward OER.[2] Further tweaking of the features of such oxide could be achieved by introducing dopant metals into the structure. Consequently, not only distorting the crystalline structure but also modifying the oxidation state of the metal content and creating vital oxygen vacancies.

$LaCoO_3$ was dually-doped by Ca^{2+} and Mn^{+2} at the A and B sites, respectively, using the Pechini method for synthesis. The influence of such an approach on the structural, morphological, and electrochemical properties of the materials were extensively studied. X-ray diffraction (XRD) was performed on a batch of $La_{1-x}Ca_xMn_xCo_{1-x}O_3$, for x={0-0.3}. The diffraction data of the synthesized perovskites was collected with a scan rate of 2° min^{-1} from 10° to 100°. The series of LCMC samples were used to prepare respective inks for drop-casting on a 5 mm diameter glassy carbon electrode with a loading of 0.751 mg cm^{-2}. The working electrode, platinum wire, and a saturated calomel reference electrode were arranged as a three electrodes cell in 1M KOH electrolyte. All the polarization tests were performed at room temperature at a scan rate of 10 mV s^{-1}. The $La_{1-x}Ca_xMn_xCo_{1-x}O_3$ samples showed distinct electrochemical activities toward OER; where the overpotentials at 10 mA cm^{-2} have ranged between 546 mV, 395 mV, 357 mV, and 438 mV (vs. RHE) for LC, LCMC9119, LCMC8228, and LCMC7337, respectively. These results confirm the enhancing effect of calcium and manganese dual-doping on top of localizing the optimal amount of doping as x=2. The faster OER kinetics of LCMC8228 were asserted by Tafel plots in Figure 1a, exhibiting the smallest value 93 mV dec^{-1} in comparison to 116, 96, and 99 mV dec^{-1} for LC, LCMC9119, LCMC7337 respectively. The tests on the corresponding ZABs were performed and exhibited low charge-discharge polarizations differences as visible in Figure 1b, with extended galvanostatic life cycles for LCMC8228. The encouraging results obtained by this strategy of dual-doping are unlocking a path for further comprehension of perovskite oxides electrocatalytic behaviours.

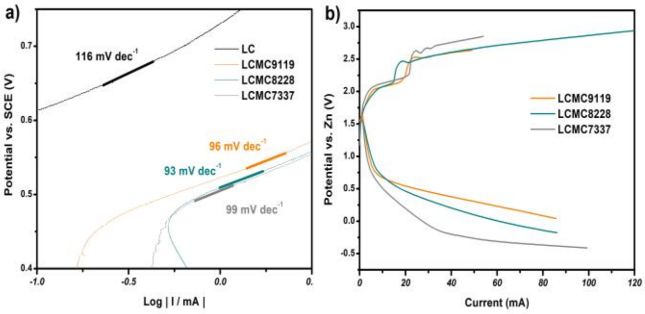

Figure 1. OER Tafel plots of the samples LC, LCMC9119, 8228, and 7337 (a). ZAB charge and discharge polarization curves of LCMC9119, 8228, and 7337 (b).

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Mohamed Elhousseini Hilal has received a science bachelor and master degree in materials science engineering in 2015 and 2017, from Sultan Moulay Slimane University in Morocco. Afterwards, he was enrolled for PhD at the key state laboratory (LOCOM), Wuhan University of Technology, China. Currently, being a visiting researcher in Energy Materials Laboratory at Muğla Sıtkı Koçman University. His research focuses on developing composite materials from metal-organic frameworks and metal oxide nanomaterials for electrochemical hydrogen production and metal-air batteries.

Presentating author: Mohamed EL. HILAL, E-mail: med.el.hilal@gmail.com tel: +90 552 868 1578

Advances in Harvesting Triboelectric Nano Energy within ZnO/Ag/Si(100)

Gizem DURAK YÜZÜAK[1,*], Seray ÖZKAN[1] and Ercüment YÜZÜAK[1]
[1]Recep Tayyip Erdoğan University, Faculty of Engineering and Architecture, Department of Energy Systems Engineering, Functional Materials Research Group, 53100, Rize, Turkey

With the progress of quantum technologies, electronic devices that we use in daily life and that require continuity are caused to become smaller and therefore the energy required by these devices is relatively low. Hereby, mankind has developed nano-micro scale energy harvesting ideas. The number of automation smart systems and sensors that equip our environment is increasing day by day, and as a result, the energy requirements of systems, many of which have to work without being connected to a network, are provided by modern and non-nature-friendly, inefficient batteries. One of the barriers limiting the development of deployable integrated sensing and actuation solutions in multifunctional systems is power shortage. In this framework, the power of these sensor networks to end their own energy generation; is very critical that it is obtained from small, inexpensive and reliable sources [1].

Triboelectric nanogenerators (TENG) are the mechanism that collects the electrostatic energy generated by the friction of at least one dielectric material with electrically different charges and operation modes are given in Fig. 1. Here, the phenomenon that directly affects the output power and has critical importance is the distribution and density of the charges, which is the electricity produced on the contact surfaces of the two materials. In other words, TENG performance is largely explained by the amount of triboelectric charge generated on the friction layer during the triboelectrification process.

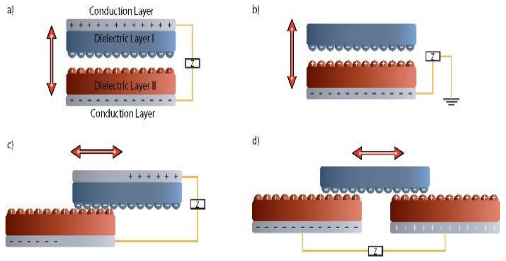

Figure 1. Schematics of triboelectrification modes **a)** Contact-separation mode **b)** Single electrode mode **c)** Sliding mode and d) Free standing triboelectric layer mode [2]

In current applications, energy is produced by using polymer-based materials as triboelectric layer in TENJs [3]. In contrast, via this study, the energy harvesting process from the waste mechanical energy, which is carried out by increasing the electrical charge difference between the layers by using these ZnO semiconductor film, is present by using triboelectric materials that are formed by using silver conductors using these electrodes.

Because of their low cost-effectiveness and strong electrical activity, ZnO films with susceptible characteristics, particularly the wurtzite phase (hexagonal symmetry), are the most extensively utilized oxide for transparent electronic applications. Friction layers made of ZnO semiconductors for triboelectric nanogenerators (TENG) can also be environmentally beneficial and long-lasting. Thin films can be utilized as friction layers to increase the triboelectric nanogenerator's output voltages. Variations in the growing conditions, such as working powers and pressures, is used to boost the triboelectric effect's magnitude in the current study. X-ray diffraction (XRD), scanning electron microscopy (SEM), semi-logarithmic I-V curves, and frequency dependent resistivity measurements are being used to evaluate the crystal structure, surface morphology, resistance, and capacitance properties of thin films. In triboelectric systems, especially below 10 Hz, it has been well known that electrical resistance and capacitance properties in the low-frequency region seem to be of high significance.

According to the results of the present study, a triboelectric nanogenerator based on semiconductor/conductor-based layers would be environmentally benign, low-cost, and have a higher output performance. According to varied sputtering pressures and target powers, the structural, and electrical values of ZnO/Ag/Si(100) films as semiconductor layers were obtained and evaluated. We established a robust mechanical energy harvesting system based on ZnO/Ag (dielectric layer I) and PET/ITO (dielectric layer II) triboelectric layers to taking utilisation TENGs' potential energy harvesting. Using load output features of the device, the mechanical force capacity of TENG was also researched and proven to be suitable for high voltage and low current applications.

Acknowledgements

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the grant number of 119M972.

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Dr. Gizem Durak Yüzüak received her bachelor's, master's, and PhD degrees in physics engineering from the University of Ankara, Turkey in 2008, 2010, and 2016, respectively. Her research is centered around nearly all branches of solid-state physics and applications. Particular interests include the nano-materials especially thin films in permanent magnets, magnetocaloric, spintronics and semi-conductors. She has published more than twenty articles in a range of journals.

Presentating author: Gizem DURAK YÜZÜAK, *e-mail:* gizemyuzuak@erdogan.edu.tr

Synthesis of Biomass-derived hierarchical porous carbon for supercapacitor electrode material

Murat YILMAZ[1], Müslüm DEMİR[1]

[1]Dept. of Chemical Engineering, Osmaniye Korkut Ata University, Osmaniye, Turkey

In recent years, supercapacitors have attracted much attention because of their long service life, cycle performance, high specific capacitance, fast charge and discharge rate, easy maintenance and safe operation [1]. In a manner of speaking, the supercapacitor has the dual functions of secondary batteries and traditional capacitors. Compared to ordinary batteries, supercapacitors have a higher power density, and it bridges the gap between these two traditional technologies, as the energy density is much higher than conventional capacitors [2].

Supercapacitors are divided into electric double-layer capacitors (EDLCs) and pseudocapacitors depending on the different charge storage process [3]. In pseudocapacitors, the energy storage process takes place by Faraday reaction on the surface of active materials, while in EDLCs, electrical charges are accumulated on the electrode with the electrolyte interface [4]. Activated carbons (ACs), carbon nanotubes and graphene as promising electrode materials for EDLCs have been widely used due to their high surface area, non-toxicity, controllable porosity, various forms of usability, and excellent electronic conductivity [5].

In this study, the use of activated carbon obtained from biomass, by producing porous activated carbon (PSAC), in supercapacitor production was investigated. The production was carried out in two steps. In the first step, biochar was obtained from biomass using hydrothermal carbonization method and Biochar-KOH mixtures were prepared in four (Biochar(g)/KOH(g) ratio as 1/0, 1/4, 1/5 and 1/6) different ratios. In the second step, these mixtures were subjected to physical (CO_2) and chemical activation (KOH) in a tubular furnace. The sample with a biochar(g):KOH(g) ratio of 1/4 was also activated in N_2 medium. Samples obtained are named as C0, C4, C5, C6 and C4_N2. In this study, the effects of CO_2, N_2 environments and KOH amount on activated carbon production were investigated.The morphological features and available functional groups on the surface of biochar were characterized using scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffractometer, and Brunauer–Emmett–Teller. The electrochemical performance analyses were performed by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy methods.

It has been observed that the amount of KOH and the CO_2 environment used in activation significantly affect the surface area and porosity of the activated carbon. In addition, in the supercapacitor application of the produced porous carbon, the specific capacitance of the electrode prepared with C4 at a current density of 0.5 A g^{-1} was measured as 148 F g^{-1}(Figure 1). Besides, the electrode prepared with C4 sample has achieved an excellent long-cycling life with only 1.3% loss of its initial capacitance over 4,000 cycles even at 5 A g^{-1}.

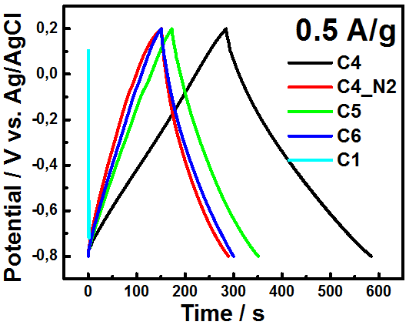

Figure 1. The GCD curves for all samples at current density of 0.5 A g^{-1}

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Dr. Murat YILMAZ is with the Department of Chemical Engineering, Osmaniye Korkut Ata University. Having graduated from Selçuk University in 2007, Murat Yılmaz obtained his M.SC in 2010 from Selçuk University and Ph.D. in 2018 from Ege University. His research interest covers energy storage, supercapacitors, adsorption and nanomaterials

Corresponding author: Murat Yılmaz, e-mail: muratyilmaz@osmaniye.edu.tr tel: +90 5077532911

Development of Activated Carbon / Bimetallic Transition Metal Phosphide Composite Materials for Electrochemical Capacitors and OER Catalysis

K. Özgün Köse[1,2] and M. Kadri Aydınol[1,2]

[1] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey

[2] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, Turkey

Among energy storage devices electrochemical capacitors (EC) stand out with high power densities, while battery and fuel cells have been used in applications requiring high energy density. There are numerous active materials developed for EC usage, transition metal phosphides are one of the most promising ones among them [1]. They react with OH- ions in the alkaline electrolyte like transition metal oxides; however, their electrical conductivities are generally higher compared to that of oxides. This character provides better power densities in electrochemical capacitors compared to the oxides [2].

In this study, composite structure is created with the bimetallic transition metal phosphides (TMP) decorated on the most commonly used material, activated carbon (AC), in electrochemical capacitors. Its structure is suitable for forming an electrical double layer, and thus, to yield superior properties in electrochemical capacitors. This nanocomposite structure was obtained by using the phosphorous functional groups left over on the surface of AC during phosphoric acid treatment in the activation process of biomass. Therefore, during AC production, phosphoric acid activation was used. After AC production stages are finished, a second impregnation was applied with transition metal salts and reduction was carried out at high temperature under Ar-H_2 gas mixture. As transition metals, nickel, manganese, copper, iron and cobalt were used. In this way, two different charge storage mechanisms resulting from double layer formation on the activated carbon surface and redox reactions on the bimetallic TMP surface is used together.

Cyclic voltammograms of the AC/bimetallic TMP structures are given in Figure 1. The redox reactions are seen in the potential range of 0.2 – 0.6 V range, as it is evident from the oxidation and reduction peaks. Nickel is kept constant in the TMP's, the others are Cu, Mn and Co. The area under the CV curve of Co-Ni composite is the biggest; therefore, it is the most promising one in EC usage. Furthermore, redox peaks are more localized in Cu-Ni composite whereas it is wider in Co-Ni composite, indicating more than one redox mechanism in Co-Ni composite.

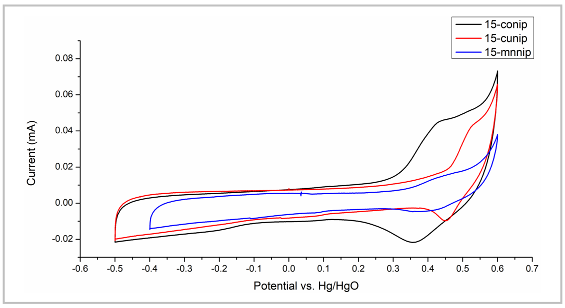

Figure 1. CV of AC/Bimetallic TMP composites.

LSV curves the AC/bimetallic TMP structures are given in Figure 2. Fe-Ni composite structure is the most promising one for OER catalyst applications according to this figure, since the overpotential of this reaction is clearly smaller on Fe-Ni.

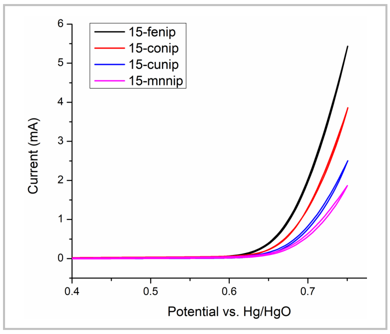

Figure 2. LSV of AC/Bimetallic TMP composites.

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Kadir Ozgun Kose obtained his B.Sc. from Department of Metallurgical and Materials Engineering in Middle East Technical University in 2014. He got his M.Sc. degree in 2017. He is currently PhD. student in the Department of Metallurgical and Materials Engineering, Middle East Technical University. His research areas mainly focus on electrochemical capacitors.

Corresponding author: Kadir Özgün Köse, email: kose@metu.edu.tr phone: +90 312 210 5831

Ti_3C_2 MXene Supercapacitor with Thin Film h-BN Separator

Alptekin Aydinli[1,2,3,4], Xuehang Wang[1], Husnu Emrah Unalan[2,3], and Yury Gogotsi[1]
[1]A. J. Drexel Nanomaterials Institute, Dept. of Materials Science and Engineering, Drexel University, Philadelphia, PA, 19104, USA
[2]Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara 06800, Turkey
[3]Energy Storage Materials and Devices Research Center (ENDAM), METU, Ankara 06800, Turkey
[4]Dept. of Materials Science and Engineering, Adana Alparslan Turkes Science and Technology University, Adana 01250, Turkey

Portable electronic devices necessitate electrochemical energy storage (EES) units that can provide high energy and power densities. Current strategies mostly focus on improving the performance of the electrode active materials. Decreasing the weight/volume fraction occupied by the inert components such as electrolyte, separator and current collector should dramatically improve the performance of EES devices, since 70-80 wt.% of the EES devices is occupied by these components. Polypropylene membrane and glassy fiber films with typical thicknesses larger than 25 µm are the conventional separator choices. Insulating 2D materials, with their flat and smooth surface, at a much smaller thickness would in fact be sufficient to act as an efficient separator [1].

Following the discovery of the first two-dimensional (2D) titanium carbide ($Ti_3C_2T_x$) in 2011, a new family of 2D transition metal carbides and nitrides named MXenes emerged. Since then, MXene family has grown quickly and continuously within the field of 2D materials. MXene has a general formula of $M_{n+1}X_nT_x$, where M is an early transition metal, X stands for carbon or nitrogen, and n = 1–3. T represents the surface termination groups, such as -O, -OH and -F, on the MXene surface. Electrochemical properties of MXenes have been widely investigated in the literature [2].

2D hexagonal boron nitride (h-BN) nanosheets, also known as ‘white graphene’ or ‘non-carbon graphene’, compose of a few layers of alternating boron and nitrogen atoms in a hexagonal order. They are shown to have very promising mechanical, thermal and electronic properties and utilized in many applications [3].

In this study, the use of thin film h-BN as an efficient separator layer in symmetric supercapacitors was demonstrated. In these devices, Ti_3C_2 was used as both the positive and negative electrodes. Spray coating technique was used to deposit both h-BN and Ti_3C_2 layer on PET substrate. Electrochemical properties such as specific capacity, rate capability and cycling stability of the fabricated supercapacitors were examined through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy.

Fabricated supercapacitors showed improved electrochemical performance in 1 M Li_2SO_4 electrolyte compared to the control device with conventional Celgard separator. As seen in Figure 1 the reduced thickness of the separator decreased the volume of the full device, significantly increasing the energy and power densities. In addition, the device with h-BN separator showed higher performance with respect to the device with Celgard separator in specific capacitance, Coulombic efficiency, series resistance and capacitance retention.

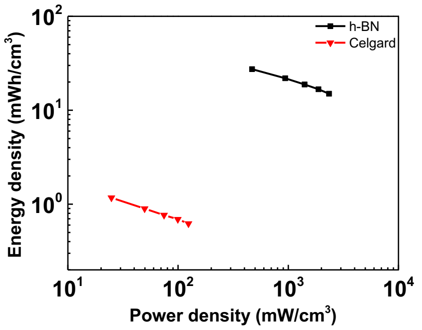

Figure 1. Power density vs. energy density of the fabricated devices.

Thanks to its significantly reduced separator thickness and increased energy/power densities, the Ti_3C_2 MXene symmetric supercapacitor device with thin film h-BN separator layer demonstrated very promising results to become a competitive alternative in energy storage systems, especially for flexible devices in which reduced thickness has significant importance.

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Acknowledgements

Alptekin Aydinli was supported by the TÜBİTAK 2214-A International Doctoral Research Fellowship Programme, No. 1059B141801094.

Alptekin Aydinli is a Research Assistant in Department of Metallurgical and Materials Engineering, Middle East Technical University. He is currently a Ph.D. candidate in the same department. He received his BS degree from Istanbul University in 2010, and MS degree from Middle East Technical University in 2013.

Corresponding author: Alptekin Aydinli, e-mail: aaydinli@metu.edu.tr tel: +90 312 210 74 85

Double layered hydroxide (Ni-Co)OOH for energy storage applications

Nourhan Mohamed, Ozden Gunes Yildiz, and Mustafa Urgen
Department of Metallurgical and Materials Engineering, Istanbul Technical University, Istanbul, Turkey

Layered double hydroxides based on nickel and cobalt are known for their promising electrochemical performance for energy storage applications due to the ease of tuning their composition, structural, electrical, and morphological properties. NiOOH is widely used for rechargeable batteries and super-capacitors. The α- Ni(OH)$_2$ exhibits higher capacitance compared to β polymorph as it is a more defective structure, with a high amount of interlamellar water and a wider potential range. However, structural transformation of the α toward β -Ni(OH)$_2$ happens under cycling conditions resulting in poor cycling stability, lower conductivity, and a narrower potential range[1]. On the other hand, Co(OH)$_2$ suffers high irreversible capacity loss because of its unstable electronic configuration and the O_2 gas evolution during the Co_{+2}/Co_{+3} transition[2]. Therefore, mixed double hydroxides based on Ni and Co are attractive because they show improved stability and capacity retention under cycling conditions. This study introduced the double hydroxide (Ni_xCo_{1-x})OOH synthesis using the anodic oxidation of Ni-Co in molten salt for the first time.

Experiment:

Self-standing nanowires substrates composed of Ni-Co were prepared by template-assisted electrodeposition in an anodic alumina membrane. Then, these alloys were anodized in molten KOH.

1. AAO membranes were prepared by anodization in 0.3M oxalic acid at 5˚C for 50 minutes at 60 V.
2. The AAO was activated by zincating for 50 seconds at 30-35˚C
3. The electrodeposition was performed using a modified Watt's solution with differet concentration of cobalt sulfate.
4. The double-layered hydroxide was prepared by anodic oxidation of Ni-Co alloys with different ratios in molten salt KOH at 200˚C.
5. Grazing incidence X-ray diffraction (GIXRD) was used to study the structure of the oxidized alloys.
6. Cyclic voltammetry (CV) was used to study the electrochemical stability of the double-layered hydroxide.
7. The morphology of the samples was studied by SEM.

Results:

GIXRD data revealed that the anodized Ni-Co alloys are composed of (Ni-Co)OOH with different concentration of Co and Ni. SEM images showed that all the anodized samples exhibited flakes-like morphology. The cyclic voltammetry shows that cobalt insertion into the NiOOH framework resulted in improved structural and electrochemical stability. The capacity retention increased with increasing the Co to Ni ratio, as shown in figure 1. For example, it was 43% for NiOOH while 73% for Ni: Co= 6:4.

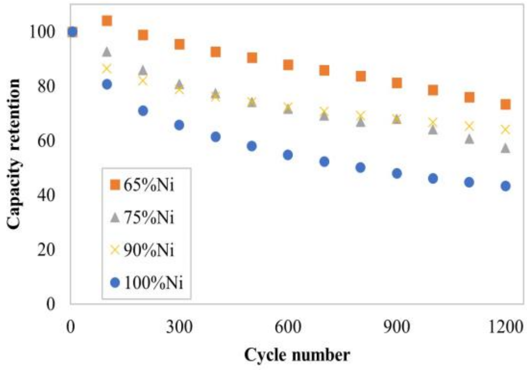

Figure1: Capacity retention of the Ni-Co alloys anodized in KOH molten salt at 200˚C.

Acknowledgment:

This project is receiving funds from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement number 764977

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Nourhan Mohamed is a Ph.D. student at the department of metallurgical and materials engineering at ITU. And graduated in physics from Fayoum University (Egypt) in 2013 and obtained M.Sc. in materials science and engineering from Picardie Julie Verne University (France) in 2017.

Presenting author: Nourhan Mohamed, e-mail:norhan.ramadan1@gmail.com, tel:05356731922

P[Th_3CNTT-TPA] based electrode material for supercapacitors

Sema Topal[1], Sebahat Topal[1], Garen Suna[1], Belkıs Ustamehmetoğlu[1], Turan Öztürk[1,2] and Esma Sezer [1]

[1]Istanbul Technical University, Department of Chemistry, 34469 Maslak İstanbul

[2] TUBITAK-UME, Chemistry Group Laboratories, PO Box 54, 41471, Gebze, Kocaeli, Turkey

Owing to the environmental stability, high charge carrier mobility, low cost, and flexibility, thiophene (Th)-based π-conjugated materials which are easy to modification for fine tuning the electronic properties have been holding a particular interest [1-2]. Thieno[3,2-b]thiophenes (TT) play an important role as their core skeleton consists of two fused rigid Th rings to limit the rotational disorder between the rings and create a better π-conjugation. Due to electron-rich structures, TT and derivatives could be employed for adjusting the band gap of organic materials [3] and in recent studies it is reported that their polymer films were found to be suitable for electronic and optoelectronic applications [4-6]. Triphenylamine (TPA) has become a valuable unit for wide range of materials such as OLEDs, solar cells, sensors, capacitors, and hole-transport devices, due to major properties of low-cost, large range of molecular designs and good hole mobilities, excellent thermal stability, high ionization potential properties, high stability during repetitive oxidation–reduction cycles and having stable radical cation after oxidations. Conjugated microporous polymers, are advanced porous material for energy storage applications. p-doped, conjugated TPA is one of the most common building units for high surface area microporous morphology possesing polymer that make it suitable to design porous cathode polymer to improve the electrochemical performance in supercapacitor and battery [7].

In this study it is aimed to use of synthetic chemistry to design new materials based TPA, CNTT and Th and to investigate structure property application relationships of these polymers for charge storage application. For this purpose, **Th_3CNTT-TPA**, was synthesized by Suzuki coupling reaction and its polymers **P[Th_3CNTT-TPA]** was prepared by electrochemical polymerization on ITO substrat. These polymer film shows reversible oxidation and reduction reactions and electro-active properties (Figure 1).

Then, capacitive properties of the **P[Th_3CNTT-TPA]** were investigated by CV, electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD) (cyclic stability properties were given in Figure 2) and spectroelectrochemical measurements. Results suggest that, **Th_3CNTT-TPA** seems a potential candidate for energy storage application.

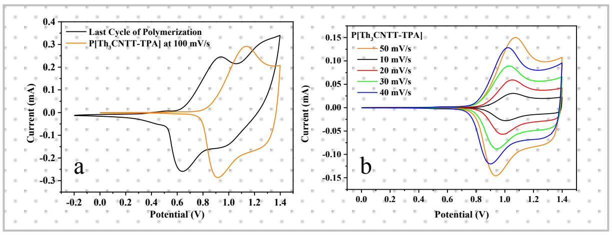

Figure 1. Comparison of the last cycle of polymerization and CV of **P[Th_3CNTT-TPA]** film at 100 mV/s (a), and CVs of the film at different scan rates in 0.1 M Bu_4NPF_6 in ACN.

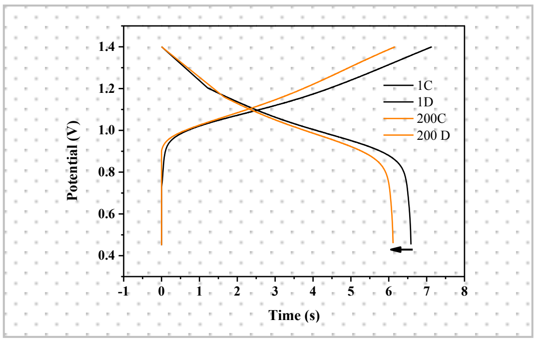

Figure 2. GCD cyclic stability of **P[Th_3CNTT-TPA]**.

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Sema Topal was born in İstanbul (Turkey); she studied chemistry at the Istanbul Technical University where she obtained an M.Sc. in 2020 under direction of Professor E. Sezer. She is currently continuing her PhD at Istanbul Technical University and working on a scientific research project about energy storage materials and her PhD studies are supported by The Scientific and Technological Research Council of Turkey TUBITAK 2211A. Her research focuses on synthesis of organic conjugated polymers and diverse electrochemical studies.

Presentating author: Sema Topal, e-mail: topals@itu.edu.tr

Modeling the distribution of ions in a electrolytic capacitor

Jami Torki[1], Ali Sari[2], Charles Joubert[3]
[1,2,3]Université Claude Bernard Lyon 1, Ecole Centrale de Lyon, INSA Lyon, CNRS, Ampère, F-69100, Villeurbanne, France

The increase of the density of electrical energy stored in energy storage systems is a crucial element in reducing the volume of on-board systems. Capacitors are made up of two conductive armatures, called electrodes, separated by a dielectric allowing opposing electric charges to be stored on each electrode. This increase can be visualized through an increase in the surface area of the electrodes (engraved, porous [1] or based on nanotubes interdigitated principle [2]).

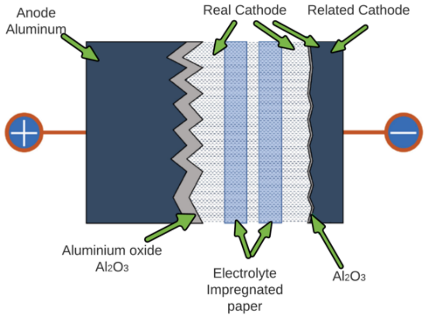

Figure 1. Aluminum electrolytic capacitor.

This work aims to develop better generation of energy storage system using concepts based on aluminum electrolytic capacitors (AEC) principle (Figure 1 [3]). The modeling will allow us to understand the physics involved in an energy storage mechanism: an electrolytic capacitor. One of the current highlights of my research is to study the density distribution of ionic species in the electrolyte in an electric field. This understanding will allow us to achieve an optimization of macroscopic parameters such as the capacitance, the Equivalent Series Resistance (ESR) or the temporal response of the system which can be deduce from microscopic analysis. To introduce my modeling, AEC consist of two aluminum electrodes (anode and related cathode), an oxide layer acting as a dielectric and an electrolyte usually boric acid or benzoic dissolved in ethylene glycol or glycerin and water [3]. These chemical mixtures allow the electrolyte to be a very good conductor, over a wide temperature range, in order to bring the negative potential of the cathode (real cathode) closer to the dielectric via ionic transport in the electrolyte. The sheets of electrolyte impregnated paper serve as physical separators limiting the risk of short circuits between the two electrodes. The thin layer of Al_2O_3 (alumina) is caused by natural oxidation of aluminum which limits corrosion.

My current research consists of studying the distribution of ion concentration, potential and electrical field in the electrolyte for different models at steady state first and then in transient regime. Indeed, the positively or negatively charged ions will be attracted by the electric potential of the electrodes. In addition, they will in turn influence the electric field. This is the coupling between the spatial charge density with the electric potential and this is why the equations for describing the interaction between the ions and the electric field is nonlinear [4]. My modeling is based on microscopic systems with simplified geometries in order to facilitate the resolution of this type of non linear equation. The first model will be a theoretical 2D model with face-to-face plane electrodes in order to compare my model with analytical solutions and check the consistency of the simulation results. The second case will be to study the impact of an etching similar to that of an anode of an AEC (Figure 1). And finally, we will consider a particular geometry allowing, like the etching, an increase in the surface of the electrode. Therefore, we can compare the results and highlight the advantages / disadvantages of each structure. The analysis of the transient regime in these three models makes it possible to study the behavior of the ions subjected to the strong electric field during the charge of the AEC. The temporal evolution of the relaxation resulting from the diffusion of the ions during the discharge of the electrolytic capacitor can also be simulated in order to characterize the electrolytic capacitors operating.

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Jami Torki obtained his B.S in Physics Department from Bourgogne University, Dijon France, in 2018. He received his Marster’s degree from University Claude Bernard Lyon 1, France in 2020. He is currently a PhD student in Electrical Engineering Department in University Claude Bernard Lyon 1. His thesis is on the modeling, design and experimental characterization of a new energy storage system using Carbon NanoTubes.

Presentating author: Jami Torki, e-mail: jami.torki@univ-lyon1.fr tel: +33 6 08 76 31 98

Ultrasonic Spray Deposition of Cobalt Based Metal Organic Frameworks for Textile-Based Supercapacitor Electrodes

Mete Batuhan Durukan[1,2 *], Asude Cetin[1], Tufan Bolukbasi[1], Husnu Emrah Unalan[1,2]

[1] Department of Metallurgical and Materials Engineering, Middle East Technical University (METU), 06800 Ankara, Turkey

[2] Energy Storage Materials and Devices Research Center (ENDAM), Middle East Technical University (METU), 06800 Ankara, Turkey

In today's industrialized world, rapid progress and increased demand on smart electronics and health monitoring systems require advancements on energy storage materials. Increasing attention has been drawn by advanced implantable/wearable devices, where the use of conventional lithium-ion batteries are not feasible.

Supercapacitors exhibit much better properties such as longer life, higher power densities and higher dynamics of charge propagation when compared to conventional capacitors and batteries. Supercapacitors would probably meet increasing energy demands in the near future especially for small-scale integrated small electronics and wearable devices.

Metal-organic frameworks (MOFs), also called as coordination polymers, assembled via node-spacers in which they have a metal centers connected with organic linkers such as imidazolate or carboxylate-based ones. These structures allow MOFs to be constructed with desired crystalline structures with extreme porosity, which makes them very good candidates to be used as energy storage materials. With these unique properties and the absolute engineerable parameters, MOFs can be tailored to have desired properties. They can complement low power output of batteries or low energy density of supercapacitors, while keeping the advantages of both type of energy storage devices. Besides the energy storage devices, MOFs are also investigated extensively for gas adsorption, biotechnology and catalysis.

In this work, cobalt (Co) based MOFs (Co-MOFs) were deposited onto conducting fabrics via ultrasonic spray deposition (USD) method. For this purpose, a well-dispersed Co-based solution was atomized into a fine mist spray to form fine droplets and deposited onto the conducting textile fabric. Following the deposition of Co-based solution, another solution involving organic linker was deposited to form Co-MOFs directly on the textile. An areal specific capacitance of 47 $mF.cm^{-2}$ was obtained at a scan rate of 10 $mV.s^{-1}$ in 1 M potassium hydroxide (KOH). Detailed analysis on the capacitive behavior will be presented in conjunction with the fabrication, post-treatment, morphology and structural characterization of the Co-MOFs.

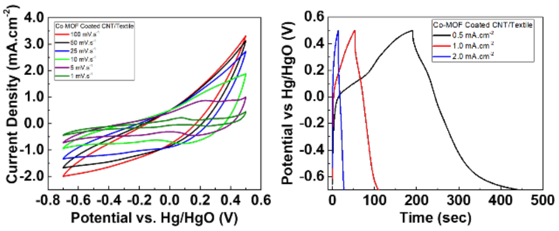

Figure 1. Cyclic voltammogram (left) and galvanostatic charge-discharge characteristics (right) of Co-MOF@conductive textiles at different scan rates and different current densities.

Acknowledgements: This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under Grant No: 119N344.

Mete Batuhan Durukan is currently a Ph.D. candidate in the Department of Metallurgical and Materials Engineering at Middle East Technical University (METU), Turkey. He obtained BS and MS degrees from Metallurgical and Materials Engineering Department of METU in 2015 and 2017, respectively. He has been working on the development of electrode active materials for supercapacitors ever since his junior year in undergraduate.

Corresponding author: Mete Batuhan Durukan, e-mail: bdurukan@metu.edu.tr tel:+905077298722

Supercapacitors Based on Functionalized Carbon Materials and Room Temperature Ionic Liquid

Ayşe Korkut[1], Betül Uralcan[1]

[1]Department of Chemical Engineering, Boğaziçi University, Bebek 34342

Supercapacitors have attracted lots of attention due to their properties like fast charge/discharge rate, long life cycle, and stability [1,2]. Neverthless, their charge storage performance is limited largely due to low conductivity through the tortous microporous structure of the electrodes and inefficient utilization of the electrode pores. We incorporate carbon quantum dots (CQDs) into thermally-exfoliated graphene oxide(TEGO) to improve the conductive network and facilitate ion diffusion deep into the electrode micropores in room temperature ionic liquid (RTIL) – based electrolytes.

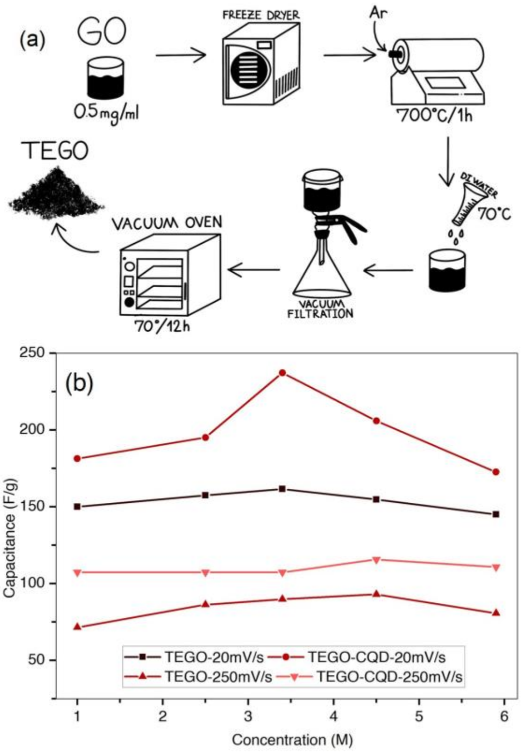

Figure 1. a) Thermally exfoliated graphene oxide (TEGO) synthesis, b) Capacitance of TEGO and TEGO-CQD as a function of ion concentration

After obtaining TEGO (Figure 1a), we characterize the structure of graphene oxide and TEGO by using X-ray Photon Spectroscopy and Raman analysis and demonstrate that reduction is executed successfully. We use electrochemical impedance spectroscopy and cyclic voltammetry to measure the effect of CQDs and solvent dilution on charge storage performance. We show that adding CQDs into TEGO improves capacitance and scan rate dependence (Figure 1b). We also demonstrate capacitance increases with dilution and reaches a maximum value at ionic liquid contents near 3.4 M.

Acknowledgments

This study is funded by the Scientific and Technological Research Council of Turkey (TUBITAK), Grant No: T118C220.

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Ayse Korkut is currently a MSc student in the Department of Chemical Engineering at Bogazici University. She graduated from Marmara University Chemical Engineering Department in 2013, and continued her undergraduate education at Bogazici University in the Department of Preschool Education. She joined the Chemical Engineering Department of Bogazici University as an MSc student in 2020. Her MSc thesis is on designing supercapacitors based on carbon electrode materials and room temperature ionic liquids.

Presenting author: Ayse Korkut, e-mail: ayse.korkut@boun.edu.tr

Optimization of energy density in supercapacitors by utilizing Artificial Neural Network-Genetic Algorithm hybrid model

Duygu Kaya [1] and Betul Uralcan [1]

[1] Bogazici University, Department of Chemical Engineering, Turkey 34342

Efficient energy storage devices are required to provide improvement of sustainable and renewable energy systems. Supercapacitors have received more attention in recent years due to higher charge/discharge efficiency, life cycle and power density. These characteristics provide potential opportunities to build advanced energy storage devices for mobile and high-power applications. A main drawback of supercapacitors is low energy density [1]. To improve the performance of supercapacitors, it is necessary to improve their energy storage capacity. The aim of this study is to optimize the capacitance of supercapacitors to obtain highly efficient energy storage devices by utilizing a hybrid artificial neural network-genetic algorithm model.

Machine learning algorithms such as artificial neural networks have become more popular for highly correlated non-linear systems instead of mechanism-based solutions. Neural-network model can exhibit rigorous solutions for such systems due to the non-linear attributes of supercapacitors. Moreover, genetic algorithm is known as effective and practical search algorithms in which the computational procedure mimics the theory of biological evolution [2-3]. Though some studies have examined the use of artificial neural networks and genetic algorithm in supercapacitors for several aspects, there is lack of the investigation on hybrid Artificial Neural Network-Genetic Algorithm model.

In this work, neural networks are performed to predict the capacitance of supercapacitors with a dataset composed of 2189 data points collected from 110 published articles. Trained neural network model is used as the fitness function for genetic algorithm to maximize the capacitance of supercapacitors. A parameter set that maximize the capacitance of supercapacitors is obtained as an output of genetic algorithm. This study enables the rational design of supercapacitors by utilizing a hybrid neural network-genetic algorithm as an optimization tool to maximize the capacitance of supercapacitors.

Acknowledgments

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Duygu Kaya graduated from Department of Chemical Engineering at Yıldız Technical University in 2019. She studied one semester in Wroclaw University of Science and Technology in 2018. She is currently in her second year of master degree in Chemical Engineering at Boğaziçi University. She is interested in studying optimization and machine learning algorithms for supercapacitors.

Presentating author: Duygu Kaya, E-mail: duygu.kaya1@boun.edu.tr

RENEWABLE HYDROGEN

Effect of Boron Doping on the Layered Iron Nickel Sulphide Nanosheets for Electrochemical Hydrogen Evolution Reaction

Esaam Jamil[1], Begüm Yarar Kaplan[2], Selmiye Alkan Gürsel[1,2], Alp Yürüm[2]

[1]Faculty of Natural Science and Engineering, Sabancı University, 34956 Istanbul, Turkey
[2]Nanotechnology Research and Application Center, Sabancı University, 34956 Istanbul, Turkey

Over the past few decades, the energy demand is increasing at rates never seen before. The fossil fuel consumption has given us an unprecedented set of problems such as green house gas emission, global warming, and climate change. More countries are adopting renewable energy resources to cater for the extra need and environmental concerns. Hydrogen fuel caught special attention of the researchers because of its versatility to be employed in zero carbon emission energy conversion applications such as PEM fuel cells which produces only water as a by-product. However, the prevalent steam reforming process for producing hydrogen, causes green house gas (CO_2) emission and is very energy intensive process. Green hydrogen production from water electrolysis is viable and sustainable option but is often restricted due to expensive noble metal catalyst platinum used both at anode and cathode side (1). There is need to replace this noble metal with earth abundant low-cost metals. Transition metals dichalcogenides based upon iron, nickel and sulphur are among the promising candidates which have shown their potential as HER electrocatalyst along with molybdenum sulphide and tungsten disulphide (2). To further improve the active sites and intrinsic catalytic activity of these electrocatalyst, there are various techniques such as making nanostructures, using support materials, controlling shape, alloying, core-shell, elemental doping, etc. (3). Doping with foreign atoms can change the band gap from insulator to semiconductor to metallic behaviour.

Hence, in this study, we see the effect of boron doping on iron nickel sulphide which can alter the basal plane to make it active along with the edges. Further, fine tuning the intrinsic activity of nanostructured and layered Fe-Ni-S chalcogenide electrocatalyst structure by varying the boron doping levels and see the improvement in the HER performance.

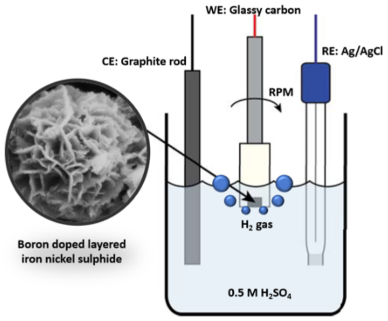

Figure 1. Three-electrode electrochemical setup for HER performance tests. The inset is the SEM image showing morphology of the obtained material.

First, we synthesized layered transition metal dichalcogenide (S) electrocatalyst based upon low-cost earth abundant metals (Ni, Fe) for hydrogen evolution reaction (HER) for low pH electrolyte. Further, by varying the boron's molar ratios, the intrinsic activity is fine tuned to improve the HER performance. Different characterization techniques employed such as XRD, XPS, SEM, and BET verified the desired structure, morphology and chemical composition. HER performance was evaluated by linear sweep voltammetry from which three important parameters: overpotential at 10 mA/cm^2, Tafel slopes and exchange current density were extracted which gave insights into the HER reaction mechanism and electrochemical kinetics. **Figure 1** shows the three-electrode electrochemical setup for HER performance tests. The results showed that low boron doping level improves the HER performance the most. These layered electrocatalysts can be grown on high surface area and highly conductive surface such as graphene to accelerate the green hydrogen generation.

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Acknowledgements

The research leading to these results has received funding from the Tübitak 1001 – Program for supporting scientific and technological research projects

Esaam Jamil is a doctorate candidate in Materials Science and Engineering Program at Sabanci University, Istanbul. Prior to this, he completed his bachelors from National University of Sciences and Technology (NUST), Islamabad, Pakistan and his masters from Sabanci University, Istanbul. His research interests include synthesis and characterization of nanostructured materials for energy conversion applications such as PEM fuel cells and water splitting for green hydrogen production

Corresponding author: Esaam Jamil, e-mail: ejamil@sabanciuniv.edu Tel: +90 553 414 5728

Enhaced CO_2 stability of nickel doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10)

Vanessa C.D. Graça[1], Francisco J.A. Loureiro[1], Laura I.V.Holz[1], Sergey M. Mikhalev[1] , Duncan P.Fagg[1]

[1] *Centre for Mechanical Technology and Automation, Mechanical Engineering Department, University of Aveiro, Aveiro, 3810-193, Portugal*

Owing to its very high equilibrium constant for hydration, yttrium-doped barium cerate, $BaCe_{1-x}Y_xO_{3-\delta}$ (BCY), can provide high protonic conductivity at low temperatures (*e.g.*, ~ 10^{-3} S cm^{-1} at 400 °C under humidified atmospheres, p_{H2O} ~ 10^{-2} atm) generating interest for its use as electrolyte in protonic ceramic fuel cell (PCFC) devices [1].

However, this composition has been, typically, discarded for real world applications, due to its very poor chemical stability in both humidified and CO_2 containing atmospheres. In this respect, the presence of amorphous intergranular phases in $BaCeO_3$ polycrystalline materials has been suggested to be the cause of the structural disintegration of this composition [1,2].

To try to overcome this limitation, we report an alternative based on the modification of the original $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10) composition by the introduction of small amounts of NiO (1 vol%). While the addition of transition metals has been widely adopted for enhancing the sinterability of these materials [1], such additions have not been previously tested as a method to improve the chemical stability and lifetime of this material.

To accomplish this goal, four different samples were pelletised and sintered: the undoped samples, BCY10 sintered at 1450 °C (BCY1450) and 1600 °C (BCY1600); and the NiO-modified samples, sintered at 1450 °C (Ni-BCY1450) and 1350 °C (Ni-BCY1350). All materials were characterised for phase composition by X-ray diffraction (XRD), and for microstructure by scanning electron microscopy, coupled with chemical analysis by Energy Energy-dispersive X-ray spectroscopy (SEM/EDS).

To evaluate the chemical stability, fresh samples were exposed to a humidified CO_2 atmosphere (p_{H2O} = 0.033 atm) at 400 °C for 30 days and electrochemical impedance spectroscopy (EIS) was used to record impedance data each three hours. The results, Figure 1, reveal that the unmodified BCY10 samples suffer a substantial drop in total conductivity in this timeframe, while the NiO-modified samples (Ni-BCY1350 and Ni-BCY1450) remain stable through the tests.

This result is important as it reveals that the simple addition of small amount of NiO (1 vol%), not only offers its typical role of decreasing the sintering temperature from 1450 to 1350 °C, but can also be successful for dramatically improving the stability of BCY10 against hydroxide formation and carbonation. The work offers a significant advance to the knowledge of this family of materials at low temperatures, potentially opening a way to use these previously discarded proton-conducting perovskite materials in real world applications.

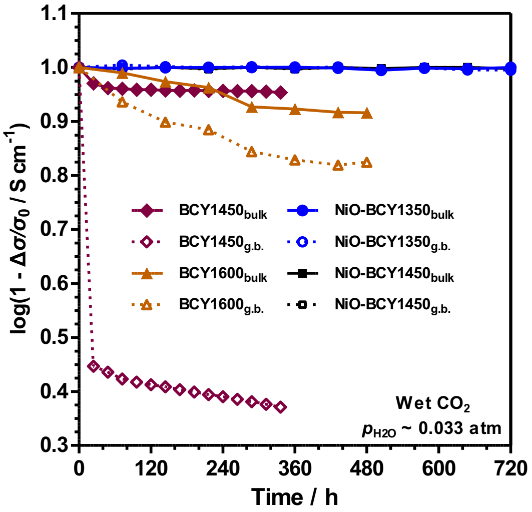

Figure 1. Bulk and grain boundary conductivities measured as function of exposure time in wet CO2 (pH2O=0.033 atm) at 400°C for pure BCY10 samples sintered at 1450 and 1600 °C and for NiO dopped BCY10 samples sintered at 1350 and 1450°C. The results are normalised to the initial values of conductivity.

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Acknowledgements

The authors acknowledge to FCT for the PhD grant SFRH/BD/130218/2017 and the projects, PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020, POCI-01-0247-FEDER-039926, POCI-01-0145-FEDER-032241, UIDB/00481/2020 and UIDP/00481/2020 and CENTRO-01-0145-FEDER-022083 - Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Vanessa C.D. Graça is a doctoral student in Nanosciences and Nanotechnology at the University of Aveiro. The topic of her phD research is the ‘Tailoring proton ceramic materials for electrochemical ammonia synthesis’.

Effect of Dual Perovskites on Hydrogen Production by Thermochemical Water Splitting

Seyfettin Berk Sanli, Ihsan Emre Yigiter, Gülhan Cakmak, Fatih Piskin, and Berke Piskin*
[1]Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey

The increasing use of fossil fuels to meet the energy needs and accordingly carbon emissions released to nature cause climate change and global warming. For this reason, researches focus on alternative energy sources to minimize the use of fossil fuels and to meet the energy demand from sustainable and clean energy for the future. Hydrogen is considered to be one of the most promising sources for renewable energy with its high energy density and being a clean energy source. Compared to gasoline, hydrogen has a higher energy density per mass (120 MJ/kg) and, unlike gasoline, being carbon-free makes it a candidate fuel for many applications[1].

Hydrogen can be generated by many methods such as cracking, reforming, gasification, thermolysis, etc. Among the solar-based hydrogen production methods, Thermochemical Water Splitting (TWS) is one of the methods that use concentrated solar energy to drive redox reactions for pure hydrogen from water. Metal oxides are one of the material groups that are used as a redox material for TWS. Although non-stoichiometric ceria ($CeO_{2-\delta}$) is considered as a benchmark material for TWS, its high-temperature requirements for reduction reaction makes the research focus onto develop alternative redox materials.

Perovskite oxides have attracted remarkable research interest attributable to their superior properties such as non-stoichiometric oxygen vacancy formation, high structural stability, flexible doping / alloying, composition variety, and low cost. $LaMnO_3$ perovskite oxides are one of the most studied metal oxide family. Especially, simultaneous doping of A-site (Sr, Ca) and B-site (Al) of $LaMnO_3$ perovskite showed promising hydrogen production amounts. As it is known, redox kinetics of perovskite materials for TWS can be increased by generating or increasing internal defects and oxygen vacancy concentration in the structure by doping. It was observed that both A-site and B-site doping increase redox performance and thus increase the H_2 yield compared to undoped $LaMnO_3$. Nevertheless, it is clearly seen that simultaneous A and B-site doping is not sufficient for H_2 yield and structural stability.

It has been observed that hetero-interfaces created in the structure improve structural stability as well as increase oxygen release and reoxidation reactions. Furthermore, it has been noted that the hetero-interfaces desired to be created can have quite different characters from their main components and exhibit superior features[2,3].

In this context, LSMA6464, LSMA6446 and LSMA5564, and LCMA 6464 perovskites were synthesized via the Pechini method. The produced perovskites have been subjected to reduction reaction at 1400 °C and oxidation reaction at 800 °C in TWS to determine their hydrogen production capacity. TWS results of LSMA6464, LSMA6446 and LSMA5564 and LCMA 6464 are shown in Table 1.

Table 1. Thermochemical Water Splitting Results of Synthesized Perovskites

Samples	**Total O_2 production (μmol/g)**	**Total H_2 production (μmol/g)**	**Efficiency (%)**
LSMA6464	215.55	257.18	59.66
LSMA6455	201.36	207.86	51.61
LSMA5564	300.34	251.34	41.84
LCMA6464	271.17	135.58	25.00

To investigate the effect of hetero-interfaces formed in LSMA:LCMA dual composite structured perovskite oxides, porous monolithic of LSMA6464:LCMA6464, LSMA6446:LCMA6464 and LSMA5564:LCMA6464 composite structure were prepared to determine the hydrogen production amount via TWS.

Acknowledgements
This work was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) (Project Number 119M420), which the authors gratefully acknowledge.

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Seyfettin Berk SANLI is currently a Master student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. He completed his BS degree at the same university in 2020. He is working at Energy Materials Laboratory and his research areas are hydrogen production, thermochemical water splitting, perovskite oxide materials.

Presentating author: Seyfettin Berk SANLI, e-mail: seyfettinberksanli@posta.mu.edu.tr, tel: +90 539 785 70 48

Combinatorial Development of LSF Based Cathode Material for IT-SOFC

Fahrettin KILIÇ[1], Havva Eda Aysal [1] and Tayfur Öztürk [2,3]

[1]Dept. of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV, USA
[2] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, TURKEY
[3] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, Turkey

SOFC is a fuel cell technology that operates at high temperatures. They are useful in large, high-power applications such as industrial stations and large-scale power plants. The electrolyte in a SOFC system is typically solid ceramic, and the system run at high temperatures (600-1000 ^{0}C). This high working temperature facilitates quick electro-catalytic reactions with non-precious materials and generates heat as byproduct for cogeneration. The efficiency of this type of fuel cell can be as high as 70%.

A SOFC is made up of electrolyte sandwiched between two electrodes. Fuel gas, such as hydrogen, is injected into the anode of the fuel cell, while oxygen, which is normally delivered by air, enters the cell through the cathode. Because of its relatively large activation energy for the oxygen reduction process, the cathode electrode is the primary contributor to the overall resistance of a SOFC, especially at intermediate and low operating temperatures. One of the most significant methods for improving cell performance in SOFCs is to reduce the polarization resistance of the cathode electrode. As a result, substantial research has been conducted on the modification and improvement of SOFC cathodes to lower oxygen reduction reaction (ORR) activation energy and resistance of the electrode.

In this study, it is aimed to fabricate composite cathodes in LSM/LSF/ScSZ ternary system and to obtain the best composition using combinatorial approach. For this purpose, thick films of composite cathodes were deposited using magnetron sputtering and were characterized using symmetric cells.

The results showed that there were three regions of favorable ASR value in ternary diagram, Fig 1. These are the middle region of the diagram, the region close to the LSM and the region close to the LSF. The lowest value in the diagram were observed as 0.33 $\Omega.cm^2$. This value in the region close to the LSM corner is relatively better than those seen in the literature [1,2].

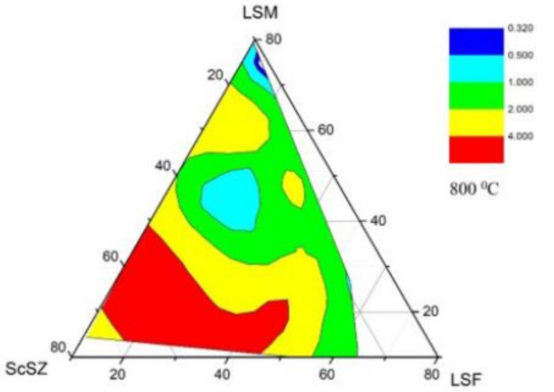

Figure 1. ASR values determined for cathode compositions in ternary diagram at 800 ^{0}C

The present study provides insights about LSM/LSF cathodes. When suitably selected, these cathodes have sufficient catalytic activity towards ORR for operating temperatures as low as 800 ^{0}C.

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Acknowledgement

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Fahrettin Kılıç is a visiting researcher in the department of Mechanical and Aerospace Engineering, West Virginia University. He received his BS and MS degree from Metallurgical and Mateirials Engineering, Middle East Technical University. He is mosty focused on solid oxide fuel cells and solid oxide electrolysis cells.

Presentating author: Fahrettin Kılıç, e-mail: fahrettinkkilic@gmail.com tel: +1 304 282 3191

Sr doped $LaMn_{0.6}Al_{0.4}O_{3-\delta}$ for H_2 production based two-step thermochemical water splitting

İhsan Emre Yiğiter, Seyfettin Berk Şanlı, Gülhan Çakmak, Fatih Pişkin, and Berke Pişkin*
[1]Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey

Climate change is one of the biggest issues in the modern-day world. Renewable energy sources have a special interest to avoid climate change. H_2 gas may be a highly attractive carbon-free alternative fuel. Solar-based two-step thermochemical water splitting (II-TWS) may offer a solution to hydrogen production from renewable sources. In this process, a metal oxide is endothermically reduced at high temperatures (>1300 °C) to create oxygen vacancies and then, the water vapor is introduced to re-oxidize the reduced metal oxide at lower temperatures like 800°C, resulting in the generation of H_2 gas[1]. There are many studied metal oxides for II-TWS. Perovskite oxides, which have an ABO_3 chemical formula, may be a suitable candidate material because they can accommodate high oxygen vacancy concentration in crystal structure and be stable under reduction and oxidation environments. The catalytic activity of perovskite oxide plays an important role in thermochemical performance. The catalytic activity might be enhanced by doping A-/B site cations since the substitution creates oxygen vacancies and structural defects[2]. In this context, $La_{1-x}Sr_xMn_{0.6}Al_{0.4}O_3$ type perovskite oxides were studied in various compositions where x= 0.4, 0.5, 0,6 in this study. It was aimed to understand the effect of strontium (Sr^{2+}) substitution to $La_{1-x}Sr_xMn_{0.6}Al_{0.4}O_3$ in the terms of structural properties and redox performance on the amount of hydrogen production.

LSMA6464, LSMA5564, and LSMA4664 powders were synthesized by Sol-gel-based Pechini method. Firstly, the stoichiometric amount of the metal nitrate precursors ($M^{+x}(NO_3)_x$) were dissolved in distilled water and citric acid was then added into the solution. The solution was heated up to 70°C with continuous stirring. The pH level of the solution was adjusted to 8 till the transparent gel was obtained and kept overnight at 70 °C. The gels were dried at 250 °C for 2 hours to remove the remaining organics and nitrates which was followed by calcination at 900°C for 6 hours. The XRD patterns were collected between $2\theta = 20°$ and 90° with a scan rate of $2°\ min^{-1}$. SEM was used to characterize surface morphology. The surface area was determined by the BET method. In the thermochemical water splitting test, 0.5 grams of LSMA powders in the tubular furnace were heated up to 1400 °C for reduction. Argon was used as carrier gas and the flow rate was set to 100 sccm. Then, the furnace was cooled down to 800°C. The water vapor was introduced for re-oxidation at $100\ \mu L \cdot min^{-1}$ by a syringe pump and the releasing gases were measured by a mass spectrometer.

Powders synthesized were identified as primitive cubic structure according to reference pattern*, as given in details Table 1. Lattice parameters were calculated by the Rietveld refinement technique and it can be realized that the lattice parameter slightly decreased when the Sr^{2+} dopant level increased. Moreover, it was observed that the morphology of powders had an equiaxed particle shape in SEM analysis. In addition to this, the higher amount of Sr^{2+} results in an increase in total surface area.

Table 1. Structural parameters of LSMA x64

Sample	Crystal structure	Lattice parameter (Å)	Volume ($Å^3$)	Surface area (m^2/g)
*$LaMnO_3$	P m -3 m	3.88	58.41	-
LSMA 6464	P m -3 m	3.836	56.44	26.48
LSMA 5564	P m -3 m	3.831	56.22	31.68
LSMA 4664	P m -3 m	3,826	56	33.52

The O_2 production performance is enhanced when the Sr amount is increased, as shown in Figure 1. The total O_2 production of LSMA4664, LSMA5564, and LSMA6464 were calculated as 341 µmol/g, 300 µmol/g, and 215 µmol/g, respectively. However, increasing Sr doping amount affects adversely the H_2 production performance and the total H_2 production decreased dramatically to 115 µmol/g at high Sr dopant level. The lowest efficiency was observed in LSMA4664. Moreover, the higher the surface area yielded, the higher the oxygen production whereas it is vice versa for hydrogen production.

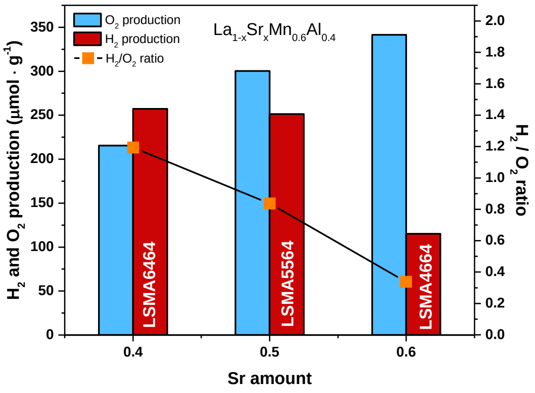

Figure 1. Hydrogen and oxygen production amounts.

Acknowledgments
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İhsan Emre Yiğiter is a metallurgy and materials engineer who works on two-step thermochemical water splitting at Energy Materials Laboratory in Department of Metallurgy and Material Engineering, Muğla Sıtkı Koçman University. He earned BS degree from the same department in 2021 where he works, and he is an applicant for a Master's degree student at the same department. His research interests are in materials for hydrogen production, perovskite oxides, Li-ion batteries, and fuel cells.

Presentating author: İhsan Emre Yiğiter e-mail: ihsanemreyigiter@posta.mu.edu.tr tel: +90 554 668 43 46

A two-step thermochemical water splitting by doped perovskite structures

Seyfettin Berk Şanlı[1] , İhsan Emre Yiğiter[1] , Fatih Pişkin[1], Berke Pişkin[1] and Gülhan Çakmak[1,*]
[1]Mugla Sıtkı Kocman University, Metallurgical and Materials Engineering Department, Mugla, Turkey

Perovskite phases are attracting significant interest because of their unique potential for many applications requiring mixed ionic and electronic conductivity. Two-step, solar thermochemical splitting of water using n redox-active metal oxides has emerged for large-scale hydrogen production. Perovskites have been proposed as alternatives to CeO2−δ because of their potential for lowering reduction temperature while maintaining high fuel productivity. In the present study, the perovskite series La1-xCaxMn1-y AlyO3 (x, y = 0.2, 0.4, 0.6, or 0.8) was fabricated using a modified Pechini method and comprehensively investigated to determine the applicability of these materials to solar H2 production via two-step thermochemical water splitting.

The studies started by determining the synthesis parameters for LCMC composition. For this purpose, LCMC4664(La4Ca6Mn6Co4O3) composition was selected and synthesized under four different conditions (1. citric acid addition, 2. citric acid addition and keeping pH ~8, 3. Citric acid and ethylene glycol addition, 4. Citric acid and ethylene glycol addition and keeping pH ~8). X-ray diffraction pattern of the resulted powders is given in Figure 1. These patterns revealed that cubic and orthorhombic crystal structure of perovskite are formed for all synthesis conditions. This has been confirmed with the Rietveld analysis.

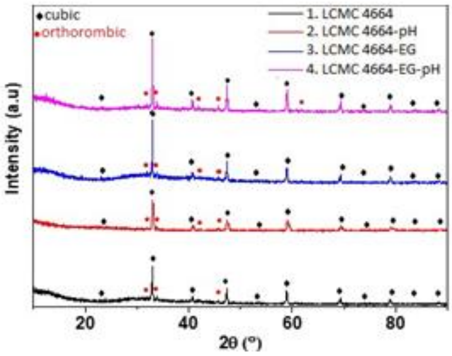

Figure 1. XRD pattern of LCMC4664 powders synthesized at four different conditions and calcined at 1300 ° C.

SEM, EDS and BET methods were used to compare other properties such as grain structure, morphology, chemical composition and surface area formed in LCMC4664 compositions synthesized with different parameters. The values obtained from the EDS analysis are summarized in Table 1. In the analysis, it is seen that the composition distribution is at the desired level for all synthesis parameters.

Table.1. EDS analysis results of LCMC4664 powders synthesized under different conditions and calcined at 1300 ° C for 6 hours

sample	La	Ca	Mn	Co
	Atomic percentages wt(%)			
LCMC4664 (1)	20,84	29,61	29,78	19,77
LCMC4664-pH (2)	21,06	29,45	29,57	19,92
LCMC4664-EG (3)	20,19	30,87	29,76	19,18
LCMC4664-EG-pH(4)	21,01	29,94	29,33	19,72

Among the powders TM:CA:EG 1:1.5:1.5 pH = 8.00 have the lowest surface area. The highest surface area is achieved for the synthesis condition of TM:CA1:1.5 pH≤1.00 (0.66m2/g). These observations are also confirmed with SEM analysis.
The study continues in the direction of determining the thermochemical water splitting properties of the powders produced.

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Seyfettin Berk ŞANLI is currently a Master student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. He completed his BS degree at the same university in 2020. He is working at Energy Materials Laboratory and his research areas are hydrogen production, thermochemical water splitting, perovskite oxide materials.

Presentating author: Seyfettin Berk ŞANLI, e-mail: seyfettinberksanli@posta.mu.edu.tr, tel: +90 539 785 70 48

Electrochemical promotion of N_2O reduction on LSCF catalyst

Laura I.V.Holz[1,2,3], Francisco J.A. Loureiro[1], Allan J.M. Araújo[4], Vanessa C.D.Graça[1], Diogo Mendes[2] , Adélio Mendes[3], Duncan P.Fagg[1]

[1] *Centre for Mechanical Technology and Automation, Mechanical Engineering Department, University of Aveiro, Aveiro, 3810-193, Portugal*

[2] *Bondalti Chemicals, S.A., Quinta da Indústria, Rua do Amoníaco Português no. 10 Beduído, Estarreja 3860-680, Portugal*

[3] LEPABE - Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[4] Materials Science and Engineering Postgraduate Program – PPGCEM, Federal University of Rio Grande do Norte – UFRN, Natal, 59078-970, Brazil

Nitrous oxide (N_2O) reduction is very important since this gas is responsible for numerous environmental problems, such as photochemical smog, acid rain, ozone layer depletion and global warming. [1].

The aim of the current work is to bridge the solid-state chemistry and heterogenous catalysis, by studying the non-Faradaic electrochemical modification of catalytic activity (NEMCA) [2] of the N_2O reduction reaction.

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ -LSCF was used as electrocatalyst due to its high availability and excellent performance as a cathode in solid oxide fuel cells (SOFCs). This material has a very high oxygen surface exchange coefficient ($K^* = 1.1 \times 10^{-3}$ cm s^{-1} at 800 °C) as well as high electronic (230 S cm^{-1} at 900 °C) and ionic conductivities (0.2 S cm^{-1} at 900 °C), essential requeriments for this application [3].

A single 3-probe cell reactor was developed, made of 8 % mol Y_2O_3 – stabilized ZrO_2 as electrolyte, LSCF as working electrode and inert gold (Au) as counter and reference electrodes.A buffer layer of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) was used to prevent the inter-reaction between the YSZ and LSCF.

The crucial aspect of this work was the use of an integrated zirconia oxygen sensor in the studies, to determine variations in the values of oxygen partial pressure (pO_2) upon polarisation, which were subsequently correlated with the extent of N_2O conversion, as predicted by thermodynamic equilibrium (**Figure 1**). The experiments performed showed that applying negative currents (*i.e* -0.05 and -0.25 A), an increase of the catalytic rate (r O_2 mol s^{-1}) was observed, resulting in a substantial increase of N_2O conversion. The Faradaic efficiency (Λ) also known as enhancement factor, was also calculated for the tested experimental conditions, and showed values that exceed unity, evidencing non-Faradaic electrochemical behaviour. The highest $\boldsymbol{\Lambda}$ value of 8.8 was obtained at the lower temperature and currents tested at 600 °C.

The current works reveals that NEMCA can be an alternative and effective tool for this green-house gas treatment, highlighting its environmental importance.

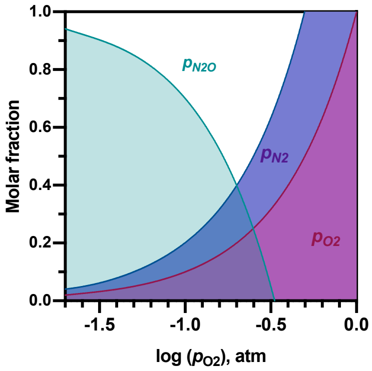

Figure 1. Thermodynamic prediction of N_2O reduction at equilibrium at 800 °C.

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Acknowledgements

Laura I. V. Holz acknowledges Fundação para a Ciência e Tecnologia (FCT) for the PhD grant PD/BDE/142837/2018.The authors also acknowledge the projects, PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020, POCI-01-0247-FEDER-039926, POCI-01-0145-FEDER-032241, UIDB/00481/2020 and UIDP/00481/2020 and CENTRO-01-0145-FEDER-022083 - Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). In addition, Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC).

Laura I.V.Holz is currently enroled in a industrial PhD programme in the frame of Refining, Petrochemical and Chemical Engineering, at University of Aveiro, in close collaboration with Bondalti Chemicals, a Portuguese Company. Her research interest covers ceramic oxides and solid oxide fuel/electrolytic cells.

Presentating author: Laura Holz, e-mail: lauraholz@ua.pt

Improved hydrogen production by the substitution of $LaMnO_3$ based perovskite oxides for thermochemical water splitting

Çağla Ünal [1,2] and Berke Pişkin[1,2*]
[1]Dept. of Metallurgical and Materials Engineering, Mugla Sıtkı Koçman University, Muğla, Turkey
[2]Energy Materials Laboratory, Mugla Sıtkı Koçman University, Muğla, Turkey

Abstract

The primary energy source of the world is provided by fossil fuels. Therefore, it becomes important to have a clean energy supply. Hydrogen plays an important role as a promising technology for long-term green energy. In this context, thermochemical methods based on solar energy come to the fore in hydrogen production. In two-step thermochemical cycles, the release of H_2 and O_2 occurs at different steps and temperatures providing pure hydrogen production without the need for any separation process. The thermodynamics and kinetics of redox reactions are one of the important factors that determine hydrogen production efficiency, as well as structural stability, which is also crucially important in the two-step thermochemical water splitting (TWS). This efficiency is strongly influenced by the structural properties of active materials used in these reactions. For this purpose, perovskite-oxides draw attention to be able to use in TWS reactions due to providing higher structural stability with allowing compositional diversity. We focused on investigating the compositional dependence of $La_{1-x}Y_xMn_{0.6}Al_{0.4}O_3$ (x=0.2, 0.4, 0.6, and 0.8) perovskite oxides to obtain higher hydrogen production by TWS.
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1. Introduction

Hydrogen has a very high energy density based on mass despite being the lightest element in the periodic table. Pure hydrogen produced from water or various organic compounds does not contain toxicity, is environmentally friendly, and is abundant in nature. The high energy efficiency of hydrogen depends on the production process and can be produced by thermochemical, electrolytic, photolytic, and biological methods. Although thermochemical methods using solar energy for hydrogen production show variable values, it is inexhaustible, free and does not produce carbon dioxide emissions [1]. In this study, the thermochemical water splitting which is solar-based for hydrogen production was carried out. Reactant material is reduced at a high temperature, creating oxygen vacancies in the oxygen lattices to produce oxygen. The reduced material is then oxidized with water to produce pure hydrogen at a lower temperature. The important thing here is that the recycled reactant material is thermally, thermodynamically, and structurally stable in redox reactions to provide high efficiency in hydrogen production. Moreover, if there is any phase transformation taking place during redox reactions, it has an adverse effect on the kinetic values of these reactions resulting decrease in cyclability [2]. And if the material exhibits the desired properties, a large amount of oxygen vacancies can be accommodated in its structure and fuel productivity increases.

Perovskite materials with their low activation energy, high catalytic activity, and high electron transfer kinetics have been used to obtain high oxygen off-stoichiometry, high reduction extent and finally to get high pure hydrogen yield at lower temperatures. The general formula of perovskite is ABO_3, where the A cation is an alkali earth metal or lanthanides with a higher radius, and the B cation is a transition metal with a lower radius, and O is the oxygen anion. The 12-fold coordination of the A cation and the 6-fold coordination of B indicates that the perovskite structure is stabilized in the cubic form. To increase hydrogen efficiency, various elements can be substituted in the A and B cations. In this study, Y and Al elements were substituted for the widely used $LaMnO_3$. Compared to La^{2+}, the use of smaller ion radii of Y^{3+} in the A-site reduces grain size and promotes the lattice distortions increase. Thus, the oxygen removal from the structure increases. Substituting Al^{3+} in the B-site causes stronger atomic bonds yielding smaller unit cell volume and increasing stability [3]. Thus, Al^{3+} substitution has a positive effect on the reaction kinetics and the re-oxidation efficiencies although the decrease in Mn content reduces the redox capacity.

Çağla Ünal is a graduate student candidate at Energy Materials Laboratory, in the Department of Metallurgical and Materials Engineering at Muğla Sıtkı Koçman University. She got her BS degree from the same university. Her bachelor thesis on the synthesis, characterization, and development of lithium-ion batteries. She is currently working on energy materials focusing on hydrogen production and lithium-ion batteries.

Presenting author: Çağla ÜNAL, e-mail: caglaaunal@hotmail.com Phone: +905531464464

It is aimed to achieve higher oxygen off-stoichiometry range. This will cause an increase in the reduction extent while also decreasing the reduction temperature in hydrogen production. In this work, LYMA 8264, LYMA 6464, LYMA 4664, and LYMA 2864 perovskite oxides were synthesized to determine the effect of Y^{3+} and Al^{3+} substitution on hydrogen production.

2. Experimental Studies

$La_{1-x}Y_xMn_{0.6}Al_{0.4}O_3$ (x=0.2, 0.4, 0.6, and 0.8) (LYMA) perovskites were synthesized by the Pechini method. $La(NO_3)_3.6H_2O$, $Y(NO_3)_3.6H_2O$, $Mn(NO_3)_2.4H_2O$, $Al(NO_3)_3.9H_2O$ were used as precursors. Citric acid was a chelating agent whereas ammonia was used to adjust pH.
First, metal nitrate salt compounds were dissolved in deionized water according to their stoichiometric ratios, respectively. After stirring this solution for a few minutes, citric acid was added to the metal cation at a ratio of 1:1.5. Then, the necessary amount of ammonia was added to ensure the appropriate pH value, and the solution was left in the magnetic stirrer until it became gel (approximately two hours). Then, the gel solution was left in the dryer at 250°C overnight and calcined at 900°C for 6 hours.

Rigaku SmartLab X-ray diffractometer (XRD) was used to identify the different phases of the synthesized perovskites with Cu-Kα wavelength (1.5406 Å) with an angle from 10 to 100° with a scan rate of 0.02° min^{-1}.

3. Results and Discussion

The XRD patterns of the synthesized $La_{0.8}Y_{0.2}Mn_{0.6}Al_{0.4}O_3$ (LYMA 8264), $La_{0.6}Y_{0.4}Mn_{0.6}Al_{0.4}O_3$ (LYMA 6464), $La_{0.4}Y_{0.6}Mn_{0.6}Al_{0.4}O_3$ (LYMA 4664), and $La_{0.2}Y_{0.8}Mn_{0.6}Al_{0.4}O_3$ (LYMA 2864) perovskites are shown in Figure 1. It was observed that further increase from 0.2 to 0.8 in the content of yttrium on A-site resulted in phase transformation from cubic to the hexagonal structure. Moreover, orthorhombic phase was also obtained for LYMA 2864 with hexagonal phase.

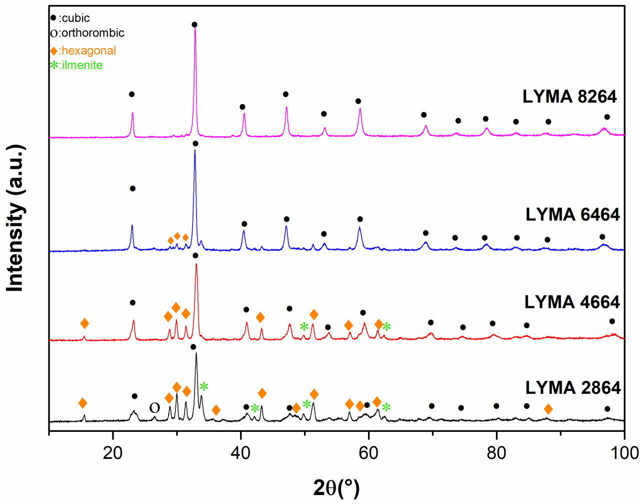

Figure 1. The XRD patterns of the synthesized LYMA8264, LYMA6464, LYMA4664, and LYMA2864 perovskites before water splitting.

Thermochemical water splitting cycles were performed to determine the oxygen and hydrogen capacity and structural stability of the LYMA perovskite oxides. TWS cycles were carried out in a high-temperature horizontal tubular furnace, coupled with a gas analyzer. The carrier gas was high purity argon (Ar) gas (~99.999%) during the cycles. The thermal reduction step of the LYMA perovskites was carried out at 1400°C where the water-splitting step was performed at 800°C.

Figure 2 shows that displays the XRD patterns of LYMA perovskite oxides after one thermochemical cycle. It was observed that the crystal structure of LYMAperovskites oxides has changed for all LYMA perovskites except LYMA 8264. LYMA 8264 perovskite oxide preserves its crystal structure after the thermochemical cycle. On the other hand, it was observed that hexagonal structure has disappeared or decreased for the other LYMA perovskites.

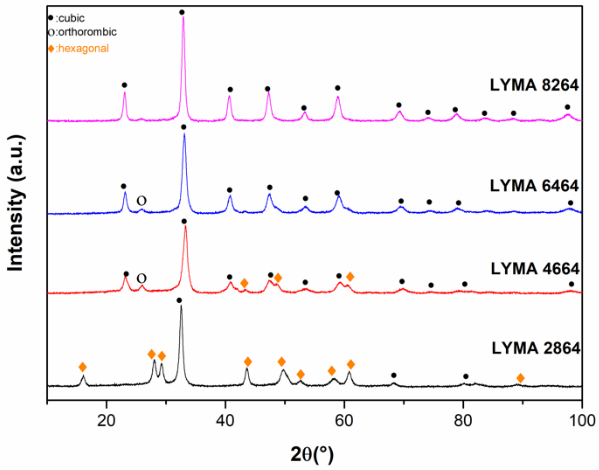

Figure 2. The XRD patterns of the synthesized LYMA8264, LYMA6464, LYMA4664, and LYMA2864 perovskites after water splitting.

Figure 3.a shows the O_2 and H_2 production capacities of LYMA perovskites. It was clearly seen that an increase in the Y content makes hydrogen production capacities increase whereas vice versa for oxygen production capacities.

Figure 3.b shows the H_2/O_2 ratio was enhanced by the further increase in Y content decrease.

Although oxygen production capacities were highest, the lowest hydrogen capacity was observed for the perovskites where Y content is 0.2. Moreover, the further substitution of Y makes the H_2/O_2 worsen.

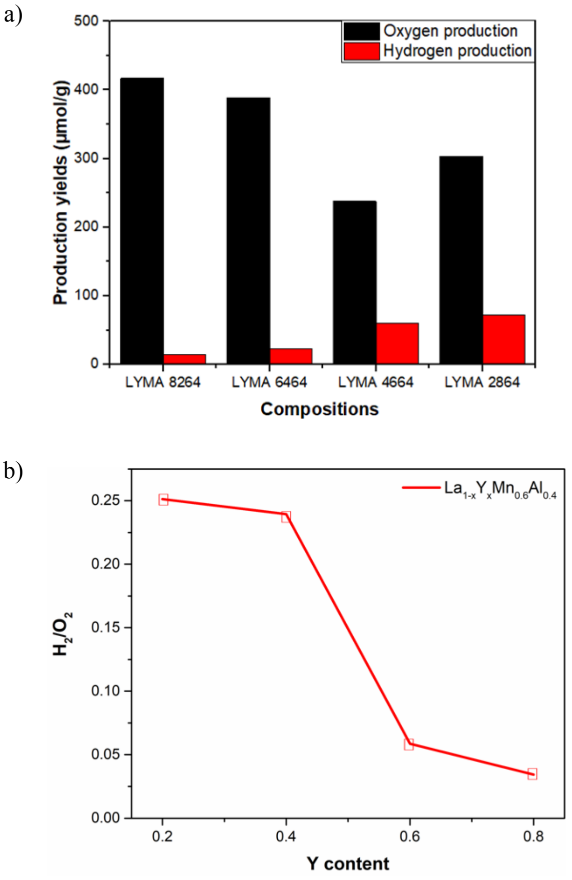

Figure 3. a) The O_2 and H_2 production capacities of LYMA8264, LYMA6464, LYMA4664, and LYMA2864 perovskites where the reduction at 1400°C and re-oxidation at 800°C. b) The H_2/O_2 ratio is estimated from the average amount of O_2 and H_2 production of LYMA perovskites as a function of Y content.

An increase in the Y content of LYMA perovskites decreases the O_2 production performance; however, it worsens the water splitting performance and resulted in lower H2 production.

4. Conclusion

In this study, $La_{1-x}Y_xMn_{0.6}Al_{0.4}O_3$ perovskites were synthesized by the Pechini method. To understand the structural effect of Y dopant, a different ratio of Y has been substituted. It was found that an increase in the amount of yttrium content resulted in cubic, orthorhombic, and hexagonal structures. After thermochemical cycling, the amount of hexagonal structure for all LYMA structures except LYMA 8264. This can be correlated with a different crystal structures of perovskites yielded with lower hydrogen production capacities by thermochemical water splitting.

Acknowledgement

This research was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) with project number 119M420, which the authors gratefully acknowledge.

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Electrochemical performance of calcium cobaltite as oxygen electrode for solid oxide cells with Pr-doped ceria active layer

Allan Araújo[1,2], Francisco Loureiro[2], Laura Holz[2], Vanessa Graça[2], João Grilo[3], Daniel Macedo[4], Carlos Paskocimas[1], Duncan Fagg[2]

[1]Materials Science and Engineering Postgraduate Program, Federal University of Rio Grande do Norte, Natal, 59078-970, Brazil

[2]Centre for Mechanical Technology and Automation – TEMA, Mechanical Engineering Department, University of Aveiro, Aveiro, 3810-193, Portugal

[3]Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, 3810-193, Portugal

[4]Materials Science and Engineering Postgraduate Program, Federal University of Paraíba, João Pessoa, 58051-900, Brazil

In recent years, the misfit-layered Ca cobaltite ($[Ca_2CoO_{3-\delta}]_{0.62}[CoO_2]$, C349) has emerged as an exciting oxygen electrode for solid oxide cells. Nonetheless, the poor ionic conductivity of C349 has prevented it from attaining a competitive performance. To overcome this limitation, efforts have relied on the formation of composite electrodes, with the addition of a predominately ion-conducting phase [1].

Previous studies have revealed the promising concept of tailoring the mixed transport properties of active layers as a strategy to enhance the kinetics of oxygen electrodes [2,3].

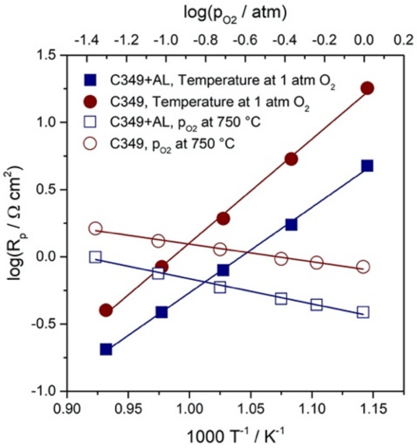

Figure 1. Temperature and oxygen partial pressure dependence of C349 and C349+CPOCo active layer (C349+AL).

Significant improvements in the performance of the C349 electrode are observed by the addition of a CPOCo active layer, as a function of the temperature and oxygen partial pressure (Figure 1). Such an improvement in performance mirrors that previously observed for similar active layers in the literature; suggested to be attributable to an extension of the surface path of the electrochemical processes, due to the provision of mixed ionic and electronic conductivity in the active layer [2,3].

The interlayer of CPOCo can offer these properties due to possessing a high ionic conductivity, combined with minor electronic conductivity arising from mixed Pr^{3+}/Pr^{4+} and Co^{2+}/Co^{3+} valence states. In this way, the current electrochemical activity is shown to be enhanced, as the CPOCo interlayer becomes an additional active surface for the oxygen processes (oxygen reduction or evolution).

This outcome is important as it provides valuable insight into future optimisation methods for this family of materials, with promising potential for application in solid oxide cells.

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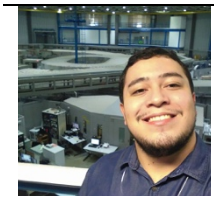
Acknowledgements

This study was financed in part by CAPES/Brazil (Finance Code 001). The Brazilian group acknowledges funding from CNPq/Brazil (200439/2019-7, 482473/2010-0, 446126/2014-4, 308548/2014-0, 307236/2018-8, 431428/2018-2 and 309430/2019-4). The Aveiro team acknowledges projects PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020 POCI-01-0145-FEDER-032241, UID/EMS/00481/2019-FCT, CENTRO-01-0145-FEDER-022083, funded by FEDER, Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and by national funds (OE), through FCT/MCTES.



Allan Araújo is currently a Ph.D. student in Materials Science and Engineering at the Federal University of Rio Grande do Norte (UFRN) - Brazil and a visiting student at the University of Aveiro - Portugal. The focus of his research is related to the optimisation of ionic and mixed ionic-electronic conductors for use as components in energy systems, such as solid oxide cells (solid oxide fuel cells/electrolysers (SOFC/SOEC)).

Corresponding author: Allan Araújo, e-mail: allan.araujo.013@ufrn.edu.br, tel: +55 (83) 996389040

Effect of B-site substitution on the structural properties of $La_{0.2}Na_{0.8}Al_{0.3}M_{0.7}O_3$(M=Mg and Mn) perovskite oxides

Müzeyyen Özdemir[1], Assist. Prof. Dr.Berke Pişkin[1]
Department of Energy, Muğla Sıtkı Koçman University,48000,Muğla,Turkey

This study focuses on solar-based thermochemical methods to obtain hydrogen, which is a clean energy source, at a low cost in one step without the need for a secondary separation process [1]. For this purpose, non-stoichiometric perovskite oxides with high redox capacity, stable and fast reaction kinetics were preferred [2].

The effect of B-sites substitution on the structural properties of $La_{0.2}Na_{0.8}Al_{0.3}M_{0.7}O_3$ (M=Mg and Mn) perovskite oxides were investigated in this study. $La_{0.2}Na_{0.8}Al_{0.3}Mn_{0.7}O_3$(LNAMn-2837),$La_{0.2}Na_{0.8}Al_{0.3}Mg_{0.7}O_3$ (LNAMg-2837) were synthesized by the Pechini method to observe the effect of structural properties on hydrogen production.

As precursors $La(NO_3)_3.6H_2O$, $Na(NO_3)$, $Al(NO_3)_2.9H_2O$, $Mn(NO_3).4H_2O$, $Mg(NO_3)_2.6H_2O$ were used to synthesize the perovskite powders. Citric acid was added as a chelating agent where ammonium solution was used to arrange the pH of the solution. After pre-calcination of the powders synthesized at 250 °C for 2 hrs, calcination was carried out at 900 °C, 1100 °C and 1300 °C for 6 hrs.

X-ray diffraction (XRD) was performed to determine the crystal structure of perovskite materials synthesized. XRD patterns were collected with a scan rate of 2°/min as shown in Figure 1 and 2. It was observed that while rhombohedral and orthorhombic structures were formed by Mn substitution, whereas Mg substitution resulted in rhombohedral and hexagonal structures for perovskites synthesized under the same experimental conditions.

LNAMn-2837 and LNAMg-2837 were synthesized via the Pechini method to be used as active materials in two-step thermochemical water splitting to evaluate hydrogen production amount. XRD studies revealed that B-site dopant has an influence on the final structure. It was observed that both perovskite oxide LNAMn2837 and LNAMg2837 structures were initially rhombohedral structures containing a small amount of orthorhombic and hexagonal structure secondary perovskite structures, respectively. It was also confirmed by decreasing orthorhombic and hexagonal secondary perovskite oxide structures that the rhombohedral structure became more stable for both compositions with increasing calcination temperature. Results of thermochemical water splitting tests were used to correlate the structural results with hydrogen production.

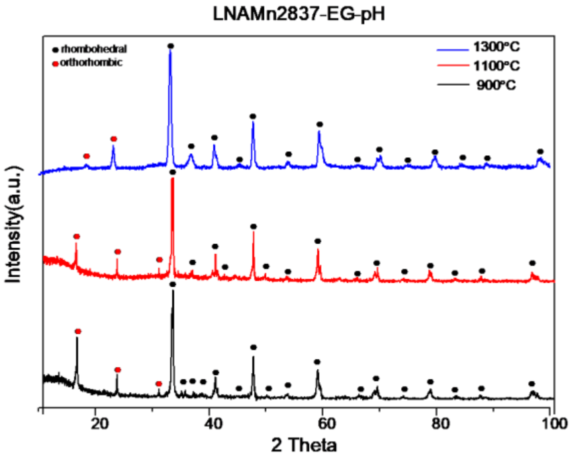


Figure 1. XRD pattern of LNAMn-2837 after the calcination 900 °C, 1100 °C, and 1300 °C 6 hrs.

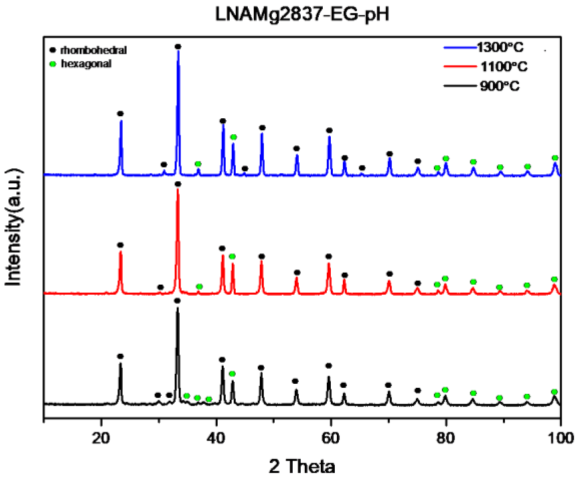


Figure 2. XRD spectrum of LNAMg-2837 after the calcination 900 °C, 1100 °C, and 1300 °C 6 hrs.

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Müzeyyen Özdemir is a graduate student at Muğla Sıtkı Kocman University, Instutue os Science, Department of Energy. She graduated from Sakarya University, Faculty of Arts and Sciences, Department of Physics in 2016. She worked as a paid physics teacher in Kütahya for 3 years.
Presentating author:Müzeyyen Özdemir, e-mail:muzeyyenozdemir@posta.mu.edu.tr tel: +90 542 235 5076

HYDROGEN STORAGE AND SEPARATION

Composition design, preparation techniques and hydrogen storage properties of high entropy alloys

Semen Klyamkin[1], Vladislav Zadorozhnyy[2], Elena Berdonosova[1], Mikhail Zadorozhnyy[2],
Korol Artem[2], Ivan Savvotin[1]
[1] Lomonosov Moscow State University, Chemistry Department, Leninskie Gory 1/3, Moscow, 119991 Russia
[2] National University of Science and Technology “MISIS”, Leninsky prospect 4, 119049 Moscow, Russia

Since the mid-2000s, alloys composed of five or more elements in equiatomic ratios have been allocated to a separate group, so called high entropy (HEA) or multi-principal element (MPE) alloys [1, 2]. Special interest in these alloys was first associated with their peculiar crystal structure and exceptional mechanical properties that has been considered in review [3].
As it was reported recently in [4], transition metal HEA can demonstrate outstanding hydrogen absorption capacity and form hydride phases with an unusual H/M ratio of 2.5 that is higher compared with individual metals and their binary intermetallic compounds. Crystall lattice strain owing to the presence of metals with very different atomic radii was considered as the main reason for this phenomenon. Later, hydrogen storage performance was studied for HEA of various compositions [5, 6].

Herein, we discuss fundamental approaches to composition design of multicomponent single-phase alloys. Based on these thermodynamic principles, we prepared a series of new HEA, for which the structure and interaction with hydrogen were characterized. A special attention was paid to the preparation techniques. Along with conventional arc melting, mechanochemical synthesis in a high-energy ball mill, electron beam melting and pendant drop melt extraction were used. Effect of the synthesis methods on the crystal structure of as-prepared alloys and their hydrides was examined by means of scanning and transmission electron microscopy, X-ray and neutron diffraction.

Hydrogen and deuterium interaction with the alloys was studied by volumetric measurements. Maximum hydrogen capacity was close to 2 H/M. The hydride formation is not completely reversibly because of high thermal stability of the hydride phases.

For $Ti_{20}Zr_{20}V_{20}Nb_{20}Ta_{20}$ BCC to FCC structure transformation upon hydrogenation was detected. Although all the methods used allowed us to obtain single-phase alloys, only the latter, resulting in formation of microwire samples, prevents the formation of secondary phases after hydrogenation.

A detailed structure analysis of the deuterides will be reported in a separate presentation by A. Korol et al.

Aknowledgment

This work was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University «The future of the planet and global environmental change» and was supported by Russian Science Foundation, project No. 19-13-00207.

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Semen Klyamkin is a professor at the Chemistry Department at Lomonosov Moscow State University. He obtained PhD degree in inorganic chemistry (1987) and Doctor of Sciences in solid state chemistry (2014). In 1993-1994 he worked in *Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, France*. He has published over 100 articles in international scientific journals. His research activity covers hydrogen storage materials, metal hydrides, gas adsorption in porous matrices (MOFs, carbons) with emphasis on high pressures, mechanochemistry, gas separation membranes.

Presentating author: Semen Klyamkin, e-mail: klyamkin@highp.chem.msu.ru, tel: +7-495-9394576

Hydrogen absorption kinetics comparison of the $LaNi_{4.4}Al_{0.3}Fe_{0.3}$-alloy based compact and the free powder bed

Ivan Romanov[1], Vasily Borzenko[1], Alexey Kazakov[1]
[1]Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia

One of the main advantages of metal hydride storage technology is the ability to quickly charge and discharge due to the high rate of interaction of intermetallic compounds with hydrogen. During this reaction, a large amount of heat is released, which is difficult to remove from the fine-dispersed powder bed of metal hydrides due to their low thermal conductivity [1], especially in large-scale reactors. This problem can be solved by forming metal hydride compacts by pressing fine intermetallic powders in a heat-conducting matrix.

This work is devoted to an experimental study and comparison of the kinetics of hydrogen absorption by an intermetallic compound (IMC) of the composition $LaNi_{4.4}Al_{0.3}Fe_{0.3}$ in form of free powder bed and a compact based on it obtained by cold pressing with using a spiral matrix of nickel-foam [2]. To calculate the kinetic parameters of the hydrogen absorption reaction, the initial rates method was used [3]. Two samples were studied: one of which was a sample of pure intermetallic compound powder weighing 50 g, and the second one was a metal-hydride compact prepared by cold pressing from 50 g of the initial intermetallic compound with a spiral matrix of nickel-foam weighing 3 g. Experimental studies in this work were carried out on a Sievert's-type test bench US-150. It allows studying the interaction with hydrogen of samples of metals and intermetallic compounds weighing from 10 to 800 g at a temperature of 243 to 673 K and a pressure of up to 15 MPa. The PCT absorption isotherms were measured at temperatures of 313, 333, and 353 K. For accurate calculations of the kinetics of the hydrogen absorption reaction, it is extremely important to observe the isothermal conditions of the system. Figure 1 shows example of the initial section of the kinetic curves with a length of 10 seconds. The curves were used to determine the duration of the initial part of the absorption process, where the conditions can be considered isothermal (temperature fluctuation less than 0.2 K). This area in Figure 1 is separated by a vertical control line. For each point in the plateau region of all the PCT isotherms, the value of this area was determined separately by analyzing the corresponding temperature curves.

The rate of hydrogen absorption increases with increasing pressure drop and temperature. It is shown that the rate of hydrogen absorption by the sample of pure IMC is significantly less dependent on temperature compared to the compact sample. In addition, the reaction rate at temperatures of 313 and 333 K is higher for the free powder bed sample, and at 353 K it is higher for the metal hydride compact. The values of the absorption constant and the activation energy of the hydrogen absorption reaction were determined for both samples. Despite the lower rate of the hydrogen absorption reaction at temperatures of 313 and 333 K, the complete relaxation of temperature and pressure occurs faster in the sample of the metal hydride compact due to the greater thermal conductivity.

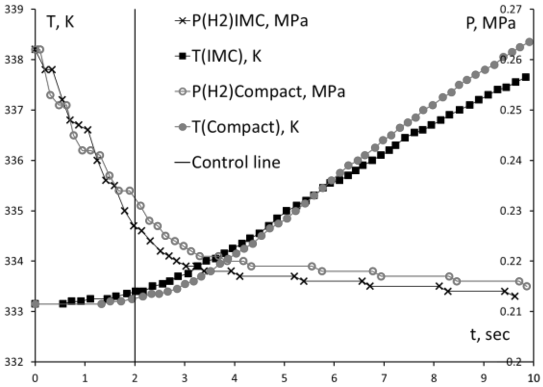

Figure 1. Initial section of the hydrogen absorption kinetic curves.

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Acknowledgements

Authors acknowledge support from the Russian Science Foundation grant No. 17-19-01738.

Mr. Ivan Romanov represents the laboratory of Hydrogen Energy Technologies of Joint Institute for High Temperatures of the Russian Academy of Sciences. Having graduated from Moscow State University in 2007. His research interest covers metal hydrides for energy applications, renewable energy and hydrogen fuel sells

Corresponding author: Ivan Romanov, e-mail: romanoff_i_a@mail.ru tel: +7 495 362 26 36

Uncovering the influence of the surface oxidation on hydrogen absorption/desorption process of magnesium ultra-thin films.

M. Blanco’ [1], C. Morales[2] , F Leardini[1], J.Ingo Flege[2], J.F. Fernández[1], I.J. Ferrer[1], J. R. Ares [1]

[1] Grupo MIRE, Dept. de Fisica de Materiales, Facultad de Ciencias, C/Tomás y Valiente 7, Universidad Autónoma de Madrid, 28049, Spain

[2]Applied Physics and Semiconductor Spectroscopy, Branderburg University of Technology Cottbus-Senfteberg, Konrad-Zuse-Strasse 1, D-03046 Cottbus, Germany

Magnesium hydride (MgH_2) is a light hydride able to accumulate high amounts of hydrogen (7.6 % wt H_2). However, thermodynamic restrictions and poor H-kinetics preclude its use in mobile applications due to the high temperatures (~300ºC) required to drive the H_2-absorption/desorption reactions. MgH_2 nanostructures are being widely investigated to overcome these drawbacks, promoting the hydrogenation process by reducing the activation energies [1] related to bulk processes such as H-diffusion, hydride nucleation, etc.

However, the critical role of the surface on the hydrogenation process has hardly been investigated. Theoretical calculations [2,3] have shown the poor ability of clean magnesium surface to dissociate the H_2-molecule, but barely experimental works have been performed [4,5]. Moreover, the high reactivity of the magnesium promotes the formation of several phases such as oxides, hydroxides and carbonates, which could drastically affect H_2-dissociation and H-diffusion into few atomic layers. However, the composition and role of those phases on the hydrogenation properties are not clarified yet, giving controversial results [6]

Therefore, the main purpose of this work is to shed light on the influence of the surface (and subsurface) composition on hydrogen-related processes. To this aim, nanocrystalline magnesium films (thickness~80 nm) were deposited by e-beam evaporation. Under ambient exposure, a 6-9 nm thick layer of oxides and hydroxides was formed onto the magnesium surface (Fig.1). Pd-capped Mg films were also synthesized for comparison purposes. The hydrogenation mechanism was investigated by “in situ” optical measurements under different temperatures and H_2-pressures. All films were characterized by profilometry, XRD, STEM (EELS and EDS) and FTIR spectroscopy.

Results show a drastic influence of surface on the hydrogenation process, even with acting the palladium catalytic layer. Activation energies and control mechanisms would be revealed, giving clues about the key influence of the surface on magnesium hydrogenation/deshydrogenation processes.

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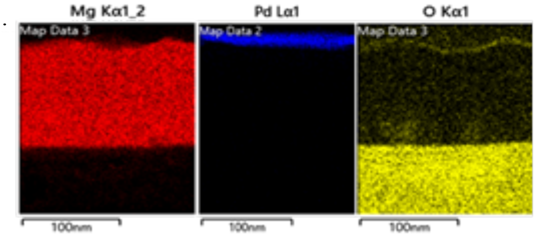

Figure 1. EDS images of Mg films after exposure to ambient conditions and palladium capped. Mg, O and Pd elements are marked

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Acknowledgements

Authors acknowledge the support from RTI2018-099794-B-I100.

Jose R. Ares is an associate professor at UAM, combining academia and research. He is currently the coordinator of University Master Degree about energy. His main research activities focus on properties of novel materials for energy storage and conversion, particularly on hydrides and sulfides to be used as hydrogen storage and thermoelectric materials, respectively.

Corresponding author: Jose Ares, e-mail: joser.ares@uam.es tel: +34 914975625

Development of Hydrogen Purification Membrane based on Pd-Mn-Ag Ternary Alloys

Mehmet Mert Köse[1,2], Hilal Aybike Can[1,2] Fatih Piskin[2,3] and Tayfur Öztürk[1,2]

[1] Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, TURKEY
[2] ENDAM, Center for Energy Storage Materials and Devices, Middle East Technical University, Ankara, TURKEY
[3] Dept. of Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University, Muğla, TURKEY

Hydrogen is well-known source of electrical energy and started to be used in domestic systems via PEM fuel cells. Studies in UK, Germany and Netherlands are showing that it is safe to blend hydrogen into natural gas pipelines within the levels of 5-20% [1].

Extracting hydrogen from the Natural Gas grids and using it in PEMFC systems requires membranes which provide hydrogen levels at least 99.97% pure hydrogen free from CO (< 10-100 ppm) and sulfur (< 2.5 ppm) [2]. Dense separation membrane already satisfies these requirements as it would separate hydrogen which is extremely pure. Currently separation membranes in use are Pd-Ag alloys, where Pd content is more than 75%.

In this study, we aim to produce Pd-Mn-Ag thin film membranes with high permeability and low cost. We make use of combinatorial deposition technique[3] so as to optimize the composition of the ternary membrane .

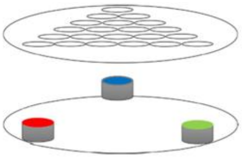

Fig.1 Combinatoırial depsition of thin film membranes

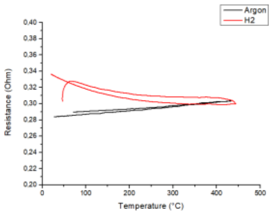

Fig.2 Resisivity change of Pd38Mn21Ag41 under argon and hydrogen as a function of temperature

Thin film membranes were prepared via sputter deposotion using 2 inch Pd, Ag and Mn targets. Substrates were glass 18 mm in diameter placed in stainless steel holder in triangular form comprising 21 mebranes, Fig.1. Conditions were adjusted such that films were typically 3 µm thick.

Thin films were then screened in terms of a reactivity index This involved the measurement of resistance of the thin film while heating to 450 °C first under argon and then under hydrogen, Fig.2 . The index was defined as $r=\rho H_2/\rho Ar$ where ρH_2 and ρAr are the resistance of the film -measured with four probe technique- under hydrogen and argon.

The position of thin film membranes in ternary system was marked in Fig.3. This comprises a total 42 thinn film membranes, i.e. two sets of films. It is seen that the embranes are distributed over a wide compositional area covering the complete ternary phase filed. It is seen structurally thin films fall into three categorties. Mn rich memebranes, Dual Phase membranes and Single phase membranes.

Reactivity index measured for the thin film membranes are shown plotted in Fig.4. Here the region close to Mn are black indicating that the measuremnt in these regions were not possible due to the fact that the films were quite brittle even without exposure to hydrogen. Therefore Mn rich compositions (shown red in Fig.3) are unstitable as separation membrane. The reactivity index has high value close to Pd-Mn line and also in region centered on Pd43Mn32Ag25. The map refers to values at 200 °C, and contour mapping is altered depending on the temperature , though the overall shape is preserved.

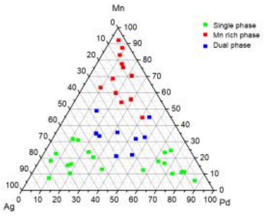

Fig.3 Structure of thin film membranes in Pd-Mn-Ag system

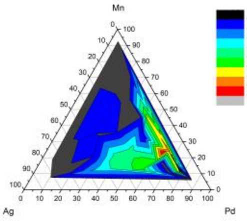

Fig.4 Map of reactivity index in Pd-Mn-Ag system at 200 °C

The results show that Pd-Mn-Ag system is quşte suitable for developing separation membranes that would function at different tenmperature. For convetional purposes, i.e.separation membrane operating betweeb 200-400 °C, two compositons are identified. These are Pd38Mn21Ag41 and Pd43Mn32Ag25.

Currently work is in progress to deposit the thin film membranes of selected composition on on nanoporous substrate to measure their permeability.

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Mehmet Mert Köse was graduated from Middle East Technical University, Department of Metallurgical and Materials Engineering. He is currently Master of Science Student in the same department.

Presentating author: Mehmet Mert Köse, e-mail: mehmetmertkose@gmail.com tel:+905543188591

High pressure hydrogen storage performance of Basolite® MOFs

Sergey Chuvikov and Semen Klyamkin
Lomonosov Moscow State University, Chemistry Department,
Leninskie Gory, 1/3, Moscow 119991, Russia

Physical compression in a high pressure vessel (up to 750 bars) remains the simplest and most efficient way to store hydrogen. One of the approaches for the increasing stored amount of gas is filled vessels with an adsorbent. Compared to various porous materials such as zeolites or carbon nanostructures, metal-organic frameworks (MOFs) demonstrate record values of excess adsorbed hydrogen up to 8,6 wt % at 77K due to high specific surface area and pore volume [1]. However, hydrogen uptake dramatically drops below 1 wt.% at room temperature and pressures up to 70-100 bars. Meanwhile, according to adsorption isotherms, saturation is not achieved under those conditions, unlike low-temperature adsorption. This suggests that the hydrogen capacity could be significantly improved by increasing the pressure [2]. Herein, we report the results of an experimental study of high-pressure hydrogen adsorption behaviour for a series of commercially available MOFs Basolite®, namely C300, Z377, Z1200, A100, and F300.

According to the XRD analysis, crystal structure parameters of C300, Z377, and Z1200 match well available data on HKUST-1, MOF-177, and ZIF-8, respectively. The main phase of the A100 corresponds to a large-pore modification of flexible MIL-53(Al) with a small amount of a narrow-pore form. The crystal structure of F300 (analogue MIL-100 (Fe)) cannot be specified because of low degree of crystallinity. The specific surface area (SSA) and pore volume (V_{pore}) values for the studied samples except F300 correlate with their original MOFs.

The hydrogen excess adsorption at 77K demonstrates pronounced maxima in the range of 15-40 bars for all studied materials regardless of their chemical composition and porous structure parameters determined by conventional N_2 low-temperature adsorption. In the high pressure region, the excess hydrogen adsorption decreases due to the alignment between the densities of hydrogen in the adsorbed and gas phase.

The adsorption isotherms at 243-293K have a more familiar Langmuir appearance: excess hydrogen uptake gradually increases at pressures up to 400-500 bar in a similar way for all samples. Meanwhile, the shape of the isotherms and the heat of adsorption calculated from the Clausius Clapeyron equation evidence different behaviour in the ultrahigh pressure range depending on the chemical nature and porous structure of MOFs.

The total hydrogen uptake and delivery capacity were estimated using the measured excess adsorption. C300 and Z1200 demonstrated the highest efficiency due to a combination of high density of the MOFs frameworks and high adsorption capacity. An optimal balance of these parameters is a key factor for practical application.

The calculated heats of hydrogen adsorption at moderate pressure for the studied materials are consistent with the previously reported results for the corresponding MOFs and lie in the range of 3.0-8.0 kJ/mol. With increasing pressure, the heat of adsorption naturally decreases and tends to zero for all MOFs except C300. In the latter case, the increase in the heat of adsorption at ultrahigh pressures is probably due to additional hydrogen binding related to reversible transformation Cu^{2+} to Cu^{+}.

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This work was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University «The future of the planet and global environmental change» and was supported by the Ministry of Science and Higher Education of the Russian Federation, project # AAAA-A16-116053110012-5.

Sergey Chuvikov is Ph.D student of chemistry of M.V. Lomonosov Moscow State University. He has been working in the field of hydrogen storage since 2009 under the supervision of Professor Semen Klyamkin. His research interests include the storage of hydrogen and methane in the field of ultrahigh gas pressures, post-synthetic functionalization of MOFs and other highly porous materials for gas storage.

Presentating author: Sergey Chuvikov, e-mail: sergey.chuvikov@gmail.com tel:+79269246650

Experimental Research of Metal Hydride-Based Heat Storage System Processes

A.V. Bezdudny [1], D.V. Blinov[1,2], V.I. Borzenko[1]
[1] Joint institute for high temperatures, Moscow, Russia;
[2] National Research University "MPEI", Moscow, Russia;

Importance and relevance of question of creating different types of cyclic thermal energy accumulation systems is driven by the growth of interest in renewable energy-based power systems. At the moment, stationary systems based on phase change materials, physical storage, compressed air, chemical transition and others. are the most commonly spread across the industry [1]. The very forward-looking in the context of complex solutions for thermal energy storage systems are metal hydrides – chemical compound of hydrogen and metal or intermetallic alloy. They are capable of reversible hydrogen storaging, purification of polluted gas (with some restraints on the initial gas mixture composition) [2], complex hydrogen compression [3] and thermal energy storage [4]

The main peculiarity of hydrogen sorption process is its high heat of reaction – approximately 40 kJ/mol for the low temperature metal hydrides of LaN_5 family.

Above mentioned feature of metal hydrides is the main technological barrier in the most developed area of metal hydride system application: storaging and purification of hydrogen. In pair with low thermal conductivity it leads to the modes of operation characterized by the mass transfer crisis [5]. On the other hand, the heat of reaction can be exploited to turn the metal hydrid device into a heat source during the sorption process.

The main goal of this study is to conduct an analysis and to experimentally research the applicabilty of single stage metal hydrid systems for the reversible thermal energy storage purproses.

In the study the results of experimental research of thermal, mass transfer and dynamic characteristics of processes in the metal hydride thermal energy storage reactor are presented. Several types of metal hydride reactors with different hydrogen capacity were used. The data about thermal power and thermal energy storage capacity are gathered. Methods for intensification of processes are proposed.

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Acknowledgements
Authors acknowledge support from the Russian Science Foundation grant No. 17-19-01738.

Bezdudny Alexander Vladimirovich, 29.04.1995. graduated Nuclear energetics and Thermal physics department of Moscow Power Engineering Institute in 2019, trainee researcher of Laboratory of hydrogen energy technologies JIHT RAS, scientific interests are hydrogen storage, metal hydrides, intermetallics, , renewable energy, thermal energy storage.
Presentating author: Bezdudny Alexander, e-mail: h2lab_bezdudny@mail.ru

Effect of Heterointerfaces on the Electrical Conductivity of $BaZr_{0.80}Y_{0.20}O_{3-\delta}$ - $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ Composite Thin Films

Taner Özdal[1], Berke Pişkin[1,2], Gülhan Çakmak[1,2] and Fatih Pişkin[1,2]
[1]Energy Materials Laboratory, Mugla Sıtkı Kocman University, Turkey
[2]Metallurgical and Materials Engineering, Mugla Sıtkı Kocman University, Turkey

Hydrogen can be produced from a variety of methods such as natural gas reforming, coal gasification, and biomass gasification. However, hydrogen (H_2) independent from the production method, could always be produced in gas mixtures containing CO, CO_2, H_2S, NO_x, etc [1]. Thus, there is a need for further separation steps. Among H_2 purification techniques, dense separation membranes are especially attractive because they could provide high purity (>99.99%) H_2. Pd-based metallic membranes have been already commercialized, however, their high cost, surface poisoning issues, and hydrogen embrittlement problems limit the comprehensive utilization [2]. On the other hand, ceramic membranes typically offer reasonable costs together with high hydrogen purity. However, they exhibit very limited hydrogen fluxes as compared to Pd-based membranes.

Among the ceramic membranes, perovskite-type oxides with ABO_3 chemical formula are extensively being studied due to their mixed ionic and electronic conductivity. However, the proton and electron conductivity of undoped perovskites are limited due to fewer amount of oxygen defects in their structure.

$$j_{H2} = \frac{RT}{4F^2L}\frac{\sigma_{H^+}\sigma_{el}}{\sigma_{H^+} + \sigma_{el}}\ln\left(\frac{P'_{H_2}}{P''_{H_2}}\right)$$

Wagner equation is used to describe H_2 flux across the dense ceramic membrane. Based on the equation, the permeability is affected by temperature, thickness, proton-electron conductivities (ambipolar), and the pressure difference between opposite sides of the membrane. Thus, to optimize the H_2 permeability, ambipolar conductivity plays a crucial role.

The selection of appropriate doping elements is one criterion to ameliorate the ambipolar conductivity. Doping with aliovalent cations deteriorates the charge balance in the perovskite structure and subsequently, oxygen vacancies are formed to ensure electronegativity. Also, it is well accepted that dopants with lower ionization potential, higher electronegativity, and larger cation size than B-site cation tend to increase conductivity. Another approach can be novel heterointerface structured materials. The formation of heterointerface can increase the oxygen vacancy concentration similar to the doping effect and can provide higher conductivity along with the interfaces [3].

In this study, the effect of $BaZr_{0.80}Y_{0.20}O_{3-\delta}$ (BZY) - $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCY) heterointerfaces on the electrical conductivity of BZY-SCY composite thin films was investigated. BZY and SCY powders, synthesized by the Pechini method, were initially pressed under 100MPa into pellets and sintered to obtain pellets with high density. BZY and SCY pellets were then used as target materials for RF magnetron sputtering. Perovskite oxide composite thin-films consist of different BZY and SCY fractions were deposited via a combinatorial material approach. BZY-SCY composite thin films with 27 different compositions were produced simultaneously on glass substrates in a single experiment. By doing so, different quantities of BZY-SCY heterointerfaces were intentionally created. Four Pt strips were deposited on the film surface to attain electrical contacts for the electrochemical measurements. Electrical conductivities of thin films were elaborately analyzed via 4-probe resistivity measurement and AC impedance spectroscopy (EIS) under H_2 atmosphere and at a temperature range of 300-500°C.

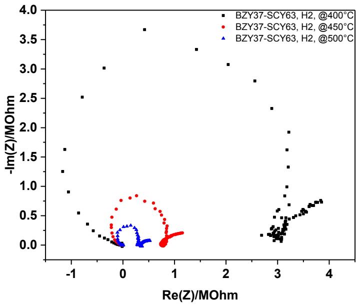

Figure 1. EIS responses of BZY (37wt.%) - SCY (63wt.%) composite thin film at 400 °C, 450 °C, and 500 °C under H_2.

In summary, the conductivity of thin-film composites was evaluated and the effect of BZY-SCY heterointerfaces was elucidated. These conductivity results will further shed light on subsequent H_2 permeability tests.

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This study is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) with project number 119M065.

Taner ÖZDAL is a materials engineer and received his bachelor degree in Metallurgical and Materials Engineering department from Muğla Sıtkı Koçman University (MSKU). He is currently a researcher in Energy Materials Laboratory, MSKU, and is studying perovskite-type oxide composites for hydrogen separation membranes. He is also interested in cathode materials for Li-ion batteries, Na-ion batteries, and solid oxide fuel cells.

Presentating author: Taner ÖZDAL, e-mail: tanerodal74@gmail.com, tel: +90 545 738 43 93

Electrochemical performance of AB$_5$ type metal hydride electrodes with carbon nanotubes

Alexey Kazakov[1], Dmitry Blinov[1,2] and Alexey Volodin[3]
[1] Joint institute for high temperatures, Moscow, Russia;
[2] National Research Institute "MPEI", Moscow, Russia
[3] Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia

Electrochemical energy storage is one of the most intensively developing areas for the renewable energy storage. Electrochemical batteries can be used not only as power sources for mobile and portable devices, but also for hybrid and electric cars and balance the load in renewable energy networks [1]. Ni-MH batteries have a number of advantages for practical applications, such as high specific energy density, resistance to overcharge / overdischarge, fast charge-discharge kinetics, environmental friendliness and safety. The main component of Ni-MH batteries, which affects their characteristics, is a hydrogen-absorbing material used as an anode. Intermetallic compounds are capable of reversibly absorbing and releasing hydrogen under normal conditions [2].

Metal hydride materials in electrochemical energy sources require to have a high reversible hydrogen capacity (> 1% mass), high catalytic activity, corrosion resistance in the electrolyte, and mechanical stability and a long service life [3]. Along with the hydrogen storage properties of metal hydrides, the preparation of metal hydride electrodes is of great importance for improvement of their electrochemical properties: metal hydride particle size [4-6], electroconductive additives [7, 8], binding components [9].

Carbon nanotubes (CNTs) are of great interest for electrochemical hydrogen storage due to their unique structural, mechanical, thermal, electronic, and electrochemical properties [10]. The applications of CNTs on the metal hydride electrode are investigated extensively [11-13].

In present study, low-Co AB$_5$ alloy La$_{0.6}$Ce$_{0.2}$Nd$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$, showed good elechtrocemical performance [14], mixed with in-lab prepared carbon nanotubes in different ratios is investigated as a negative electrode. Effect of carbon nanotubes on electrochemical performance (discharge capacities, high rate dischargeability, hydrogen diffusion and cyclic stability) of cold-pressed pelletized metal hydride electrodes are studied

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Acknowledgements
Authors acknowledge support from the Russian Science Foundation grant No. 17-19-01738.

Kazakov Alexey Nikolaevich, 09.08.1987. graduated Chemical department of Moscow state university in 2010, researcher of Laboratory of hydrogen energy technologies JIHT RAS, scientific interests are hydrogen storage, metal hydrides, intermetallics, electrochemistry, renewable energy, biohydrogen

Presentating author: Alexey Kazakov, e-mail: kazakoffalex09@gmail.com tel:+7-926-454-6098

Structure investigation of multi-base-component alloys and their hydrides

Korol Artem[1], Vladislav Zadorozhnyy[1], Elena Berdonosova[2], Mikhail Zadorozhnyy[1], Semen Klyamkin[2] and Polina Borisova[3]

[1] National University of Science and Technology “MISIS”,
College of New Materials & Nanotechnology, Physical Materials Science Department, Moscow, Russia
[2] Lomonosov Moscow State University, Chemistry Department, Moscow, Russia
[3]National Research Centre “Kurchatov Institute”, Moscow, Russia

Nowadays, the theme of materials for hydrogen storage has become an important topic. As far as hydrogen is renewable and does not pollute the environment, it is a promising fuel for various applications. Therefore, there is a need for efficient storage materials. For this purpose, hydride-forming alloys are considered as promising materials due to their ability to store large amounts of hydrogen safely and compactly. Among metal hydride materials, a special group of multi-base-component (MBC) alloys can be distinguished. These alloys known as “high-entropy alloys”, which include 5 or more elements with concentrations ranging from 5 to 35% [1] have attracted special attention due to their exceptional mechanical properties, good crack resistance, high strength, and plasticity, particularly at high temperatures [2, 3]. Besides, the presence of elements with high affinity for hydrogen in some MBC alloys and crystal lattice distortion due to big difference in atomic radii of components cause record hydrogen absorption capacity [4].

In the present work, structure investigations of the new type of the multi-base-component alloys of the following compositions: $Ti_{20}Zr_{20}V_{20}Nb_{20}Ta_{20}$, $Ti_{20}Zr_{20}V_{15}Nb_{15}Ta_{15}Hf_{15}$ and $Ti_{25}Zr_{25}V_{15}Nb_{15}Ta_{20}$, have been performed. Transmission electron microscope, scanning electron microscope, X-ray and neutron diffraction (Fig.1) were used for this purpose. In order to examine the location of hydrogen atoms within metallic crystal lattice as a function of MBC composition and preparation method a series of deuterides was synthesized.

Hydrogen storage performance of the alloys was evaluated by volumetric measurements. As it was shown, all studied alloys form hydide phases of high thermal stability with maximum hydrogen capacity close to 2 H/M. Low hydride decomposition pressure allowed us to preserve the hydrogen-saturated phases for subsequent structural analysis

Aknowledgment

This work was supported by the RFBR, project No. 20-32-90042 and RSF progect No. 19-13-00207.

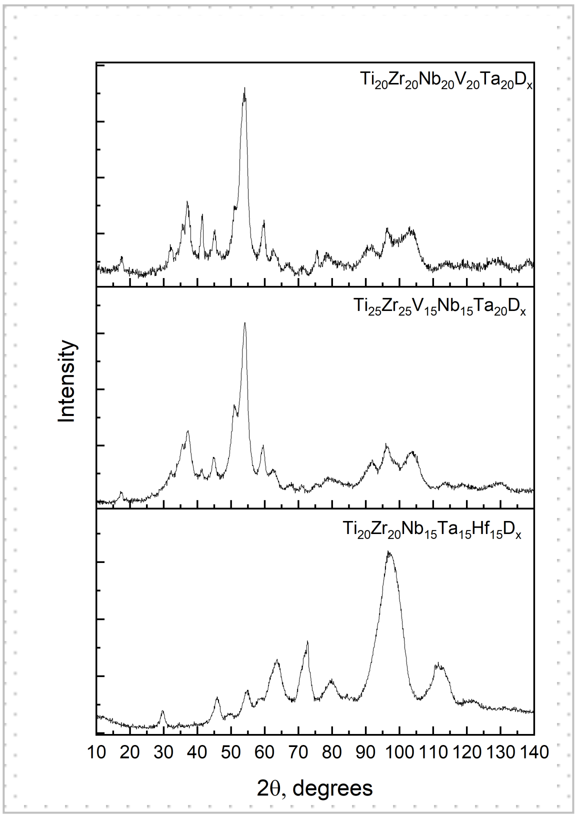

Figure 1. Neutron diffraction patterns of studied alloys

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Artem Korol received bachelor’s degree in Materials Science at National University of Science and Technology "MISIS", Moscow, Russia (2020). His thesis was titled *Synthesis and investigation of hydride-forming multi-principal-component alloys for reversible hydrogen storage.* Korol presented six oral and poster presentations at scientific conferences. He works now at State Research Center “TsNIIchermet” Moscow, Russia (junior researcher), National Research Center “Kurchatov Institute”, Moscow, Russia (research laboratory assistant) National University of Science and Technology “MISIS”, Moscow, Russia (research laboratory assistant).

Presentating author: Artem Korol, e-mail: artemkorol1998@gmail.com tel: +79803718135

Artificial Neural Network (Ann) for Pressure- Concentration- Temperature (P-C-T) Curves of Metal Hydrides

ZK Simelane[1], A, Kolesnikov [2] and M, Lototskyy [3]
[1]Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
[2]Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
[3]South African Institute for Advanced Materials Chemistry, University of Western Cape, Cape Town, South Africa

Currently metal hydrides are studied for the purpose of being used as hydrogen storage in fuel cell-powered electric cars and in batteries [2]. Artificial Neural Networks (ANN) can be referred to a class of algorithms that has an ability to obtain hidden regularities from data, and the data may be incomplete, distorted, and even contradictory. If there is connection between the input and output data the neural network is able to tune in to it with accuracy [1].

An artificial neural model for Pressure- Temperature-Concentration (P-C-T) curves of Metal Hydrides was investigated, for this purpose the artificial neural network (ANN) method was used. The major purpose of this research project is to build and develop a model for fuel cell based on the artificial neural networks. In this research project; a model of phase diagrams for hydride forming metals and alloys with hydrogen gas which are referred to as PCT diagrams were developed.

The double-layer (ANN [2-14-1-1]) model was developed for absorption; a model that trains 2 elements (P&T, P&C or C&T) and calculates the 3rd one (P/C/T). The model was then improved for a better fit from 14 neurons to 18 neurons for desorption (ANN [2-14-1-1]). 407 total datasets were collected from the University of Western Cape experiment, 285 samples (70%) were used for training, 61 samples (15%) were used for validation and the remaining 61 samples (15%) was used for testing. The training stopped when the error goal or the maximum number of epochs was reached.

Performance metrics; goodness of fit (R^2) and mean square error (MSE) were used to assess the performance of the developed model. From the results, the model had an overall MSE of 0.3783 and an R^2 of 0.9928 for absorption and an overall MSE of 0.2830 and an R^2 of 0.9956.

The post-training regression analysis plotted showed the linear regression fit to the data points, matching the predicted output to the actual target. An R value is very close to 1 which means there is a close relationship between outputs and targets and that indicated a good fit. MSE value showed that the network learned better, as the number of epoch increased.

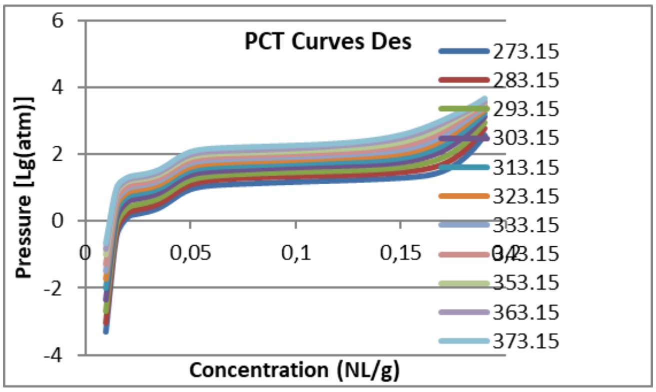

Figure 1. PCT curves for desorption results obtained from ANN model using experimental data from UWC.

It was verified that the predicted values of ANN coincide well with the experimental results. Matlab neural network modelling tool is a very suitable tool for calculations in engineering, and can also serve as a visualization tool of simulation models in artificial intelligence applications.

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Acknowledgements

Author acknowledges support from Tshwane University of Technology Prof. A. Kolesnikov for supervising, the University of Western Cape Dr. M. Lototskyy for the provision of data used on this experiment and the National Research Foundation for funding during the study.

Miss Ziphezinhle Khethiwe Simelane is with the Department of Chemical and Metallurgical Engineering, Tshwane University of Technology. Having graduated from TUT in 2018 and from MUT in 2017. She obtained her N.Dip in 2017 and her BTech in 2018. Her research interest covers Hydrogen storage application, Artificial intelligence and Data analysis.

Corresponding author: Ziphezinhle Khethiwe Simelane , e-mail: ziphezinhle03@gmail.com tel: +27 724 728939

FUEL CELLS AND ELECTROLYSERS

Materials development for proton ceramic cells

Olivier JOUBERT
Université de Nantes & CNRS

This study will be dedicated to the development of materials used in proton ceramic cells and more precisely to the ceramic electrolyte: optimization of the microstructure of the material via accurate monitoring of the synthesis and temperature treatment steps. The objective is to reach a total conductivity level above 0.1 mS/cm for operating temperatures below 600°C in order to prevent premature aging of SO cells performance. I will focus the presentation on BZCY solid solution showing properties which are compromise between the high proton conductivity of BCY and the stability of BZY. This material requires high sintering temperatures (≈1600°C) and new sintering process are needed. One example will be presented, the cold sintering process (CSP) which enable to obtain dense BZCY type electrolyte and the influence of CSP parameters on ionic conductivity will be discussed.

Olivier JOUBERT (1965) is presently full professor in Chemistry of Materials at University of Nantes and is Chair of electrochemical storage and conversion of energy group (ST2E) of "Institut des Matériaux Jean Rouxel (CNRS-IMN)". The major research interests of professor JOUBERT revolve around development of new materials for technological applications such as high and intermediate temperature ceramic Solid Oxide (SO) fuel or electrolyser cells (SOFC and SOEC). He is co-author of 120 publications, 25 invited talks and 5 patents. Olivier Joubert is chairing the French Research Network on Hydrogen Energy which assembles all French academic research groups in the field of electrolysis production and storage of hydrogen and also its conversion to electricity using fuel cell.

Presentating author: Olivier Joubert , e-mail: Olivier.Joubert@cnrs-imn.fr

Nitride materials as possible electrodes for NH_3 reversible fuel cells

Vanessa C.D.Graça, Laura I.V.Holz, Maria A.Salvador, Sergey M.Mikhalev, Francisco J.A.Loureiro, Duncan P.Fagg

Centre for Mechanical Technology and Automation, Mechanical Engineering Department, University of Aveiro, Aveiro, 3810-193, Portugal

A principal aim of the EU 2030 climate & energy framework is the reduction of CO_2 emissions by the development of new technologies for industries and processes[1]. In this respect, ammonia (NH_3) is a key chemical that is produced in vast quantities worldwide as a precursor in a range of products that are vital to society, such as fertilizers and medicines. Moreover, due to its high energy density and the formation of only H_2O and N_2 upon its combustion, it also has been proposed as a potential carbon-free fuel [2].

The current industrial route for ammonia production is the Haber- Bosch process, which employs Fe-based catalysts to synthesize ammonia from nitrogen and hydrogen at high pressures (100-300bar) in the temperature range 300-550ºC [3]. Despite this prevalence, the process has a very high energy consumption, with low equilibrium conversion (10-15%) and produces 300 million metric tons of CO_2 per year due to its continued reliance on hydrogen produced from natural gas [3].

New greener concepts for NH_3 production and utilisation are, therefore, urgently needed.

The current work aims to offer potetnial materials for a highly attractive alternative to mitigate this problem, based on the electrochemical synthesis of NH_3 directly from H_2O and N_2,. with the input of renewable electricity, using a Proton Ceramic Electrolyser Cell (PCEC), Fig.1. Such a process can form NH_3 without CO_2 generation. Moreover, it can also provide a method for the chemical storage of renewable electricity, generating a route to balance renewable energy supply and demand, by the formation of a transportable chemical product of high energy density.

At this juncture, it is also important to highlight that the reverse operation of the electrochemical cell of Fig.1, would correspond to a fuel cell, where NH_3 would be combusted to form the products of H_2O and N_2, while also directly producing electricity and heat.

Despite this attraction, and the apparent similarity of these two devices, previous work on these concepts are scarce. For this reason, the current presentation aims to emphasise the challenges of these processes and the critical funcionalitites that are required in each case with respect the NH_3 electrode. Discussion will then progress to decribe some recent work of our group on the development of a range of nitride materials as possible NH_3-electrodes for these devices.

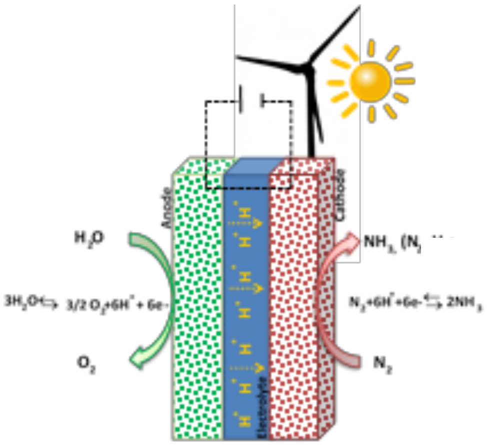

Figure 1. Electrochemical NH_3 production using a protonic membrane.

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Acknowledgements

The authors acknowledge the Fundação para a Ciência e Tecnologia (FCT) for the PhD grants SFRH/BD/130218/2017, PD/BDE/142837/2018 and the projects, PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020, POCI-01-0247-FEDER-039926, POCI-01-0145-FEDER-032241, UIDB/00481/2020 and UIDP/00481/2020 and CENTRO-01-0145-FEDER-022083 - Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Dr. Duncan Fagg is currently employed as a Principal Researcher in the University of Aveiro, Portugal. He obtained his B.SC in Chemstry and Materials science Nottingham University 1992 and Ph.D. in Chemistry Aberdeen University 1997. He has over 20 years of research experience with previous placements in CICECO Aveiro, Portugal, ICV Autonomous University Madrid, Spain, Dept.Chemical Engineering, Patras Greece, School of Chemistry, St-Andrews University Scotland, and Risø DTU National Laboratory for Sustainable Energy, Roskilde Denmark. He is the author of over 100 international scientific publications in areas covering Solid Oxide Fuel Cells (SOFC), Solid Oxide Electrolyser Cells (SOEC), Oxygen separation membranes, Hydrogen separation membranes, Hydrogen Storage..
Presentating author: Duncan Fagg, e-mail: duncan@ua.pt

Hydrogen generation by PEM electrolysis – a numerical investigation

Elena Carcadea[1], Mihai Varlam[1], Daniela Ion-Ebrasu[1], Konstantin Petrov[2], Catalin Jianu[1], Laurentiu Patularu[1] and Dorin Schitea[1]

[1]National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, Uzinei Street, No. 4, P.O. Box 7 Raureni, 240050, Rm. Valcea, Romania

[2]Institute of Electrochemistry and Energy Systems “Academician Evgeni Budevski”, Acad. Georgi Bonchev Str., Block 10 1113 Sofia, Bulgaria

A numerical and experimental investigation of a Proton Exchange Membrane (PEM) electrolyser has been carried out in order to study the effect of flow fields and membrane electrode assembly (MEA) characteristics on the overall performance. These components account for about half of the cost of a PEM electrolyser and a quarter of the cost of a complete hydrogen production system by electrolysis. In this context, an optimization by mathematical modelling followed by an experimental demonstration has been carried out.

Bipolar plates represent key components in a PEM electrolyser (Fig. 1) because it must ensure the even distribution of fluids (water, hydrogen and oxygen) to the reaction areas. An uneven distribution of fluids may negatively influence the heat transfer in the cell and implicitly, its performance.

The performance of the PEM electrolysis cell depends on the reaction kinetics that occurs inside the catalyst layer. It is necessary to analyze the three-phase interaction (membrane-catalyst-water) and the species transport (water, hydrogen and oxygen) to and from the catalyst layer to the adjacent layers (membrane and gas diffusion layer). Different properties of MEAs are numerically simulated in order to understand their influence on the performance.

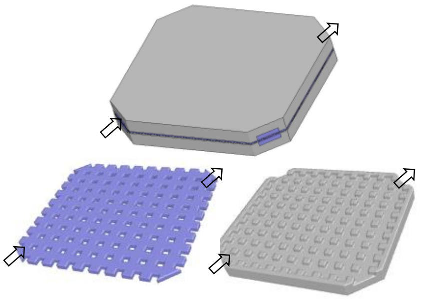
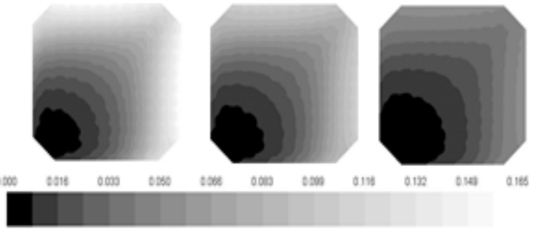


Figure 1. PEM electrolyser (up), fluid flow channels (bottom, left) and bipolar plate (bottom, right).

ANSYS Multiphysics 17.0 with the Fuel Cell and Electrolysis Model has been used to solve the conservation of mass, momentum, species, energy and charge equations. The 3D CFD model analyzed the influence of design (bipolar plate configuration, membrane thickness) and operating parameters (voltage, pressure, temperature) on the PEM electrolyser performance. The simulations were carried out using specific boundary conditions (mass flow rates, species mass fractions) and properties (porosity, permeability). Different properties of MEAs and bipolar plates have been taken into account in order to understand their influence over the electrochemical process and performance. The simulations carried out revealed that (i) the pin dimensions from the bipolar plate do not have a big influence on electrolyser performance, (ii) a higher active area of the catalyst can lead to an increase of the performance, (iii) an optimum membrane thickness (50 microns) was obtained.

The aim of PEM electrolyser optimisation is to maximize the hydrogen production. Fig. 2 presents the hydrogen mass fraction in the catalyst layer for various membrane thicknesses. It can be noticed that starting from the inlet, where there is no hydrogen (only water is supplied), the generation starts to takes place as the reaction proceed therefore, the mass fraction of hydrogen increases. A maximum hydrogen mass fraction of 0.165 was obtained for the 50 microns thickness as compared to only 0.111 for 75 microns and 0.056 for the 160 microns. In terms of mass flow rate, we obtained a hydrogen generation rate at the outlet of the PEM electrolyser of 0.06 mg/s for the 50 microns membrane, 0.049 mg/s for 75 microns and 0.032 mg/s for 50 microns at 2V cell potential difference.



(a) (b) (c)

Figure 2. Hydrogen mass fraction in catalyst layer for various membrane thicknesses at 2V: (a) 50, (b)75, (c)160 microns.

Our analysis was intended to give an insight into physical mechanisms that can influence a PEM electrolyser and to optimize some parameters in order to maximize the hydrogen production. The CFD modelling is the easiest way to evaluate the dynamic behaviour of the processes and to establish the effect of different changes in materials, configurations and operating conditions for any electrochemical device or system.

Acknowledgements
This work was supported by Nucleus Programme - PN 19 11 and IIN CNHPC.

Dr. Carcadea Elena is coordinating ICSI Energy, a department of the National Research and Development Institute for Cryogenics and Isotopic Technologies ICSI Rm. Valcea, Romania. The research activity is directed towards optimization of hydrogen technologies and electrochemical devices involved in energy production and storage (fuel cells, electrolysers, batteries) by both mathematical modeling and experimental tests. She is member of the Romanian Association for Hydrogen Energy and represents the institute to Hydrogen Europe Research and European Clean Hydrogen Alliance.

Presentating author: Elena Carcadea, e-mail:elena.carcadea@icsi.ro tel:+40.350.733.890/ ext 200

Impact of Anode Loading on the CO Tolerance of $Ti_{0,8}Mo_{0,5}O_2$-C supported Pt Electrocatalyst

Ceyhun Yıldırım[1,2], E.Sena Kazan[1,3], Osman Öztürk[2] , Irina Borbath[4], András Tompos[4], M.Suha Yazici[1]
1. TUBITAK Marmara Research Centre, Energy Institute, Gebze-Turkey
2. Department of Physics, Gebze Technical University, Gebze-Turkey
3. Department of Chemical Engineering, Gebze Technical University, Gebze-Turkey
4. Research Centre for Natural Sciences, Hungarian Academy of Sciences (RCNS HAS), Budapest, Hungary

Fuel impurities especially trace amount of CO cause dramatic losses on the performance and lifetime of PEMFCs. Further purification of H_2 to remove CO or develop a CO-tolerant catalyst can be part of the strategies. Pt/Ru bimetallic electrocatalysts (ECs) are available against the CO poisoning effect, but high cost is the hindering factor for widespread usage.

$Ti_{0.7}Mo_{0.3}O_2$ was investigated as an alternative support material for anode catalyst due to its higher corrosion resistance in acidic media [1]. Park et al. stated that Pt-Ti alloy structure has better ORR activity than commercial C-supported Pt [2]. Addition of Mo to the PtRu EC structure resulted superior CO tolerance [3]. It has been shown that the stoichiometric ratio between Ti and Mo have significant impact on the CO tolerance [4].

$Ti_{0.8}Mo_{0.2}O_2$ was sythesized and used as anode electrode in PEM fuel cell testing [5]. MEAs containing 0.5 and 1.5 mg/cm^2 Pt on Pt/$Ti_{0.8}Mo_{0.2}O_2$/C catalyst were used as anode while 0.6 mg/cm^2 Pt on Pt/C were used as cathode. The MEAs were conditioned by working with pure H_2 and impedance/polarization curves were taken. Then, anode gas was switched to H_2-100ppmCO mixture for measurements. **Hata! Başvuru kaynağı bulunamadı.** shows impedance response of two different loading under hydrogen and 100 ppm CO. Impedance sweep experiments were performed at different current densities (5kHz-0,1Hz frequency and amplitude: %10 of DC current).

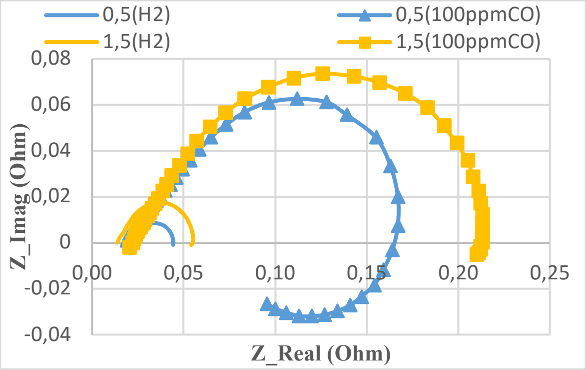


Figure 1. Electrochemical Impedance Spectra under pure H_2 and 100ppmCO contained hydrogen

Hata! Başvuru kaynağı bulunamadı. shows the polarization curves of the MEAs with 0,5mgPt/cm^2 and 1,5mgPt/cm^2, taken at 80 °C cell temperature, 100% humidity and 15psig back-pressure.

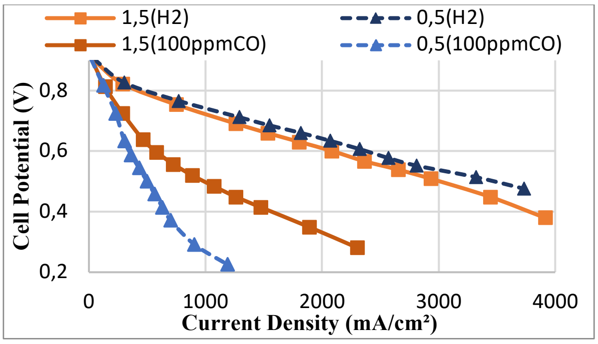


Figure 2. Polarization curves under pure hydrogen and 100ppmCO contained hydrogen

Results under different loadings, humidity and back-pressures will be discussed and presented for CO containing fuels.

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Assoc. Prof. Mehmet Suha Yazici is currently Chief Research Scientist at TUBITAK Marmara Research Center. His current research focus is on the use of Pt alternative catalysts and graphene for PEM fuel cells. He has several patents/publications on electrochemical systems in power generation and energy storage.

Corresponding author: M. Suha Yazici, e-mail: suha.yazici@tubitak.gov.tr, phone: +90-555-846-4575

High Performance electrospun Pt/C/Sulfonated Silica/P(VDF-TrFE) fibrous cathodes for PEM fuel cells

Bilal Iskandarani[1], Selmiye Alkan Gürsel [1] and Begüm Yarar Kaplan [2]
[1] Sabancı University, Faculty of Engineering and Natural Science, Istanbul, 34956, Turkey
[2] Sabancı University Nanotechnology Research and Application Center (SUNUM), Istanbul, 34956, Turkey

Polymer electrolyte membrane fuel cells (PEMFC) are on the cliff to be widely commercialized. However , cost and performance issues hinders their spread utilization [1]. Electrospinning has proven to be a handy tool to fabricate PEMFC electrode with enhanced performance. On one side, it provides exposes platinum to the surface increasing their utilization. On another, it provides the required porositiy for the facile inward diffusion of gas reactants and the outward expulsion of water [2]. In this sense, PVDF and its copolymers emerged as promising carrier polymer due to their hydrophobic character serving in better preventing electrode flooding [3]. In addition to its porous structure, P(VDF-TrFE) has proven to retain water which is thought to help maintain enough water for an optimum PEMFC performance without leading to flooding [4].

Furthermore, Nafion® free electrodes have been under invesigation. This is due to its high cost and unsatisfactory performance at low relative humidity. For this reason, Sulfonated silica (S-SiO_2) is thought to be a promising ceramic-based candidate to substitute Nafion® [5].

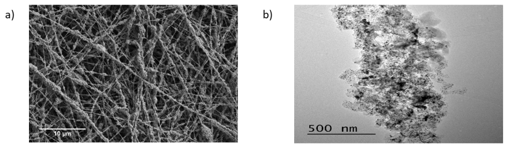

Figure 1.a) SEM and b)TEM images P(VDF-TrFE)-based Pt/C/S-SiO_2 electrospun fibrous material

In the current work, PVDF and P(VDF-TrFE) carrier- based fibrous materials containing Pt/C and S-SiO_2 were fabricated using electrospinning. The electrospun fibrous material (Figure 1) have shown adequate and continuous distribution of both Pt/C and S-SiO_2 particles along the carrier polymer fiber. This is of siginicant importance to ensure a continuous conduction of protons and electrons throughout the electrode leading to enhanced performance.

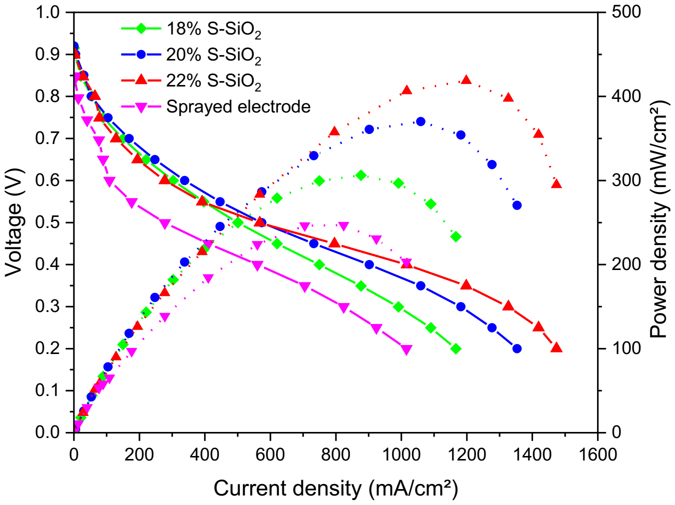

Figure 2. Polarization curve of P(VDF-TrFE)-carrier-based Pt/C/S-SiO_2 MEA containing cathode

The fibous electrodes of different S-SiO_2 loadings were assembled in an MEA against a sprayed electrode. Polarization curves at both fully and partially humidified conditions were collected. The results were complimented by performing electrochemical Impedance spectroscopy (EIS). The electrode with the highest S-SiO_2 loading recorded 418.77 mW/cm^2 maximum power output which is siginificantly higher than that of the brushed electrode. Furthermore, TrFE-based electrodes have shown better performance at lower humidity levels.

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Bilal Iskandarani is currently a PhD Candidate at Sabancı University Materials Science and Nanoengineering Department, conducting research at Sabancı University Nanotechnology Application Center. He obtained her M.Sc. in Molecular Inorganic Chemistry in 2014 from the Lebanese University-Beirut . His research interests are Electrode and membrane materials for Polymer electrolyte membrane fuel cells (PEMFC)

Presentating author: Bilal Iskandarani , e-mail:bilal@sabanciuniv.edu tel: +90 (552) 3371704

Heterogeneous A-site Deficient / Stoichiometric (La, Ca)CoO_3 Electrodes for Solid Oxide Cells

Mehmet Sezer[1], Ali Şems Ahsen[2], Aligul Buyukaksoy[1]
[1]Department of Materials Science and Engineering, Gebze Technical University, Gebze, Kocaeli 41400, Turkey
[2]Department of Physics, Gebze Technical University, Gebze, Kocaeli 41400, Turkey

Improvements in the long-term performance stability of cathode components are critical for the development of economically viable solid oxide fuel cells. Thin-film La0.6Ca0.4CoO3 (LCC) electrodes showed excellent activity in our recent study. However, after long-term exposure to 700 °C, substantial performance degradation, i.e., a 26-fold increase in area-specific resistance (ASR) due to changes in surface chemistry, such as CaO + La2O3 segregation, took place.

The aim of the present research is to improve the performance and stability of LCC cathodes by using them in combination with their A-site deficient modifications (def-LCC), which are known to i) be abundant in oxygen vacancies and ii) exhibit slower cation diffusion than stoichiometric LCC. The former property provides faster oxygen reduction, while the latter enhances the stability of the surface chemistry. In this study, we aimed at developing heterogeneous LCC/def-LCC electrodes in two different combinations i.e., LCC film+def-LCC overlayer and def-LCC+LCC overlayer, and thereby achieving high performance and stability. Electrochemical impedance spectroscopy (EIS) measurements conducted on symmetrical half-cells at 700°C indicated that def-LCC and LCC films, and def-LCC+LCC overlayer exhibited nearly the same electrochemical performances, while LCC + def-LCC overlayer combination yielded a much lower area specific resistance (ASR) in comparison to the rest of the samples (ca. 0.08 Ω.cm2). However, upon prolonged exposure to 700 ° for 100 hours, a 2.0-, 1.85- and 4.0-fold increases in ASR were recorded in the cases of def-LCC, LCC + thin def-LCC layer and def-LCC + thin LCC layer, respectively. X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the reasons behind the long-term performance stability improvements.

Synthesis of Thermally Reduced Graphene Oxide Welded Graphene Aerogel Support Material for PEM fuel cells

Meryem Samancı[1], Ayşe Bayrakçeken Yurtcan[2]
[1] Faculty of Engineering, Department of Chemical Engineering, , Atatürk University, Erzurum 25240, Turkey
[2] Department of Nanoscience and Nanoengineering, Atatürk University, Erzurum 25240, Turkey

Fuel cells are considered one of the most promising power sources for mobile and stationary applications due to their high energy conversion efficiency, low operating temperature, low pollutant emissions, easy fuel feed and ease of use. A fuel cell is a device that converts chemical energy directly into electricity. Among the different fuel cell types, the proton exchange membrane (PEM) fuel cell has shown great potential in mobile applications due to low operating temperature, solid state electrolyte and compactness.

Carbonaceous nanomaterials have unusual dimensions and surface properties (eg morphological, electrical, optical and mechanical) that are effective in enhancing the energy conversion performance of fuel cells. Specifically, carbonaceous materials improve the electrochemical active surface area (ECSA) of the electrocatalyst, which provides a high amount of mass transfer to the electrocatalyst. Among these materials, the most remarkable one is the modified graphene (graphene oxide, reduced graphene oxide, graphene aerogel) structures.

In this study, thermally reduced graphene oxide and its associated graphene aerogel synthesis were performed to be used as support material in PEM fuel cells. In the synthesis of Pt electrocatalyst, 1,5-dimethyl platinum cyclooctadiene Pt(COD)Me_2 precursor was used as Pt source. Supercritical carbon dioxide ($ScCO_2$) deposition technique was used in the catalyst synthesis [1]. It is aimed to use platinum (Pt) in the most efficient way with this technique. Electrochemical and physicochemical analyzes were performed on the synthesized materials. In this way, it will be tried to reach the catalyst that gives the best results in the PEM fuel cell.

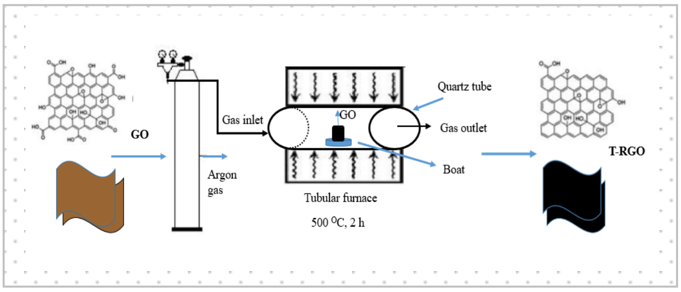


Figure 1. Thermal reduced graphene oxide synthesis.

Graphene oxide synthesized by the Hummer method was used as the precursor material in the synthesis of reduced graphene oxide [2]. Reduced graphene oxide (RGO) is very similar to the original graphene. The reduction can be done by thermally (annealing, microwave, light), chemically (a reducing agent, photocatalyst, electrochemistry, hydrothermal reaction) or a combination of these methods. In this study, the synthesis of reduced graphene oxide was carried out by thermal reduction to graphite oxide (Figure 1). The specified amount of GO was placed in the tubular furnace and kept in argon (Ar) atmosphere at 500 °C for 2 hours. The heating rate of the oven is set at 10 ^{0}C/min. Digital photographs of synthesized graphene oxide and thermally reduced graphene oxide are given in Figure 2.

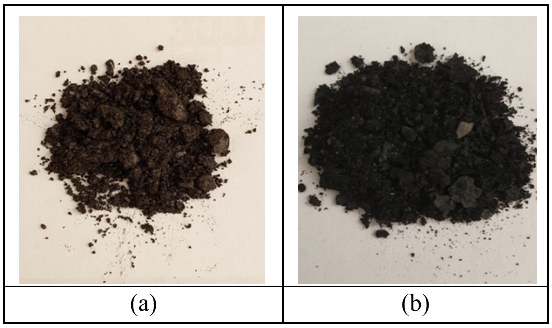

(a) (b)

Figure 2. Digital photographs of (a) graphene oxide and (b) thermally reduced graphene oxide.

Graphene aerogel (GA) has attracted the attention of researchers due to its unique electronic, thermal, mechanical, chemical properties and potential technical applications and its completely 3-dimensional (3D) structure. Regarding graphene aerogel synthesis, there are four most commonly used methods. These have been described as hydrothermal reduction, sol-gel, template-directed reduction and chemical reduction. The most widely used method is the sol-gel method.

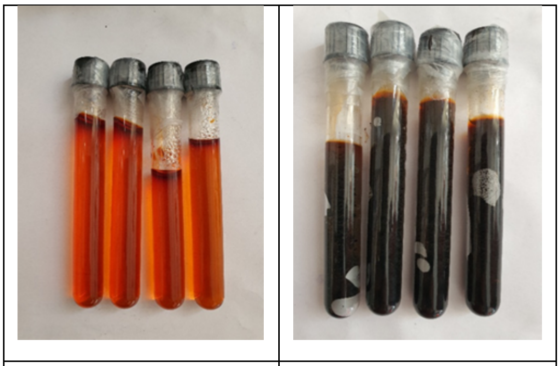

(a) (b)

Figure 3. Digital photographs after gelation of (a) CA and (b) GA

Aerogels are synthesized by the reaction of resorcinol and formaldehyde. Sodium carbonate (Na_2CO_3) was used as a catalyst. Drying process was carried out in $ScCO_2$ environment after gelation and solvent exchange with acetone. As a result of these processes, the hydrogel structure has been achieved. Finally, aerogel structures were obtained after being kept in the pyrolysis furnace in nitrogen environment for 4 hours at 1000 ^{0}C [3]. Unlike carbon aerogel (CA) synthesis, graphene aerogel synthesis was made by adding T-RGO to the sol-gel solution at a certain amount (Figure 3). Thus, electrochemical and physicochemical changes in the structure of T-RGO added to aerogel will be examined.

In the synthesis of Pt electrocatalyst, 1,5-dimethyl platinum cyclooctadiene Pt(COD)Me_2 precursor was used as Pt source. Catalyst synthesis consists of two stages. The first stage is the adsorption of Pt precursor over graphene and the second stage is the thermal reduction of these precursors to Pt. First of all, the support material and Pt precursor were mixed in certain proportions and placed in the reactor. The reactor temperature is set to 80 °C. By adjusting the reactor pressure to 3500 psi, CO_2 was introduced into the system. Under these conditions, it was kept for 24 h in order for the Pt precursor to dissolve well and adsorb to the support surface. After the adsorption process, the sample is removed from the reactor and thermally reduced in N_2 environment at 500 °C for 3 hours in a tubular oven. Thus, Pt was transformed into metallic form.

The following characterization methods were used for the characterization of the support material. Structural properties (such as surface area, pore diameters, pore size distribution) were determined by nitrogen adsorption/ desorption isotherm analysis using the Brunauer, Emmett and Teller (BET) method. Micromeritics 3Flex 3-port BET surface area device was used for surface area analysis.

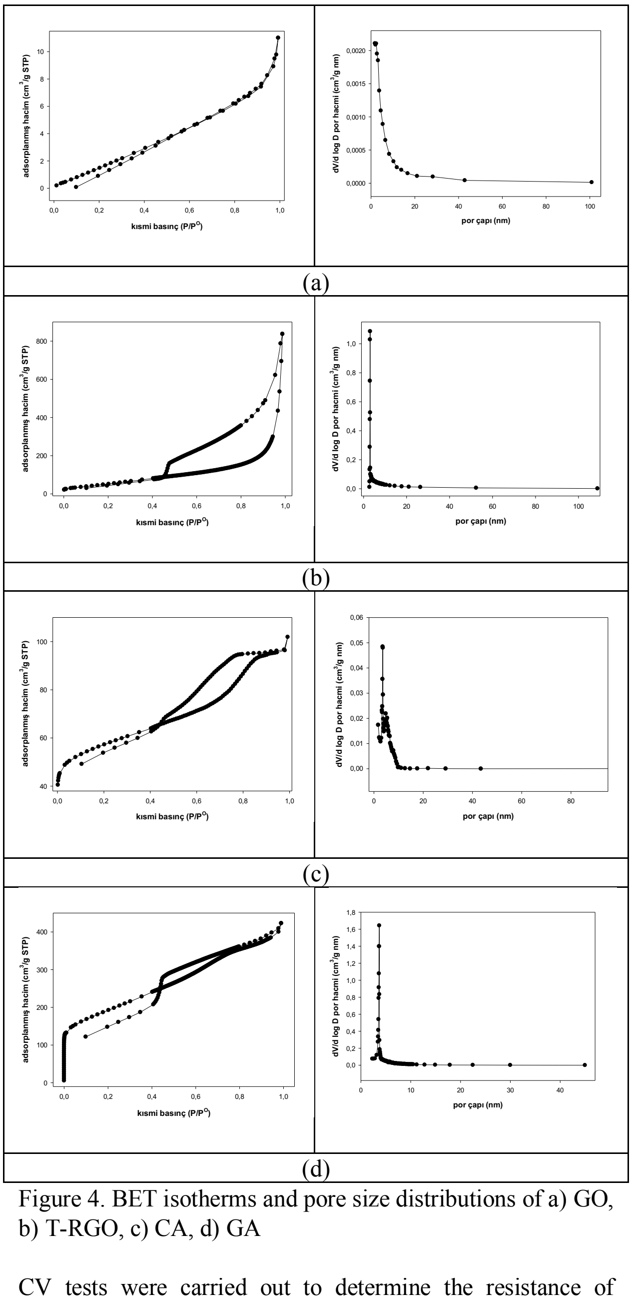
Electrochemical characterizations of the synthesized materials were made by cyclic voltammetry (CV) method, which was obtained from Pine Instrument, combined with Versastat 3 potentiostat and rotating disk electrode system. CV analyzes were performed with a standard three-electrode electrochemical cell system consisting of the working (glassy carbon; GC), reference (Ag/AgCl) and counter (Pt wire) electrodes. Experiments were performed in Perchloric acid, $HClO_4$ (0.1 M) electrolyte.

Table 1. BET analysis results of synthesized materials

Material	**BET surface area (m^2/g)**	**Average pore diameter (nm)**	**BJH pore volume (cm^3/g)**	**Average particle size (nm)**
GO	10.51	4.85	0.016	570.93
T-RGO	213.37	13.28	1.287	28.12
CA	202.86	2.91	0.108	29.58
GA	668.77	3.61	0.619	8.97

Multipoint BET surface area, BJH pore volume data of graphene support material are given in Table 1 and BJH pore size distribution values and nitrogen adsorption-desorption isotherm curves are given in Figure 4. According to the results of the BET analysis, when GO was subjected to thermal treatment, the surface area increased from 10.51 m^2/g to 213.37 m^2/g. This indicates that the carboxylic and hydroxylic structures in GO are considerably reduced during the thermal processing. The surface area of graphene aerogel synthesized by adding T-RGO to carbon aerogel increased from 202.86 m^2/g to 668.77 m^2/g.

Figure 4 shows that, according to the classification made by IUPAC, it is compatible with GO for Type III, T-RGO for Type V and aerogel for Type IV isotherms. Type III isotherm is an indicator of non-porous or macroporous solids, and this isotherm occurs in systems where the adsorbent-adsorbent interaction is very weak. Type IV and Type V isotherms are characteristic of mesoporous solids. In addition, aerogels conform to the H2 type hysteresis curve. H2-type hysteresis is a characteristic of spherical agglomerate systems, but solids giving such hysteresis do not have a well-defined pore size distribution and pore shape.



(a)

(b)

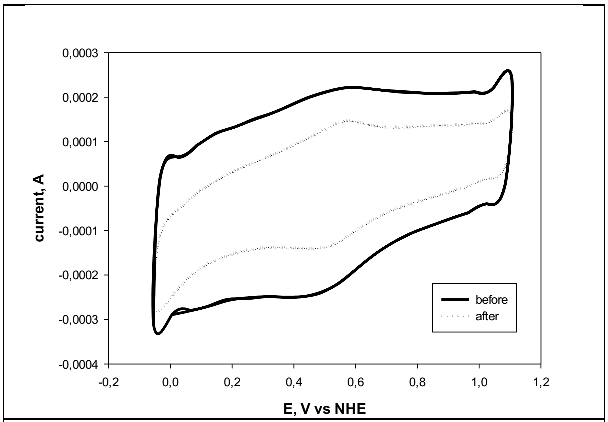
(c)

(d)

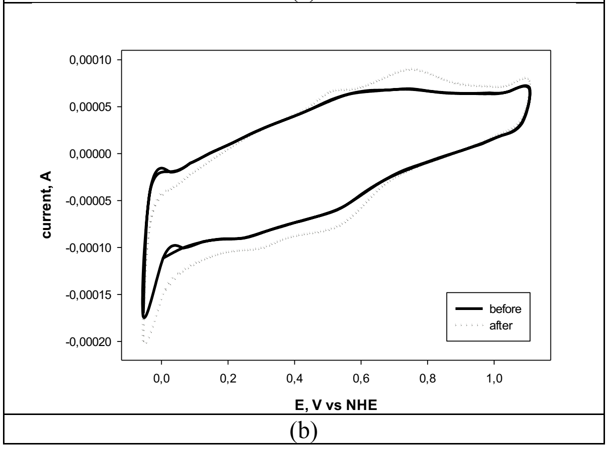
Figure 4. BET isotherms and pore size distributions of a) GO, b) T-RGO, c) CA, d) GA

CV tests were carried out to determine the resistance of synthesized T-RGO, CA and GA materials against carbon corrosion under harsh conditions. CV voltammograms of the support materials exposed to corrosion for 24 h were drawn before and after corrosion test. CV curves of T-RGO, CA and GA are given in Figure 5.

Current-voltage curves of T-RGO, CA and GAs showed that the aerogel based support materials are more resistant to corrosion. It is seen that T-RGO support material has bigger double layer capacitance than the other materials which can be attributed to its higher pore volume. It is seen that the oxidation peaks of the CA and GA supports between 0.4-0.9 V become much more pronounced after corrosion. These peaks are caused by surface oxides formed as a result of hydroquinone-quinone (HQ-Q) redox reactions occurring on the surface of the aerogel [4].



(a)



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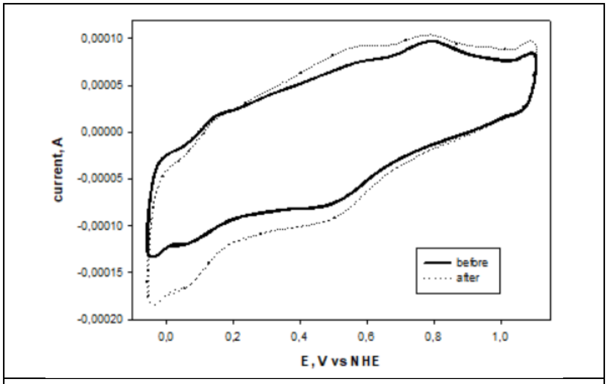

(c)

Figure 5. CV results of support materials a) T-RGO, b) CA, c) GA

Various studies are conducted to increase the performance of PEM fuel cells. In this study, thermally reduced graphene oxide, which is one of the modified graphene structures, was synthesized. Then, the GA synthesis was made by sol-gel method. A structural comparison of CA and GA has been made. The effect of T-RGO additive on aerogel was investigated physicochemically and electrochemically. Pt loading will be made to the synthesized support materials with the supercritical carbon dioxide deposition technique. PEM fuel cell tests and CV measurements of the synthesized electrocatalysts will be done. Our aim in this work is to develop support and catalyst materials for PEM fuel cells to provide better energy conversion and higher performance.

Acknowledgment

This work is supported by the Scientific Research Projects (BAP) Coordination Unit of Atatürk University with FDK-2020-8560 project number. Thank you to BAP for their support.

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Meryem Samancı received the BS degree in the Department of Chemical Engineering from Atatürk University Turkey in 2012, and MSc degree in the department of Process and Reactor Designs from Atatürk University in 2015. Since 2017, she has been continuing studies her Ph.D degree in the Department of Process and Reactor Designs at Atatürk University.

Presentating author: Meryem Samancı, e-mail:meryemsamanci@gmail.com tel: 0539 322 51 04

Enhancing the electrochemical performance of misfit calcium cobaltite electrodes for reversible solid oxide cells

Francisco J. A. Loureiro*[1], Allan M. Araújo[1,2], Laura I. V. Holz[1], Vanessa C. D. Graça[1], João P. F. Grilo[3], Daniel A. Macedo[1], Carlos A. Paskocimas[1], Duncan P. Fagg[1]

[1] Centre for Mechanical Technology and Automation – TEMA, Mechanical Engineering Department, University of Aveiro, Aveiro, 3810-193, Portugal

[2] Materials Science and Engineering Postgraduate Program – PPGCEM, Federal University of Rio Grande do Norte – UFRN, Natal, 59078-970, Brazil

[3] Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, 3810-193, Portugal

[4] Materials Science and Engineering Postgraduate Program – PPCEM, Federal University of Paraíba – UFPB, João Pessoa, 58051-900, Brazil

A growing interest in the development of Reversible Solid Oxide Cells (R-SOCs) for energy production or electrolysis has increased the demand for new electrode materials that can offer superior electrochemical performance. Calcium cobaltites have emerged as an attractive alternative, due to their excellent thermal compatibility with standard electrolytes that may privilege these compounds among state-of-the-art SOC electrodes. Nonetheless, to date, their electrochemical performances have been strongly limited by poor levels of oxygen ion transport [1]. In this work we, thus, report on a new composite electrode containing the misfit calcium cobaltite $[Ca_2CoO_{3-\delta}]_{0.62}[CoO_2]$ (C349) phase combined with $Ce_{0.8}Pr_{0.2}O_{1.9}$ (CPO). The CPO component of the composite is chosen due to being a material that offer both a high level of oxide-ion transport and a minor p-type electronic contribution [2]. A comparative study is presented between these composites and the standard, high performing, electrode material $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), in terms of their microstructure, number of depositions, and resultant electrochemical properties. Our results demonstrate that the addition of CPO to the C349 electrode can successfully lower the total polarisation resistance by over a factor of 4 (Figure 1).

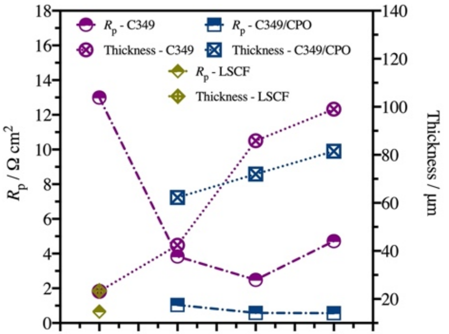

Figure 1. Evolution of R_p and thickeness of the electrode layer as a function of the number of depositions.

These electrodes are also shown to be highly sensitive to electrode microstructure; and increases in the number of depositions, beyond that of the standard LSCF electrode, can significantly expand the electrochemically active region for oxygen exchange at the gas/electrode interface, minimising losses associated with both diffusion and surface polarisations. Such tailoring permits the best C349/CPO composite electrode to attain high levels of electrochemical performance that rival the standard LSCF material. This successful result is highly relevant, as it can provide insight into the most critical optimisation factors for similar SOC electrodes that intrinsically suffer from similarly low levels of ionic transport.

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Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. Allan J. M. Araújo acknowledges the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/Brazil, reference number 200439/2019-7). João P. F. Grilo, Carlos A. Paskocimas and Daniel A. Macedo also thank CNPq/Brazil (482473/2010-0, 446126/2014-4, 308548/2014-0, 307236/2018-8, 431428/2018-2 and 309430/2019-4). Laura I. V. Holz acknowledges Fundação para a Ciência e Tecnologia (FCT) for the PhD grant PD/BDE/142837/2018. The authors also acknowledge the projects, PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020, POCI-01-0247-FEDER-039926, POCI-01-0145-FEDER-032241, UIDB/00481/2020 and UIDP/00481/2020 and CENTRO-01-0145-FEDER-022083 - Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Dr. Francisco Loureiro obtained his PhD in Engineering of Refining, Petrochemistry and Chemistry in 2019, at the University of Aveiro. He is currently working as a doctorate researcher in Centre for Mechanical Technology and Automation (TEMA) at the Department of Mechanical Engineering of the University of Aveiro. His research interest covers proton conducting ceramic oxides, solid oxide fuel/electrolytic cells.

Presenting author: Dr. Francisco Loureiro, e-mail: francisco.loureiro@ua.pt

Optimization of the flow-field for solid oxide fuel cell thin sheet interconnectors

Bora Timurkutluk [1,2] and Emre Ucar [1,2]
[1]Nigde Omer Halisdemir University, Mechanical Engineering Department, 51245, Nigde, Turkey
[2]Nigde Omer Halisdemir University Prof. Dr. T. Nejat Veziroglu Clean Energy Research Center, 51245, Nigde, Turkey

Abstract

In SOFC system, the interconnector component that ensures the homogeneous distribution of the gases and the collection of the generated current is very important. Conventional metallic interconnectors are formed by high precision machining from a thick interconnector material. In addition to this forming, high precision grinding is also required to collect the current effectively. However, these stages are not cost and time effective. In addition, interconnectors made of thick material lead to stacks with low specific (W/kg) and volumetric power density (W/m3). In our previous study, rubber pad forming was proposed to fabricate SOFC interconnectors from thin Crofer sheets with 0.2 mm thickness instead of machining of thick bulk material. Optimization of the channel geometry (i.e. channel width, channel depth and rib angle) of the interconnector, so that it can be manufactured by rubber pad forming of thin sheets succesfully, was also performed. However, this optimization was evaluated based on the formability. In this respect, the channel geometry may not be the geometry that provides the highest power density. In this study, therefore, it is aimed to optimize the channel geometry according to the power output to further improve the specific and volumetric power density of SOFC stacks with formed thin metal interconnectors.

Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device that converts the chemical energy of hydrogen or hydrocarbon fuels directly into electrical energy and useful heat at high operating temperatures (600-1000 °C). A typical SOFC consists of a membrane electrode assembly (MEA) made of anode and cathode electrodes coated on an electrolyte, current collecting plates, sealing and current collector materials such as conductive meshes and pastes. This structure is also known as single cell or short stack. On the other hand, interconnector plates or interconnectors are also needed with flow channels, allowing a homogeneous distribution of the fuel and oxidant in the stack as well as connecting the single cells electrically. Since the interconnectors operate under both reduction and oxidation atmospheres as well as at high operating temperatures, they should have the following features: high electronic conductivity, good chemical and thermal stability, gas tightness and compatible thermal expansion coefficient with MEA components. Metallic SOFC interconnectors have some superior advantages over the ceramic alternatives including high mechanical strength, high thermal and electronic conductivity, ease of fabrication and availability [1].

On the other hand, beside the high material cost, high temperature corrosion leading to formation of an oxide scale on the interconnector surface is one of the challenging issues. In this respect, there exist studies in the literature regarding cost reduction [2, 3] or corrosion-preventing coating on interconnectors [4, 5] and different metal alloys as an interconnector material [6] to improve the performance and service life of SOFC stacks. Nevertheless, the main role of SOFC interconnectors is the effective collection of the current generated and the homogeneous distribution of reactant gases. Therefore, SOFC performance can vary significantly with the interconnector design since the flow-field geometry significantly affects the reactant gases transport as well as heat and momentum transfers. For this reason, numerous studies in the literature focused on the effects of flow channel designs, flow patterns or flow configurations on SOFC performance by numerical simulations.

Among these studies, Saied et al. [7] numerically investigated the performance of the planar solid oxide fuel cell having helical, single-entry serpentine parallel, modified parallel, double-entry serpentine and triple-entry serpentine flow channels. The results indicated that the triple-entry serpentine design provides a homogenous distribution for both fuel and oxygen throughout the active surface area and as a result a high current of approximately 23.3 A is obtained from this design, which is 5.18% higher compared to other designs studied. Huang et al. [8] experimentally and numerically investigated the flow homogeneity and its effect on the planar SOFC performance having various interconnector designs. The effect of Reynolds number was also considered in the study. They reported an increase of 11.1% in the maximum power density value with a new design having guide vanes equally spaced around the feed header of the double-inlet/single-outlet flow configuration. They also stated that Reynolds number should be between 20 and 50 and between 200 and 300 for the anode and cathode side, respectively, to achieve a reasonable power density. Bhattacharya et al. [9] numerically compared the performance of anode-supported SOFCs having straight and serpentine channel geometry.

Bora Timurkutluk

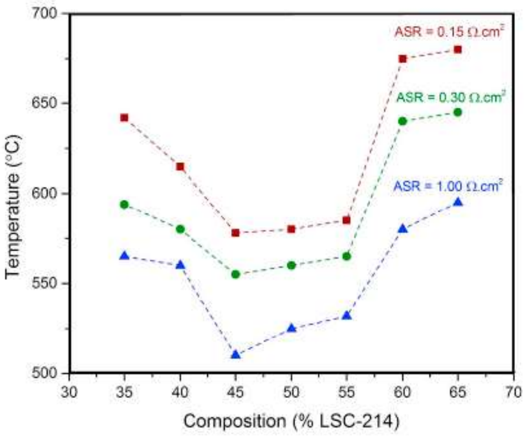
Dr. Bora Timurkutluk is Director of Prof. Dr. T. Nejat Veziroglu Clean Energy Research Center at Nigde Omer Halisdemir University, Turkey. He is also Head of Mechanical Engineering Department. His research interests focus on design, modeling, fabrication and development of solid oxide and PEM fuel cell/electrolyzer and components as well as fuel cell-based energy conversion systems.

Corresponding author: Bora Timurkutluk , e-mail: bora.timurkutluk@ohu.edu.tr tel: +90388 225 22 45

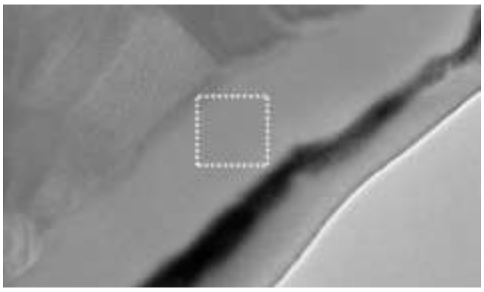
Development of polyamorphous cathodes materials for IT-SOFCs

Ramin Babazadeh Dizaj[1,2], Tayfur Öztürk [1,2]
[1] *Dept. of Metallurgical and Materials Engineering, Middle East Technical University, 06800 Ankara, Turkey*
[2] *Center for Energy Materials and Storage Devices, Middle East Technical Univerity*

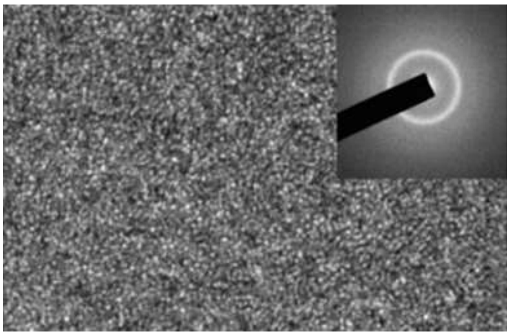
There is a considerable interest in lowering the operating temperature of solid oxide fuel cells. In this respect, (La,Sr)CoO3-(La,Sr)2CoO4 dual phase oxides have attracted much attention as cathode materials due to their enhanced oxygen reduction reaction kinetics[1,2]. Moreover there is much interest to develop these cathodes in amorphous state which not only leads to significantly improved cathode performance, but also are associated with a strong resistance to Sr segregation making them as a suitable choice for IT-SOFCs[3].



Variation of temperature where ASR= 0.15, 0.30 and 1.0 Ω cm2 with composition. Note that temperature is minimum at LSC113- 45%LSC214. (Sari et al 20018)



TEM image of a portion of symmetric cell with LSC113 -50 % LSC214 cathode. Granular region is electrolyte and dotted square shows a portion of a cathode where SAD is taken (Sari et al, 2018)



TEM image of co-sputtered cathode LSC113 -50 % LSC214. Note that in co-sputtered state the cathode is amorphous (Sari et al, 2018)

In the current study so as to further improve the stability, a third oxide was introduced into the system. Over 20 cathodes compositions, all based on (La,Sr)CoO3-(La,Sr)2CoO4-(Gd,Ce)O2 ternary system, were sputter deposited in combinatorial geometry. A target operating temperature of 550oC was selected and the full cell performances were measured in each cell so as to identify the best cathode composition. Scenarios how to best keep the amorphous structure at elevated temperatures and with prolonged use are discussed.

Acknowledgement
Financial support for this work was provided by TUBITAK with project number 217M628, which we gratefully acknowledge.

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Ramin Babazadeh Dizaj has worked on parallel robot 3D-printers and the filament materials in his bachelor's degree in Mechanical Engineering department, University of Tabriz, Iran. Then he started his master's degree in Metallurgical and Materials Engineering department of Middle East Technical University, Turkey. He is currently working on development of polyamorphous cathode for IT-SOFCs.

Presentating author: Ramin Babazadeh Dizaj, e-mail:ramin.dizaj@metu.edu.tr tel:+905526758780

Effect of Fe Alloying On The Electrochemical Performance and Long-Term Stability of Ni Thin Film Electrodes

M. Ünsal Ünver[1] and Aligül Büyükaksoy[1,2]

[1] Department of Materials Science and Engineering, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey

[2] Institute of Nanotechnology, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey

Because of the interruption and variability in renewable energy sources, interest in reversible solid oxide cells increased. A reversible solid oxide cell (RSOC) can be operated in both fuel and electrolysis mode, which converts fuels into electricity and heat in a fuel cell (SOFC) mode and reversible in electrolysis (SOEC) mode. The most common and widely used material for the fuel electrode is porous cermet consisting of Ni and YSZ (yttria stabilized zirconia). The main drawback of the Ni-YSZ electrodes is the degradation of the Ni therefore commercialization of that electrode is prevented. The main reason for this performance loss in Ni-based electrodes during long-term operation is the coarsening and migration of Nickel.

In this study, to slow down coarsening, the Ni phase is alloyed with Fe. In contrast to the literature in this research, Ni-Fe alloys were produced as thin-film electrodes via the polymeric solution method. The polymeric precursor method allows molecular level mixing and fine particle size without even at low temperatures (400 °C). Symmetrical half-cells were obtained by coating the prepared polymeric Ni-Fe alloy on a dense YSZ substrate. Long-term electrochemical performance measurements of Ni and Ni-Fe thin film electrodes for 100 hours at 800 °C performed by electrochemical impedance spectroscopy. The relationship between microstructure and stability was investigated via scanning electron microscopy analyses.

Mustafa Unsal Unver received his B.Sc and M.Sc degrees in Materials Science and Engineering from Gebze Technical University, in 2014 and in 2018 respectively. He is currently working towards his Ph.D degree. His research interests are solid oxide cells, ceramic processing, piezoelectric ceramics.

Presentating author: Mustafa Unsal Unver, e-mail: munver@gtu.edu.tr tel: +90 535 465 53 33

High Performance LSF based fuel electrodes for Solid Oxide Fuel Cells

Buse Bilbey[1], Aligül Büyükaksoy[1,2]

[1] Department of Materials Science and Engineering, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey

[2] Institute of Nanotechnology, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey

Conventionally, the choice of anode material is the Ni-YSZ composite, and these composites consist of an electrocatalyst (metallic Ni) and an oxygen ion conductor (yttria-stabilized zirconia-YSZ). The regions where gas phases also meet are called triple-phase boundaries (TPBs), and electrochemical reactions take place at the TPBs. The main disadvantage of Ni-based anodes is the coarsening of Ni and migration leading to de-wetting from the electrolyte substrate. Moreover, the interruption of the reducing atmosphere source leads to a phase change from metallic Ni to oxidized NiO, and this volume change leads to mechanical degradation. This degradation lowers or even breaks the TPBs and leads to the unstable performance of the anode.

Because of these mentioned problems, we suggest using ceramic anodes as an alternative to Ni-based anodes. In this study, we decided to use lanthanum strontium ferrite (LSF) as anode material, which is mixed ionic and electronic conducting (MIEC) perovskite-type oxide and one of the most preferred cathode choices for Solid Oxide Fuel Cells (SOFCs). In the oxidizing atmosphere, Fe valance change from +3 to +4 allows LSF to use as cathode material. Thus, Fe valances are changing from +3 to +2 in reducing the atmosphere of the LSF based electrode allows use as an alternative to Ni-based anodes via n-type character. Also, LSF based anodes could be a promising choice at the redox cycles. Moreover, LSF can use as symmetrical SOFC material.

In this present study, we aim to analyze LSF-based electrodes as SOFC anodes. The LSF-based electrodes were produced by the polymeric precursor method which, was deposited onto YSZ electrolyte pellets via the spin coating method. Even at the begging of our research, we have achieved less than 0.35 $\Omega.cm^2$ ASR anode at 800˚C in the reducing atmosphere by electrochemical impedance spectroscopy (EIS) measurements for 6LSF (La:0,6) in Figure 1. For improve performance different LSF stoichiometries and pre-heat treatment effect on the EIS analyzed. The EIS response, phase and microstructure of 8LSF (La:0,8) (Figure 2) and was investigated.

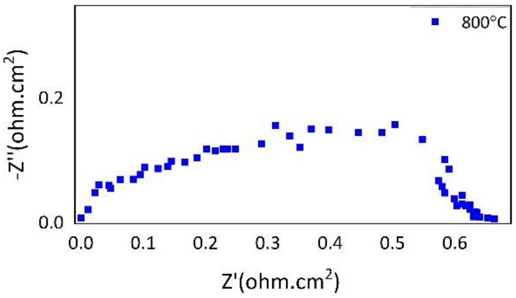

Figure 1. Electrochemical impedance spectroscopy result of 6LSF thin film at 800°C.

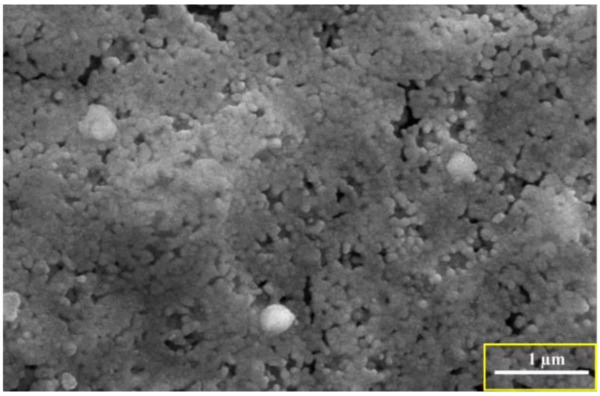

Figure 2. Microstructure analysis of 8LSF anode after exposure of %10 H_2- %90 Ar atmosphere by Scanning Electron Microscopy

Buse Bilbey obtained her M.SC degree from Materials Science and Engineering at Gebze Technical University in 2020. She is currently working towards her PhD. degree, focusing on Solid Oxide Cells at the same department.

Corresponding author: Buse Bilbey, e-mail: bbilbey@gtu.edu.tr tel: +90 535 858 70 04

Sulfonated Silica-Based Proton Conductive Hybrid Electrospun Membranes for Low Humidity Operation of PEM Fuel Cells

Naeimeh Rajabalizadeh Mojarrad[1], Ahmet Can Kırlıoğlu[1], Selmiye Alkan Gürsel [1,2] and Begüm Yarar Kaplan [2]

[1] Sabancı University, Faculty of Engineering and Natural Sciences, 34956, Istanbul, Turkey
[2] Sabancı University Nanotechnology Research and Application Center (SUNUM), 34956, Istanbul, Turkey

Novel membranes with different compositions and architectures are required for the commercialization of PEM fuel cells. Electrospinning is a versatile fabrication technique to form nanofiber composite/hybrid fuel cell membranes compared to solution-cast polymer blends. Among the other hybrid or composite membranes, silica-based membranes for PEM fuel cells have various advantages such as low cost, high water retention capacity, and relatively high ionic conductivity [1]. In this respect, hybrid membrane fabrication with organic and inorganic constituents via electrospinning technique is considered attractive due to the long-range organization of hydrophilic and hydrophobic parts in the nanoscale [2].

In this work, we combined sulfonated silica, which is cheap and stable at low humidity, with a carrier polymer via electrospinning technique to obtain mechanically strong, proton conductive, long-range ordered organic/inorganic interfaces. Thus, it is aimed to obtain high conductivity and high power output at both low and high humidity feed gas conditions by means of electrospinning and sulfonated silica.

Here, sol-gel process was used to carry out the reaction between tetraethyl orthosilicate (TEOS) and 3-(trihydroxysilyl)-1-propanesulfonic acid (or 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane). By means of this method sulfonated silica sol-gel were synthesized in a single step without further modifications. After that the prepared sol-gels were mixed with PVDF as the carrier polymer, then mixture was utilized to fabricate electrospun membranes. Firstly, the electrospinning solution and electrospinning parameters were optimized to achieve a homogeneous nanofiber network. After obtaining a nanofiber hybrid mat, it was hot-pressed and annealed into a denser mat form. Consequently, scanning electron microscopy (SEM) technique was used to analyze the nanofiber structure and morphology. The ionic conductivity, water uptake and mechanical strength of the resultant hybrid membranes were also examined. As seen in SEM micrograph, homogeneous fiber mat was obtained (**Figure 1**). Electrospun membranes showed enhanced mechanical strength and relatively high ionic conductivity at low humidity. Moreover, membrane-electrode-assemblies

(MEAs) were fabricated by using hybrid electrospun membranes and commercial catalyst sprayed electrodes, and fuel cell tests were also performed at different feed gas humidity conditions.

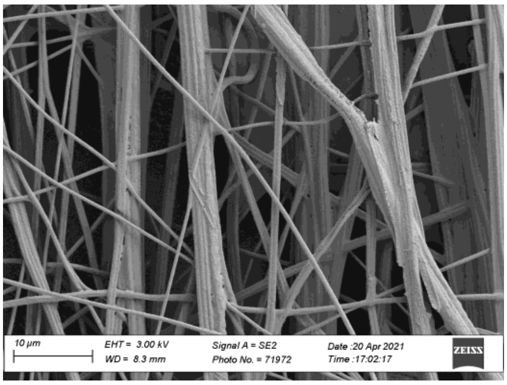

Figure 1. SEM micrograph of hybrid electrospun membranes

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Naeimeh Rajabalizadeh Mojarrad is currently PhD candidate at Sabancı University Materials Science and Nanoengineering Department. She obtained her bachelor degree at Ceramic Engineering from Tabriz University and M.Sc. in Materials Science and Nanoengineering from Sabancı University. Her research interest is membrane material for Polymer electrolyte membrane fuel cells (PEMFC)

Presentating author: Naeimeh Rajabalizadeh Mojarrad, e-mail:nrajabalizadeh@sabanciuniv.edu
tel: +90 (505) 1305942

Synthesis and characterization of carbon supported PdCu for direct glycerol fuel cells

Kübranur Agtoprak[1], Merve D. Özcan[1], Ramiz G. Akay[1], Ayşe N. Akin[1]
[1] Chemical Engineering Department, Kocaeli University, Kocaeli,4100 , Turkey

The growing amount of biodiesel produced worldwide leads to more than two million tons of glycerol entering the market yearly. Glycerol is used in the pharmaceuticals, cosmetics and food industries. However, the current production rate already surpasses the capacities needed by these industries[1]. Therefore, in this study, glycerol as a biodiesel by-product will be evaluated directly in the glycerol fuel cell. Cheap and easily found glycerol is an important alternative as a fuel. One of the most important problems in fuel cells are the performance and cost of the catalysts, which make the reaction faster. Alternatively, the use of catalysts produced from less costly metal powders will be explored within the scope of this project.

Fuel cell reactions of glycerol are as follows;

Anode reaction $C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 14H^+ + 14e^-$

Cathode reaction $14H^+ + 14e^- + (7/2)O_2 \rightarrow 7\,H_2O$

Overall reaction $C_3H_8O_3 + (7/2)O_2 \rightarrow 3CO_2 + 7H_2O$

Theoretical energy densities of some fuels and glycerol;

- Methanol: 4820 Wh/L
- Ethanol: 6280 Wh/L
- Glycerol: 6400 Wh/L
- Ethylene Glycol: 5800 Wh/L[2].

PdCu/C (PdCu 20 wt%) catalyst was synthesized via microwave assisted and conventional polyol methods. Firstly, Pd acetate and copper acetate salts were dissolved separately in ethylene glycol. Then the carbon was dissolved in ethylene glycol. The solutions were mixed separately for 30 minutes. The solution was combined in a carbon flask and pH adjusted. In the reaction medium mixed with magnetic stirrer, pH adjustment was made with 1M NaOH solution. When the desired pH setting was reached, NaBH4 was added. Then the reaction vessel was heated in a domestic Arçelik brand MD674 model microwave oven and the reaction was achieved. The reaction time was measured with a stopwatch and immediately after the reaction, the reaction vessel was removed from the microwave oven and placed in the ice bath. The catalyst aged in an ice bath for one day was placed in the filter set and filtered with the help of a vacuum pump. Subsequently, the catalyst was washed and dried at 80 °C for 18 hours.

The XRD patterns for the commercial Pd/C electrocatalyst exhibited peaks located at $2\theta = 41.1$, 46.68 and 68.24 which are characteristic of a face-centered cubic structure for Pd and correspond to their (111), (200) and (220) planes, respectively.

In additon, the XRD pattern for the PdCu/C electrocatalyst shows a shifting values, their values were $2\theta = 40.38$, 47.00 and 68.60, which correspond to its (111), (200) and (220) planes, respectively.The Pd(111) peak position of PdCu/C was slightly shifted from the peak of Pd/C, indicating the formation of PdCu alloy nanostructures.The average grain size calculated by the Debye-Scherrer equation using the (111) plane peak of the PdCu/C catalyst is 3.51 nm.

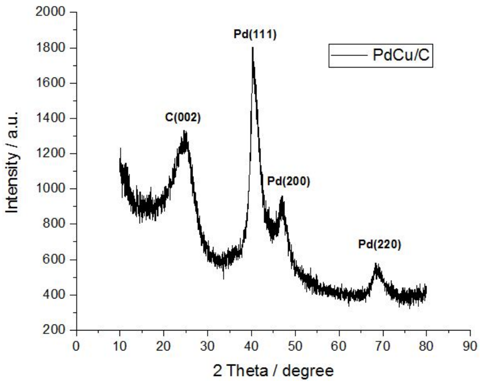

Figure 1. XRD patterns of PdCu/C catalyst.

As seen from the CV results, current densities of 14,406 mA/mg and 4,088 mA/mg were obtained for commercial PdCu/C and Pd/C, respectively.

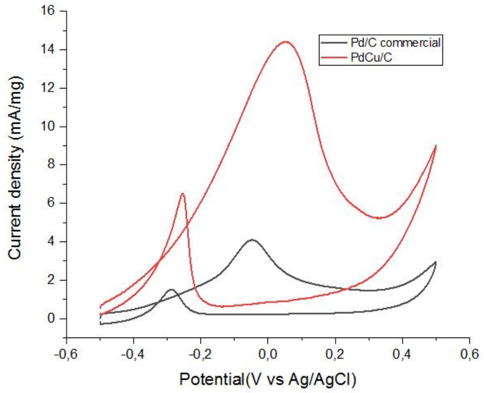

Figure 2. Cyclic voltammetry of PdCu/C and Pd/C commercial in 1 M KOH and 1 M G. Scan rate: $50mVs^{-1}$.

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Acknowledgements

The work was supported by Kocaeli University BAP which the Authors gratefully acknowledge.

MSc Kübranur Ağtoprak is with the Department of Chemical Engineering, Kocaeli University. Having graduated from Selçuk University in 2018, Chemical Engineering. Her research interests are fuel cells, electrocatalysts and nanotechnology.

Corresponding author: Kübranur Ağtoprak, e-mail: kubranuragtoprak@gmail.com tel: +90 534 012 3236

Anion Exchange Membrane Development for Direct Glycerol Fuel Cell

Ceyda Elif Meydan[1], Ramiz G. Akay [1]
[1]Chemical Engineering Departmennt, Kocaeli University, Kocaeli,4100,Turkey

Fuel cells are energy converter technologies that are thought to have a critical importance and place in a more environmentalist and efficient energy system. Problems of hydrogen production, distribution and storage have increased the interest in liquid fuel cells.Direct glycerol fuel cell can work in both acidic and alkaline media. Many types of fuel can be used, such as methanol, ethanol, formic acid, glucose, ethylene glycol, glycerol.Glycerol is a low-cost, renewable fuel with high energy density, non-toxic, non-volatile and non-flammable. Glycerol, the main by-product of biodiesel production, can be produced in large quantities at low cost[2].

Efforts have been made to develop alkaline anion exchange membrane fuel cells due to their high energy conversion efficiencies, high power density and low pollutant formation.Anion exchange membrane fuel cells have advantages over proton exchange membrane fuel cells due to their advantages such as cathode kinetics and ohmic polarization.Anion exchange membrane fuel cells must have high ionic conductivity, excellent chemical and mechanical stability throughout their lifetime.Various polymers such as poly(arylene ether ketone), polysulfone, poly (2,6-dimethyl-1,4-phenylene-oxide) have been synthesized and used as membranes in this type of fuel cells.

Polybenzimidazole (PBI) has received much attention due to its excellent thermal stability and good chemical stability.In this study, polybenzimidazole (PBI) / ionic liquid functionalized graphene oxide (IL-GO) composite AEMs were synthesized and characterized.

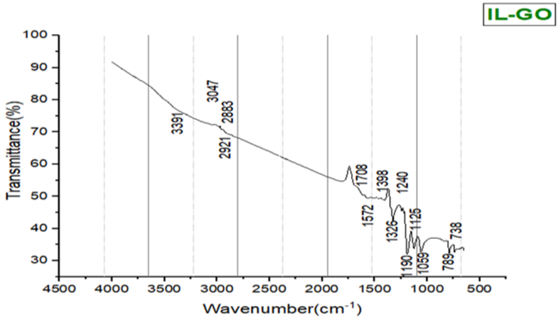

Figure 1. FTIR of ILGO.

The broad peak at 3391 cm-1 is due to the stretching vibration of the hydroxyl groups of GO in Fig.1. The 1572 cm-1 peak is caused by imidazolium groups [3].For IL-GO, several new peaks can be observed at 2981, 2833 and 1572 cm, leading to the conclusion that GO binds successfully with IL-NH_2.

Membrane	Conductivity of 1M KOH Doped Membranes (S/cm) (25°C)	Conductivity of 2M KOH Doped Membranes (S/cm) (25°C)	Conductivity of 2M KOH Doped Membranes (S/cm) (60°C)
PBI	0,008	0,026	0,091
%0,5 ILGO /PBI	0,009	0,006	0,221
%1 ILGO/PBI	0,007	0,066	0,005
%1,5 ILGO/PBI	0,007	0,005	0,005
%2 ILGO/ PBI	0,01	0,157	0,042

Figure 2. Conductivity of ILGO/PBI membrane.

The alkali resistance of the membranes is one of the important factors affecting the ion conductivity and fuel cell performance. According to the above data, it can be said that the IL-GO additive made to the membranes increases the ionic conductivity.

In general, the conductivity of AEMs should be above 10−2 S cm-1 at room temperature to meet the basic conductivity requirement of fuel cells .In addition, it has been shown in the literature that imidazolium-based ionic liquids have good alkaline stability and high conductivity [1].

In the literature, the conductivity value for KOH doped PBI at 25°C is 9.10-2 S/cm, H_2SO_4 Doped PBI is 5.10-2 S/cm, H_3PO_4 doped PBI is 2.10-2 S/cm [4].The conductivity of nanocomposite AEMs has increased with increasing temperature, resulting in faster migration of ions and higher diffusion at higher temperature.

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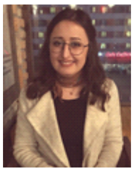

Ceyda Elif Meydan is a master student at Kocaeli University, Department of Chemical Engineering. She focused on membrane development for liquid fuel cells in her master's thesis.

Presentating author:Ceyda Elif Meydan e-mail:ceydameydan4141@gmail.com tel:05397689786

CATALYST AND ACTIVE MATERIAL SYNTESIS

How to increase the catalytic efficacy of platinum-based nanocatalysts for hydrogen generation from the hydrolysis of ammonia borane

Saim Özkar

Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey.

Hydrolysis is the best way of releasing H_2 from ammonia borane (AB) in the presence of catalysts (Equation 1).[1]

$$H_3NBH_3(aq) + 2H_2O(l) \rightarrow NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \qquad (1)$$

Significant achievements have been obtained in increasing the rate of releasing H_2 from AB by employing transition metal nanoparticles (NPs) as catalysts.[2,3,4] Pt is one of the most active transition metals providing high turnover frequency (TOF) for hydrogen generation from the hydrolysis of AB. However, the high price of this precious metal hampers its large-scale applications in catalyzing the hydrolysis of AB. Achieving high catalytic performance with the smallest amount of metal is critical for any catalytic applications of noble metals. While continuous efforts have been devoted to improve the catalytic activity of non-noble metals, an immense challenge in the field is the enhancement of utilization efficiency and catalytic performance, and thus ultimately lowering the cost of noble metal catalysts. For example, reducing the particle size of Pt catalysts to nanoregime increases their surface area and thus, the number of active sites for catalysis.[5] However, colloidal metal NPs are unstable and tend to aggregate to larger particles, which greatly hampers their recyclability and catalytic performance.[6] A proper way of overcoming this problem is the immobilization of Pt NPs on a support with large surface area, such as oxides, carbonaceous materials, metal-organic frameworks. The catalytic activity and stability of supported Pt NPs depend on the particle size and size distribution, surface area of support, and strength of metal-support interaction. Selecting suitable supports is of paramount importance in obtaining NPs which are stable and still catalytically active. Using the supporting materials with large surface area certainly helps to increase the catalytic activity of Pt NPs. The strength of platinum-support interaction turns to be crucial for catalytic activity and stability of NPs on the support surface. Although no mathematical correlation between the catalytic activity and the strength of metal-support interaction could be obtained yet, almost all the highly active Pt catalysts have high Pt 4f binding energy as determined by XPS analysis. Increasing the lifetime and reusability of nanocatalysts can certainly help to improve the atom efficiency of Pt catalysts. Lifetime is used as a measure of stability which correlates well to the strength of metal-support interaction relative to metal-metal bond while reusability is mainly determined by the isolability of nanocatalysts for subsequent runs. At this point it would help to differentiate the recyclability and reusability of nanocatalysts in the present case of hydrolysis. A recyclability test is performed by adding a new batch of AB to the reactor, when the hydrolysis is complete, for the subsequent cycle of hydrolysis without isolating the catalyst or removing the reaction solution from the reactor. Actually, it would not make any difference whether the whole amount of AB is added at once in the commencement or portion wise in the successive cycles. It is noteworthy that the recyclability test can serve to measure the lifetime of catalyst when performed by adding sufficient amount of AB until the cease of H_2 generation.[7] Thus, recyclability measures the durability of catalysts. On the contrary, reusability test is performed by isolating the catalyst from reaction solution after completion of hydrolysis in the first run and re-dispersing in a new batch of AB for the subsequent run, whereby the retaining activity of catalyst is measured.[8] In other words, reusability test serves in measuring the stability of catalysts, which is an important parameter to be considered in large scale industrial application. Low reusability is largely caused by material loss during the isolation of catalyst from solution and re-dispersing in a new reaction solution for the succeeding run of catalytic reaction.[9]

A short prelude on the mechanism of catalytic hydrolysis of AB will give insight to understand and appreciate the reported achievements in enhancing the catalytic performance of Pt based catalysts in hydrolysis of AB: The activation of AB molecule on the surface of metal NPs proceeds in the form of dissociative adsorption through interaction between the metal and hydridic hydrogens of borane moiety and the resultant -BH_2 species promotes the dissociation of H_2O which has been suggested to be the rate-determining step in the transition metal catalyzed hydrolysis of AB.[10,11,12] This is followed by the formation and desorption of H_2 molecule from the nanoparticle surface and the -$BH_2(OH)$ species continues with further hydrolysis.

The progresses in developing highly efficient platinum(0) nanocatalysts which have been reported to be active catalysts in H_2 generation from the hydrolysis of AB will be discussed along with the available parameters including temperature, particle size, surface area of the catalyst or support, the catalyst to substrate ratio used in the catalysis, Arrhenius activation energy obtained for the catalytic hydrolysis, TOF, and the XPS determined Pt 4f binding energy.

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Photoelectrochemical Water Oxidation using $BiVO_4$ Photoanodes

Sarp Kaya[1,2]
[1] Department of Chemistry, Koç University, 34450 Istanbul, Turkey
[2] Koç University Tüpraş Energy Center (KUTEM), 34450 Istanbul, Turkey

Photoelectrochemical (PEC) water splitting is an ultimate strategy to convert the energy of the Sun to the energy stored in the chemical bonds of molecular hydrogen and oxygen. Photoelectrodes made of earth-abundant elements have poor surface catalytic activity thus catalysts are commonly incorporated onto their surfaces to boost the activities.

$BiVO_4$ is one of few promising oxide semiconductor light-absorbing materials for use as a photoanode in the oxygen evolution side of the water-splitting PECs. The typical efficiencies of unmodified $BiVO_4$ photoanodes for water oxidation are not impressive as they suffer from excessive electron-hole recombination and poor charge transport that is correlated to the bulk and surface defect densities. Therefore, strategies such as morphology control, doping, and pairing with oxygen evolution catalysts to alleviate one or more of these limitations have been developed. PEC turnovers are dramatically enhanced by the incorporation of co-catalysts. There are several catalysts shown to be rather effective in the water oxidation reaction, however, there is an ongoing debate about the origin of the enhancement in the activity. It has been argued that catalysts decrease the recombination rate of the charge carriers at the photoanode surfaces without being truly involved in the oxidation reaction. Their involvement in charge transport and utilization depends on the catalyst amount and active phase.

In this talk, the viable strategies to enhance the surface activities of $BiVO_4$ photoanodes will be presented. In addition to facile recombination dynamics of the charge carriers both in bulk and in the surface region, electron trapping at the interface under illumination significantly hampers the water oxidation kinetics. Surface modification and doping as well as co-catalyst incorporation have a significant impact on the elimination of the electron trapping process and facilitates charge transport. The effects of nitrogen doping [1], oxygen vacancies [2], cobalt doping, and $Co(OH)_2$ catalyst incorporation [3] on the charge transfer kinetics will be discussed.

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Sarp Kaya received his PhD in Physical Chemistry in 2007 after completing his studies on ultrathin metal oxide layers at Fritz Haber Institute of the Max Plank Society and Humboldt University. During his post-doctoral studies at Stanford University (2007-2010) and following research activities as a scientist at SLAC National Accelerator Laboratory (2010-2014) and Joint Center of Artificial Photosynthesis (JCAP) (2011-2014) he heavily utilized synchrotron radiation for investigations on gas-solid and liquid-solid interfaces. He has joined the Department of Chemistry, Koç University in 2013. He has also been co-director of Koç University Tüpraş Energy Center (KUTEM) since 2019.

Presentating author: Sarp Kaya, e-mail: sarpkaya@ku.edu.tr tel: +90 (212) 338 1378

How A-site doping strategy influences the OER activity on La-based parent perovskite oxides through oxidation state and lattice distortion

Tuncay Erdil[1], Mustafa Doguhan Oguz [1], Ersu Lokcu[3] and Cigdem Toparli [1,2]
[1]Middle East Technical University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Ankara, Turkey
[2] ENDAM, Center for Energy Materials and Storage Devices, Middle East Technical University, Ankara, Turkey
[3] Eskisehir Osmangazi University, Department of Metallurgical and Materials Engineering, Eskisehir, Turkey

Climate change has stimulated great interest in developing clean and renewable solutions for energy conversion and storage[1]. Emerging technologies for solutions, like unitized regenerative fuel cells, metal-air batteries, and water electrolyzers, depend on the reliable catalyst materials suited for long term application in alkaline environments. In particular, the demanding reaction in these systems is the oxygen evolution reaction involving complex multielectron/proton transfer processes and thus sluggish kinetic. At present, the state-of-the-art OER catalysts are IrO_2 and RuO_2. However, the high cost and scarcity of these materials severely prevent the wide-scale application of these systems. Perovskite oxide (e.g., single perovskite expressed as ABO_3) electrocatalysts are particularly considered next-generation OER catalysts due to their adjustable physicochemical properties and, as a consequence, their catalytic properties by substitution of ions in the A and B sites. Perovskite oxide materials offer great potential to improve the efficiency of metal-air batteries, fuel cells, and water electrolyzer due to their unique 3d electronic structures and structure flexibility[2,3]. Recently, surface self-reconstruction of perovskite oxides during OER has been shown via in situ and operando spectroscopic techniques. To approach this problem, management of A-site element and altering the tolerance factor of perovskite oxide has been offered [4,5]. Yet, the understanding on A-site influence on the structural stability and establishing the dynamic correlation between structure and activity are still missing. Thus, it is highly desirable to develop the A-site design strategies to reveal the coherent structure-activity correlation in the OER process. In this context, double perovskite La_2CoMnO_6 would be potentially active for OER and pave the way for A-site doping strategy. This study systematically investigates the influence of A-site doping on the OER activity of La_2CoMnO_6 (LCM) parent perovskite oxide catalysts. Here, we performed the sol-gel-derived polymeric citrate gel method to fabricate the perovskite oxide catalysts. X-ray diffraction (XRD) was used to examine the crystal structure of the A-LCM (A-site doped LCM) powders. The elemental concentration of A-LCM was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

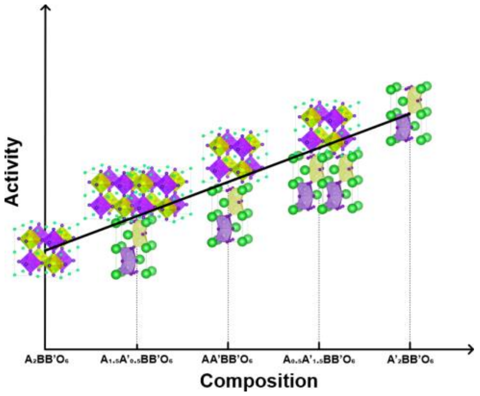

Figure 1: A-site dependent crystal structure management and thus activity. Hexagonal Ba_2CoMnO_6 shows the highest activity.

X-ray photoelectron spectroscopy (XPS) was applied to study the valance state of the oxides. Finally, electrochemical tests were performed using a rotating disk electrode (RDE) in alkaline media. The results show that both lattice parameters and valance states of the B-site oxides have immense influence on the OER the catalytic activity of A-LCM.

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Tuncay Erdil completed his bachelor's degree from Middle East Technical University at the Metallurgical and Materials Engineering Department. He is currently a master's student in the same department and working on developing bifunctional oxygen electrocatalysts in the Electrochemical Energy Materials Laboratory. Presentating author: Tuncay Erdil, e-mail:erdil.tuncay@metu.edu.tr

Effect of lateritic Ni ores on the crystal structure and electrochemical properties of NMC cathodes

Semih Engün[1,2], K. Burak Dermenci[1] and Servet Turan[1]
[1]Dept. of Materials Science and Engineering, Eskisehir Technical University, 26555, Eskisehir, TURKEY
[2]Dept. of Metallurgical and Materials Engineering, Zonguldak Bulent Ecevit University, Zonguldak, 67100, TURKEY

Mixed hydroxide precipitate (MHP) is an intermediate product of lateritic ores, which is considerably found in Turkey's western part. MHP includes a significant amount of Ni, Mn and Co elements as well as Mg. On the other hand, some impurities into the MHP such as Mg [1], Zn [2], Si [3], Ca [4], Cr, Al and Fe [5,6] and Cu [7] have already been used for a doping purpose of ($LiNi_xMn_yCo_{1-x-y}$) (NMC) cathodes which became popular thanks to their high energy density for Li-ion batteries. When most of these impurity elements improve the electrochemical properties of NMC by enhancing structural stability and Li-ion diffusion, some of them can worsen. In this regard, a trade-off needs to be considered in deciding the appropriate MHP amount to improve the electrochemical performance of NMC cathodes. Moreover, the direct usage of the by-product consisting of Nickel-based raw material will provide environmental and economic benefits by eliminating the hydrometallurgical purifying step.

This study discussed the potential use of intermediate MHP product as an alternative Ni and Co source and a multielement substitution element in NMC cathodes. NMC111 and NMC622 cathodes were synthesized by solid-state and pechini methods. Solid-state synthesis carried out by oxide and hydroxide/carbonate-based precursors with stoichiometric amount MHP. On the other hand, the pechini process was carried out using nitrate-based precursors with a stoichiometric amount of MHP. For each synthesis procedure, different amounts of MHP were added to the precursors between 2 % wt and 20 % wt. The synthesis flowchart of the study was given in Figure 1.

X-ray powder diffraction (XRD) was performed to determine the crystal structure of powders. The morphology of powders was assessed by scanning electron microscope (SEM). Galvanostatic charge-discharge was performed to discuss the electrochemical performance of the cathodes. The CR2032 type coin cells were cycled at 0.1C rate (1C=271 $mAhg^{-1}$) between the 2.75-4.25 V vs. Li/Li^+ potential range. The Gibbs Free Energy and Enthalpy calculations of synthesized NMC powders with oxide and hydroxide/carbonate precursors were performed. The thermodynamic software (HSC) was used to calculate the thermodynamic data up to calcination temperature.

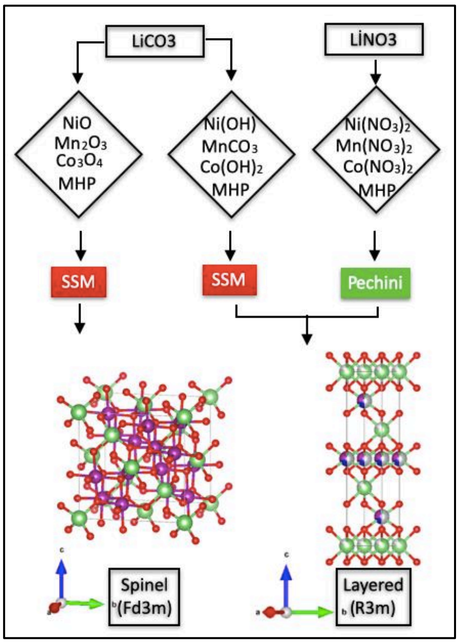

Figure 1. Synthesis flowchart of NMC cathodes with different precursors.

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Acknowledgments

The authors acknowledge support from the Eskişehir Technical University Scientific Research Projects Unit with the grant number 1803F057.

Semih Engün is a Research Assistant of Metallurgical and Materials Engineering at the Zonguldak Bülent Ecevit University. He received B.Sc. in 2012 and M.Sc in 2016 in the Department of Materials Science and Engineering from Anadolu University in Eskisehir. He is a PhD candidate in the Department of Materials Science and Engineering at Eskisehir Technical University. His research interests include Lithium-ion batteries, solid-state batteries and electron backscattered diffraction (EBSD) techniques.

Corresponding author: Semih Engün, e-mail: semihengun@beun.edu.tr tel: +90 372 291 19 73.

Replacement of Cobalt with Copper in NCA Cathode Materials

Ozgul KELES[1], Dila SİVLİN[1]

Department of Metallurgy and Materials Engineering, Istanbul Technical University, Ayazaga Campus, 34469 Istanbul, Turkey

Car producers are investing electric vehicle production to reduce carbondioxide emission [1]. To outperform gasoline cars, the electric vehicles must have powerful batteries. Even though many battery type is avalible, lithium-ion batteries are the most suitable ones for the electric vehicles. As any other battery types, lithium-ion batteries consists of anode, cathode, electrolyte and separator [2]. Among them, cathode materials are the crucial component, because they hugely affect the battery performance [3]. So far, $LiNi_{0.8}Co_{0.15}A_{0.05}O_2$ (NCA) cathodes are preffered due to their high power and safety. However, NCA cathodes -so that electric vehicles- are under attack due to cobalt which is a toxic material. Cobalt content and electric vehicle production for reducing carbondioxide emission cause a contradiction both in science and in industry.

Each element provides a specific property to NCA. Nickel is responsible for capacity, cobalt prevents diffusion of nickel to the lithium layers and aluminum reduces oxygen release and increases safety [4,5,6]. To eliminate cobalt, it should be understood its role and the mechanism of the problems that caused by cobalt.

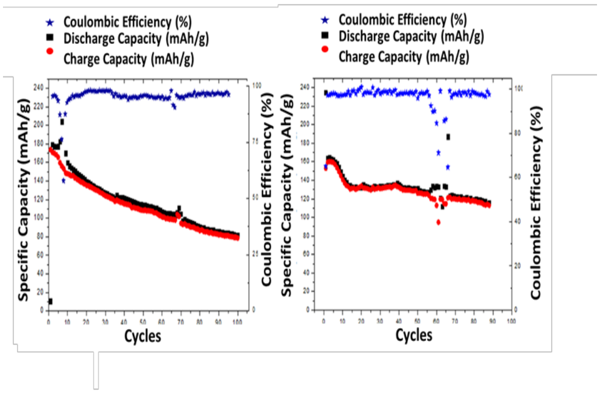

Figure 1. Electochemical performances of the cathodes

Alternative stochiometries are investigated to reduce cobalt content as much as possible [7]. Yet in these stoichiometries, crystal stability is detrimentally affected and eventually electrochemical performance becomes inadequate for high energy application. In this study, we used copper as an alternative and NCuA cathodes were produced by coprecipitation method. Also, NCA cathode materials are produced to compare these two cathodes. Depending on the doped material pH value in the experiments are varied. Metal solution molarity, NaOH molarity, temperature, stirring rate parameters kept constant during the experiment. After the experiments, precipitates are filtered and washed with distilled water several times. The precipitates are dried at 120°C, 12 hours and then two step heat treatment was applied. XRD analysis is used to investigate the crystal structure, SEM analyse is used to investigate the morphology.

Fig.1 shows the electrochemical performance of the cathodes. First discharge capacities of the cathodes are found to be 173.78 mah/g for NCA and 151.75 mah/g for NCuA cathodes. Capacity retentions of the samples are found to be 80.66% and 57.21% for NCuA and NCA cathodes, respectively. Even though the first discharge capacity of NCuA cathode is lower than the NCA capacity retention of NCuA is better than the NCA cathode. The main reason of NCuA having lower capacity could be related with the valance state of the Ni. If Ni exists in 3+ state, than only one electron is sacrificed for capacity as a result lower capacity is obtained.

Also, it could be said that NCuA has more stabile crystal structure. As it can be understood by the XRD analysis, NCuA has higher I003/I104 ratio and lower R value which shows that it has good crystal stability. Due to NCuA having more stabile and strong crystal structure, it has better capacity retention after one hundred cycles. It endured lithium intercalation/ deintercalation better than the NCA cathodes.

This study shows that Cu replacement in NCA cathode structure can be considered as an alternative cathode material. We believe that with a more detailed and focus study, NCuA cathodes become a challenger for NCA cathodes and open a path for commercialization of more eco-friendly electric vehicles.

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Synthesis of NMC Cathode Active Material from Battery Grade Metal Sulphates Obtained from MHP (Mixed Nickel-Cobalt-Manganese Hydroxide Precipitate)

Şerif Kaya

R&D Department META NİKEL KOBALT MADENCİLİK SAN. VE TİC. A.Ş. Manisa/Türkiye

In this work, battery grade nickel, cobalt and manganese sulphates were obtained from MHP (Mixed Nickel-Cobalt-Manganese Hydroxide Precipitate) via hydrometallurgical techniques namely leaching, precipitation, solvent extraction and ion exchange. After obtaining the battery grade refined metal sulphates, NMC-622 type precursor material was synthesized via co-precipitation method. The obtained precursor was lithiated with commercial grade lithium carbonate. The lithiation parameters were determined as pre-calcination at 450 ˚C for 6 hours and calcination at 820 ˚C for 15 hours in order to obtain the cathode active material. The lithiated cathode active material was then coated onto Al current collector and the electrochemical performance of the cathode active material was investigated as a half cell relative to the Li anode in button cell size. Half-cell electrochemical characterization test results showed that 181 mAh/g capacity was obtained within the first two formation cycles which was conducted at 0.1 C. After the first two formation cycles, 170 mAh/g capacity was obtained at 0.5 C. The electrochemical experiments were conducted between 2.8 V - 4.3 V charge and discharge potential, respectively. The charge and discharge currents were determined according to the reference capacity given in the literature as 170 mAh/g for NMC-622 chemistry. Finally, %93 capacity retention was obtained after 50 charge and discharge cycles.

Recovery of Li,Ni,Co and Mn From Spent Lithium-ion Batteries

Fırat Tekmanlı[1,2], M. Kadri Aydınol [1,2]
[1]Dept. of Metallurgical and Materials Engineering, Middle East Technical University, 06800, Ankara, Turkey
[2]Center for Energy Materials and Storage Devices, Middle East Technical University, 06800, Ankara, Turkey

Recycling of spent lithium-ion batteries has attracted wide attention because of their high content of valuable and hazardous metals. One of the difficulties for effective metal recovery is the separation of different metals from the solution after leaching. In my research, a full hydrometallurgical process is being developed to selectively recover valuable metals (Ni, Co, Li and Mn) from cathode scrap of spent lithium ion batteries.

Currently, pyrometallurgical and hydrometallurgical processes are the main technologies for recycling metals from spent LiBs and other waste streams. A typical pyrometallurgy process involves high temperature burning of organic materials, reduction and smelting of metal/oxides, refining and separation of cobalt after leaching. Lithium is lost in slag because of its high reactivity and it will be pretty much difficult to be recovered. Hydrometallurgical method is recently considered as a favoured technology for spent LiBs recycling as the recovery process and also it is expected to be shortened with more controllable environmental impact than a pyrometallurgical process has.

The leaching experiments were performed while charging a known amount of cathode scrap powder in the known amount of leaching reagents. Effect of leaching reagents composition, stirring speed, pulp density, leaching time and temperature during the leaching was examined. The slurry was taken for analysis, at selected time intervals. After leaching, the slurry was filtered and washed, then the residue was dried overnight. The residue and pregnant leach solution are analyzed with ICP-OES, ICP-MS and C,S devices. Also XRD analysis of scraps were conducted both pre-leach and after-leach stages.

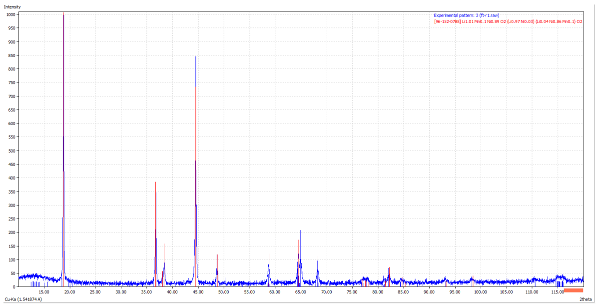

Figure 1. XRD pattern of cathode scrap powders.

The X-ray diffraction of the cathode scrap powder (Fig. 1) shows that Li(Ni,Co,Mn)O2 is identified as the major phase. First of all, battery pack is teared apart and dismantled to seperate anode-cathode-seperator. Then carefully the cathode is removed after conducting multimeter test to ensure there was no any potential left in the battery. Aluminum foils are getting used to be current collector at cathodes. This foil was going to be removed first. For this reason basic reagents were used and their concentrations are studied.

After removing aluminum from cathode, acid leach was conducted. Valuable metals are dissolved in a certain and studied amount of acid. Then selectively all these metals were tried to be precipitated in a simultaneous way.

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Mr. Fırat Tekmanlı received his bachelor's degree from Department of Metallurgical and Materials Engineering in Middle East Technical University in 2020. He is currently master student in the Department of Metallurgical and Materials Engineering, Middle East Technical University. His research areas mainly focus on recycle of lithium-ion batteries and production of cathodes for NMC lithium-ion batteries.

Presentating author: Fırat Tekmanlı, e-mail: firat.tekmanli@metu.edu.tr tel: +90 553 257 53 15

Effect of carbon support type on anode electrocatalyst for EOR performance

Emine Sena Kazan[1], Mahmut Bayramoğlu [1], Canan Arslan [1]

[1]Dept. of Chemical Engineering, Gebze Technical University, Kocaeli, Turkey

Abstract

Ethanol electrooxidation reaction (EOR) has great importance since the fully completed EOR provides a considerable amount of energy. In order to achieve this goal, various types of anode electrocatalysts are studied in the literature. Carbon supports are widely used to increase the catalytic activity and catalytic surface area of a catalyst. This study was conducted to compare the effect of two different carbon support materials (carbon black and graphite) on the same non-noble metal-based anode electrocatalyst for EOR in alkaline media. Physicochemical characterizations of the catalysts were investigated via XRD, SEM, and TEM analysis. Electrocatalytic performances of the catalysts were investigated via cyclic voltammetry (CV) and Linear Sweep Voltammetry (LSV). The stabilities of the catalysts were investigated by the chronoamperometry (CA) technique.

1.Introduction

Fuel cells are one of the most significant alternative energy generation systems since they allow to use various kinds of fuels such as, hydrocarbons, hydrogen, methanol, ethanol and etc. Among them ethanol has a great importance since it has a very high theoretical energy density. Moreover, it is a carbon-neutral, non-toxic, economical fuel and can be produced, transported and, stored so easily. Ethanol must be electrooxidized to provide energy and in order to achieve this goal, there must be a suitable electrocatalyst [1-2].

Direct Ethanol Fuel Cells (DEFCs) are used for generating electrical energy from ethanol. This system can be operated in both acidic and alkaline environment however, studies showed that the kinetics of ethanol electrooxidation reaction (EOR) in alkaline media is faster than acidic media. Therefore, studies are started to focus on Alkaline Direct Ethanol Fuel Cells (ADEFCs). Alkaline media allows to the system to use non-noble metal based anode electrocatalysts for EOR. Unlike noble metal based anode electrocatalysts, non-noble metal based anode electrocatalysts are cheaper, have more resistance to catalytic poisioning, more available and show a good performance as a noble metal based anode electrocatalyst [3].

Support materials increase the catalytic activity and the surface area of the catalysts. Chosing a proper support material is vital for EOR since it effects the measured current density and stability. In literature, carbon based support materials are widely used. Among them, Vulcan is a well-known support material and it is known that it increases catalytic activity of noble metal based anode electrocatalysts.

In this study, two different carbon based catalyst support materials were used to prepare Ni-Mo_2C anode electrocatalyst. The electrocatalytic performances of the electrocatalysts were investigated and compared in alkaline media.

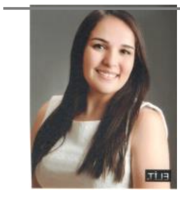
2. Experimental

$NiCl_2.6H_2O$ (Sigma Aldrich), Mo_2C (-325 mesh, 99.5% Aldrich), Hydrazine Hydrate (64-65%, Sigma Aldrich), Vulcan XC- 72 (Cabott Corporation), Graphite, Ethylene glycol (Merck), NaOH (Sigma Aldrich), ethanol (Merck). All the chemicals were used as received without further purifications.

The preparation of the Ni-Mo_2C/C and Ni-Mo_2C/G is inspired by the Ref. [4]. The Ni-Mo_2C/C (or Ni-Mo_2C/G) catalysts were synthesized as follows: 5 ml of 0.1M $NiCl_2.6H_2O$ in Ethylene Glycol (EG) and 3 mL of pure EG were taken and mixed with the specified amounts of Vulcan XC72 (or graphite) and Mo_2C. Then, the temperature was brought to 120 ºC. Next, 0.5 mL hydrazine hydrate was added. After, 1.5 mL 0.5 M NaOH (in EG) solution was added and stirred for 20 minutes. Finally, it was cooled to the room temperature, diluted with ethanol, filtered, washed with distilled water, and dried. The amount of the Ni, Mo_2C and carbon support were decided according to preliminary tests. Accordingly, the carbon support amount is %30 by weight. The Ni amount is %75 by weight.

Physical characterization of the catalysts were made by XRD, SEM (XL-30 SFEG, Philips, Eindhoven, Holland) and, TEM (Hitachi-HT7700) analysis. The XRD analyses were performed with Bruker D8 Advance device (40Kw, 40mA), with a Cu Kα radiation over a 2θ range from 2° - 90° and with 3° min^{-1} scanning rate.

Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), and Chronoamperometry (CA) experiments were performed with using VersaSTAT3 Potentiostat/Galvanostat (Princeton Applied Research). Electrochemical characterizations of the catalysts were performed by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and, chronoamperometry (CA). For all the electrochemical characterization experiments, a Pt wire was used as the counter electrode, Ag/AgCl was used as the reference electrode and, Glassy Carbon Electrode was used as working electrode (WE). The diameter of the GCE used in this study was 3 mm (CHI Instruments).



Emine Sena Kazan completed her undergraduate education in Chemical Engineering Department of Istanbul University in 2016. Then, she started working as a research assistant at Gebze Technical University afterwards, completed her master's degree and then started her doctorate education and is still continuing.

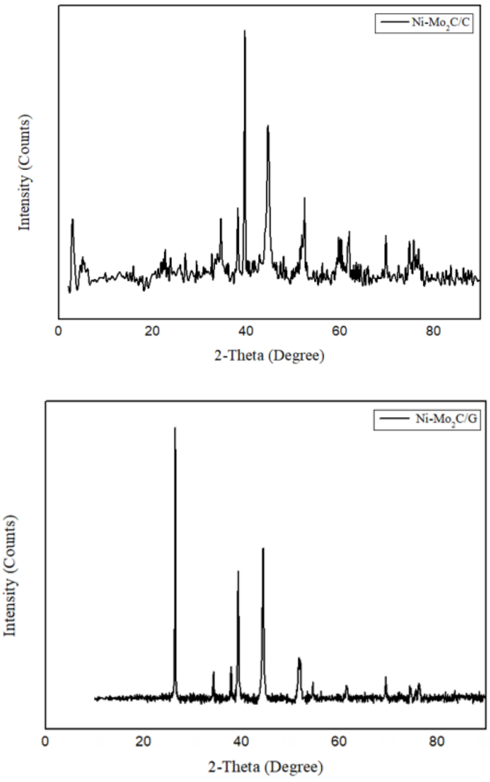
Corresponding author: Emine Sena Kazan, e-mail: eskazan@gtu.edu.tr tel: 0262 605 2140

Emine Sena Kazan

3. Results and Discussion

3.1. Physical Characterization

XRD diffractograms of the synthesized compounds are given in Fig. 1, it was seen that the peaks observed at 2θ = 44.32, 51.74, 76.95 can be attributed to the surfaces of nickel 111, 200, and 220. [5]. The diffraction peaks at 2 θ = 34.39, 38.00, 39.44, 52.13, 61.57, 69.57, 74.68, 75.57 in Fig. 1 are attributed to the (100), (002), (101), (102), (110), (103), (112) and (201) crystal planes of Mo_2C [6]. Lastly, the diffraction peaks at 2θ = 24.341, 46.540 show the surfaces of (200) and (10) of Vulcan XC 72 and, the peak at 2θ = 26.46, 54.87 show the surfaces of (002) and (004) of graphite.



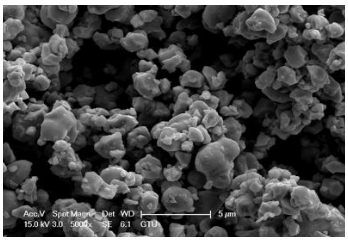
a)

b)

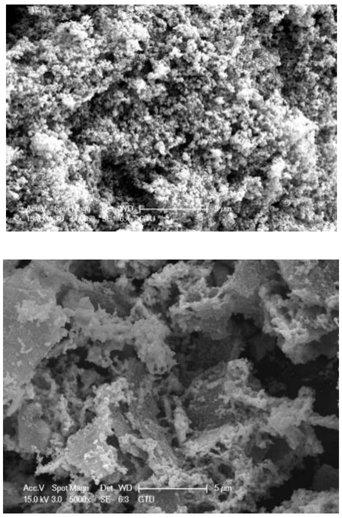
Fig. 1. XRD results of a) Ni-Mo_2C/C, b) Ni-Mo_2C/G.

As seen, the nickel peaks are highly apparent thus, it shows that the nickel salt is very well reduced to elemental nickel. Moreover, there are not any additional peaks observed on Ni-Mo_2C/C and Ni-Mo_2C/G catalysts which shows that there are no other nickel species (such as nickel oxide or nickel hydroxide) in the catalysts.

SEM analysis results of the synthesized catalysts are given in Fig. 2. Fig. 2a shows that the surface structure of Mo_2C. The surface structure of Ni-Mo_2C/C and Ni-Mo_2C/G dramatically changed with the addition of Mo_2C. As seen, spherical shaped Mo_2C nanoparticles are well and intensely disturbed on the surface of Ni particles.



a)



b)

c)

Fig. 2. SEM analysis results of a) Mo_2C, b) Ni-Mo_2C/C and, Ni-Mo_2C/G.

3.2. Electrochemical Characterization

CV experiments were conducted in both 0.1M NaOH solution and 0.05M NaOH + 0.5M Ethanol at 0.01 V s-1 scan rate. In 0.1M NaOH solution, the catalysts form NiOOH species which has a high degree of electrocatalytic activity. Then EOR was performed in 0.05M NaOH + 0.5M Ethanol solution.

Fig. 3a shows the voltammograms of Ni-Mo_2C/C and Ni-Mo_2C/G in 0.1 M NaOH solution and Fig. 3b shows the voltammograms of the catalysts in 0.05M NaOH+0.5M Ethanol at 0.01 Vs^{-1} scan rate. The oxidative and reductive peaks of the catalysts seem similar however observed that the peaks in both samples are similar however their intensities are different. Comparing to Vulcan XC 72, graphite has increased the catalytic activity slightly more. The $Ni(OH)_2$/ NiOOH transformation can be observed from the peaks between 0.65-0.7 V in Fig 3b [4]. The transformation of $Ni(OH)_2$ to NiOOH starts and reaches its maximum at a potential value around 0.7 V, because of the oxidation process of ethanol [6, 7].

As known, a better catalyst is generally characterized by a more negative onset potential and higher current density therefore, onset potential is an important parameter [8]. The onset potentials and the maximum current densities of the catalysts are shown in Table 1. Fig. 3b indicates that the both catalysts have similar onset potentials however, Ni-Mo_2C/G showed higher current density with a slighter positive shift at the onset potential. That means, Ni-Mo_2C/C may show a better durability that Ni-Mo_2C/G. Table 1 shows the maximum current densities and onset potentials of the catalysts.

Table 1
Maximum current Densities and onset potentials of the catalystst in 0.05M NaOH + 0.5M Ethanol

Catalyst	Maximum Current Density (mA cm^{-2})	Onset Potential (V)
Ni-Mo_2C/C	11.4	0.46
Ni-Mo_2C/G	12.7	0.46

Besides, there is Reversible Electron Transfer Followed by an Irreversible Homogeneous Chemical Reaction mechanism: ErCi mechanism in both samples [9]. However, Ni-Mo_2C/C have a larger cathodic peak which can be resulted in a more stable catalyst for EOR in an alkaline medium.

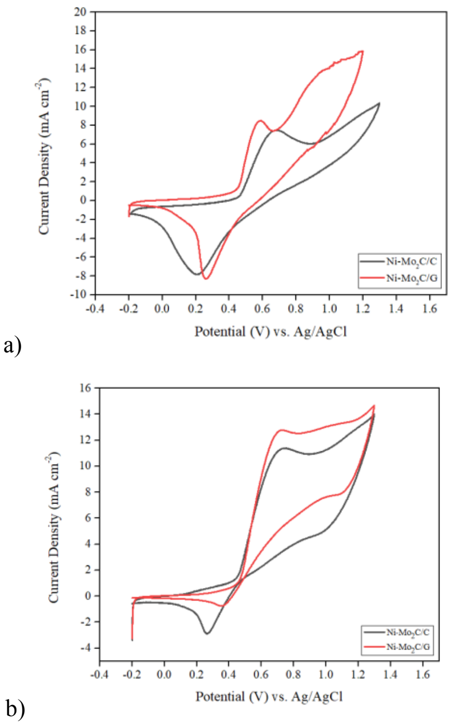


Fig. 3. CV voltammograms of the catalysts with 0.01 V s^{-1} scan rate in a) 0.1M NaOH, b) 0.05M NaOH + 0.5M Ethanol.

Fig. 4 represents the LSV results of the catalysts. As seen, the Ni-Mo_2C/G has a higher current density than Ni-Mo_2C/C shows better electrocatalytic activity at different scan rates. By using the Randles-Sevcik formula, the diffusion coefficients of thee catalysts can be calculated. The slope of the i_p vs. $\nu^{1/2}$ graph (see Fig. 4c and 4d) is used to obtain the diffusion coefficients. The Randles-Sevcik formula is given below:

$$i_p = 0.4463nFAC\left(\frac{nF\nu D}{RT}\right)^{1/2} \quad (1)$$

where i_p is the current density (A), F is the Faraday constant (96485 C mol^{-1}), A is the electrode geometric surface area (in this study it is 0.07 cm^2), R is the gas constant (J K^{-1} mol^{-1}), D is the diffusion coefficient (cm^2 s^{-1}), C is the concentration (mol cm^{-3}), T is the temperature (K), ν is scan rate (V s^{-1}) and n is the number of electrons transferred in the redox which was taken as 2.8 according to the literature [10]. The diffusion coefficient of Ni-Mo_2C/C and Ni-Mo_2C/G would be calculated as 3.74x10^{-9}, and 34.89x10^{-9} cm^2 s^{-1}, respectively. Consequently, a higher diffusion coefficient value indicates a higher reaction kinetics so that it would be easier to control the diffusion.

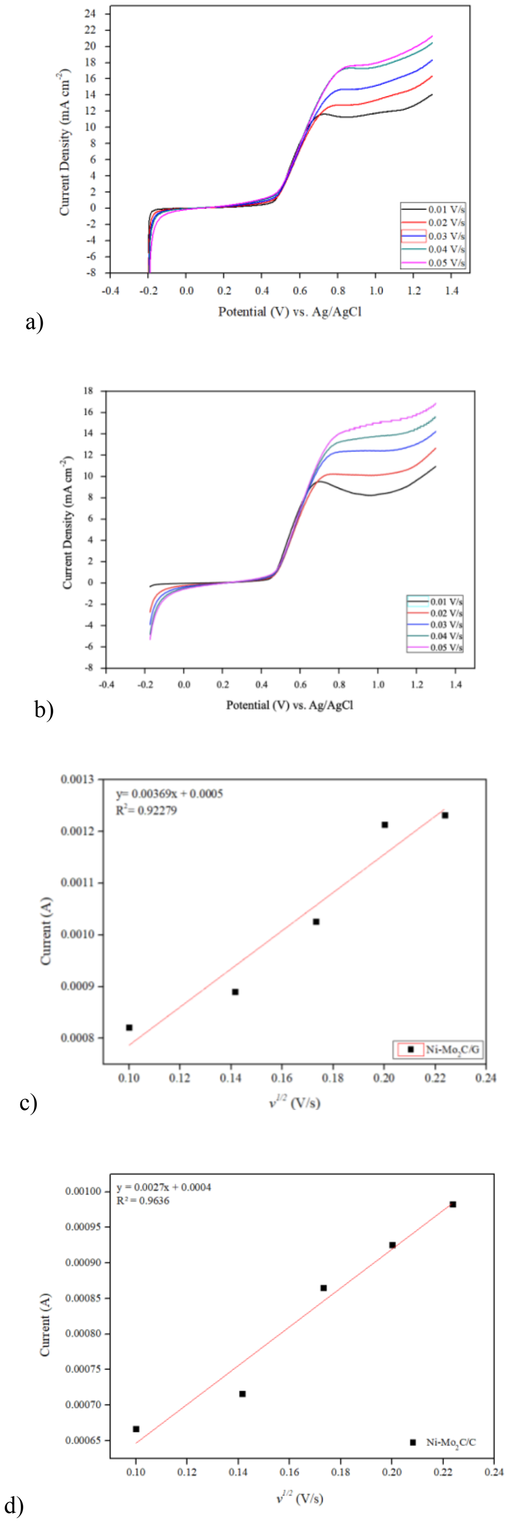


Fig. 4. LSV results in 0.05M NaOH+0.5M Ethanol solution with various scan rates of a) Ni-Mo_2C/G, b) Ni-Mo_2C/C and, i_p vs. $\nu^{1/2}$ graph of c) Ni-Mo_2C/G, d) Ni-Mo_2C/C.

To see the durability of the catalysts, chronoamperometry experiments were conducted for 1200s in 0.05M NaOH+0.5M Ethanol solution. Fig. 5 shows the current density-time curves of the catalysts. As expected from the onset potentials, current density of Ni-Mo_2C/G was sharply decreased earlier than Ni-Mo_2C/C next, decrease continued slighter for both of the catalysts. It would be a result of polarization current density caused by the adsorption of ethanol in the first place. Then, the current densities of the catalysts decrease very slightly because of the tendency to equilibrium of the adsorption rate and electrochemical reaction rate of ethanol [12].

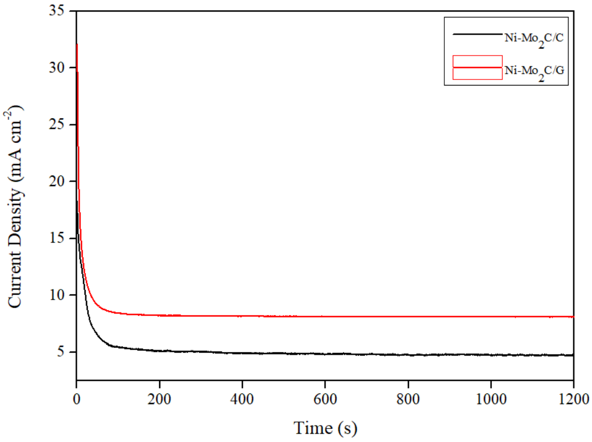


Fig. 5. CA results of Ni-Mo$_2$C/C and Ni-Mo$_2$C/G in 0.05M NaOH + 0.5M Ethanol solution.

4. Conclusion

In this study, two different carbon supports namely, Vulcan XC 72 and graphite were used as catalysts support material for Ni-Mo$_2$C electrocatalyst. The catalytic activities, diffusion coefficients and durabilities of the Ni-Mo$_2$C/C and Ni-Mo$_2$C/G were compared in alkaline media. In the catalyst's compositions, the active sites were Ni and the carbon supports were introduced to the catalysts to increase the catalytic activity. The obtained anodic current densities of Ni-Mo$_2$C/C and Ni-Mo$_2$C/G are 11.4 mA cm^{-2} 12.7 mA cm^{-2}, respectively. The stability and catalytic poisoning tolerance of the Ni-Mo$_2$C/C was slightly better than the Ni-Mo$_2$C/G. Accordingly, the results of the study are promising for the further studies on EOR and provide useful data for ADEFC system.

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Enhancing the OER activity of benchmark $BaSrCoFeO_6$ electrocatalysts through A-site doping strategy

Tuncay Erdil[1], Ersu Lokcu[3] and Cigdem Toparli [1,2]
[1]Middle East Technical University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Ankara, Turkey
[2] ENDAM, Center for Energy Materials and Storage Devices, Middle East Technical University, Ankara, Turkey
[3] Eskisehir Osmangazi University, Department of Metallurgical and Materials Engineering, Eskisehir, Turkey

Energy demand and consumption have been increasing rapidly because of population growth and industrial expansion in today's world. Carbon dioxide emission, which increases progressively due to fossil energy production, is a significant environmental concern. Therefore, using renewable energy systems and efficient energy conversion devices, finding new electrochemical energy storage systems is essential to decrease environmental pollution concerns while meeting the growing energy demand. Oxygen evolution reaction (OER) is the key process in various electrochemical energy systems, such as rechargeable metal-air batteries, water splitting devices, and fuel cell technologies. The challenge here is that OER has the slowest kinetics of all the counterpart half-reactions. Hence, today extensive research interest has focused on developing efficient electrocatalysts for OER [1]. The current state-of-the-art OER catalysts are IrO_2 and RuO_2. However, the high cost and scarcity of these materials severely prevent the wide-scale application of these systems. Next-generation OER catalysts include Perovskite oxide (e.g., single perovskite expressed as ABO_3) due to their adjustable physicochemical properties and, as a consequence, their catalytic properties by substitution of ions in the A and B sites. Metal-air batteries, fuel cells, and water electrolyzers all have a lot of potential with perovskite oxide materials due to perovskite's unique 3d electronic structures and structure flexibility[2,3]. To approach this problem, A-site management and altering the tolerance factor of perovskite oxide has a good option[4,5]. However, the effect of A site's impact on structural stability and creating a dynamic correlation between structure and activity have a lack of knowledge. Thus, it is highly desirable to develop the A-site design strategies to reveal the coherent structure-activity correlation in the OER process. In this context, benchmark electrocatalysts $BaSrCoFeO_6$ would be potentially active for OER and offer a way for A-site doping strategy. This study investigates the influence of A-site doping on the OER activity of $BaSrCoFeO_6$ (BSCF) parent perovskite oxide catalysts. Here, we performed the sol-gel-derived polymeric citrate gel method to fabricate the perovskite oxide catalysts. X-ray diffraction (XRD) was used to examine the crystal structure of the BACF (A: Ca, La, Sr) powders. X-ray photoelectron spectroscopy (XPS) was applied to study the valance state of the oxides. Finally, electrochemical tests were performed using a rotating disk electrode (RDE) in alkaline media. The results show that both lattice parameters and valance states of the B-site oxides have an immense influence on the OER catalytic activity of BACF.

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Tuncay Erdil completed his bachelor's degree from Middle East Technical University at the Metallurgical and Materials Engineering Department. He is currently a master's student in the same department and working on developing bifunctional oxygen electrocatalysts in the Electrochemical Energy Materials Laboratory. Presentating author: Tuncay Erdil, e-mail:erdil.tuncay@metu.edu.tr

Characterisation of CdS thin films electrodeposited on conductive glass for application in solar cells

Shikhamir Eminov [1], Akif Aliyev[2], Jafar Guliyev[1], Khuraman Jalilova[1], Vusala Majidzade[2]
[1]Institute of Physics NAN of Azerbaijan, H. Javid ave 131, Baku, Azerbaijan
[2]Institute of Catalysis and Inorganic Chemistry NAN of Azerbaijan H. Javid ave 113, Baku, Azerbaijan

Cadmium sulfide (CdS) is a semiconductor compound of II-VI group. This material has been widely used in applications such as transistors, photodetectors, light emitting diodes, sensors, and solar cells. It is extensively used in the CuInSe and CdTe-based solar cells as buffer layers. The optimum thickness and the optoelectronics properties of CdS thin films like optical band gap, electrical resistivity, structure, and composition, etc. are to be considered for its use functional material.

In this work we report the synthesis of CdS thin films electrochemically deposited over optically transparent conducting ITO-glass substrates and their characterization by various techniques like XRD, SEM, and EDX and optical transmission spectroscopy. We have chosen the electrochemical deposition route to the deposition because it offers deposition over a large area and other advantages such as a low-temperature operation, flexible process control and economic. Before the deposition process of CdS, ITO covered glass substrate has been cleaned using Methanol, Acetone, Trichloroethylene, and Distilled water. The stoichiometric CdS films were successfully deposited on ITO glass substrate using electrodeposition technique from nonaqueous solution of 0.055 M $CdCl_2$ and 0.19 M elemental sulfur, dissolved in ethylene glycol at 110-120°C. The electrodeposition of CdS thin films was carried out potentiostatically using a 2-electrode system. Then after CdS films were annealed at 200°C for a different time and studied its influence on the optical transmission, bandgap, and electrical resistivity.

The surface microstructure was observed using scanning electron microscope (SEM) JEOL model JSM 5600 LV, Energy Dispersion X-ray analysis (EDX) Germany) was also done (using Bruker Nano GmbH, Berlin), to confirm the presence of possible elements in the deposited film.

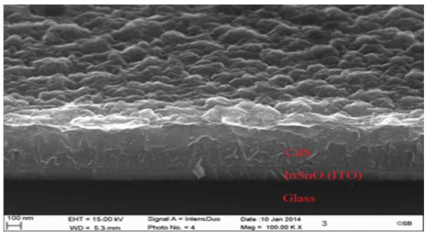

Figure 1. SEM cross-section image of glass/ITO/CdS structure

The SEM cross-section image of the as-deposited CdS layers with thickness in a range of 200-300 nm (fig.1) shows the good coverage of the ITO surface by the CdS grains. However, the visual non-uniformity at the surface of the CdS thin films can be due to the high surface roughness of the underlying glass/ITO substrate and also can be due to the upward growth nature of the electrodeposited layers. As can be seen from the SEM image in fig.2 the film has fine grains with a diameter in the range of about 30-200 nm.

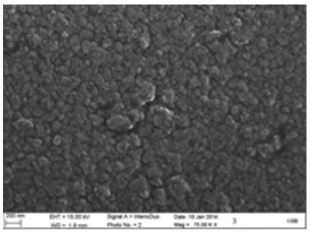

Figure 2. SEM image of the grains of CdS

EDX analysis shows that the composition of Cd and S may be considered to be stoichiometric.

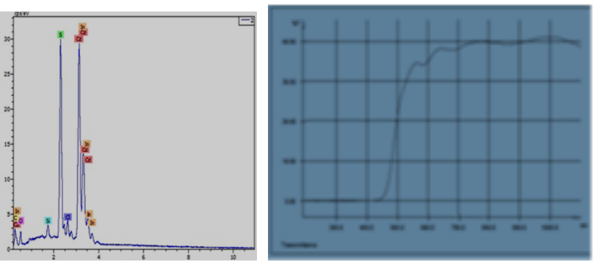

Figure 3. EDAX spectra of CdS film

The optical studies indicate that the electrodeposited CdS layers have direct bandgaps in the range (2.53 - 2.5 8) eV for the as-deposited and (2.42 - 2.48) eV after annealing at 420°C for 30 minutes in the air. The optical band gap of as-grown CdS is measured to be 2.42 eV, XRD analysis shows that the as deposited and annealed CdS layers are polycrystalline with hexagonal crystal structure and preferentially oriented along (200) planes. The hot probe method confirms the n-type conductivity of the CdS film. Hall probe data shows the resistivity of the films was in the order of 10^3 Ωcm. Observed data signifies its future use in the many optoelectronics devices.

Dr. Akif Aliyev works at the Institute of Catalysis and Inorganic Chemistry of the National Academy of Sciences of Azerbaijan. 1978 graduated from Baku State University. In 1986, Akif Aliyev obtained a PhD in Chemistry, and in 2010, a Doctor Science of Chemistry. His research interests covers hydrogen energy, photoelectrochemistry, solar cells, and semiconductors electrodeposition.

Corresponding author: Akif Aliyev, e-mail: akifaliyev55@mail.ru; tel: +994 55 742 58 89

SYSTEMS AND APPLICATIONS

Enabling the success of the hydrogen-energy chain through international cooperation

Fermin Cuevas[1], François Aguey-Zinsou[2], Junxian Zhang[1] and Michel Latroche[1]
[1]Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France
[2]Merlin Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

Hydrogen is considered worldwide as an essential vector for freeing our societies from fossil fuels and effectively initiating the energy transition. Offering high energy density, hydrogen can be used for mobile, stationary, or industrial applications of all sizes. This perspective on the crucial role of hydrogen is shared by a growing number of countries (e.g., Australia, China, France, Germany, Japan, Republic of Korea, United States of America…), which are publishing ambitious roadmaps for the development of hydrogen and fuel cell technologies, supported by substantial financial efforts. Turkey also takes an active part in this direction through the definition of priority areas aiming to define a national roadmap [1].

This contribution highlights the vision of different countries on hydrogen-energy, with especial emphasis on French, German, and European policies [2] as well as the Australian case. Even though all these countries share the common vision of boosting the hydrogen chain for attaining a carbon-free world, strategies differ depending on national energy policies. But, as a common rule, all underline the needs of establishing international collaboration in research and development to share knowledge on hydrogen technologies and/or to accelerate import-export hydrogen markets. Thus, the implementation of international cooperation tools is a key factor to enable the success of the hydrogen vector. In this context, the International Research Network FACES (Figure 1) was created in 2020 [3]. The IRN-FACES is the collaborative French-Australian research network on energy materials and integrated systems for electrochemical storage and hydrogen energy. Its expertise concerns not only the hydrogen chain but also electrochemical energy storage. IRN-FACES aims and expertise in the framework of international collaborations will be presented.

Figure1: IRN-FACES: **I**nternational **R**esearch **N**etwork - **F**rench-**A**ustralian research network on **C**onversion and **E**nergy **S**torage

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Fermin Cuevas obtained in 1996 his PhD in Physics at Autonoma University of Madrid (Spain). After postdoctoral studies at MPI-Stuttgart (Germany) and CNRS-Thiais (France), he became in 2002 permanent researcher at CNRS. His main research activities are hydrogen storage in solids as well as electrode materials for Ni-MH and Li-ion batteries. Currently, he is leader of the Interaction of Hydrogen and Matter group at the East Paris Institute of Chemistry and Materials Science, co-head of the hydrogen storage axis at the French Research Network on Hydrogen Energy, and French coordinator of the International Research Network FACES, the French-Australian research network on Conversion and Energy Storage

Presentating author: Fermin Cuevas, e-mail: cuevas@icmpe.cnrs.fr tel: +33 149 781 225

Thermally-driven Hydrogen Compression Utilising Metal Hydrides

Mykhaylo Lototskyy [1]

[1] HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, Bellville, South Africa

Hydrogen compression is a major contributor to capital costs and maintenance hours in the infrastructure related to storage, distribution and end-use of hydrogen. Conventionally used mechanical hydrogen compressors have a number of disadvantages including a complicated design, insufficient reliability, high operating costs, a probability of hydrogen leakage and hydrogen contamination [1-3].

A promising alternative is a thermally driven metal hydride hydrogen compressor (MHHC) whose operation is based on the reversible interaction of hydride-forming alloys with hydrogen gas. MHHC's have a number of advantages including practically unlimited (up to 5000 bar) discharge pressure, good scalability (from several litres to tens normal cubic metres of hydrogen per an hour), modular design, simplicity in service and operation, as well as the possibility to utilise low-grade heat and high purity of the delivered hydrogen. In addition, the MHHC does not contain moving parts that simplifies its design, increases reliability, and eliminates noise and vibration [4-6].

This presentation overviews R&D activities related to the thermally-driven hydrogen compression utilising metal hydrides. The focus is put on the interrelation between properties of metal hydride materials and their hydrogen compression performances, first of all, operating pressure – temperature range, process productivity and efficiency. Typical design features of the hydrogen compression systems and ways of their optimization are considered as well. Finally, a brief techno-economic analysis of the MHHC's benchmarked against alternative hydrogen compression technologies (mechanical and electrochemical) is presented, and their promising application niches are outlined.

Acknowledgement

This work is funded by the Department of Science and Innovation (DSI) of South Africa (HySA project KP6-S02).

Table 1. Recently developed industrial-scale MHHC's

#	Manufacturer	Pressure range [bar]	Productivity [Nm^3/h]
1	HYSTORSYS AS (Norway)	5–200	5
2	SAIAMC / UWC (South Africa)	3–200	5
3	IPCP RAS, SKTBE (Russia)	3–160	15
4	HYSTORE Technologies (Cyprus)	7–220	2.5

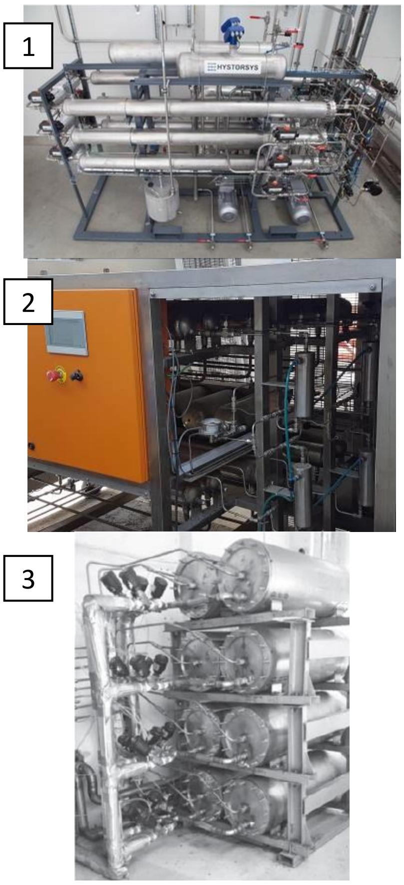

Figure 1. Industrial-scale MHHC's (see Table 1).

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Key Programme Manager / Senior Lecturer at the University of the Western Cape (UWC), South African Institute for Advanced Material Chemistry (SAIAMC), HySA Systems Centre of Competence, Bellville, South Africa. Internationally recognized researcher in the fields of hydrogen energy and technology, hydrogen storage, material science and applications of metal hydrides. 114 SCOPUS-indexed publications cited 3097 times; h-index 30

Presentating author: Mykhaylo Lototskyy, e-mail: mlototskyy@uwc.ac.za tel: +27 21 9599314

Feasibility study of fuel cell powered forklift truck

G. Radica[1], I. Tolj[1], M. V. Lototskyy[2] , S. Pasupathi[2]

[1] University of Split, Faculty of Electrical and Mechanical Engineering and Naval Architecture, Split, Croatia

[2] HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, Bellville, South Africa

This paper describes a hybrid system of PEM FC forklifts that use PEM fuel cells and a battery as a source of electricity. Hybrid systems consist of a fuel cell system, which is the primary energy source, and an energy storage system, ie a battery, which provides an additional source of electricity or power. The complete hybrid drive system includes a hydrogen supply system, a PEM fuel cells stack and its regulator, a DC voltage regulator, a battery, an energy management regulator, and the forklift itself. Based on the conducted techno-economic analysis, and the comparison of battery electric forklifts and forklifts with PEM fuel cells, it is shown that despite high capital costs, the use of forklifts with PEM fuel cells can reduce the total cost of ownership by 10%. Fuel-powered forklifts can reduce charging costs by up to 80% and require 75% less space compared to battery charging infrastructure. In addition, fuel cells provide constant power during shifts, while battery performance deteriorates in line with SOC reduction. Thanks to proven performance, short refueling time and the potential to increase productivity, fuel cells can compete with life-cycle batteries.

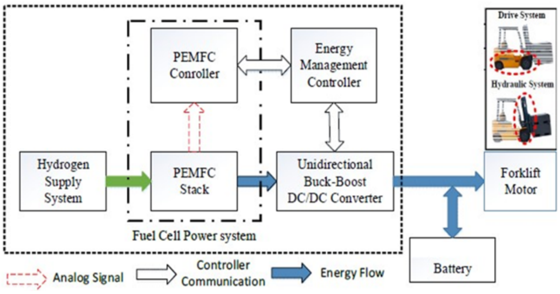

Figure 1: Hybrid forklift configuration diagram.

Acknowledgements

This work is funded by the Department of Science and Technology within the HySA Programme (HySA Systems projects KP3-S02, KP6-S02 and KP6-S03), and Impala Platinum Limited; South Africa. Also, this project is founded by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778307.

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Full professor at the Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split. Chair of Heat Engines. Head of Laboratory for Heat EnginesResearcher has years-long experience with heat engines and implementing new technology in engine diagnostic. He is author of lots paper which deals with hybrid energy systems, expert systems, testing, diagnosing and optimization. Researcher introduced a new systems of monitoring and controlling engine. Researcher participated on several international Scientific projects.

Presentating author:Gojmir Radica, e-mail: goradica@fesb.hr tel:+ 385 21 305955

Transient CFD Analysis of 1 kW Air-Cooled PEM Fuel Cell Stack During Startup

Ivan Tolj[1], Gojmir Radica[1]and Željko Penga[1]
[1]Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, R. Boškovića 32, 21000 Split, Croatia

Start-up and variable load operation of a 1 kW air-cooled stack is investigated via computational fluid dynamics (CFD) analysis. The results of the transient analysis indicate that the temperatures inside the air-cooled stack are up to 27 °C higher when compared to the temperatures on the outside walls of the bipolar plates and this indicates a requirement for development of a new method for PEM fuel cell operation to increase the relative humidity of the reactants internally and prevent membrane dehydration. The novelty of this work is the method for increasing the relative humidity along the active area of the cell by intentionally increasing the pressure drop across the flow field, resulting in higher performance of the cell. The CFD model also investigates the influence of altering the bipolar plate material on the overall heat transfer inside the cell in order to achieve a similar effect with success in both cases.

Small scale air-cooled stacks are interesting for mobile applications such as portable power generators and as power supply units for remotely controlled or autonomous unmanned aerial vehicles (UAVs). Air-cooling is interesting for PEM fuel cell applications because it reduces the price and complexity of the system by removing the necessity for coolant loop. However, since commonly used materials for PEM fuel cell bipolar plates are characterized by poor thermal conductivity, air-cooling does not result in uniform temperature distribution along the active area of the cell and results in membrane dehydration. For such systems special care must be admitted in determining the required air mass flow rate to result in the desired temperature inside the flow field, instead of solely along the outside walls of the bipolar plates due to high temperature gradient between the flow field of the cell and the outskirts with cooling ribs. In previous studies a new method was developed for improved performance of PEM fuel cells without any form of external humidification, termed coolant induced variable temperature flow field [1-4], but since it is not convenient to use coolant fluid in this case it is not applicable. For this reason another method is developed based on controlling the water vapor saturation pressure by intentionally increasing the pressure gradient along the cell in such manner that the water generated inside the cell, is sufficient to humidify the membrane, even at higher operating temperatures and transient operating conditions. This method is completely new and has not been previously implemented, as well as the type of transient analysis shown in this work. It is also demonstrated that the thermal conductivity of the bipolar plates makes a significant difference in the resulting transient heat transfer.

CFD model is developed based on the single-cell geometry from the experimental 1 kW air-cooled stack developed by Proton Energy Systems™. The stack, geometry and mesh are shown in Figure 1. Since the total duration of flow time for reaching steady-state from start-up was roughly 1000 seconds, the stack is modeled as a single-cell with symmetry boundary conditions.

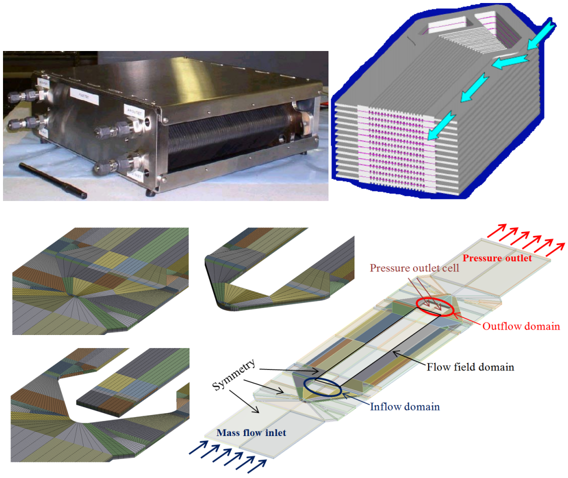

Figure 1. 1 kW air-cooled stack without external humidification (above left); cooling ribs with annotated air flow (above right); mesh and geometry with annotated boundary conditions (below) [1].

This work shows that it is possible to achieve higher operating efficiency, i.e. higher membrane water content, by controlling the heat transfer inside the cell via using different bipolar plate materials or new method for enhancing the pressure drop along the cell. This would be beneficial for portable PEM fuel cell applications and result in longer durability of the cell. This method will be further investigated in a future study.

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Dr. Tolj is an Assistant Professor in the Department of Thermodynamics and Heat Engines, Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split. His activities focus on thermodynamics, thermal engineering and fuel cell power systems.

Presentating author: Ivan Tolj, e-mail: itolj@fesb.hr tel: +385 21 305 948

Advancing the Promise of Low-Temperature Molten Sodium Batteries

Erik D. Spoerke
Sandia National Laboratories Albuquerque, NM USA

Traditional molten sodium batteries, such as those based on sodium-sulfur (NaS) and sodium-nickel chloride (ZEBRA) chemistries, have promised cost-effective, reliable energy storage for decades but high costs, tied to operation near 300°C, have limited widespread utilization and deployment.Here, we describe a promising new class of low temperature molten sodium-halide batteries that operates at dramatically reduced temperatures near 100°C, promising lower costs and improved lifetimes.Through innovation of new molten salt catholytes, solid state separators, and improved charge transfer at critical interfaces, we have demonstrated high voltage (>3V) molten sodium batteries that exhibit stable, resilient cycling for more than 8 months.These batteries may offer a path to safe, cost-effective, reliable energy storage, key to emerging grid-scale and long-duration applications.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Erik D. Spoerke, Ph.D. is currently a Principal Research and Development Materials Scientist in the Electronic, Optical, and Nano Materials Department at Sandia National Laboratories.Erik's widely published and patented research efforts span a diverse materials portfolio, with an emphasis on combining elements of chemistry, biology, and materials science to study and develop functional materials ranging from novel electrochemical materials to synthetic biological analogs and functional supramolecular thin films. Much of his current research passion focuses on ion-conducting materials aimed at the development of solid state electrolytes, functional separators, environmental barriers, and even ionic filters for next generation ion-mediated technologies. In the last 10 years, he has worked on battery technologies including supercapacitors, lithium ion batteries, bio-inspired batteries, and metal-based batteries. He is currently the Materials Team Lead for Sandia's Energy Storage Program, and he is focused on developing a new generation low-temperature, molten sodium batteries intended for grid-scale energy storage.

Materials Technology Gaps for Low Cost Grid Energy Storage

Babu Chalamala, Valerio De Angelis, Erik Spoerke and Clifford Ho

Sandia National Laboratories

Deep decarbonization of the electric grid will require a range of low cost energy storage technologies to satisfy the needs from short duration power quality applications to longer duration and seasonal energy storage requirements. There is general consensus in the industry that battery energy storage systems, particularly Li-ion, can be cost-effective for short duration applications. In addition to Li-ion batteries, emerging modular energy storage technologies like zinc and sodium-based batteries flow batteries, have potential to be cost effective for some longer duration applications. For deeper decarbonization and transition to fossil-free generation, the grid also needs cost effective long duration and seasonal energy storage options. Currently, pumped hydro storage provides most of the existing long duration capacity, but this capacity amounts to 15 min of ride through. The grid needs a range of long duration and seasonal storage solutions for varied application needs. This paper gives an overview of materials technologies options for low cost grid energy storage and potential solutions for longer duration and seasonal storage.

Dr. Babu Chalamala is Manager of the Energy Storage Technology and Systems Department at Sandia National Laboratory,. Prior to joining Sandia in August 2015, he was a Corporate Fellow at SunEdison (formerly MEMC Electronic Materials) for five years, where he led R&D and product development in grid scale energy storage. Before that, he founded two startup companies commercializing large format lithium batteries and digital x-ray sources. Earlier, as a research staff member at Motorola, Research Triangle Institute, and Texas Instruments, he made contribution to the development of electronic materials and device technologies. He received his B.Tech degree in Electronics and Communications Engineering from Sri Venkateswara University and his PhD degree in Physics from the University of North Texas. He is a Fellow of the IEEE and Academy of Sciences St Louis, a Life Member of the Electrochemical Society, and a Member of the Materials Research Society. As chair of the IEEE Photonics Society Technical Committee on Displays, he was instrumental in launching the IEEE/OSA Journal of Display Technology. He has been an active member of the Materials Research Society for twenty years and served as General Chair of the 2006 MRS Fall Meeting. He was a guest editor of the MRS Bulletin, Proceedings of the IEEE, and the IEEE Journal on Selected Topics in Quantum Electronics, and served on the editorial boards of the Proceedings of the IEEE and IEEE Access. He received the 2015 James Eads Award of the Academy of Sciences St Louis.

Development of rechargeable zinc manganese dioxide batteries from concept through product to market

Sanjoy Banerjee

CUNY Energy Institute and Urban Electric Power, Inc

A high performance, low environmental impact battery to enable widespread deployment of grid-scale energy storage was developed at the City University of New York (CUNY) Energy Institute. The Institute was founded in 2008 with the mission to develop sustainable energy technologies with low carbon footprints. One focus was energy storage to assure capacity from renewable but intermittent generation such as solar and wind power. To this end, zinc anode batteries were researched with federal, notably DOE Office of Electricity, ARPA-E, and New York State, support. The work resulted in a 'green' rechargeable battery concept with earth abundant manganese dioxide (MnO2) and zinc (Zn) as the non-toxic, easily recyclable and inexpensive, active constituents. These materials are widely used in the ubiquitous and safe primary alkaline cells, but these cells cannot be repeatedly charged and discharged. The breakthrough made at the Energy Institute was to find dopants and processing methods for the manganese dioxide which enabled access to its full two electron producing capacity through thousands of charge-discharge cycles.

Both Zn and MnO2 are non-toxic, and have lower CO2 emissions when compared to other rechargeable batteries. Life cycle CO2 emissions from Zn-MnO2 batteries are seven times lower than lithium batteries and four times lower than lead batteries. Additionally, lead recycling is energy intensive and has a significant environmental impact and lithium recycling has not fully matured. In contrast, Zn and MnO2 can be recycled by low energy consuming chemical processes allowing the Zn-MnO2 battery to further reduce its greenhouse gas footprint.

To commercialize the concept, Urban Electric Power Inc. (UEP) was spun-off from the CUNY Energy Institute to manufacture, market, and deploy rechargeable large-format Zn-MnO2 batteries**.** When manufactured at GWh/year scale, battery packs will cost less than $50/kWh leading to energy storage systems with a levelized cost of energy (LCOE) below $0.05/kWh, widely identified as the target for widespread adoption of grid scale energy storage.

In this presentation, we will discuss the evolution of the Zn-MnO2 rechargeable battery concept from its beginnings at the Energy Institute, through development of prototypes for grid energy storage, to manufacture of commercial products at UEP, and their deployment to provide power backup during grid outages, and to provide storage capacity that support solar and wind generation.

Sanjoy Banerjee is a Distinguished Professor of Chemical Engineering, City College of New York and Director of the City University of New York (CUNY) Energy Institute. Banerjee is also the Founder and Chairman of Urban Electric Power, spun out of the CUNY Energy Institute to develop 'beyond lithium' batteries. Banerjee was recruited from UC Santa Barbara, where he had been Department Chair and previously taught at Berkeley, McMaster University, and worked at Atomic Energy of Canada, as Director of the Applied Science Division. He has also served as Mitsubishi Professor at the University of Tokyo, the Burgers Professor at TU Delft, and at ETH Zurich. He has also served on several advisory boards: NASA Fluid Physics, the oil- industry Flow Assurance Consortium, and the Advisory Committee on Reactor Safeguards, congressionally mandated to advise on nuclear facilities.

Presentating author: Sanjoy Banerjee e-mail: banerjee@ccny.cuny.edu, sanjoy@urbanelectricpower.com

Current Status and Future Prospect of Li-Ion Battery Technology in Turkey

Ahmet Altınay[1]
[1]Aspilsan Enerji A.Ş Design, Innovation and Product Development Center, ODTÜ Teknokent, ANKARA

Ever since Sony released first commercial lithium – ion cells, lithium-ion battery technology still draws attention as a promising Energy storage technology regarding to have high Energy density, low discharge characteristics, and long life cycles. The technology then became one of the most researched topics in academia and in the R&D facilities all around the world.

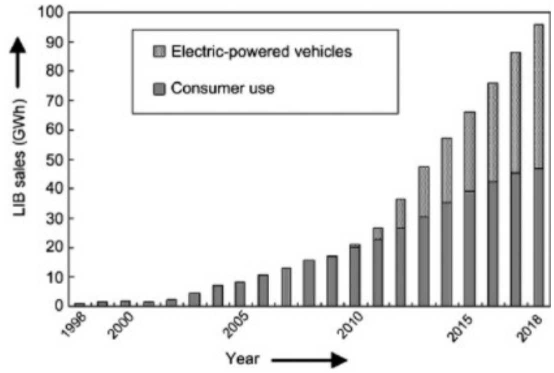

Figure 1. Demand for lithium ion batteries [1]

In Europe a research initiative, BATTERY 2030+, has a vision of advancing the sustainable batteries of the future, providing European industry with disruptive technologies and a competitive edge throughout the battery value chain and enabling Europe to reach the goals of a climate-neutral society envisaged in the European Green Deal [2]. The main objectives will be to facilitate and monitor the implementation of the BATTERY 2030+ roadmap, and contribute to European curricula in battery Technologies.

As years progressed more and more companies started replacing old NiCd, NiMH, lead – acid batteries with more energy dense and more powerful li – ion batteries. With the rise of renewable energy installations and electrified transportation applications starting from 2010's the need for lithium ion technology also increased. With this prospect, Turkish industry and academia directed their focus on several R&D projects and initiatives on the issue. However, no attempt has been made until ASPİLSAN Enerji started working on 250 MWh/year plant in 2020.

As we look to the opportunity of domestic battery manufacturing as this market grows, one challenge for Turkey is that Turkey is not a large producer of minerals such as lithium, manganese, cobalt, or graphite—all important components of today's lithium-ion batteries. However, there is a big potential to build an ecosystem countrywide to produce and enrich those minerals.

Benefits from Domestic EV Battery Manufacturing will be more resilient supply chains, economic opportunity in global markets, job opportunities, more affordable battery cells, reduced emmisions and simultaneously advancing Energy storage systems and Technologies.

There will be also challenges to domestic battery cell manufacturing like low demand, insufficient funds, insecure supply chain, bringing technologies from innovation to deployment.

With keeping mind on Battery 2030+ roadmap and challenges and opportunities, in its Design, Innovation and Product Development Center of ASPILSAN Energy, is focused on lithium ion battery cell design, material development and material characterization for commercial use.

In the initial phase cylindrical type cells will be produced in the plant, with pouch and/or prismatic cell production plans as a second phase.

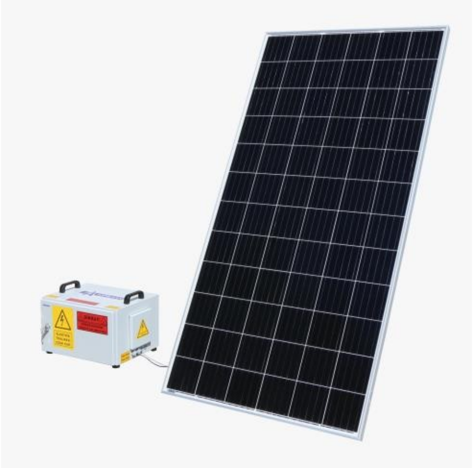

Figure 2. Solar panel coupled with ASPİLSAN Enerji mini energy storage system

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Dr. Ahmet Altınay obtained his Bachelor's Degree in Chemistry (2006), Master's Degree (2014), PhD (2020) from Hacettepe University. After 8 years of experience in Aluminum production and Energy sector, started working at ASPİLSAN Enerji in 2016 as Research and Development Manager which he continues to this day.

Presentating author: Dr. Ahmet Altınay, e-mail: ahmet.altinay@aspilsan.com tel: +905324658688

Appendix

POSTERS AT ENTRY LEVEL DESIGN EXHIBITION

DESIGN REQUIREMENTS AND MATERIAL SELECTION FOR BATTERY PACKS IN ELECTRIC VEHICLES

Salih Alcin[1], Cahit Gunes[1], Sebnem Temel[1], Hande Ozturk[1], Ekin Zeki[1], Gurkan Pekoz[1], Ozgul Keles[1], Sebahattin Gurmen[1]

[1]Istanbul Technical University

Electric vehicles are getting more popular each year due to the global struggle for reducing CO_2 emissions. Governments are promoting the production and use of electric vehicles to reduce their carbon footprints. In the 2000s and early 2010s, electric vehicles were quite expensive due to their production costs and were not preferred over internal combustion engines [1]. However, today thanks to the developing battery and production technologies, affordable and commercially successful electric vehicles have started to be introduced to market. The main problem of electric vehicles today is their high charging times compared to their mid-range ranges. Using material design, possible solutions to this problem were investigated and two possible solutions were found for this problem. The first is to produce batteries with higher energy density for electric vehicles, and the second is to reduce the weight of electric vehicle components. A battery pack is a component of electric vehicles that contains and controls battery cells. This component is unique to for each electric vehicle. The weight of battery packs ranges from 400 to 500 kg, which is about 30% of the weight of vehicles [2]. Reducing the weight of the pack through material design will significantly increase the ratio of electric vehicle range to charging time.

In this study, battery pack components (battery cells, conductive parts, battery management system, battery thermal management system, battery modules, etc.) were examined in detail to make materials and process selection in light of the boundary conditions determined. Then, the current technology roadmaps on battery cells and battery packs are investigated. Finally, a technology roadmap was proposed for Turkey (see Figure 1).

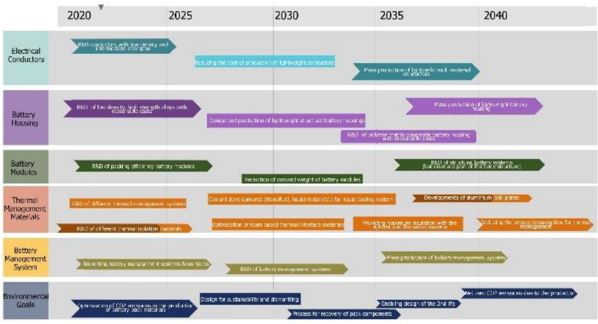

Figure 1. Proposed technology roadmap on battery packs for Turkey

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He was born in 1998 in Ankara. He went to Istanbul Technical University, where he got his Bachelor's Degree in Metallurgical and Material Engineering. He is currently doing his master's degree in Production Metallurgy and Technologies at ITU. Energy storage systems, production technologies and composite materials are his fields of interest.

Presentating Author: Salih Alcin E-mail: alcins16@itu.edu.tr Phone: +90 507 434 20 84

Design Requirements and Roadmaps for Cathodes Used in Electric Vehicles

Sertac Celik[1], Fatih Kaan Gullu[1], Yigit Hamza Yildiz[1], Selahattin Cat[1], Ozgul Keles[1] and Sebahattin Gurmen[1]
[1]Istanbul Technical University

Electric vehicle technology has been developing rapidly in recent years. Increase in the use of electric vehicles in the automobile industry, studies on Li-Ion electric vehicle batteries have attracted great attention. One of the most important parts of Li-ion batteries is cathodes. Cathodes have important design requirements that affect properties. In this study, it is aimed to investigate the effect of design requirements on cathode properties and to prepare cathode-specific a technological roadmap for Turkey.

A detailed literature survey was conducted to observe effect of these requirements on cathode performance. Then, cathode selection criteria were defined and effectiveness of available applications were examined in detail. Design requirements that affect cathode performance are morphology, particle size, production methods, and coating and doping methods. Effects of design requirements on cathodes are determined by examining 14 different cathode types that are used in lithium-ion batteries. Afterward, electrochemical performances depending on production methods were observed. Different particle sizes were observed in different production methods. In general, as particle size decreased, higher values were obtained for initial discharge capacity and cycle stability. It is thought that there will be progress towards nanometer size. When coating and doping methods are applied, there is an improvement in their electrochemical performance. In this way, the performance of low-cost and low-performance cathode types can be improved.

While preparing technological roadmap for cathodes, a future plan for Turkey has been put forward. Then, the roadmaps of other countries are examined focusing on the needs of electric vehicles. Electrochemical performances and advanced technology studies were also evaluated. Ethical and environmental problems in battery production have been taken into account. As a result, a road map including targets between 2020-2040 has been proposed for Turkey as seen in Figure 1.

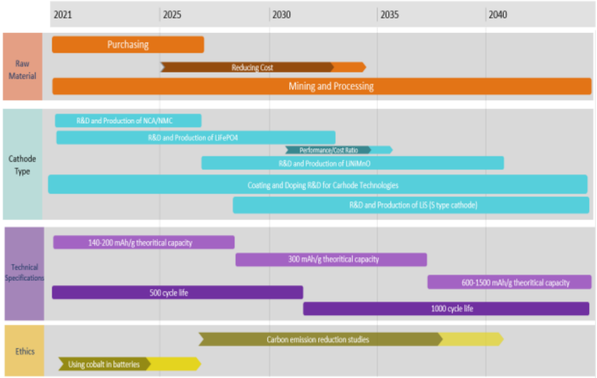

Figure 1. Proposed technological roadmap for Turkey

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Sertac Celik was born in 1998 in Sanliurfa. He graduated from the Department of Metallurgical and Materials Engineering at Istanbul Technical University in 2021. He is currently doing his master's degree in Ceramic Engineering at Istanbul Technical University. Lithium-ion batteries, ceramic materials, production metallurgy and powder metallurgy are his main areas of interest.

Presentating Author: Sertac Celik, E-mail: celikse16@itu.edu.tr Phone: +90 546 962 54 01

Comparison of Recycling Methods for Lithium-Ion Batteries

Orhun Oguz[1], Oytun Berkman[1], Yunus Emre Gul[1], Ahmet Suat Gursoy[1], Emre Bayboga[1], Ozgul Keles[1] and Sebahattin Gurmen[1]
[1]Istanbul Technical University

Today, the decreasing resources or the instability of the available resources have led the world to recycle in many areas. In recent years, the interest in lithium-ion batteries has led to high production and, accordingly, to the formation of a large amount of waste lithium-ion batteries. Also, the value of many metals such as lithium and cobalt used in the construction of lithium-ion batteries is increasing rapidly day by day while cobalt production in the world is largely dependent on a single country and can be extracted under very difficult conditions. In order to prevent the environmental and economic impact of these wastes, which are formed and rapidly increasing, and at the same time to provide a secondary production route for the valuable metals contained in these batteries, recycling has a crucial importance.

Many countries are aware of the importance of lithium-ion batteries in the aimed clean world and the resulting increasing waste. In line with this purpose, countries form roadmaps to determine aims, assisting organizations and budgets. There is also a significant amount of used batteries in Turkey and this amount is expected to increase exponentially in the coming years. With the presence of valuable institutions already working in the battery field, Turkey also has a high potential for battery development and recycling.

As for the recycling methods, There are two main methods for recycling lithium-ion batteries, these are pyrometallurgy and hydrometallurgy. However, there are two alternative methods such as bioleaching and electroextraction which are recently developed. Also, pre-treatments are also carried out before conducting these methods in order to make the recycling process more efficient.

In this study, cost, complexity, recovery, throughput, duration and energy consumption values of the recycling methods are analyzed, compared and a detailed understanding of which recycling process is more feasible in which situation is brought to attention. As a result, while bioleaching is seen to be more upfront for laboratory applications, the combination of pyrometallurgical and hydrometallurgical processes is more feasible in industrial applications.

A flowchart is built for easy traceability of these recycling methods as seen in Figure 1. Finally, by showing the high recycling potential in Turkey and evaluating the different roadmaps made around the world, a battery roadmap is proposed to give insight for whom would like to take a step about lithium-ion battery recycling in Turkey. With the potential in Turkey, it is possible to reach the recycling rates as high as the pioneer countries about the battery technology in the world.

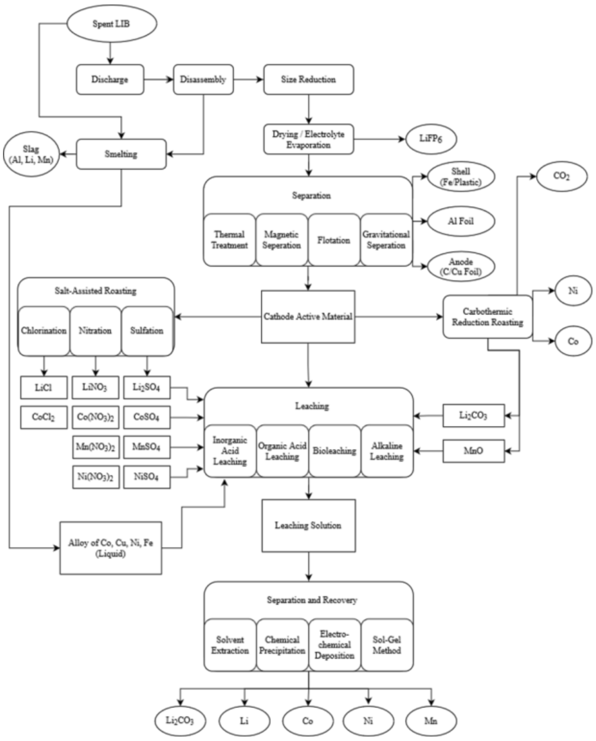

Figure 1. Flowchart for recycling process of spent lithium-ion batteries.

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Orhun Oguz was born in 1997 in Kayseri, Turkey. After graduating from Galatasaray High School, he completed his undergraduate education at Istanbul Technical University, Department of Metallurgical and Materials Engineering. Currently, he continues his education with a Master's program in Materials Science and Engineering at Istanbul Technical University.

Presentating author: Orhun Oguz, e-mail: oguzo16@itu.edu.tr tel: +90 537 647 56 10

Anode Design Requirements and Materials Selection for Electric Vehicles

Arda Durer[1], Elif Sarikas[1], Yagiz Arslan[1], Melike Korkman[1], Anil Savran[1], Ozgul Keles[1], Sebahattin Gurmen[1]

[1]Istanbul Technical University

Today, to reduce the amount of carbon emissions, alternative energy sources have been utilized. Electric vehicles are one of the applications that emerged as a result of this orientation.

In this study, technology roadmaps of countries are compared and the parameters affecting battery performances are analyzed for better material selection especially anodes.

In technology roadmaps, besides technologically proven graphite anodes silicon-based anode materials and lithium titanate oxides, which are also used in some commercial applications, the potentials of MXene, pure silicon, pure lithium, oxides of transition metals and graphene-based anode materials have had a great attention.

In graphite anodes, the properties, potentials and production methods of synthetic and natural graphite were examined. The production of natural anodes depends on natural resources and requires less energy in its production compared to synthetic anodes. In addition, the potential of Turkey regarding the production of anode materials used in batteries was also studied. While drawing attention to the number of graphite ores in Turkey, a technology roadmap including graphite and silicon-based anodes, which have the highest commercial potential for our country, was proposed within the future plans. The main point here is that silicon-based anodes can be used together with graphite anodes to reach commercial use in the short to medium term. Based on this fact, it was determined by examining the academic studies and the products available in EV market that the silicon content of graphite-based anodes may reach up to 30% by weight for the long term in line with the R&D studies.

He was born in 1998 in Manisa. He went to Istanbul Technical University, where he got his Bachelor's Degree in Metallurgical and Material Engineering. He is currently doing his master's degree in Materials Engineering at ITU. Energy storage systems, nanotechnology applications and semiconductors are his fields of interest.

Arda DURER, durer16@itu.edu.tr, +905343121484

Design of 1 MW Energy Storage System for Renewable Energy - Li-ion Batteries

Berkhan Karadede, Özge Karataş, İbrahim Dereli, Cansu Şimşek, Aykut Şahbazoğlu, Eren Sefer

To solve climate crisis, an energy transition is inevitable from fossil fuels to renewable and cleaner sources. Solar panels and wind turbines cannot be continuously available. Energy storage systems offer shifting excessive energy to temporarily replace renewables. For example, solar panels cannot produce energy at nights and required to shift daily production. 1-10 Hours of energy must be stored to succeed shifting (IEEE Std 2030.2-2015, 2015).

A battery system can be designed. However, this kind of system should work for at least ten years. The design should also include safety, ease of use, potential hazard to environment, and durability in different climate and conditions. Lithium Ion batteries show good lifetime and energy density values together (Linden & Reddy, 2019). Considering Lithium Ion is not harmful than lead and cadmium-based systems, it is a great option to choose. The only problem may be related with increased capital costs, but lifetime improvements remove the necessity of repeating that spending in short periods of time.

Li-Ion is a logical choice for operation. However, Li-Ions also have different variations. To find a suitable type, a data set collected from Samsung brand batteries. Each battery has the same dimensions and they all produced from the same factory. Table 1 gives capacity, power, cost and lifecycle values. However, Lifecycle over cost index is the most important one. If that value is high. It means that it is more profitable to use for long times. LiFePO4 wins a huge gap from that perspective. Additionally, LiFePO4 is safest option than any of the batteries listed below (Linden & Reddy, 2019). Nickel and Cobalt metals are also valuable and LFP consist none of them. Consequently, the battery system is assembled by using LFP option.

Table 1. Lithium Battery Comparisons taken from cylindrical products commeacially available.

Cathode type	*LiNiMnCoO2*	*LiCoO2*	*LiFePO4*	*LiNiCoAl*	*LiMn2O4*
Weight (g)	45	45	40	50	50
Capacity (Ah)	2.5	2	1.1	3.2	3.2
Nominal voltage	3.6	3.6	3.2	3.65	3.75
Watt-hour	9	7.2	3.52	11.68	12
Cost ($) / cell	2.5	2.36	2.19	2.55	2.29
Cost ($) / Watt-hour	3.6	3.1	1.6	4.6	5.2
Life cycle	1200	250	2000	1000	300
Life cycle/cost	333.3	81.9	1244.3	65.5	57.3

The design starts with packing a massive prismatic unit cell weight 5.3 kgs. The capacity is 272 Ah with a standard LFP voltage 3.2 volts. 5 of these cells connected serially in a rack creating 16 volts with the same capacity of 272 Ah. Then 9 of them are serially connected to create a module with 144 volts. This voltage level is still low. 6 serially connected modules solve it and create 864 volts. That 6 modules unification is called a cluster. Combining 9 cluster creates a power of 1MW with 2 MWh energy capacity. The battery costs reach 170000$ with 16000 kgs mass. Additional equipment brings the cost 240000$.

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