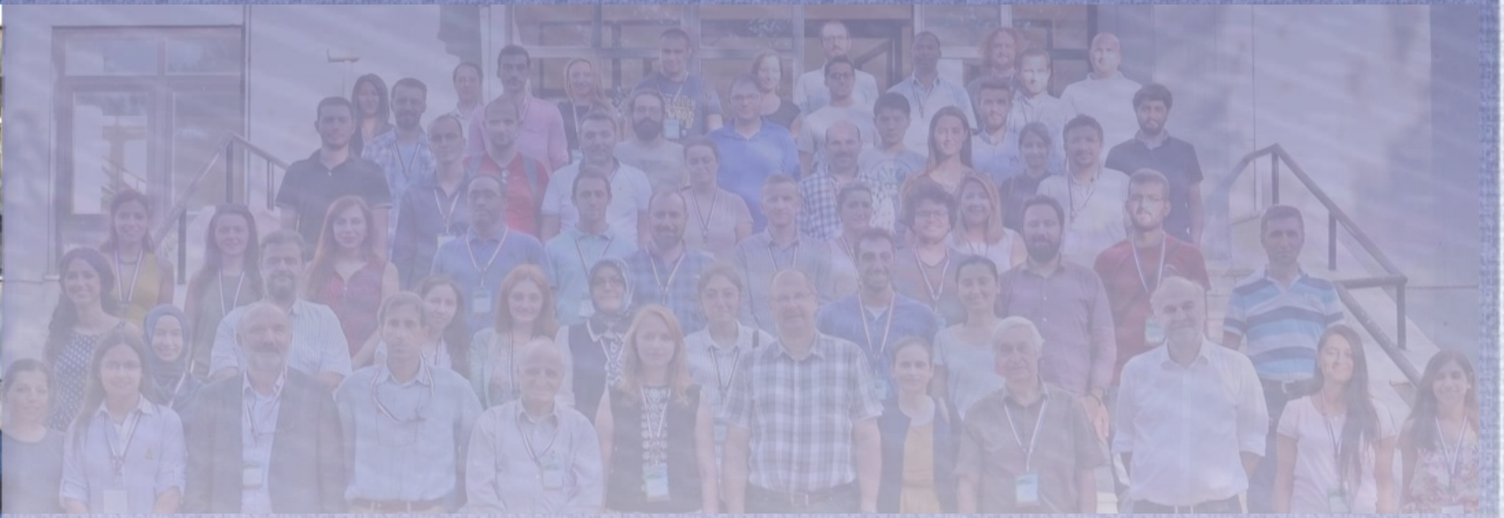
1st International Symposium on Materials for Energy Storage and Conversion

11-13 September 2019, Akyaka

7-9 September 2015, METU, Ankara

Book of Abstracts/Proceedings



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mESC-IS 2021

The First International Symposium on Materials for Energy Storage and Conversion

Edited by
Ezgi Onur Şahin and Tayfur Öztürk

7-9 September 2015

Convention Center-METU, Ankara, Turkey

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PREFACE

This activity has stemmed from very successful similar activities organized in past years with the involvement of two **COST** Actions namely **MP1103** Nanostructured Materials for Solid Hydrogen Storage and **MP 1004** Hybrid Energy Storage Devices and Systems for Mobile and Stationary Applications**.** Such activities included Barcelona meeting on "Energy Storage in the Grid" and "IDHEA" in Nantes**.**

This initial idea has evolved into the current symposium where it now encompasses three activity areas; namely solid state hydrogen storage (SSHS), batteries and fuel cells. The symposium, as formed, have a fair balance of plenary sessions covering cross-cutting issues and the state of the art reviews as well as parallel sessions with contributed papers and poster presentations.

This symposium just follows a summer school on energy materials taken place in the Department of Metallurgical and Materials Engineering, METU. This had two bases; one comprised overviews on such topics as SSHS, supercapacitors, batteries and fuel cells. The other comprised material characterization techniques with an emphasis on in-situ experiments. It is my opinion and I think our colleagues who made this school possible would agree that it was well-worth their effort. 80 trainees from a variety of countries in different disciplines, some early in their graduate study, some quite experienced have benefitted greatly from this experience.

As organizing committee, it is our intention to continue the summer school in coming years. Also we have reached the decision that we shall continue the symposium with two years interval, next symposia to be taking place in 2017 in Cappadocia.

This event was made possible with the contribution of COST action MP1103 both to the summer school and the symposium, which we gratefully acknowledge. We also acknowledge the support of our respective universities in a number of ways. The symposium is made by all of us, from new researchers who are going to make their first presentation, not counting those whose wealth of knowledge all of us are going to benefit.

Tayfur Öztürk
on behalf of mESC-IS Organizing Committee

Organisation

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^{m}ESC-IS 2015 Program

Cultural and Convention Center
Middle East Technical University
Ankara

September 7th Monday 2015

08:30 - 17:30	Registration		
09:00 - 09:40	Opening Session		
	Hall A **Chair: Amelia Montone**		
09:40 - 10:20	The role of hydrogen in the future energy economy (page 17) **Andreas Züttel**		
10:20 - 10:45	Coffee Break		
	Hall A **Chair: Andreas Züttel**		
10:45 - 11:15	Solid state hydrogen storage: New materials and technologies from COST Action MP1103 (page 18) **Amelia Montone**		
11:15 - 11:45	Transition metal nanoparticles in low temperature catalysis (page 19) **Saim Özkar**		
11:45 - 12:15	Hydrogen & fuel cell research in Turkey (page 20) **Mehmet Süha Yazıcı**		
12:15 - 12:45	Hydrogen containing solids - new perspectives (page 21) **Torben R. Jensen**		
12:45 - 14:00	Lunch Break		
	Hall A **Chair: Luca Pasquini**	**Hall B** **Chair: Şaban Patat**	**Hall C** **Chair: İnci Eroğlu**
14:00 - 14:30	Kinetics and thermodynamics of hydrogen sorption in Mg-Ti nanoclusters (page 22) **Luca Pasquini**	Revealing surface species on electrochemical cell electrodes in operando (page 27) **Sarp Kaya**	Structure, phase transitions, dielectric and transport properties of Bismuth Vanadate-based BILAMEVOX ionic conductors (page 32) **Ekaterina Politova**
14:30 - 14:50	Magnesium hydrides and their phase transitions (page 23) **Vaclav Paidar**	High capacity graphene/A-MnO_2 nanocomposite cathodes for Li-O_2 batteries (page 28) **Hatem Akbulut**	New mixed electron-proton conducting $Ln_{6X}Zr_XMoO_{12+\delta}$ (Ln=La, Nd, Sm, Gd, Dy, Ho) materials (page 33) **S.N. Savvin, A.V. Shlyakhtina, I.V. Kolbanev, L.G. Shcherbakova, J.C. Ruiz-Morales and P. Nunez**

14:50 - 15:10	Correlation between the microstructure and hydrogen storage properties of nanocrystalline Mg-based alloys processed by different severe plastic deformation routes (page 24) **Adam Revesz and Marcell Gajdics**	Pseudo capacity properties of titanate nanotubes and their high rate capabilities as a Li-ion battery anode (page 29) **Alp Yurum, Miad Yarali, Emre Bicer and Selmiye Alkan Gürsel**	Effect of hydrophobic nanoparticles on PEM fuel cell performance (page 34) **Gökçe S. Avcıoğlu, Berker Fıçıcılar and İnci Eroğlu**
15:10 - 15:30	Thermal Plasma Synthesis of Mg-Ni Nanoparticles (page 25) **Burak Aktekin, Gülhan Çakmak and Tayfur Öztürk**	Lithium super ionic conduction in $LiBH_4$/Silica nanocomposites (page 30) **Peter Ngene, Suwarno Suwarno, Didier Blanchard and Petra de Jongh**	Stacking of the direct borohydride/peroxide fuel cell system by the solution distribution network (page 35) **Merve Gördesel, Göksel Günlü, Ayşe Elif Şanlı and Bekir Zühtü Uysal**
15:30 - 15:50	H_2 real gas effect simulation in a non-continous single stage AB_2 compressor (page 26) **Andres R Galvis, Leardini Fabrice, Julio Bodega, Jose R Ares and Jose Francisco Fernandez**	Multiscale modelling efforts to reconcile diverse experimental observations on lithiation of $LiFePO_4$ cathodes (page 31) **Oncu Akyildiz, Aziz Abdellahi, Rahul Malik, Gerbrand Ceder and Katsuyo Thornton**	Improving the performance of direct borohydride/peroxide fuel cell system by the modification of anode and cathode (page 36) **Ayşe Elif Şanlı, Merve Gördesel, Göksel Günlü and Bekir Zühtü Uysal**
15:50 - 16:15	Coffee break		
	September 7th Monday 2015		
16:15 - 16:45	**Hall A** An optical analysis of the hydrogen permeation properties of Pd-based alloys (page 37) **Bernard Dam**		
	Hall A **Chair: Bernard Dam**	**Hall B** **Chair: Kadri Aydınol**	**Hall C** **Chair: Yüksel Kaplan**
16:45 - 17:05	Ternary hydrogen seperation membranes via combinatorial approach (page 38) **Fatih Pişkin and Tayfur Öztürk**	NaSbSn compound as negative material for Na cells at room temperature (page 42) **Milena Martine, Mathilde Bouchard, Franziska Thoss, Grzegorz Parzych, Juergen Eckert and Lars Giebeler**	Polybenzimidazole/silica hybrid membranes for high temperature PEM fuel cells (page 46) **Yilser Devrim, Huseyin Devrim and Inci Eroglu**
17:05 - 17:25	New insights on deformation/decomposition mechanisms of $KAlH_4$ (page 39) **Jose Ramon Ares, Junxian Zhang, Thibault Charpentier, Fermin Cuevas and Michel Latroche**	SnO_2/pyrolyzed bacterial cellulose composites as anode materials for Na-ion battery (page 43) **Burcu Dursun, Taner Şar, Meltem Akbaş and Rezan Demir-Çakan**	Modeling of polymer electrolyte membrane fuel cell and sensitivity analysis (page 47) **Dilara Gülçin Çağlayan, Berna Sezgin, Yılser Devrim and İnci Eroğlu**
17:25 - 17:45	In-situ raman study of H-> D exchange in Υ-Mg $(BH_4)_2$ (page 40) **Olena Zavorotynska, Stefano Deledda, Guanqio Li, Motoaki Matsuo, Shin-Ichi Orimo and Bjorn Hauback**	An aqueous rechargeable sodium battery cathode based on $NaFePO_4$ for large scale energy storage systems (page 44) **Serkan Sevinc, Burak Tekin and Rezan Demir Cakan**	High proton conductive PVA/PAMPS/Triazole composite membrane for PEMFC PEM-membrane (page 48) **Mustafa Erkartal, Seyma Dadı, Hakan Usta, Murat Çıtır and Ünal Şen**

17:45 - 18:05	NMR studies of molecular dynamics in complex metal borohydrides (page 41) **Anton Gradišek**	Improved lithium-sulfur batteries by preventing Li_2S formation (page 45) **Elif Ceylan Cengiz and Rezan Demir Çakan**	Modelling of PEM water electrolysis and determining operating parameters for different anode catalysts (page 49) **Mehmet Fatih Kaya and Nesrin Demİr**

September 8th Tuesday 2015	
	Hall A **Chair: Hiroshi Inoue**
09:00 - 09:30	Metal hydrides in batteries and semiconducting devices (page 50) **Dag Noréus**
09:30 - 10:00	TiNi-based intermetallic compounds for Ni-MH batteries: challanges and opportunities (page 51) **Fermin Cuevas**
10:00 - 10:30	Nanostructured metal hydrides for hydrogen storage and metal hydride batteries: the role of magnesium (page 52) **Volodymyr Yartys**
10:30 - 11:00	Coffee Break
	Hall A **Chair: Yury Gogotsi**
11:00 - 11:30	Properties of carbons in electrochemical capacitors involving various types of electrolytes (page 53) **François Béguin**
11:30 - 12:00	Lithium-ion batteries: from conception to development and beyond (page 54) **Rachid Yazami**
12:00 - 12:30	Updates on Battery 500 project: collaborative research with ASELSAN (page 55) **Ho-Cheol Kim**
12:30 - 15:30	Lunch Break **Poster Sessions** **Exhibition Hall**
	Poster Session: SS Hydrogen Storage 12:30- 15:30 September 8th Tuesday 2015
	Hydrogen adsorption on Au@Pd nanoparticles: a first principles study (page 56) **Mario Sandoval, Romina Luna, Aline Pereira, Estela González, Paula Jasen, Miranda Caetano and Alfredo Juan**
	Structure of TiFe alloy synthesized by ball milling (page 57) **Bilel Hosni, Chokri Khaldi, Omar Elkedim and Nouredine Fenineche**
	Optimization of properties of sprayed In_2O_3 semiconductor: effect of precursor's molarity (page 58) **Hamza Bendjedidi, Abdallah Attaf, Hanane Saidi, Adel Bouhdjar, Youcef Benkhetta, Wafa Bounif, Imen Bouhaf Kherkhachi and Rahil Azizi**
	Production of carbon encapsulated metal nanoparticles by spark discharge generator (page 59) **Pelin Livan, Cavit Eyövge and Tayfur Öztürk**
	Hydrogen as an energy carrier: artificial neural network system proposal for the storage of hydrogen in MOFs (page 60) **Zeynep Yıldız**
	Hydrogen storage in the gas discharge microelectric devices with porous zeolite cathodes (page 61) **Kıvılcım Köseoğlu and Bahtiyar Salamov**
	Numerical study of hydrogen purification by filtering through a metal hydride bed (page 62) **Valerij Artemov, onstantin Minko and Georgij Yan'Kov**
	An evaluation of mechanical properties of nanostrucutred Al alloy processed by SPD (page 63) **Aferdita Priftaj Vevecka, and Urim Buzra**
	DFT investigation of AlH_3 polimorfs – electronic structure quide to the hydrogen storage applications (page 64) **Milijana Savić, Jana Radaković and Katarina Batalović**

	Computational Determination of Endohedral Hydrogen Storage Capacity of Small Boron Nitride Nanocages (page 65) **Armağan Kinal and Sinan Sayhan**
	Charge/discharge performance correlated to magnetic clusters on metal hydride surfaces (page 66) **Yang Shen, Dag Noréus, Björn Skårman, Hilmar Vidarsson and Sofia Kontos**
	Use of Electro-deoxidation in the Synthesis of Hydrogen Storage Alloys (page 67) **Nurten Başak Hatırnaz, Duygu Özdemir and Mustafa Anik**
	A DFT study on electronic properties of MgH_2 with charged vacancies (page 68) **Francisco Gaztañaga, Romina Luna, Paula Jasen and Alfredo Juan**
	Underground hydrogen storage in geological formations: a techno-economic analysis (page 69) **Ejaz Gül**
	Exhibition Hall **Poster Session: Batteries and Supercapacitors 12:30- 15:30 8 September 2015**
	Anomaly in the electronic structure of the NaxCoO$_2$-y cathode as a source of its step-like discharge curve (page 70) **Jannina Molenda**
	An Oxygen Cathode Embedded with a Bi-functional Catalyst to Enhace the Electrochemical Performance of Lithium Air Batteries (page 71) **Mehmet Nurullah Ates, Sanjeev Mukerjee and K.M. Abraham**
	Free standing flexible graphene cathodes for Li-air batteries (page 72) **Seyma Ozcan, Tugrul Cetinkaya, Mahmud Tokur, Hasan Algul and Hatem Akbulut**
	High reversible Si/graphene composite anodes for Li-on battery (page 73) **Mahmud Tokur, Seyma Ozcan, Hasan Algül, Tugrul Cetinkaya, Mehmet Uysal and Hatem Akbulut**
	The effect of $LiBF_4$ salt concentration in EC-DMC based electrolyte on the stability of nanostructured $LiMn_2O_4$ cathode (page 74) **Şeyma Karaal, Hilal Köse, Ali Osman Aydın and Hatem Akbulut**
	Pt/Bi_2O_3 catalysts for rechargeable Lithium-air batteries (page 75) **Mehmed Selim Çögenli, Tansel Şener, Dino Tonti and Ayşe Bayrakçeken Yurtcan**
	Effect of surface treatment with boiled alkaline solution on electrochemical properties of ZrNi alloy electrode (page 76) **Akihiro Matsuyama, Hironori Mizutani, Takumi Kozuka and Hiroshi Inoue**
	$VO_2(B)$ as anode material for aqueous Li-ion batteries and as a catalyst for hydrogen storage material MgH_2 (page 77) **Sanja Milošević, Nikola Cvjetićanin, Luca Pasquini, Radojka Vujasin, Igor Milanović, Sandra Kurko and Jasmina Grbović Novaković**
	The electrochemical properties of doped $LiMn_xM_{(1-x)}PO_4$ synthesized by spray pyrolysis (page 78) **Mehmet Kadri Aydınol and Esin Akça**
	Electrochemical properties of $LiCo_{1-x}B_xO_2$ cathodes for Li-ion batteries (page 79) **Erdinc Oz, Serkan Demirel, Emine Altin, Sevda Avci and Serdar Altin**
	Nickel foam-supported porous Sn-Cu electrode for Li-ion batteries (page 80) **Hasan Algül, Mahmud Tokur, Seyma Ozcan, Mehmet Uysal, Tugrul Cetinkaya, Ahmet Alp and Hatem Akbulut**
	Al stabilized $Li_7La_3Zr_2O_{12}$ solid electrolytes for all-solid state Li-ion batteries (page 81) **Kamil Burak Dermenci, Eren Çekiç and Servet Turan**
	A new coating for improving the electrochemical performance of cathode materials (page 82) **Makhonina Elena, Medvedeva Anna, Dubasova Valeriya, Volkov Vyacheslav and Politov Yurii**
	Li-Al-Mg as potential anode material for Li-ion batteries (page 83) **Grzegorz Parzych, Miléna Martine, Franziska Thoss, Lars Giebeler and Jürgen Eckert**
	Low-density silicon thin films as anodes in lithium-ion batteries (page 84) **M. Taha Demirkan, Lynn Trahey and Tansel Karabacak**
	Production and characterization of free-standing ZnO/SnO_2/MWCNT ternary nanocomposite Li-ion battery anode (page 85) **Hilal Köse, Şeyma Karaal, Ali Osman Aydin and Hatem Akbulut**
	$LiFePO_4$/C nano plates sythesis via ultrasound assisted precursor precipitation (page 86) **Şafak Doğu and Mehmet Kadri Aydınol**
	Silicon carbide derived carbon for energy storage applications (page 87) **Emre Kayali and Göknur Büke**

	Self-organization of titanate nanotubes on functionalized graphene as a novel hybrid electrode for lithium-ion batteries (page 88) **Anaguli Abulizi, Adnan Taşdemir, Selmiye Alkan, Veera Sadhu, Essam Jamil, Sajjad Ghobadi and Alp Yürüm**
	The effects of Ca and Nb co-doping on the electrochemical properties of $Li_4Ti_5O_{12}$ as anode material for lithium ion battery (page 89) **Fatma Kilic Dokan, Halil Sahan and Saban Patat**
	Preparation and characterization of $Na_{0.44}MnO_2$ cathode materials for novel Na-ion batteries (page 90) **Serkan Demirel, Erdinç Öz, Emine Altın, Serdar Altın and Sevda Avcı**
	Cost-effective cathode material for Na-ion batteries - $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ (page 91) **Dominika Baster, Piotr Trzaska, Łukasz Kondracki and Janina Molenda**
	Synthesis of hydrothermal carbon/SnO_2 anode materials for Na-ion batteries (page 92) **Ayşen Zerey, Burcu Dursun and Rezan Demir Çakan**
	Investigation of the concentration effect of V(V) ion on vanadium redox battery system by cyclic voltammetric and electrochemical impedimetric methods (page 93) **Metin Gençten, Hürmüs Gürsu and Yücel Şahin**
	Free standing polyaniline/CNT electrodes and their electrochemical performance (page 94) **Dilek Çakıroğlu and Fevzi Çakmak Cebeci**
	Capacitive energy storage with carbon aerogel, carbon xerogel and their polypyrrole composites (page 95) **Meryem Samancı, Elif Daş and Ayse Bayrakceken Yurtcan**
	Carbon nanotube - conducting polymer electrodes for electrochromic supercapacitors (page 96) **Recep Yüksel, Ali Çırpan and Hüsnü Emrah Ünalan**
	CuO/graphene oxide nanocomposite for supercapacitors (page 97) **Gamze Bozkurt, Elif Daş, Ayse Bayrakçeken Yurtcan and Abdulkadir Özer**
	Carbon nanotube-cobalt oxide nanocomposites for high performance supercapacitors (page 98) **Mete Batuhan Durukan, Recep Yüksel and Hüsnü Emrah Ünalan**
	Binder free direct hydrothermal growth of $Zn_xNi_{3-x}O_4$ as superior electrode material for supercapacitor applications (page 99) **Kush Upadhyay, Rodrigo Della Noce, S. Eugénio, R.G. Duarte, T. Moura E Silva, M.J. Carmezim and M.F. Montemor**
	Electrochemical synthesis of poly(1-(chrysenyl)-2,5-di(2-thienyl)-1H-pyrrole-co-pyrrole) for supercapacitor applications (page 100) **Hakan Görçay, İlhami Çelik and Yücel Şahin**
	Exhibition Hall **Poster Session: Fuel Cells and Electrolysers 12:30- 15:30 September 8th Tuesday 2015**
	Performance of stainless steel 316L electrodes with modified surface to be used in alkaline water electrolyzers (page 101), **María Lavorante and Juan Isidro Franco**
	Order-disorder high temperature phase transformation in $La_{5.5}WO_{11.25}$ proton conducting phospor (page 102) **Stanislav N. Savvin, A.V. Shlyakhtina, D.A. Belov, A.N. Shchegolikhin, I.V. Kolbanev, O.K. Karyagina and L.G. Shcherbakova**
	Comparison of two different catalyst preparation methods for graphene nanoplatelet supported platinum catalysts (page 103) **Elif Daş, Ayse Bayrakceken Yurtcan, Selmiye Alkan Gursel and Lale Isikel Sanli**
	Preparation of graphene nanoplatelet supported platinum catalysts by supercritical carbon dioxide deposition (page 104) **Elif Daş, Ayse Bayrakceken Yurtcan, Selmiye Alkan Gürsel and Lale Isikel Sanli**
	Durability of carbon/conducting polymer composite supported Pt catalysts prepared by supercritical carbon dioxide deposition (page 105) **Gamze Bozkurt, Fulya Memioğlu and Ayşe Bayrakçeken Yurtcan**
	Modeling and sensitivity analysis of high temperature PEM Fuel cells by using comsol multiphysics (page 106) **Berna Sezgin, Dilara Gülçin Çağlayan, İnci Eroğlu and Yılser Devrim**
	Utilization of polystyrene/SiO_2 core-shell particles covered with PDMS as superhydrophobic material in MPL of PEM fuel cells (page 107) **Ayşenur Öztürk and Ayşe Bayrakçeken Yurtcan**
	Superhydrophobic polydimethylsiloxane/silica coating for micro porous layer of PEM fuel cell and effects of calcination temperature on the wetting behavior (page 108) **Ayşenur Öztürk and Ayşe Bayrakçeken Yurtcan**
	Biomass-based carbon aerogels for oxygen reduction reaction in polymer membrane fuel cells (page 109) **Qiong Cai and Magda Titirici**
	Modeling the water transport in a PEM fuel cell cathode using COMSOL (page 110) **Volkan Işık, Gokce S. Avcioglu and Inci Eroglu**

	Some technological aspects of developing PEMFC stacks for unmanned aerial vehicles (page 111) **Bartłomiej Lis, Magdalena Dudek, Krzysztof Sornek, Mariusz Korkosz, Piotr Bogusz and Piotr Wygonik**		
	Semi-IPN system electrolyte membranes composed of sulfonated poly(arylene ether ketone) block copolymer and organosiloxane based hybrid network(page 112) **Kyuhyun Kang, Dukjoon Kim**		
	Fasteners selection for stacked direct borohdyride/peroxide fuel cell system (page 113) **Süleyman Kürşat Özden, Merve Gordesel, Melek Gülatik Sertkaya, Eyüp Şemsi Yilmaz, Belkıs Canan, Göksel GÜnlÜ and Ayse Elif Sanli**		
	Sputter deposited Au-Pd bimetallic catalysts for direct formic acid fuel cells (page 114) **Mehmed Selim Çögenli and Ayşe Bayrakçeken Yurtcan**		
	Investigation of mechanical properties of Crofer 22 APU sheets for SOFC applications (page 115) **Murat Canavar, Serkan Toros, Bora Timurkutluk and Yuksel Kaplan**		
	Investigation of thermal cycle properties of glass-ceramic sealant for SOFC (page 116) **Murat Canavar, Abdullah Mat, Selahhattin Celik, Bora Timurkutluk and Yuksel Kaplan**		
	Investigation of micro-tube solid oxide fuel cell fabrication parameters by produced phase inversion method (page 117) **Abdullah Mat, Berkan İşeri, Levent Furkan Kabasakaloğlu, Hakan Yaşar, Ufuk Küçük, Murat Canavar, Ömer Genç, Serkan Toros, Bora Timurkutluk, Sadik Kuliyev and Yüksel Kaplan**		
	Structure evolution and conductivity hysteresis in 3+/5+ niobates pyrochlores (page 118) **AV Shlyakhtina, D.A. Belov, A.B. Borunova and K.S. Pygalskiy**		
	Oxygen vacancy and interstitial transport in the pyrochlore- and fluorite-like $Pr_{2\pm x}Zr_{2\pm x}O_{7\pm\delta}$ (page 119) **João Carlos de Castro Abrantes, E. Gomes, A.V. Shlyakhtina, A.N. Shchegolikhin and L.G. Shcherbakova**		
	The phase formation and properties of Nd_2MoO_6 compounds, doped by Pb (page 120) **Valentina Voronkova, Ekaterina Orlova, Dmitrii Belov and Elena Kharitonova**		
	Fluorite-like compounds with high anionic conductivity in Nd_2MoO_6 - Bi_2O_3 system (page 121) **Elena Kharitonova, Valentina Voronkova, Dmitrii Belov and Ekaterina Orlova**		
	Synthesis of apatite type $La_{10-x}Sr_xSi_6O_{27-0.5x}$ powders for IT-SOFC using sol-gel process (page 122) **Yangzhou Ma, Nouredine Fenineche, Michel Moliere, Omar Elkedim and Hanlin Liao**		
	Combinatorial development of metal hydrides for thermal coupling of solid oxide fuel cells (page 123) **Doğancan Sarı, Fatih Pişkin, Volodymyr Yartys, Yener Kuru, Y. Eren Kalay, Tayfur Öztürk**		
	Development of anodes for direct oxidation of methane fuel in solid oxide fuel cells (page 124) **Yelda Akdeniz, Bora Timurkutluk and Cigdem Timurkutluk**		
	September 8th Tuesday 2015		
	Hall B **Chair: Dag Noreus**	**Hall A** **Chair: Rezan Demir-Çakan**	**Hall C** **Chair: Enrico Traversa**
15:30 - 16:00	Electrochemical properties of Ti-V-Cr-Ni alloy negative electrodes for use in Ni-MH battery (page 125) **Hiroshi Inoue**	Aqueous and Non-aqueous Electrolytes Lithium-Sulfur Batteries (page 130) **Rezan Demir-Çakan, Elif Ceylan Cengiz, Serkan Sevinç, Burak Tekin Ali Ata, Mathieu Morcrette and and Jean-Marie Tarascon**	Development of a commercial HT-PEM fuel cell stack module (page 135) **Thomas Steenberg, Hans Aage Hjuler, Hector Rodrigo Garcia, Yilsir Devrim, Huseyin Devrim and Omer Erdemir**
16:00 - 16:20	The importance of surface area for metal hydride electrodes (page 126) **Dag Noréus and Zhou Ye**	Critical Materials and Cell-level design considerations for high energy density and low cost lithium-sulfur battery (page 131) **Damla Eroğlu, Kevin Zavadil and Kevin Gallagher**	Electrochemical performance and long term stability of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ (y=0.2 and 0.8) cathode thin films prepared by liquid precursor deposition (page 136) **Can Sındıraç, Aligül Büyükaksoy, Sedat Akkurt and Viola I. Birss**

16:20 - 16:40	Activation of a AB_2 negative electrode material for Ni-MH battery (page 127) **Semra Tan, Yang Shen , Ezgi Onur-Şahin, Dag Noréus and Tayfur Öztürk**	Effect of Ag-coating on the electrochemical performance of $LiFePO_4$ cathode material (page 132) **Hüseyin Göktepe, Halil Şahan and Şaban Patat**	Investigation of micro-tube solid oxide fuel cell fabrication using extrusion method (page 137) **Abdullah Mat, Hakan Yaşar, Ufuk Küçük, Berkan İşeri, Levent Furkan Kabasakaloğlu, Murat Canavar, Uğur Çatık, Bora Timurkutluk, İbrahim Pamuk and Yüksel Kaplan**
16:40 - 17:00	The influence of the temperature on the electrochemical properties of the AB_5-type metal hydride anode (page 128) **Chokri Khaldi and Jilani Lamloumi**	Development and characterization of new layered cathode materials for Li-ion batteries (page 133) **Berke Pişkin and Mehmet Kadri Aydınol**	Utilization of anomalous oxygen reduction rate at hetero interface of $(La_{0.8}Sr_{0.2})CoO_{3-\delta}/(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$ for solid oxide fuel cell cathodes (page 138) **Ziya Çağrı Torunoğlu, Oktay Demircan, Y. Eren Kalay, Tayfur Öztürk and Yener Kuru**
17:00 - 17:20	Role of KOH in the hydrogen storage properties of Li-Mg-N-H system (page 129) **Gökhan Gizer, Claudio Pistidda and Martin Dornheim**	Magnetic interactions in Mn-based Li-ion batteries and the effects on the battery performance (page 134) **Serdar Altın, Ali Bayri, Erdinç Öz, Serkan Demirel, Emine Altın and Sevda Avcı**	Investigation of temperature distribution and performance on single SOFC stack with/without machined gas channels (page 139) **Esra Şanlı, Volkan Uysal, Murat Canavar, Abdullah Mat, Selahattin Çelik, Yüksel Kaplan, Bora Timurkutluk and Ömer Genç**
20:00	**Symposium Dinner**		

September 9th Wednesday 2015	
	Hall A **Chair: Detlef Stolten**
09:00 - 09:30	2D Carbides (Mxenes) for energy storage (page 140) **Yury Gogotsi**
09:30 - 10:00	Mesoporous MCM-41 material for hydrogen storage: A Review (page 141) **Yuda Yürüm**
10:00 - 10:30	Status and potential of PEM technology for transportation and the related hydrogen infrastructure (page 142) **Detlef Stolten**
10:30 - 11:00	Coffee Break
11:00 - 11:30	Development of renewable hydrogen energy systems (page 143) **İnci Eroğlu**
11:30 - 12:00	Chemically stable materials for the development of reversible solid oxide fuel based on proton conducting electrolytes (page 144) **Enrico Traversa**
12:00 - 12:30	Recent advances on micro-level modeling of solid oxide fuel cells (page 145) **Mahmut Mat**

12:30 - 14:00	Lunch Break		
14:00 - 14:30	Oxygen reduction kinetics on perovskite oxides in solid oxide fuel cells: Effects of dissimilar interfaces and surfaces (page 146) **Bilge Yıldız**		
	Hall C **Chair: Fermin Cuevas**	**Hall B** **Chair: Jose R. Ares**	**Hall A** **Chair: Bilge Yıldız**
14:30 - 14:50	Effect of the rare earth on the structural and hydrogen sorption properties of A_2Ni_7 (A= Y or Sn) (page 147) **Veronique Charbonnier, Michel Latroche, Junxian Zhang, Lionel Goubault and Patrick Bernard**	Tungsten disulfide nanoparticles as a medium for hydrogen storage (page 150) **Alex Laikhtman, Alla Zak, Hoi Ri Moon, Marius Enachescu and Meltem Sezen**	Effect of patterned catalyst layer on gas evolution behaviour in regenerative fuel cells (page 153) **Ömer Faruk Selamet, Shohji Tsushima, Shuichiro Hirai, Fukai Katsuyuki, Jao Ting-Chu and Takashi Sasabe**
14:50 - 15:10	Synthesis of A_2B_7 type hydrogen storage alloys in the molten salt (page 148) **Alanur Binal Aybar, Duygu Akmanbay and Mustafa Anık**	Synthesis of palladium incorporated MCM-41 via microwave irradiation and investigation of its hydrogen storage properties (page 151) **Ezgi Dündar Tekkaya and Yuda Yürüm**	Effects of fabrication parameters on the performance of solid oxide electrolyzer cell (page 154) **Hatice Korkmaz, Bora Timurkutluk and Cigdem Timurkutluk**
15:10 - 15:30	In-situ formation of Mg-Ni intermetallics by a two-step electrochemical technique (page 149) **İshak Karakaya, Fuat Erden and Metehan Erdoğan**	Decoration of graphene sheets by Pd/Al_2O_3 particle pairs: Synthesis, characterization and applications in hydrogen storage (page 152) **Zahra Gohari Bajestani and Yuda Yürüm**	Preparation and characterization of N-doped graphene as a metal free catalyst for the oxygen reduction reactions in acidic and alkaline media (page 155) **Edip Bayram, Gizem Yılmaz, Merve Bilge Adanalı and Sanjeev Mukerjee**
15:30 - 16:00	Coffee Break		

	Hall C **Chair: Volodymyr Yartys**	**Hall B** **Chair: Hatem Akbulut**
16:00 - 16:20	Preparation of carbon supported LiH and $LiNH_2$ nanoparticles (page 156) **Peter Bramwell, Krijn de Jong and Petra de Jong**	Electrochemical performance of silver coated $Li_{1.3}Mn_{0.666}Co_{0.167}Ni_{0.167}O_{2.4}$ cathode active material for rechargeable Li-ion batteries (page 159) **Halil Şahan, Şaban Patat, Fatma Kılıçdokan, Burcu Özdemir and Ahmet Ülgen**
16:20 - 16:40	Characterization of the electronic structure of transition-metal catalysts by magnetic resonance spectroscopy (page 157) **Özlen Erdem**	Production and characterization of silicon particles with nanowired surfaces for secondary Li-ion battery anode (page 160) **Burcu Kayıplar and Mehmet Kadri Aydınol**
16:40 -17:00	Hydrogen decrepitation of Mg rich intermetallics (page 158) **Altekin Aydınlı, Burak Aktekin and Tayfur Öztürk**	W-doped $LiCoO_2$: Effect of different starting chemicals, doping contents and additional doping elements (page 161) **Atıl Büyükburç and Mehmet Kadri Aydınol**
17:00 -17:30	**Closing Session** **Hall A**	

ABSTRACTS

The Role of Hydrogen in the Future Energy Economy

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The storage of renewable energy is the greatest challange for the transition from the fossil aera to a sustainable future. The world economy is growing due to the spreading industrialisation and global population will saturate at approx. 10 billion people in 2050. Due to the economic growth worldwide the energy demand will tripple in the comming 35 years. This is only possible if renewable energy i.e. solar energy becomes the major source of energy and if the materials cycles will be closed in the near future. During the last century the industrialized parts of the world operated based on mining resources and depositing waste with the consequence of a global shortage in resources (Fig. 1).

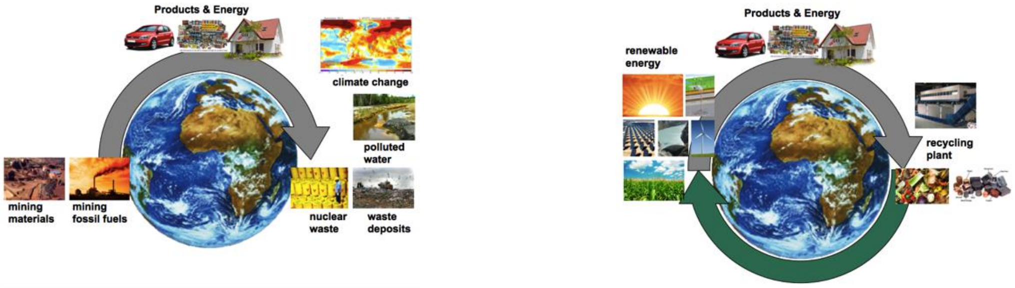

Fig. 1 Open cycle established during industrialization (left) and closed cycle based on renewable energy and complete recycling of materials, i.e. no deposition (right)

Hydrogen produced from renewable energy leads to a closed cycle, because the water relesed from the combustion condenses in the atmosphere. The challange in the large scale application of hydrogen is the storage with a high gravimetric and volumetric density. based on todays knowledge a hydrogen storage is limited to about 20 mass% and 70 kg/m^3. Therefore the maximum energy density of hydrogen based energy storage is limited to approx. 50% of the energy density in fossil fuels. The main reason is that the host material of the hydrogen storage is not oxidized in the combustion. In order to achiev a comparable energy density of fossil fuels, hydogen has to be stored in hydrocarbons (synthetic fuels), where the CO_2 is extracted from the atmosphere. The latter requires energy in order to increase the concentration from 400 ppm to pure CO_2, corresponding about 5% of the heating value of the hydrocarbon. However, the process working close to the thermodynamic limit is not know yet. Furthermore, the reduction of CO_2 to hydrogen is based on the Sabatier to Methane or on the rewersed water gas shift reaction and Fischer-Tropsch synthesis to an unspecific hydrocarbon. The surface of metal hydrides can offer new reaction paths and catalytic centers with atomic hydrogen.

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Solid state hydrogen storage: new materials and technologies from COST Action MP 1103

Amelia Montone

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Hydrogen storage is one of the main bottlenecks to implement a low-carbon energy system based on hydrogen. Solid state hydrogen storage offers enormous advantages (safety, high Hydrogen volumetric density) compared to other storage methods i.e. gas and liquid storage. However, the main drawbacks are too thermal stability, low Hydrogen gravimetric density and stability of the system due to the effects of hydrogen cycling that should be improved prior to implementation.

The European Action MP1103 “Nanostructured Materials for Solid State Hydrogen Storage”, supported by the intergovernmental framework for European Cooperation in Science and Technology (COST), deals with the future of energy storage and aims to set up a competitive and coordinated network capable to define new and unexplored ways for Solid State Hydrogen Storage (SSHS) by innovative and interdisciplinary research. COST Action MP1103 comprises 27 COST countries, 1 COST Near Neighbor Countries and 4 International Partner Countries, which altogether incorporate more than 260 researchers from different fields.

Four Working Groups activate the scientific debate and the consequent synergy:

- Synthesis of novel materials with optimized properties,
- High resolution and high sensitivity characterization of atomic level structure and microstructural features,
- Characterization of hydrogen storage properties both at the laboratory level and at the scale of prototype tanks,
- Computational modelling of processes relevant to SSHS.

The Action is focused on several lightweight nanostructured materials suitable to allow the commercial diffusion of the technologies related to the use of hydrogen for energy storage and energy transport. The material taken into account are widely considered as the best potential solution to the challenge of the Solid State Hydrogen Storage compatible with the technological constrains. The investigation of the performances of these materials and their chemical physical characterization are biased in order to satisfy all technological aspects necessary for the design of hydrogen storage tanks and to plan their realization on large scale.

Amelia Montone, Degree in Physics in 1984 (Rome University “La Sapienza”). From 1988 Researcher at ENEA, Research Centre of Casaccia, Rome. Research work has been on applications of electron microscopy methods to material science problems. In the last ten years her research is focused on synthesis, microstructural and thermal characterization on nanocomposite for hydrogen storage,. She has published more than 110 publications in international journals. Project scientific leader in national and European projects on hydrogen storage materials. ENEA scientific coordinator of Hydrostore-Industria 2015. Management board member of EERA-Joint Programme on Advanced Materials and Processes for Energy Application (AMPEA), Chair of the COST Action MP1103 (Nanostructured materials for solid-state hydrogen storage), 25/10/2011-25/10/2015, President of SISM (Italian Society for Microscopical Sciences) from 2008 to 2013. E-mail: amelia.montone@enea.it

Transition metal nanoparticles in low temperature catalysis

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Thanks to the large fraction of surface atom over the bulk [1], transition metal nanoparticles are much more active catalysts in many reactions than the larger particles [2]. However, transition metal nanoparticles are thermodynamically not stable against the aggregation [3], which causes to a rapid decrease in the catalytic activity. Therefore, metal nanoparticles need to be kinetically stabilized without affecting the catalytic activity [4]. Stable metal nanoparticles can be obtained by using suitable stabilizing ligands or supporting materials, without blocking the catalytically active surface sites. By this way, one can obtain highly active and long-lived metal nanoparticles catalyst. Designing the stabilizing ligand environment, it is possible to generate stable and yet catalytically active metal nanoparticles [5]. Tuning the activity versus stability by modifying the stabilizer enables us to generate metal nanoparticles, which can catalyze many reactions even at low temperature. Examples of room temperature hydrogen generation, hydrogenation, and dehydrogenation will be presented.

The first example is the acid induced catalytic hydrogenation of neat acetone [6]. Complete hydrogenation of acetone to 2-propanol can be achieved at 22 °C in the presence of Ir(0) nanoparticles plus hydrogen chloride which is formed from the hydrogen reduction of iridium(I) precursor $[(COD)\ IrCl]_2$.

The second example is the catalytic hydrogenation of aromatics by using ruthenium [7,8] and iridium [9] nanoparticles at room temperature. Particularly, ruthenium(0) nanoparticles encapsulated within the supercages of zeolite Y show superb catalytic activity in hydrogenation of neat benzene and other aromatics such as toluene, xylene and mesitylene at room temperature [7]. Furthermore, reducing the particle size of porous support materials from micrometer to nanometer regime leads to an enormous increase in catalytic activity of guest metal nanoparticles.

The hydrogen generation from ammonia borane can be achieved at room temperature by using transition metal(0) nanoparticles, which are stabilized by suitable ligands or supporting materials with large surface area [10]. Also the results of the most recent studies on the catalytic use of metal(0) nanoparticles in the room temperature hydrolytic dehydrogenation of ammonia borane will be presented.

Rhodium(0) nanoparticles supported on silica nanospheres with particles size smaller than 25 nanometer are found to be highly active catalyst in hydrogen generation from the methanolysis of ammonia borane at room temperature. Rhodium nanoparticles can be in situ generated from the reduction of rhodium(III) ions impregnated on nanosilica during the methanolysis of ammonia borane at room temperature. As shown in Figure 1, the formation of rhodium(0) nanoparticles can be followed by monitoring the hydrogen gas generated during the catalytic methanolysis of ammonia borane, which is used as reporter reaction.

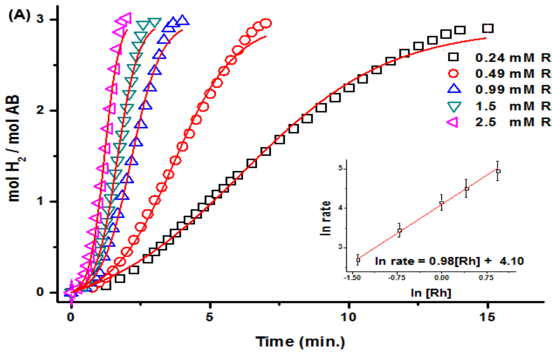

Figure 1. Plots of mol H_2 evolved per mole of ammonia borane versus time for the methanolysis of 200 mM ammonia borane in different metal concentrations at 25.0 ± 0.5 °C. Inset: Plot of hydrogen generation rate versus the concentration of rhodium (both in logaritmic scale.).

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S Saim Özkar was born in Elâzığ in 1949, completed his undergraduate study in chemical engineering at the Technical University of Istanbul in 1972, and then worked for two years in industry. He received his Ph.D. in inorganic chemistry at the Technical University of Munich, Germany in 1976 before joining the Department of Chemistry, Middle East Technical University as an Assistant Professor in 1979, where he is now a Full Professor. He spent one year at the Max Planck Institute in Mülheim as Alexander von Humboldt-Foundation Scholar in 1986, 2 years at University of Toronto as visiting professor in 1988-1990, and 9 months at Colorado State University as Fulbright Fellow in 2000. His current research interests involve the transition metal nanoparticles; synthesis, characterisation, and catalytic applications in hydrogen generation, hydrogenation, and oxidation.

Hydrogen & Fuel Cell Research in Turkey

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There has been growing worldwide interest in renewable hydrogen economy and fuel cell technology, as reflected in the dramatic increase in public and private sector product introductions. This presentation will review Turkish state on hydrogen and fuel cell research.

The Turkish Scientific and Technical Research Council (TUBITAK) has been the main driver for hydrogen and fuel cell research at academic and industrial level in Turkey. More than $15 million has been spent on hydrogen and fuel cell research in the last 10 years. Last two years, hydrogen and fuel cell research is identified as energy priority area and funded under what is called 1003. Currently, universities, companies and research centers are supported by the program. Research arm of TUBITAK, Marmara Research Centre (MRC) has been working on new technology development with emphasis on fuel cell system prototypes, transportation applications and gasification and reforming research. One of the state of the art research carried by the MRC is development of a fuel cell Combined Heat and power (CHP) system in which a 5 kWe fuel cell system is combined with 30 kWth reformer system. Further continuation of this research is expected through Renewable Energy Directorate. Team at MRC has been working on enzymatic fuel cell for future aspect. MRC also involved with hydrogen production through gasification processes as hydrogen, liquid fuels being final products.

The Turkish Ministry of Energy supported the International Centre for Hydrogen Energy Technologies (ICHET) through a trust fund administered by UNIDO to implement hydrogen and fuel cell demonstrations in Turkey until Renewable Energy Directorate took over the Center. ICHET acted as a catalyst to involve Turkey in international hydrogen and fuel cell platforms for the duration of its activities. ICHET took a proactive role by supporting pre-feasibility studies on various technologies before turning feasible proposals into full scale projects. A few to name are: “Hydrogen Bus Pilot Project for Istanbul”; “Market Potential for Hydrogen Production from Hydrogen Sulphide in Black Sea”; “Hydrogen Generation Using City Wastes”; and “Process for One Stage Production of $NaBH_4$ from Borax”. On the demonstrations side, universities, small and big companies, public entities have all been involved in these projects for widespread acceptance of hydrogen technologies. One of the most successful of these was establishment of Turkey’s first hydrogen filling station in Istanbul. ICHET provided comprehensive support for R&D activities involving both industry and academia. The purpose of this approach was to turn academic R&D programs and expertise into product development and industrial commercialization. One example was to produce 3 kW fuel cell systems in Turkey. Within this project, a consortium specially formed to develop a 3 kW fuel cell. Partners from academia, industry and R&D organizations have involved each having individual expertise in the areas of catalysts, membranes, system assembly, electronics and control.

Several Turkish universities have engineering faculties with research programs on hydrogen and fuel cell subjects. METU, ITU, Nigde University, YTU, GTU, Sabancı University are a few to name but there are many others getting into wider involvement.

Corporate activities are very limited, and even though there is involvement with gas production companies to produce hydrogen, fuel cell development is restricted to only a few companies.

For acceptable level of achievements on the subject, there has to be coherent action by various organizations (Ministries of Energy, Defense, and Transportation, universities, research centers, companies) to implement effective policies for the benefit of Turkey. A “National Hydrogen Energy Roadmap” would encourage nationwide involvement in this aspect. Past, current and future of hydrogen and fuel cell activities in Turkey will be discussed in this presentation.

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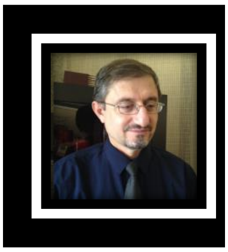

Assoc. Prof. Mehmet Suha Yazici is an electrochemical engineer with over 20 years of academic and industrial research experience in the area of electrochemical energy conversion (batteries and fuel cells). In addition to his scientific research, he had worked on project and program management for new product development and collaborative research with membership to The Electrochemical Society (ECS), the International Society of Electrochemistry (ISE) and International Association of Hydrogen Energy (IAHE). Currently working at MRC Energy Institute and acting as country representative for the International Society of Electrochemistry (ISE).

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Hydrogen containing solids – new perspectives

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Hydrogen is recognized as a potential and extremely interesting energy carrier, which can facilitate efficient utilization of unevenly distributed renewable energy [1]. Here we report an overview of our recent research results within new light weight hydrogen containing materials: (***i***) Mechano-chemical synthesis of novel metal borohydrides, (***ii***) Systematic trends in structure and composition, (***iii***) New types of hydrides and (***iv***) Studies of their properties for hydrogen storage, as ion conductors or towards novel multi-functional materials.

We have recently explored mechano-chemical and solvent based methods for synthesis of new hydrides and have discovered new series of bi- and tri-metallic borohydrides, typically containing alkali metals and di- or tri-positive cations. Apparently, the structural complexity increase with the increasing size of the alkali metal and also the tendency to form mixed borohydride-halide compounds and ternary chlorides increase [2, 3]. Both synthesis and hydrogen release and uptake reactions often occur via several coupled chemical reactions, which can be utilized to stabilize boron in the solid state. A fascinating structural chemistry is discovered within metal borohydrides, e.g. interpenetrated 'MOF-like' networks or zeolite-type structures with up to 30% 'empty' space in the porous structures with chemical bonding ranging from ionic to more covalent and containing composite polynuclear complex anions in the solid state [3]. The most open-structured borohydrides with 30% 'empty' space in the porous structures, γ–$Mg(BH_4)_2$, M = Mg or Mn, which additionally can physisorp molecular hydrogen, e.g. γ–$Mg(BH_4)_2\cdot{\sim}1H_2$, $\rho_m = {\sim}18$ wt% H_2 [4]. This is the first hydride storing both chemically bonded hydrogen (14.9 wt% H_2) and additionally physisorped molecular hydrogen.

Recently, we stabilized NH_4BH_4 with extreme hydrogen density, 24.5 wt% H_2, as $NH_4Ca(BH_4)_3$ (15.7 wt% H_2) with higher stability and decomposition temperature, T_{dec} = 97 °C [5]. A number of other ammonium metal borohydrides have also been investigated.

Recently, a series of new fast Li-ion conductors, $LiM(BH_4)_3Cl$, M = La, Ce, Gd, Pr or Nd [6,7], which simultaneously store significant amounts of hydrogen was discovered. The high conductivity is due to unoccupied cation position around the large cubane like composite anions. DFT structural optimisation suggest that these compounds are stabilised by higher entropy rather than lower energy [6].

A series of 30 new complex hydride perovskite-type materials and new synthesis protocols involving rare earth elements was recently presented [5]. Photophysical, electronic and hydrogen storage properties was discovered along with trends in structural behaviour and may have 'multi-functionality'. In this view, homopolar hydridic di-hydrogen contacts arise as a potential tool to tailor crystal symmetries, hence merging concepts of molecular chemistry with ceramic-like host lattices. Furthermore, anion-mixing provides a link to the known ABX_3 halide perovskites. The new series of perovskite type metal borohydrides [5]. We conclude, that the chemistry of hydrides is very divers, towards rational design of multi-functional materials and that there is still room to discover the magic hydrogen storage material that can be the successor for gasoline.

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Torben R. Jensen

Torben received his Ph.D. degree in materials chemistry and did postdoctoral research at Risø National Laboratory and DESY, Hasylab, Hamburg. He became Assistant Professor (2000) and Research Associate Professor (2002) at the Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University. He was awarded a *Steno* research stipend (2002), a *Carlsberg* research stipend (2005) and a D. Sc. degree (2014). He published ~200 papers within synthesis, structural, physical and chemical properties of new inorganic materials and utilisation of synchrotron X-ray diffraction.

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Kinetics and thermodynamics of hydrogen sorption in Mg-Ti nanostructures

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Tuning the thermodynamics of hydride formation is a formidable materials science problem, yet the payback in case of success could be enormous. At the same time, it is desirable to achieve extremely fast kinetics of hydrogen (H) sorption. In this work, we focus on specific issues that may be effective for knowledge-based modification of the Mg-H system. We study two different Mg-Ti nanostructures grown by physical deposition techniques (Figure 1): i) Mg-Ti nanoparticles (NPs) by inert gas condensation (IGC) with two independent vapour sources, and ii) Mg (30 nm) / Ti (5nm) / Pd (5nm) three-layered nanodots (NDs) by molecular beam epitaxy (MBE) on substrates covered by nano-porous ultra-thin alumina masks.

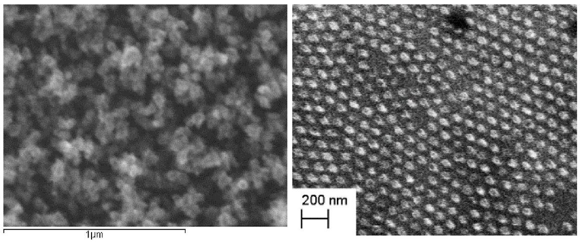

Figure 1. left: Mg-Ti NPs grown by IGC using two independent vapour sources; right: Mg/Ti/Pd three-layered NDs grown by MBE on porous ultra-thin alumina masks.

X-ray diffraction and electron microscopy show that, despite the immiscibility of Mg and Ti, Mg-Ti NPs nucleate and grow in the gas phase as a metastable *hcp* solid solution. After H-absorption, the solution decomposes into nanosized hydrides MgH$_2$ and TiH$_2$. The resulting nanophase material, characterized by the presence of many interfaces, exhibits excellent H-sorption kinetics (Figure 2), with reaction times as short as few hundred seconds even at the relatively low temperature of 250 °C. The thermodynamics, as determined by pressure-composition-isotherms and van't Hoff plot, shows no significant changes from that of bulk MgH$_2$.

Differently, small yet measurable thermodynamic changes are detected in Mg/Ti/Pd NDs. Optical hydrogenography permits to observe both the H-absorption and H-desorption isotherms at low temperature (Figure 3). With decreasing NDs size, from 300 to 50 nm, the equilibrium pressure increases and the van't Hoff plot suggests that the hydride formation enthalpy is reduced by about 5 kJ/mol H$_2$.

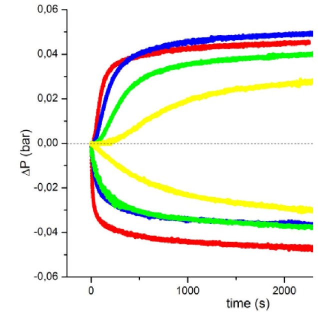

Figure 2. Isothermal pressure changes during H-sorption / in Mg-Ti NPs. The reaction speeds up with increasing temperature (from 205 to 250 °C in steps of 15 °C).

These size-dependent changes are discussed within the frame of an elastic constraint model [1], which takes into account the effect of a stiff MgO layer on the NDs lateral surface.

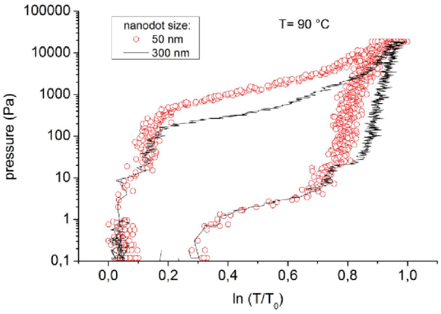

Figure 3. Hydrogenography on Mg/Ti/Pd nanodots of two different sizes.

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Magnesium hydrides and their phase transitions

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Magnesium hydride is a well known material with large hydrogen storage ability, its mass absorption capacity is 7.6 wt. %. However, there are major drawbacks as slow absorption kinetics or elevated decomposition temperature. Such undesirable behaviour is a consequence of strong Mg-H bonds in magnesium hydrides. It can be anticipated that the structures with higher energies are less stable and so more suitable for practical applications.

Three different crystal structures were reported for magnesium dihydrides: α-MgH_2 with rutile tetragonal structure at ambient conditions, β-MgH_2 with fluorite-type structure and γ-MgH_2 with orthorhombic structure, both latter structures arising at high pressure. While for the high-pressure phase β-MgH_2, the volume-per-formula is about 8.5% lower with respect to the reference α-MgH_2 phase at ambient conditions, the volume-per-formula is only about 1.4% lower for the γ-MgH_2 phase. The α-MgH_2 and γ-MgH_2 phases coexist between the pressures of 0 and 9 GPa. The β-MgH_2 phase appeared during compression at the pressure that lowered the volume-per-formula down by about 21% of the reference volume, but the β-MgH_2 phase persisted during decompression to the volume-per-formula that was 8.4% lower than the reference one. The number of magnesium nearest-neighbour hydrogen atoms in α-MgH_2 and in γ-MgH_2 is six in both structures what is directly related to only small differences among the volumes-per-formula. On the other hand, the number of magnesium nearest-neighbour hydrogen atoms in β-MgH_2 is eight indicating that the phase transition α to β is associated with a qualitative change of the magnesium-hydrogen bonding revealed by the magnesium atom coordination.

The distance between the hydrogen atom in an interstitial position and the neighbouring metallic atoms (H-M) varies with the interstitial site type. Assuming a hydride with the fluorite structure, with the lattice parameter a_f, the H-M distances are $a_f/2$ for the octahedral interstitial position and $a_f\sqrt{3}/4$ (about 0.433 a_f) for the tetrahedral interstitial position. The metallic atoms are in the fluorite structure on the atomic sites of the FCC lattice and the hydrogen atoms occupy the tetrahedral interstitial sites giving thus the MH_2 stoichiometry. When the hydrogen atom is put at the centre of the triangular metallic faces, the H-M distances further decrease to $a_f/\sqrt{6}$ (about 0.408 a_f). The number of the metallic nearest-neighbours decreases from 6 for the octahedral interstitial position, via 4 for the tetrahedral interstitial position, down to 3 for the planar triangular face. In fact, the latter case corresponds to the rutile hydride structure. For the constant formula-cell-volume of the MH_2 metallic dihydrade, the tetragonal rutile lattice parameter is about 0.909 a_f assuming that the c_r/a_r ratio is equal to 2/3, what is almost the case for αMgH_2, $c_r/a_r = 0.6686$. The H-M distances are then $(11/18\sqrt{2})\ a_r$ (about 0.432 a_r), i.e. about 0.393 a_f, that is even lower than $a_f/\sqrt{6}$ (about 0.408 a_f). Therefore, considering the transition from the rutile to fluorite structures and assuming the preservation of the formula-cell volume, the H-M distances is increased by about 10.2% (from about 0.393 a_f to 0.433 a_f).

When the metallic atoms in the fluorite structure stay at their sublattice and the hydrogen atoms from the planes alternating the metallic planes are shifted, the rutile topology can be formed. Assuming a constant per-formula-volume of the rutile and fluorite crystals, the lattice *a*-parameter of rutile is 1.2849 times larger than the ½<110> FCC vector what becomes the rutile *a*-parameter. Hence, to reach the correct rutile dimensions starting from the topological projection, the cubic FCC lattice has to be extended in the x- and y-directions about 28% and simultaneously compressed along the z-axis about 53%. This lattice deformation can be compared with the Bain path of the FCC-BCC transition where the in plane extension is only about 12% and the z-contraction about 29%. For the fluorite-rutile transition, these numbers are about twice larger.

Another way how the FCC-BCC transition can occur is Zener shear along the (111) FCC plane. The lattice uniaxial deformations additional to the Zener shear are much smaller than the Bain deformation carrying the whole structural transition. This is why the diffusionless martensitic transformations are realized by the shear deformations and not by triple uniaxial straining. It can be anticipated that a similar behaviour can be expected also in the case of the rutile-fluorite transition.

It is hence desirable to look for the ways how the basic rutile structure of MgH_2 could be transformed into the fluorite structure with better properties for hydrogen storage.

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Correlation between the microstructure and hydrogen storage properties of nanocrystalline Mg-based alloys processed by different severe plastic deformation routes

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Magnesium is considered as one of the most attractive hydrogen storage materials, mainly because of high storage capacity (7.6 wt.%), lightweight and low cost. Nevertheless, high thermodynamic stability, high hydrogen desorption temperature and relatively poor hydrogen absorption-desorption kinetics impedes the use of Mg in industrial applications. To improve the hydrogen storage properties of magnesium, nano-sized Mg powders have been produced by mechanical alloying. Among Mg-based alloys, binary Mg-Ni is the most remarkable due to its favorable thermodynamics.

In the present study ball-milled (BM) nanocrystalline Mg_2Ni powders were subjected to intense plastic straining by cold rolling (CR), high-pressure torsion (HPT) and equal-channel angular pressing (ECAP).

Morphology studies were performed on a FEI QUANTA 3D dual beam scanning electron microscope. Repeated dehydriding-hydriding cycles was carried out in a Sievert's-type apparatus. Local area X-ray diffraction (XRD) measurements were carried out on a Rigaku high resolution double crystal diffractometer with negligible instrumental broadening equipped with a fine focus rotating copper anode (Nonius, FR 591). The symmetrical Ge (220) primary monochromator produced monochromatic Cu Kα radiation. Diffraction patterns were registered by FUJI Imaging Plate (IP), BAS MS2025.

The recorded X-ray diffraction patterns have been evaluated by the Convolutional whole profile fitting (CMWP) procedure developed by Ungár and co-workers, which includes the direct fit of the whole measured X-ray diffractogram by the sum of background, theoretically constructed profile functions and measured instrumental profile [1]. The line profile analysis provides size parameters of the microstructure, i.e. median (m) and variance (σ) of crystallite size distribution, as well as strain parameters, like average dislocation density From the available data of m and σ the average coherent crystallite size can be determined as $\langle D\rangle = m\exp(2.5\sigma^2)$. In the model, it is assumed that the coherent crystallite size obeys a log-normal size distribution.

The CMWP analysis revealed that HPT results in further refinement of the microstructure after BM incorporating increased amount of lattice defects. The amount of absorbed hydrogen increased by about 30-50% after HPT, mainly due to the lattice defects [2].

The ECAP deformation of the BM powders results in a moderate crystallite size reduction, while the distribution of the coherently scattering domains preserves its homogeneity. On contrary, the CR specimens undergoes different evolution, i.e. considerable broadening of the crystallite-size distribution is realized after 4 CR passes accompanied with a rapid crystallite size increase. Hydrogen absorption measurements revealed that both ECAP and CR reduces the storage capacity of the BM Mg_2Ni powders, however, the broader crystallite size distribution of the CR 4x sample is coupled with an enhanced kinetics [3].

As a summary, it is concluded that the amount of equivalent strain of the different SPD techniques, the deformation geometry, and the resulting nanostructure and microstructure are together responsible for the H-storage behavior of nanocrystalline Mg_2Ni alloys.

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Thermal Plasma Synthesis of Mg-Ni Nanoparticles

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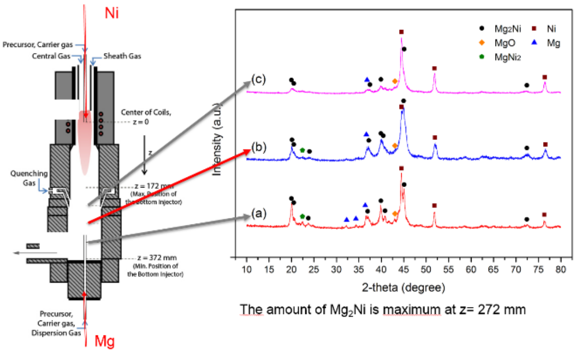
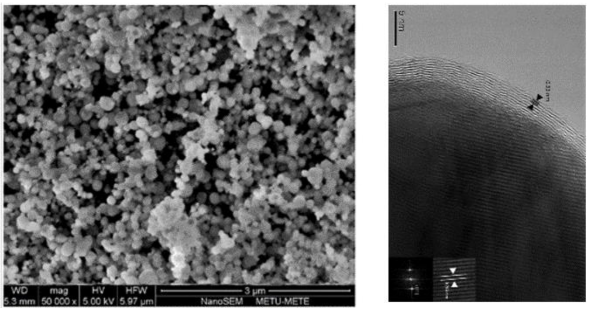
There is a considerable interest in developing magnesium and magnesium alloys in the form of nanoparticles for hydrogen storage purposes. In this study, the possibility of synthesizing Mg-Ni nanoparticles was investigated using inductively coupled R.F. plasma. In this method, starting materials were fed into plasma torch where the temperature is high enough (up to ~10,000 K) for complete vaporization of powder which then condenses into nanoparticles further down in the reactor.



The amount of Mg_2Ni is maximum at z= 272 mm

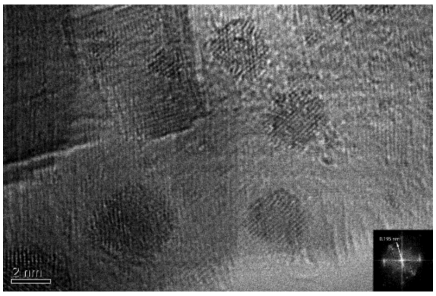
Schematic representation of thermal plasma torch (left) and XRD of Mg2Ni synthesized when Mg injected at different locations.

Plasma reactor used in the current study incorporated two injection probes located axially in the torch one from the top and the other from the bottom. Starting materials were either elemental powders or pre-alloyed compounds. Ni upon feeding to plasma torch can easily be processed to sizes less than 100 nm. Special precautions are necessary to produce Mg nanopowders due to its reactivity. The study, to a greater part, has concentrated on the synthesis of Mg_2Ni nanoparticles. The use of pre-alloyed Mg_2Ni powder as precursor leads to its disintegration in the plasma, condensing into separate phases and therefore was not suitable for the synthesis of Mg2Ni nanoparticles.



Mg2Ni nanoparrticles snthsized with thermal plazma. The particle size is around 90 nm (left). Carbonencapsulated Ni partcle(right)

The study showed that Mg2Ni can be synthesized quite successfully with the use of elemental powders provided that elements are fed into the plasma at carefully controlled positions. While the fraction of Mg2Ni was quite substantial, it co-existed with other phases and therefore additional treatments would be necessary for separation. It was shown that a substantial size reduction was possible with thermal plasma where Mg2Ni could be produced in sizes around 100 nm. The significance of these observations was discussed with regard to the potential of thermal plasma processing in yielding nanoparticles of metallic alloys and compounds.



Mg nanoparticles(5-6 nm in size) embedded in carboneous matrix

Attempts were also made to encapsulate Mg-Ni nanoparticles with carbon. For this purpose the precursor materials were co-fed with methane to thermal plasma. Ni could successfully be encapsulated, but this was not the case with Mg. There the structure was Mg particles of extremely small sizes ,i.e. 5-6 nm, embedded in a carboneous matrix. Hydrogenation of these particles were also reported

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H_2 real gas effect simulation in a non-continous single stage AB_2 compressor

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A simulation program in Matlab was developed to study the influence of applying different equations of state in a realistic non-continous first stage hydride compressor. The whole simulation contains three main stages. In the first one, Three real hydrogen equations of state have been compared with the ideal model in order to analyzed the variation in the behavior of the gas at pressures between 0 and 1000 bar and at the absorption/desorption temperatures in the compressor, which are 296K and 353K, respectively [1,2,3]. In the second part, these models have been employed to analyzed the real behavior of the hydrogen at the absorption and desorption stages. P-c-T curves at room temperature (296K) for two alloys: $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ and $Ti_{0.9}Zr_{0.1}Mn_{1.34}V_{0.3}$, were measured in order to contrast the difference of using each model. Finally, the main input to the program comprises either experimental and/or simulated Pressure-Composition Isotherm (P-c-T) curves, wich are fitted by the Fang et al model [4]. This approach models the three main regions of the hydride formation with two main equations that take into account the effect of the temperature in the calculation of the new P-c-T at a different temperature. The first equation simulates the alpha and beta phases, while the second one models the plateau or alpha-beta zone. Furthermore, for each equation several mathematical coefficients have to be found in order to simulate the P-c-T at low and high temperature, 23 and 80 C respectively. Moreover, three equations of state have been employed in order to analyzed the real behaviour of the gas at the absorption and desorption stages [1,2,3]. The P-c-T curves at room temperature (23ºC) of the two alloys were taken in order to contrast these experimental data with the simulation fit of the P-c-T in the compressor program as shown in figure 1. The simulation was developed varying mainly the volume and mass of the alloy. The three models of equation of state provides almost the same answer for the simulated high temperature working point as it is seen in Figure 1. In this communication, it will be reported the effects of using real h2 gas models in the simulation of hydring and dehydring stages and its repercussion in a non-continous single stage compressor.

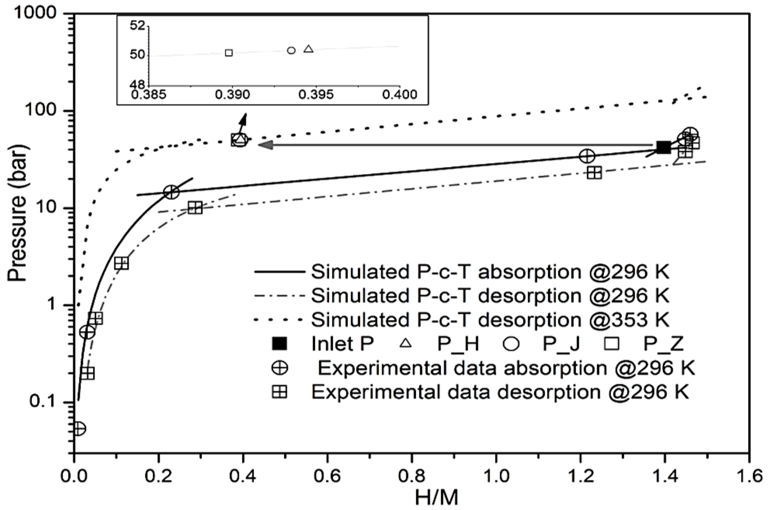

Figure 1. Simulation of the perfomance of a hydride compressor stage based on $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$. The black continuous arrow shows the transition from the low temperature to the simulated high temperature working point with the different equation of state, which are enlarged in the inset curve.

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Revealing Surface Species on Electrochemical Cell Electrodes in Operando

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Development of efficient fuel cell and electrochemical cell devices to retrieve energy in a renewable manner lies in the molecular level understanding of the conversion processes taking place at surfaces and interfaces. These processes involve complicated bond breaking and formation at the surfaces as well as charge transfer through interfaces which are challenging to track under operational conditions. I will address the nature of these interfacial processes using core level spectroscopy by leveraging its atomic sensitivity and give several examples of fuel cell and electrolysis reactions to demonstrate the importance of probing the surface under operating conditions. Oxygen reduction reaction (ORR) taking place on the platinum cathode in proton exchange membrane fuel cells [1], water splitting reactions including oxygen evolution reaction (OER) over IrO_2 [2]and hydrogen evolution reaction (HER) over MoS_x [3] reveal that different species dominate on the surface under different operational conditions and surface activities are directly related to the stabilities of those intermediate species and possible structural rearrangements of the catalyst material.

Ambient pressure x-ray photoelectron spectroscopy (XPS) is a powerful approach to obtain new surface sensitive information about interfacial processes using a novel electrochemical cell (EC) that allows for electrochemical potential control [4]. Other operando techniques have been facing challenges to provide such information since most often these are lacking sufficient surface sensitivity to probe catalysis of electrochemical reactions occurring at the catalyst-electrolyte interface. Here a particular advantage has been taken by using the new XPS system allowing for pressures up to 100 Torr.

EC cells were designed in order to study the surfaces of interest in operando, i.e. as the cells are in catalytic reaction operation in the presence of gases. The basic schematics of the EC cells is depicted in Figure 1. A Nafion membrane was used as the proton conductor and electrode materials were loaded on both sides of the membrane, representing cathode and anodes, respectively. The working electrode is the surface under XPS investigation whereas the counter electrode is isolated from the gas cell ambient.

In operando investigations reveal that the identification of OH intermediates is essential during ORR on Pt but also the process becomes more efficient when the OH is non-hydrated [1]. This will have important implications for the design of new fuel cell systems when it comes to the level of hydration. I will also demonstrate that indeed IrO_2 changes it oxidation state during OER but only in the surface region [2]. Furthermore, the amount of OH on the surface becomes less as the catalyst is turning over during the reaction. These results cast clear evidence towards one particular proposed mechanism for OER related to the peroxide route. Finally I will show that MoS_x converts into MoS_2 during HER that increases the amount of active MoS_2 edge sites [3].

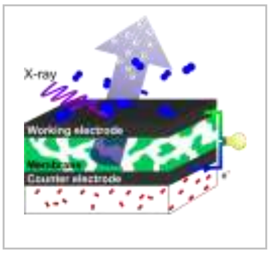

Figure 1. Schematic representation of the electrochemical cell. Working and counter electrodes are separated by a Nafion membrane. X-ray beam approaches to the sample at a grazing incidence and the measurements are performed at normal emission geometry.

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High Capacity Graphene/α-MnO_2 Nanocomposite Cathodes for Li-O_2 Batteries

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Among batteries, the lithium–air battery has recently captured worldwide attention due to its ultrahigh specific energy density of 11.140 Wh kg^{-1}, rivalling that of gasoline. A typical non-aqueous lithium–air battery consists of a metallic lithium anode, an electrolyte with a lithium salt dissolved in an aprotic solvent and a porous O_2-breathing cathode. However, despite the extensive research effort devoted to its practical implementation, several issues with the electrodes and electrolytes have limited the performance of lithium–air batteries to a few charge–discharge cycles and a low rate capability. Therefore, an extremely effective carbon cathode for high performance Li–O_2 batteries must be designed and produced.

In the carbon cathode materials, Graphene nanosheets (GNSs) have been reported as ideal cathode materials for Li-O_2 batteries because of their unique morphology and structure which provide both diffusion channels for O_2 and active sites for cathode reactions. On the other hand, α-MnO_2 catalysts help full to increase the reversibility of the lithium-oxygen interactions due to hollandite type crystal structure of MnO_2 consists 2x2 tunnels. In the study, graphene was produced by chemical treatment methods. The α-MnO_2 one dimensional nanowire catalysts was synthesized by microwave hydrothermal method. After producing the graphene and α-MnO_2 catalysts, Graphene/α-MnO_2 nanocomposite electrodes were produced using planetary ball milling. For preparation of the nanocomposite electrode, PVDF binder dissolved in NMP solution, selected amount of graphene and α-MnO_2 catalysts were added into the stainless steel bowl and mechanically alloyed using planetary ball milling. After then, obtained mixture was cast on the nickel foam and dried at 100 °C in a vacuum oven. In order to investigate effect of α-MnO_2 catalyst on the electrochemical reaction of lithium and oxygen, content of the α-MnO_2 was altered in the composite electrode. Prepared nanocomposite electrode was characterized using scanning electron microscopy, x-ray diffraction and Raman spectroscopy. To investigate electrochemical behaviour of the produced Graphene/α-MnO_2 nanocomposite air breathing cathodes, ECC-Air test cell (purchased from EL-Cell in Germany) was used. In the test cell, lithium foil was used as anode material, produced nanocomposite electrode was used as cathode electrode, the working and counter electrode was separated with glass fibre separator. The electrochemical cycling test of the nanocomposite electrode was performed between 2.15 V and 4.25 V in the ECC-Air test cell using 1 atm oxygen pressure. For further electrochemical characterization, electrochemical impedance spectroscopy of the electrodes was investigated with the Nyquist plots in the frequency range of 1000 kHz to 0.1 Hz with AC amplitude of 10 mV.

Keywords: Graphene, α-MnO_2, composite, Li-O_2.

Acknowledgments

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Pseudocapacitive properties of titanate nanotubes & their high rate capabilities as a lithium-ion battery anode

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Improvement of lithium-ion electrodes with high charge and discharge capacities is in high need especially for electronic devices and electric vehicles [1]. For that reaso, development of ion transport in the crystal structure is needed [2]. The general idea is synthesizing nanometer scale particles. Reducing the particle size helps the ion diffusion in the structure [3]. Titanate nanotubes are promising materials because of their special morphology and high specific surface area. The nanotubes are formed by rolling-up of titanate nanosheets [4]. These titanates provide high rate capability and low volume expansion upon lithiation [5]. More importantly their tubular structure helps the transport of ions through the crystal.

In this study, we synthesized titanate nanotubes and modified the interlayer distance by changing the pH. For the characterization XRD (Figure 1), SEM (Figure 2) and BET (Figure 3) techniques were used. In addition, the effect of interlayer distance on energy capacity and rate capability was investigated.

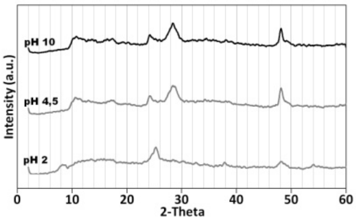

Figure 1. The effect of pH on crystal structure of titanates.

The shortest interlayer distance was observed at pH 4,5. Getting further away from this point, interlayer distances increased and this also increased the nanotube diameter. Conversely, specific surface area reaches its maximum value at pH 4,5. Potential-capacity profiles of TiO_2 nanoparticles showed distinct potential plateaus. Nevertheless, a very fast capacity drop was observed for TiO_2 particles. On the other hand, for titanates, broad peaks appear in CV measurements. For titanates capacities higher than 700 mAh/g were obtained. More importantly, titanates showed exceptional rate capabilities especially at wider interlayer distances due to higher mobility of ions in the structure (Figure 4). It was found that interlayer distance plays an important role in rate capability. However the material still needs some modifications to stabilize the capacity.

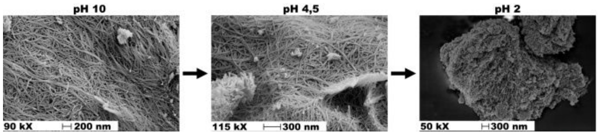

Figure 2. SEM images of titanates after being treated at various pH values.

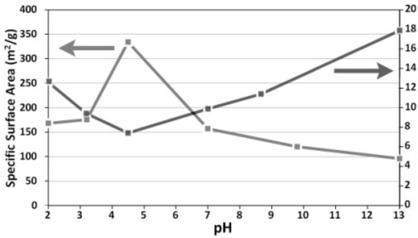

Figure 3. Surface area and interlayer distance values at various pH values.

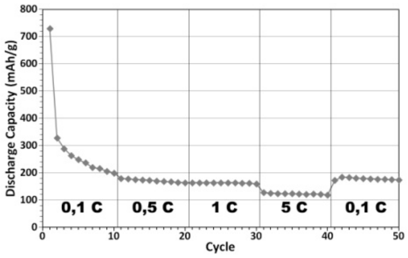

Figure 3. Surface area and interlayer distance values at various pH values.

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Lithium Superionic Conduction in $LiBH_4$/Silica Nanocomposites

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One of the key challenge in the field of battery technology is the development of solid state fast ionic conductors that will facilitate the realization of all solid-state rechargeable cells[1]. The light weight complex hydrides especially those based on lithium are very promising materials for reversible hydrogen storage and also for ions conductor in all solid-state Li batteries. High Li^+ mobility has been reported in several Li based complex hydrides such as $LiBH_4$, $Li_2(BH_4)(NH_2)$, $LiAlH_4$, Li_3AlH_6, $LiNH_2$ and Li_2NH[2]. Unfortunately, these materials do not show sufficient ionic conductivity at ambient temperatures which is required for most battery applications.

Very recently, we showed for the first time that the Li-ion conductivity of $LiBH_4$ at room temperature can be increased by about three orders of magnitude (Figure 1) when confined in mesoporous silica scaffolds.[3]. NMR results indicate that this increase in Li-ion condictivity is due to a very high Li^+ mobility in the nanoconfined $LiBH_4$ located close to the interface with the SiO_2 pore walls[4-5]. DSC and Quasi-elastic neutron scattering (QENS) studies reveals that this fraction at the SiO_2-$LiBH_4$ interface does not undergo solid-solid transition as in the macrocrystalline $LiBH_4$, while the remaining nanoconfined $LiBH_4$ that are far from the SiO_2 pore walls displays a significantly lower solid-solid transition temperatures than for crystalline $LiBH_4$[5]. These suggest that confinement of $LiBH_4$ in the nanoporous silica led to stabilization of the high temperature hexagonal phase (which is known to have very high Li^+ mobility), resulting in increased Li^+ conduction in the nanocomposites even at room temperatures.

In this contribution we will show how the Li-ion conduction in the nanocomposites is influenced by the physico-chemical properties of the mesoporous silica scaffolds such as the nature of the silica material, its pore size, specific surface area and the surface functional groups. We will discuss how the critical parameters can be tunned inorder to optimise the performance of $LiBH_4/SiO_2$ nanocomposites as a solid state electrolyte. In addition we will show Li-ion conductivity of $LiBH_4$ confined in other nanoporous scaffolds like Al_2O_3, TiO_2 and ZrO_2, and discuss how the properties of these support materials influences the the Li^+ conductivitiy of nanoconfined $LiBH_4$.

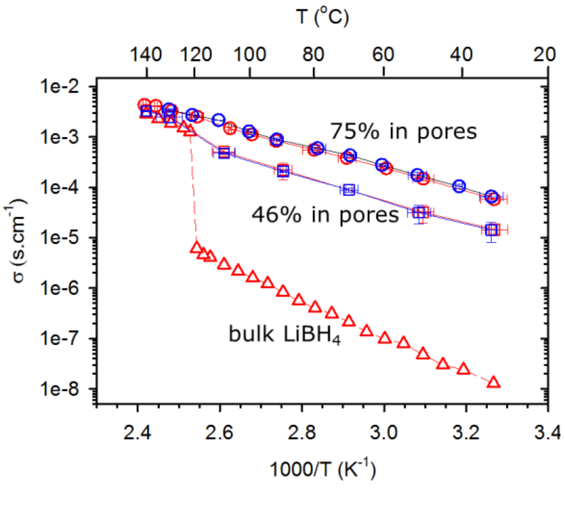

Figure 1. Arrhenius plots of the ionic conductivities of bulk $LiBH_4$ and $LiBH_4/SiO_2$ nanocomposites with different pore fillings.

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Multiscale modeling efforts to reconcile diverse experimental observations on lithiation of $LiFePO_4$ cathodes

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Secondary lithium ion batteries available today, performance of which heavily depend on the intercalation compound used in the cathode, have yet to meet the requirements for the hybrid and electric vehicle industry. Thus, efforts to develop an understanding of the lithiation/delithiation mechanisms of the cathode materials that have potential for higher energy and power densities has increased substantially. Lithium iron phosphate ($LiFePO_4$, LFP) is among the most investigated intercalation compound due to its long cycle life, good thermal stability, natural abundance, safety and low cost. Despite the low electronic conductivity of LFP, the composite cathodes that are made from carbon coated LFP nano particles can achieve high rates and capacities. The experiments that are conducted in order to understand the underlying mechanism have resulted in several different observations and theories.

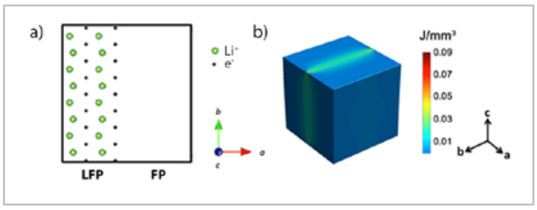

Figure 1. a) Chemical interfacial energy calculation by DFT and b) continuum scale elastic strain energy calculation for the bc-interface when $x_{Li}=0.5$. Respective values for interfacial and volume averaged elastic strain energies are 0.115 J/m^2 and 3.7 MJ/m^3 [1].

In situ and *ex situ* microstructural investigations indicate that LFP cathode particles have a two-phase microstructure in general (lithium poor (FP) and rich (LFP) phases). During Li insertion, phase separation may take place within a single particle and/or across separate particles. Phase boundaries (LFP-FP interface) with many different orientations have been reported in investigations examining a single particle. Correspondingly, various theories have been developed to examine various limiting cases wherein the limiting factor can be from the electrochemical reaction at the particle surface, the diffusivity of lithium in the particles, nucleation, or phase boundary mobility. Among these are the core-shell [2], anisotropic-growth [3] and domino cascade [4] models. A solid solution pathway was also proposed [5]. The emergence of these diverse observations and theories is due to the highly anisotropic nature of LFP (in terms of the lithium diffusivity, elastic constants, misfit strains, and surface and interfacial energies) and the increased effect of surfaces and interfaces to materials thermodynamic and kinetic properties with the increasing area/volume ratio as the particle sizes approach to the nano scale.

By combining density functional theory calculations (for anisotropic interfacial energies and several topotactic reaction pathways) with continuum scale elastic strain energy density calculations it is possible to gain insights on this complex phenomena. This talk will cover some of our recent findings on the thermodynamic stability of several interfaces, solid solution phases and phase transformation kinetics.

This work was partially supported by the Turkish Scientific and Technical Research Council, TUBITAK, grant no. 113F091.

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Structure, phase transitions, dielectric and transport properties of bismuth vanadate-based BILAMEVOX ionic conductors

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Oxides based on the bismuth vanadate $Bi_4V_2O_{11-y}$ reveal high ionic conductivity ~ 0.01 S/cm at temperatures < 900 K. They are promising for development of electrolytes for portable SOFC devices. Rather low thermodynamic stability of these oxide in reducing atmosphere comprises their main drawback and stimulates studies of composition modifications aimed to improve their stability.

In this work, crystal structure parameters, phase transitions, dielectric and transport properties of ceramic solid solutions $(Bi_{1-y}La_y)_4(V_{1-x}M_x)_2O_{11-z}$ (BILAMEVOX) with $x, y < 0.3$, Me = Zr, Ga, Fe, Cu, have been studied. The introduction of La and M cations may ensure enhancement of thermodynamic stability of these compositions.

Ceramic samples were prepared by the solid state reaction method at temperatures < 1100 K. Phase formation, structure and microstructure parameters of ceramics were studied by means of DTA/DSC, X-ray diffraction, IR-spectroscopy, and atomic force microscopy methods. Dielectric properties, conductivity and phase transitions of ceramics were studied by the *ac* impedance spectroscopy in the temperature range of 300 – 950 K and in the frequency range of 100 Hz – 1 MHz.

The concentration and temperature stability regions of monoclinic α-, orthorhombic β- and tetragonal γ- and γ'-polymorph modifications have been determined, with α-phase existing at $x<0.06$ in all the systems studied, while the tetragonal γ'- phase stabilizing at $x>0.10$.

The α-β and β-γ reversible phase transitions were revealed in the conductivity, dielectric permittivity and dielectric loss temperature dependences of ceramic solid solutions studied. It was determined that temperatures of these transitions decreased with increasing x. The first order α-β, β-γ and γ'-γ phase transitions are marked with anomalies in temperature dependences of heat capacity and dielectric permittivity.

Ferroelectric origin of the α-phase compositions was proved using the piezoforce microscopy methods. At temperatures <600 K, effect of dielectric relaxation was revealed in the BILAMEVOX samples. This effect is caused by the formation of dipoles relaxing in alternating field in course of ionic transport.

Slow kinetics of structural phase transitions was revealed and explained by the presence of oxygen ion vacancies in the crystal lattice and their "pinning" on ferroelectric domain walls responsible for large thermal hysteresis of the α-β phase transitions.

Temperature dependences of total conductivity revealed Arrhenius type behavior typical of ionic conductors. Total conductivity of BILAMEVOX ceramics decreases to two orders in comparison to the initial value at room temperature, and to one order at 900 K. In temperature domain of the orthorhombic β-phase, conductivity enhances to an order when x value increases to 0.08. At room temperature conductivity value does not exceed 10^{-6} S/cm, though increases more than 6 orders at temperatures near 800 K.

The BILAZRVOX ceramics were studied using the impedance method. In frequency dependences of dielectric losses Z"/Z'(*f*) two relaxation peaks were observed, with their frequency positions depending on x value and temperature. In the impedance Z"(Z') plots marked semicircles were observed for both α- and β-phase compositions in high frequency range. This effect points to the contribution of fast ionic diffusion on grain boundaries and/or ferroelectric domains along with the bulk mechanism of fast oxygen ions migration through vacant positions in oxygen sublattice.

The data obtained allow us to conclude that changes in composition govern the crystal structure, phase transitions and transport properties of the BILAMEVOX ceramics studied. The possibility of their application for the electrolytes for IT-SOFC development is discussed.

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NEW MIXED ELECTRON-PROTON CONDUCTING $Ln_{6-x}Zr_xMoO_{12+\delta}$ (Ln= La, Nd, Sm, Gd, Dy, Ho) MATERIALS

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Lanthanide based oxides, such as fluorite-like rare-earth molybdates and tungstates or Ce/Zr pyrochlores generally possess much better chemical stability than the perovskites ($BaCeO_3$ and $BaZrO_3$) and as will be discussed later some of them seem to lack any grain boundary contribution to the total conductivity.

$Ln_{5.4}Zr_{0.6}MoO_{12+\delta}$ (Ln= Nd, Sm, Gd, Ho, Dy (06LnZMO), $Sm_5ZrMoO_{12.5}$ (1SZMO) and $La_{5.8}Zr_{0.2}MoO_{12.1}$ (02LZMO) were prepared using the mechanical activation method. The mechanically activated mixtures of the oxides were unaxially pressed at 914 MPa and sintered at 1400ºC and 1600ºC for 3 h. The geometric density of the as-prepared ceramics ranged from 80.5 to 92.5% of the theoretical one. All samples were characterized both structurally and electrically. The temperature dependence of the total (electronic and ionic) grain interior conductivity in different dry and wet atmospheres (air, Ar, Ar-5% H_2) was extracted from impedance spectra obtained using a Solartron 1260 frequency response analyzer. Total ac conductivity as a function of the oxygen partial pressure $p(O_2)$ under reducing conditions in the atmosphere of CO/CO_2, while under oxidizing conditions dry oxygen and Ar were mixed in different ratios to yield atmospheres with $p(O_2)$ ranging from $\approx 1\times10^{-5}$ atm to ≈ 1 atm at 800 ºC.

All reflections observed in the patterns of 06SZMO, 06DZMO, 06HoZMO were indexed on a face-centred cubic lattice (space group $Fm\overline{3}m$), which resulted in quite similar cell parameters for both phases. Indexing of the main reflections in the XRD pattern of 02LZMO allowed us to determine parameters of the fluorite-like rhombohedral $R\overline{3}$ subcell. The XRD profile of 06NZMO showed clearly that the sample consists 2 fluorite phases. Although no changes in the sample's phase composition were detected, their unit cell parameters decreased substantially on reduction. The fluorite-like $Ln_{5.4}Zr_{0.6}MoO_{12.3-\delta}$ (Ln = Nd, Sm, Ho, Dy) have similar total conductivity of the order of $5\cdot10^{-4}$ S/cm at 800ºC in air. Although no changes in the sample's phase composition were detected, their unit cell parameters decreased substantially on reduction. Their conductivity seems to be dominated by ionic defects at low temperatures (Fig.1), while at high temperatures or under the atmosphere of Ar-5% H_2 electronic conduction prevails. Under oxidizing conditions electron holes were found to be dominant charge carriers in 02LZMO and 06NZMO at high and intermediate temperatures respectively. We argue that proton conduction may exist in 06NZMO, 06SZMO, 06DZMO and 06HoZMO in the temperature range of 250–530°C in wet atmospheres. The relative contribution of protons to the total conductivity of $Ln_{6-x}Zr_xMoO_{12+x/2-\delta}$ in air gradually decreases on going from La to Ho. 06NZMO demonstrated much better hydration characteristics than the rest of the molybdates did under mild reducing conditions. Among the samples studied, $La_{5.8}Zr_{0.2}MoO_{12.1}$ showed the highest total conductivity in wet air (about 2.5×10^{-5} S/cm at 500°C), which was found to be entirely due to the bulk transport. The total conductivity of $La_{5.8}Zr_{0.2}MoO_{12.1}$ was found to be dominated by ionic charge carriers at intermediate oxygen partial pressures and high temperatures. On Zr^{4+} doping the oxygen vacancies concentration and ionic conductivity decreases (for example in $Sm_{5.4}Zr_{0.6}MoO_{12+\delta}$ and $Sm_5ZrMoO_{12.5}$) [1].

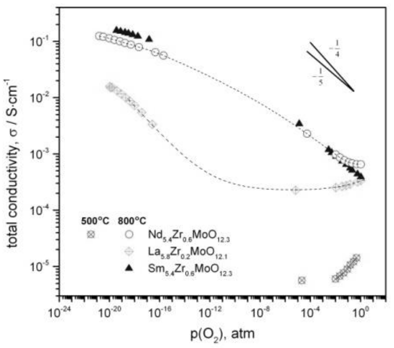

Fig.1. The total conductivity of 02LZMO, 06NZMO, 06SZMO as a function of oxygen partial pressure. Broken lines are guides to the eye.

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Effect of PTFE nanoparticles in catalyst layer on PEM fuel cell performance

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Fuel cells are regarded as viable devices for clean energy alternatives. They are commercially used in stationary and portable applications. They are the devices that generate electricity in a simpler way compared to combustion of fuels via splitting H_2 gas into protons and electrons. The only products of this process are water as an exhaust and excess heat of reaction. Polymer electrolyte membrane (PEM) fuel cells are more preferable in some applications than other fuel cell types because of its simplicity, quiescence, and quick start up. However, in order to more widen its application field, understanding thermal and water effect onto the performance and durability is essential.

A PEM fuel cell electrode is one of the most important components of a PEM fuel cell where the electrochemical reactions take place. In an electrode electrons travel through electrically conductive solids; protons travel through the Nafion ionomer and the reactant gases travel only through the voids. In order to enhance the performance of a PEM fuel cell, electrode structure should be designed as optimum for electron, gas and liquid transport. To achieve enhanced performance and durability providing net water transport through the membrane electrode assembly is essential. In other words, membrane electrode assemblies handle high liquid water saturation levels however; excess liquid water should be removed from the cell in order not to block the reactant gases to reach the active catalyst sides. For this purpose, hydrophobic nanoparticles like Polytetrafluoroethylene (PTFE) can be added to the catalyst layer structure. By this way, paths for gas and liquid transport can be provided.

The aim of this work is to create hydrophobic channels through the catalyst layer. With this modification, reactant starvation is alleviated. To create these channels, PTFE® suspension is added into catalyst ink. Structural changes due to addition of hydrophobic nanoparticles through the catalyst layer are studied by impedance spectroscopy, and fuel cell performance tests.

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Stacking of the Direct Borohydride/peroxide fuel cell system by the solution distribution network

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Fuel cells offer a promising alternative as a power generation technologies for large-, medium- and small-scale applications. Liquid hydrogen carriers such as methanol, ethanol and borohydrides are replaced with hydrogen gas. $NaBH_4/H_2O_2$ system shows the higher theoretical energy density of 17 kWh kg^{-1} than that of H_2 (3.28 kWh kg^{-1}). Depending of some parameters such as cell materials, operating conditions and cell chemistry, the cell performance decreases. System Engineering (SE) issues include the design of flow fields, the fuel and oxidant management, thermal (heat) management and mass transport.

The main important problems on stacking of DBPFC are the increasing of stack temperature, O_2 gas evolution at the cathode because of the fast kinetics of the peroxide with Pt electrode and H_2 gas evaluation at the anode. Hydrogen gas can be generated from the borohydride, it reacts the metal catalysis, at the anode side. Hydrogen generation not only decreases fuel utilization but also lowers the cell performance. Moreover, peroxide reduces indirectly and generates O_2 gas at the cathode. The gas evaluations cause the maldistribution in liquid fuel cells. Moreover when the cells are stacked, the components of the cell can be damaged because of the stack temperature increase. High temperature in the cell raises the temperature of fuel/oxidant and accelerates the oxidation and reduction reactions on the catalyst layers. Therefore gas evaluation rate increases. Firstly, a commercial fuel cell stack type was used for performance tests. It was observed that the diffusion layers and catalyst layers in the cells placed in the middle of the stack were damaged because of both the temperature increased and gas evaluated (Figure 1).

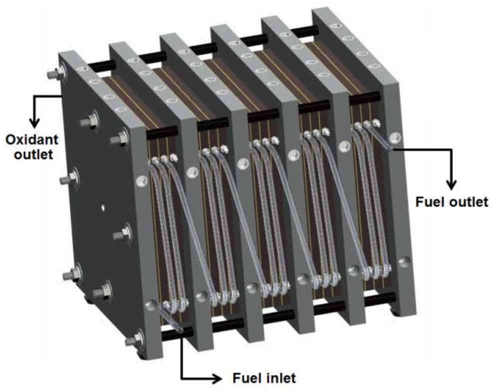

Figure 1. Commercial fuel cell used in the performance test

Presented in this paper is an important engineering factor for successful stacking design of DBPFC. To reduce damage of the cells in the middle of the stack we developed the **Independent Cell Liquid Distribution Network (ICLDS).** Schematic of the system is given in Figure 1. So that temperature can be controlled, the gas evaluation decreased and destruction of the components was prevented.

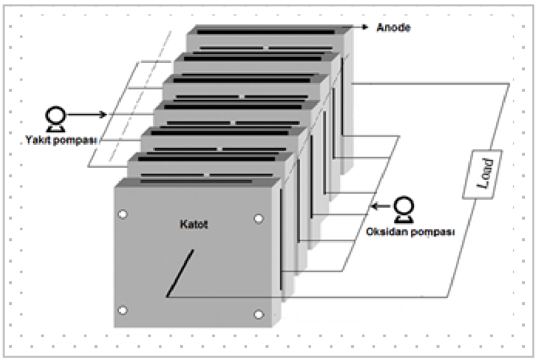

Figure 2. The fuel cell stack designed with ICLDN.

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Improving the performance of direct boroydride/peroxide fuel cell system by the modification of anode and cathode

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Direct borohdyride/peroxide fuel cells use the basic borohydride solution as a liquid fuel and the acidic peroxide solution as an oxidant. Electricity is produced via the following reactions:

$$NaBH_4 + 4H_2O_2 \rightarrow NaBO_2 + 6H_20 \qquad E^0_{cell} = 2.11\ V$$

$NaBH_4$ is chemically stable, can be easily stored and handled. Borohydride can oxidized to metaborate and water with generating 8 electrons theoretically. The electron numbers generated are 7-8 for Au electrode, 4-6 for Pd electrode, 4 for Ni electrode and 2-4 for Pt electrode.

On the other hand hydrogen peroxide (H_2O_2) reduces electrochemically to water or decomposes into oxygen and water:

$$4\,H_2O_2 \rightarrow 4H_2O + 2O_2$$

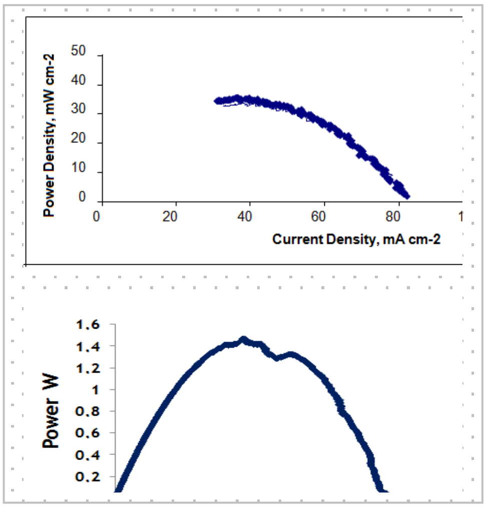
$$4H_2O_2 + 8e^- \rightarrow 8OH^- \qquad E^0 = 0.87\ V\ (vs\ SHE)$$

Pt is the most commonly used electrocatalyst for both O_2 and H_2O_2 reductions. But it is also promote the undesirable H_2O_2 decomposition causing the fast kinetic of H_2O_2 reduction reaction on Pt surface. For both electrocatalysis it is expected the problems of the undesired reactions on anode surface and cathode surface may be prevented at least minimized by modification of the electrocatalysis.

Electrooxidation of borohydride and hydrogen peroxide mainly depend on the catalyst materials. Hosseini et al were investigated the electrooxidation of borohydride on the bimetalic PdNi electrode by the electrochemical methods of cyclic voltammetry (CV) and impedance spectroscopy **[1].** It was observed that current densities on PdNi electrode are greater than that of Pd electrode. Selverani et al. developed Prussian Blue (PB) modified Pt electrode to reduction of H_2O_2 and reported that Pt/PB electrode improved the H_2O_2 reduction process **[2]**.

In the present study, we used a commercial pressed membran-electrode-assembly (Pd anode/Nafion 115 membran/Pt cathode). Pt/PB electrode and Pd-Ni electrode were prepared by depositing electrochemically thin films on the electrode surfaces under galvanostatic conditions at the constant currents. $NiSO_4$ solution and PB solution [$FeCl_3.6H_2O$ + $K_3(Fe(CN)_6)$] were used as the electrochemical deposition solutions.

The performance curves after and before the electrochemical treatment are shown in Figure 1. The maximum cell power is 35 mW cm^{-2} at the current density of 40 mA cm^{-2} and cell potential of 0.8 V. after the anodic and cathodic modifications, the cell power increased up to 175 mW cm^{-2} at the current density of 140 mA cm^{-2} and the cell voltage of 1 V.



Figures 1. Power curves of DBPFC a) befor treatment, b) after treatment

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This work has being done at Nevsan Energy Laboratories founded by the project of (Project No: 635.TGSD.2010;) and has been supported by TUBITAK (The Scientific and Technological Research Council of Turkey; Project No: 113M097and 111M806).

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An optical analysis of the hydrogen permeation properties of Pd-based alloys

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We recently developed an optical method to measure the permeation of thin film samples in a combinatorial way [1]. Using this method we analysed the behaviour of the Pd-Cu system. We reproduce the optimum Cu concentration for permeation found in bulk. However, an analysis of the microstructure suggests that not only composition, but also the presence of heterogeneous phase boundaries is essential to obtain a high permeation [2].

In short our combinatorial method works as follows. Using magnetron sputtering compositional gradient samples of a potential membrane material are codeposited on 3 inch wafers and covered by an yttrium indicator layer. As a last step, a grid of Pd dots is produced through the use of a shadow mask. When taking the sample out of the vacuum system, the yttrium surface oxidizes leaving the Pd dots as the only location for the dissociative ad- and absorption of hydrogen. Upon exposing such a sample to hydrogen, it will then enter the sample through the Pd dots towards both the yttrium and the underlaying layer to be studied. Since the lateral permeation of hydrogen in yttrium is very small, while its affinity for hydrogen is very large, the lateral hydrogen progression is determined by the membrane layer. The front of the hydrogen diffusion can be observed through the coloration of the yttrium layer, when hydrogen leaks into it (see fig.1).

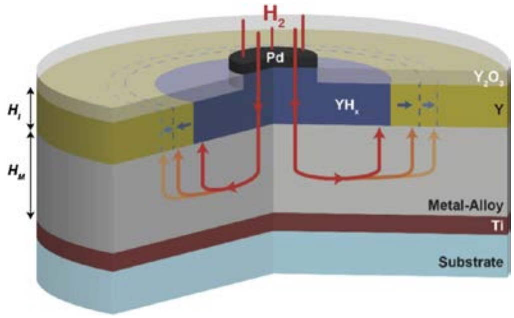

Fig.1: Schematic picture showing the geometry of our thin film samples in which we study the lateral permeation of hydrogen through the metal alloy.

By following the coloration front in time, we are able to derive the permeation, albeit in a planar geometry and of course neglecting any surface catalytic issues. The beauty of the method is that by comparing the coloration fronts originating from different Pd dots we can compare the permeation within different sections of the thin film and thus correlate it to the underlying composition of the membrane material.

Using this method we analyzed several binary and ternary alloy membranes. In particular, we studied the well-known Pd-Cu system and verified that the maximum permeation is obtained for 48% Pd. This optimum was explained as being due to be located within the bcc phase, but having the maximum possible Pd content (hence at the bcc/fcc phase boundary). While our films reveal the same optimum as the bulk (micron thick) membranes, an electron microscopy study showed a quite different phase behaviour. In our thin films the optimum is positioned within a mixed fcc/bcc phase. This mixed phase appears to be extended over a much larger part of the phase diagram, as compared to the classical phase diagram. It is not clear whether our films constitute a meta-stable phase. Alternatively, the phase diagram might not adequately respresent the equilibrium at low temperatures.

The question than remains what determines the optimum permeation. So far our microstructural analysis indicates that the presence of heterogeneous fcc/bcc phase boundaries is essential to obtain a high permeation. Samples having the same concentration in which we suppress such boundaries, do not show a high permeation.

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Ternary Hydrogen Separation Membranes via Combinatorial Approach

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Hydrogen can be produced from a wide range resources such as fossil fuels, biomass and water. However, hydrogen production currently is dominated by fossil fuels mostly via steam reforming of natural gas/methane and coal gasification. The methods in question yield hydrogen in a gas mixture such as CO, CO_2 and H_2S [1]. Thus there is a necessity to separate hydrogen from the gas mixture so as to obtain it in a pure form. Hydrogen separation membranes effectively allow extraction of hydrogen from mixed gases. Hydrogen separated in this way may be used in fuel cells to generate electricity or may be fed directly to the natural gas grid. It is likely that the current network of natural gas will soon be transformed into a “gas” grid where hydrogen would be an essential ingredient [2]. All these require the use of efficient separation membranes, which when made possible would lead to an easy availability of hydrogen as is currently the case for natural gas. Thus the separation membranes has a much wider scope than normally anticipated and therefore there would be a need for separation membranes that are more efficient and in particular of low cost. Among the hydrogen separation membranes, metallic membranes are particularly attractive due to their very high hydrogen selectivity and the relatively high hydrogen permeability. Pd and Pd alloys i.e. Pd77Ag23, are fairly convenient as a separation membrane and they are commercially available in the market. However, the hydrogen embrittlement together with the high-cost of Pd restricts the use of Pd based membranes in industrial applications. Therefore, efforts have concentrated on either reducing the Pd content of the membranes or to find new alternatives which were free of Pd.

Pd-free membranes based on b.c.c. structure are particularly attractive. This is due to the fact that metals such as Nb, V and Ta are far superior than f.c.c. Pd with respect to hydrogen permeability. However, b.c.c. membranes extremely suffer from hydrogen embrittlement due to their very high level of hydrogen solubility. The efforts to produce mechanically durable membranes have therefore concentrated on reducing the level of hydrogen solubility while maintaining the high permeability. The developing improved membranes via both alloying Pd and finding alternative Pd free compositions are not always successful and require extended coordinated efforts. Therefore traditional approach of synthesizing one membrane composition at a time and testing it for permeability are not always very suitable. A method that would allow the synthesis of material library and which may then be evaluated by a screening technique is a highly useful approach to develop new membranes best suited for the purpose.

In the current work a method is described which can be used to identify material compositions in a ternary alloy systems that would be suitable as separation membranes. The method allow the production of multiple material compositions in the form of thin film membranes. This was achieved using a purpose built magnetron sputtering deposition unit incorporating a 6 inch diameter substrate holder.

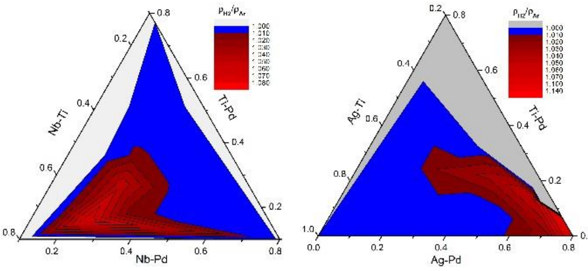

Figure 1. The resistivity mapping of Pd-Nb-Ti (left) and PdAgNi (right) ternary systems at 350 °C.

The system incorporates three sputter targets arranged in triangular fashion positioned vertically and axially to yield a uniform film thickness over an extended area in the substrate. The substrate holder was in the form of a magazine comprising a total of 21 disc shape substrates each 18 mm in diameter arranged in triangular form aligned with the sputter targets underneath. This allows the deposition of 21 thin film membranes in a single experiment each with a different composition. The membranes may then be screened using permeability testing, or alternatively a preliminary evaluation could be made with resistivity measurement. The method was applied to Pd-Nb-Ti, Pd-Ag-Ti and Pd-Ag-Ni alloy systems where the membranes covered a considerable portion of the ternary phase diagram. Results using resistivity measurement allow mapping of ternary compositions. The covered portion of related ternary systems and the resistivity mapping results are given in Figure 1.

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New insights on the formation/ decomposition mechanism of $KAlH_4$

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Alanates have attracted much attention as hydrogen storage media after the achievement of reversible hydrogenation of $NaAlH_4$ by adding $TiCl_3$ as an additive [1]. Later, many mono-alkali and bi-alkali alanates have been studied aiming to find suitable hydrogenation properties for storage applications. However, the role of the additive in the H-properties of alanates still remains unclear.

$KAlH_4$ has the peculiarity of being the unique mono-alkali alanate that reversibly stores hydrogen under moderate pressure (~1 MPa) without using any additives. This offers the possibility to investigate hydrogen absorption/desorption processes with and without additives and therfore to better understand their role. Moreover, $KAlH_4$ is a promising hydrogen storage media with a capacity of 5.7 wt.% H. However, its hydrogenation properties have been scarcely investigated [2,3]. The hydrogen absorption/desorption reactions in $KAlH_4$ are expected to follow the same reactional pathway as for other alkali alanates, namely:

$$3KH + Al + 3/2H_2 \leftrightarrow K_3AlH_6$$

$$K_3AlH_6 + 2Al + 3H_2 \leftrightarrow 3KAlH_4$$

However, recent studies reveal the existence of intermediate phases during the formation/decomposition process [4]. The composition of these phases is reported to strongly depend on the synthesis conditions of $KAlH_4$, a fact that opens new questions about the reactional pathway in alanates.

In this work, $KAlH_4$ was synthetised by mechanochemistry of KH and Al powders under H_2 pressure (8 MPa) using an tight vial equipped with temperature and pressure sensors [5]. This method provides much faster $KAlH_4$ formation than thermally driven routes. The influence of several MCl_3 additives (M = Ti, Sc, La) on $KAlH_4$ formation has been studied (Fig. 1). Reaction pathways were analyzed with the help of ex-situ X-Ray diffraction and Nuclear Magnetic Resonance analysis. Thermal stability of $KAlH_4$ was investigated by Differential Scanning Calorimetry and reversible hydrogen storage was characterized by the Sieverts' method. The rate limiting step as well as the activation energy of the absorption/desorption reactions have been obtained and compared to those observed for other alanates. We will discuss the existence of novel reactional pathways that shed new light on the formation/decomposition mechanisms and the role of the additives.

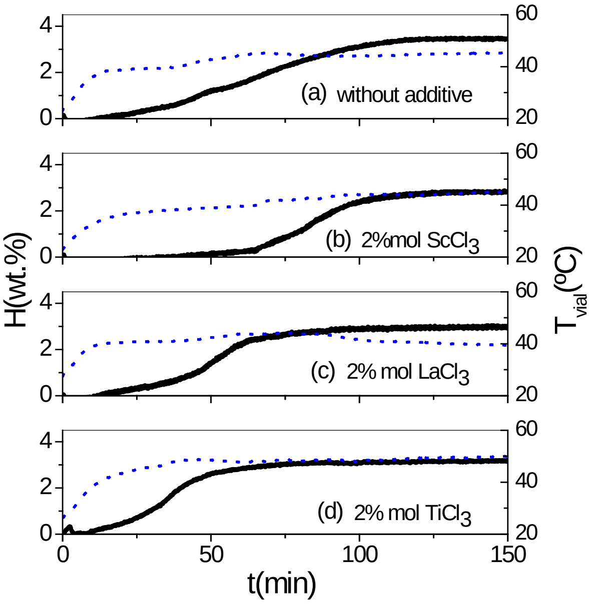

Figure. Hydrogen uptake (left scale, full lines) and vial temperature (right scale, blue dotted lines) variations during mechanochemistry of (a) KH+Al, (b) KH+Al+ $ScCl_3$, (c) KH+Al+$LaCl_3$, and (d) KH+Al+$TiCl_3$ mixtures.

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In-situ Raman Study of H → D Exchange in γ-$Mg(BH_4)_2$

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Isotope spectroscopy can provide useful insight into molecular structure and bonding. Due to the large mass difference of H and D, vibrational spectra of the molecular groups containing the two isotopes are easily distinguished and can be used to study the mechanisms of various intermolecular processes. Isotope spectroscopy of complex hydrides, for example $LiBH_4$ and $Mg(BH_4)_2$, have been used to investigate synthesis, diffusion, decomposition and also thermodynamic properties [1-3]. In this work *in-situ* isotope Raman spectroscopy was applied to study the H-D exchange in $Mg(BH_4)_2$ between 300 and 543 K.

Commercial γ-$Mg(BH_4)_2$ was used in this study. This phase polymorph is a rare example of the porous hydride with high specific surface area [4]. The sample was soaked in 0.3MPa D_2 at 300 K and gradually heated at 5 K/min rate. Simultaneously Raman spectra were recorded. with a Nicolet Almega micro-Raman spectroscope with 532 nm excitation wavelength. The first evidence of H-D exchange appeared at 373 K as a peak at 1717 cm^{-1} and assigned to the B-D stretching mode in BDH_3. With increasing temperature, we were able to record well-resolved peaks due to the B-D stretching in various $BH_{4-x}D_x$ ions [5].

Isotope-exchange reactions were also followed isothermally at several steps (Figure 1). allowing for the reaction kinetics studies. Spectral features were assigned to various $BH_{4-x}D_x$ species by means of symmetry correlation and 2D correlation analyses [6].

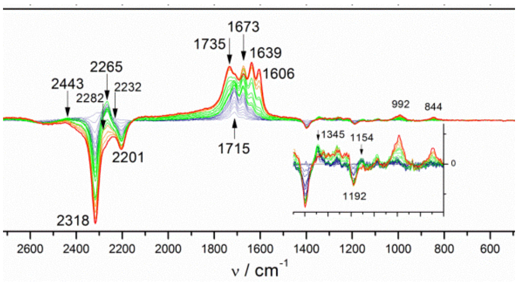

Figure 1. Subtracted in-situ Raman spectra of H→D exchange in γ-$Mg(BH_4)_2$ at 413 K.

Our work has shown that the isotopic exchange in the porous high SSA γ-$Mg(BH_4)_2$ at appreciable rates occurs on a minute time scale already at 373 K and only at 0.3 bar D_2 pressure. These are the mildest exchange conditions observed in stable ionic borohydrides. The *in-situ* study has shown also that the gas-solid isotopic reaction follows the $BH_4^- + D^\bullet \rightarrow BH_3D^- + H^\bullet$ mechanism at least at the initial reaction steps. Ex-situ deuteration of porous $Mg(BH_4)_2$ and its dense phase polymorph indicated that the intrinsic porosity of the hydride is the key behind the high isotopic exchange rates. It implies that the solid-state H(D) diffusion is considerably slower than the gas-solid H-D exchange reaction at the surface and it is a rate-limiting steps for hydrogen desorption and absorption in $Mg(BH_4)_2$.

The approach of the *in-situ* spectroscopic scrambling can be utilized to the wide veriety of materials and problems.

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Dr. Olena Zavorotynska obtained her Specialist degree in Physics from Kyiv-Mohyla Academy in Kyiv, Ukraine, in 2006. She continued her studies in the University of Turin, Italy, where she earned her PhD degree in Materials Science in 2010 under the supervision of Prof. Giuseppe Spoto. The work was mainly focused on characterization of the materials' surfaces (zeolites, MOFs, polymers) with variable-temperature vibrational spectroscopy of probe molecules. In 2010-2012 she worked as the research assistant in University of Turin, studying metal borohydrides for hydrogen storage applications. She continues this research at present at the Institute for Energy Technology in Norway, where she works as post doctorate fellow since 2012 in the group of Prof. Bjørn Hauback.

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NMR Studies of Molecular Dynamics in Complex Metal Borohydrides

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Borohydrides are promising hydrogen storage materials due to their high gravimetric hydrogen content, with systems such as $LiBH_4$ containing almost 20 wt. % of hydrogen. However, hydrogen in these systems is chemically bound and has to be released through a chemical reaction, often requiring high temperatures to take place ($LiBH_4$ decomposes at 450 °C, which is not practical for on-board storage in a car, where the working temperature of a fuel cell is around 100 °C). In order to reduce the decomposition temperature, new systems have been synthesized, introducing additional elements and thus destabilizing the structure.

A thorough understanding of internal dynamic processes that take place in borohydrides is desired in order to help designing systems with even better properties. For this purpose, Nuclear Magnetic Resonance (NMR) is a powerful tool, both in view of determining local structure and to study molecular dynamics.

I will present NMR studies of two systems, $LiZn_2(BH_4)_5$[1] and $Sr(BH_4)_2(NH_3)_2$[2]. Both decompose slightly above 100 °C and, although none of them releases only pure hydrogen, are good candidates to study dynamics processes of atomic groups, providing link between the microscopic and the bulk properties of these systems.

Molecular dynamics was investigated experimentally by ^{1}H, ^{11}B, and ^{7}Li NMR spectrum and spin−lattice relaxation techniques. Different thermally activated reorientational processes of BH_4 tetrahedra about their 2-fold and 3-fold symmetry axes were identified from the temperature-dependent spin−lattice relaxation rates and were quantified by their activation energies, in relation to the structural details.

In $LiZn_2(BH_4)_5$, we found two different components in relaxation, related to two different types of BH_4 tetrahedra (see Fig. 1). On the other hand, $Sr(BH_4)_2(NH_3)_2$ contains two types of hydrogen containing units (BH_4 and NH_3) and dynamics of both appears to be strongly influencing one another.

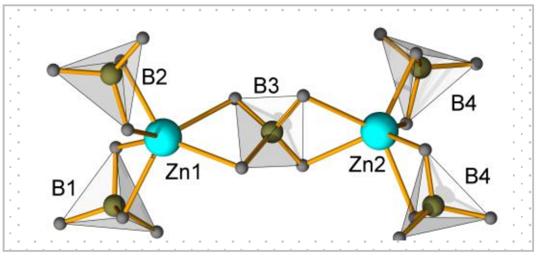

Figure 1. Anion structure in $LiZn_2(BH_4)_5$

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NaSbSn compound as negative material for Na cells at room temperature

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Lithium-ion battery technology is widely spread in our daily life and is considered as potential candidate for the electric vehicles' market and stationary applications. Due to limited resources and high cost of lithium precursors, it is necessary to have alternative batteries. Sodium-based batteries offer the opportunity for large scale stationary storage devices in smart electrical grids, especially due to the cost balance of the resources. Despite the fact that efforts have been successful to develop cathode materials, few families of anode materials have been reported in the literature [1]. SbSn alloys have recently shown promising performances when used as anode in sodium batteries [2, 3].

In this study, a presodiated compound of nominal composition NaSbSn was investigated in half cells versus metallic sodium with different electrode formulations. The conductive additive significantly influences the capacity reversibility. At a rate of 30 mA/g, a reversible capacity of ca. 380 mAh/g could be sustained over 10 cycles.

The pristine material consists of amorphous regions with two crystalline phases including a Sn-rich phase and an unidentified one. This last same phase was also found for other compositions during our investigation of the Na-Sb-Sn system at room temperature [4]. NaSbSn compound has the specificity to be desodiated or sodiated at the first cycle. The structural changes were investigated by *ex-situ* XRD measurements. In both cases, during desodiation of the electrodes, a well-crystallized SbSn alloy phase has been observed for the two first desodiations (Fig. 1) which differs from the observations described by Darwiche *et al.* [3]. The presodiated NaSbSn electrodes behave therefore differently than the SbSn electrodes. Furthermore, the evolution of the structural changes during sodiation/desodiation upon cycling is dependent on the starting point. The patterns obtained after each sodiation are different if Na ions are inserted or removed first into or from the pristine material. At fully discharged state, an increase of crystallinity is observed upon cycling when Na ions are removed from the pristine material at first (Fig. 1a). This behavior is different from the pristine material where Na ions are first inserted (Fig. 1b).

The presodiated NaSbSn electrodes show interesting feature. Preliminary results will be presented as starting point for discussions.

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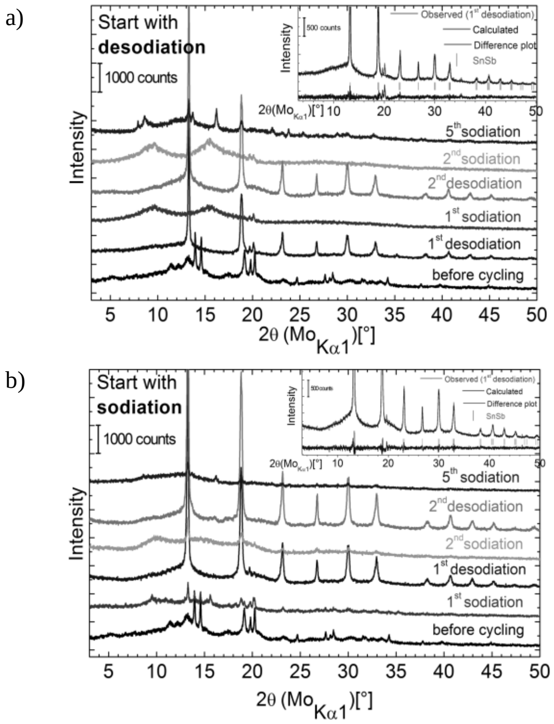

Figure 1. *Ex-situ* XRD patterns of NaSnSb electrodes start with desodiation (a) and sodiation (b), after the 1st, 2nd and 5th sodiation/desodiation. Inset: Rietveld refinements of the SnSb phase recovered after the 1st desodiation.

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After a 4-months stay in the laboratory of Prof. Jeff Dahn (Halifax, Canada) as summer student working on intermetallics for lithium ions batteries, a master degree in Material Science was obtained at the University of Strasbourg (France). Currently in the 2^{nd} year of the PhD studies, intermetallics used as negative electrode materials for sodium batteries are in focus of study.

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SnO_2/ pyrolyzed bacterial cellulose composites as anode materials for Na-ion battery

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Li-ion batteries have been successfully utilized as a power source in hybrid electric vehicles (HEV) and mobile electronic devices such as mobile phones and lap-top computers. But, the relative abundance of lithium in the Earth's crust is limited to be only 20 ppm and so lithium resources are expensive. Recently, sodium-ion (Na-ion) batteries have emerged as an attractive electrochemical power source for energy storage and conversion, owing to nature's abundance of sodium [1, 2].

Tin oxide is an attractive material as a potential anode material in sodium-ion battery because of high volumetric and gravimetric capacities. But SnO_2 suffers from an extremely large volume change during charge and discharge, resulting in electrode degradation and fast capacity fading [3, 4]. To overcome these problems and enhance the cycling stability, one of the most effective method is to deposit nanostructured active materials into a three-dimensional conductive porous network [5].

Herein, we report an easy, low cost and environmentally benign SnO_2/ pyrolyzed bacterial celluloses (PBCs) composite. PBCs with microfibril network have three-dimensional porous structure. Pure SnO_2 nanoparticles (NPs) with narrow size distribution have been synthesized with a non-aqueous, simple and surfactant free method. Then those synthesized SnO_2 NPs were added into the bacterial cellulose production environments leading to BC coated SnO_2 composites. After carbonization at a moderate temperature under an inert atmosphere, SnO_2 NPs decorated PBCs (SnO_2/PBC) are obtained.

The morphology and structure of SnO_2/PBC were characterized by X-ray diffraction, thermogravimetric analysis, transmission and scanning electron microscopy. All the identified peaks are assigned to tetragonal SnO_2 and according to TEM images, SnO_2 have small size (~13 nm) covered with cellulose fibers.

To understand the sodium storage properties of the as-prepared samples, a series of electrochemical measurements were performed. Figure 1 shows the SnO_2/PBC composite acting as anode material for Na-ion batteries.

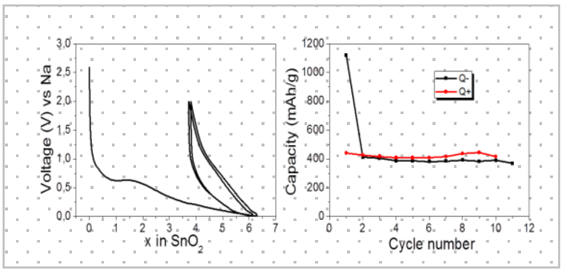

Figure 1. Cycling performance of SnO2/PBC composite

As it is seen in Figure 1 the first cycle in the sodium system is not reversible which should be due to the SEI layer formation and decomposition of SnO_2 to Sn. Following cycles are reasonable reversible in which the alloying reaction takes place between Sn and Na. The composite electrode Na-storage capacity shows 400 mAh/g with an good capacity stability.

In this contribution, we will be discussing the role of electrolyte additives and nanoparticle loading into the cycle performance of the cells.

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An aqueous rechargeable sodium battery cathode based on $NaFePO_4$ for large scale energy storage systems

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Long cycle life, low cost, environmental benignness and low risk of safety are very important parameters for Energy Storage Systems (ESSs). Abundant and non-toxic raw materials and stable storage systems as well are required for stationary applications. Although the Lithium Ion Batteries (LIBs) have highest energy density[1] and long cycle life[2], they are not applicable for large-scale applications due to the limited source of lithium. Furhermore, usage of toxic and flammable electrolytes leads security problems. Therefore, development of low cost and safer materials is critical. Sodium is of interest not only with chemical-physical properties similar to that of Li but also sodium's abundancy and cheaper price compared to Li. Sodium Ion Batteries (NIBs) are considered as a potential alternative for rechargeable batteries.

Moreover, usage of sodium in aqueous electrolytes which has 10 fold higher ionic conductivity than organic electrolyte may prevent security issues and resolve energy storage problems for large scale systems at high power rate. In this study, $NaFePO_4$ cathode material was synthesized by electrochemical sodiation of $LiFePO_4$ in 1M $NaNO_3$ solution. Then, half-cell electrochemical proprerties were tested in order to investigate effect of dissolved oxygen, pH and type of the salt and salt concentration.

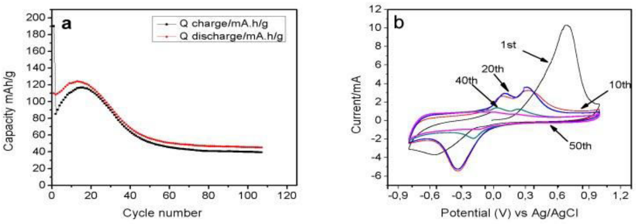

Fig 1. a) Charge/discharge profile of sodiated $LiFePO_4$
b) CV analyses of $LiFePO_4$ and $NaFePO_4$ at 5mV/s.

$NaFePO_4$ shows (Figure 1a) rapid capacity fading due to dissolved oxygen[3] and structural deformation.This could observed clearly in Cyclic Voltammetry (Figure 1b) after 50th cycle, oxidation and reduction plato were almost disappeared. Na extraction occurs in two voltage plateaus separated by an intermediate phase Na_xFePO_4 (x 2/3), whereas three phases ($FePO_4$, $Na_{2/3}FePO_4$ and $NaFePO_4$) appear simultaneously during Na insertion (Figure 1b) as clearly seen in reduction peak.

The samples are characterized by various techniques; scanning electron microscopy (SEM), X-ray diffraction (XRD), BET to analyse composition, morphology, particle size and surface area of cathode material.
In conclusion, sodium cathode material($NaFePO_4$) was synthesized by electrochemical sodiation of $LiFePO_4$ and utilized in aqueous batteries. Electrochemical responds showed $NaFePO_4$ is promising candidate for large scale energy storage systems with its outstanding rate capability, safety characteristics and lower price as well.

Acknowledgements
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Improved Lithium-Sulfur Batteries by Preventing Li_2S Formation

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Lithium-sulfur batteries offer high theoretical capacity (1672 mAh/g), high energy density and low cost, but their non-stability and rapid capacity fade result in short cycle life and limit their usage. The reasons are (i) the use of a lithium metal anode which may cause safety problems with liquid electrolytes, (ii) the low active material utilization due to the insulating nature of sulfur, (iii) the soluble polysulfide species generated during the battery operation, which diffuse throughout the separator and deposit on the lithium electrode resulting in a loss of active material, (iv) the irreversible deposition of non-soluble lithium sulphide (Li_2S) both at the cathode and lithium anode. Li_2S formation is one of the most important problems for Li-S batteries that it has low electrochemical activity and blocks carbon framework. In this contribution, we present how Li_2S formation might be dentrimetal to the Li-S batteries.

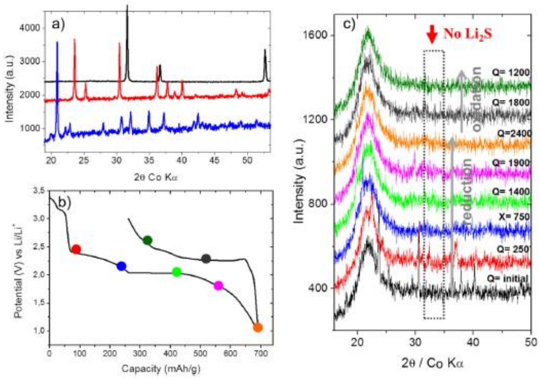

Fig. 1. a) XRD pattern of the chemically formed of lithiated V_2O_5 (Black: Li_2S, Red: V_2O_5, Blue: $Li_{1.03}V_2O_5$), b) first discharge-charge profile of MCS+V_2O_5, c) in-situ XRD observation showing no Li_2S formation.

First of all, the formation of solid and insulating Li_2S in a porous carbon/sulfur composite was initially examined using by detailed analytical techniques such as in-situ XRD, post-mortem analysis of TEM and SEM. Later on, in order to avoid Li_2S formation, either the addition of an electrochemically active metal oxide, V_2O_5, which oxidizes Li_2S to longer chain of polysulfides or tuning the cut-off voltages are suggested.

XRD pattern of Li_2S, V_2O_5, and $Li_{1.03}V_2O_5$ are shown in Fig. 1a. The first charge-discharge profile of the MCS in the presence of V_2O_5 additive (Fig. 1b) together with the corresponding in-situ XRD patterns (Fig. 1c) did not reveal the formation of Li_2S.

Fig. 2a shows that the discharge capacity decreases with the increasing of the discharge cut-off voltage and the best capacity retention being reached when the cycling is limited to the 1.8-3.0 V range (Fig. 2b).

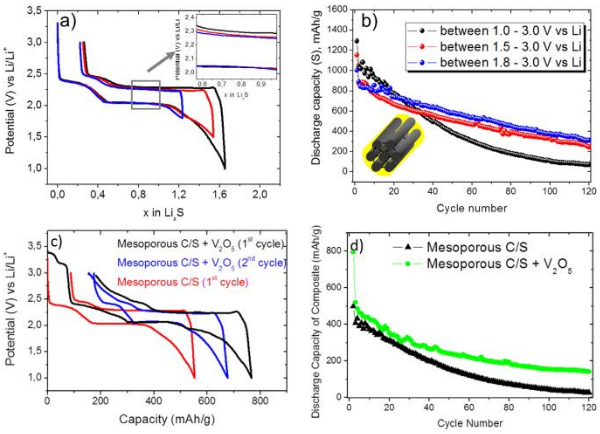

Fig. 2. a) First discharge-charge profile of the MCS at different cut-off voltages, b) cycling performances of the MCS at different cut-off voltages, c) First charge-discharge profile of MCS and MCS+V_2O_5 d) cycling performance of MCS and MCS+V_2O_5 composite.

As a whole, for the MCS composite alone, a sharper capacity fading is observed. However, in the case of MCS+V_2O_5 composite, the capacity after the 120 cycles was retained at higher values, 150 mAh/g (Fig. 2d) together with a lower decay rate, 0.59% per cycle. It can be seen that the MCS+V_2O_5 composite cathode offers 125 mAh/g higher capacities than the MCS cathode in the absence of the V_2O_5 additive.

Acknowledgements

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Polybenzimidazole/Silica Hybrid Membranes for High Temperature PEM Fuel Cells

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Proton exchange membrane (PEM) fuel cells are potential candidates for transportation, power plant generation/ cogeneration, and portable power applications. PEM fuel cells operating at high temperatures have received a great deal of attention in recent years due to the their numerous advantages, which include increased reaction kinetics, easier water management and a better tolerance to CO [1].

Many different types or groups of membranes are used for high temperature PEM fuel cell (HT-PEM) and of these the poly(2,2′-mphenylene-5,5′-bibenzimidazole) (PBI) based membranes are amongst the most widely used and studied. PBI-based HT-PEM fuel cell technology, unlike Nafion-based technology, is currently still in the research stage [2].

The use of PBI/silica hybrid membranes as an electrolyte material could potentially enhance the performance and stability of the fuel cell. Moreover, the use of silica ss a filler also increases the aciddoping level in the PBI membrane, thereby enhancing proton conductivity. The aim of this work is to developed hybrid membrane based on PBI membranes that contain silica nanoparticles. PBI polymer was synthesized in the laboratory according to a procedure described in a previous work [3].

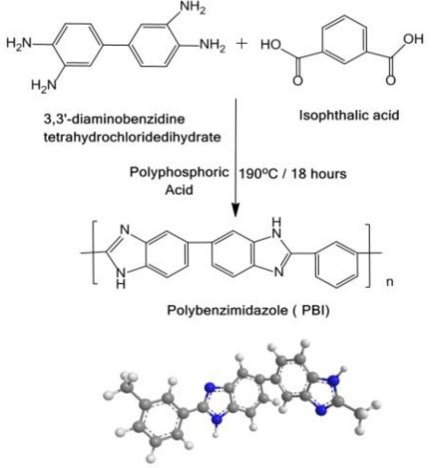

Figure 1. Reaction scheme of the PBI polymer.

The membranes were cast from a PBI polymer synthesized in the laboratory, and the modified membranes contained nano-sized silica as a filler. Both standard and hybrid membranes were cast using the following procedure. First, the polymer solution in DMAc was cast onto glass plates. The plates were then placed in an oven at 80^{o}C for approximately 12 h. The membranes were then immersed in an 85 wt.% H_3PO_4 bath for a minimum of five days to ensure steady-state conditions for the H_3PO_4 absorption process under ambient temperature. The membranes were physically/chemically and electrochemically characterized for use as electrolytes in HT-PEM fuel cells.

Membrane Electrode Assemblies (MEA)s were fabricated by Ultrasonic Coating Technique. A catalyst ink was prepared by dispersing a carbon-supported catalyst (70 wt.% Pt/C) in a mixture of DMAc and PBI by sonication. The catalyst ink was ultrasonic-sprayed onto the GDLs by the Sono-Tek 'Exacta-coat' ultrasonic spray instrument. After the catalyst ink was sprayed onto the GDL, the electrodes were left to the oven at 190^{o}C for 2 hours to remove the solvent traces. Then the catalyst ink onto the GDLs, MEA was prepared by pressing GDLs onto the both sides of the phosphoric acid doped PBI membrane at 150^{o}C for 5 min.

The PBI/silica hybrid membranes were tested in a single cell with a 25 cm^{2} active area operating at the temperature range of 160 to 180°C. Non-humidified air and hydrogen were supplied at ambient pressure to the cathode and anode, respectively. The gas stoichiometry was 1.5 and 2.5 for hydrogen and air, respectively. The PBI/silica hybrid membrane showed the best performance at 160◦C. As a result, hybrid PBI/silica membrane has exhibited improved mechanical strength, high proton conductivities, and single cell performance compared to the pristine PBI membrane. The results suggest that PBI/Silica-based hybride membranes are promising electrolytes for HT-PEM fuel cells.

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Modeling Of Polymer Electrolyte Membrane Fuel Cell and Sensitivity Analysis

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Fuel Cells are electrochemical reactors which converts chemical energy to the electrical energy. They consist of anode and cathode compartment in which redox reactions take place. The electrical energy is obtained by these reactions, typically oxidation on the anode side and reduction on the cathode side. The direct conversion of chemical energy to the electrical energy yields higher efficiency, and the hydrogen and oxygen fed to the reactor only produces water. Therefore, fuel cells have high power density, low or zero emissions, long cell and stack life and low corrosion; in addition, they are promising alternative energy resource for the future due to their sustainability [1].

Fuel cells can be classified according to the electrolyte involved in the system. Polymer Electrolyte Membrane (PEM) Fuel Cells usually include perfluorosulfonated polymer electrolyte which behaves like insulator for electrons and conductor for protons. Nafion® produced by DuPont has become an industrial standard for the polymer electrolyte. The catalyst layer can be found on both sides of the membrane, and it is followed by gas diffusion layers which distributes the reactant gases to the active area uniformly[2]. Finally, bipolar plates collect the current and complete the circuit. The operation temperature varies between 50-100 °C, above 100 °C the Nafion deformation is observed.

A three dimensional model of Polymer Electrolyte Membrane(PEM) Fuel Cell having an active area of 25 cm^2 has been investigated in order to examine the parameters affecting the performance of the cell and to provide the best conditions for the operation. The system is modeled by using COMSOL Multiphysics which is a commercial software package. It solves the model by finite element method. Steady-state, single-phase and isothermal is assumed while demonstrating the mass and momentum transport phenomena as well as the electrochemical current circumstances occurring in the gas diffusion layers, catalyst layer and polymer electrolyte in the model. In addition, the pressure drop is neglected, so the system is assumed to operate under isobaric conditions. The flow of gases within the system is modeled by using Navier-Stokes equation, for the multicomponent diffusion Maxwell-Stefan equation is used. Moreover, Tafel equation is used to model the electrochemical kinetics of the system.

The model is solved with the operation temperature 65 °C and the operation pressure is taken as 1.2 bar. Pure hydrogen and air is used as reactants. Polarization curve, membrane current density, concentration profiles of both reactants and product are obtained as results of the model. The domain constructed in COMSOL Multiphysics is given in Figure1.

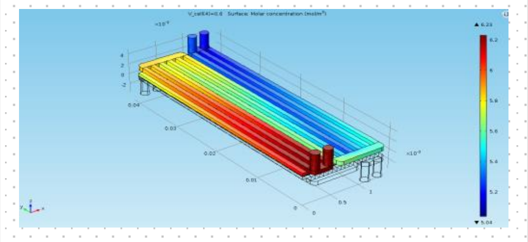

Figure 1. Domain used in Comsol Multiphysics.

It is seen that temperature has a crucial role in the operation conditions. Therefore, sensitivity analysis for temperature is performed. The model is solved for different temperatures ranging from 60-75 °C. While constructing the analysis mass flow rate of hydrogen and air is kept constant. In other words, changing volumetric flow rate of reactants due to the temperature variation is balanced by keeping their mass flow rate constant. By doing so, only parameter affecting the system becomes temperature.

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High Proton Conductive PVA/PAMPS/Triazole Composite Membrane for PEMFC

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Proton exchange membrane fuel cells (PEMFCs) are one of the most innovative research areas in search of novel power sources, especially because of their no to low greenhouse gas emissions, high efficiency, diverse fuel options and low maintenance costs. Today, most common membranes are based on the perfluorosulfonic acid structure, and the well-known is Nafion, a trademark of Dupont. Nafion has a relatively high stability in mechanical terms and dimensions owing to its PTFE backbone, meanwhile, ionically bonded sulfonic acid functional groups enable protons to be transfered through the membrane. Nafion has such advantages, but it also has limitations and drawbacks such as high costs, methanol crossover and a rapid decrease in proton conductivity above 80 ^{0}C [1-5]

Physically blended membranes that consist of hydrocarbon matrix significantly draw attention because they are cost-effective and suitable to be tailored. PVA is widely used as a matrix component in blended membranes because of its well forming film ability, hydrophilic structure, chemical and mechanical stability, but it has poor proton conductivity.[1-3] PAMPS, which is derived from AMPS (2-acrylamido-2-methylpropanesulfonic acid), is an acidic polymer that shows a higher proton conductivity than partially hydrated Nafion. As a result of chemical structure, PAMPS is able to exhibit much endurance of water when compared to Nafion and polystyrene sulfonic acid (PSSA). It thus can be a suitable membrane material for fuel cell operation at high temperatures.[1-4] 1H 1,2,4-triazole is reported to promote productive proton conduction in a polymer electrolyte membrane (PEM). 1H-1,2,4-triazole may conduct proton through either the vehicle mechanism or Grotthuss mechanism. [5]

In this study, the proton exchange membranes composed of PVA, PAMPS and 1,2,4-Triazole were synthesized. Membranes were prepared physically blending and then solvent-casting methods. Flexible, transparent membranes with high thermal stability and good mechanical properties were obtained. The characterization of the membranes is carried out by using Fourier transform infrared (FTIR) spectroscopy for the interpolymer interactions, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for the thermal properties, and scanning electron microscopy (SEM) for the morphological properties. Proton conductivities in the anhydrous state measured from room temperature to 150 ^{0} C by using impedance spectroscopy. The proton conductivity of the composite membrane achieves up 2×10-3 S cm $^{-1}$ at 150 ^{0}C under anhydrous conditions

Figure 1. photographs of the membrane

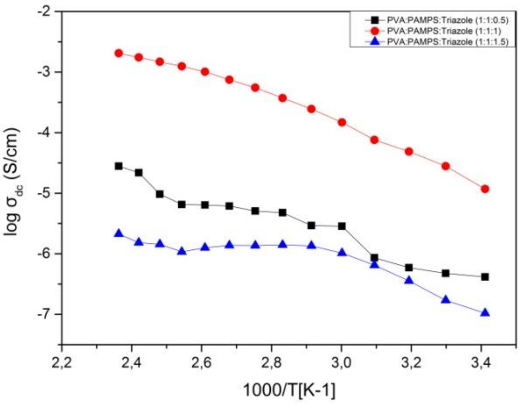

Figure 2. the DC conductivity plots of the membranes

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Modelling of PEM Water Electrolysis and Determining Operating Parameters for Different Anode Catalysts

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Global warming, greenhouse gas emissions and air pollution effects led researcher to carry out further studies on clean and sustainable energy systems. Hydrogen energy shows great potential as sustainable energy production methods. Hydrogen, that are not available in nature, is one of the best solution of alternative energy research due to converting into electricity very efficiently using fuel cell and storing high pressure in less space and light weight. Hydrogen can be produced different way and water electrolysis is easiest and practical method [1]. Chemical reaction process that are conducted in water electrolysis split water to oxygen and hydrogen molecules. These reactions are reverse process of proton exchange membrane (PEM) fuel cells. PEM water electrolysis systems are enviromentally friendly and can simply integrate renewable energy sources such as photovoltaic and wind power. These advantages of PEM water electrolyser led researcher to develop this technology providing hydrogen economy [2-5]. Basic reactions that are conducted PEM water electrolysis electrodes are different for anode and cathode side.These reactions can be seen in **Fig.1.**

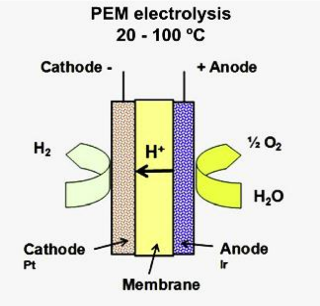

Figure 1. Schematic of the operating principle of PEM water electrolyis [6]

At the anode side water is separated into oxygen, protons and electrons.

$$2H_2O_{(liq)} + 2e^- \rightarrow H_{2(g)} + 2OH^-{}_{(aq)}$$

At the cathode side protons goes through membrane and combines with electrons which is conducted by external circuit to generate hydrogen gas.

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

The net reaction of PEM electrolysis is:

$$H_2O_{(liq)} \rightarrow H_{2(g)} + 0.5O_{2(g)}$$

Due to the simplicity of net reaction, reactions that are conducted in membrane and electrodes are very complex because of two phase flow conditions. It is necessary to overcome some problems for better operating conditions of PEM electrolysis cell. For this reason numerical modellings are very important tools to predict experimental works. Aim of this study is generating simple and useful numerical model to determine working parameters of PEM electrolysis cells based on Butler-Volmer kinetics on the electrode surface and reactions that are consisted through membrane. In this model different anode catalyst layers such as Pt, Pt-Ir are used to observe difference of water consumption and hydrogen production in the flow channel. In this work Comsol Multiphysics software is used for numerical calculations. The various parameters that are affected cell performance are investigated such as pressure, temperature, flow rate of water and current density. Model is used to optimize cell parameters in particular value. Performance curve (V-I) is validated by experimental datas. For simplicity flow is laminar, stable and steady state conditions. For all phases momentum and continuity equations are used to observe velocity and mass fractions of species.

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Metal hydrides in batteries and semiconducting devices

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$$H^{-} \leftrightarrow H \leftrightarrow H^{+}$$

Hydrogen is a very polarizable atom

The hydride ion contains weakly bonded electrons around a +1 proton. In a sense one can see it a way to store electrons. When the electron is included in a more conventional octet around for example an oxygen atom, energy is released. This is essentially the principle behind both NiMH batteries and fuel cells.

Polarizable also means an easily deformable electron density. This can have as consequence that small atomic structural changes can have profound impact on the electric conducting properties in conducting and semiconducting metal hydrides.

Both these important aspects have been developed during the more than 40 years long quest for finding metal hydrides suitable for hydrogen storage systems since the “oil crisis”. The focus on metal hydride storage systems has, however, become less when Toyota chose to select high pressure gaseous storage for their fuel cell vehicle. Toyota will, however, use NiMH batteries for almost their entire Hybrid Electric Vehicles (HEV) models and Fuel Cell Vehicles (FCV).

Photovoltaic solar cells based on different semiconducting systems are presently getting established on a rapidly expanding market. Several of the new metal hydrides discovered in the search for metal hydride storage systems have bandgaps that are well suited for photovoltaic applications. The polarizable hydride ion offers also a possibility to tune the bandgap opening up for a more effective use of the solar radiation in multiple junction solar cells.

NiMH batteries and solar cells have not been much in focus in the more traditional metal hydride community. This paper with give some examples of the possibility to find interesting materials in these aspects from the large number of new systems that have been discovered in the above quest for hydrogen storage materials.

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TiNi-based intermetallic compounds for Ni-*M*H batteries: challenges and opportunities

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Several families of AB_n intermetallic compounds can be used as active material for negative electrodes in Ni-*M*H batteries [1]. Here, *A* and *B* stand for metals forming stable and unstable hydrides, respectively. Today, AB_5 to AB_3 compounds with typical discharge capacities of 320 to 380 mAh/g, respectively, are used in commercial Ni-*M*H batteries [2]. However, they all contain expensive rare-earth elements and their mass capacity is limited by their high molecular weight. As an alternative, stoichiometric *AB* intermetallic compounds crystallizing in the CsCl-type structure, such as TiNi and its derivatives, are foreseen as promising electrode materials.

TiNi absorbs hydrogen reversibly by solid-gas reaction, forming β-$TiNiH_{1.4}$ hydride at normal conditions of pressure and temperature [3]. Following the electrochemical reaction, TiNi typically exhibits a reversible capacity of 150 mAh/g at C/10 regime, which only represents 40% of its total hydrogen content [4]. In-situ neutron diffraction measurements have demonstrated that such a limited reversible capacity is exclusively provided by hydrogen solubility in the β-hydride phase (from TiNiH to $TiNiH_{1.4}$) [5]. Recovery of the full storage capacity of TiNi (350 mAh/g) is expected to be attained if TiNiH hydride is destabilized by suitable chemical substitutions.

The physicochemical properties of TiNi are extremely sensitive to chemical substitutions. This statement has been extensively investigated in relation with the outstanding properties of TiNi as shape memory alloy [6]. Chemical substitutions on both *A*-type and *B*-type sublattices are possible which allow tuning the shape memory properties of TiNi-based compounds to specific applications.

In this context, we have explored the effect of chemical substitutions on the solid-gas and electrochemical properties of TiNi. In particular, our studies have considered the substitution of Ti by Zr on the *A*-type site [4,7], and the substitution of Ni by Pd [8,9], Co or Cu [10] on the *B*-type site.

From a fundamental point of view, these works demonstrate that *i)* the hydrogen content, crystal structure and stability of TiNi-based hydrides strongly depend on substitution effects, *ii)* the solid-gas hydrogenation properties are governed by the electronic modifications, rather than geometric ones, induced by the element substitution studied in this work, and *iii)* the electrochemical properties of TiNi-based electrodes are extremely sensitive to chemical substitutions. As for practical implications on Ni-*M*H batteries, we here demonstrate that TiNi-based compounds can potentially provide discharge capacities as high as 600 mAh/g. However, a compromise between high reversible capacity and extended cycle-life is observed so far. Best results by now have been obtained for the Ti(Ni,Cu) system for which capacities close to 300 mAh/g are obtained with reasonable cycle-life. Strategies to further improve these interesting properties will be addressed during the conference.

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Fermin Cuevas

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Nanostructured metal hydrides for H storage and metal hydride batteries: the role of magnesium

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Intermetallic hydrides demonstrate a close interrelation between their crystal chemistry and hydrogen storage behaviours thus allowing optimization of the H storage performance. Hydrogen accommodation in the metal lattice is typically accompanied by a few percent increase of the interatomic metal–metal distances, while the H atoms fill the available interstices in the intermetallic structures. However, in a number of cases a formation of the metal hydride leads to rebuilding of the metal sublattice. Such a rebuilding is of particular interest as it could be related to the unconventional metal–hydrogen bonding in the hydrides thus formed. The present paper reviews our recent work on investigating of the role of magnesium on the hydrogen storage behaviours in the alloys formed with nickel and rare earth metals. Studied materials included cost efficient advanced metal hydride battery anode La–Mg–Ni H alloys offering benefits of high discharge capacity of 400 mAh/g, high drain discharge, good performance at sub-zero temperatures and increased cycle stability in the Ni-MH battery applications.

Despite significant differences in chemistry between the rare earth metals and magnesium, Mg forms extensive solid solutions in the RE-Ni intermetallic alloys, reaching up to 67 % for the $RENi_3$ alloys crystallizing with a $PuNi_3$ type trigonal structure.

The following hydrides will be in focus:

(a)$(La,Pr,Nd)_{3-x}Mg_xNi_9$ (*$PuNi_3$* type) hydrides with $(La,Pr,Nd)_2MgNi_9$ stoichiometry;

(b) Mg-rich $LaMg_2Ni_9$-H_2 (D_2) system studied at pressures up to 1,000 bar;

(c) $MgNi_2H_3$ hydride synthesized at H_2/D_2 pressure of 28 kBar and 300 °C.

These studies revealed that magnesium plays a decisive role in determining the thermodynamic properties, reversible H storage and electrochemical capacity and the mechanism of the metal-hydrogen bonding in the studied hydrides.

The most important features include [1-5]:

(a) Increase of Mg content and a replacement of La by Pr and Nd causes a significant destabilization of the hydrides with a possibility to variate the enthalpy of decomposition between 24 and 35.9 kJ/mol H_2.

(b) Magnesium significantly affects the bonding mechanism of metal-hydrogen interactions studied in detail for the $(La,Pr,Nd)_2MgNi_9$ hydrides. A prominent and the most important feature of the hydrides is in the local ordering of the hydrogen sublattice built by stacking of the MgH_6 octahedra and NiH_4 tetrahedra.

(c) The hydrogenation properties of Mg-rich compounds become principally different from those for $LaNi_3$. $LaNi_5$-assisted hydrogenation of $MgNi_2$ in the $LaMg_2Ni_9$ hybrid structure takes place.

(d) Even though synthesized at 28 kBar H_2, $MgNi_2H_3$ is stable at ambient conditions due to the strong covalent bonding in the present in the rebuilt structure buckled Ni-H-Ni-H nets.

(e) Optimization of the content of Mg and Nd allows to increase diffusion rate of hydrogen and to achieve superior performance of the MH anodes at high current densities.

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Properties of carbons in electrochemical capacitors involving various types of electrolytes

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Supercapacitors (or ultracapacitors, or electrochemical capacitors) based on activated carbon electrodes are an energy storage device which has been the object of important research in the last decade [1,2]. They provide higher energy density than dielectric capacitors, while demonstrating higher power density than batteries [3,4]. Therefore, they are particularly adapted for applications which require energy in bursts during short periods of time, e.g., automobiles, tramways, buses, cranes, forklifts, wind turbines and in opening emergency doors of airplanes. Since the basic operating principle of supercapacitors is the electrostatic attraction of ions at the electrode/electrolyte interface, the commercially available supercapacitors demonstrate a high degree of reversibility, being able to withstand millions of charge/discharge cycles.

Owing to their high electrical conductivity, low cost and availability at ease, porous carbons are used as electrode materials in supercapacitors. Activated carbons (AC) provide high surface area, and their porosity can be tailored to the desired pore size distribution by varying the activation process or type of precursor. The correlation of ion size of the electrolytic system to the pore size of carbons has opened new research horizons in the field of supercapacitors [5,6]. Besides the pure electrostatic attraction of ions (electrical double-layer charging which plays in all kinds of electrochemical capacitors), the performance of capacitors can be enhanced by pseudocapacitive contributions. The later might be related with the presence of surface oxygenated and nitrogenated functionalities, electrochemical hydrogen storage, carbon interface with redox species [7,8].

The energy density of supercapacitors depends on the square of the operating voltage, which is controlled by the stability window of the electrolyte [7]. Aqueous electrolytes have a limited stability window up to 0.7–0.8 V in acidic and alkaline pH value [9] and up to 1.8–1.9 V in neutral pH value [10], while non-aqueous electrolytes have a stability window up to 2.7–2.8 V [11]. However, aqueous electrolytes give much higher capacitance values in comparison to organic electrolytes.

This presentation will review the basic role played by carbon materials in energy density enhancement of supercapacitors. A part of the discussion is also dedicated to the contributions of hydrogen storage and carbon/electrolyte interface to the overall capacitance. Finally, the importance of the electrolytic systems on the voltage, and consequently energy density, is also considered.

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François Béguin is Professor in Poznan University of Technology, where he leads a research group on energy storage systems. In the case of supercapacitors, his recent activities are dedicated to asymmetric and hybrid capacitors and to environment friendly systems. In 2013, he edited a book entitled “Supercapacitors: materials, systems and applications”. From 2006 to 2012, he was appointed in the French Agency for Research (ANR) as director of programs on Fuel Cells and Energy Storage Systems.

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Lithium ion batteries; from conception to development and beyond

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In this presentation we will briefly cover the major milestones of lithium ion battery (LIB) development, which led to today's success story. Both academic and industry research contributed to emergence and commercialization of LIB, starting from the 70's to the early 90's when Sony launched mass production.

Primary lithium batteries were in the market in the 70's. However, making the rechargeable version was one of the most challenging and risk taking step in battery development history.

Since early 90's until today, LIB experienced an exponential market increase and have become by far the dominating power source system for a broad range of market segments, including mobile electronics ("3C"), electric vehicles (EV) and stationary energy storage (ES). Over 15 billion LIB cells were produced by industry in 2014, mostly in Asia.

Despite tremendous LIB performance enhancement in energy density, power density, cycle life, shelf life, reliability, safety and cost over the last 25 years, today' LIB do not meet some of the stringent market demands and expectations in particular regarding the EV application. In fact, EV customers expect their car to perform as current gasoline powered cars, i. e. filling the gas tank in less than 10 minutes, drive for over 500 km per tank and keep the car for over 10 years. Today no battery technology allows complying with these requirements. Therefore, more R&D is being conducted worldwide to further improve LIB or develop new battery chemistry beyond LIB' with higher energy, power and life performances.

Some of the options will be discussed at both new chemistry and battery management levels.

Rachid Yazami is a Visiting Professor at the School of Materials Science and Engineering, NTU and serves as the Energy Storage Programs Director at ERIAN. Prof. Yazami served as a Visiting Associate at the California Institute of Technology in collaboration with JPL/NASA for 10 years (2000-2010). In 2007, while with Caltech he founded CFX Battery Inc. (now Contour Energy Systems), a startup company on fluorine based primary and rechargeable batteries located in Azusa, California. More recently, Yazami founded KVI Pte Ltd in Singapore. KVI develops systems for battery management through thermodynamics data aimed at enhancing battery life and safety.

Updates on Battery 500 project: collaborative research with ASELSAN

Ho-Cheol Kim and Team

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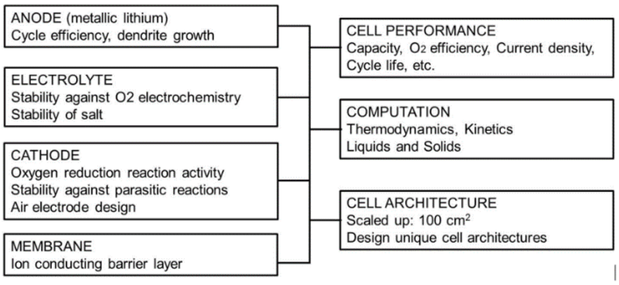
IBM Battery 500 project is an international R&D collaboration on rechargeable lithium-air batteries (LAB). The project kicked-off in summer 2009 as a grand challenge project in IBM Research-Almaden Research Center. Project name reflects the target of the project: to realize high energy battery that enables 500 miles of drive with single charge. The theoretical specific energy of LAB is 3458 Wh/kg (energy density: 3445 Wh/L), which is more than 8 times higher than that of lithium-ion batteries (LIB) (theoretical specific energy and energy density of LIB is approximately 400 Wh/kg and 1400 Wh/L, respectively). Considering the energy consumption for 1 mile driving with modern vehicles is about 300 Wh, 150 kWh battery will enable 500 miles of driving. If we assume the weight of battery as 300 kg, specific energy of 500 Wh/kg is needed to realize battery of 150 kWh. 500 Wh/kg is approximately 15% of the theoretical specific energy of LAB. The fact that state-of-the-art LIB has been achieved over 60% of theoretical specific energy (close to 50% for energy density) is intriguing for realizing 15% of theoretical value of LAB.



Challenges and research activity of Battery 500 project.

The research effort during the first phase of the project has been focused on understanding fundamentals of lithium-oxygen electrochemistry. Collaboration participants from Germany, Japan and Korea had been working closely with IBM team and addressed critical material issues for operating LAB with non-aqueous electrolytes. The project turns into the second phase from this year (2015) and the focus has been shifted more into demonstration of research prototype of the LAB at the end of the second phase. International collaboration continues for the second phase and the participants from Turkey, Spain, Korea and Germany are working together for the project.

In this presentation, I will discuss the collaborative R&D effort of Battery 500 coalition to tackle challenges associated with materials science and engineering. As shown in Figure 1, paramount challenge of LAB is the stability of component materials such as anode, electrolyte and cathode. I'll update the progress we have made in research of component materials along with focus on cathode materials where ASELSAN's effort makes critical contribution to the project.

Dr. Ho-Cheol Kim manages Energy Research Department at IBM Research-Almaden Research Center located at San Jose, CA. He joined IBM Research in 2001 after his Post-Doctoral research at University of Massachusetts at Amherst. He received his Ph. D. in Polymer Science from Seoul National University in Korea. His research has been focused on nano-structured materials (organic and inorganic) and their applications to eletronic devices. Recently he actively explores materials and devices for energy storage, in particular high energy metal-air batteries for electric vehicles and grid storage. He won the IBM Almaden Fund for Innovation (2005) and the IBM Research Division Award (2005, 2013). He has authored/co-authored over 110 research publications and holds over 80 granted/pending US patents.

Hydrogen adsorption on Au@Pd nanoparticles: a first principles study

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The necessity to find an alternative environment-friendly energy carrier is critical to address the global warming and shrinking fossil fuel supplies issues The use of hydrogen as an energy vector has proven to be an interesting alternative. The consolidation of high efficient hydrogen technologies relies on the search and development of storage materials able to provide high H_2 storage density and good H_2 sorption properties. Lately, bimetallic nanomaterials have attracted much attention due to their potential technological applications [1-2]. Experimental and theoretical studies have shown that bimetallic nanoparticles (NPs) present interesting properties due to their nano-sized structure, geometry and composition [3].

Here, first-principles calculations based on the density functional theory (DFT) were applied to study the H_2 adsorption on metallic nanoparticle. Model for Au@Pd nanoparticle (NP) with icosahedral geometry has been used. The Au@Pd NP is composed of a central core of Au atoms, coated by a surface of Pd atoms, as shown in Figure 1. The adsorption of the H_2 molecule was determined at each adsorption site by considering different H-H bond orientations respect to the center of each site.

The calculations were performed using the Vienna Ab initio Simulation Package (VASP) [4]. The projector augmented wave (PAW) pseudopotential was used to account for the electron-ion core interaction, using the PW91 functional as generalized gradient approximation (GGA) for the exchange-correlation term. The Brillouin-zone was sampled using the Gamma k-point only. For the plane-wave basis set a cut-off of 700 eV was used. All the structures have been optimized until the forces acting in each ion are less that 10^{-4} eV/Å.

Our calculations indicate that, for almost all adsorption sites, there is no energy barrier for H_2 dissociation at the surface of Au@Pd icosahedral nanoparticles, and the H_2 molecule spontaneously dissociate. The only exceptions are for the AE and AV sites. Besides, the adsorption energies for dissociated cases have a difference of about 1.3 eV lower than the non-dissociated cases.

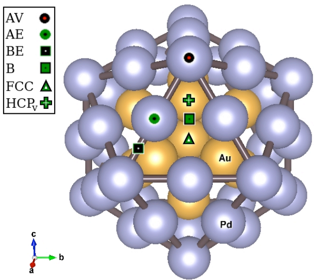

Figure 1. Schematic representation of the icosahedral Au@Pd NP. AV indicates the Atop Vertex, AE the Atop Edge, BE the Bridge Edge, B the Bridge sites. The FCC and HCP_V refer the hollow sites, in which, the subscript V denotes the sites that are near the Vertex of the nanoparticle surface.

The most energetically favorable adsorption sites were found to be the BE and HCP_V with the H_2 in the side-on orientation, with similar adsorption energies, -1.44 and -1.45 eV, respectively. For the BE site, the H_2 molecule is adsorbed in the diagonal orientation to the Pd-Pd connection, while for HCP_V it is adsorbed along the Pd-Pd connection.

Dodecahedral nanoparticles were also studied. Electronic properties, such as DOS, the d-band center, and COOP analysis are investigated. The results show that the H_2 adsorption properties strongly depend on the geometry of the nanoparticles and further studies are needed to development of bimetallic nanoparticles tuned for applications in hydrogen technology.

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Structure of TiFe alloy synthesized by ball milling

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The hydrogen is considered as the answer to the numerous problems associated with our current reliance on oil[1]. Numerous studies have been performed to develop hydride hydrogen storage, such as AB_n (A-rare earth or transition metal; B-transition metal; n=1, 2 or 5). The AB-type alloys are known as promising less expensive materials for hydrogen storage, for example, the TiFe is an interesting alloy because of its relatively high hydrogenation capacity (1.9%), excellent cyclability and low price[2].

Commercial elemental powders of Ti and Fe were stoichiometrically loaded into stainless steel vials (volume 50ml) with three stainless steel balls in a glove box filled with argon. 2%alcohol was added . The ball to powder weight ratio is 5. The milling was carried out in a planetary high energy ball mill (Retsch PM 400) at speed of 400 rpm under argon atmosphere at room temperature. In order to avoid the increase of temperature during the BM, the milling was paused 30min after every 30 min of operation. the mechanically alloyed powders were examined using X-Ray diffraction (XRD), the morphologies of the powder were characterized by scanning electron microscopy.

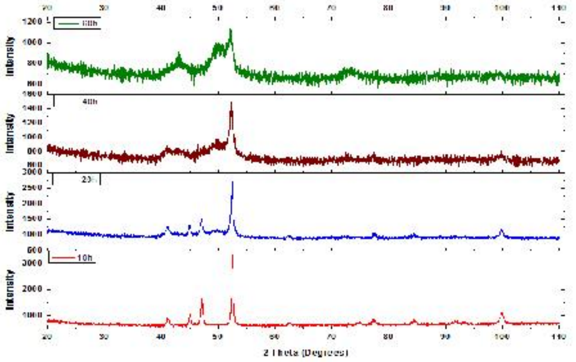
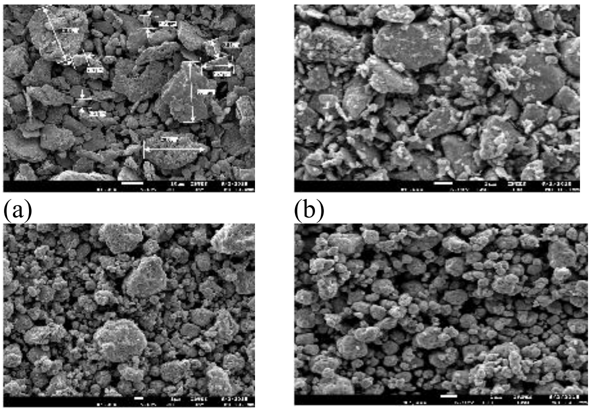


Fig1 XRD patterns of mechanical alloying TiFe milled for 10h, 20h, 40h and 60h.

With increasing the milling time, the peak intensties of the pure metals decrease. the sample milled for 40h seemed to become amorphous, the peaks from TiFe phase for 60h is broadened compared with those for TiFe (40h).


(a) (b)

(c) (d)

Fig2: SEM micrographs of TiFe alloy powders milled for various times 10h(a), 20h(b), 40h(c) and 60h(d).

The morphologies of the particle after milling for 10h are discernable. By increasing the milling time , the average particle size decreases. For the sample milled for 20h , we noted an appearance of small particles less than 15 µm , this is a sign of fracturing After milling for 60h, the size distribution is generally normalized.

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molarity effect on the properties of In_2O_3 for semiconducting devices application

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***Abstract**:* In this work, transparent conductive Indium oxide thin films were deposited on glass substrates by ultrasonic spray technique. We have studied the effect of precursor molarity by varying from 0,05 to 0,3 mol/l at substrate temperature 400°C.

To investigate the influence of precursor molarity on the properties of indium oxide thin films, several characterizations were carried out such as: XRD to determine the grains size, SEM for microstructural study and to determine films thickness and UV-Vis-Nir Spectroscopy for optical studies like the optical gap and the disorder, and Four-Point probes method were used for electrical measurements such as the conductivity.

***Keywords*:** Indium oxide, Optical properties, Spray Ultrasonic, Structural and electrical properties, TCO.

1. INTRODUCTION:

Indium oxide belong among transparent conducting oxides are widely used in various applications thanks to their low resistivity, high optical transparency and wide band gap. These applications include using in solar applications and transparent electrodes in various optoelectronic devices [1], liquid crystal displays [2], light-emitting diodes [3], the barrier layers in tunnel junctions [4], the active layers of gas sensors [5] or the material for ultraviolet lasers [6]. Therefore, there have been a lot of works on investigations of their growth conditions and studying their properties in dependence on the synthesis methods ranging from such as evaporation, sputtering, chemical pyrolysis to metal organic chemical vapour deposition [6–8], thermal oxidation [9] pulsed laser deposition (PLD) [10–12], atomic-layer epitaxial growth [13], spin coating [14] and the sol–gel method [15]. In_2O_3 thin films have a good adherence to the substrate surface and high chemical inertness [16]. The material properties, described in the literature often differ considerably from each other. One important reason for this is that the preparation conditions are different and consequently the oxidation state of the samples is different. In_2O_3 can appear in two stable modifications as body centred (bcc) cubic (a=10.118 Å) and rhombohedral (rh) (a=5.478 Å and c=14.51 Å) [17]. They can be stabilized by choosing appropriate deposition conditions or synthesis methods [18-20]. The band gap of both is currently a subject of discussion and it seems to be that this material exhibits indirect transitions [21]. The values for the indirect and direct gaps of the cubic phase are between 2.1 to 3.1 eV and between 3.1 to 3.7 eV [22]. In the case of the rhombohedral In_2O_3 phase the indirect gap was estimated to be in the range from 3.0 to 3.3 eV, whereas the direct gap can be expected 3.3 and 3.4 eV [23, 24].

2. EXPERIMENTAL PROCEDURE

Indium oxide thin films were prepared by spraying an alcoholic solution containing indium chloride $InCl_3$ on glass substrates using ultrasonic spray process, substrates were degreased in successive rinses with acetone, ethanol, and distilled water for 5 min. the films were deposited in 400°C, and we have varied the precursor molarity from 0,05 to 0,3 mol/l in atmospheric pressure. The films were characterized by means of morphological, structural, optical and electrical methods. The surface morphology of the films was observed using a JEOL, model JSM 6301F Scanning Microscopy by field effect and the films thickness were calculated from the obtained micrographs. The X ray diffraction studies were carried out using a D8 ADVANCED BRUKER diffractometer with copper anode having a wavelength $\lambda = 1.5418$A°, the crystallite size were estimated to study the effect of the molarity. The UV–VIS–NIR transmittance measurements were performed PerkinElmer LAMBDA1050 UV/VIS/NIR Spectrometer in the spectral range 300–1500 nm. The electrical conductivity of the films was determined by four-point probes method at the temperature 25°C. The type of the semiconductor was determined from Hall measurements at room temperature.

3. RESULTS AND DISCUSSION:

3.1 Structural properties of In_2O_3 thin films:

Typical SEM images, of the surfaces of the Indium Oxide films deposited at different precursor molarities are shown in Figure.1.

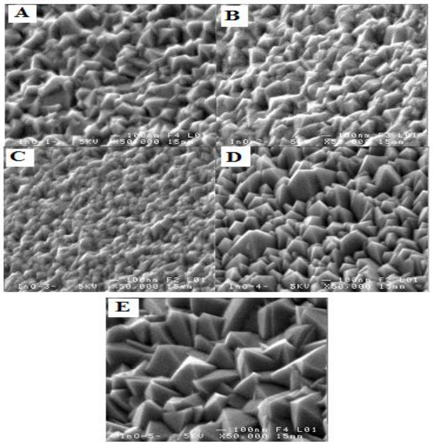

Figure 1. micrographs SEM, A :(M=0,05), B :(M=0,075), C :(M=0,1), D :(M=0,2), E :(M=0,3).

Note that no cracks are observed on large scan area for all samples. The films are continuous and in fact consist of grains like small pyramids. In addition, the shape of grains didn't change with molarities increasing because there is no change in the preferential orientation (400), V.S. Vaishnav et al observed that the shape of

Production of carbon encapsulated metal nanoparticles by spark discharge generator

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Nanoparticles have an outstanding role in the field of energy production and storage due to their unique properties. It is offer necessary to encapsulate these particles for a variety of purposes: to prevent agglomeration, environmental oxidation and to confine particles so as to minimize volume expansion. For such purposes, carbon is an ideal material for protection. It is known that materials such as Fe, Co, Ni can easily be encapsulated by carbonaceous materials. Recently, an attempt has been made to encapsulate Mg with limited success. In order to determine underlying mechanism in the process of encapsulation, a systematic study was carried out using a variety of metals W, Nb, V, Zr, Ti, Si, Cu, Ag, Al, Zn, Sn. In this study, encapsulation was carried out with a spark discharge generator were the metal was made one at the electrode against graphite. The collected nanoparticles were characterized by transmission electron microscopy (TEM) and the quality of encapsulation was determined with lattice imaging. Utilization of spark discharge generator enables a simple and easily operated process which provides the direct production and observation of carbon encapsulated metal nanoparticles.

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Hydrogen as an Energy Carrier: Artificial Neural Network System Proposal for the Storage of Hydrogen in Metal Organic Frameworks

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In this study, artificial neural network model was developed for prediction hydrogen gas storage capacities of porous Metal-Organic Frameworks.

Hydrogen is one of the leading candidates as an energy carrier of the future because of its high energy content and clean burning, potentially renewable nature. A particularly daunting challenge facing its use in transportation, however, is the development of a safe and practical storage system [1]. Porous metal–organic frameworks (MOFs), a new type of porous crystalline materials, have shown great potential for the storage of gases such as hydrogen, methane and carbon dioxide due to their high surface area and porosity, tunable pore size and shape and functional sites which can be readily immobilized to optimize their storage capacity [2].

In recent years, artificial neural network (ANN) models have been commonly used to examine relationships in complex nonlinear data sets [3]. The optimum ANN topology comprise of 3 input neurons, 7 hidden neurons and 1 output neurons using tangent function and purelin activation functions in hidden and output layers, respectively. Surface area, adsorption enthalpy, temperature and pressure were selected as input parameters.

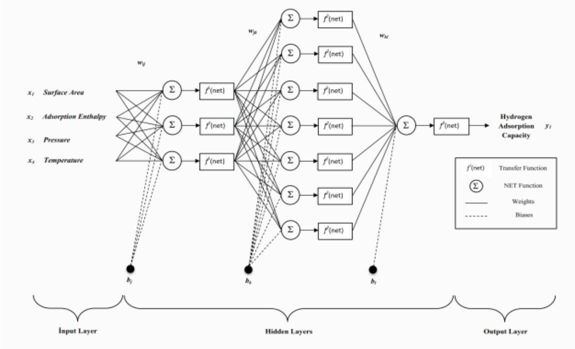

Figure 1. Multi layers artificial neural network architecture

As seen in Table 1, MOFs data are divided into 2 groups. Used data were divide into two portions of training (73%), and testing (27%). ANN results were observed as a good agreement with root mean squared error (RMSE) of 0.121 and correlation coefficient of 0.9857.

Table 1. Data of metal organic frameworks used in ANN.

	Metal Organic Frameworks[a]	SA_{BET}[d] [m^2 g^{-1}]	ΔH_{ads}[c] [kj mol^{-1}]	P [atm]	T [K]	H_2 Upt.[b] [wt%]
Calibrating Data	$Cu(ttpm)_2 0.7CuCl_2$	2506	8.40	1	77	2.80
	$Cu_2(becb)$	1840	8.90	1	77	2.12
	NOTT-112, $Cu_2(bbtei)$	3800	5.64	1	77	1.90
	SNU-6, $Cu_2(bpndc)_2(4.4'\text{-}bpy)$	2590	7.74	1	77	1.68
	$Be_{12}(OH)_{12}(btb)_4$	4030	5.50	1	77	1.60
	PCN-9(Co), $Co_4O(tatb)_{8/3}$	1064	10.10	1	77	1.53
	IRMOF-3, $Zn_4O(abdc)_3$	2639	5.30	1	77	1.51
	PCN-9(Mn), $Mn_4O(tatb)_{8/3}$	836	8.70	1	77	1.26
	UMCM-2, $Zn_4O(t^2dc)(btb)_{4/3}$	5200	6.40	1	77	1.28
	$Cd_5(tz)_9(NO_3)_3$	310	13.50	1	77	0.75
	$Cd_2(tzc)_2$	230	11.40	1	77	0.55
Testing Data	$Cu_3(btei)$	3730	9.20	1	77	2.29
	IRMOF-3-Amph-b	2052	5.70	1	77	1.73
	$Zn(bpe)(tfbdc)_3$	512	6.20	1	77	1.04
	Cu(diyb)	435	8.60	1	77	0.57

[a] Abbreviations: becb= 5.5′-(1.3-phenylenebis(ethyne-2.1-diyl))diisophthalate. bbtei= 5.5′.5′′-(benzene-1.3.5-triyltris(benzene-4.1-diyl))triisophthalate. bpndc= benzophenone-4.4′-dicarboxylate. btb = benzene-1.3.5-tribenzoate. tatb = 4.4′.4′′-s-triazine-2.4.6-triyltribenzoate. abdc = 2-aminobenzene-1.4-dicarboxylate. bpe = 1.2-bis(4-pyridyl)ethane. tfbdc = tetrafluoroterephthalate. tz = tetrazolate. btei = 5.5′.5′′-(benzene-1.3.5-triyltris(ethyne-2.1-diyl))triisophthalate. diyb = 4.4′-(1.4-phenylene)bis(imidazol-1-ide) [b] At 77 K per 1 atm per wt% [c] Adsorption enthalpy [d] Brunauere-Emmette-Teller.

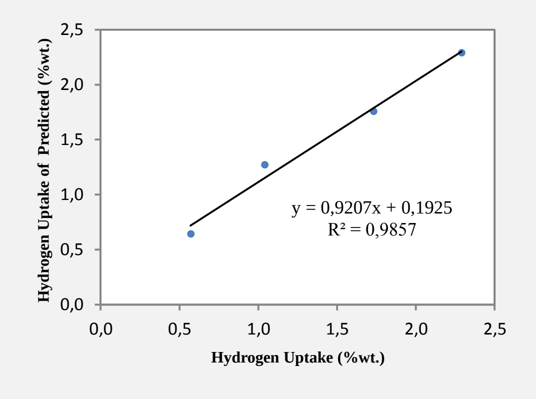

Figure 2. Comparison of best ANN model testing performance

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Hydrogen storage in the gas discharge microelectronic devices with porous zeolite cathodes

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H_2 has gained considerable attention as an alternate energy source because of its high energy content, renewable source and non-polluting nature [1]. Zeolites as H_2 storage materials are investigated broadly [2,3] due to their pore structure offers a high internal surface area, which is a useful attribute for the physisorption of H_2 [4] and it is found that as small molecules such as molecular H_2 can be easily absorbed into a flexible nanoscaffold of zeolites. In this work, we have studied experimentally the current transport processes in a planar gas discharge microelectronic device (GDED) with a wide pressure range up to atmospheric pressure (AP) (28-760 Torr) at electrode gap d (50 μm), and diameter D (22 mm) of the active areas for porous zeolite (ZC) and GaAs semiconductor cathode (SC) (Figure 1) in an air and hydrogen dc microdischarges. The GDED with SC cannot effectively operate at AP in air media compared with SC in H_2 media and ZC. Operating efficiently of the system will be based on the use of ZC, which is a good absorber of gas molecules in their nanopores. Thus, the discharge initiates from the surface and channels of the ZC, unlike conventional planar GDED with GaAs SC [5].

Porous cathodes are used for plasma light source applications with very low supply voltage and power consumption. The microstructures and performance of the ZCs are found to depend sensitively on the channel morphology and nature of the nanopores. Specific geometry of the zeolite channels structure and the strong electric field in the nanopores supply an efficient electron multiplication and related excitation of gas atoms. The use of gas discharge gap with nanoporous ZC gives rise to increase in the plasma emission intensity. The total plasma emission intensity of GDED with ZC is higher than plasma emission for chamber with GaAs photocathode. This device might find an application in for generating and sustaining a stable, uniform and homogeneous non-thermal AP plasma. In summary, these results promise of H_2 gas can be absorbed into a pores and nanoscaffold of zeolites and properties of cheap and natural zeolite provides efficiently work for plasma light source applications. The unique electronic properties of nanopores clinoptilolite make them also good candidate materials in the electronic industry, so that silicon-based technologies could be replaced or supplemented by nanoporous zeolitelike materials. Therefore, we confirm that the porous zeolites is a suitable as solid state H_2 storage electrode materials for energy storage and conversion in GDED and can serve as a source of UV-radiation if pressure and electric field are sufficiently high [6].

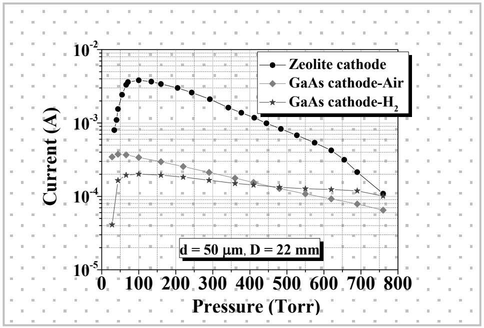

Figure 1. Current changes as a function of pressure for discharge system with ZC, GaAs SC in air and H_2 gas at feeding voltage U_0 = 1 kV.

Acknowledgments
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Numerical study of hydrogen purification by filtering through a metal hydride bed

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Selectively absorbing hydrogen, metal hydrides can be used for hydrogen purification – separating hydrogen from the unabsorbed gas and providing high-purity hydrogen. Impurities have a negative influence on the performance of metal hydride devices; some admixtures such as H_2S or CO have poisonous effects [1], CO_2 can contaminate metal hydrides [1] and inert admixtures such as N_2 slow down the reaction of hydrogen sorption [2]. The primary factors that limit the sorption rate of hydrogen from the gas mixtures containing inert impurities are the reduction of the effective thermal conductivity and increasing the temperature of the metal hydride bed, decreasing the hydrogen partial pressure in the system by increasing the amount of impurities. To clean the hydrogen from the gas mixture, metal hydrides may be used in a method similar to pressure swing absorption (PSA-like method) [3], or in the method based on filtering the mixture through a metal hydride bed [3].

In this work, a mathematical model, which was previously developed to analyse the processes in metal hydride systems for hydrogen storage and purification [4], was used. The present paper describes a mathematical models and a numerical study of heat and mass transfer processes in a metal hydride reactor for hydrogen purification which based on filtering the mixture through a metal hydride bed. Available data from the literature were used for verification of the mathematical models. The verification results showed that these models describe the heat and mass transfer processes for this system quite accurately.

The metal hydride tank examined in this work had a cylindrical geometry. Two designs were considered: tank without aluminium foam (reactor no. 1) and tank with aluminium foam (reactor no.2). The intermediate region filled with $LaNi_5$. The reactor had fixed lengh 400 mm. The calculations were performed for fixed temperature of metal hydride reactor wall and the different radii of the reactor (r_0 = 5–20 mm). The effects of various parameters on the effectiveness of metal hydride systems for hydrogen purification were studied.

For example, Fig. 1 shows the dependence of average fraction of the transformed material X at a time when the amount of loss of hydrogen increases sharply (the mole fraction of hydrogen at the outlet reaches 0.05) from specific (per unit area) mixture flow rate G_m (mole fraction at inlet: H_2 – 75%, N_2 – 25%).

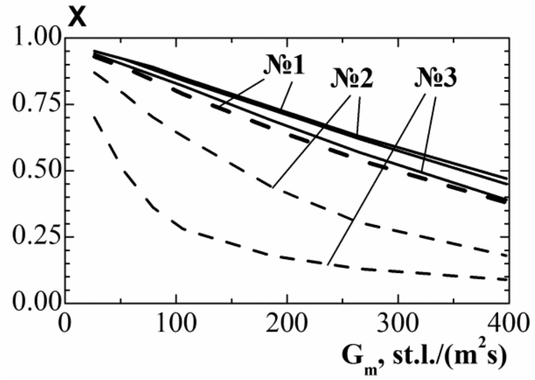

Figure 1. The dependence of X at a time when the amount of loss of hydrogen increases sharply (the mole fraction of hydrogen at the outlet reaches 0.05) from G_m. P = 0.8 MPa. Dash line – reactor no. 1; Solid line – reactor no. 2; r_0 = 1 – 5 mm; 2 – 10 mm; 3 – 20 mm.

The results illustrate that the major factors which reduce the rate of sorption and consequently the efficiency of the system is increasing the temperature of reactor and pressure drop due to filtering the mixture through the metal hydride bed with low permeability. It is shown that the use of an aluminum foam and an appropriate selection pressure at the reactor inlet allow to realize an effective system for hydrogen purification from impurities.

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AN EVALUATION OF MECHANICAL PROPERTIES OF NANOSTRUCTURED AL ALLOY PROCESSED BY SPD.

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Abstract

The novel multi-functional materials produced from the broad and multidisciplinary field that is nowadays called nanotechnology, can be used for sustainable energy production, transformation and use. Magnesium, aluminium or Mg–Al alloys in the form of bulk materials with nanograins, are envisaged as some of the potential optimal materials for hydrogen storage. During the last decades, fabrication of bulk nanostructured or ultrafine grained metals and alloys, using severe plastic deformation (SPD) processing, has been evolving as a rapidly advancing direction of nanomaterials science, aimed at developing materials with new mechanical and functional properties for advanced applications. Among various SPD processes, Equal Channel Angular Pressing (ECAP), is the most well developed processing technique.

In the present work, the technologically interesting aluminium alloy AA6061 was selected for study. The strain rate sensitivity of AA6061 has been investigated in a conventional grain sized (CG) state and in two different ultrafine grained (UFG) conditions, processed by ECAP, for 2 and 6 passes at 100° C. Strain rate jump tests in compression were performed at different temperatures, and the strain-rate sensitivity (SRS) exponent m was determined. It is shown that both UFG microstructures, exhibit a strongly increased strain-rate sensitivity (SRS) compared to CG state.

In order to evaluate the level of homogeneity within the pressed samples, microhardness measurements were also recorded along the orthogonal axes of billets processed by ECAP. The results from this investigation demonstrate that the structure is almost homogenous throughout the cross-sectional plane of the billet.

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DFT investigation of AlH_3 polimorfs – electronic structure quide to the hydrogen storage applications

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Air pollution due to the use of the fossil fuels in traffic and industry is one of the main problems that modern civilization faces nowadays. The need for environmental-friendly and sustainable energy solutions lead many experts to predict that the world economy in the following decades will try to free its dependence on fossil fuels and will be increasingly reliant on hydrogen. One of the main unsolved problems for the wide use of hydrogen energy is finding the safe and technologically and economically feasible method of hydrogen storage. Hence, material-based hydrogen storage is the subject of numerous ongoing research.

The ideal storage material should be safe, non-toxic, and inexpensive, and contain at least 6.4 wt% of hydrogen. One compound with all these characteristics is aluminum hydride (alane). AlH_3 has very large hydrogen content (10,1 wt% [1]) and crystallizes in several polymorphic modification, some of them being α-alane (space group *R-3c*), α'-alane, β-alane (space group *Fd-3m*), δ-alane, ε-alane and γ-alane (space group *Pnnm*) [2]. All of these polymorphs are metastable at room temperature, and very sensitive to the environmental conditions. Therefore, in order to design Al-based material for room-temperature hydrogen storage, the knowledge of the stability of all hydride phases and effects of impurities and modifications on the properties of interest is imperative.

In our work we investigate the properties of tree aluminum hydride polymorphs, α-alane, β-alane and γ-alane. The unit cells of the studied hydride phases are shown in the figure 1. The electronic structure and stability of the hydride phases is addressed using density functional theory (DFT) based calculations. The band structure calculations are performed using a Full Potential (Linearized) Augmented Plane-Waves plus local orbitals (FP (L)APW + lo) method as implemented in WIEN2k program packuage. The vibrational frequencies and zero point energy (ZPE) for the investigated compounds are calculated with the Vienna Ab initio Simulation Package (VASP). The crystal structure of all studied compounds is fully optimized with respect to unit cell parameters and atomic positions.

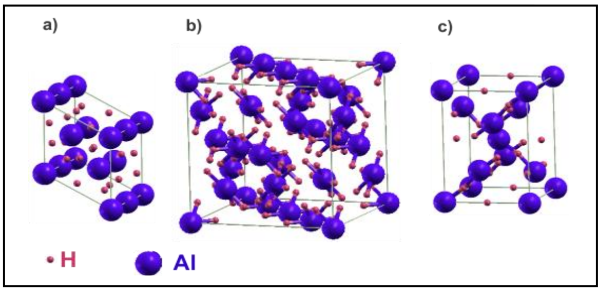

Figure 1. The unit cells of a) α-AlH_3, b) β-AlH_3, c) γ-AlH_3.

The influence of crystal structure on the stability of aluminum hydrides is studied in detail. Further, the electronic structure, the bulk moduls and charge transfer based on the Bader's AIM theory of hydrides are disscussed. Comparing to the starting metal-aluminum, we follow the influence of hydride formation and crystal structure change on the electronic structure modifications.

The investigation of the stability of defects and impurities in the aluminum hydride phases is aimed toward understanding the role of potential dopants in stabilization of aluminum hydride phases.

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Computational Determination of Endohedral Hydrogen Storage Capacity of Small Boron Nitride Nanocages

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87% of the global energy consumption in year 2013 is originated from fossil fuels. This huge consumption is the greatest reason of the global warming since large amount of carbon dioxide, the most dangerous greenhouse gas, is being released. Scientists are trying to find new, clean and reproducible alternative(s) to fossil fuels such as solar energy, wind power, biofuels, geothermal energy, etc. Another very important alternative is the hydrogen energy. H_2 gas can be produced using a variety of sources e.g. water, biomass, natural gas, etc. The chemical energy stored in a fixed amount of hydrogen is almost three times larger than that stored in the same amount of an ordinary fossil fuel [1]. In recent years, hydrogen energy has attracted excessive amount of attention of both scientific institutions and industrial companies, because it has a potential to use in hydrogen-powered fuel cell vehicles and/or hydrogen-fueled internal combustion engine vehicles for mobile power applications [1-3].

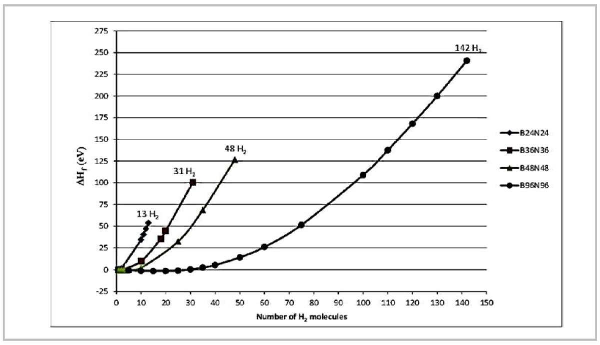

Figure 1. Variation of formation heats of the complexes with the hydrogen molecule doping

The use of hydrogen for the above mentioned applications requires an efficient, safe, and stable storage medium. Therefore, many hydrogen storage materials have been investigated both experimentally and computationally such as carbon based materials, metal hydrides, metal-organic frameworks and organic polymers. Shortly after their discovery [4], boron- nitride nanotubes, BNNTs, were tested as new material for hydrogen storage [5]. These studies resulted in that boron nitride nanotubes could store up to 4.2 wt% hydrogen at room temperature and also their hydrogen storage capability was better than carbon nanotubes. Recently, it was discovered that a porous BN material called HBBN-1 could store hydrogen up to 5.6 wt% under 3MPa pressure [6], These findings can be accepted as an indication of the necessity of further investigation on hydrogen storage capabilities of BN nano-structures.

In this study, endohedral hydrogen storage capability (gravimetric density as wt%) of several selected BN nanocages (B_nN_n where n = 12, 24, 36, 48 and 96) were computationally investigated by several quantum chemical methods. Initially, we compared performances of the PM6-DH2, PM7, B3LYP methods with the help of the ωB97X-D method, known to be accurate for systems including non-covalent interactions. PM6-DH2 predicted the stabilities of hydrogen doped BN nanocages as accurately as ωB97X-D with a computation time of ten thousand times faster. Therefore, this method was employed to determine endohedral hydrogen storage capability of the $B_{24}N_{24}$, $B_{36}N_{36}$, $B_{48}N_{48}$, and $B_{96}N_{96}$ nanocages (Figure 1), whose hydrogen storage percentages are calculated to be 4.40, 6.67, 8.12 and 12.01, respectively. $B_{96}N_{96}$ can endohedrally store up to 142 H_2 molecules. Hence, it can be concluded that the BN nanocages and the larger structures built from them may be good candidate materials for hydrogen storage

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Charge/discharge performance correlated to magnetic clusters in metal hydride surfaces

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Metal hydrides used in commercial hydride batteries (NiMH) are based on AB_5 to $AB_{3.3}$ alloys, where A are electropositive metals usually containing mixtures the rare earth elements. Nickel constitutes the major part of B elements. Depending on the targeted performance Al, Co, Mg and Mn are also commonly occurring alloying elements. As several have a significant electropositivity they can be easily corroded in the alkaline electrolyte used in NiMH batteries. To inhibit the corrosion it is important to form a thin protective layer on the alloy particles. This usually forms during the initial formation of the NiMH batteries, during which the alloy particle cracks up into a smaller particles and fresh surface is exposed to the electrolyte. A small fraction of the electropositive metals in the surface is corroded liberating nickel that forms small clusters.[1-4] These clusters are presumed to be responsible for improving the reactions that transfer hydrogen in and out of the alloy particles. They also show a complicated magnetic behaviour combining para-, ferro- and superparamagnetism. By following the development of the magnetization and correlate it to the polarization of the electrodes, we can model the reaction paths at the surface.

In this work, a surface treatment method was used to stimulate the reaction paths at surface of an ($La_{20}\,Ce_7\,Pr_1\,Nd_4\,Al_2\,Mn_5\,Co_6\,Ni_{55}$) alloy. The treatment comprises three steps: decrepitating the alloy by cycling it using hydrogen gas; oxidizing the obtained hydride alloy powder and boiling the oxidized powder in potassium hydroxide. After the treatment, magnetic nickel clusters can be liberated in metal hydride surfaces which contribute to a fast initial activation and improved high-rate dischargeability.

Composition and surface morphology of the alloy after surface treatment were studied by XRD, SEM and TEM. Electrochemical characterization was investigated by half cell test. Magnetic properties of different samples were measured. The magnetization curves for the metal hydride before and after surface treatment are given in Figure 1. Original alloy shows paramagentism, the magnetization increases after hydrogen treatment. Samples show mixture of superparamagnetism and ferromagnetism after potassium hydroxide boiling, and the magnetization increases within the increasing boiling time which we interpret as an increased amount of magnetic nickel clusters. The electrochemical performance correlated to magnetic clusters in metal hydride surfaces after surface treatment will be discussed and specific positions and amount of liberated magnetic nickel clusters will be studied by XPS to better understand the reaction paths at the surface.

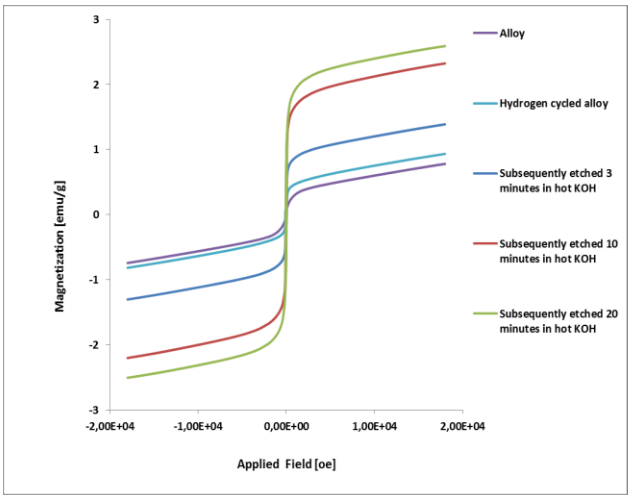

Figure 1. Magnetization curves for the alloy, hydrogen cycled alloy, subsequently etched 3 minutes in hot potassium hydroxide, subsequently etched 10 minutes in hot potassium hydroxide and subsequently etched 20 minutes in hot potassium hydroxide.

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Use of Electro-deoxidation in the Synthesis of Hydrogen Storage Alloys

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La-Ni based alloys are being used in the commercial secondary nickel metal hydride batteries. Economical synthesis of these alloys may cause large scale utilization of them especially in the electrical vehicles. The electro-deoxidation, which is accepted as the revolutionary technique in the extractive metallurgy, is very promising in the hydrogen storage alloy synthesis since it provides direct synthesis of the alloys from their oxide raw materials. In this study AB_3 type La-Mg-Ni-Co alloys were synthesized from sintered mixture of La_2O_3 + MgO + NiO + CoO in the molten salt by the electro-deoxidation method at 800°C and the electrochemical hydrogen storage characteristics of the synthesized alloys were observed. Sintering resulted in formation of the non-hygroscopic La_2NiO_4, $LaNiO_3$, $La_3Ni_2O_{6.84}$, $La_3Ni_2O_{6.35}$ and $La_4Ni_3O_9$ phases depending on the Co content of the oxide mixture. The X-ray diffraction peaks indicated that the target La-Ni phase formed within 2 h electrolysis and all the remaining oxygen-containing phases disappeared after 6 h electrolysis process. It was observed that the discharge capacities of the alloys synthesized by the electro-deoxidation technique in this work have either equal or even superior (due to more porous structure) electrode performances as compared to the performances of the same alloys synthesized by the traditional techniques.

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A DFT study on electronic properties of MgH_2 with charged vacancies

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The magnesium is considered a very promising element for hydrogen storage due to its high storage capacity (7.5 wt.%H) and its low cost. Magnesium absorbs gaseous hydrogen forming magnesium hydride (MgH_2), in a reversible reaction. The MgH_2 can cristallize in differrent phases, particularlly we study the β-phases (*P4/mnm*) [1]. Nevertheless, the Mg-H bond is to strong for this reazon several experimental and theoretical research works have been employed in this regard, like doping with different transition metals and point defects [2]. In this work we study the electronic properties of H, Mg and the complex H-Mg vacancies with different charge states induces in solid MgH_2.

We perform first principles calculation based on DFT as implimented in VASP code [3]. The projector augmented wave (PAW) pseudopotential is used to account for the electron–ion core interaction, using the PW91 functional as generalized gradient approximation (GGA) for the exchange–correlation term. The Brillouin-zone is sampled using a 7 x 7 x 7 Monkhorst-Pack k-point mesh for surfaces. For the plane-wave basis set a cut-off of 700 eV was used. All the structures are optimized in such a way that the forces acting in each ion are less that 10^{-3} ev/Å.

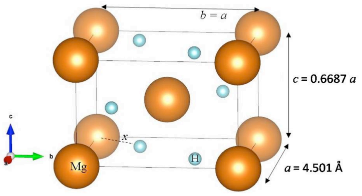

Figure 1. Unit cell of MgH_2 where $x = 0.304$ Å.

The supercell used to perform all calculations contains 24 Mg and 48 H atoms. The presence of an H vacancy (VH), or a Mg vacancy (VMg) or an H-Mg mixed vacancy (VMg-H) were introduced removing one H and/or one Mg atom from the center of the cell.

Fig. 2 shows the total density of states (DOS) curve for pure MgH_2 without defects. We notice the semiconductor behavior of pure hydride, the band gap obtained is 3.76 eV. This value is in good agreement with others reported in the literature. Fig. 3 shows the total DOS curves for MgH_2 with different type of vacancies and charged states. In this Figure we can see that the semiconductor feature of hydride remains. The most important change occurs when we consider VH. The peak around level Fermi is called trap state. These state types lower the effective current density and charge carrier mobility in the semiconductor. In addition to this, we note a Fermi level shift towards conduction band (CB) then the semiconductor behavior is like a n-semiconductor. The neutral and negative charged states present similar behavior, nevertheless the positive charge state in VH has a reduction on gap energy between trap states and CB. When VMg is considered there is a slight band gap reduction with respt to MgH_2 without defects, of around 1.6 %. For the complex VMg-H we see a similar behavior to the VMg, then the VMg has a predominant rol in this case. The band gap energy practically does not change for the charge states of the VMg and VMg-H.

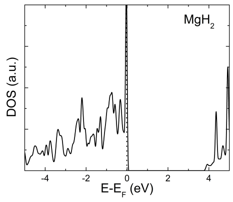

Figure 2. Density of states curve for pure MgH_2 without defects.

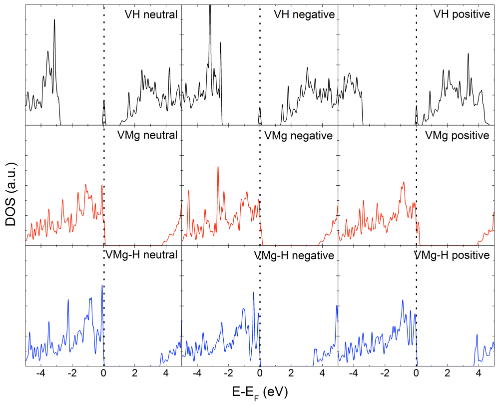

Figure 3. Density of states curve for pure MgH_2 with vacancy defects .

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Underground Hydrogen Storage in Geological Formations: A Techno-economic Analysis of Geologic Storage Options

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Geologic storage is used extensively in the oil, natural gas, and compressed air energy industries. The basic drive for geological storage is that the cost per volume-stored is 3 to 5 times less than surface storage. Geostorage of hydrogen has been considered in connection with large-scale use of hydrogen. The Government of Pakistan, Department of Energy was interested in large scale hydrogen geostorage, which could offer substantial buffer capacity to meet possible disruptions in supply or changing seasonal demands. Four geostorage site options were considered which included hard rock cavern, salt cavern, aquifer, and depleted gas reservoir located at Kotal, Kehwra, Dhadhar and Dharki respectively.

The Department of Energy was interested in assessing the techno-economic feasibility of these four types of geologic hydrogen storage options. Consequently, this study was undertaken to develop a viable and comprehensive techno-economic analysis methodology to assess the benefits and costs entailed in developing and operating an underground geologic storage facility for hydrogen storage.

Firstly, geotechnical analysis was carried out to assess the feasibility of four sites from geotechnical poit of view. This analysis included variables like strata, pressure, voids volume, moisture content, volume of the reservoir etc. Secondly, economic analysis was done by using two approaches; the analysis of a techno-economical factors matrix and the traditional cost benefit (levelized cost) method. In the factors matrix analysis, a matrix comprising selected techno-economical factors was formulated. These factors included possibility of leakage, cost of site development including wells, capital cost, contamination, accessibility, injection of gas, withdrawal of gas, possibility of repeated use, maintenance costs, sustainability, environmental effects, and design life. Opinion of technical and economic experts was collected by questionnaire and interviews. Field visits to four geologic sites were also carried out. Collected data was analyzed by three methods, statistical analysis of the factors matrix to determine the relative rating of four geologic options, the digital analysis by using computer assisted qualitative data software (CAQDAS) to obtain digitally iterated and attenuated models, and the economathical analysis of the four options using Newton-Leibniz integration formula to determine numerical values of the ratings.

Results of geotechnical analysis showed that salt caverns had substantial promise due to self sealing nature of the salt and consequently less leakage of the stored gas. However, salt caverns can store less gas compared to depleted gas reservoir. Depleted gas reservoir had known production history and had proven gas storage capability but it had leakage losses. However, these leakages could be controlled by treatment of site with impermeable liners. Aquifer was having porous strata and more losses due to leakage alongwith the accessibility and development issues as the site was located in the difficult terrain. However, aquifer had a greater a greater advantage of easy mining. Hard rock cavern required mining and placement of impermeable liners represented a complicated storage option.

Results of economic analysis were different. Statistical analysis of techno-economic factors matrix showed that depleted gas reservoir was the best option followed by aquifer. The digital analysis gave iterated and attenuated models with representative equations for each option. The representative equation of depleted gas reservoir had the highest value of coefficient of determination R^2 which represented greater accuracy of the trend. The economathical analysis indicated highest value for depleted gas reservoir. Similarly, cost benefit analysis using levelized cost method also indicated that depleted gas reservoir is the least cost option for geologic storage of hydrogen.

At the end, a comparison of the different analysis methods was carried out and its was observed that geotechnical and economic analysis results of the four geologic storage options were supporting and confirming each other. However, it should be noted that none of the hydrogen storage options fullfil all the desired requirements and the selection of a particular option depends on many geotechnical, geographical and environmental factors besides economic considerations.

The study helps to develop understanding of geostorage of hydrogen and its costs and benefits.

Ejaz Gul is an emerging scholar in the field of economic analysis. He has been associated with United Nationations Organization for the economic analysis of socio-developmental projects in Liberia. He has number of research and scholary papers to his credit in the international famous journals. He has recently conducted research on economic analysis of energy alternatives in which he has introduced a new concept of digital and econo-mathical analysis. He has also introduced the spatial contour maps of social inequality in the arena of social scieces. He is member of number of internaltional bodies including American Ecnomic Association.

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Anomaly in the electronic structure of the Na_xCoO_{2-y} cathode as a source of its step-like discharge curve

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Recently, Na_xCoO_2 has attracted much attention because of its unusual electronic and electrochemical properties. At high sodium concentration (x ≈ 0.65-0.75) it exhibits remarkable high values of thermoelectric power combined with metallic character of electrical conductivity, which was first reported in early 1980s [1]. Namely layered sodium cobaltate with high sodium doping was intensively investigated as promising material for thermoelectric application [2]. Moreover, interest in Na_xCoO_2 system significantly increased after discovery of superconductivity below 4.5 K in the hydrated compound $Na_xCoO_2 \cdot H_2O$ (x ≈ 0.3) in 2003 [3]. Electrochemical studies on Na_xCoO_2 (x ≈ 0.65 - 0.85) revealed unusual electrochemical behavior, establishing itself in a form of a step-like shape of the voltage curve [1, 4]. Moreover, previous examination of sodium intercalation into Na_xCoO_2 indicated a strong dependence of EMF of cells on conditions of preparation of the cathode material (T, pO_2), which affected structure of ionic and electronic defects in the compound [1, 5].

In this work we would like to show a new approach to an explanation of the nature of the discharge–charge curve of $Na/Na^+/Na_xCoO_{2-y}$ batteries, which can justify the existence of the step-like characteristics. This is still an open problem, which until now had no proper description in the literature. On the basis of comprehensive experimental studies of physicochemical properties of Na_xCoO_{2-y} cathode material (XRD, electrical conductivity, thermoelectric power, electronic specific heat) supported by calculations performed using the DFT method with accounting for chemical disorder [6], it has been shown that the observed step-like character of the discharge curve reflects the variation of the chemical potential of electrons (Fermi level) in the density of states of Na_xCoO_{2-y}, which is anomalously perturbed by the presence of the oxygen vacancy defects and sodium ordering. Our studies of structural, electronic and thermal properties of Na_xCoO_{2-y} cathode material in the characteristic points of discharge curve it is on the pseudo-plateaux and on the potential jumps, show non-monotonous variations of its transport properties (metallic/ semiconducting/ metallic/ semiconducting/metallic) during sodium intercalation which indicate that the density of states at the Fermi level is anomalously (either finite or vanishing) [7-9]. This effect is coherently supported by the shape of calculated density of states (DOS) of Na_xCoO_{2-y} having included oxygen defects and sodium ordering.

Acknowledgements
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An Oxygen Cathode Embedded with a Bi-functional Catalyst to Enhace the Electrochemical Performance of Lithium Air Batteries

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To achieve a 300-mile (500 km) driving range on a single charge in an all-electrical vehicle, classical lithium ion batteries with cathodes containing even up to one reversible electron transfer per metal need to be replaced with higher energy density batteries. In order to overcome the constraints imposed on the reversible capacity of cathode materials by the intercalation reaction, it would be necessary to change the electrode reaction to one of dispalcemetn reaction involving multiple electron (Li) transfer per metal reversibly. As an example of such a system, the serendipitous invention[1] of rechargeable lithium-air (i.e. Li/O_2) batteries in non-aqueous media has opened new horizons in redesigning battery energy storage systems.

Several technical issues pertaining to the Li air battery have been documented[2,3]. Among them, appropriate catalysts to enhance the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics in non-aqueous electrolytes are for the development of a practical battery. In this report, we address this issue by introducing new metal oxide cathode catalysts. Our work is aimed at several objectives; i-) to promote full reduction of molecular oxygen to Li_2O to enhance the energy density of the battery ii-) to lower the activation energy of oxygen reduction reaction which improves the power density of the battery, and iii-) to improve the cyclability of Li air batteries.

Our preliminary results with the metal oxide catalyst in Li air cells have suggested that the catalyst improved the ORR and OER kinetics, leading to higher discharge voltages and lower charge voltages with an overall improvemnet in the cell's rechargeability. Figure 1a and 1b show galvanostaticly charged and discharged Li air cells with bare (Ketjen Black) KB300 cathodes and those embedded with the catalyst, respectively. It is clear that catalyzed cell enhanced the ORR voltage (cell discharge) response by around 150 mV which will ultimately enhance the power output of the cell. Improvement was observed in the OER process as well. For example, during charging, the catalyzed cell delivered approximately 220 mAh/g capacity below 4V, while the uncatalyzed cell delivered around 120 mAh/g at the same potential region. This suggests that during the initial oxidation process the cell mechanism changes to a process assisted by the catalyst. Another noteworthy difference between catalyzed and uncatalyzed cells is that after 6 cycles the uncatalyzed cell's discharge capacity faded rapidly whereas the catalyzed cell continued to cycle without discharge capacity fade. Overall, our cell cycling studies suggested that the metal oxide in the porous carbon electrode catalyzed both the OER and ORR reactions.

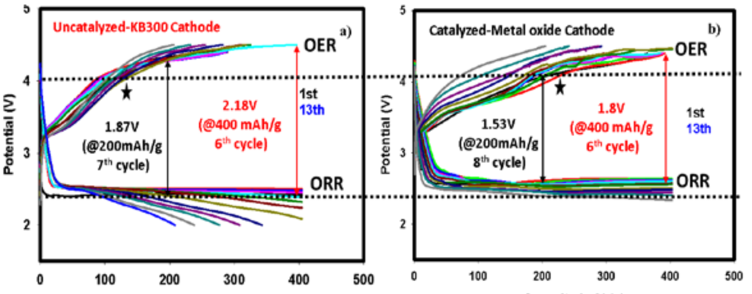

Figure 1. Charge-discharge profiles of a-) uncatalyzed b-) catalyzed cells run at 0.1mA/cm^2 current rate and cycled between 2 and 4.5V by limiting the capacity to 400mAh/g. The electrolyte consisted of 1M $LiPF_6$ dissolved in TEGDME solvent.

Further work to unravel the ORR and OER mechanisms is underway and the results will be presented in the meeting. We will be demonstrating the structure-property relationship of the catalyzed and uncatalyzed cathodes using X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy and x ray absorption spectroscopy techniques.

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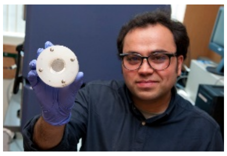

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Free Standing Fexible Graphene Cathodes For Li-Air Batteries

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The lithium-air battery, which theoretical energy density is much higher than the other energy storage devices, has gained worldwide attention. In lithium-air cathode materials, graphene containing materials have been reported as ideal cathode materials due to their large theoretical specific surface area, chemical stability, high electrical conductivity and charge Capacity. In this study; three free-standing flexible graphene cathodes were produced with different thickness by vacuum filtration technique. For preparation of the graphene electrodes, graphene oxide papers were chemically reduced. Surface morphology of the produced graphene cathodes were characterized by using scanning electron microscopy (SEM) and energy dispersive spectroscopy was conducted to understand elemental composition of the graphene oxide paper. X-ray diffraction (XRD) technique and Raman spectroscopy were carried out to investigate the structure of the graphene oxide paper. Moreover, specific surface area and porosity distribution of the graphene oxide paper was performed using Brunauer–Emmett–Teller (BET) method from N_2 adsorption and desorption isotherms and the pore size distribution curves were calculated using the Barrett–Joyner–Halenda (BJH) algorithm on the desorption branch. Electrochemical performance of the free-standing graphene electrodes was assessed in ECC-Air test cell from 1.5 V to 4.5 V at a constant current density .

Keywords: Li-Air batteries, Graphene, Air breathing cathode

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High Reversible Si/Graphene Composite Anodes for Lithium Ion battery

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Due to their high energy density, long cycle life, high safety and low cost, lithium ion batteries are good choice for portable electronic devices such as laptops, mobile phones and hybrid electric vehicles. Carbon materials such as graphite are widely used as anodes in lithium ion battery applications. However, the limiting factor for using portable devices is the theoretical specific capacity of negative electrode material of graphite (372 mAh/g). Silicon is promising alternative material due to its higher capacity of 4200 mAh/g. However, silicon cannot be used singly, because of its lower conductivity and poor cycling stability during the electrochemical process. Graphene has large theoretical surface area and high electrical conductivity and discharge capacity. Aim of this study, synthesis of Si/Graphene composite anode and take both advantages of Si and graphene.

In this study, Silicon/Graphene composite electrodes were produced by mechanical alloying method to increase capacity retention and reversibility of the composite anode. For this aim, three Si/Graphene composite anodes were produced with dispersing different amounts of Graphene (10wt.%, 30wt.% and 50wt.%) into composite structure to investigate effect of Graphene contents on the electrochemical performance of the composite electrodes. The surface morphology of the produced electrodes was characterized using scanning electron microscopy (SEM) 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 produced Si/Graphene electrodes was investigated by charge/discharge and cyclic voltammetry tests from 0.05V to 1.5V in CR2016 test cells. The resistances of the cells were investigated using ac impedance technique. This study proved that dispersing Graphene and increasing content of the Graphene remarkably increase the discharge capacity of the Si/Graphene composite anodes.

Keywords: Silicon/Graphene, composite anode, mechanical alloying, Li-Ion batteries.

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The Effect of $LiBF_4$ Salt Concentration in EC-DMC Based Electrolyte on the Stability of Nanostructured $LiMn_2O_4$ Cathode

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Li-ion batteries are used in many applications such as portable electronics, cellular phones and laptop computers. In addition, there is a great interest in using Li-ion batteries in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ positive electrodes are known as the most commonly used and commercially available cathode electrode materials for rechargeable Li-ion batteries. Among these cathodes, spinel $LiMn_2O_4$ and its derivatives have some advantages such as easy preparation, inexpensiveness, more abundance of manganese resources, non-toxicity and environmental friendly. These merits make $LiMn_2O_4$ an ideal cathode material for lithium-ion batteries. However, at elevated temperatures it exhibits poor performance so the capacity rapidly degrades with cycling[2,3]. One of the basic elements of batteries is the electrolyte, which must fulfill many strict requirements as high conductivity, low impedance of passivation layers, as well as chemical and electrochemical stability over a wide range of temperature [4]. Most commonly, $LiPF_6$ solutions in ethylene carbonate (EC) as cyclic carbonate and dimethyl carbonate (DMC) as linear carbonate are used for lithium ion battery, in commercial fabrication [5]. Compared with $LiPF_6$, $LiBF_4$ has some advantages such as better thermal stability and lower sensitivity toward environmental moisture and its solution provides lower charge-transfer resistance, especially at low temperatures [6].

In this work, the optimum $LiBF_4$ salt concentration was studied for EC-DMC based electrolytes to determine the effect of electrolyte solutions on the stability of nanostructred $LiMn_2O_4$ cathode materials. For providing higher ionic conductivity, the optimum solvent values were kept in the ratio of 2:1 (w/w) EC:DMC. In order to obtain 0.8, 1.0, 1.2 and 1.4 m homogenously $LiBF_4$ electrolyte solutions, calculated amounts of $LiBF_4$ salts were added to EC:DMC (2:1) solvents and stirred about 10 h in a glove box. The produced electrolyte solutions were used to assemble half-cells containing metallic Li anode and nanostructured $LiMn_2O_4$ cathode materials (Fig. 1). Electrochemical tests were performed for investigating the effect of $LiBF_4$ salt concentration on the electrochemical performance of nanostructured $LiMn_2O_4$ cathode material at room temperature. After 100 charge-discharge cycles, electrochemical impedance measurement was conducted by EIS. Then the cells were disassembled and the cathode materials were taken out, rinsed with EC and dried at 35^{o}C for four hours. Obtained cathode materials were analyzed by Raman, SEM and XRD to examine the effect of electrolyte solutions on the stability of nanostructured $LiMn_2O_4$ cathode materials. Finally, for EC-DMC based electrolyte solutions, the optimum $LiBF_4$ salt concentration was found and results showed that higher salt concentration provides higher electrochemical capacity and higher stability for the bare nanostructured $LiMn_2O_4$ cathode material.

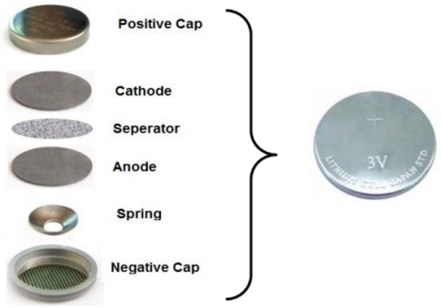

Figure 1. Li-ion battery design

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Pt/Bi_2O_3 Catalysts for Rechargeable Lithium-Air Batteries

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In the past decades, lithium-ion batteries (LIBs) have been considered as the most effective and practical technology for power supply of small electronic devices a due to their flexible design, long lifespan, high energy density, high power density [1]. However, they can just supply 150 km of range for electric vehicles. Instead, many research groups have been developing rechargeable lithium–air batteries, because of the far higher theoretical energy density than that of conventional batteries like LIBs. A Li-air battery cell is generally composed of a Li-based anode, a porous cathode, and an electrolyte in which Li^+ ions flow from one electrode to the other. These electrochemical devices (Figure 1) directly convert fuels to electricity carried by proton, hydroxide ion or lithium ion at room temperature and rely heavily on oxygen reduction reaction (ORR) and the reverse reaction, oxygen evolution reaction (OER) electrocatalysts [2].

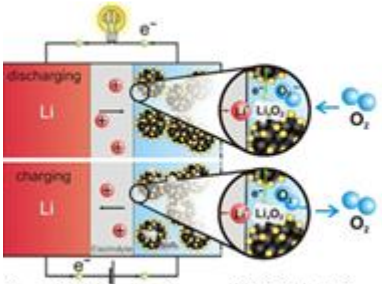

Figure 1. Schematic diagram of a Li-O_2 batteries

Preliminary stability testing of the most active oxide, revealed only very small changes in ORR activity suggesting that oxide materials can serve as reasonably stable ORR catalysts in fuel cells and metal–air batteries [3]. Single-cell measurements showed that catalysts can greatly influence the discharge and charge voltages of Li-O_2 batteries, where Au is the most active for oxygen reduction reaction (ORR) (during discharge) and Pt is the most active for oxygen evolution reaction (OER) kinetics (during charging) [4]. Catalyst development is needed to reduce the ORR/OER potential losses and to increase the Li-air battery roundtrip efficiency [4]. This study revealed the strong influence of both Pt in the active OER kinetics and Bi_2O_3 in the active ORR kinetics catalysts on the charge and discharge voltages of rechargeable Li–O_2 batteries.

In this study, Bi_2O_3 supported Pt catalyst was prepared by using microwave irradiation technique. Firstly, required amounts of Bi_2O_3 and aqueous solution of H_2PtCl_6 added in ethylene glycol and then stirred for 30 min.

Then the resulting mixture was reduced in microwave oven. After microwave treatment, the mixture was cooled down with cold water, then filtered, washed with acetone and deionized water and finally dried at 100°C for 12 h.

Bi_2O_3 supported Pt cathode materials for Li-air battery were synthesized. The structural properties of the obtained Pt/Bi_2O_3 nanoparticles were characterized by energy dispersion spectroscopy (EDS) (Table 1) and scanning electron microscopy (SEM) (Figure 2).

Tablo 1. EDS results of prepared catalysts

Sample	O		Bi		Pt	
	Wt %	At %	Wt %	At %	Wt %	At %
Bi_2O_3	4.47	37.20	95.53	62.79	-	-
Pt/Bi_2O_3	5.20	41.49	80.87	49.40	13.93	9.12

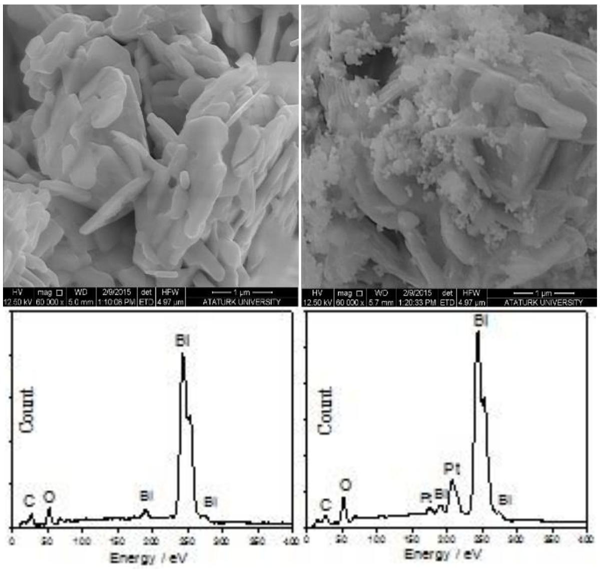

Figure 2. SEM images and EDS results of a) Bi_2O_3 b) Pt/Bi_2O_3

These materials will also be characterized with XRD, TEM and will be tested for single-cell measurements for charge and discharge activity in Li-air battery.

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Effect of Surface Treatment with Boiled Alkaline Solution on Electrochemical Properties of the ZrNi Alloy Electrode

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The ZrNi alloy has hydrogen storage capacity of 2.0 mass% H_2 [1], which corresponds to charge capacity of 536 mAh g^{-1}. So it can be expected as negative electrode active material for Nickel-metal hydride (Ni-MH) batteries. However, the discharge capacity of ZrNi alloy was reported 62 mAh g^{-1} [2], because the alloy surface was covered with the passive film like ZrO_2 to inhibit charge-discharge reactions [3]. To remove the passive film of Laves-phase hydrogen storage alloys, for example, the surface treatment with boiling alkaline solution is useful [4]. In this study, we carried out surface modification of the ZrNi electrode with the boiling alkaline solution and evaluated its electrochemical properties.

The ZrNi alloy ingot was prepared by arc-melting. The alloy ingot was pulverized to sieve particles under 40 µm in diameter. The alloy powders were analyzed by X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX). In the electrochemical tests, the alloy powder was mixed with Cu powder and polyvinyl alcohol aqueous solution to make a paste. The paste was loaded in a porous Ni as a current collector to make a negative electrode. The surface treatment of electrode was immersed in a boiling 6 M KOH solution for 4 h. The positive and reference electrode were a $NiOOH/Ni(OH)_2$ and a Hg/HgO electrode, respectively. The electrolyte solution was 6 M KOH + 1 M LiOH. In the charge-discharge cycle tests, the negative electrode was charged at 100 mA g^{-1} for 5 h and discharged at 10 mA g^{-1} to the cut off potential of -0.5 V vs. Hg/HgO at 333 K. After each charging, the circuit was kept open for 10 min.

XRD analysis exhibited that the main phase of the ZrNi powders was the B33-type CrB structure. Small diffraction peaks assigned to $Ni(OH)_2$ were additionally detected after surface treatment. XPS spectra showed that the untreated ZrNi surface was covered with ZrO_2, whereas $Ni(OH)_2$ appeared on the alloy after surface treatment. In the SEM-EDX results after surface treatment, white deposits whose size mean was about 200 nm were observed and the Ni and O contents were higher than that of the untreated ZrNi. From these results, $Ni(OH)_2$ was deposited by the surface treatment.

Figure 1 shows the charge-discharge curves of the untreated and the treated ZrNi electrode. The initial discharge capacity of the untreated ZrNi electrode was 18 mAh g^{-1} but that of the treated ZrNi electrode was increased up to 320 mAh g^{-1}. The initial discharge capacity was greatly improved by the surface treatment, suggesting that $Ni(OH)_2$ was easily converted into metallic Ni during charging. Therefore, the metallic Ni became catalytic sites to improve the surface electrochemical reaction.

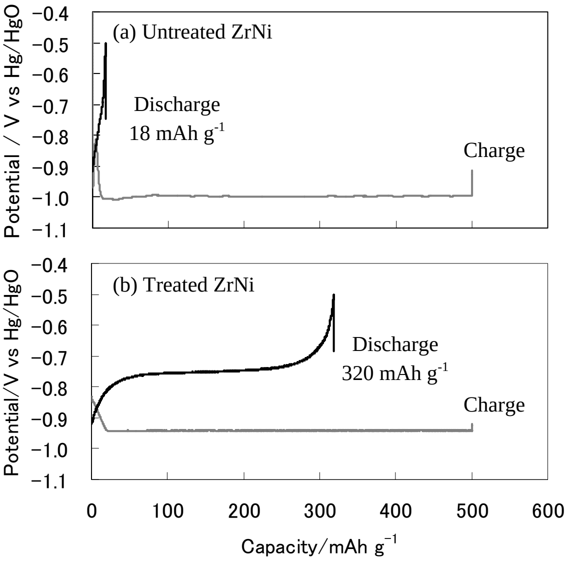

Figure 1.The intial charge-discharge curves (a) the untreated ZrNi and (b) the treated ZrNi electrode. Specific charge and discharge currents were 100 and 10 mA g^{-1} at 333K.

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VO_2(B) as anode material for aqueous Li-ion batteries and as a catalyst for hydrogen storage material MgH_2

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Meeting the future demand for alternative, environmental friendly source of energy, we focused our investigation on materials for solid stage hydrogen storage, as well as on materials for electricity storage i.e. Li-ion batteries.

Synthesized VO_2, polymorph type B, is a material which can meet the requirements of electrode material for organic and aqueous Li-ion batteries. Since aqueous Li-ion batteries are still the challenge as a novel type of Li-ion batteries, we focused our research on anode material and VO_2(B) gave the satisfying results. The charging/discharging curves of $VO_2(B)|LiNO_3(sat.)|LiCr_{0.15}Mn_{1.85}O_4$ battery are shown in Figure 1. Charging and discharging become very stable after twenty cycles and remain stable until the 50th cycle. Although there is no constant voltage plateau during discharging, discharge capacity is very high and exceptionally stable. After twenty cycles the discharge capacity becomes constant and amounts 170 mAh g^{-1}. The capacity fade after 50 cycles is only 4% [1].

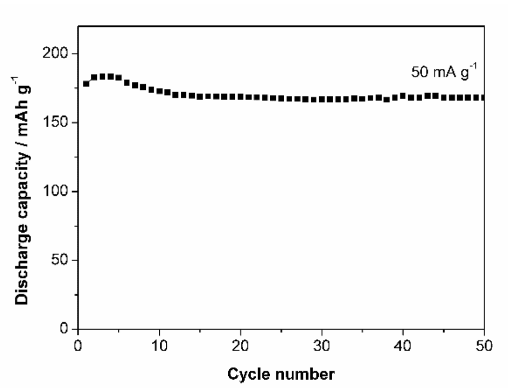

Figure 1. The discharge capacity of cell at 50 mA g^{-1}

On the other hand VO_2(B) is promising candidate for enhancement of desorption reaction of MgH_2. Nanocomposite material MgH_2–VO_2(B) by mechanical milling, with a share of 85wt.% of MgH_2. The purpose was to reduce high desorption temperature and to improve cyclability of MgH_2. Thermal analysis show change in morphology of DSC curve as well as the reduction of desorption temperature onset from 455°C (MgH_2) to 400°C (nanocomposite). Cyclability testing was performed on Sievert's type apparatus Hydrogen Sorption Analyzer (HSA) and the results show excellent overlap of curves of synthesized nanocomposite even at lower temperature (360, 350 and 340°C) with sustainable capacity (see Figure 2). The maximum capacity of released hydrogen is reached in 75 second from MV15 composite.

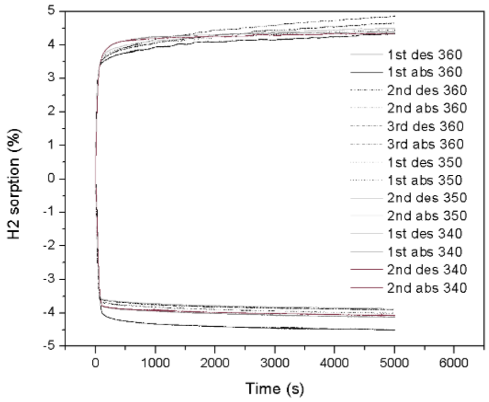

Figure 2. HSA curves of nanocomposite at different temperatures

The excellent performance of VO_2(B) as anodic material in Li-ion batteries and catalytic activity in material for hydrogen storage can be explained by vacant structure and hollowed 3D morphology of synthesized VO_2(B).

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The Electrochemical Properties of Doped $LiMn_xM_{(1-x)}PO_4$ Synthesized By Spray Pyrolysis

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Introduction

Over the last few decades, much research has been done on olivine structured lithium manganese phosphate ($LiMnPO_4$) as a cathode active material for Li-ion batteries. The reason why this phospho-olivine attracts much attention for the energy storage application is its high energy density and low cost. $LiMnPO_4$ has 170 mAh/g theoretical capacity with 4.1 V average voltage; however, it suffers from low electrical and ionic conductivity due to low lithium diffusion kinetics. There are different approaches to overcome the conductivity problems of $LiMnPO_4$; minimizing the particle size [1], coating the particles with carbon [2], and metal ion doping [3,4]. On the other hand, several synthesis routes such as hydrothermal method [5], solid-state reaction [6], sol-gel method [2], polyol reaction [7], and spray pyrolysis [8] were utilized to eliminate the weaknesses of $LiMnPO_4$. In this study, metal ion doped $LiMn_xM_{(1-x)}PO_4$ (where M is Co, Cr, Mo, V and W) was synthesized by spray pyrolysis followed by dry ball milling to achieve high electrochemical performance. Co, Cr, Mo, V and W cations were used to partially substitute Mn atoms.

Experimental

The precursor solution was prepared by dissolving $LiNO_3$, $Mn(NO_3)_2 \cdot 6H_2O$, H_3PO_4, and dopant source in DI water. The concentration of the Li^+, Mn^{2+}, PO_4^{3-}, and the related dopant were all set to give $Li/Mn/M/PO_4$= 1/1/0.95/0.05/1 ratio. The precursor solution was atomized by an ultrasonic nebulizer. The droplets were then transferred to the furnace by Ar and H_2 gas mixture with a flow rate of 4 lt/min. The droplets were converted to the solid particles through a series of processes such as evaporation of the solvent, precipitation, drying, pyrolysis and, sintering within the furnace at 500 °C. The particles were collected at the furnace exit by an electrostatic precipitator. The obtained particles were then milled with 10 wt.% carbon black by a planetary ball-milling.

Characterization

X-ray diffraction was performed on a Rigaku DMAX 2200 by using Cu Kα radiation to determine the crystalline phases. Rietveld method was used to refine the lattice parameters and calculate occupancy of the host and dopant atoms. The surface morphologies of the particles were examined by FEI Nova Nano 430 Field Emission Scanning Electron Microscopy. The electrochemical performance was investigated by using coin-type cells. The cells were charged and discharged with different rates on the Solartron 1480 multi channel battery tester.

The particles synthesized by spray pyrolysis were in the shape of hallow or porous spheres as provided in Figure 1. These samples had good electrochemical performance, achieving discharge capacities of 70-100 mAh/g, Figure 2.

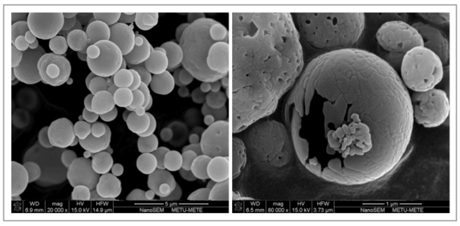

Figure 1. SEM images of the sphere structure synthesized by spray pyrolysis.

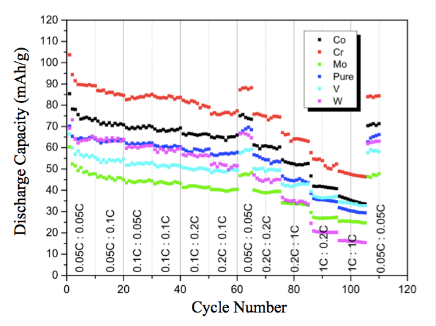

Figure 2. The discharge capacity vs cycle number graph of the pure and doped samples.

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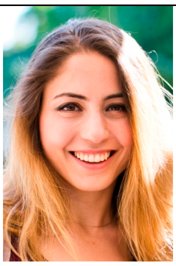

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Electrochemical Properties of $LiCo_{1-x}B_xO_2$ cathodes for Li-ion Batteries

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In this work, we investigated the physical properties of layered $LiCoO_2$ cathode material doped with Boron (B) for Cobalt (Co) sites. For this study, $LiCo_{1-x}B_xO_2$, x=0, 0.125, 0.250, 0.375, 0,5, 0,75 and 1 cathode materials were synthesized in the bulk form via solid state reaction technique at 750 ^{0}C in Oxygen atmosphere. Microstructural, magnetic and electrical resistivity properties of the samples were investigated systematically. These materials are used to fabricate CR2032 coin cell batteries and their battery performances are determined and compared (Figure 1).

Our investigations show that x=0,125 and 0.250 samples have the same crystal structure as $LiCoO_2$ without detectable impurity phases. This result show that the Boron ions incorporate the structure succesfully for $x \leq 0.25$. However, as the boron content increases further, significant amount of impurity phases appear and eventually distroys the layered structure.

In this study, the structural and electrochemical properties of boron doped LiCO2 cathode materials have been investigated in detail. It is found that solubility limit of boron in LiCoO2 was determined as $x \leq 0.25$. The results indicate that the cycle performance of the battery increases significantly with boron doping process for $x \leq 0.25$. Furthermore, the boron impurity was also positively affected the lattice adaptation to the insertion/extraction of lithium, and prevents the structural first-order transition, which relates with the Verwey transition, in $Li_{0.5}CoO_2$ [1,2].

Although, the batteries produced with the $LiCo_{0.875}B_{0.125}O_2$ and $LiCo_{0.750}B_{0.250}O_2$ cathodes have lower capacity than the pure $LiCoO_2$, they have a significantly better capacity retention than pure $LiCoO_2$ for long cycling. So it is concluded that the small amount of boron can be used in the commercial batteries for long cycling life.

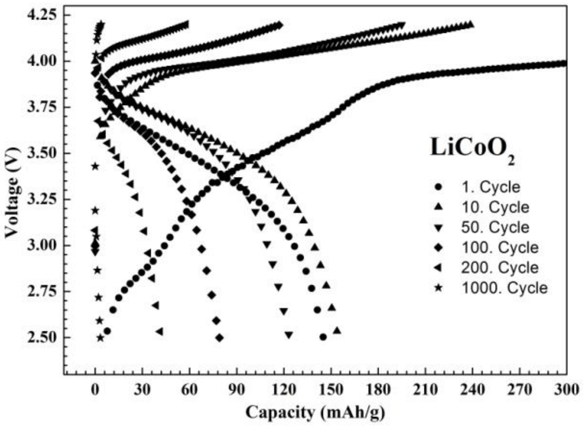

Figure 1. Capacity-Voltage graph for 1000 cycle of $LiCoO_2$ sample.

Keywords: Li-ion batteries, boron, enhancement, cycling performance.

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Nickel Foam-Supported Porous Sn-Cu Electrode for Lithium-Ion Batteries

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In the past decade, tin based anodes have been extremely focused as an alternative to graphite anode, because of its high theoretical capacity of 990 mAh/g [1]. However, pulverization of electrode during lithiation and de-lithiation process, which caused from high volume expansion and consequent rapid capacity fading is one of the main disadvantages [2]. To improve electrochemical performance of pure Sn anodes, Sn–M intermetallic compounds have been designed to provide an inactive phase that acts as buffer matrix against volumetric changes and contribute conductivity reported as one effective solution. These matrix systems are Sn–Ni [3], Sn–Co [4], Sn–Cu [5] etc. Nickel substrates with foam structure have been used as current collectors to enhance the electrochemical performance of Sn electrode, since the porous structure of nickel foam will accommodate stresses and electrode pulverization because of the volume expansion and also maximize the utilization of active materials by ensuring that the electrolyte is easily diffused into the anode materials [6].

In this study, Sn-Cu was electrodeposited onto the porous nickel foam substrate under pulse electrodeposition conditions. Pulse electrodeposition was carried out at three different peak current densities of 10, 20 and 40 mA/cm^2 for 5 minutes in a bath containing 40 g/L $SnCl_2.2H_2O$, 30 g/L $CuSO_4.5H_2O$, 164 g/L $K_4P_2O_7$ and 19 g/L Glycin. Surface morphology of Sn-Cu electrodeposited Ni foam electrode was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was conducted to understand the elemental surface composition of composites. X-ray diffraction (XRD) analysis was carried out to investigate the structure of Sn-Ni foam electrode. The electrochemical performance of electrodes has been investigated by charge/discharge tests, cyclic voltammetric experiments and the ac impedance technique. The results yielded encouraging discharge capacities since Ni foam behaves as a stress bearing support and electronic conductivity component.

Keywords: : *Li batteries; Ni foam; Pulse electrodeposition; electrochemical behavior; stress bearing, discharge capacity*.

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Al stabilized $Li_7La_3Zr_2O_{12}$ solid electrolytes for all-solid state Li-ion batteries

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All Solid State Lithium Ion Batteries (ASS-LIB) have been attracting more attention due to their advantages in terms of high temperature stability, energy density and safety. Oxide ceramic electrolytes are one of the best solid electrolytes with their decomposition voltages higher than 5.5 V (vs. Li), stability and high ionic conductivities[1].

$Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte is one of the most studied electrolytes because of its exceptional high stability against Li metal, air and moisture. thermal stability and approx. 10^{-4} S/cm total conductivity of LLZO at 25°C is competitive with liquid electrolytes [2]. There are two polymorphs of LLZO reported so far. Tetragonal polymorph – the low temperature stable form of LLZO – has approx. 10^{-6} S/cm Li^+ conductivity [3]. However, cubic polymorph – high temperature stable form of LLZO – rises up to 5.11 x 10^{-4} S/cm. Stabilizing cubic structure can be either increasing synthesis temperature where the cubic phase is stable or doping with stabilizers during synthesis. For example, Al addition increases Li^+ ion conductivity within the range of 10^{-4} S/cm. When Al^{3+} ions are introduced in the structure, it substitutes for Li^+ ions leaving two vacancies of Li sites behind. It's found that, below 0.204 moles of Al addition could not stabilize cubic form since Li vacancy concentration is insufficient. If the Al addition is higher than 0.389 moles, it exceeds Al solubility in cubic form and a second phase of $LaAlO_3$ is formed[4].

In this study, 0.30 % Al containing LLZO is produced via Solid State Reaction Method. Sintering behaviour and microstructural evaluation is also studied. First of all, Li_2CO_3 (Merck) was dried at 200°C whereas La_2O_3 (Sigma-Aldrich) and ZrO_2 (Inframat) were dried at 900°C before mixing. Al_2O_3 was used to stabilize cubic phase. Stoichiometric amounts of powders were mixed in agate mortar grinder (Retsch RM200). 15 % of excess lithium was added in order to compensate lithium losses during the calcination. Powders were calcined twice at 900°C and 980°C for 12 hours. Between each calcination step, powders were re-ground. After that, 2 g of calcined powders were isostatically pressed into pellet at 290 MPa. Then, the pellets were sintered at 1100 and 1150 °C for 12h and 24h within a powder bed. Alumina crucible was used for all heat treatments. 2°C/min heating rate was selected in order to minimize unexpected lithium losses during heat treatments. After each experiment, pellets were ground using 2-propanol as coolant and their crystal structures were determined by X-Ray Diffractometer (XRD - Rigaku MiniFlex 600). Pellets were also polished using appropriate polishing media (alcohol based 0.25 micron diamond solution) before microstructural analysis. Then, microstructure and elemental analysis of each pellet were carried out by Scanning Electron Microscope (SEM- Zeiss SUPRA 50VP) and Energy Dispersive Spectrometer EDS (Oxford INCA). Due to surface ion-exchange when contacting with water as reported in literature [5], water was avoided in every treatment of pellets.

According to the XRD results, at 1150 °C - 12h and 1150 °C - 24h sintering conditions, cubic form of LLZO was stabilized. However, at 1100 °C for both 12h and 24h, minute amount of tetragonal LLZO was present. No other impurity phases were detected from XRD patterns.

SEM/BSE micrographs from polished surfaces showed porous but highly homogeneous LLZO microstructures. At 1100°C for both 12h and 24h samples, elemental analysis showed that there are unreacted products due to the insufficient diffusion. When the temperature was increased to 1150 °C, impurity phases were not detected in the microstructure considering that the diffusion was completed. Elemental map on the 1100°C – 24h sample illustrated that Al, La, Zr and O distribution were homogeneous at highly dense regions of the microstructure, but Al deposits were identified near the pores which is believed to be the reason of Li losses. Both intergranular and transgranular type of fracture were seen from the micrographs of fractured surfaces. Pores were found to be distrubuted along the pellet body and smaller grains were collected at triple junctions of bigger grains.

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A New Coating for Improving the Electrochemical Performance of Cathode Materials

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Lithium-ion batteries (LIBs) now dominate the energy storage market for portable electronic devices. However, their widespread use as high-energy storage devices for electric and hybrid vehicles requires further improvement in their energy density, safety, and operation time. Cathode materials play the most important role for the battery electrochemical performance. Layered compounds of the $LiNi_xMn_yCo_{1-x-y}O_2$ family are promising candidates for the positive electrode of high-energy LIBs due to their high discharge capacity and relative thermal and structural stabilities. To enhance the cyclability of these materials, protective coatings can be applied.

In the present study, we synthesized $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ compound and obtained a new mixed alumina–carbon coating by a simple soft chemical route. The inclusion of carbon in the coating composition can compensate the impedance growth during cycling and prevent a loss of electrical contact between particles. The presence of alumina and carbon on the surface of coated samples is proved by ICP-AES, chemical analysis, XP spectroscopy, TEM and SEM microscopy and electron diffraction. The electrochemical behavior of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ with the mixed alumina–carbon coating (LNMC-AC) is studied and compared with that of the bare sample (LNMC) and alumina-coated $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ (LNMC-A). The electrochemical performance of the cathodes based on the compounds under study is evaluated with the use of coin-type cells at 25°C. The negative electrode is lithium foil; the electrolyte solution is 1M $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate in the weight ratio of 1:1:1.

According to the X-ray powder diffraction data for LNMC-AC and LNMC-A, the coatings obtained have no or little influence on the LNMC crystal structure (crystal symmetry R-3m). The elemental mapping images (SEM) demonstrate the uniformity of the Al_2O_3 coating for both samples. The thickness of coating layers is about or less than 25 nm (TEM images). Our electron diffraction analysis indicates that some fraction of the Al_2O_3 coating may create an epitaxial „shell‟ film for „core‟ particles of LNMC-AC.

Fig. 1a represents the cycling performance of the two materials (LNMC and LNMC-AC) at a current rate of 10 mA g^{-1}. The capacity retention of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ electrode with alumina–carbon coating is remarkably enhanced. The capacity loss after 110 cycles was 9.1% for LNMC-AC and 16.9% for LNMC, respectively. The rate capabilities of Li/LNMC, Li/LNMC-A, and Li/LNMC-AC cells are shown in Fig. 1b. The cells were charged at the constant current density of 10 mA g^{-1} (0.1 C rate) and discharged at different current densities up to 500 mA g^{-1} (5 C).

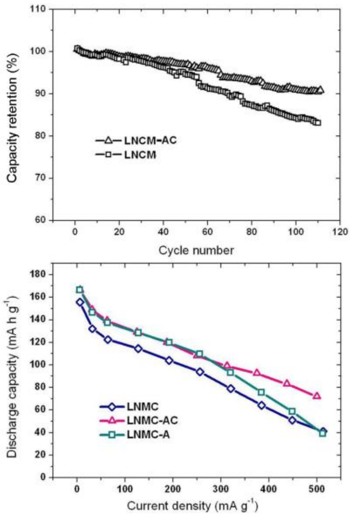

Figure 1. (a) Cycling behavior of coated LNMC-AC and bare LNMC samples and (b) comparison of rate capabilities of the same samples and the sample LNMC-A.

These data show that the sample with the Al_2O_3–C coating has a better electrochemical performance compared with the pristine one and with the sample coated with pure alumina and shows more stable cycling at high rates.

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Li-Al-Mg as potential anode material for Li-ion batteries

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Secondary lithium ion batteries are widely used as energy sources for mobile devices due to their balance of high energy density with high power density compared to other energy storage materials. However, the development of the modern portable devices increases the demand for batteries with a higher performance. The present batteries operate using intercalation processes, which require an electrode material with open crystallographic structure. An interesting alternative to this mechanism is to use lithium alloying metals as negative electrodes [1]. One of the most detailed studied systems is lithium-aluminum [2-4]. The main drawback of the system is that the delithiation during discharge causes a rapid degradation of the electrode, mainly due to formation of α-LiAl phase.

We investigate the addition of magnesium in Li-Al system in order to stabilize the active phase. Presumably, the electrodes based on Li-Al-Mg alloys will have reasonable capacities. On the other hand, phase transformations during cycling are expected to have a minimal impact on the electrodes' integrity preventing them from degradation.

In this study, several Li-Al-Mg compositions were prepared by melting pure metal elements in a sealed tantalum tube in an oxygen- and water-free environment. The obtained materials were pulverized by a milling process. The powders were wet-chemically and structurally analyzed. They contain different proportions of the binary phases LiAl and/or Li3Mg7 and/or Li3Mg17. Prepared electrodes were assembled in coin cells and electrochemically studied. Depending on binary phases' ratio, the initial capacities vary from 200 mAh/g to 1000 mAh/g.

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Low-Density Silicon Thin Films as Anodes in Lithium-ion Batteries

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Silicon has become one of the most promising anode material for Li-ion batteries because of its high theoretical capacity (~3580-4200 mAh/g), which is the highest known value among all materials in nature to the day. Besides this significant advantage, Si anode materials suffer from several problems which have created difficulties for its commercial use. The major problem with silicon anodes is its more than ~400% volume change during the insertion/extraction of lithium ions. This volume change causes mechanical instability, capacity fading in batteries. In order to achieve higher cycling performance without pulverization or delamination, the mechanical breakdown due to the volume change must be compensated.

In this work, several Si thin film samples with different densities were fabricated at different deposition gas working pressure values in order to study the effect of the density on the mechanical stability and electrochemical properties of Si thin film anodes for Li-ion batteries. Conventional dense Si thin film anodes (with density of ~ 2.27 g/cm^3) showed substantial change from the initial capacity of 2320 mAh/g to 830 mAh/g at the 100th cycle. Electrochemical performances of less dense films with the densities of 1.77 g/cm^3 and 1.99 g/cm^3 have gotten worse compared to the conventional Si thin film. However, by decreasing the density further, films with density values of 1.67 g/cm^3 and 1.64 g/cm^3 have provided excellent capacity retention. (Figure 1) The specific capacity values of those films decrease at a low rate and stabilize after ~ 80th-90th cycle with reasonable high capacity values of ~530 mAh/g and ~650 mAh/g for films of 1.67 g/cm^3 and 1.64 g/cm^3 density values, respectively. This enhancement might be because of the high porosity of these films which provides broader pathway and spacing for atoms leading to better mechanical stability.

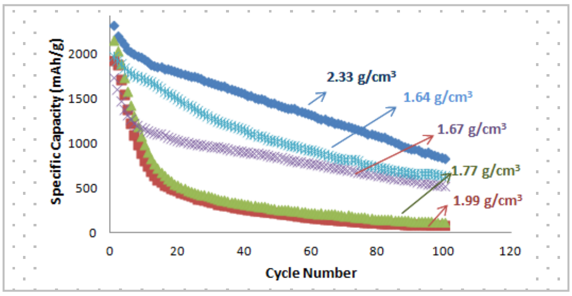
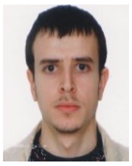


Figure 1. Specific capacity values of Si thin film anodes of different densities for 100 cycles.



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Production and characterization of free-standing ZnO/SnO$_2$/MWCNT ternary nanocomposite Li-ion battery anode

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For electrochemical energy conversion and storage devices, lithium ion batteries (LIBs) are one of the most promising candidates in the scientific and industrial fields [1]. To obtain high capacity and long-lasting batteries, several studies are performed on cathode and anode materials. The studies on the improvement of anode materials have been widely reported for metal oxide based electrodes. Especially, zinc and tin dioxide based materials are being used as active anode materials for rechargeable lithium batteries, because theoretical capacity of ZnO (978 mAhg^{-1}) and SnO$_2$ (1491 mAhg^{-1}) has been estimated to be superior to that of graphite (372 mAhg^{-1}) [2,3]. However, as far as known from previous works, these high capacity anode materials usually suffer severe capacity fading, because of the quick aggregation of metal particles and the huge volume expansion during Li$^+$ insertion/extraction cycles [4]. So, to prevent the pulverization of the anodes and electrical detachment of active materials, MWCNT buckypaper substrates are considered as a buffer material during the battery applications. CNT buckypapers are self-supporting networks of CNT assemblies randomly arranged and held together by van der Waals interactions at the tube–tube junctions [5]. In Figure 1, it is illustrated the accommodation of the stresses arisen from the volume increase during charging process by using highly porous MWCNT network coated with a thin layer of the metal oxides. In literature, ZnO-MWCNT and SnO$_2$–MWCNT nanocomposite materials were extensively studied as binary composites [2,5].

In this work, high capacity ZnO/SnO$_2$/MWCNT ternary nanocomposite films were prepared as free-standing anode materials by sol–gel spin coating method to increase the electrochemical discharge capacity of the Li-ion battery electrodes. The structural properties of free-standing buckypaper composite film anodes were characterized by FEG-SEM (Field Emission Gun - Scanning Electron microscopy), EDS (Energy Dispersive X-ray Spectroscopy) and XRD (X-ray Diffraction) techniques. Electrochemical performance tests, CV (Cyclic Voltammetry) and EIS (Electrochemical Impedance Spectroscopy) analyses of free-standing anodes assembled in the CR2016 coin cell type Li-ion batteries were also performed. The cells were charged and discharged at 25 °C between fixed voltage limits (2.5 V to 0.2 V). After 100 cycles, ZnO/SnO$_2$/MWCNT free-standing anode showed as high as 487 mAh g^{-1} discharge capacity. MWCNT buckypaper substrates provided the prevention of mechanical disintegration and anode pulverization of the electrode. The results indicated that the ZnO/SnO$_2$/MWCNT ternary nanocomposite anode produced by spin coating supplied beneficial outputs according to binary nanocomposite structures to increase electrochemical energy storage performance of anode electrode for Li-ion batteries. The simple method for the design of core-shell structure on MWCNTs (core) of ZnO/SnO$_2$ (shell) nanocomposite with a high capacity coupled with an excellent cycling performance may open up a new opportunity of ZnO/SnO$_2$ based anode materials for next generation application Li-ion batteries as ternary nanocomposites with MWCNTs.

Keywords: Li-ion battery, metal oxide/MWCNT nanocomposites, sol-gel synthesis, spin coating, electrochemical characterization.

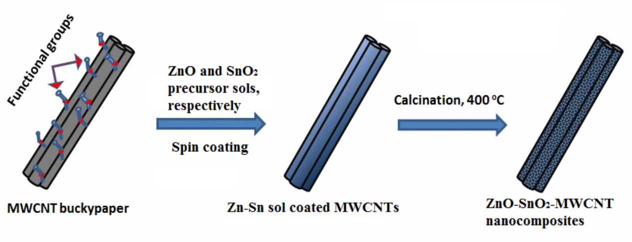

Figure 1. The illustration of ZnO/SnO$_2$/MWCNT nanocomposite production.

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$LiFePO_4$/C nano plates sythesis via ultrasound assisted precursor precipitation

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After the discovery of olivine type $LiFePO_4$ as a promising cathode candidate for lithium-ion batteries[1], it displayed outstanding cycling stability and safety against oxide materials because of its more stable oxygen atoms shared by octahedral-PO_6 and tetrahedral-FeO_4. Pioneer research studies have consolidated into low electronic conductivity ($\sim10^{-9}$ Scm^{-1}) and slow lithium ion diffusion which causes poor rate capability at quick charging ($\sim1.8\times10^{-14}$ $cm^2\ s^{-1}$)[2]. To increase conductivity by increasing Li ions diffusion rate is widely aimed by both carbon coating and size refinement[3,4].

Using hydrothermal methods are resulted in micron sized particles rather than nano sized structures[5]. However aquous precipitation techniques are easily controllable for synthesis of small particles[6]. In order to gain control on size distribution and provide better homogeneity, subsequential synthesis method through vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) precursor is the most promising technique for the mass production of $LiFePO_4$. Although it is reported as inexpensive, resulted in high performance cathode; micron size, bad reproducible examples were synthesized besides oxidation sensitivity of vivianite[5].

In this study, to control on size and morphology, sequential synthesis strategies are proposed for carbon coated $LiFePO_4$ nano plates via ultrasound (US) assisted vivianite precursor precipitation in aqous suspesion (eqn. 1 and 2). Resulted precursor crystals meet the nano size target with low cost, low temperature synthesis (Fig.1). Ultrasound irradiation, during precipitation, gives control on reaction and crystallization mechanisms with higher reproducibility and size refinement.

$$3\ LiOH + H_3PO_4 \rightarrow Li_3PO_4 + 3\ H_2O \qquad (1)$$

$$3\ FeSO_4 + 3\ Li_3PO_4 \rightarrow Fe_3(PO_4)_2 + 3Li_2SO_4 + Li_3PO_4 \qquad (2)$$

$$Fe_3(PO_4)_2{\cdot}8H_2O_{(s)} + Li_3PO_{4\,(s)} \rightarrow 3\ LiFePO_{4\,(s)} + H_2O \qquad (3)$$

We use restricted solubility of Li_3PO_4, as both phosphate and then lithium sources, controlled with US wave induction. US waves manage the reaction rate by increasing high solubilization and temperature in a very short time. Insonation reduces both induction time and metastable zone width for nucleation so that crystallization process becomes uniform and controllable[7]. Mass transportation is also homogenized by rapid shock waves reducing aglomeration and crytallite size. Reducing media is also maintained by US produced radicals.

For increasing conductivity and preserving the size and morphology of precursor crystals, carbon encapsulation strategy was applied with sucrose impregnation and drying method followed by heat treatment in reducing atmosphere at 350 °C and 700 °C.

XRD patterns support that vivanite nano plates can be obtained with strong preferred orientation at (010). Than they serve to sythesize conductive $LiFePO_4$/C nano plates with reliable electrochemical cathode performance (Fig.2). Final $LiFePO_4$/C has little impurity of Li_3PO_4 by US assistance.

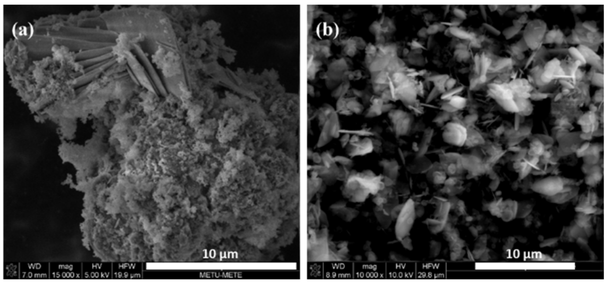

Figure 1. Vivianite structures synthesized with (b) and without (a) US assistance

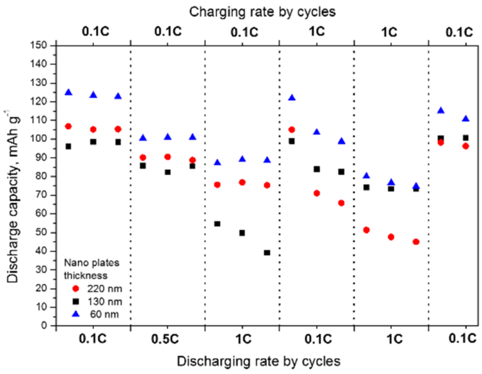

Figure 2. Capacity results of $LiFePO_4$/C nano plate cathodes

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Silicon Carbide Derived Carbon for Energy Storage Applications

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Many kinds of anode materials have been studied for lithium ion battery since its birth. However, graphitic carbon is still the only commercially available product. On the other hand, addition of elements like Si, with high Li storage capacity, is an attractive method to modify these carbonaceous anode materials. In this study, Si doped carbon is produced not by the addition of Si into carbon, but extraction of Si from SiC through high-temperature vacuum annealing. Tests showed that Si doped carbon that is derived from SiC is a promising candidate for the Li-ion battery applications.

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Self-organization of Titanate Nanotubes on Functionalized Graphene as a Novel Hybrid Electrode for Lithium-ion Batteries

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There are many studies in academic realm to develop materials for energy storage in order to be used in portable devices of electronic industry. By having a large application area, lithium ion batteries (LIBs) are the most preferred energy storage sources in terms of not only their lower weight, higher energy capacity, and performance but also longer life time, lower cost and greater reliability when compared to other types of batteries[1]. Despite all, many materials are being tried to improve these properties of LIBs. Graphene based materials are the most promising candidates for LIBs due to their high electrical conductivity, good mechanical behavior and good electrochemical properties such that enable it to be doped with other functional, dense and high energy materials[2] [3]. In this research, two novel graphene based materials were synthesized and characterized for lithium ion batteries. Self-organized titanate nanotubes ($H_2Ti_3O_7$) are dispersed on both nitrogen doped reduced graphene oxide (N-rGO) and polypyrrole/ reduced graphene oxide nanocomposites (PPy/rGO). Anatase was synthesized by Sol-Gel method and then processed with hydrothermal treatment to obtain micron size titanate nanotubes (figure 1). N-doped graphene has been prepared by annealing GO with NH_3 and PPy/rGO nanocomposite was prepared by in-situ polymerization of pyrrole in the presence of GO. Self-organization of the nanotubes on graphene was achieved by mixing them in certain ratios and treating them under a second hydrothermal process. Several characterizations were performed on novel hybrids of $H_2Ti_3O_7$/N-rGO and $H_2Ti_3O_7$/PPy/rGO. The structural and morphological analysis of the samples were performed by X-ray diffraction (XRD), Brunauer-Emmentt-Teller (BET) analysis, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and RAMAN spectroscopy. Cyclic voltmeter (CV) was operated to explore the oxidation-reduction relation with current-voltage parameters. Charge-discharge tests were employed to evaluate energy storage capacity corresponding to applied voltage and current to characterize their performance and durability. It is found that these samples remain stable and save their energy capacities in high current values due to the enhanced Li^+ ion and electron mobility.

Figure 1. SEM image of Titanate Nanotubes

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The effects of Ca and Nb co-doping on the electrochemical properties of $Li_4Ti_5O_{12}$ as anode material for lithium ion battery

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The lithium ion batteries are widely employed as the main power source for portable electronic devices. Among the electrode materials, $Li_4Ti_5O_{12}$ has attracted much interest owing to the potential application as an anode material for power lithium-ion batteries[1,2]. The spinel $Li_4Ti_5O_{12}$ has a stable and high working potential (about 1.55 V vs Li/Li+), which can avoid the formation of the solid-electrolyte interphase (SEI) layer (usually occurring below 1.0 V Li/Li+) and the deposition of lithium dendrites. In addition, $Li_4Ti_5O_{12}$ also exhibits excellent safety, high structural stability, and thermodynamic stability due to its zero volume change in the charge−discharge process. However, , $Li_4Ti_5O_{12}$ exhibits poor electronic and lithium ionic conductivities, thereby limiting itself in high rate charge/ discharge application. To improve the conductivities, several effective ways have been proposed, including synthesizing nano-sized $Li_4Ti_5O_{12}$, doping with aliovalent ions (V^{5+}, Nb^{5+}, Zn^{3+}, Cr^{3+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Br -, F-) in Li, Ti or O sites [3-4].

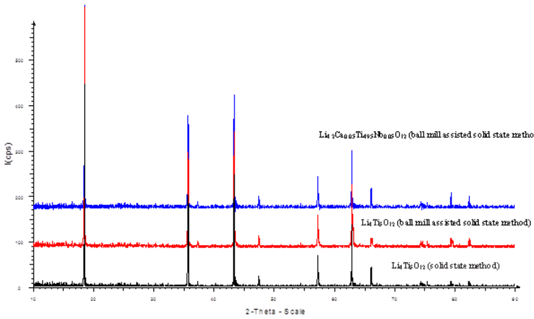

Figure 1. XRD patterns of the samples

We report on the effect of Ca and Nb co-doping on the conductivity and electrochemical performance of $Li_4Ti_5O_{12}$. Pristine $Li_4Ti_5O_{12}$ and co-doped $Li_{4.2}Ca_{0.05}Ti_{4.95}Nb_{0.05}O_{12}$ materials were synthesized by a solid state and ball mill assisted solid state methods using stoichiometric amounts of Li_2CO_3, TiO2, Nb_2O_5 and $CaCO_3$ as Li, Ti ,Nb and Ca sources, respectively. Excess Li was added to compensate for lithium volatilization during the sintering process.

The structural and electrochemical properties of the prepared powders were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and their electrochemical properties as the anode material for lithium ion batteries were investigated by galvanostatic charge and discharge tests.

Figure 1 shows the XRD spektrum of $Li_4Ti_5O_{12}$ and $Li_{4.2}Ca_{0.05}Ti_{4.95}Nb_{0.05}O_{12}$. All major diffraction peaks can be indexed into a cubic spinel structure with a Fd-3 m space group,indicating that small amount of Ca^{2+} ve Nb $^{5+}$co-doping does not change the basic structure of $Li_4Ti_5O_{12}$. In addition, no other peaks are detectable, suggesting the high purity of the products.

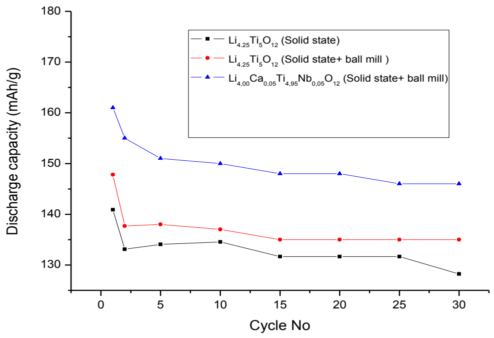

Figure 2. Cycle performance curves of the pristine $Li_4Ti_5O_{12}$ and co-doped $Li_{4.2}Ca_{0.05}Ti_{4.95}Nb_{0.05}O_{12}$

Figure 2 shows the cycle performance curves of the samples, The electrochemical property results demonstrate that $Li_{4.2}Ca_{0.05}Ti_{4.95}Nb_{0.05}O_{12}$ synthesized by ball mill assisted method shows a much higher cycling stability in comparison with un-doped $Li_4Ti_5O_{12}$ synthesized by both solid state and ball mill assisted solid state methods.

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Preparation and Characterization of $Na_{0.44}MnO_2$ Cathode Materials For Novel Na-ion Batteries

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Li-ion batteries are the most interesting and the promising technology among the energy storage systems. The operating voltage and high energy density of these batteries make them popular for portable electronic devices and electric vehicles. However, major problems awaits the Li-ion batteries in the future such as the limited resources of lithium raw materials and as a consequence, increasing prices of the raw materials [1]. Because of these drawbacks, researchers have focused alternative battery systems [2]. In this scope, novel Na-ion batteries have the potential to replace the Li-ion batteries in the future. Na-ion batteries have similar electrochemical characteristics and operational mechanisms as Li-ion batteries. Also the sodium resources, unlike Litihum, are inexhaustible around the world [1,3].

In this study, nominal compositions of $Na_{0.44}MnO_2$ were prepared using conventional solid-state reaction technique. Appropriate amounts of reagent grade Na_2O_2 and MnO_2 were mixed in agate mortar for 1 h to give the nominal composition. Two separate batches of powders were pressed into pellets and after 750 ^{o}C 24h heat treatment was applied in air.

Afterwards, the microstructure characteriztions were examined with X-ray diffraction (XRD), scanning electron microscope (SEM) and Energy-dispersive X-ray (EDX) analysis.

For the electrochemical performance analysis, we fabricated the $Na_{0.44}MnO_2$ electrodes. To fabricate the $Na_{0.44}MnO_2$ cathode materials, $Na_{0.44}MnO_2$ active materials, acetylene black and polyvinylidene fluoride (%80:%10:%10) were mixed into slurries in N-methyl-2-pyrrolidone into an agate mortar. They were then cast on aluminum foils with a Micrometer Adjustable Film Applicator blade and then dried at 110^{o}C for 10h to obtain several electrode laminates.

For the battery, CR-2032 type coin-cells with pure Na metals as the counter electrode were assembled in the glove box with the $NaPF_6$ electrolyte. The cells were cycled by 8 channel battery analyzer system at 1C current rate. Also the cyclic voltammograms (CV) of the cells were measured with MTI-BST8-STAT-EIS-LD Single Channel Potentiostat/Galvanostat workstation from 3 to 3.8 V at a scan rate of 0.1 mV s^{-1}.

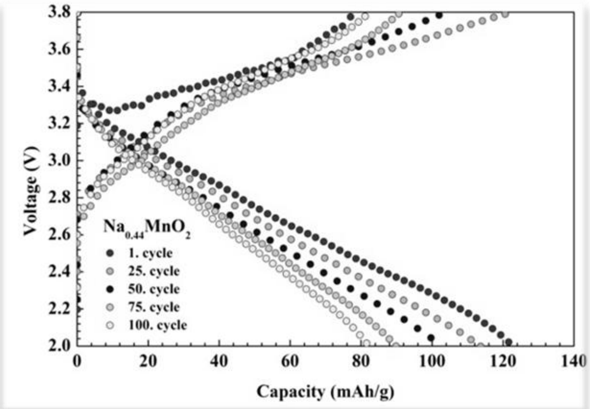

Figure 1. Cycle performance of $Na_{0.44}MnO_2$ Na-ion battery.

Figure 1 shows the charge discharge curve of the batteries with $Na_{0.44}MnO_2$ cathodes up to 100 cycles. The battery cells are activated until 3.8 V and then they are cycled between 2.0 and 3.8 V. As the obtained conclusion, $Na_{0.44}MnO_2$ cathode materials has got aproximately 120 mAh/g capacity value. Also we showed that after 100 cycle, discharge capacity value decreasing to aproximately 82 mAh/g. According to obtained experimental results we can say easily which is good for a novel Na-ion battery.

Acknowledgement

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Cost-effective cathode material for Na-ion batteries - $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$

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Energy conversion and storage is one of the great challenges of the last decades. Hence, efficient, safe, low-cost, and environmentally friendly storage systems are required to response modern society's needs. The technology of Li-ion batteries is one of the most promising among energy storage systems due to many advantages and wide range of applications (portable electronic devices, hybrid and electric vehicles). Sodium-ion batteries were proposed as a low cost alternative to Li-ion batteries, and rapid progress has been made in developing high capacity cathode materials. The cathode material is a key component that has significant influence on the final performance and cost of batteries. Ideal candidates from the economic point of view would be Fe-based cathodes. Yabuuchi et al. [1] proposed a new electrode material, P2-$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$, that delivers 190 $mAh \cdot g^{-1}$ of reversible capacity in the sodium cells with the electrochemically active Fe^{3+}/Fe^{4+} redox.

This work presents synthesis method of P2- $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ by a solid-state reaction with Na_2CO_3 (POCH, 99.8%), Fe_2O_3 (POCH, 99%), $MnCO_3$ (Chempur, > 99.9%) used as substrates. The crystal structure and mechanism of charge transport in $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ is discussed. The obtained material were applied as cathodes in $Na/Na^+/Na_xFe_{1/2}Mn_{1/2}O_2$-type cells. Specific capacity, reversibility and stability during charge-discharge cycles were evaluated to characterize electrochemical properties of the cells. In order to explain mechanism of charge transport, low-temperature electrical conductivity and thermoelectric power were performed by a 4-probe AC method and dynamic method, respectively.

XRD analysis of Na_xCoO_{2-y} showed single phase material having $P6_3/mmc$ space group (Fig.1) and unit cell parameters: a = 0.29223(9) nm and c = 1.12582(8) nm, which are in good agrement with results obtained by Mortemard de Boisse et al. [2]. Fig. 2 shows exemplary electrochemical data for $Na/Na^+/Na_xFe_{1/2}Mn_{1/2}O_2$ cells. The obtained discharge capacity of examined cell is observed for $Na_xFe_{1/2}Mn_{1/2}O_2$ (100 $mAh \cdot g^{-1}$) with voltage in the range 2.0-3.0 V delivering energy density over 250 $mWh \cdot g^{-1}$. The observed wide range of potential plateau is interesting from application point of view.

Acknowledgements
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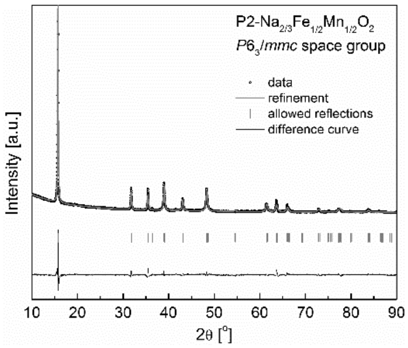

Figure 1. XRD pattern with Rietveld refinement for the synthesized $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$.

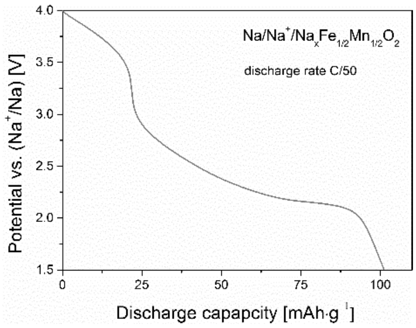

Figure 2. Discharge curve for $Na/Na^+/Na_xFe_{1/2}Mn_{1/2}O_2$ cell.

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Synthesis of Hydrothermal Carbon/SnO2 Anode Materials for Na-ion Batteries

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Na-ion batteries are considered to be alternative to Li-ion batteries owing to the natural abundance of sodium. They have emerged as an attractive electrochemical power source for large-scale electrical energy storage (EES). The development of suitable anode materials for Na-ion batteries has been studied a considerable effort. SnO_2 is a promising alternative anode material for Na-ion batteries. However, SnO_2 suffers from an extremely large volume change during charge and discharge, resulting in electrode degradation and fast capacity fading [1]. Embedding SnO_2 in carbon matrices can effectively suppress the volume expansion of the SnO_2 electrode. Carbon nanocomposites where the carbon can act as both a conductive additive and a physical buffering layer for the large volume change are also good alternatives to improve the performance on SnO_2 in NIBs [2-7].

In this study, SnO_2/carbon nanocomposite has been synthesized using hydrothermal carbonization of biomass in the presence of SnO_2 nanoparticle, since biomasses are eco-friendly energy sources and they are very qualified carbon sources. By the help of biomass conversion to carbon, not only wastes can be recycled, but also carbon can be acquired with low cost. Hydrothermal Carbonization (HTC) is one of the most used techniques to form carbonaceous material from biomass. It has been successfully applied as an anode material for sodium-ion batteries.

Pure SnO_2 nanoparticles (NPs) with narrow size distribution was synthesized with an aqueous, simple and surfactant free method. SnO_2 NPs are then disperssed into the biomass contaning aqueous solution to purse HTC. After carbonization at a moderate temperature under an inert atmosphere, hydrothermal carbon-coated SnO_2 NPs are obtained.

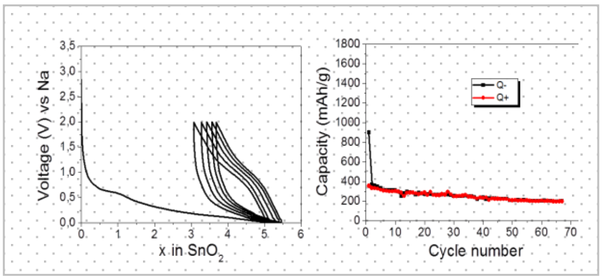

Figure 1. Cycling performance of SnO_2/C composite

The morphology and structure of SnO_2/carbon nanocomposites were characterized by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy and BET analyses. According to XRD, all the identified peaks are assigned to tetragonal SnO_2.

The electrochemical performances of SnO_2/C composite were evaluated by galvonastatic test. The experimental results show that the well-designed SnO_2/C composite electrode has great potential as an anode for sodium ion batteries. Approximately 250 mAh/g (Figure 1) capacity is obtained for Na-storage. The above results prove that carbon coated SnO_2 nanoparticle composite could be an option to utilize as electrode materials in sodium-ion batteries.

Acknowledgements

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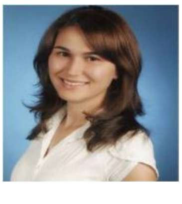

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Investigation of the concentration effect of V(V) ion on vanadium redox battery system by cyclic voltammetric and electrochemical impedimetric methods

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Energy explained the capacity of work ability of objects and system, is an important need for the human life. The dependence of energy has been increased during the human history and it has come to the highest level in the today’s knowledge society. The improving technology and developing new devices allow to increasing the need of energy day to day. Since most of needed energy consumed electric energy form, production and storage of it becomes an important issue.

Vanadium redox batteries (VRB) consisting of vanadium ions at different oxidation statement in sulrufic acid solutions inside of both cell are new generation energy storage system which was discovered and employed in University of New South Wales (UNSW) for the first time [1-3]. Concentraion of vanadium ions effects radically the capatiy and perfomance of this system [4].

In this study, we have investigated the concentration effects of V(V) ions on electrochemical behaviors of the system by cyclic voltammetric and electrochemical impedimetric methods (Fig. 1 and Fig. 2). Anodic and cathodic peak currents and redox capacities were determined by cyclic voltammetry. Solution resistance (Rs), charge transfer resistance (Rct) and Warburg impedance values were also studied with electrochemical impedance spectroscopy. When concentration of V(V) ions increased from 0.02 M to 0.2 M, anodic and cathodic peak currents increased and impedance values decreased.

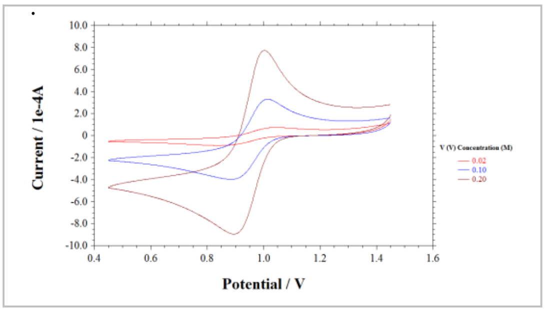

Figure 1. Cyclic voltammograms of sulfuric acid solutions having different concentration of V(V) ions

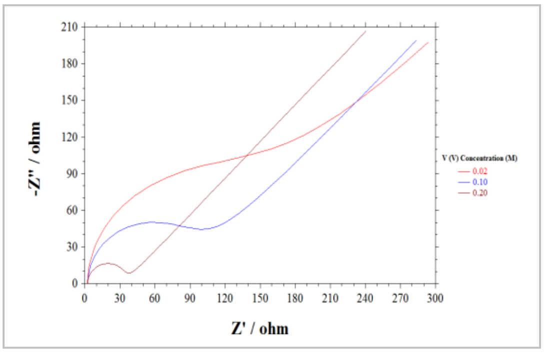

Figure 2. Electrochemical impedance spectra of sulfuric acid solutions having different concentration of V(V) ions

It was resulted that concentration of vanadium ions are significant parameters for VRB system and it was affects the peak currents, capacities and impedimetric values.

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Free Standing Polyaniline/CNT Electrodes and Their Electrochemical Performance

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Supercapacitors or electrochemical double layer capacitors are one of the most important research topics in the energy storage field because they fill the gap between batteries and commercial electrostatic capacitors providing higher energy density than electrostatic capacitors and higher power density than batteries. They have also fast response time and exceptional cycle life. Carbon based materials have required fundemantal properties, such as high specific surface area, good conductivity, and porous structure, to fabricate high performance supercapacitor electrodes.

After introduction of multi-walled carbon nanotubes (MWCNTs) to the scientific community by S. Iijima, carbon nanotubes (CNT) became a very popular electrode active material in supercapacitor applications because of its well-defined porosity, chemical stability, and more importantly its high conductivity that might lead high power density. These characteristics are essential for high charge storage which is called double-layer capacitance. Two forms of CNTs, which vertically aligned carbon nanotubes (VA-CNTs) and the other one is entangled carbon nanotubes (EN-CNTs)can be used as an electrode material in supercapacitors.

Implementing CNTs with a conducting polymer which will give additional charge storage, called pseudo-capacitance, into a supercapacitor electrode structure ensures to achieve enhanced capacitive behavior. The reason of this is that supercapacitor will store the charge physically in the double-layer and also chemically in the polymer in this way. Among all conducting polymers, polyaniline (PANi) has been studied extensively due to its high conductivity, high theoretical capacitance, good faradic redox reversibility, and high stability in air and solutions.

In the present work, VA-CNTs were synthesized by thermal chemical vapor deposition (CVD) at 750˚C on the 1 cm x 1 cm silicon wafer chips. Si wafer substrates were coated with 300 nm of SiO_2, 10 nm of Al_2O_3 as buffer layer and 1 nm of Fe catalyst layer by e-beam evaporation technique. Free standing ENCNT film without any binder was prepared from vertically aligned CNT. ENCNT/PANi hybrid supercapacitor electrodes were fabricated via pulse electrodeposition of PANi. Morphological characterization of the electrodes were studied with SEM and TEM. Electrochemical performances of two different supercapacitor cells were evaluated in aqueous electrolyte by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) test methods. Supercapacitor cell assembled with ENCNT/PANi electrode showed more promising results than one with ENCNT electrode (Figure 1).

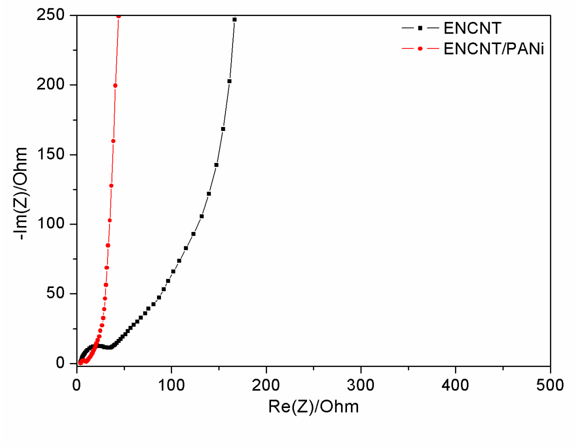

Figure 1. EIS data of ENCNT and ENCNT/PANi electrodes

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Capacitive energy storage with carbon aerogel, carbon xerogel and their polypyrrole composites

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Electrochemical double layer capacitor (EDLC), which is a type of capacitor and also known as supercapacitor, is an electrochemical capacitor which have high energy density. These supercapacitors can be divided into three parts depending on the electrode used as follows;

- Double-layer capacitors; with carbon electrodes or derivatives
- Pseudocapacitors; with electrodes made of metal oxides or conducting polymers
- Hybrid capacitors; electrodes exhibit both double-layer and pseudocapacitance

There are different types of carbon and conducting polymer materials used in supercapacitors. The investigation of carbon aerogels derived from resorcinol–formaldehyde as electrode materials for EDLCs is currently an active research area. This is due to the controllable pore size distribution, large surface area, and high electrical conductivity of carbon aerogels. The synthesis procedure is given in Figure 1.

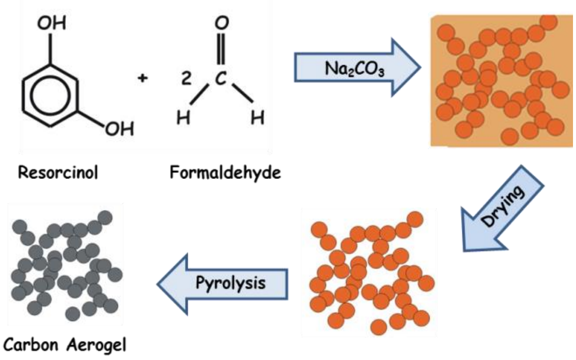

Figure 1. Synthesis of carbon aerogel

In this study, carbon aerogel was synthesized by using resorcinol-formaldehyde route (CA). The carbon xerogel structures were obtained starting by the same material but using ambient drying instead of supercritical drying. Ambient drying is achieved either by subsequent drying of RF aerogel (CK) or drying after the solvent exchange of RF aerogel by acetone (CKA). The composites with polypyrrole (PPy) were prepared by in situ oxidative polymerization of pyrrole [1] on carbon aerogel and xerogel structures. The surface areas and pore volumes of the materials obtained from nitrogen adsorption-desorption analysis is given in Table 1.

Table 1. Structural properties of the materials

Material	BET surface area (m^2/g)	BJH pore volume hacmi (cm^3/g)	DR micropore volume (cm^3/g)
CA1	500.2	0.4059	0.2135
CK1A	12.1	0.0156	0.0061
CK1	6.8	0.0112	0.0021
CA1/PPy	216.5	0.2884	0.0795
CK1A/PPy	100.7	0.1416	0.0354
CK1/PPy	14.5	0.0326	0.0032

The specific capacitances of the corresponding materials are given in Table 2. The specific capacitances are increased with the addition of PPy.

Table 2. Specific capacitances of the materials

Material	Specific capacitance (F/g)
CA1	156
CK1A	103
CK1	67
CA1/PPy	247
CK1A/PPy	206
CK1/PPy	199

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Acknowledgement

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Carbon Nanotube - Conducting Polymer Electrodes for Electrochromic Supercapacitors

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Supercapacitor devices are complementing batteries with their high power and moderate energy densities. There are commercial batteries that show the remaining battery power through a gauge by means of a thermochromic indicator that measures the heat resistance. Likewise, what if the supercapacitors are made to reveal their stored capacity? One could use electrochromic polymeric materials for this purpose to reflect the stored capacity via color change. A new conducting polymer is emerged as a promising active material both for its electrochromic and electrochemical properties combined in a single device. In this work, we report on the fabrication and characterization of supercapacitors with single walled carbon nanotube (SWNT) and a novel conducting polymer (CP) network electrodes. Vacuum filtered SWNT thin films in this work provided high surface area, high conductivity and high transparency for the electrochromic polymer. CP was deposited onto SWNT thin films by drop-casting and experienced multiple color changes with respect to its charged state. Electrochemical properties such as specific capacity and cycling ability of electrochromic supercapacitors were then investigated through cyclic voltammetry, chronopotentiometry, electrochemical impedance spectroscopy. Specific capacitance of SWNT/CP nanocomposite electrodes was obtained to be 112 F/g, which was higher than that of bare SWNT electrodes. We will present a detailed analysis of the electrochromic and electrochemical properties of the fabricated supercapacitor electrodes. Our results reveal the potential of the use of SWNT/CP in supercapacitor electrodes that can be fabricated through simple solution based methods and the method investigated herein can be simply adapted to industrial scale fabrication.

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CuO/Graphene oxide nanocomposite for supercapacitors

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The development of energy storage system is very important because of the limited utility of fossil fuels. One of the energy storage systems, supercapacitors, have various advantages such as fast charge-discharge, long life, safety high power density and environmental compliance [1]. Capacitors containing metal oxide such as NiO, CuO, MnO_2, Fe_3O_4, Fe_2O_3, MoO_3, TiO_2, RuO_2, SnO_2, V_2O_5 and Co_3O_4 have high capacitance but electrical conductivity of these capacitors are low. Therefore electrochemical stability of the metal oxide-supported graphene hybrid capacitors have been developed [2]. In this study, a composite is prepared by using chemical precipitation method by using copper (II) oxide (CuO) and graphene oxide (GO) prepared by modified Hummers method.

The morphology of the CuO/GO composite was determined by using scanning electron microscope (SEM). Figure 1 shows the dispersion of CuO on GO.

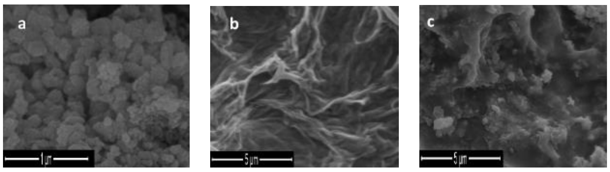

Figure 1. SEM images of the prepared a) CuO b) GO c) CuO/GO

Figure 2 shows the XRD pattern of the CuO and CuO/GO composite material. The XRD pattern of CuO/GO composite is similar to that of free CuO, indicating that the CuO/GO composite has been well synthesized. The diffraction peaks of C did not observed in the XRD image of nanocomposite due to the rather homogeneous dispersion of the composite and disorder stacking of graphene oxide layer [3]. In addition to this, the diffraction peaks coincide well with the standard pattern of CuO. The electrochemical performance of the CuO/GO composite is investigated by cyclic voltammetry measurements (CV) before and after potential cycling (1000 cycle). The presence of anodic and cathodic peaks at between 0.3-0.4V in the CV curve are proof of the fact that the origin of capacitance in the composite is mainly from the surface redox reactions.

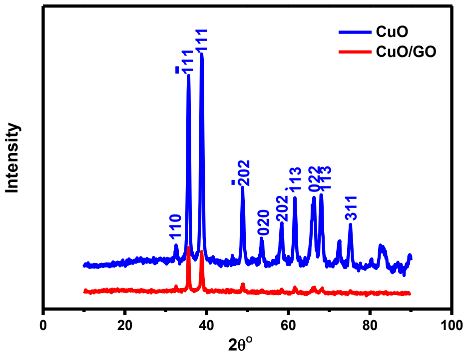

Figure 2. XRD pattern of CuO and CuO/GO

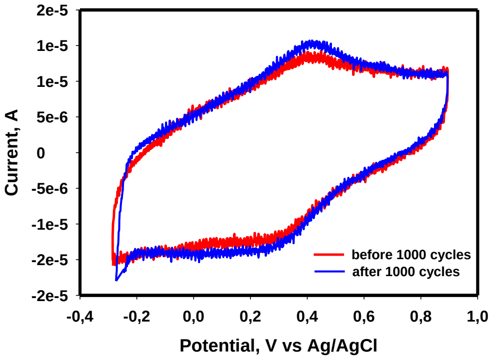

Figure 3. CuO/GO CV curve at 50mVs

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Carbon Nanotube- Cobalt Oxide Nanocomposites for High Performance Supercapacitors

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Depletion of energy sources created urgency to develop advanced energy storage devices. 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.

While the double layered supercapacitors that uses carbon materials with high surface areas are commercialized; metal oxide active materials has attracted much more attention in recent years. This is because of their pseudocapacitive behavior; high redox activity and high reversibility. Cobalt oxides (Co_3O_4 and CoO) are reported to have high pseudocapacitive properties, which make them promising electrode materials for supercapacitors. Hybrid capacitors using multi-walled carbon nanotubes and cobalt oxides are reported to have high capacitance values; however, research on electrodeposition of cobalt oxide onto carbon nanotubes and supercapacitors fabricated by this means remained elusive.

In this work, single walled-carbon nanotube (SWNT) thin films and cobalt oxide hybrids were prepared via different electrodeposition techniques, such as cyclic voltammetry, chronopotentiometry and chronoamperometry. SWNT thin films were fabricated via vacuum filtration method onto glass substrates and cobalt oxides were electrodeposited from a cobalt acetate solution. Different cobalt oxides were obtained through changing the annealing temperature. The capacitive behavior of the hybrid supercapacitors was investigated through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. A result of 18.3 $mF.cm^{-2}$ capacitance was obtained through cyclic voltammetry scan done with 20 mV/s scan rate. A detailed analysis on the capacitive behavior will be presented with the comparison of oxidation states and morphology of the active materials.

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Binder free direct hydrothermal growth of $Zn_xNi_{3-x}O_4$ as superior electrode material for supercapacitor applications.

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The Growing population, rapid industrial developments and depleting fossil fuel has increased the demands of cleaner, renewable and cost effective energy harnessing and storage devices. It has led the scientist to focus on the development of efficient environmentally friendly high power energy resources. Supercapacitor has drawn more attention and is highly studied in the field of energy storage devices because of its very long life cycle, faster charge-discharge rates and extremely high power density as compared to batteries. There are various synthesis methods for the synthesis of electrode materials like chemical precipitation, sol-gel, chemical vapor deposition, electrostatic spray deposition, electrodeposition and hydrothermal. In this work hydrothermal route has used for the direct growth of nanostructure on the carbon fiber paper. The advantages of using hydrothermal route for the direct growth on the carbon fiber paper are the electrode will be free from binder and cuductive additives which results in the enhancement of the electrode's electronic property, scale-up ability and easy processing[1-3].

Herein we first time report the hydrothermal synthesis of $Zn_xNi_{3-x}O_4$ binder free directly grown on the carbon fiber paper for supercapacitor application. The precursor for the synthesis were $Zi(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and Urea taken in an optimized ratio and dissolved in 75ml DI water and stirred for 30 minutes to get a clear solution. The whole solution was then transferred into 100 ml teflon autoclave and the carbon fiber substrates were dipped into it. The autoclave was sealed and kept at 130 ºC for 5 h in an electric oven. After naturally cooling to room temperature the substrate was removed and washed with DI water and ethanol for several times to remove the excess deposit from the surface and then kept for drying overnight at 70 ºC. Then the substrate was annealed in air at 250 ºC for different time duration say 2 h, 3 h and 4 h at a heating rate of 1ºC min^{-1} to get the pure crystalline phase. Then electrode was physically and electrochemically characterized by following techniques: scanning electron microscopy (SEM), X-ray diffractometry (XRD), Raman spectroscopy, cyclic voltammetry, and chronopotentiometry (charge-discharge measurements).

The electrochemical behaviour was checked for all the electrodes and the best performance was obtained for the electrode annealed at 300 ºC. Cyclic voltammetry was done for all the electrodes in the potential window of 0-0.55 V in 2 M KOH solution at different scan rates. Charge discharge was also performed at different current density and it has shown the excellent rate capability even at higher current density. The specific capacitance of 770 F g^{-1} was obtained at 1 A g^{-1} and it has shown excellent capacitance retention around 99 % after 1000 cycles.

In conclusion, $Zn_xNi_{3-x}O_4$ was synthesized directly on the substrate by hydrothermal root and it had shown the excellent capacitive behaviour. Its high cyclic stability and high rate capabilities can play an important role in designing hybrid electrochemical supercapacitors.

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Electrochemical synthesis of poly(1-(chrysenyl)-2,5-di(2-thienyl)-1H-pyrrole-co-pyrrole) for supercapacitor applications

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Energy and energy storage have become one of the most important issues to achieve a clean and sustainable world In this respect, electrochemical energy storage devices such as batteries, fuel cells, and electrochemical supercapacitors have been recognized as the most important portion of the various energy storage technologies [1]. Electrochemical capacitors, also called supercapacitors (SCs), one of the promising energy storage devices due to their high power density, ultrafast charging-discharging rate, long-cycle-life, low cost and excellent stability [2-3]. Polypyrrole has been widely used for supercapacitor applications because of its high electrical conductivity, high capacitance, stability, and low cost with potential applications for energy storage in wind power systems and electric vehicles [4].

In this work, 1-(chrysenyl)-2,5-di(2-thienyl)-1H-pyrrole monomer was synthesized chemically. ^{1}H-NMR and ^{13}C-NMR spectroscopic methods were used to characterize the monomer. Then, electrocopolymerization of 1-(chrysenyl)-2,5-di(2-thienyl)-1H-pyrrole with pyrrole was carried out in an dichloromethane solution containing 0.1 M tetrabuthylammonium perchlorate by cyclic voltammetry method. The capacitive properties of the conductive copolymer electrode were investigated by electrochemical impedance spectroscopy. The specific capacitance, solution resistance (Rs), charge transfer resistance (Rct) values of the modified copolymer electrode were calculated from the Nyquist diagram (Fig. 1).

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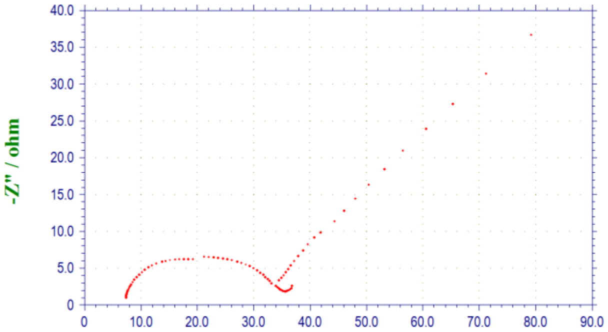

Fig. 1. Nyquist diagram of modified copolymer electrode in potassium hydroxide electrolyte solution.

Because of the low impedance values of modified copolymer electrode, it can be used an electrode material for supercapacitor applications.

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Performance of stainless steel 316L electrodes with modified surface to be used in alkaline water electrolyzers

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Water electrolysis could provide a method to storage the excess of renewable energy (from the wind and the sun) as hydrogen. There exist different kinds of water electrolysers as alkaline, proton exchange membrane, high pressure, high temperature and solid polymer. The advantages offered by alkaline water electrolysis, such as accuracy, simplicity, robustness and being well known, make it suitable for that purpose.

In this work we carried out the performance analysis of four different kinds of stainless steel 316L electrodes to be used in alkaline water electrolyzers for the production of hydrogen. The proposed electrodes were: electrodes in their original condition (as marketed), electrodes with chemical pickling treatment, mechanized electrodes with straight-parallel topology and combined electrodes (with straight parallel topology and chemical pickling treatment). The chemical pickling process consists of firstly treating the electrodes with a solution of hydrocloric acid 1 M during 1 hour at 60° C, and secondly with nitric acid 5% w/w, during 5 minutes at room temperature. This process was explained in detail in Lavorante et al. 2014. [1] The purpose of the chemical pickling is to increase the surface area of the electrode by creating roughness; the straight-parallel topology is another way to increase the surface area in an enclosed way. The electrodes were tested in a special electrolytic cell that allows establishing the distance between them. [2] Each experience (with one type of electrodes) was made four times, all of them at 30,1°C as initial temperature and potasiumm hydroxide 30% w/w as electrolyte solution. Current measurements were made at a certain potential between 0.0 and 3.0 V, changing the applied voltage differences 0.1 V, every 30 seconds. The results obtained in the four experiences were averaged together with the purpose of construct the graphical representations.

The behaviour of all these electrodes was studied under two different distances (5.3 and 5.5 milimeters) in order to determine their performance in each of the situations. The results obtained were shown in the graphical representations below. **Figure 1** is the graphical representation of the current density as a function of the applied voltage differences at 5.3 milimiters as distance between electrodes, **Figure 2** is the same representation but at 5.5 milimeters between electrodes. The mechanized electrodes with straight-parallel topology present the best performance in all distances examined.

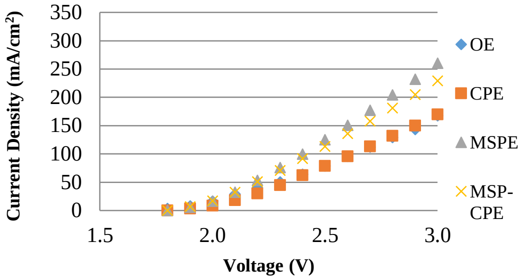

Figure 1. Graphical representation of current density as a function of applied voltage differences for the systems of: original electrodes (EO); chemical pickling electrodes (CPE); mechanized electrodes with straight-parallel topology (MSPE) and mechanized electrodes with straight-parallel topology and chemical pickling treatment (MSP-CPE), at 5.3 mm as distance between electrodes.

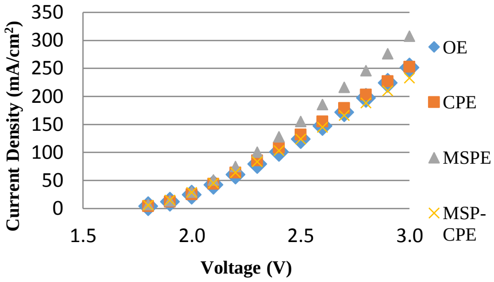

Figure 2. Graphical representation of current density as a function of applied voltage differences for the systems of: EO; CPE; MSPE and MSP-CPE, at 5.5 mm as distance between electrodes.

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ORDER-DISORDER HIGH-TEMPERATURE PHASE TRANSFORMATION IN $La_{5.5}WO_{11.25}$ PROTON CONDUCTING PHOSPHOR

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Among the $Ln_{5.5}WO_{12-\delta}$ (26.7 mol.% WO_3; Ln = La, Nd) family of rear-earth tungstates, $La_{5.5}WO_{12-\delta}$ has attracted particular interest because of its high proton conductivity reaching 1.5×10^{-3} S/cm at 600°C in wet atmosphere [1–3]. The average crystal structure of $La_{5.5}WO_{12-\delta}$ was described as cubic and its relation to fluorite was established [1,4,5]. We have recently shown that Zr-doped rare-earth molybdates $Ln_{5.4}Zr_{0.6}MoO_{12.3}$ (Ln=Nd, Sm, Dy) and $La_{5.8}Zr_{0.2}MoO_{12.1}$ possess appreciable mixed electron-proton conductivity in the low and intermediate temperature range [6,7]. Unfortunately, due to the tendency to form complex superstructures with large unit cells, the precise determination of the crystal structure of fluorite-like rare-earth molybdates and tungstates has been problematic [8]. The purpose of this study is to demonstrate that a cubic (F) to rhombohedral (R) phase transformation takes place in $La_{5.5}WO_{11.25}$ between 1600 ºC and 1650ºC and discuss its implications for the proton conductivity.

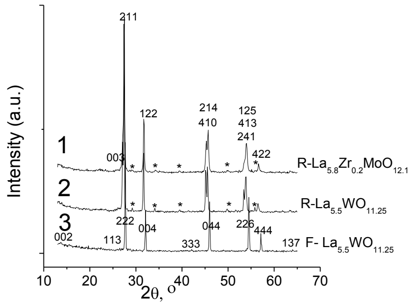

Fig.1 XRD patterns of (1) R-$La_{5.8}Zr_{0.2}MoO_{12.1}$ (1600°C, 3h), (2) R-$La_{5.5}WO_{11.25}$ (1600°C, 3h), (3) F- $La_{5.5}WO_{11.25}$ (1650°C, 3h; HKL indexation in accordance with [1]).

The mechanically activated mixtures of the oxides(La_2O_3, ZrO_2, MoO_3 or WO_3) were unaxially pressed at 914 MPa and sintered at 1400, 1600 or 1650ºC for 3 h. All samples were characterized both structurally (XRD, Raman) and electrically (ac-impedance studies using a Solartron 1260 frequency response analyzer and NorECs ProboStat cell) in dry and wet atmospheres. High-temperature transformation in the $La_{5.5}WO_{11.25}$ was observed to occur between 1600 and 1650°C in air. The color of the samples changed from dirty-yellow (R-$La_{5.5}WO_{11.25}$, 1600°C, 3h) to beige (F-$La_{5.5}WO_{11.25}$,1650°C, 3h). XRD data show different structure types: low-temperature R-$La_{5.5}WO_{11.25}$ (Fig.1, curve 2) and high-temperature F- $La_{5.5}WO_{11.25}$ (Fig.1, curve 3). R-$La_{5.8}Zr_{0.2}MoO_{12.1}$ (1600°C, 3h) (Fig.1, curve 1), investigated early [7] has pure yellow color. The XRD pattern of the rhombohedral $La_{5.5}WO_{11.25}$ (SG $R\bar{3}$) looks very similar to that of $La_{5.8}Zr_{0.2}MoO_{12.1}$. Order-disorder R-F structure transformation in the temperature interval 1600-1650ºC was observed in the $La_{5.5}WO_{11.25}$. Raman spectroscopic studies revealed the presence 2 parent cubic and rhombohedral type structures. The total conductivity and luminescence of low- and high temperature phases in dry and wet atmospheres are being investigated.

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Comparison of Two Different Catalyst Preparation Methods for Graphene Nanoplatelet Supported Platinum Catalysts

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Proton exchange membrane fuel cell (PEMFC) is one of the fuel cells which has high power densities, low weight, cost, volume and operation temperature, and rapid start up. The most important part is the membrane electrode assembly (MEA) in which the half cell reactions and proton conduction occur. The activities of the fuel cell electrocatalysts depend on several parameters such as the catalyst preparation technique, type of carbon support and graphene (G) seemed to be a good candidate [1], properties of the precursor, accessibility of the metal on the support, and testing conditions [2].

Supercritical carbon dioxide ($scCO_2$) deposition technique is used to prepare Pt/G in $scCO_2$ at 35˚C and 10 MPa by adsorbing the Pt organometallic precursor on graphene. The adsorbed precursor was converted to Pt with thermal treatment at 400˚C in nitrogen atmosphere.

Microwave irradiation method was also used for the preparation of Pt/G catalyst. Briefly, required amounts of graphene and aqueous solution of H_2PtCl_6 added in 50mL ethylene glycol and then stirred for 30 min. Then the resulting mixture was reduced in microwave oven for 60s.

In this study, we compared two facile and effective approach to synthesize Pt nanoparticles uniformly dispersed on G. The support metarial and prepared catalysts were characterized by using TGA, SEM, XRD, TEM and PEM fuel cell performance tests.

TEM results (Fig.1.) showed that $scCO_2$ deposition method resulted in a more homogeneously distributed and smaller Pt nanoparticles than microwave irradiation.

PEM fuel cell performance tests showed also a better result for Pt/G prepared with $scCO_2$ deposition when compared to Pt/G prepared with microwave irradiation (Fig.2.).

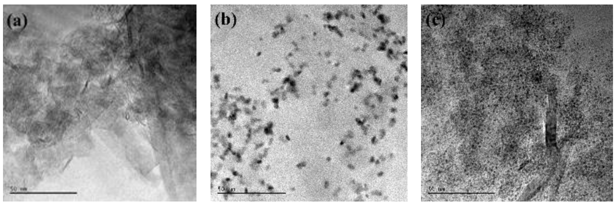

Figure 1. TEM images of (a) graphene (b) Pt/G microwave and (c) Pt/G $scCO_2$ deposition

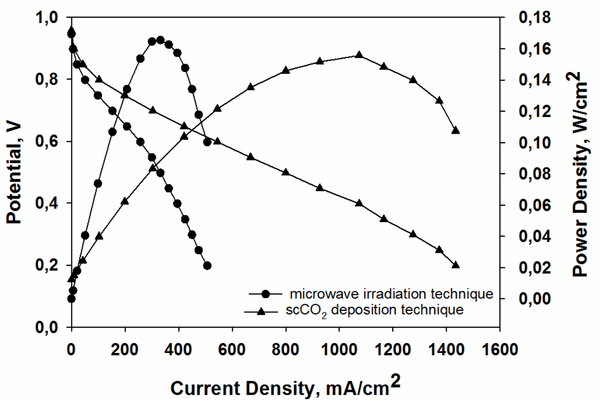

Figure 2. PEM fuel cell performance test results

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Preparation of Graphene Nanoplatelet Supported Platinum Catalysts by Supercritical Carbon Dioxide Deposition

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The use of a 2-D carbon nanostructure, graphene, as a support material for the dispersion of Pt nanoparticles provides new ways to develop advanced electrocatalyst materials for fuel cells. Several different methods were utilized to deposit platinum on different carbon supports.

Supercritical carbon dioxide ($scCO_2$) deposition is one of the alternative techniques to incorporate metals on supports. The technique involves the dissolution of a metallic precursor in the $scCO_2$ phase and the exposure of the support to this solution. After adsorption of the precursor on the support, the precursor is reduced to its metallic form by various methods. Fig. 1. shows the experimental setup of $scCO_2$ deposition [1, 2].

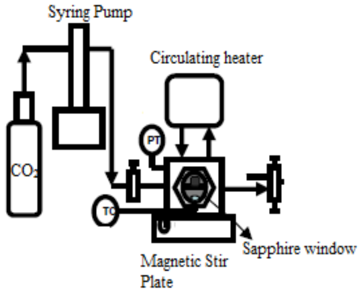

Figure 1. Experimental setup for supercritical deposition

In this study, Pt nanoparticles on graphene nanoplatelets (1-5 nm thick, surface area of 750 m²/g) were achieved by using $scCO_2$ deposition method by using 1,5-dimethyl platinum cyclooctadien (Me_2PtCOD) as the Pt organometallic precursor. This precursor was firstly dissolved in $scCO_2$ (at 35˚C and 10 MPa) and then adsorbed on the graphene nanoplatelets material. The precursor was decomposed to metallic Pt with the heat treatment at 400˚C for 4 h in nitrogen atmosphere. The precursor amounts dissolved in the high pressure vessel was changed in order to get catalysts having different Pt loadings over the graphene nanoplatelet. The graphene nanoplatelet and prepared catalysts were characterized by using TGA, TEM and PEM fuel cell performance tests.

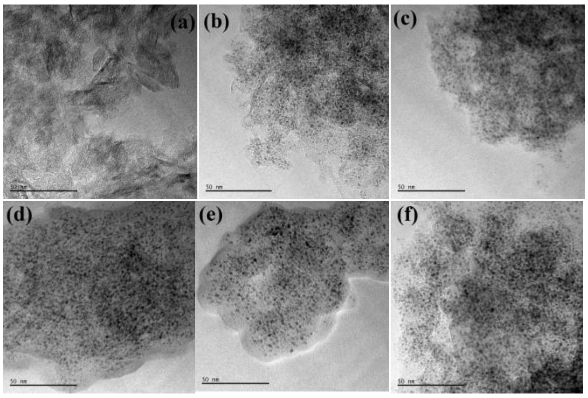

Figure 2. Tem images of (a) plain graphene (b)Pt/G (5.7%) (c)Pt/G (18.4%) (d)Pt/G (27%) (e)Pt/G (28%) (f)Pt/G (30%)

Pt loadings in between 5.7-30.4% were obtained over the graphene nanoplatelet. TGA measurements in air atmosphere were used to determine the Pt loading over the graphene support material. TEM results showed the homogeneity of the Pt nanoparticles and the average particle size decreased with decreasing Pt content. PEM fuel cell performance tests also proved that the catalytic activities are highly depended on the size and dispersion of the metal nanoparticles on the support material as well as the particle interactions with the support materials.

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Durability of carbon/conducting polymer composite supported Pt catalysts prepared by supercritical carbon dioxide deposition

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Carbon supported catalysts are commonly used ones in PEM fuel cell electrodes. During the long term operations carbon tend to corrode via carbon corrosion. An alternative to plain carbon can be conducting polymer/carbon composite in order to decrease the carbon corrosion [1]. Therefore PPy/Carbon supported Pt catalysts seems to be an alternative in order to decrease the performace losses in PEMFCs due to carbon corrosion. Supercritical carbon dioxide ($scCO_2$) deposition method provides a better dispersion of the metallic nanoparticles over the support material [2]. In this study, PPy/carbon composites were used as the support material for the Pt nanoparticles. Pt nanoparticles were decorated on this composite by using $scCO_2$ deposition method.

Composite material was synthesized by in situ chemical oxidative polymerization of pyrrole over carbon support (C, Vulcan XC 72, Cabot) [2]. $ScCO_2$ deposition procedure is similar to the reference given elsewhere [2]. The composite and the catalyst were characterized by using BET, TGA, XRD, TEM and CV techniques. Cyclic voltammetric experiments were carried out via a standard three electrode cell configuration. Aging tests were carried out either by potential cycling (upto 1000 cycle) or potential hold at 1.2 V [3].

TEM results showed that highly dispersed and small and spherical nanoparticles can be obtained over the composite material by using $scCO_2$ deposition method (Figure 1).

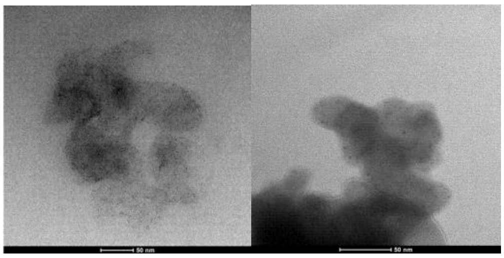

Figure 1. TEM images of the prepared catalyst

The multipoint BET surface area of the composite material was found as 77 m^2/g. The plain carbon surface area of 250 m^2/g was decreased with the addition of PPy because of blockage of the pores of the carbon with PPy. TGA technique was used to determine the Pt loading over the composite material and the Pt loading over the composite material was found at around 10%.

ESA of the catalyst is calculated by taking into account the average of adsorption and desorption areas of the cyclic voltammograms. Hydrogen oxidation reaction (HOR) activity of the catalyst before and after carbon corrosion is given Figure 2. ESA loss is calculated as 49% after carbon corrosion which is a bit higher than the ESA loss after Pt dissolution/agglomeration test (43%).

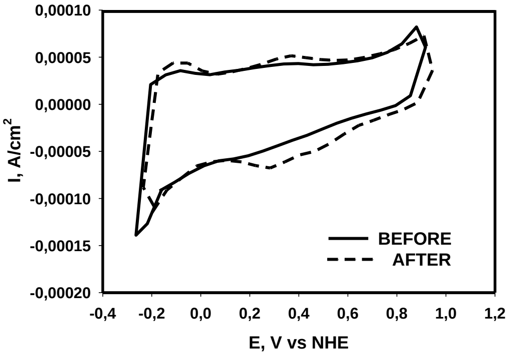

Figure 2. Cyclic voltammogram before and after carbon corrosion test

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Modeling and Sensitivity Analysis of High Temperature PEM Fuel Cells by using Comsol Multiphysics

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A fuel cell is an energy conversion device that directly converts the chemical energy of a fuel into electrical work through an electrochemical reaction. The fuel at the anode is oxidized to release electrons that are then transferred to the cathode side. At the cathode, these electrons are used for reducing the oxidant. During the red-ox reactions, the flow of electrons from anode to cathode is the current produced by the fuel cell and an electrical potential difference exists between the two electrodes. The theoretical efficiency of fuel cells is higher than the theoretical efficiencies of heat engines. A fuel cell is silent and mechanically stable since there are no moving parts, which yields the potential for higher reliability. Moreover, fuel cells are clean and sustainable alternative energy resources for future because they use hydrogen and oxygen as reactants; therefore the only product is water at the end of the reaction.[1]

Fuel Cells are generally classified based on the electrolyte they use. Polymer Electrolyte Membrane (PEM) Fuel Cells involve solid polymer membrane which should possess high proton conductivity. Proton Exchange Membrane Fuel Cells operate in the range of 50 – 100 ^{o}C and at this range of temperature PEMFCs have been implemented using perfluorinated polymers like Nafion as electrolyte. However, to employ this kind of materials entails a series of disadvantages at low temperatures such as water management problem and higher CO content. Therefore, high temperature operation is an alternative solution in order to overcome this situation. High temperature PEMFCs are generally operated at between 150-200 ^{o}C and Polybenzimidazole (PBI) membrane the one that is the most suitable to be used in this sort of fuel cells.[2]

Modeling of a high temperature PEM fuel cell has an essential role for the optimization of parameters affecting the performance of the fuel cell. In order to achieve the highest efficiency, three dimensional mathematical modeling of a high temperature PEM fuel cell is performed by using commercial software package, COMSOL Multiphysics. In order to simulate and analyze the performance of high temperature PEM fuel cell, operation is assumed to be isothermal, steady state and single phase operation. Moreover, pressure drop within the cell is neglected; therefore, the system is also assumed to be isobaric.

The model contains transport of gas in the gas flow channels and transport of electrical current in the solid phase. Water and ion transport in the polymer electrolyte has been modeled by using Stefan-Maxwell equation while reactants gas flow in the channels has been modeled by using Navier-Stokes equations.

The model is developed as having a single flow channel with 25 cm^2 active area, 170 oC operating temperature and 0.6 V operating voltage. Pure hydrogen is used as fuel and air is used as oxygen source. The generated domain with meshes is illustrated in Figure 1.

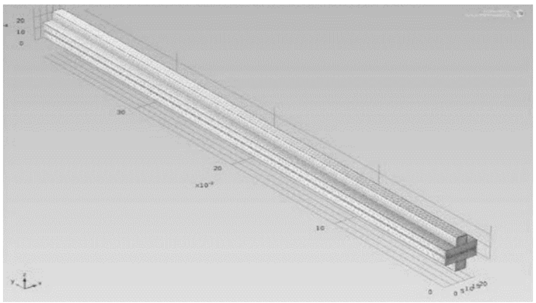

Figure 1. Domain of Single Channel PEMFC

For sensitivity analysis, firstly, the domain is modeled at constant hydrogen inlet velocity but different air inlet velocities. In other words, change in air inlet velocity results change in volumetric flow rate and therefore mass flow rate. After that, mathematical modeling in Comsol Multiphysics is performed at different cell lengths to find its optimum value. At the end of the simulations, critical parameters affecting the performance of the fuel cell are determined as air inlet velocity and the cell length.

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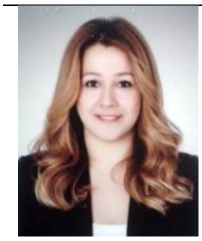

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Utilization of polystyrene/SiO_2 core-shell particles covered with PDMS as superhydrophobic material in MPL of PEM fuel cells

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One of the most critical problem in PEM fuel cell system is ensuring effective water management. Lower amount of water causes decreasing membrane proton conductivity, induces contact resistance between the membrane and catalyst layer and thereof it has severely adverse effect on the fuel cell performance. Excess water also deteriorates obtained power from the cell because of accumulation of liquid water. Flooding leads to plugging of active catalytic sites and prevents mass transfer of reactants. Preparation of superhydrophobic surfaces for fuel cell components is the common concept to find a way out this critical problem. The surfaces that includes optimum level of hydrophobic agents serve as good water repellants [1].

Micro porous layer (MPL) is the part of gas diffusion layer and comprises of carbon powder and hydrophobic agent. Coating gas diffusion layer with MPL has many advantages for fuel cell dynamic performance, especially at water management. Fluorinated polymers are used conventionally as hydrophobic materials in MPL**.** This study differs from the others with using polydimethylsiloxane (PDMS) polymer to provide hydrophobicity. The features of PDMS such as thermal stability, flexibility, non-toxicity, robust hydrophobicity, low surface energy and glass transition temperature makes PDMS favorable material [1].

There are two approaches encountered in the literature for fabrication of superhydrophobic surfaces: 1) Adding hydrophobic agent 2) Roughening the surface structure. In this study, polystyrene/silica core shell particles were synthesized firstly to be used as coating skeleton and then they were treated with PDMS polymer in hexane. It is aimed utilizing from combine effects of hydrophobic agent and inorganic particles to construct robust superhydrophobic surface for MPL in PEM fuel cell. Hexane solution was selected as solvent for PDMS coating onto the core-shell particles [2].

PDMS having molecular weight of 236.5 g/mole and hexane as solvent media were used. Prepared hydrophobic particles will be used in the MPL structure and constructed membrane electrode assemblies with these MPLs will be tested and evaluated in terms of PEM fuel cell performance (Figure 1). The materials will also be characterized by using FTIR.

Figure-1: Experimental procedure

SEM images of the prepared particles and also PS/SiO_2/PDMS coated GDLs are given in Figure 2. The GDL surface getting more dense with an increase in PDMS amount.

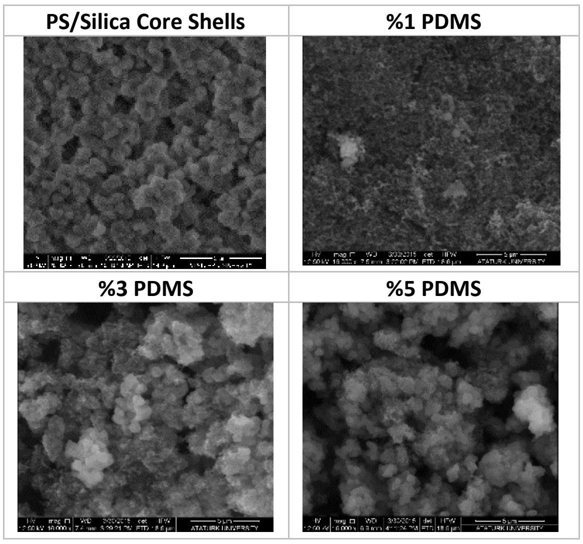

Figure-2: SEM images of PS/Silica/PDMS coatings on GDL surface with different PDMS loadings

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Superhydrophobic polydimethylsiloxane/silica coating for micro porous layer of PEM fuel cell and effects of calcination temperature on the wetting behavior

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One of the major issues in proton exchange membrane fuel cells (PEM) is water management. The polymer electrolyte membranes have to be humidified sufficiently for proton conductivity. If the membrane begins drying out, proton transfer from anode to cathode side leaves off and cell performance decreases drastically. On the other hand, excess water amount is also undesirable circumstance inside the cell. This situation is called “flooding”, especially at cathode side. Excess liquid water clogs active reagons of catalyst layers, gas diffusion media, flow channels and causes the deterioration of cell performance. Preparing superhydrophobic surfaces for cell components simplifies the controlling of water amount in the cell. [1]

In this work, polydimethylsiloxane (PDMS) was used as hydrophobic agent instead of fluorine polymers. PDMS is a silicone based polymer and it has low surface tension, low glass transition temperature, high flexibility, high thermal and chemical resistances, optical transparency and non-toxicity. Beside the high water repellency property of PDMS, it was aimed to contribute superhydrophobicity by roughening the surface. For this reason, silica nanoparticles were used as inorganic substance to gain rough structure to surface. In this study, it was utilised from PDMS/SiO_2 consolidative forces for superhydrophobicity. Calcination temperatures were considered as an affecting factor for superhydrophobicity. PDMS/silica coated MPL for PEM fuel cell was prepared and the effect of calcination temperature on the superhydrophobicity of the material and performance of fuel cell was investigated. The procedure for PDMS/silica preparation is given in Figure 1. [2]

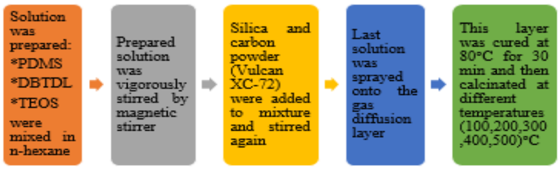

Figure-1: Flow chart of experimental procedure

SEM images of the GDLs with PDMS/silica material calcined at different temperatures are given in Figure 2. This GDLs will be tested in PEM fuel cell.

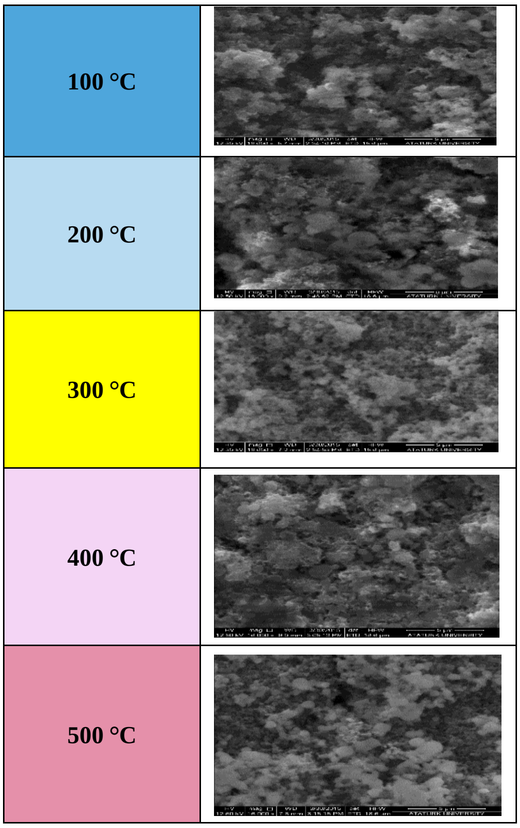

Figure-2: SEM images of GDLs obtained at different calcination temperatures

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Biomass-based carbon aerogels for oxygen reduction reaction in polymer membrane fuel cells

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Polymer electrolyte membrane fuel cells (PEMFCs) are considered as a promising sustainable technology for automotive and stationary applications, however, have many challenges to overcome for mass commercialization. One of the main challenges is associated with the oxygen electrode where carbon supported platinum is used as the catalyst for oxygen reduction reaction (ORR), giving rise to high cost (because of Pt), degradation of performance related to the migration, agglomeration and dissolution of Pt particles, and carbon corrosion during start-up/shut down cycling which may be induced by the presence of Pt [1-2].

This paper reports our research on using biomass-derived N-doped carbon aerogels (N-CA) as next generation ORR catalysts in the oxygen electrode of PEMFCs. N-doped carbons recently appear to be attractive catalyst/electrode materials in low temperature alkaline and PEMFCs, and have shown prolonged stability and low cost promise [3-6]. The N-CA materials are derived from biomass using inexpensive process (i.e. Hydrothermal Carbonisation). They can be easily tailored to have different physicochemical functionalities and micro (< 2 nm), meso (2-50 nm), and macro (> 50 nm) porosity [3, 4]. In this work we optimise the N-CA materials by controlling the level of nitrogen doping, hybridising the N-doped carbons with transitional metals such as Fe and Co, and controlling the pore size and particle size of the resulting materials, to achive high ORR performance in acidic environment. The optimised materials are then taken into real PEMFC single cells to test the electrochemical performance (e.g. the polarisation curves and electrochemical impedance spectroscopy (EIS)) to elucidate materials effects on the electrochemical performance.

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Modeling the Water Transport in a PEM Fuel Cell Cathode Using COMSOL

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Energy is mostly produced from fossil fuels; however, fossil fuels are limited in amount and sooner or later will be depleted. Moreover, fossil fuels causing serious environmental problems such as global warming and climate changes since using them in order to produce energy emits too much CO_2 and other greenhouse gases (GHG) to the atmosphere. Therefore, fuel cells should be good solution for this crucial problem.

Fuel cells are the electrochemical reactors that convert chemical energy in the fuels (mostly hydrogen) to the electrical energy. Redox reactions take place both at the anode and at the cathode; reduction of hydrogen, or the fuel, takes place at anode and the oxidation of oxygen occurs at cathode. Due to the fact that there is not any intermediate steps like in the internal combustion engines (ICEs), efficiencies of the fuel cells are much higher than ICEs. Moreover, power density of the fuel cells are also higher, that is, there is less volume and less weight needed for the fuel cells. Also, one of the most important feature of fuel cells is that there is not any GHG emissions [1].

Fuel cells are categorized with respect to their membrane structures. Proton exchange membrane, also called polymer electrode membrane, fuel cells (PEM) include perfluorosulfonated electrolyte. The membrane allows protons to pass to the cathode side; however, it does not allow electrons to pass from mebrane. Electrones are forced to follow a different path and electricity is produced. The name of the membrane is Nafion^{TM} which is produced by Dupont company. At both sides of the polymer membrane thin catalyst layer are placed. It is followed by gas diffusion layers which distributes the gas homogeneously. Bipolar plates complete the circuit and collect the current.

A three dimensional model of PEM fuel cell having an active area of 5 cm^2 has been investigated in order to model the water transport at the cathode of a PEM fuel cell. During the modeling COMSOL Multiphysics 4.4 Software which has a commercial fuel cell package was used. Finite elements method are used in COMSOL. Moreover, some assumptions were made which are temperature is constant, gas mixture is ideal gas, flow is laminar. Furthermore, pressure drop is neglected and isobaric assumption was made [2]. Navier-Stokes equation is used to model the flow in the system. In addition, Maxwell-Stefan equations is used for multicomponent diffusion and the electrochemical kinetics in the system is modelled by using Tafel equation.

In the model pure hydrogen and air are used as the reactants; temperature and the pressure of the model are 65 ^oC and 1.2 bar, respectively. After conctructing the model, polarization curve, membrane current density and concentration profiles of both reactants and product are investigated. Used model can be seen in Figure 1.

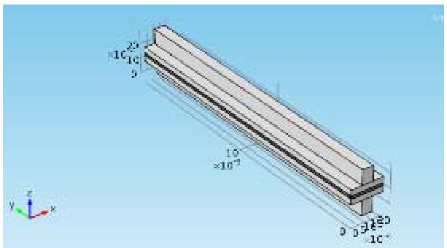

Figure 1:*Model Used in COMSOL Multiphysics*

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I am a senior chemical engineering student at Middle East Technical University, Ankara, Turkey. I have taken the course 'Topics in Chemical Engineering' in my last semester and I have been working on modeling of PEM Fuel Cell with COMSOL.

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Some technological aspects of developing hybrid power system for unmanned aerial vehicles

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Unmanned aerial vehicles (UAVs) are mainly used for surveying and surveillance. These applications have very specific constraints: power, cost, weight, space, and flight endurance. Fuel cells show growing applications for unmanned aerial vehicles (UAVs) because of their energy densities that excess 800 Wh/kg as compared to advanced batteries (energy densities of 150 Wh/kg). The additional advantages of FCs vs. advanced batteries are: reduced weight size, lower life cycle cost, extended run times, reduced and lower life cycle cost.

Some of sizes, the aircraft-powering fuel cells have been recently built as final yields of many research projects contracted between scientific institutions and industry companies involved in UAVs and the field of fuel cells in the USA, Europe, and Asia.

The purpose of this paper was to present some results on application of an elaborated hybrid electrical system (a battery and hydrogen-oxygen fuel cells) as a power unit in electrical motors for small unmanned aerial vehicles. The scope of the work included: **(1)** Designing and manufacturing an unmanned aerial vehicle.**(2)** Electrochemical and analytical investigations of a 300-W elaborated PEMFC stack, as well as a 600-W hybrid electrical system (a battery and PEMFC stack). **(3)**Technical analysis of the possibility of hydrogen storage for PEMFC stacks during a one-hour flight. **(4)** Selection and modification of a commercially viable electric motor. **(5)** Comprehensive studies on the integration of the electric motor with the PEMFC stack or the hybrid electrical system. **(6)**Preliminary tests of elaborated electrochemical power sources during the UAV flight.

Polymer electrolyte membrane fuel cells (PEMFCs) seem to be the best choice for the main electrical power supply in unmanned aerial vehicles (UAVs). They operate at low temperatures, and can be cooled by air (mainly fans or streamlined air), or a liquid medium. The PEMFC stacks (H-series) produced by Horizon Singapore were selected as the main components for constructing a power source involving fuel cells. The open-cathode air-cooled H-series PEMFC has a simple, efficient, easily-modified design, which greatly lowers its weight. Therefore, we have chosen a 300-Watt H-PEMFC stack for our studies. The paramteres were tailored to the to the requirements of the electric motor management controller. The first main electrical modification was aimed at lowering the starting voltage of PEMFC stack. The battery Li-Pol was also added to increase power of the system. Fig.1 presents the U-I curves recorded for hybrid system

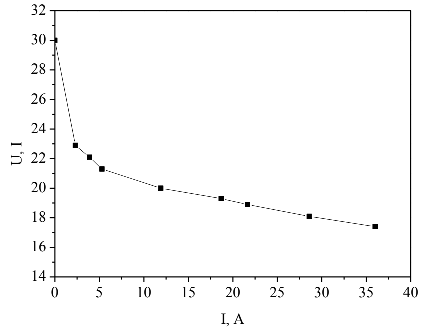

Fig.1 The U-I curves recorded for designed hybrid system

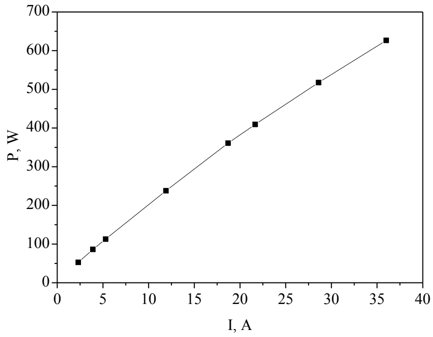

Fig 2. The P-I curves obtained for designed hybrid system.

Comprehensive studies on the integration of the electric motor with the PEMFC stack or the hybrid electrical system was also presented and analyzed.

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Semi-IPN system electrolyte membranes composed of sulfonated poly(arylene ether ketone) block copolymer and organosiloxane based hybrid network

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A semi-interpenetrating polymer network (semi-IPN) proton exchange membrane is prepared from the sulfonated poly(arylene ether ketone) block copolymer and organosiloxane-based organic/inorganic hybrid network. The organosiloxane network is synthesized from 3-glycidyloxypropyltrimethoxysiane and 1-hydroxyethane-1,1-diphosphonic acid. The methanol permeability is illustrated in Fig.1. and it is much lower than Nafion® 117 under addition of the organosiloxane network. The proton conductivity is illustrated in Fig.2. the proton conductivity increases with an increase the organosiloxane network content; the membrane containing the 20-24 wt% organosiloxane network shows higher conductivity than Nafion® 117 . Chemical synthesis of the semi-IPN membranes is identified using FTIR and thermal stability was analyzed by the thermal gravimetric (TGA) method. And its ionic cluster dimension of the membrane was analyzed by the small angle X-ray scattering (SAXS) technique. The water uptake, ion exchange capacity (IEC), oxidative stability and mechanical properties of the semi-IPN membrane were investigated for their applications in proton exchange membrane fuel cells.

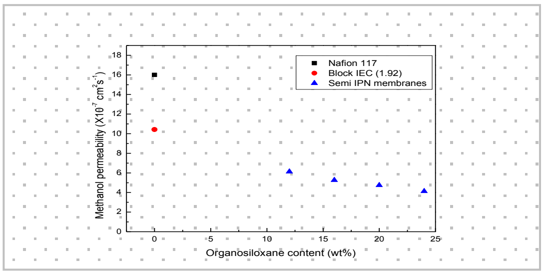

Figure 1. Methanol permeability of semi-IPN membranes .

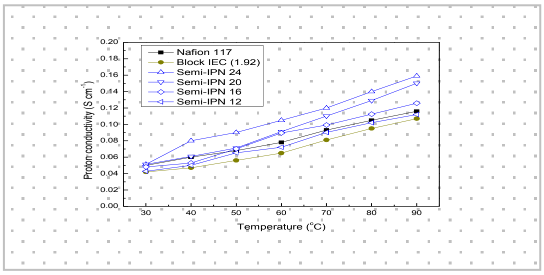

Figure 2. Proton conductivity of semi-IPN membranes.

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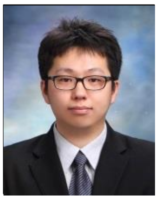

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Fasteners selection for stacked direct borohdyride/peroxide fuel cell system

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Liquid fuel cells such as direct methanol fuel cell, ethanol fuel cell, borohydride fuel cell or peroxide fuel cell require expensive materials for the stack control. Liquid fuel cells have some advantages rather than PEMFCs and are getting more interests because of their high energy density, high theoretical cell potential and the use of easy-to-carry and to manage of liquid fuel as well as the low temperature operation.

On the other hand the system must be controlled strictly by the balance of plant (BOP). The engineering of Liquid Fuel Cell is complicated by the physical/chemical processes and the complexity of BOP. BOP control must be significant part of the system. In a liquid fuel cell the equipment of BOP are different from that of PEMFC.

In DBPFCs, the alkaline borohydride solution is fed to the anode and acidic peroxide solution is fed to the cathode. The strongly acidic and basic solutions have conductivity on the order of 200 mS cm^{-1}. Therefore considering that peroxide and alkaline solutions are corrosive, fasteners of the system should be selected from materials which are the acid- and base-resistant.

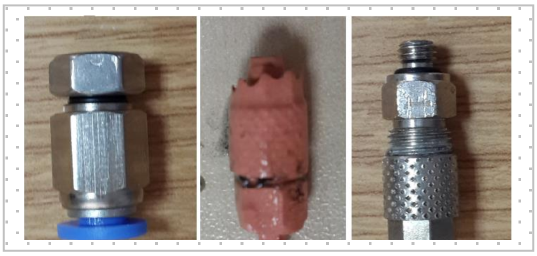

Figure 1. The manifolds used in the DBPFC system; the stainless steel at the anode, the chrome at the cathode.

The fasteners commercially available are manufactured from the stainless steel (SS-304). While it is suitable for the anode side, acidic hydrogen peroxide caused to deformation of the stainless steel (Figure 1.b). Therefore in the DBPFC system, the manifolds used were made from stainless steel at the anode side and from chrome at the cathode side (Figure 1).

Current collectors which are the other important components in the cell are made from spring steel material because of its ability to resist deformation and no deterioration of the shape.

Liquid pumps have a great importance in the fuel cell system. It is also required to have the corrosion resistance against to damage caused by the acidic and basic solutions. In the DBPFC system the micro-gear pumps manufactured by KNF and FOURONLY were used to feed. It was observed that KNF pumps were more chemical resistant than FOURONLY pumps. However the peristaltic pump (Masterflex) offers the best solution because the fuel and oxidant don't contact directly with internal parts of pump (Figure 4). But it can't be controlled electronically. Therefore we are still working on the selection of proper pump and other fasteners for the DBPFC system. The pumps tested in our system are shown in Figure 2.

Figure 2. The pumps used in the fuel cell system

Photo of the presenting author

20X25 mm

She was graduated from Erciyes university, Electric&Electronics Engineering. She is project assistant at Tubitak Project (113M097)

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Melek Gülatik

Sputter Deposited Au-Pd Bimetallic Catalysts for Direct Formic Acid Fuel Cells

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A fuel cell is an electrochemical system that continuously converts chemical energy of fuel into electrical energy and heat with high thermodynamic efficiency. Direct formic acid fuel cells (DFAFCs) are promising alternatives to hydrogen proton exchange membrane fuel cells (PEMFC) for electronic applications. Palladium and platinum have very similar properties because they belong to the same group in the periodic table. Some experiments showed that Au-Pd nanoparticles can be used as electrode catalysts for DFAFCs [1].

When a formic acid fuel cell uses platinum as the anode catalyst, there are two reactions that can occur. Consider the below reaction equations [2]. When formic acid is used as the fuel, the catalyst can be poisoned. Formic Acid Oxidized by Pt to CO and CO_2:

$$Pt + HCOOH \longrightarrow Pt + CO + H_2O$$
$$Pt + HCOOH \longrightarrow Pt + CO_2 + 2H^+ + 2e^-$$

This can cause significant problems for the fuel cell. When CO is present, a bond between the platinum and the CO is formed (Pt-CO). Because of this bond, reactions can no longer take place at the platinum site that has been bonded to. This bonding of the CO to the platinum site is the poisoning of the cell taking place. As more CO bonds to the active platinum sites, the cell performance will continually degrade, until the cell does not function [3].

Pd-based catalysts have recently drawn attention because they can catalyze the oxidation of formic acid by a direct path that reduces the poisoning effect associated with conventional Pt catalysts [3]. The University of Illinois has performed research on formic acid fuel cells, and found that palladium catalysts can help to avoid the poisoning issues of the anode [2].

Formic Acid Oxidized by Pd into CO_2:

$$Pd + HCOOH \longrightarrow Pd + CO_2 + 2H^+ + 2e^-$$

In this study, Au-Pd bimetallic catalysts was prepared by using sputter deposition. In this study, an RF sputtering system was employed to deposit Au-Pd catalyst onto Sigracet GDL 34 BC carbon paper by changing the sputtering time (45, 90, 180 and 540 s) in order to get different thicknesses. The electrodes were called with respect to their sputtering time. Structural properties were determined by using SEM images, mapping and EDS (Fig. 1). The increase in the Au-Pd quantity of deposition with an increase in sputter deposition time is observed from the mapping and EDS of the electrodes (Table 1).

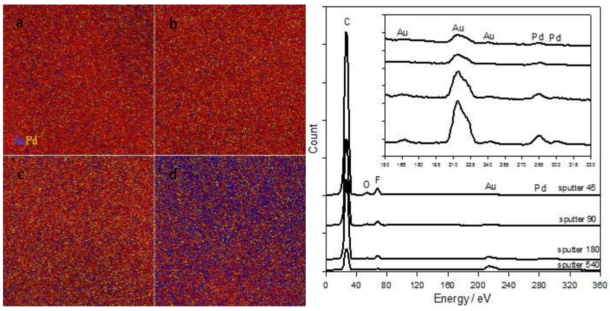

Figure 1. Mapping and EDS of the Au-Pd sputter deposited of (a) sputter45, (b) sputter90, (c) sputter180 and (d) sputter540.

Table 1. EDS results of sputter electrodes

Electrodes Wt%	C	Au	Pd
Sputter45	97.63	2.09	0.29
Sputter90	94.79	4.24	0.97
Sputter180	87.21	10.17	2.62
Sputter540	61.49	30.25	8.26

Sputtered electrodes will be used at anode electrode side for DFAFCs then will be compared with other studies in the literature.

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Investigation of Mechanical Properties of Crofer 22 APU Sheets for SOFC Applications

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Solid oxide fuel cells (SOFCs) use metal or ceramic based materials as an interconnector material. Although ceramic interconnectors provides high corrosion resistance and electrical conductivity, they are vulnerable to temperature gradients and have machining problems due to their fragile nature. Therefore, metallic interconnectors are generally employed in SOFC applications. Beside their main role of current collection, the interconnectors should provide the reactant gases to the reaction zones and remove the products from the reaction zones. Thus, they generally include machined flow channels. However, this requires the use of thick interconnector increasing both the size and cost of the system. Alternatively, the metallic interconnectors with flow channels can be fabricated via press shop by using sheet metals. On the other hand, the effects of the parameter of this design such as the thickness of the interconnector and channel size on the species, current and mass distribution in the cell so the cell performance as well as on the press shop fabrication parameters need to be determined for the optimum design. This can be done by experimental studies which require very long time and material consumption. Alternatively, the optimum fabrication and interconnector parameters can be decided by finite element simulation of the stamping process. To do so, the mechanical properties of the interconnector need to be obtained. Although Crofer 22 APU is the most commonly used SOFC metallic interconnector material, some of its mechanical properties especially required for the simulation of stamping are still unknown. Therefore in this study, the tensile test was performed to the Crofer 22 APU sheets under various temperature (25-300 ^{o}C) and strain rates (5-500 mm/min). The required mechanical properties like yield strength, anisotropies (0^{o} - 45^{o} - 90^{o}) and stress-strain flow curves were determined.

Murat Canavar was born in 1980, and grew up Istanbul. He earned Bachelors and MSc degrees from Nigde University. Canavar has been both working as a research assistant and maintaining PhD studies at Nigde University since 2013. His interests cover termodynamics, heat transfer, numerical analysis and clean energy applications as like pSOFC, PEM and DMFC.

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Investigation of Thermal Cycle Properties of Glass-Ceramic Sealant for SOFC

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Solid oxide fuel cells (SOFCs) may provide the clean energy needs of the world due to their excellent features such as high energy conversation efficiency, compact structure, quite operation and different fuel usage options. However, some problems must be solved before fully commercializing the technology. Providing a gas-tight connection between both two interconnectors and interconnector and electrolyte is one of the most important problems. Numerous studies have been performed to evolve a suitable glass-ceramic sealant material for SOCF operation conditions. Sintering temperature, compressing pressure and sealing thickness were optimized in our previous experimental study [1]. In this study, on the other hand, the thermal cycle parameters such as number of the thermal cycles, heating and cooling rates during start-up and shut down, respectively are experimentally investigated to find out the degradation of glass-ceramic material bonding strength depending on the sealant fabrication parameters optimized previously.

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Murat Canavar was born in 1980, and grew up Istanbul. He earned Bachelors and MSc degrees from Nigde University. Canavar has been both working as a research assistant and maintaining PhD studies at Nigde University since 2013. His interests cover termodynamics, heat transfer, numerical analysis and clean energy applications as like pSOFC, PEM and DMFC.

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Investigation of Micro Tube Solid Oxide Fuel Cell Fabrication Parameters by Produced Phase Inversion Method

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Fuel cell is a device which transforms directly the chemical energy into the electrical energy. Among them, solid oxide fuel cell (SOFC) can directly produce electrical energy by using pure hydrogen as a fuel. They can also utilize hydrocarbons. SOFCs are fabricated by ceramic based materials and their working tempratures are between 500 and 1000°C.

Currently, tube formed SOFC's support layers are produced by the extrusion method. Recently, superior microstructres are obtained by combined the extrusion and phase inversion method [1,2]. Phase inversion method is based on obtaining hollow fiber microstructures which decrease gas transport resistance. Thus, the more power density can be obtained from cell by decreasing the consantration overpotential of the cell.

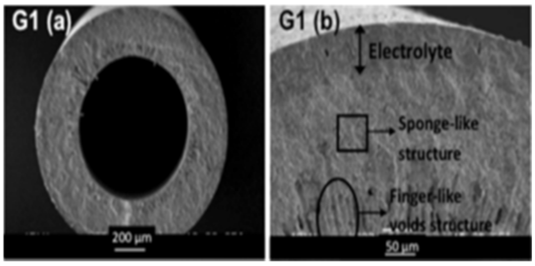

Figure 1 Hollow fiber micro-tube SOFC (a) and its microstructure (b) [1]

Anode support layer with two different pores structure can be fabricated via single-step extrusion together with phase inversion. Finger like porous structures form at the regions far away from the electrolyte layer and a sponge like porous structure forms at the regions close to the electrolyte layer. Thus, the electrochemical reaction zones are increased close to the electrolyte where the electrochemical reactions occur in the sponge like structure and easy gas transport can be provided by the finger like porous structure obtained at the inner side of the micro-tube. Fig. 1 shows the obtained anode structure by phase inversion method. The studies in the literature showed that the obtained microstructure has a significant effect on the system efficiency.

In this work, the effects of different non-solvent materials on the pore structure of the anode support layer is studied. Experimental studies showed that the cell performance increases with the porosity up to a certain limit and then the performance tends to decrease indicating that the control of the porosity is significant to improve the cell performance.

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STRUCTURE EVOLUTION AND CONDUCTIVITY HYSTERESIS IN 3+/5+ NIOBATES PYROCHLORES

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The 3+/5+ pyrochlore ($A_2(B^{3+}B^{5+})_2O_7$) family can be obtained by inserting two cations with valences of 3+ and 5+ in the B site [1-3]. The niobates and tantalates in the 3+/5+ family have the pyrochlore (P) structure only when the trivalent cation on the B site has the smallest radius (Lu and Sc) and only for some Ln^{3+} ions on the A site, as indicated in Fig. 1. The main purpose of this work is to study the variation of the structure and conductivity (in air and Ar) in the Ln_2ScNbO_7 (Ln = La, Ho, Yb) rare-earth niobate series and Sm_2ScTaO_7.

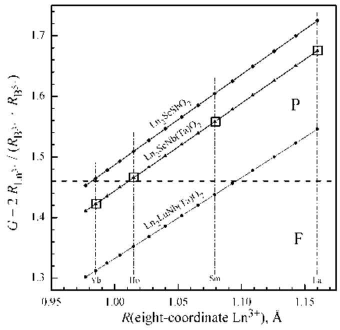

Fig. 1. Tolerance factor *G* as a function of ionic radius for $Ln^{3+}_{(CN =8)}$ on the A site of some 3+/5+ pyrochlores (P).

The Ln_2ScNbO_7 (Ln= La, Ho, Yb) niobates were prepared using mechanical activation of La_2O_3, Ho_2O_3, Yb_2O_3, Sc_2O_3 and Nb_2O_5 (preannealing of La_2O_3 and Ho_2O_3 at 1000 °C for 2 h, Aronov mill). Sm_2ScTaO_7 was synthesized in a similar way. Green compacts were fired at 1400 for 20 h, 1500 °C for 10 h or at 1600 °C for 5 h. X-ray diffraction (XRD) patterns were collected on a DRON-3M automatic diffractometer. The conductivity of the samples was determined by impedance spectroscopy in the range 250–930°C using two-probe measurements in a NorECs ProboStat cell. The La_2ScNbO_7 pyrochlore and fluorite-like Ho_2ScNbO_7 were studied by impedance spectroscopy measurements using heating–cooling cycles in air (heating rate of 2°C/min).

According to our results, La_2ScNbO_7 crystallizes in the pyrochlore structure (Fd3m), whereas Ho_2ScNbO_7 and Yb_2ScNbO_7 crystallize in the fluorite structure (Fm3m), related to the pyrochlore structure type. We have measured the bulk conductivity of the Ln_2ScNbO_7 (Ln = La, Ho, Yb) compounds in air (Fig. 2). The Arrhenius plot of conductivity for the fluorite-like compounds $Ho(Yb)_2ScNbO_7$ has the form of a straight line throughout the temperature range studied: 250–930 °C.

One distinctive feature of the 3+/5+ pyrochlores is that their conductivity is essentially constant in some temperature range: 500 to 600 °C for La_2ScNbO_7 and 700 to 800 °C for Sm_2ScTaO_7.

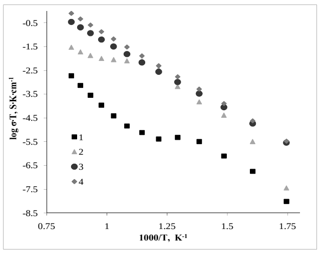

Fig.2 Temperature dependences of bulk conductivity for (1) P-La_2ScNbO_7; (2) P-Sm_2ScTaO_7, (3) F-Ho_2ScNbO_7, and (4) F-Yb_2ScNbO_7 in air.

The conductivity of Ln_2ScNbO_7 (Ln = La, Ho, Yb) in air increases as the ionic radius of Ln decreases. The conductivity of fluorite Yb_2ScNbO_7 and Ho_2ScNbO_7 is higher than that of pyrochlore La_2ScNbO_7 (1.3×10^{-4}, 6.15×10^{-5}, and 1.066×10^{-7} S/cm at 750 °C, respectively). The perfect pyrochlore phase La_2ScNbO_7 has been shown for the first time to have an anomalously broad thermal hysteresis of conductivity. Since the effect may also be due to proton conductivity in the same temperature range, we plan to make measurements in dry and wet argon.We have studied the structure and conductivity of 3+/5+ pyrochlores: La, Ho, and Yb niobates and Sm tantalate. In the Ln_2ScNbO_7 (Ln= La, Ho, Yb) series, the conductivity hysteresis loop area decreases considerably as a result of the pyrochlore-to-fluorite structural transition due to the lanthanide contraction, which can be used to follow the disappearance of pyrochlore microdomains in the fluorite lattice in the 3+/5+ compounds. To ascertain this possibility, proton conduction in La_2ScNbO_7 and Sm_2ScTaO_7 should be ruled out.

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-00680).

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OXYGEN VACANCY AND INTERSTITIAL TRANSPORT IN THE PYROCHLORE- AND FLUORITE-LIKE $Pr_{2\pm x}Zr_{2\pm x}O_{7\pm\delta}$

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The studies on the pyrochlore type rare-earth zirconates having multiple valences, in particular with Pr, are limited [1-4]. The rare-earth ions having multiple valences are likely to exhibit electronic as well as ionic conductivities. The higher stability of Pr^{3+} compared to the Ce^{3+} is expected to make $Pr_2Zr_2O_7$ a better MIEC. Due to the large solubility limits for Pr or Zr excess in the pyrochlore structure, it is possible to prepare solid solutions with huge stoichiometry deviations.

$$(2\text{-}x)ZrO_2+(1+x/2)Pr_2O_3\rightarrow$$
$$(2\text{-}x)Zr_{Zr}^{\times}+xPr_{Zr}'+2Pr_{Pr}^{\times}+(7\text{-}x/2)O_O^{\times}+x/2V_O^{\bullet\bullet} \qquad (1)$$
$$(2+x)ZrO_2+(1\text{-}x/2)Pr_2O_3\rightarrow$$
$$(2\text{-}x)Pr_{Pr}^{\times}+xZr_{Pr}^{\bullet}+2Zr_{Zr}^{\times}+7O_O^{\times}+x/2O''_i \qquad (2)$$

These equations are based on ionic compensation for dopant effects, and we expect to observe, in the both cases, an increase of the ionic conductivity. Oxygen vacancies will be dominant for Pr-rich compositions, while interstitial oxygen will be responsible for the ionic conductivity of Zr-rich compositions.

Using coprecipitation followed by heat treatment at 1550 °C for 4 h, we prepared pyrochlore - and fluorite -like PrZrO solid solutions containing 18, 26.6, 30, 33.3, 35.5, 54, and 60 mol % Pr_2O_3.

Conductivity measurements were made in air between 300 and 750°C, and versus oxygen partial pressure between 700 and 1000°C, during reoxidation and after reduction with a mixture of 95% N_2 and 5% H_2. The electrical measurements, both in reducing atmosphere and in air, were made by impedance spectroscopy in the frequency range of 20 Hz to 1 MHz, using a Hewlett-Packard 4284A precision LCR bridge.

Thermomechanical analysis (TMA) curves were obtained in air between 30 and 900°C at a heating rate of 10°C/min and a load of 100 mN using a PerkinElmer TMA 7 analyzer and flat tip probe.

Electrical measurements confirm the composition effects as expected by equations 1 and 2, with an increase of conductivity for non-stoichiometric compositions. The increase of conductivity for high oxygen partial pressure is attributed to the p-type electronic conductivity.

Linear TEC of the $Pr_3ZrO_{6.5}$ (60% Pr_2O_3) material has nonlinear behavior. It is important to separate out the chemical expansion contribution from pure thermal contribution [5]. In nonstoichiometric PrZrO ceramics the chemical expansion contribution is related to the interaction of the solids with gas atmosphere (Pr3+/Pr4+ active electrochemical couple).

Defect chemistry analysis was used to interpret the experimental results.

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-00680) and by the Presidium of the Russian Academy of Sciences (program Synthesis of Inorganic Substances with Controlled Properties and Fabrication of Related Functional Materials, grant no. 17/2015).

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The phase formation and properties of Nd_2MoO_6 compounds, doped by Pb

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The compounds with different compositions (1:3, 1:2, 5:6, 1:1) were discovered in binary Ln_2O_3 - MoO_3 systems in the range from 25 to 50 mol.% of Ln_2O_3. Among these compounds the cubic $La_2Mo_2O_9$ and $Pr_2Mo_2O_9$ (1:2) have high oxygen conductivity [1,2], whereas fluorite-type compounds with the 5:6 composition, $Nd_5Mo_3O_{16}$ and $Pr_5Mo_3O_{16}$, are mixed ion-electron conductors [3]. The compounds with 1:1 composition, Ln_2MoO_6, or oxymolybdates [4] with large rare-earth cations (La, Pr, Nd) are synthesized at 900°C in the monoclinic phase. At temperatures above 1000°C they have tetragonal noncentrosymmetric layered structure (sp. gr. $P\bar{4}2m$) with fluorite Ln_2O_2-layers and layers of Mo-tetrahedra alternation. All other rare-earth oxymolybdates starting with Sm-molybdate, have monoclinic structure. It should be noted that PbO has a layered structure constructed of fluorite Pb_2O_2 layers similar to fluorite layers in the oxymolybdates with large cations. Therefore it is of interest to examine the conditions of synthesis, polymorphism, thermal and conductive properties of molybdates in the binary Nd_2MoO_6 - PbO cut of ternary Nd_2O_3-MoO_3-PbO system.

Polycrystalline samples Nd_2MoO_6:Pb with different Pb content (10, 20, 33.3, 40, 50, 60 mol% PbO in ternary Nd_2O_3-MoO_3-PbO system) were obtained by solid state reaction in air. XRD characterization was performed with DRON-2.0 diffractometer (Cu Kα-radiation). Differential scanning calorimetry (DSC) has been made using NETZSCH STA 449C equipment. Conductivity and dielectric permittivity were measured using a Tesla BM 431 E bridge (20-1000° C, 1 MHz) and Novocontrol Beta-N impedance analyzer (200-950° C, 0.06 Hz - 3 MHz).

Pure sample and samples with a low content of Pb (10 and 20 mol.% PbO) are synthesized in the monoclinic phase at 900°C and in the tetragonal at 1000°C. The compounds containing 33 – 60 mol.% PbO are tetragonal at 900°C and the attempts to synthesize them in the monoclinic phase were unsuccessful. In the case of samples with large lead content (33 – 60 mol.% PbO) one can observe the peaks on the DSC curves near 820 ºC, endothermic while heating and exothermic while cooling. The permittivity temperature dependence measurements for these samples also revealed the λ-type anomaly at the same temperature range (fig. 1). The conductivity of Pb-containing compounds increased stepwise by about 1.5 orders of magnitude compared to pure sample reaching 10^{-2}Sm/cm at about 900°C (fig. 2).

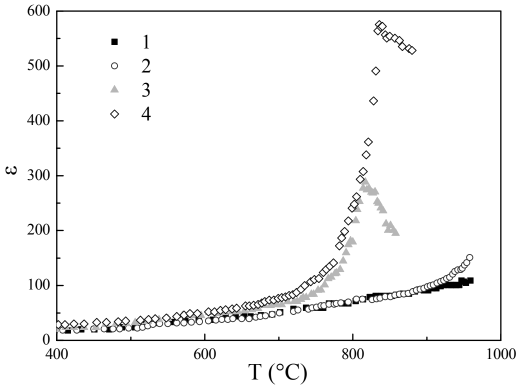

Figure 1. Permittivity temperature dependences for the samples with different PbO content: (1) 0mol.%, (2) 20mol.%, (3) 33.3mol.%, (4) 60mol.%.

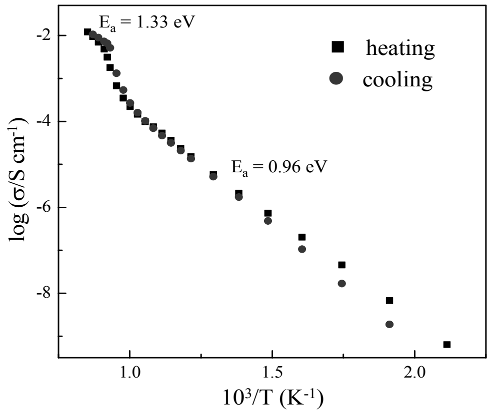

Figure 2. Bulk conductivity for the samples 33.3mol.% PbO

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Fluorite-like compounds with high anionic conductivity in Nd_2MoO_6 - Bi_2O_3 system

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Bi_2O_3-based compounds attract attention as materials with high anionic conductivity. The high temperature cubic phase of pure Bi_2O_3 has extremely high oxygen conductivity close to 3 S/cm [1]. At room temperature this phase may be stabilized by partial substitution bismuth with calcium and rare earth elements. In [2, 3] authors obtained Bi_2O_3-based materials with high oxygen conductivity (~ 1 S/cm at 800 ºC) at codoping Bi_2O_3 with tungsten and dysprosium or tungsten and lanthanium. It should be noted that in the binary Ln_2O_3-MeO_3 (Ln = La, Nd, Pr, Me = Mo, W) systems there are compounds with high anionic ($La_2Mo_2O_9$), mixed oxygen-electronic ($Nd_5Mo_3O_{16}$), and proton (La_6WO_{12}) conductivity were found. Ln_2O_3-Bi_2O_3-MeO_3 ternary systems are poorly understood. The purpose of this work - the synthesis of compounds in Nd_2MoO_6-Bi_2O_3 cut of Nd_2O_3 - MoO_3 - Bi_2O_3 ternary system and study of their electrical properties.

Polycrystalline samples in Nd_2MoO_6-Bi_2O_3 cut were obtained by solid state synthesis in air at maximum firing temperature 800-1050 °C depending on sample compositions. Wide area of solid solutions was found in this system. From $5Nd_2O_3{\times}5MoO_3{\times}90Bi_2O_3$ to $20Nd_2O_3{\times}20MoO_3{\times}60Bi_2O_3$ the samples have cubic fluorite-like structure. Samples with less bismuth concentration (to $25Nd_2O_3{\times}25MoO_3{\times}50Bi_2O_3$) were tetragonal resulted from distortion of fluorite structure. Cell parameters a and c of tetragonal compounds close to that of cubic solid solutions. The samples containing 47 - 10 mol.% Bi_2O_3 are mixture of phases based on Nd_2MoO_6 and $25Nd_2O_3{\times}25MoO_3{\times}50Bi_2O_3$ compounds.

The thermal expansion coefficient of the samples weakly depends on the amount of bismuth and close to $17{\times}10^{-6}$ 1/K.

An intensive diffuse peak is observed on dielectric permittivity temperature dependence for all samples with cubic and tetragonal structure. This peak moves into low temperatures with decrease of bismuth concentration, from 770 °C (50 mol.% Bi_2O_3) to 570 °C (85 mol.% Bi_2O_3). The nature of this peak is not clear.

The samples with tetragonal and cubic structure demonstrate high conductivity (Figure 1). For the samples with 50 - 60 mol.% Bi_2O_3 conductivity is weakly dependent on bismuth content and reaches 0.05 S/cm at 800 °C.

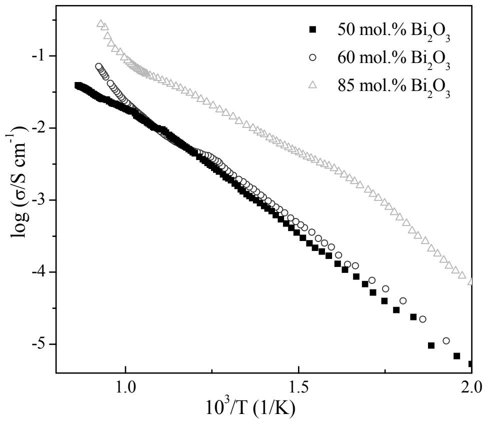

Figure 1. Conductivity temperature dependence for the samples with different Bi_2O_3 content

With increasing of Bi_2O_3 concentration the conductivity grows on an order of magnitude. Sample with 85 mol.% Bi_2O_3 demonstrate the conductivity close to 0.2 S/cm, which is comparable with the results of [2-4]. Conductivity temperature dependences for all measured samples may be approximated by Arrhenius law with activation energy near 0.8 eV. It is assumed that, as the conductivity of Bi_2O_3, the conductivity of compounds in Nd_2MoO_6-Bi_2O_3 cut may be caused by the diffusion of oxygen anions into the structure.

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Valentina Voronkova

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Synthesis of apatite type $La_{10-x}Sr_xSi_6O_{27-0.5x}$ powders for IT-SOFC using sol-gel process

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Solid oxygen ionic conductors have attracted much attention as electrolyte materials for solid oxide fuel cells (SOFCs), which are high efficiency energy conversion devices [1]. The devices generate electrical power directly from the oxidation of the fuel and electrolytes are responsible for the transport of the ions produced during the reaction [2, 3]. Thus, the ionic electrolyte strongly influences the cells performance; it must be dense enough to isolate the gas flux and create a negligible electronic transport contribution. Apatite-type lanthanum silicates with the general formula $La_{10-x}Si_6O_{27-1.5x}$ (LSO) have been investigated as ionic conductors with different stoichiometry i.e. with either oxygen ions deficiency or excess and with different dopants [4-6]. They exhibit higher oxide ion conductivity at intermediate temperatures than a typical ytttria-stabilized zirconia (YSZ) SOFC electrolyte (4 mS·cm-1 at 500 ℃ vs. 1 mS·cm-1) [7-10].

Alkaline earth metal elements, such as Mg, Sr and Ba, [6] have been evaluated as dopant able to occupy La sites, the most frequent element being Sr due to its ionic radius similar to that of La. In this paper we present the synthesis of Sr-doped $La_{10}Si_6O_{27}$ with optimized sol-gel process. The synthesis parameters have been investigated to obtain pure, high crystalline degree powders. The mechanisms occurring in the sol-gel reactions are discussed to improve the formation process of the sol.

The related parameters involved in the synthesis process have been discussed, including: the pH value of precursor solution, Sr doping effect, calcination time and temperature. The optimized combination of parameters has been summarized to reduce synthesis costs and improve synthesis efficiency. Fig. 1 shows the morphology of the dry gel treated with optimized process.

By optimizing the sol-gel process, pure apatite powders have been obtained from a temperature as low as 800℃ and have been characterized using scanning electron microscopy, X-ray diffraction. The sintering processing was developed with the temperature 1500℃ for the crystallization process study and actual application in fuel cells..

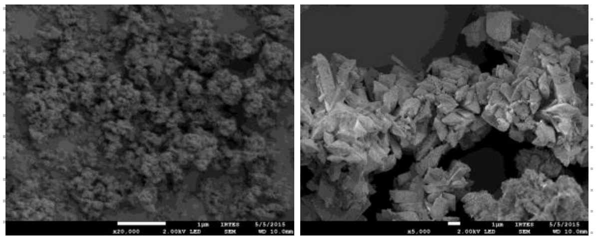

Figure 1. SEM figures for the morphologies of dry gels as the precursors before calcination. (left. Treated by optimized parameters; right. Treated by the parameters of unsuitable pH values)

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Combinatorial development of metal hydrides for thermal coupling of solid oxide fuel cells

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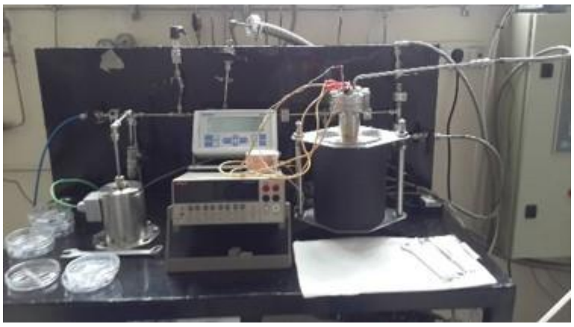
Thermal coupling of SOFC is desirable for improved energy efficiency. This might be achieved with the use of metal hydrides with operating characteristics tuned with those of SOFC. In this respect IT SOFCs offer better possibilities since their temperature range is quite moderate and suitable for a range of hydrides.

In this study, a target temperature in the range 550-650 C is selected and a study is to be carried out to determine metal hydrides that would function at this temperature range. The study follows a combinatorial approach where ternary alloys were deposited over a wide compositional range, screened for their sorption properties via resistivity measurement. We illustrate the use of combinatorial method within this context and finally give results for ternary system for Ti-V-Fe.

Acknowledgement
The work is a part of ERAFRICA collaborative program between Norway, Turkey, Egypt and South Africa with a TÜBİTAK support (114M128) which we gratefully acknowledge.

Magnetron sputtering with three guns used in combinatorial development



Set-up used for resistivity measurement

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Development of Anodes for Direct Oxidation of Methane Fuel in Solid Oxide Fuel Cells

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Due to transportation and storage problems of hydrogen, hydrocarbons can be used as an alternative fuel for solid oxide fuel cells (SOFCs). However, conventional Ni-based anodes exhibit an excellent catalytic activity towards the hydrocarbon cracking reaction and thus the carbon deposition occurs in the anode [1-2]. The deposited carbons quickly deactivate the anode by covering the active surface of the anode catalyst [3]. As a result, a significant degradation in the cell performance can be possibly seen. In this work, the anode structure is modified by the addition of copper and ceria to increase the coking resistance of the cell [4]. In this respect, the anodes are infiltrated by different amounts of Cu and CeO_2 nitrates via the wet impregnation technique to investigate the effects of Cu and CeO_2 loadings on the carbon tolerance of the cell. The effect of the anode porosity is also considered in the study. The carbon resistance thus the service life of the cell with Cu/CeO_2/Ni/YSZ anodes is found to be significantly higher than that of conventional Ni-based anodes under direct dry methane fuel. To investigate the effect of the infiltrated phases, the cell without infiltration is tested in dry methane. It is observed that anode is deactivated due to carbon deposition just after 2 h as shown in Fig. 1.

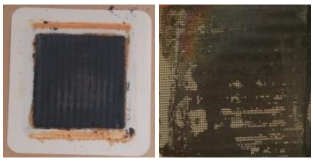

Fig. 1- The photo of the anode without infiltration after operated with dry methane fuel

Then, the anode is infiltrated with 1M solutions of Cu and Ce-nitrate. First the effect of Cu content (1-4 mL) is studied to optimize the Cu loading while the amount of Ce-nitrate solution is kept as 3 mL.The performance variation of the cell is shown in Figure 2. It is seen the optimum Cu content is 3 mL. Tests are realized on the constant current density at 0.7 V to analyse the voltage degradation for 5h at 700 °C. Then the amount of Ce-nitrate solution (1-4 mL) is considered. The Cu loading is kept constant as 3 mL for these cases. The cell whose anode is infiltrated by 2 mL of Ce-nitrate and 3 mL of Cu-nitrate solutions shows the best performance as shown in Fig.3.

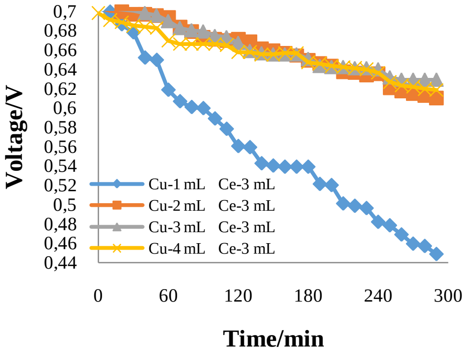

Fig. 2- Voltage-time curve of different Cu amounts infiltrated SOFC anodes

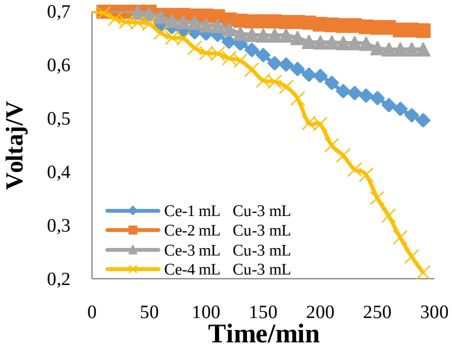

Fig. 3- Voltage-time curve of different amounts of CeO_2 infiltrated SOFC anodes

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Electrochemical properties of Ti-V-Cr-Ni alloy negative electrodes for use in nickel-metal hydride battery

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Rare Earth-based AB_5-type hydrogen storage alloys and superlattice alloys are used as negative electrodes for commercial nickel-metal hydride (Ni-MH) batteries. For improving specific energy of Ni-MH batteries, new high capacity hydrogen storage alloys need to be developed. We have paid attention to V-based alloys as the next high capacity alloy because they had high volumetric hydrogen storage capacity and did not include rare earth elements, which are easily subject to speculative transactions. In our previous study, we found that the $TiV_{0.9}Ni_{0.5}$ electrode had the highest discharge capacity (390 mAh g^{-1}) among $TiV_{1.4-x}Ni_x$ ($0 \leq x \leq 1$) electrodes [1] and the $TiV_{2.1}Ni_{0.3}$ alloy, which was the primary phase of $TiV_{0.9}Ni_{0.5}$, had a much higher discharge capacity (540 mAh g^{-1}) than the original alloy [2]. Some surface modifications of the $TiV_{2.1}Ni_{0.3}$ alloy were effective for increasing discharge capacity [3,4], but ineffective for improving charge-discharge cycle stability. Moreover, we demonstrated that bulk modification such as partial substitution of V with Cr was effective for significantly improving the cycle durability [5, 6]. In this study we investigated electrochemical properties of various Ti-V-Cr-Ni alloys as a basic composition of $TiV_{1.7}Cr_{0.4}Ni_{0.3}$.

$TiV_{2.1-x}Cr_xNi_{0.3}$ (x=0.4-1.0) alloys were composed of two phases like the $TiV_{2.1}Ni_{0.3}$ alloy, but the content of each phase changed with Cr content. The primary and the secondary phases had body-centered cubic (bcc) and TiNi-based structures, respectively. The $TiV_{1.7}Cr_{0.4}Ni_{0.3}$ electrode exhibited the maximum discharge capacity ($C_{\max}$) of ca. 440 mAh g^{-1} at the second cycle, and its cycle stability was greatly improved compared to the $TiV_{2.1}Ni_{0.3}$ alloy electrode. Over x=0.4, $C_{\max}$ was decreased with an increase in Cr content, while cycle number for initial activation was increased. Cycle stability was improved with increasing the Cr content of the primary phase. High-rate dischargeability (HRD) of the $TiV_{1.7}Cr_{0.4}Ni_{0.3}$ electrode was the best, and lowered for the alloy electrodes with higher Cr contents.

$Ti_xV_{1.7}Cr_{0.4}Ni_{0.3}$ (x=0.9-1.1) alloys were also composed of the primary phase with bcc structure and the secondary phase with TiNi-based structure. With increasing the x value, the Ti content of the primary phase was increased, but the Cr content was decreased. The V vontent of the primary phase was x=1.0 > x=0.9 > x=1.1. $C_{\max}$ was the highest for x=1.0, while cycle stability and HRD were lowered with increasing the Ti content.

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The importance of surface area for metal hydride electrodes

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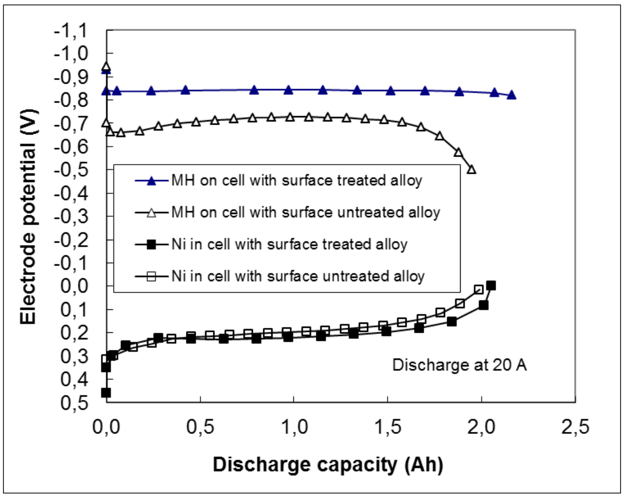
A surface treatment aiming to increase the electrochemical metal hydride charge/discharge reaction kinetics has been developed. It comprises a washing of oxidized, pre-hydrided AB_5 alloy particles in a hot KOH solution. This results in a large active specific area, which is a very efficient way to improve charge and discharge rate capabilities of the metal hydride electrode. The treatment also leads to strong magnetization, making it possible to lift the powder with a simple permanent magnet, indicating that nickel liberated in the surface layer is playing an essential role in the improved reaction kinetics.

The surface-treated alloy was investigated and compared with an untreated alloy in both half cells and sealed cells. The overpotential of each step in the discharge process was analysed in detail, and it was found that the electrode polarisation depends on the current density per active area. Both untreated and treated alloy powder had similar current densities per active area. But due to the larger surface area the latter exhibits superior kinetics. A NiMH cell with a surface-treated alloy has very good rate capability, only limited by the kinetics of the Ni electrode.



The electrode potential of a MH electrode and a Ni-electrode vs. Hg/HgO electrode during a 10 C discharge of 2 subC cells having a surface treated- and standard AB_5 alloy, respectively

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Activation of an AB$_2$ negative electrode material for Ni-MH battery

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AB$_2$ type hydrogen storage alloys are promising negative electrode materials for NiMH batteries. Such alloys when suitably adjusted demonstrate high electrochemical discharge capacity and good cycle life, but suffer from disadvantage that they require many charge-discharge cycles for activation. This is often attributed to the dense Zr oxide film formed on the particle surface acting as a barrier for hydrogen diffusion. A number of methods have been proposed over the years to solve the activation problem; Ni or Cu encapsulation via electroless plating, fluorination, alkaline treatment etc.

In this study, the activation behavior of AB$_2$ type alloy was investigated by several treatments; surface treatments; ball milling, hot alkaline treatment and surface coating. The relative success of these treatments were compared through galvanostatic cycling at 50 mA/g and 320 mA/g. As-received AB$_2$ ($Ti_{12}Zr_{21.5}V_{10.0}Ni_{38.1}Mn_{13.6}Cr_{4.5}Sn_{0.3}$) showed almost no capacity during the first few cycles. The maximum capacity without treatment attained was around 220 mAh/g. The value was reduced to 70 mAh/g at the higher rate. Milling of the powder introduced some activation, but most pronounced effect was obtained with boiling KOH treatment. This has resulted in a remarkable improvement in electrochemical performance of the alloy. After 20 minute-treatment, the electrode showed a capacity of 200 mAh/g in the first cycle. Highest capacity was obtained after 80 minutes treatment which yielded a value of 400 mAh/g.

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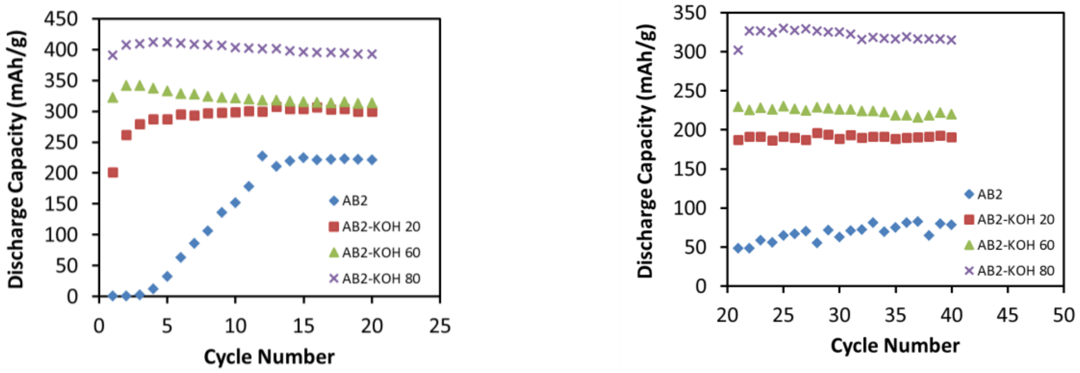

Discharge capacity vs. cycle number profiles of pristine and KOH treated AB$_2$ cycled at low (left) and high (right) rates

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The influence of the temperature on the electrochemical properties of the AB_5-type metal hydride anode

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Numerous studies have been performed to develop more efficient AB_5 hydrogen storage alloys, used as negative electrodes in nickel-metal hydride accumulators, in particular mono-and polysubstituted $LaNi_5$ parent compound [1-5]. Several compositions have been studied and the best results in terms of electrochemical performance were obtained with the tri-substituted $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ currently commercialized.

In our previous work [6-10], the electrochemical properties of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy used in commercialized nickel-metal hydride batteries were studied at room temperature. However, the temperature characteristic of the aforementioned alloy has never been researched until now. In this paper, the effect of temperature on the electrochemical properties of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ commercialized alloy were studied, using different electrochemical techniques, such as, the chronopotentiometry, the chronoamperometry, the electrochemical impedance spectroscopy and the potentiodynamic polarization. It was found that the effect of environmental temperature on the electrochemical properties was significantly observed. Different characteristic parameters of the absorption-desorption reaction of hydrogen by the commercialized alloy have been determined, such as the enthalpy change, the entropy change and the activation energy (Fig. 1). The study of the corrosive behavior, of the commercialized electrode, was evaluated at different temperatures.

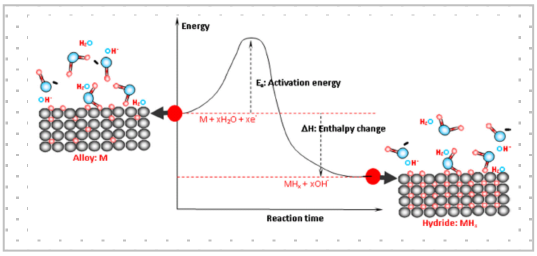

Figure 1. the parameters characterizing the hydruration reaction, such as the enthalpy change and the activation energy, of the intermetallic alloy.

All the obtained results show that the increased temperature promotes the subsequent growth of the active surface of the electrode and consequently the improvement of the kinetic properties of absorption and desorption of hydrogen. On the other hand, it accelerates the oxidation through the formation of an oxide film on the surface of the electrode, thereby degrading the kinetic properties and reduces the active surface. Thus, it is reasonable to consider the compromise of the double effect of increasing temperature.

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Role of KH in the hydrogen storage properties of Li-Mg-N-H system

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Hydrogen is an attractive energy carrier since it can be produced from renewable energy sources and has the possibility to supply energy demand for the future. Hydrogen storage holds an important place in hydrogen applications. Safe, economical and efficient way of storing hydrogen is essential for its application. Considerable efforts have been devoted to develop Metal-N-H based materials with the pioneering of Chen *et al* [1]. Its high capacity (5.6 wt. %), reversibility and reaction kinetics at moderate conditions (≈200°C) attracted the interest for Li-Mg-N-H system composed of $Mg(NH_2)_2$ and 2LiH [2]. Hydrogen sorption from the system can be described by the reaction shown in Equation (1).

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2MgN_2H_2 + 2H_2 \quad (1)$$

Theoretical calculations predicted operating temperature 90°C at equilibrium hydrogen pressure of 1 bar, which almost satisfies requirements of a PEMFC [2]. However, due to high kinetic barriers,initially hydrogen desorption could only be achieved at 220°C [3]. Considerable efforts have been undertaken to reduce the desorption temperature of the system [4]. Wang et al. found that peak desorption of the system decreased from 186°C to 132°C for $Mg(NH_2)_2$ - 1.9LiH-0.1KH system [5]. Unfortunately studies are usually focusing to the first dehydrogenation of material. Long term cycling of materials should be also considered for an application. Liu et al. showed that dehydrogenation/hydrogenation properties of KF added Mg(NH2)2-2LiH system was almost identical to those of pristine sample during cycling above 250°C for dehydrogenation and 210°C for hydrogenation [6]. Superior effect of K-based additives is diminishing when the material is cycled at high temperatures. This behavior is not very understood yet and it is very important to understand the role of additive for further development. For this purpose two samples were synthesized. Figure 1 shows the DTA of KH added and pristine samples before and after cycling. Peak temperature of the reaction was at 164°C when KH was added. After 20 cycle peak temperature was shifted to 213°C. Superior properties of KH were not observed after 20 cycle.

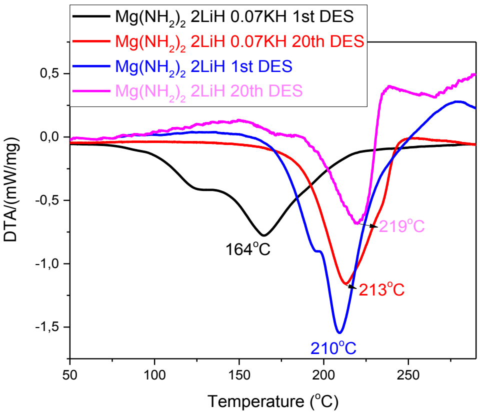

Figure 1: DTA of KH added and pristine samples before and after 20 cycle.

In this work effect of KH to the kinetics of Li-Mg-N-H system was investigated with Sievert's volumetric method; in situ and ex situ PXRD experiments were performed at Lund University Max II facility. For thermal characterization DTA TG-MS was used. Investigations showed that $Mg(NH_2)_2$-2LiH-0.07KOH system can reversibly store 4 wt.% H_2 at 220 °C.

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Aqueous and Non-aqueous Electrolytes Lithium-Sulfur Batteries

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The development of alternative low cost battery technologies is becoming essential. Thus, the obvious solutions could be either to switch back to aqueous electrolytes or to develop post lithium ion battery technologies (e.g. Li-S batteries) which could offer three fold energy densities than that of the current Li-ion batteries.

In spite of the large number of efforts on Li-S batteries in aprotic organic electrolytes, there is almost no study showing the potential application of this system in aqueous electrolyte. Recently we have developed for the first time an aqueous electrolyte Li/ion-polysulphide battery coupling a well-known cathode material ($LiMn_2O_4$) with dissolved polysulphides as anode[1,2]. The use of aqueous electrolyte in the field of Li-S batteries was suggested more than two decades ago by Licht and co-workers[3] and put in practice few years later for polysulphides-based batteries as well as solar cells. In 2013, Visco *et al.* have developed a high performance rechargeable Li-S battery using Li_2S in an aqueous cathode[4].

Herein, we will first focus the aqueous electrolyte Li-ion/polysulfide battery concept by the use of ceramic membrane (Fig 1.)[1]. Further searching for cost reduction, an obvious implementation is to replace the ceramic membrane in which we will be discussing the same concept with an ion-selective polymer membrane namely a perfluorosulfonate ionomer (Nafion)[2]. Last but not least, polysulfide batteries in aqueous and non-aqueous electrolyte systems will be compared in terms of energy density, power rate capability and cycle life.

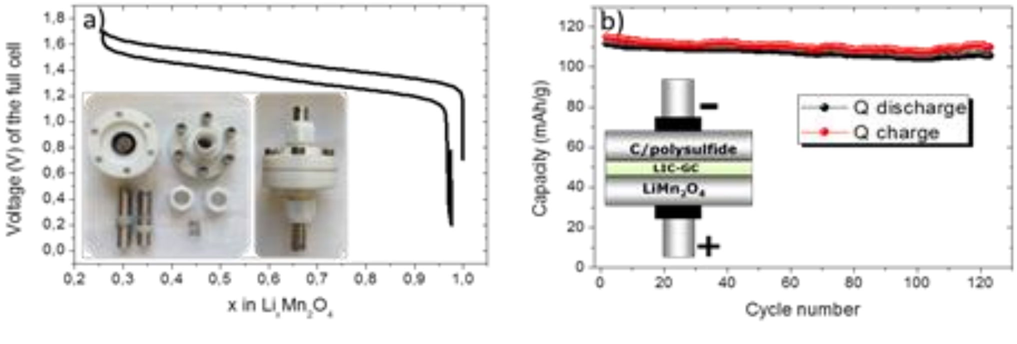

Fig. 1 First galvanostatic charge-discharge profile of the $LiMn_2O_4$/polysulfide full cell at a current density of C/2 b) cycling performance of the cell in 0.5 M Li_2SO_4 containing aqueous electrolyte[1]

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Critical Materials- and Cell-Level Design Considerations for High Energy Density and Low Cost Lithium-Sulfur Battery

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In the search for rechargeable batteries for the electric vehicles with high energy density and low cost, Li-S chemistry has gained significant attention due to its very high theoretical specific energy of 2567 Wh/kg in addition to the low cost, natural abundance and non-toxicity of elemental sulfur [1].

Battery chemistries are evaluated based on their theoretical specific energy, which is calculated considering only the active materials mass; however the conclusions can be significantly different when one considers the systems-level properties [2]. Therefore, a thorough materials-to-system analysis that projects the systems-level specific energy, energy density and cost of the battery pack designed specifically for the electric vehicle applications is required. In this study, a materials-to-system analysis for the Li-S electric vehicle battery that links the materials chemistry and physics to the cell-level design is presented. The techno-economic model used in this study is based on the bottom-up Battery Performance and Cost (BatPaC) model developed previously for the Li-ion chemistries [3,4].

Excess Li amount at the anode, useable specific capacity of the active material, electrolyte volume fraction, sulfur to carbon ratio and kinetics at the cathode are identified as the critical electrode- and cell-level design considerations. The systems-level energy density, specific energy and cost of the Li-S transportation battery as a function of these design considerations are projected and discussed. Electrode loading is identified as a key parameter to relate the battery cost for useable energy to the investigated design considerations. The analysis projects that electrode loadings higher than 8 mAh/cm^2 are required for the Li-S batteries to achieve the high energy density and low cost requirements of the electric vehicle applications. The critical development pathway for the high energy density and low cost Li-S transportation battery is identified as stabilizing Li anode at high current densities with a limited excess of Li and maintaining cell capacity at high S loadings in an electrolyte starved cathode.

Acknowledgments

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Effect of Ag -coating on the electrochemical performance of $LiFePO_4$ cathode material

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$LiFePO_4$ has been extensively studied as the most promising cathode material of lithium-ion batteries because of its low cost, acceptable environmental characteristics, and good safety compared with layered oxides such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. In addition, $LiFePO_4$ has a large theoretical capacity (170 mAhg^{-}1), and aflat discharge potential of 3.4 V versus Li/Li^{+}[1] Despite these unique features, it suffers from low electronic conductivity ($\sigma=10^{-9}$ Scm^{-1}),thereby resulting in poor electrochemical performance. In order to enhance the electronic conductivity, several groups have oriented their research in the same area. In the literature, two types of approaches have been reported to address the specific problems. First, is the reduction of particle size which consequently reduces the lithium ion diffusion path length and second is the preparation of composites with continuous conductive coating, such as carbon graphene , metal doping metal oxide coating and surface modifications by nanosized metals [2] Here, we tried an nanosized silver coating on $LiFePO_4$ particles synthesized by hydrothermal method in order to improve the electronic conductivity.The treatment expected to positive effect both charge-discharge capacity and the cyclability [3].

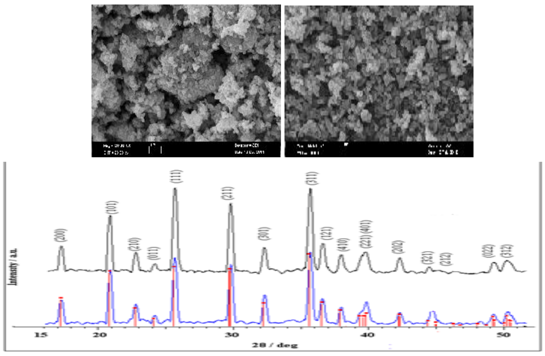

Figure 1. XRD and SEM data of bare and %2 Ag coated $LiFePO_4$

Surface modification of $LiFePO_4$ by silver coating was tried using silver nitrate solution as in literature [4]. The weight ratio of Ag/ $LiFePO_4$ was %2wt. The electrochemical performance was investigated by galvanostatic charge /discharge experiments and also we used XRD, SEM, for charecterization. The conductivity of samples was measured by the four-point probe method. Fig 1 shows the XRD patterns of bare and %2 Ag coated $LiFePO_4$. Both samples with an olivine structure indexed to the orthorhombic Pnma space group (JCPDS card no. 81-1173) and the difraction peaks of the silver were not observed because the low silver content of %2 wt. SEM images both samples also shown in Fig 1.It can bee seen that the Ag coated sample owns less agglomeration and scatters more uniform than the bare one. The electronic conductivity of Ag coated was measured to be about $1.3*10^{-2}$Scm^{-1}.

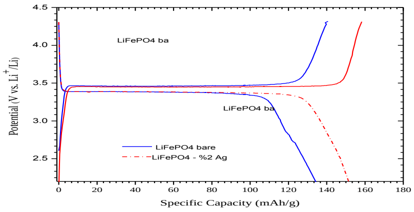

Figure 2. The initial charge and discharge profiles of bare and %2 Ag coated $LiFePO_4$.

Fig 2. shows the first charge/discharge capacity of both samples was tested at 0.1C in the voltage range between 2.2 and 4.4V and Fig 3 shows the rate performance of bare and %2 Ag coated $LiFePO_4$ by galvanostatic cycling at various C (0,1-2 C) rate. The first discharge capacities and rate performance of %2 Ag coated $LiFePO_4$ higher than bare $LiFePO_4$ sample. Therefore, the Ag coating can be powerful method to enhance the conductivity and preserve the capacity even at the high current densities.

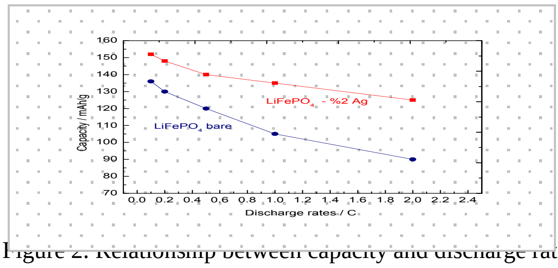

Figure 2. Relationship between capacity and discharge rate of the bare and %2 Ag coated $LiFePO_4$

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Development and Characterization of New Layered Cathode Materials for Lithium Ion Batteries

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Lithium ion batteries are now widely used especially in mobile applications as a power source. In the case of Li-ion batteries, certain properties such as energy density, cycle life, safety, electrical conductivity and rate capability have great importance. $LiCoO_2$ has been used as a cathode material for Li-ion batteries for many years. However, capacity of the currently used layered $LiCoO_2$ cathodes is limited to perform 50% of its theoretical capacity (140 mAh/g) [1]. In this regard, novel layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode materials have been investigated as an alternative cathodes searching for higher capacity, cycle life, rate capability and safety. $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathodes exhibit higher capacity that of close to 200 mAh/g with enhanced safety [2]. This high capacity can be associated with the improved chemical stability. However, the rate capability is the most important deficiency which should be improved for new layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode materials. Moreover, the electrochemical performance of cathode is strongly affected by powder properties such as morphology, surface area and composition. Therefore, spray pyrolysis method was used to obtain spherical fine-sized morphology followed by heat treatment will to obtain better electrochemical activity [3].

The precursor powders were prepared using aquaous solution via spray pyrolysis. $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode material was produced by using solutions of lithium nitrate ($LiNO_3$), nickel (II) nitrate hexahydrate ($N_2NiO_6.6H_2O$), manganese (II) nitrate tetrahydrate (Mn $(NO_3).4H_2O$ and cobalt (II) nitrate hexahydtare ($Co(NO_3)_2.6H_2O$) with the mole ratio of 1:1/3:1/3:1/3, repectively. The total concentration of the solution is 0.5 M with additives of citric acid and ethylene glycol. Spray pyrolysis was used to obtain spherical fine-sized particles which then heat treated between 800^{0}C - 1000^{0}C. Different time-temperature combinations were tried and an undefined peak of new layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ was observed which heat treated at 1000^{0}C. Therefore, temperature range between 800^{0}C and 900^{0}C was chosen as heat treatment temperature. X-Ray Diffraction (XRD) pattern of obtained layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode material showed good [006]/[102] and [108]/[110] doublets indicating layered structure and good hexagonal ordering as shown in Figure 1.

Precursor concentration, droplet size, gas flow rate and temperature are the main parameters affecting the particle properties. Therefore, these parameters were optimized to obtain particles with spherical fine-sized and narrow size distribution. The morphology of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ observed by scanning electron microscopy (SEM) and average particle size was between 0.4 and 0.6 μm, as shown in Figure 2. With proper cathode composition, experimental parameters and electrode design, improved electrochemical properties was achieved.

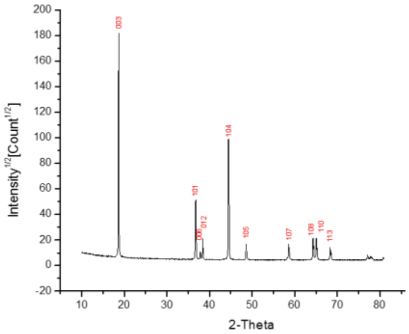

Figure 1. XRD spectrum of layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode materials produced by using spray pyrolysis and then heat treated.

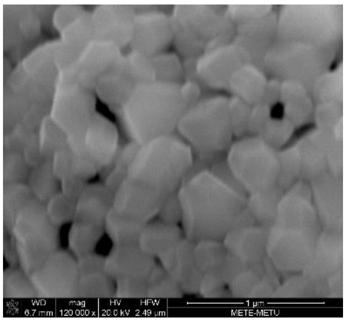

Figure 2.SEM images of studied layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode materials produced by using spray pyrolysis and then heat treated.

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Magnetic Interactions in Mn Based Li-ion batteries and the Effects on the Battery Performance

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In the everyday life the most common electrodes for rechargeable Li-ion batteries are $LiMn_2O_4$, containing transition metal oxides with unpaired electrons in d-shells. In these materials magnetic interactions can be induced by pressure, temperature, applied magnetic field or crystal field in the lattice. Especially, during the charge and discharge processes, due to the changes in the crystal field, the magnetic states of the transition metals can change as low spin (LS), intermediate spin (IS) or high spin (HS) as seen in the Figure 1. The doping or substitutions of the Mn ions by the other elements can cause the change of the effective magnetic moment of the Mn ions due to the change of the enviroment and valence value of them. So, the magnetic properties of the Mn ions can also cause the change of the structural, electrical and electrochemical performance of the cell. After a certain number of cycle of the battery, the lattice parameters of the active cathode material expand and the crystal field decreases as seen the illustrated scheme of the Figure 2. Thus, the spin state changes and/or Jahn-Teller distortion is induced due to the decrease in the splitting energy between eg and t_2g states. In this study, we report the strong correlation between the magnetic structure of the cathode materials and their battery performances in Li-ion batteries, Figure 3. Thus, if the effective magnetic moment of the Mn ions can be controlled, it can be possible to prevent the capacity loss after repeated cycling, which is the main problem of the rechargable batteries.

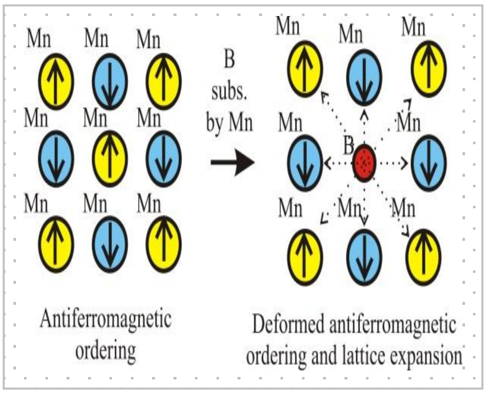

Figure 2. The nano-clustering of the Mn ions and the doping or substution can cause an expantion of the cell for a special direction in the magnetic perspective. B indicate the non-magnetic doping elements with smaller size than Mn

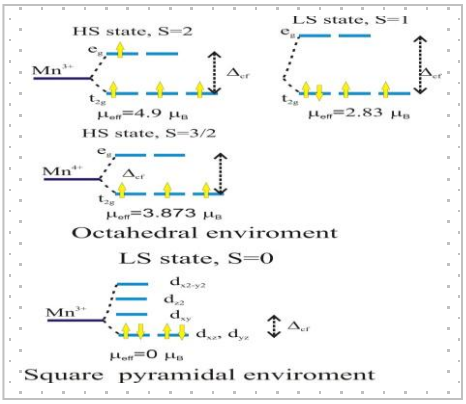

Figure 1. Valance state of Mn ions for different enviroments.

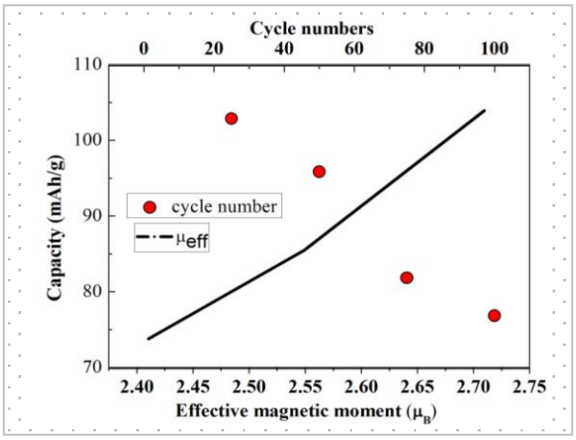

Figure 3. The effective magnetic moment and cycle number dependency of the LiMn-ion cell. It is clear that the decrease of the capacity by the increasing cycle is also related to decrease of the effective magnetic moment.

Keywords: Li-iyon batteries, magnetic properties, spin transition

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Development of a commercial HTPEM fuel cell stack module

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Danish Power Systems (DPS) and Teksis Ileri Teknolojiler (TIT) collaborate on the development of a commercial HTPEM stack module. The aim of this collaboration is to develop a low cost stack module that will be used as a range extender in a utility vehicle for airport ground operations. DPS is developing the HTPEM fuel cell technology and related components and TIT are developing a low cost modular stack concept.

The work presented here focuses on recent results obtained by DPS regarding the degradation of PBI membranes used in membrane electrode assemblies (MEAs) under various operating conditions in addition to the latest developments on achieving an increased platinum utilization. Furthermore, the modular stack concept from TIT will be presented.

DPS has demonstrated an average degradation rate of 9 µV/h over the first 10.000 hours (Figure 1) has been achieved during long-term MEA testing under dry hydrogen and air at 0.23 A/cm^2 with a cell lifetime of more than 14.000 hours.

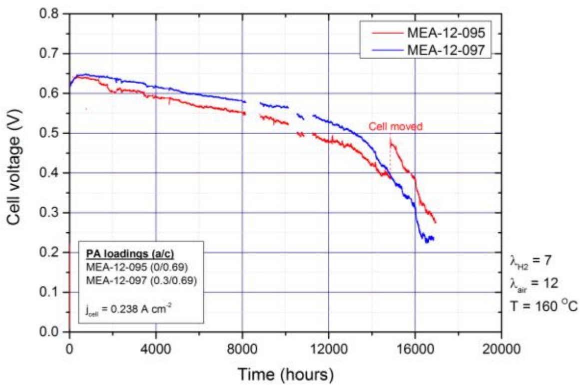

Figure 1. Results from long term testing of DPS MEAs. Operated at a constant current (0.23 mA/cm^2) using H_2 and air. 10 cm^2 active area.

Long-term testing on MEAs subjected to testing using wet hydrogen (30 mole %) have shown similar rates of degradation over the first 2.600 hours. Scanning electron microscopy, transmission electron microscopy and x-ray diffraction analyses have been used to investigate the modes of degradation occurring within the catalyst layers and membrane.

TIT have developed a low cost modular stack concept (Figure 2), which enables simple scaling of stack voltage and current, a high level of robustness and easy service and maintanence. It was aimed by this promising design to reduce the fuel cell system complication such as reactants stoichiometry, coolant requirements for heat management, pressure drop in monifolds, flow field design, uniform current collection, stack compression, reliable sealing etc. by developing stacks smaller in size followed by connecting them in series or parallel depending on the power requirement.

The presentation includes design and cost considerations, flow plates, cooling system, gaskets and stack assembly.

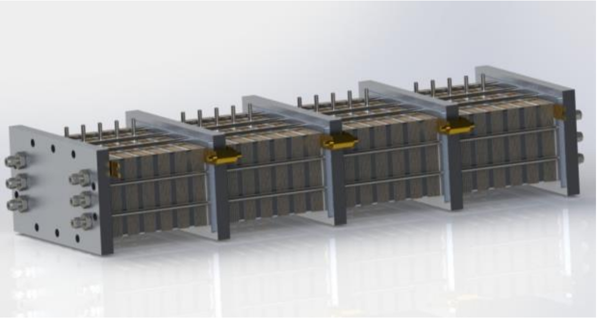

Figure 2. Drawing of the 5 kW HTPEM stack design.

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Electrochemical Performance and Long Term Stability of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ (y = 0.2 and 0.8) Cathode Thin Films Prepared by Liquid Precursor Deposition

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Micro Solid Oxide Fuel Cells (µSOFCs) are energy conversion devices that operate at 400 – 600 °C. A µSOFC usually consists of thin electrodes, separated by a thin film electrolyte (thicknesses < 1 µm) supported on a silicon substrate [1]. Therefore, the facile fabrication of the thin anode and cathode layers that also perform well under µSOFC operating conditions is of great interest.

(La,Sr)(Co,Fe)O_3 (LSCF) is widely used in solid oxide fuel cells (SOFCs) as a cathode material, due to its high surface oxygen exchange coefficent and its mixed ionic and electronic conductivity. Although LSCF has been widely investigated in both anode and electrolyte supported SOFCs in both high (800 – 1000 °C) and intermediete (600 - 800 °C) temperature ranges [2-3], its fabrication in the form of thin films and the resulting electrochemical performance has only rarely been investigated [4]. Furthermore, the long-term stabilty of thin film LSCF cathodes, a vital prerequisite for their use in µSOFCs, has not been investigated to date to the best of our knowledge. For this reason, in this study, cathodes having two widely used compositions of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ (y = 0.2 and 0.8) (LSCF) were fabricated by spin coating of their respective polymeric precursors on dense $Ce_{0.9}Gd_{0.1}O_3$ (CGO) substrate pellets. Scanning electron microscopy (SEM) studies showed that uniform thin films with thicknesses less than 1 µm were obtained by this relatively low cost and effective fabrication method.

The electrochemical performance and the long term stability of the symmetrical LSCF/CGO/LSCF cells were investigated by impedance spectroscopy. Figure 1 shows that similar electrochemical performances to that reported in the literature for LSCF-based thin film cathodes were obtained (Figure 1). Long term stabilty studies showed that the cathode polarization resistance increased by at least 20% after exposure to stagnant air for 120 hours at 600 °C, most of which is attributed to deleterious microstructural evolution of the electrodes.

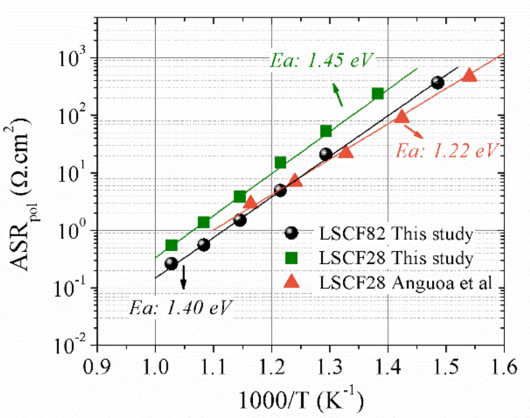

Figure 1. Temperature dependence of the total electrode polarization resistance obtained from symmetrical cells basaed on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF28) and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF82) as thin film electrodes, separated by CGO, with the data collected in stagnant air. For comparison, the resistance of LSCF28 cathode thin films, reported in the literature [4], is also shown.

Acknowledgements

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Investigation of Micro-Tube Solid Oxide Fuel Cell Fabrication Using Extrusion Method

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Solid oxide fuel cells (SOFCs) are high efficient energy generators which convert the chemical energy of hydrogen and hydrocarbon fuels into electrical energy. SOFCs are usually designed in two types as planar and tube. However, both type SOFCs are planned to be used on stationary applications because of long start-up time, late response to the dynamic loads and heavy weight.

The power density of tubular SOFCs is known to be inversely proportional to the tube diameter i.e. the power density increases with decreasing the tube diameter [1]. Tube shaped SOFCs which have less than 5 mm diameter are called micro-tubular SOFCs. Micro-tubular SOFCs provide the advantages of tube shaped SOFCs such as high power density, mechanic strength, fast start-up and shut-down and high thermal cycling behaviour [2].

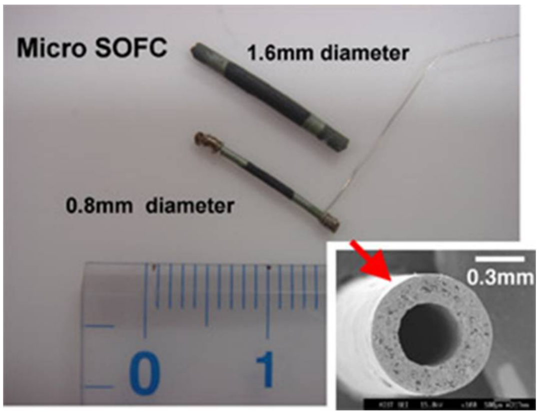

Figure 1 Micro-tube SOFC [3]

Tubular SOFCs are usually produced by the extrusion method. In this method, the parameters such as viscosity of the ceramic slurry, extrusion speed and mold temperature needs to be optimized for a high performance. The most important part of the extrusion machine is mold part where the ceramic solution takes the form of a tube. In this section, the homogeneity of the ceramic slurry is provided while passing through the mold apparatus. In this way, distortion doesn't occur in the produced tube. Furthermore, the mold must be brought to the appropriate temperature to shape the ceramic material easily. The mold should also be designed very precisely because the tube diameter and wall thickness are formed during the mold stage.

In this study, a mold design was made for the production of micro-tubular SOFC with an outer diameter of 3 to 4.5 mm. NiO/YSZ anode mixtures with different production parameters such as mold temperature, viscosity, content are fabricated. The results showed that the mold temperature is very important for the fabrication of the micro-tube support layer. The extrusion and pre-sintering temperatures for the anode support are selected as 40-70ºC and 800-1200ºC, respectively and their effect on the quality of the electrolyte layer were examined.

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Utilization of Anomalous Oxygen Reduction Rate at Hetero Interface of $(La_{0,8}Sr_{0,2})CoO_{3-\delta}/(La_{0,5}Sr_{0,5})_2CoO_{4-\delta}$ for Solid Oxide Fuel Cell Cathodes

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Perovskite type $(La_{1-x}Sr_x)CoO_{3-\delta}$and the related compounds have been studied as one of the promising candidates for the cathode of intermediate temperature (500-700 ^oC) solid oxide fuel cells (IT-SOFCs); they show high mixed electronic/ionic conductivity and high electro-catalytic activity.

Despite their advantages, the main problem in utilization of perovskite type $(La_{1-x}Sr_x)CoO_{3-\delta}$ and all other relevant derivatives in SOFCs is oxygen reduction rate (ORR), which is mainly hindered by dissociative adsorption of oxygen at the cathode surface along with bulk ionic transport at intermediate temperatures. Nonetheless, anomalously enhanced oxygen reduction kinetic around the $(La_{0,8}Sr_{0,2})CoO_{3-\delta}/(La_{0,5}Sr_{0,5})_2CoO_{4\pm\delta}$ interface has been reported in recent years. Exploiting this interface induced ORR enhancement can decrease operation temperature of SOFC cathode, extending the chemical stability of cathode together with emerging the probability of using new anode materials operating at lower temperatures and so used not to be compatible with IT-SOFC cathode.

In this work, $(La_{0,8}Sr_{0,2})CoO_{3-\delta}$ and $(La_{0,5}Sr_{0,5})_2CoO_{4\pm\delta}$nano-powderswere obtained through low temperature solution based methods either by separately or as dual phase synthesis from initial solution, which was followed by phase analysis with conventional XRD (with CuK_α) to ensure absence of any undesired phase and SEM/EDS analysis to control morphology, powder size and stoichiometry of cations. Separately obtained nano-powders from each oxide were mixed in certain proportions and ball-milled with ZrO_2 balls in an organic container. Rietveld analysis has been carried out based on conventional XRD results to reveal particle sizes and fractions of each expected phases assuming no dislocation on the particles.

Ball-milled powders in certain proportions as well as dual phase synthesis powders were used to prepare slurry. In slurry preparation fish oil, toluene, PEG, BBP and PVB were used. After addition of each chemical, slurry was ball milled for 15 min period. Each slurry was applied as 0.5cmX0.5cm squares onto $(Ce_{0.9}Gd_{0.1})O_{2-\delta}$ which was synthesized via Pechini method, calcined at 800 ^oC, pressed into 1.4 cm diameter-0.1 cm thickness pellets and sintered at 1300 ^oC. After application of slurries onto both sides of GDC pellets and making symmetric cells, it was fired at initial calcination temperatures of powders namely 800 ^oC so that avoiding irreversible formation of higher temperature equilibrium oxygen vacancies. Then gold paste was applied onto cathodes as well as gold wires and fired at 500 ^oC for 2 hours. Eventual symmetric cells were characterized via in-situ potentiostatic electrochemical impedance spectroscopy (EIS) with a frequency range between 1MHz-5mHz and 10 mV perturbation voltage amplitude under different oxygen partial pressure and temperature combinations. Oxygen partial pressures were 0.01, 0.1 and 0.21 atm and temperatures were 400, 500, 550, 600, 650 and 700 ^oC. Surface oxygen exchange constant and oxygen ion diffusivity were tried to be extracted from in situ EIS results along with determination of rate limiting step for corresponding conditions. The proportion giving the highest density of interfaces, best ORR and hence the lowest possible temperature is chosen as candidate for eventual cathode.

Since none of the thin film and/or surface decorated performances is expected to be functional due to probable high temperature cracking problems on the films as well as cost efficiency, dual phase synthesis examinations are expected to be outstanding.

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Investigation of Temperature Distribution and Performance of SOFC Short Stack with/without Machined Gas Channelles

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Solid oxide fuel cells (SOFCs) generate electrical power via electrochemical reactions. Non-uniform reaction distribution on the cell active area may lead to a temperature gradient in the cell which may result in micro or macro cracks because of the thermal stresses generated [1]. This certainly causes the degradation of SOFC performance. To avoid this problem, two flow field areas are proposed in this study i.e. first one has machined parallel gas channels and second one has no machined gas channels to decide the optimum design for better temperature gradient and performance from 81 cm^2 active area electrolyte supported cell which is produced in Prof. Dr. T. Nejat Veziroglu CERC at Nigde University. The effects of SOFC operation conditions such as current (20-80 ampers), temperatures (700-750-800 °C) and, hydrogen and oxygen mass flow rates (1-4 and 2-8 L/min, respectively) on the anode side gas temperatures are experimantally investigated. To measure the temperatures in the anode gas channels, 7 different points are decided and K-type thermocouples are placed as shown in Figure 1.

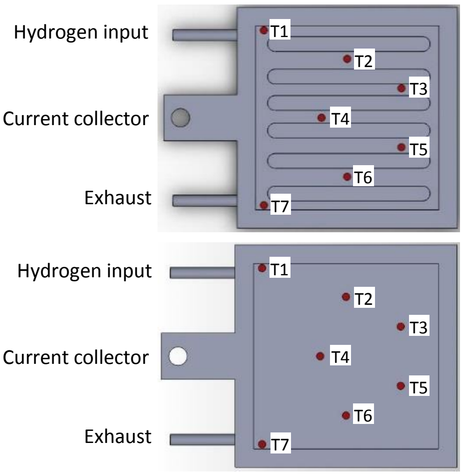

Figure 1. Measurements points in two designs.

Glass-ceramic materials are used to provide gas tightness between the interconnector and thermocouple probes. This structure is illustrated by Figure 2.

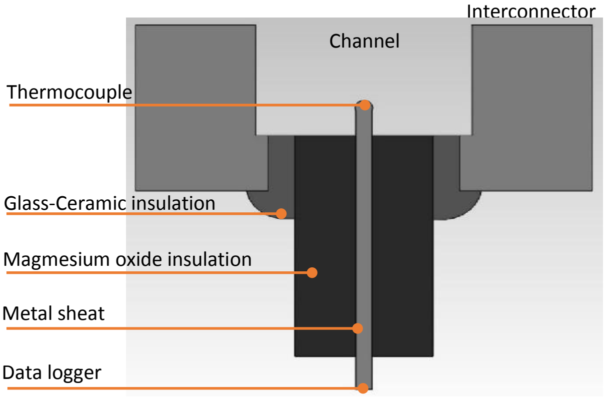

Figure 2. Thermocouple placement on the anode interconnector

After satisfying steady-state conditions in the single stack, temperature datas are recorded by Pico DataLogger (T-08) for one hour and then performance results are obtained by Arbin FCTS at different flow rates, temperatures and currents.

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Murat Canavar was born in 1980, and grew up Istanbul. He earned Bachelors and MSc degrees from Nigde University. Canavar has been both working as a research assistant and maintaining PhD studies at Nigde University since 2013. His interests cover termodynamics, heat transfer, numerical analysis and clean energy applications such as SOFC, PEM and DMFC.

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2D Carbides (MXenes) for Energy Storage

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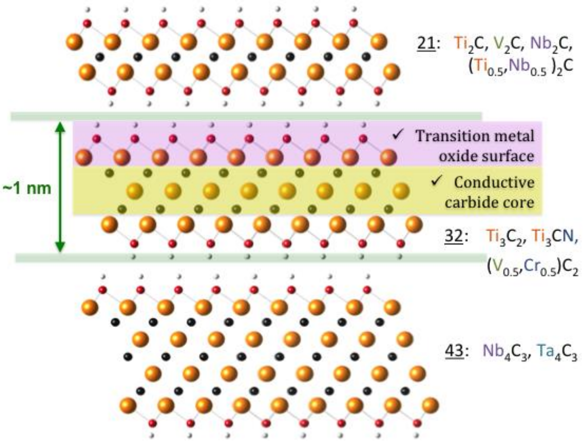
Recently a new family of two-dimensional (2D) early transition metal carbides (Ti_2C, Ti_3C_2, Nb_4C_3, etc.) and carbonitrides, called MXenes, was discovered by Drexel University scientists.[1,2] Selective etching of the A-group element from a MAX phase results in formation of 2D $M_{n+1}X_n$ solids, labeled “MXene”. MXenes combine the metallic conductivity of transition metal carbide layers with the hydrophilic nature of their mostly hydroxyl or oxygen terminated surfaces. In essence, they behave as “conductive clays”. We observed intercalation of Li^+, Na^+, Mg^{2+}, K^+, NH_4^+, and Al^{3+} ions between the 2D MXene layers.[3] In most cases, the cations intercalated spontaneously. The intercalation of some ions, notably Al^{3+}, can be promoted electrochemically.

MXenes have shown much promise for electrochemical energy storage systems.[4-6] We explored the potential of MXenes as anode materials for Li-ion and Ni-ion batteries, and their use in electrochemical capacitors. We studied a range of MXenes with different chemistries (e.g., Ti_2C, Nb_2C, Ti_3C_2), and electrode architectures in lithium and sodium ion batteries using both experimental and theoretical approaches. A very high volumetric capacitance of flexible Ti_3C_2 electrodes of up to 900 F/cm^3 was observed in aqueous electrolytes. This study provides a basis for exploring a large family of 2D carbides and carbonitrides in electrochemical energy storage applications using single- and multivalent ions.



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Yury Gogotsi is Distinguished University Professor and Trustee Chair of Materials Science and Engineering at Drexel University. He is the founding Director of the A.J. Drexel Nanomaterials Institute and Associate Editor of *ACS Nano*. He works on nanostructured carbons and two-dimensional carbides for energy related and biomedical applications. His work on selective extraction synthesis of carbon and carbide nanomaterials with tunable structure and porosity had a strong impact on the field of capacitive energy storage. He has co-authored 2 books, more than 450 journal papers and obtained more than 50 patents. He has received numerous national and international awards for his research. He was recognized as Highly Cited Researcher by Thomson-Reuters in 2014 and elected a Fellow of AAAS, MRS, ECS and ACerS and a member of the World Academy of Ceramics.

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Mesoporous MCM-41 Material for Hydrogen Storage: A Review

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The limited resources of fossil fuels and the rising demand of energy is a matter of fact, which is closely related to the environmental issues. Hence, green technologies have been developed to reduce the consumption of fossil fuels. Hydrogen that is an environmental friendly energy carrier is one of the best alternatives to the fossil fuel sources for both stationary and mobile applications. For this reason although there is an increasing demand for hydrogen production, its storage is the bottleneck against widespread use of hydrogen due to its low volumetric density.

In order to meet the commercial needs, the Department of Energy (DOE) of the United States has targeted system level hydrogen storage capacity of 5.5 wt% (1.8 kWh/kg) and 0.040 kg/L (1.3 kWh/L) by the FY 2015 which requires a much higher gravimetric and volumetric capacity of the material alone [1]. Reversibility, feasibility and safety are also matters of concern for the development of storage systems. Hence, it is an attractive research topic to maintain the DOE targeted hydrogen uptake and develop new materials.

The hydrogen storage capacity of the materials is investigated at both room and cryogenic temperatures. The reported experimental results on the hydrogen storage of carbon based materials scatter over a range of 1.5-10 wt% depending on the temperature and pressure [2-4]. Despite the fact that metal hydrides allow high amount of hydrogen storage (up to 7.6 wt%), the cost of the material, the sensitivity to the impurities in the gas and poor reversibility of the stored hydrogen are the major drawbacks [5, 6]. It has been reported that zeolites may store up to 4.5 wt% of hydrogen at 77 K [7]. The reason why zeolites are considered for hydrogen storage is because they do have porous structure which enables high volume for the storage [8].

MCM-41, which is a type of zeolite with uniform pore structure and high surface area is a member of family of mesoporous materials according to IUPAC (International Union of Pure and Applied Chemistry) classification. It was first discovered by Mobil researchers [9]. Since its discovery, MCM-41 has been mainly used for catalytic purposes as well as adsorption, separation, environmental applications and petrochemical industry [10]. As a result of the promising results obtained in gas adsorption researches, there are a number of researches in which MCM-41 is now also considered as hydrogen storage media with a maximum reported hydrogen uptake of 1.68 wt% [11-14]. However, there is not any review specifically on the hydrogen storage of MCM-41. Therefore, the main scope of this paper is to highlight the recent studies on the use of MCM-41 as hydrogen storage media as well as its synthesis conditions and the effect of loading metal on the storage capacity.

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Yuda Yürüm is a full professor at the Faculty of Engineering and Natural Sciences of Sabanci University (Istanbul, Turkey) since 1999. He received both his BSc degree and MSc degree in Chemical Engineering from Middle East Technical University in 1969 and 1970, respectively. In 1974, he received his doctoral degree in Chemistry from Hacettepe University. Prof. Dr. Yürüm acted as the Principal Investigator of 25 national and international projects since 1976. He is author or editor of 5 books and has chapters in 6 international scientific books, 114 refereed international scientific articles and about 150 presentations in international symposia. He has more than 2300 citations to his scientific work

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Status and Potential of PEM Technology for Transportation and the Related Hydrogen Infrastructure

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For reduced CO_2 emission in transportation there are just two pathways available: enhanced efficiency or fuel switch. The option of carbon capture is applies only for bigger and preferably stationary applications, mostly for power plants. Whereas efficiency improvements of power trains and whole cars are the short-term way to CO_2 savings, the impact of these measures is limited to the 20 - 30 % range compared to today's best practices. In view of an 80 % CO_2 reduction goal a fuel switch is unavoidable.

Battery electric drives may serve for short distances and smaller cars, like in daily commuting, fuel cells electric drive trains can serve as full substitutes for existing drive trains covering the whole range of vehicles from sub-compact to full size cars and SUVs and a reasonable cruising range of about 500 km with the option to refuel in about seven minutes. The worldwide status of the automotive development and the major challenges to be resolved will be outlined and the advantages of a potential technology shift will be presented from a macro-economic and societal point of view.

The major advantage of the fuel cell technology is the fuel switch to hydrogen, since hydrogen is a clean and carbon free secondary energy carrier. A barrier for implementation poses the very different nature of hydrogen as a gas compared to liquid fuel used for transportation today in that a new infrastructure is needed. Based on a study assuming a high market penetration of hydrogen electric vehicles and renewable energy in Germany it can be concluded that a dedicated hydrogen infrastructure poses no cost barrier for implementation. It will even help reduce the cost of grid extension by combining the power grid and a gas grid which is underground and needs, ceteris paribus, a smaller footprint and less investment. The value chain from renewable energy production, storage and distribution all the way down to the use in automobiles will be discussed and the societal advantages will be outlined.

Detlef Stolten studied metallurgy/ceramics at and later received his PhD from the University of Technology at Clausthal/Germany. He worked for over 10 years in the industry as a scientist first with the Robert Bosch GmbH, Stuttgart and then with Daimler Benz/Dornier, Friedrichshafen. Since 1998 he has been with the Juelich Research Center as the Director of the Institute for Energy and Climate Research – Fuel Cells. In 2000 he became a full professor for Fuel Cell Technology at the University of Technology Aachen, Germany. His research activities are focused on energy process engineering for DMFC, HT-PEFC and SOFC systems, i.e. electrochemistry, stack technology, reforming process and systems engineering as well as systems analysis. Fostering the cooperation between research and industry he was in charge of the NRW – Fuel Cell Network from 2000 through 2005. Former activities of Prof. Stolten include Member of the Board of the Research Association of Electrochemistry (AGEF) in Germany: Member of the Advisory Council of the European Hydrogen and Fuel Cell Technology Platform,(2004 – today). He represents Germany in the Executive Committee of the IEA Annex Advanced Fuel Cells. He chaired the Steering Panel for the Strategic Research Agenda of the Platform and was chairman of the Quality Assurance Panel for the Implementation Plan. Being a member of the Technology/Engineering Working Group he has been contributing to the GROCC (Global Roundtable on Climate Change), Columbia University, New York since 2005. He represents the Helmholtz-Community within the advisory board of the 'Programmgesellschaft Nationale Organisation Wasserstoff- und Brennstoffzellentechnologie GmbH (NOW)', the major agency for project funding of the German Federal Ministries for Transport, Economics and Research. Prof. Stolten currently is the Chairman of the ExCo of the IEA Implementing Agreement Advanced Fuel Cells. He represents Germany in the Executive Committee of the IEA Annex Advanced Fuel Cells and is co-chairman of IEA's Expert Group on Science for Energy. He is on the advisory board of the journal Fuel Cells and the Chair of the World Hydrogen Energy Conference which was held in May, 2010. Prof. Stolten is the Chair of the 2nd International Conference on Energy Process Engineering (2nd ICEPE) hold in June, 2011. Since 2011 he is Member of the Advisory Board of the VDI- GVC (Association of German Engineers- Chemical and Process Engineering).

Development of renewable hydrogen energy systems

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Today, we are consuming the solar energy accumulated on earth in million years as fossil fuels at a rate which is much faster than it is stored by photosynthesis. Alternative energy sources such as solar, wind, wave, geothermal and nuclear are today’s need of carbon neutral technologies either as replacement of some of the existing ones or as producing new sources such as; biofuel, biogas and hydrogen, to increase the energy supplement of the world. Besides the source, today’s engineers are very much concerned about how to utilize these energies in a more efficient way. There is a solution for future, a new energy carrier system that is hydrogen. Hydrogen can be produced from primary energy sources, it can be stored and it can be converted directly to electricity in fuel cells efficiently when it is needed. Hydrogen energy system is bio-analog strategy for the sustainable future. Photosynthesis is the most efficient way to store solar energy. Plants, algae and photosynthetic microorganisms have developed their energy transduction centers and they know how to do this energy transformation and storage. Man exploit photobiological and photobiomimetic production of hydrogen. Biological hydrogen production processes, namely biophotolysis, dark fermentation and photofermentation, offer the prospect of producing hydrogen from renewable sources. Rhodobacter species are photosynthetic purple non-sulfur bacteria that can produce hydrogen from small-chain organic acids derived from biomass at the expense of light energy.

Since the fuel consumption rate is very high, biohydrogen need to be produced at a much faster rate with new strategies based on energy bionics. These processes should provide a net energy gain, be economically competitive, and be producible in large quantities without reducing the food supplies. Further research is needed in all fields to be competitive with conventional technologies.

Hydrogen- powered fuel cell electric vehicle option is a clue for 21st century’s people how to change their consumption habits for a sustainable future.

Inci Eroglu

Inci Eroglu is Professor in Middle East Technical University Chemical Engineering and Biotechnology Departments, where she leads a research group on Fuel Cell Technolagy and also co-leader of METU Biohydrogen Research Group Since 1990, her research has been concentrated on biological hydrogen production, alkaline and proton exchange membrane fuel cells. She is an author of more than 100 scientific articles related to hydrogen energy, published in journals and international conference proceedings and co-author of several book chapters. She represented Turkey in International Energy Agency- Hydrogen Implementation Agreement (IEA- HIA Task-21). She is a member of the Executive Board of International Association of Hydrogen Energy (IAHE) since 2006. She is an elected member of the METU University Senate.

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Chemically stable materials for the development of reversible solid oxide fuel cells based on proton conducting electrolytes

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The high cost of solid oxide fuel cells (SOFCs), associated with their high operating temperatures, hampers their broad use and causes long-term stability problems. A step forward towards reducing the SOFC working temperature at 600°C or below can be the use of high temperature proton conductor (HTPC) oxides as electrolytes, due to their lower activation energy for proton conduction (0.3-0.6 eV), with respect to oxygen-ion conducting electrolytes [1]. We have recently made significant progresses following various strategies [2] in the development of chemically-stable HTPC electrolytes by improving the sinterability of Y-doped barium zirconate (BZY) [3], which offers excellent chemical stability against CO_2 and H_2O reaction and high bulk conductivity [4], but low conductivity values for sintered pellets due to the presence of blocking grain boundaries. Co-doping BZY with Pr allowed obtaining a chemically stable, sinterable electrolyte that showed a conductivity of 0.01 S/cm at 600°C.

However, efficient cathodes need to be developed to avoid polarization losses at such a low temperature [5]. We followed a rational approach to tailor the cathode materials with low overpotential, considering that the materials should concurrently possess electron, proton and oxygen-ion conductivities, given the different species involved in the cathode reactions, and we succeeded in obtaining an area specific resistance as low as 0.157 Ω cm^2 at 600°C [6].

The development of these materials allowed us to start investigation on solid oxide electrolysis cells (SOECs), where the use of HTPC electrolytes can alleviate the problems encountered with oxygen-ion electrolytes, which are high working temperatures, dilution of the produced H_2, and fuel electrode oxidation [7]. We were recently able to report first on the SOEC test using BZY electrolytes [8].

In this presentation, the past work on protonic SOFCs will be briefly summarized, and then the recent work on SOECs will be presented. In addition, preliminary results of the recent efforts in scaling up both planar and microtubular cells and in improving the performance through the tailoring of the nanostructure of cathode materials will be shown.

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Enrico Traversa

Professor Enrico Traversa's wide ranging research interests fall within the general framework of nanostructured materials for sustainable development including energy, environment, and healthcare. His recent research activity on solid oxide fuel cells (SOFCs), includes work on chemically stable proton conducting oxide electrolytes, miniaturized SOFCs, hydrocarbon-fueled SOFCs, and reversible SOFCs for energy storage. He has authored more than 500 scientific papers, with over 330 published in refereed international journals, has 16 patents, and has edited 30 books and special issues on journals. He is listed in the Essential Science Indicators/Web of Science as a highly cited researcher, both in the Materials Science and Chemistry categories, and has an h-index of 50.

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Recent Advances on Micro-Level Modeling of Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) are ceramic based electrochemical devices operating at high temperatures and generates electricity and useful heat energy utilizing various fuels at a high efficiency. The main structure of the cell comprises a dense electrolyte coated with two porous anode and cathode electrodes. The electrolyte is responsible for the transfer of oxide ion while the electrochemical reactions take place in the electrodes. The cell performance is limited by the number of reaction zones known as triple/three phase boundaries (TPBs). Therefore, the electrodes play a crucial role in achieving high power as well as long service life. When the requirements that SOFC electrodes should meet are considered, the most successful electrode materials seem to be composite ones including ionic and electronic conductive phases with pores for the gas transport. However, this combination is not enough alone since the contiguous contact of these three phases within the electrodes is also necessary to obtain electrochemically active reaction zones. The number of these areas can be a useful metric for predicting the cell performance or provide a relationship between the performance and microstructure. The determination of the electrochemical reaction zones at micro-scale and the microstructural parameters influencing their density are required to link the microstructure to the performance.

Therefore in this paper, micro-modeling studies of SOFC electrodes through advanced microstructural characterization are reviewed.

Dr. Mat was born in 1968, Giresun, Turkey. He graduated from Istanbul Technical University as a mechanical engineer in 1989. He completed his MsC again in the same University. Receiving Turkish Higher Educational Council scholarship, he attended Northeastern University for his PhD studies. After serving as a Post-Doc in Northeastern for a while, Dr. Mat started in Nigde University, as an assistant Professor in 1998. He was promoted to associate professor and full professor positions in 2001 and 2007 respectively. He is the president of Meliksah University since June 2013.. Dr. Mat served as advisor for a number companies in Turkey and developed a solid oxide fuel cell and Pem Electrolyser and filed several patents during these studies. Dr. Mat is also recipient of several prestigious awards such as outstanding young scientist award (Turkish national Academy of Sciences, TUBA), TUBITAK Encouragement award, METU Parlar award. Dr Mat is author or coauthor of more than 50 scientific journal papers and holds two national and an international patents.

Oxygen reduction kinetics on perovskite oxides in solid-oxide fuel cells: effects of dissimilar interfaces and surfaces

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Interfaces between dissimilar oxides are attracting significant interest for their potential role in accelerating charge transport and surface reaction kinetics. If well understood and controlled, they can provide a new way to enable high-performance solid-oxide fuel cells, separation membranes as well as fast switching memristors. For example, recent studies have demonstrated that cobaltite hetero-interfaces exhibit orders of magnitude faster oxygen reduction kinetics compared with either single phase. The interfacial strain fields and electronic interactions between the two phases as well as the effect of these interactions on the surface chemistry are the likely mediators behind such an unprecedented enhancement. The underlying mechanisms must be understood quantitatively, so that we can go beyond isolated and empirically found interface or surface structures to rationally designing dissimilar oxide interfaces with superior properties. Towards this goal, we used a novel combination of in-situ scanning tunneling spectroscopy, high energy x-ray photoelectron spectroscopy and density functional theory calculations. In this talk, I will present our results on the local electronic structure, defect chemistry and surface chemistry at nanometer resolution in model thin films, multilayers and vertically aligned nanostructures. These recent results are encouraging for an improved understanding of oxide hetero-interfaces and surfaces at elevated temperatures, and could enable the discovery of new interfaces with fast oxygen transport and oxygen reduction kinetics.

Professor **Bilge Yildiz** Bilge Yildiz is an associate 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 degree at MIT in 2003 and her BSc degree from Hacettepe University in Turkey in 1999. After working at Argonne National Laboratory as research staff, she returned to MIT as an assistant professor in 2007. Her research centers on molecular-level studies of oxygen exchange kinetics on surfaces at elevated temperatures, under stress and in reactive gases, by combining in situ surface sensitive experiments with first-principles calculations and novel atomistic simulations. The scientific insights derived from her research impact the design of novel surface chemistries for efficient and durable solid oxide fuel/electrolysis cells, and for corrosion resistant films in a wide range of extreme environments as in nuclear energy generation and oil exploration. She was the recipient of the Charles Tobias Young Investigator Award of the Electrochemical Society in 2012, the Somiya Award of the International Union of Materials Research Societies for international collaboration in 2012, and an NSF CAREER award in 2011.

Effect of the rare earth on the structural and hydrogen sorption properties of A_2Ni_7 (A = Y or Sm)

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To meet the continuously increasing demand in energy density, the development of new intermetallic alloys as negative electrode for Nickel-Metal Hydride (Ni-MH) batteries is sublect of numbers studies [1]. The optimum alloy should meet the requirements for a high specific capacity, good cycling stability and low cost.

Recently, some research groups have reported that the A_2Ni_7 (A = La, Mg) compounds present interesting discharge capacity (400 mAh/g) and relative good cycle life [2-4]. Those alloys can be described as the stacking of [A_2B_4] and [AB_5] subunits along the c axis. The La-Mg-Ni system has been largely studied, but A_2Ni_7 systems with other rare earths have been rarely reported [5]. In the present work, Sm_2Ni_7 and Y_2Ni_7 compounds have been synthesized. X-ray diffraction and EPMA indicate that both compounds were successfully synthesized. Their hydrogenation properties and electrochemical performance will be presented.

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Synthesis of A_2B_7 Type Hydrogen Storage Alloys in the Molten Salt

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$La_2(Ni_{1-x}Co_x)_7$ x = 0, 0.05, 0.1, 0.2 type hydrogen storage alloys were synthesized in the molten $CaCl_2$ electrolyte at 850°C and the charge/discharge characteristics of the synthesized alloys were observed. Sintering (at 1200°C for 3 h) caused the hygroscopic La_2O_3 to disappear and the non-hygroscopic La_2NiO_4 and $LaNiO_3$ to form. LaOCl was observed to form chemically upon contact of the sintered pellet with the melt [1]. The X-ray diffraction peaks indicated that the sinter products reduced to $LaNi_5$ within 4 h electro-deoxidation process. The reduction kinetics of LaOCl was relatively slow. This sluggish reduction caused formation of the target La_2Ni_7 phase only after 6 h electro-deoxidation. The final La_2Ni_7 alloy structure with small amount of retained $LaNi_5$ was obtained after 10 h electro-deoxidation and this structure did not change upon further electrolysis. The presence and increase in the cobalt content of the alloy did not change the reduction scheme and the alloy phase structure of the alloy [2]. The electrode performance of the alloys, however, improved as cobalt content of the alloy increased. While the maximum discharge capacity of La_2Ni_7 was 207 mA h g^{-1}, that of $La_2(Ni_{0.8}Co_{0.2})_7$ was 332 mA h g^{-1} (Figure 1). The results obtained in this study showed that the electro-deoxidation technique is very promising in the synthesizing of the high performance hydrogen storage alloys.

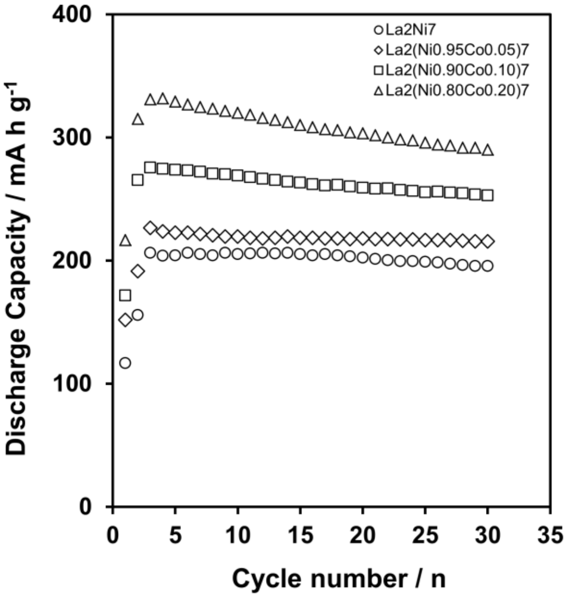

Figure 1. Discharge capacities of the synthesized alloys.

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In-situ Formation of Mg-Ni Intermetallics by a two-step Electrochemical Technique

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Mg_2Ni is a low-cost, light weight and lowtoxic hydrogen storage material. Hydrogenation reaction of Mg_2Ni results in the formation of 3.6 % wt. hydrogen containing Mg_2NiH_4 [1]. Reversible characteristics of Mg_2Ni was also reported in the literature [1]. It is commonly believed that the hydriding properties of Mg_2NiH_4 strongly depend on their nanometer scale structures in terms of thermodynamic and kinetic aspects [2].

Production of Mg_2Ni was found to be difficult by conventional melting mainly due to large melting point and vapor pressure differences between Mg and Ni. Other alternative routes for producing Mg_2Ni includes mechanical alloying, vacuum induction melting, vacuum arc melting, combustion synthesis, melt-spinning, repetitive rolling and isothermal evaporation casting. However, difficulties arise during handling, preparation and combination of Mg and Ni due to highly reactive nature of especially magnesium. This is one of the reasons that limits application area of Mg_2Ni besides its high working temperature and poor hydrogen desorption dynamics [3]. However, the desorption dynamics can be significantly improved by the use of nanostructured Mg_2Ni [3]. On the other hand, it is difficult and requires very long processing durations to achieve nanostructured Mg_2Ni by above processes.

Alternatively, electrodeoxidation of MgO-NiO mixtures were attempted [4] to form nanostructured Mg-Ni intermetallics. Complete reduction of NiO was achieved, but Mg_2Ni formation was not successful while $MgNi_2$ formation was obtained only in part. However, stepwise changes of applied potential during electrodeoxidation of NiO in an $MgCl_2$ containing electrolyte yielded the appearance of Mg_2Ni [5]. Therefore, successful electrodeoxidation of NiO to form Ni was complemented by $MgCl_2$ electrolysis to form Mg_2Ni. In this approach, electrochemical reduction of NiO particles to nickel powder was followed by in-situ formation of Mg-Ni intermetallics. Molten salt electrolysis of $MgCl_2$ was performed on the electrochemically formed nickel powder at the cathode of the same cell. By this way, nickel powder and magnesium were brought in contact with each other to form the intermetallic particles. The flow sheet for Mg_2Ni formation by the proposed method can be seen in Figure 1.

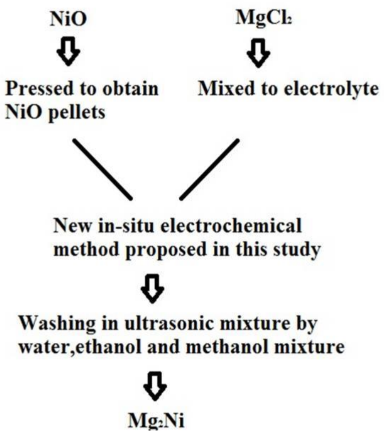

Figure 1. Mg_2Ni formation by the proposed method.

The products were characterized by XRD and SEM analysis. The quantitative results from Rigaku showed that more than 50 percent of the input Ni was converted to Mg-Ni intermetallics. Above findings were supported by Rietveld Refinement Method conducted by Maud and by mass balance of the samples.

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Tungsten disulfide nanoparticles as a medium for hydrogen storage

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The use of hydrogen in a distributed system requires an effective, safe, and stable storage solution. Nanostructured materials such as inorganic nanotubes (INT) and inorganic fullerene-like (IF) nanoparticles are appealing because of their extremely high surface area and layered structure, where potentially many sites can either chemi- or physisorb hydrogen. A newly developed technology enables the synthesis and production of pure IF and INT phases of WS_2 in commercial quantities, beyond tens of kg. This is why we initiated a project to test WS_2 INT and IF as possible candidates for hydrogen storage. These materials may allow hydrogen to be either chemi- or physisorbed inside their crystalline structure, inside hollow core of fullerenes/nanotubes or in the open interstitial pore spaces between the nanoparticles or nanotubes, on the surface or in the open interstitial pore spaces of nanotubes' powder mesh. Exposure to high pressure molecular hydrogen at 77-720 K was found to have measurable but limited absorption rate - up to 0.36 wt.%. Whereas treatment of the WS_2-INT and WS_2-IF by hydrogen and deuterium activated by microwave (MW) or radiofrequency (RF) plasma resulted in much higher value of absorbed hydrogen of ~0.5-1.5 wt.% so far. These results could be attributed to more effective interaction of activated vs. molecular hydrogen with nanoparticles substrate surface due to the strong either chemisorption of MW plasma activated hydrogen compared to weaker physisorption of molecular hydrogen, or to higher energy and momentum of the hydrogen molecules in the RF plasma. In addition, plasma originated ions and electrons interact with the nanoparticles and then can produce new or modify existing defects and pores, and so contribute to hydrogen diffusion and its stability following exposure to ambient atmosphere.

To determine the chemical nature of so absorbed deuterium, micro-Raman measurements were performed (see Fig. 1). For the RF plasma deuterated samples, a small peak centered at ~2970 cm^{-1} was observed. This feature was previously attributed to the D–D stretching mode, and, therefore, its appearance in our spectra proves that deuterium is present in the molecular form, as D_2. To finally prove that the Raman feature measured at 2970 cm^{-1} is indeed due to D_2, both IF and INT RF plasma deuterated samples were heated in vacuum to 450 ºC for 90 min. The intensity of the above Raman peak decreased to nearly zero supporting our assumptions.

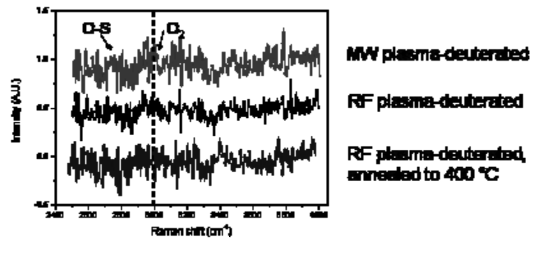

Figure 1. Micro-Raman spectra of the deuterated WS_2 nanoparticles.

TEM investigation of the deuterated WS_2 nanoparticles showed some increase of the interlayer distance as compared to reference materials along with changes in the defects distribution.

To investigate the possible effect of ions on both types of the target materials (IF and INT), they were exposed to FIB of Ga^+ ions for different doses. Following ion bombardments, the samples were analyzed by SEM, EDS, and micro-Raman. The primary effect was in the drastic change of the near surface structure and morphology of the bombarded region. From SEM images, melting or sublimation with subsequent recrystallization of the nanoparticles takes place. This is confirmed by micro-Raman measurements showing degradation of the crystalline perfection by decrease in the intensities of the characteristic peaks of WS_2. However, no contamination, oxidation, or decomposition of the substrate materials was detected after FIB treatments. These results can explain why physisorbed hydrogen is stable at the room temperature in the plasma-treated IF and INT, indicating that such "melting" could happen then resulting in closing some of the pores through which hydrogen atoms diffuse inside these layered nanoparticles.

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Dr. Alex Laikhtman obtained his PhD in Physical Chemistry (Technion, Haifa) on the subject of electron, photon and ion interactions with diamond surfaces. Before that he studied toward B.Sc and M.Sc in chemistry in the same institution.
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Synthesis of Palladium Incorporated MCM-41 via Microwave Irradiation and Investigation of Its Hydrogen Storage Properties

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The demand to new energy sources due to the shortage of fossil fuels makes hydrogen one of the best alternatives as it is an environmental friendly energy carrier. However, the limitations in the hydrogen storage due to its low density stand as a bottleneck against the effective use of hydrogen. Metal hydrides, porous carbon structures, and mesoporous silica materials attracts attention as hydrogen storage media [1]. MCM-41 that is a mesoporous zeolite may be considered as a good candidate as it has large surface area and pore size, uniform pore distribution [2, 3].

Aqueous solution of sodium silicate with 27 wt.% SiO_2 (AppliChem Inc.) was used as silica source and hexadecyl trimethyl ammonium bromide (98%, ABCR Gmbh) was used as surfactant. Pd loaded MCM-41 was synthesized using Palladium (II) chloride (99.99%, Aldrich Chem Co.). The surfactant was slowly dissolved in deionized water at 40 °C. Sodium silicate was added dropwise to the surfactant and stirred until the mixture was homogenized. The mixture with pH adjusted to 11 is then microwave heated at 90 & 120 W for 30 min. The resultant product was then filtered, washed with distilled water until the pH is neutralized. Pd was incorporated to the dried solid that was synthesized at 120 W before calcination with a weight ratio of 10:100 Pd: MCM-41. The aqueous solution of MCM-41 and Palladium (II) chloride was stirred at room temperature for 24 h. After the mixture was homogenized, it was centrifuged, dried at 80°C for 24 h, and calcined as described.

The morphology and structure of the Pd doped MCM-41 were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The functional groups on the MCM-41 surface were investigated by Fourier transform infrared spectroscopy (FTIR). The surface area, pore size and adsorption capacity of MCM-41 were measured by Brunauer-Emmett-Teller (BET) method. The hydrogen adsorption capacity measurements were conducted at ambient temperature (298 K) and up to 10 bar pressure by the Intelligent Gravimetric Analyzer (IGA).

The adsorption and desorption isotherms of the samples show the characteristics of Type IV according to IUPAC classification (Figure 1). The linear increase in the adsorption isotherms at low pressures ($P/P_0<0.25$) is attributed to the monolayer adsorption of N_2 on the pore walls [3]. The sharp increase at $0.25<P/P_0<0.40$ is due to the capillary condensation inside the walls. The long plateau at $P/P_0>0.40$ show that as a result of the saturation of the capillary condensation the adsorption continues on the surface of the sample [2]. The narrow hysteresis of the samples as well as the sharp increase at low pressures are characteristics of mesoporous materials.

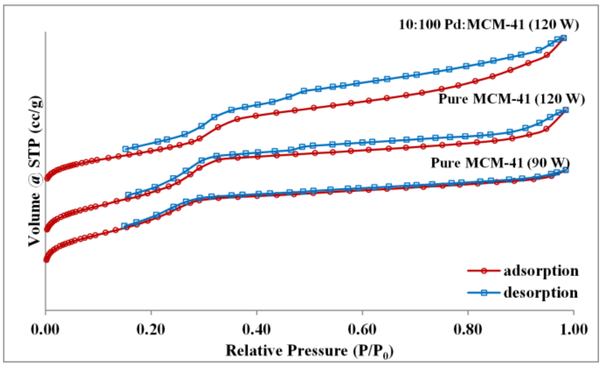

Figure 1 Nitrogen adsorption-desorption isotherms at 77 K

It was observed that pure MCM-41 had large surface area 1447-1115 m^2/g and roughly 3.18-3.54 nm pore size according to calculations with DFT method. High specific surface area and large pore size of the samples suggested that the synthesized MCM-41 can be proper candidate for hydrogen storage.

The hydrogen storage capacities of pure MCM-41 and. 10:100 Pd:MCM-41 samples were measured at ambient temperature (298K) with increasing pressure up to 10 bar. The results showed that pure MCM-41 had hydrogen uptake of 0.69 and 0.83 wt% for samples synthesized at 90 and 120 W, respectively and Pd incorporation enhanced the hydrogen uptake of MCM-41.

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Decoration of graphene sheets by Pd/Al_2O_3 particle pairs: synthesis, characterization and applications in hydrogen storage

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Abstract

In this study reduced graphene oxide was prepared from natural graphite by Hummers' method. Few layers graphene was decorated by Alumina and Palladium with an incipient wetness impregnation method and it was used as hydrogen adsorbent. The hydrogen adsorption isotherm of the RGO-Pd/Al_2O_3 was determined at room temperature and pressures up to 10 bar.

Keywords: Graphene, hydrogen storage, adsorption isotherm.

Introduction

Recently, graphene, a single atomic layer sheet of sp^2 bonded carbon, has gained tremendous attention because of its unique properties such as high surface area and electrical mobility. It was proposed that graphene has a great potential to become an ideal substrate for hydrogen storage application. Studies revealed that dispersion of transition metals such as Pd on carbon materials improves hydrogen storage capacity by chemical adsorption [1]. In this work we decorated reduced graphene oxide (RGO) by Pd/Al_2O_3 particles (RGO-Pd/Al_2O_3) via incipient wetness impregnation method and effect of Pd/Al_2O_3 particles on hydrogen adsorption capacity of RGO was studied.

Experiment

Graphene oxide (GO) was obtained by the modified Hummers' method. Certain amount of GO was dispersed in water and sonicated for 2 hours. Alumina and palladium were added to the solution. After drying, the solid mixture was reduced by thermal treatment at 1000 °C.

Samples were characterized by X-ray diffraction (XRD), Raman spectroscopic analysis and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDS) analysis. Specific surface area of samples was determined by analyzing the standard nitrogen adsorption isotherms (BET) at 77 K. The hydrogen adsorption isotherms were measured at room temperature up to 10 bar by the Intelligent Gravimetric Analyzer (IGA).

Results and discussion

Firstly, graphite, GO and RGO samples were characterized by XRD and Raman spectroscopy. Interlayer spacing (d-spacing) of 3.3 A° and 8.37 A° were calculated for graphite and GO, respectively. Reduction of GO to RGO was confirmed by appereance of (002) peak, characteristic peak for RGO, and absence of (001) peak, characteristic peak for GO, in XRD patterns of samples [2]. Raman spectroscopy was used to find the structural information required to define the density of defects in graphene sheets. After oxidation, a high I_D/I_G=0.88 was observed in Raman spectrum of GO due to existence of large amount of oxygen containing functional groups. Reduced samples, RGO and RGO-Pd/Al_2O_3, exhibited higher I_D/I_G ratios of 1.02 and 1.1, respectively. The latter obseravtion is possibly a result of the presence of more defects and added particles [1]. Fig. 1 ascribes the SEM image of RGO and RGO-Pd/Al_2O_3. Transparent flaky graphene sheets were observed in Figure.1a that is the indicative of exfoliated graphene sheets with layered structure. Fig.1b displays homogeneous dispersion of Pd/Al_2O_3 particles on the exfoliated graphene sheets. Presence of dual particles, as shown by Fig 1.b inset, throughout the sample can be attributed to deposition of Al_2O_3 and Pd particles on the graphene sheets simultaneously. Elemental analysis of RGO-Pd/Al_2O_3 sample was shown in Fig. 1c. Appearance of the peaks at ~1.8 and ~2.8 keV indicates the presence of Al and Pd in the sample, respectively.

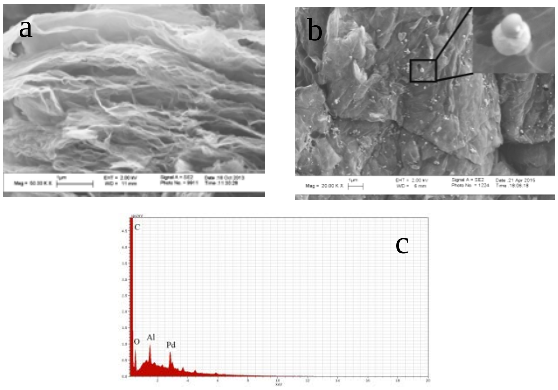

Figure 1. SEM images of (a) RGO (b) RGO-Pd/Al_2O_3 and (c) EDS spectrum of RGO-Pd/Al_2O_3.

Results of IGA showed the enhancement of the hydrogen storage capacity in Pd/Al_2O_3 decorated graphene compare to pristine graphene specimen.

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Effect of patterned catalyst layer on gas evolution behavior in regenerative fuel cells

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Regenerative fuel cells (RFC) are instruments which combine fuel cell and electrolyzers at one device. RFCs can produce highly pure hydrogen up to 99.9999 % [1] at an elevated pressure with high efficiency and can directly store it for utilization in the same device to generate electricity. Recently, it has been achieved that the round-trip efficiency of 42.2 % which is close to fuel cell single device efficiency and far above to today's ICEs [2].

In an earlier study, it has been proved that the water accumulation on the cathode compartment (hydrogen side) reduces the electrolyzer cell performance due to the mass transfer limitations [3]. The gas evolution behavior from a conventional Membrane Electrode Assembly (MEA) has already been investigated in previous study [4].

Reducing the amount of precious catalyst loading on the membrane is one of the targets in fuel cells and electrolyzers. On the other hand, the area under the rib is affected from flooding at high current densities. Likewise, gas accumulation and residing for longer time was proved to happen under the ribs in regenerative fuel cells [4]. Therefore, two phase behavior of patterned MEA is investigated in this study.

Pattern of the catalyst layer is designed to have strips with 1 mm width for each loadings (i.e. lower and standard loadings) by using a micro-inject printing technique. Lower catalyst loading is applied to under the rib and thus, the area under the channel contains standard catalyst loading as shown in Figure 1. The cell has five channels and therefore five lower and six standard loadings is applied to membrane, while fabrication MEA. Only the cathode side is fabricated with standard loading, while anode remains with standard MEA pattern. The cell is assembled and tested in both modes – electrolyzer and fuel cell. Test results are compared with the standard MEA's. The temporal variation of gas-water two phase variation of the cell with patterned MEA is shown in Figure 2. In fuel cell mode, more homogenous water accumulation is observed with patterned MEA.

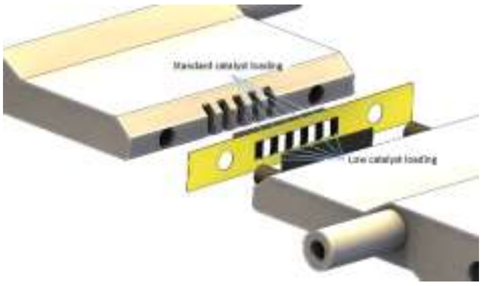

Figure 1. Patterned MEA and regenerative fuel cell design

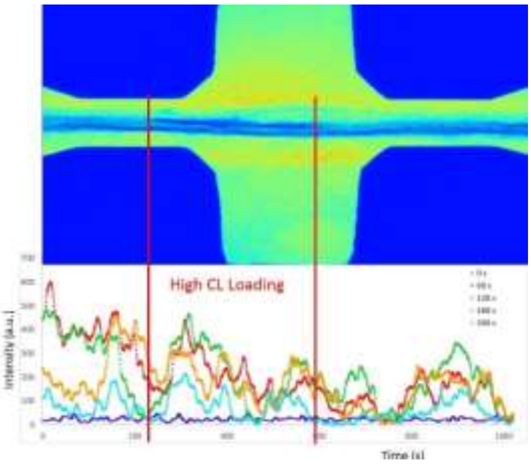

Figure 2.Temporal variation of intensity profile for the patterned MEA in electrolysis mode.

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Effects of Fabrication Parameters on the Performance of Solid Oxide Electrolyzer Cell

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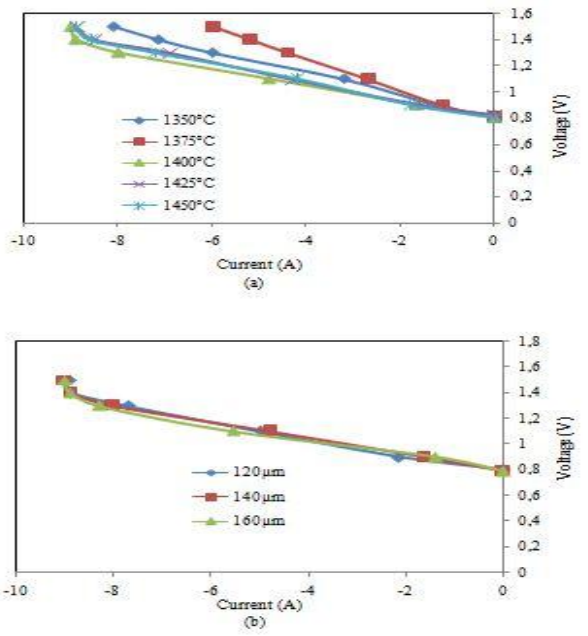
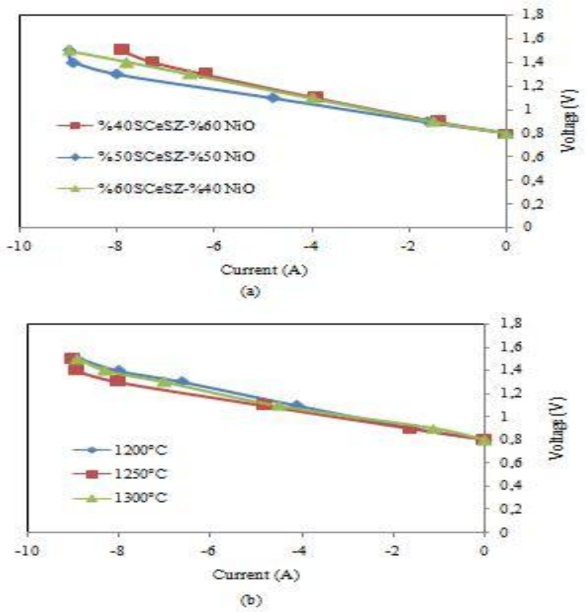
In the present work, ScSZ based electrolyte supported solid oxide electrolyzer cells are fabricated via tape casting and screen printing techniques. Since the performance of the cell is directly related with the fabrication parameters, the effects of the electrolyte/electrode sintering temperatures and thicknesses as well as the composition of both electrodes on the hydrogen production rate are investigated experimentally. The performances of the cells with different properties are measured under the same operational conditions to optimize the selected fabrication parameters.The effect of the electrolyte sintering temperature and thickness on the cell performance are shown in Figure 1. The change in the cell performance with cathode composition and sintering temperature, on the other hand, are illustrated in Figure 2.



(a)

(b)

Fig.-1. The effect of the electrolyte sintering temperature (a)and electrolyte thicknesses (b) on the cell performance



(a)

(b)

Fig.-2. The effect of the cathode composition (a) and cathode sintering temperature (b)on the cell performance

The results show that the fabrication parameters considered for the solid oxide electrolyzercell are found to have a significant effect on the hydrogen production.

Hatice Korkmaz was born in 1990, and grew up Kayseri. She earned graduate from İstanbul Aydın University and masterdegrees from Nigde University. Korkmaz has beenboth workingas a project assistant and maintainig MSc studiesat Nigde University since 2013. She interests termodynamics, heat transfer, numerical analysis and clean energy applications as like SOFC and SOEC.

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Preperation and characterization of N-doped graphene as a matal free catalyst for the oxygen reduction reactions in acidic and alkaline media

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Development of state-of-the-art electrocatalysts with inexpensive and commercially available materials to facilitate sluggish cathodic oxygen reduction reaction (ORR) is a key issue in the development of fuel cells and air batteries [1]. Nitrogen-doped carbons are generally accepted as a potential substitute for platinum-based catalysts due to their high ORR activities, low cost and excellent tolerance toward methanol [2]. Among these materials, nitrogen doped graphene (N-GN), has attracted growing interest in the past few years.

This study reports a low cost procedure for the synthesis of N-GN through an organic sol-jel methode by direct pyrolysis of grapheneoxite (GO) and melamine gel mixture. Melamine, a low cost industrial chemical, was chosen as the N source and spacer to prevent the reaggregation of GO sheets. With the annealing of dried GO-melamine gel in Ar atmosphere at 1050 °C, N atoms were doped into the GO sheets, resulting in the formation of N-GN. Efficiently avoided reaggregation with melamine as spacing through gelation process, the obtained N-GN showed high spesific surface area (SSA) of 585 m^2/g. The scanning electron microscopy (SEM) images of the N-GN catalyst and GO are shown in Figure 1. The GO contains flakes and 3D particles that have size of tens of nanometers. After the nitrogen doping process, typical crumpled silk veil wave-like morphology and porous architecture of graphene structure was observed. The Raman spectra of N-GN exhibit two remarkable peaks at around 1345 and 1575 cm^{-1} corresponding to the well-defined D band and G band, respectively. The intensity ratio (I_D/I_G) of the D to G bands of GO (0.84) was decreased to 0.73 for heated GO (rGO) and 0.40 for N-GN catalyst. This indicates that partial sp^2 domains were restored at different levels, and the graphitic degree of N-GN samples was also improved to the reduction effect and "self-repairing" of the graphene layer at high temperature consistent with the SEM results. X-ray photoelectron spectroscopy (XPS) characterizations were performed to analyze the elemental composition and nitrogen bonding configurations in N-GN catalyst. With a content of GO in dried mixture of %15, the doping level of 1.6% (N atom %) has been achieved. The high resolution XPS showed that five different N containing species have been formed on graphene sheets and pyridine-like nitrogen is the main component in our N-GN catalyst.

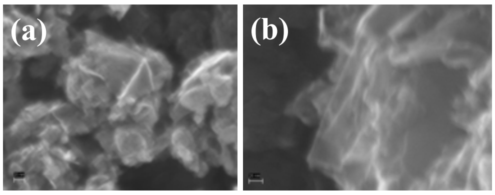

Figure 1. SEM images of **(a)** GO and **(b)** N-GN samples.

The electrocatalytic activity of N-GN catalyst was assessed by cyclic voltammetry (CV) in 0.1 M KOH and 0.1 M $HClO_4$ solution saturated with nitrogen or oxygen at different scan rates. To further investigate the electrocatalytic activity of the catalyst, linear sweep voltammetric (LSV) measurements were performed and the results have been given in Figure 2.

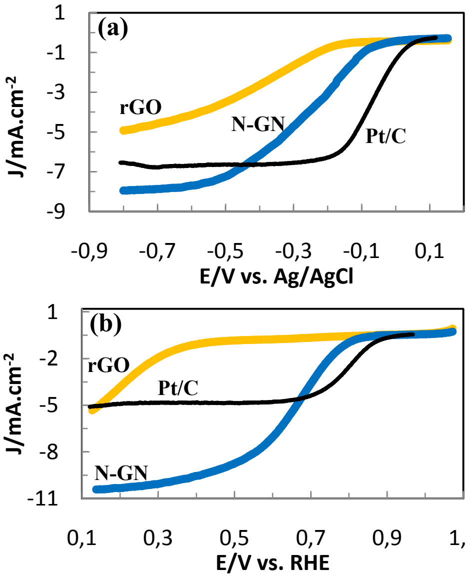

Figure 2. LSV curves of samples on RDE in O_2 saturated **(a)** 0.1 M KOH and **(b)** 0.1 M $HClO_4$ solutions at a rotation speed of 1600 rpm.

In spite of the poor N content, N-GN samples exhibited much enhanced ORR activity in terms of current density and onset potential in both acidic and alkali media giving valuable information about the ORR mechanism of N-GN catalysts.

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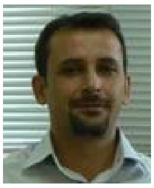

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Preparation of Carbon supported LiH and $LiNH_2$ Nanoparticles

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The Li-N-H system is of great interest to hydrogen storage due to its ability to store 6.5 wt% of hydrogen[1]. Unfortunately the system suffers from a number of issues such as high temperature hydrgen release and the release of ammonia which is a poison for a cell. Many apparochaes have been taken to improve on these aspects and one such method is nanoconfinement which, in the case of other light metal hydrides has yielded big improvements in hydrogen storage properties[2]. However, there are very few examples of this being applied to the Li-N-H system[3] as many of its components are insoluble in most solvents and decompose before melting. This prevents the use of techniques such as solution impregnation and melt infiltration. therefore a procedure for preparing these materials has been developed.

Two different nanocomposites have been successfully prepared, LiH/C and $LiNH_2$/C (figure 1), which has so far not been achieved before. The procedure consists of two steps: first solution impregnation of butyllithium and subsequent decomposition under hydrogen yields LiH nanoparticles. The second step involves treatment of this nanocomposite with ammonia gas to form $LiNH_2$. Nanoconfinement of both compounds yields reduced hydrogen release temperatures compared to the bulk and physical mixture systems, due to a combination of particle size effects and interaction with the carbon support itself. Particle sizes can be tuned from 100 nm to 6 nm depending on the preparation conditions. The LiH/C nanocomposite begins release of hydrogen at 150 °C when supported on a carbon aerogel with average pore diameter of 6 nm, a reduction of roughly 200 °C compared to a LiH/C physical mixture. The $LiNH_2$/C nanocomposite shows release of both ammonia and hydrogen, although the latter is believed to be due to reaction with the support. The ammonia release profile is significantly altered upon nanoconfinement, yielding ammonia release as low as 50 °C compared to 300 °C in the $LiNH_2$/C physical mixture. At lower loadings no hydrogen is released, yielding exclusively ammonia.

The effects of support type, temperature and precursor used in solution impregnation as well as pore size and loading have all been investigated for both materials. In general the use of lower temperatures to decompose butyllithium to LiH and a tertiary butyllithium precursor instead of n-butyllithium yield significantly smaller LiH and $LiNH_2$ particles. Carbon aerogels are a better suited support due to their more robust pore structure while graphitic supports cause the release of ammonia at higher temperatures in the case of $LiNH_2$/C nanocomposites. Smaller pores, which facilitate the formation of smaller particles, allow the release of ammonia at lower temperatures. In short a procedure for preparing two novel nanocomposites has been developed and a variety of conditions can be used to tune the particle size and gas emission profile. This provides many unique opportunities for applying these new materials to applications that include hydrogen storage, ammonia storage and battery technology.

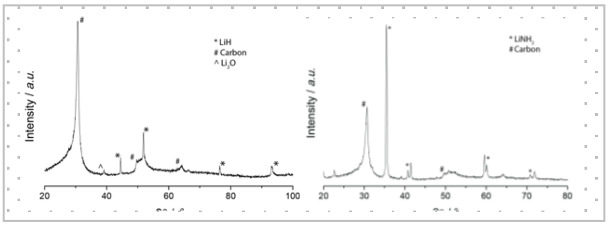

Figure 1. X-ray diffraction patterns for the LiH/C (left) and $LiNH_2$/C nanocomposites supported on high surface area graphite.

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Characterization of the Electronic Structure of Transition-Metal Catalysts by Magnetic Resonance Spectroscopy

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Hydrogen will play a crucial role in future renewable energy technologies and will enable clean energy storage. Many microorganisms use molecular hydrogen as an energy source or protons as an electron sink where hydrogenases are used as catalysts [1a]. Inspired from nature, synthetic transition metal catalysts which mimic the function of the active site (Figure 1a) of [FeFe] hydrogenases have been developed [1-5]. These cataylsts are also used in recently developed fuel cells [1b]. This presentation will mainly focus on the characterization of the electronic structure of bio-inspired catalysts in various spin and oxidation states giving insight into their redox cycles [2-5]. By means of magnetic resonance spectroscopy, local information on the spin properties of such catalysts can be understood. Interaction of the unpaired electron with the applied field gives information about the electronic properties of the metal center. The local symmetry of the metal center up to 0.1 nm from the unpaired electron can be investigated by continuous wave electron paramagnetic resonance (CW EPR). Furthermore, advanced pulsed EPR techniques such as hyperfine sublevel correlation (HYSCORE) and electron nuclear double resonance (ENDOR) can be used to track the hyperfine interactions of the nuclei and the unpaired electron (Figure 2). This reveals information about the spin density distribution over the molecule which is especially important when the crystal structure of a molecule cannot be obtained in certain oxidation states. In this presentation, several examples (e.g., Figure 1b,c) will be presented where a theory-supported spectroscopic approach (with FT-IR, EPR, Moessbauer, as well as DFT) is applied for understanding structure-function relationship. It will be shown that not only the metal-core and direct ligands, but also the second coordination sphere have influence on the activity of the transition-metal catalysts [3, 4].

The investigation of trapped intermediates in their diamagnetic (e.g. Fe(II)) and paramagnetic (e.g. Fe(I), Fe(III)) states provides a comprehensive understanding of the working principles of such complexes and leads to newly designed, highly efficient catalysts which work under mild conditions. Apart from hydrogen conversion catalysts, a HYSCORE investigation for a boron containing iron complex will be discussed for which ^{11,10}B was resolved even residing remotely (2-3 bond-distance) from the metal center. The latter might be useful when investigating borohydrides as hydrogen storage materials.

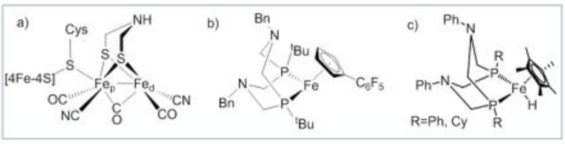

Figure 1. Active site of [FeFe] hydrogenase (a), bio-inspired catalyts presented in Ref. 5 (b), and Ref. 3 (c).

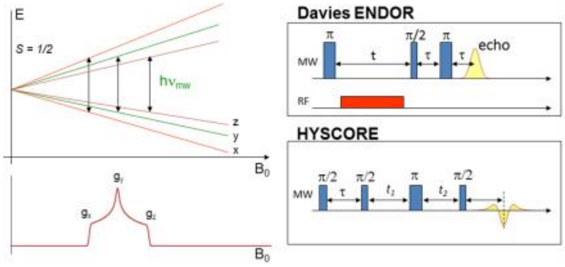

Figure 2. Left: resonance condition for EPR; Right: examples of advanced pulsed EPR techniques where microwave (MW) and radio frequency (RF) pulses are applied.

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Hydrogen decrepitation of Mg rich intermetallics

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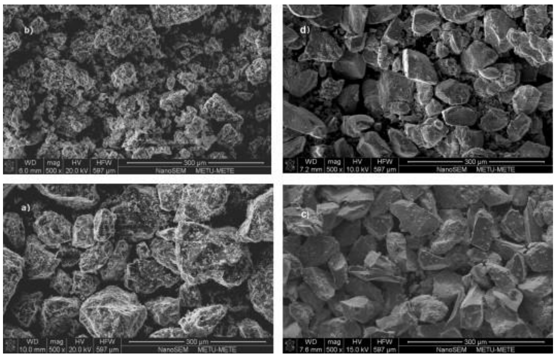
Hydrogen decrepitation is an efficient size reduction method used in the material processing. The method can be used in metals, alloys and intermetallic compounds that react with hydrogen. It typically consists of several cycles of hydrogenation and dehydrogenation treatments. The size reduction that occurs as a result of this treatment originates from volume changes associated with hydriding and dehydriding reactions.

The process of hydrogen decrepitation was of considerable interest in the 90s within the context of high performance magnets. The so-called "HDDR" treatment leads to a substantial reduction in grain/particle size of sintered/bonded magnets with highly improved coercive properties. In this treatment the alloy, e.g., NdFeB, upon hydrogenation disproportionates into a multiphase structure which, when brought to elevated temperature under vacuum, dehydrogenates, and the phases recombine together re-forming the original phase with a drastic reduction in particle size. Size reduction brought about by hydrogen decrepitation was also of interest in hydrogen storage alloys. With coarse powders, the reaction rate is often sluggish in such alloys. This makes it necessary to refine the powders. Thus, several cycles of hydrogenations are applied to the powders so as to improve their sorption kinetics. This is often referred as activation treatment where freshly generated surfaces arising from decrepitation reacts with hydrogen more easily.

A more deliberate use of decrepitation treatment was made in the production of hydrogen storage tanks. Rather than processing the powders to a fine size, the alloys are packed in storage tanks in the form of relatively coarse powders and they are then in-situ decrepitated by applying several cycles of hydrogenation and dehydrogenation. This ability of in-situ particle refinement is a considerable advantage in the production of hydrogen storage tanks. Although size reduction resulting from hydrogen decrepitation can be usefully employed to activate/improve the sorption kinetics, the same may also be associated with some adverse effects. With continued use, as a result of decrepitation, particles in storage tanks are more efficiently packed which leads to a creation of space between the storage material and the tank wall resulting in some loss of thermal conductivity . A more serious adverse effect occurs in negative electrode material in alkaline batteries. Metal hydride in the negative electrode as it decrepitates may lead to enhanced corrosion and thus lead to a loss of capacity with cycling [8].



SEM micrographs for; (a) Mg2Ni, starting powder, (b) Mg2Ni, hydrided powder after the tenth cycle, (c) Mg2Cu, starting powder and (d) Mg2Cu, hydrided powder after the tenth cycle. Note that original particle morphology in Mg2Cu is essentially the same before and after cycling.

In this study an investigation was carried out into hydrogen decrepitation of Mg rich intermetallics, namely Mg_2Ni and Mg_2Cu. These intermetallics are quite similar to each other except for the fact that Mg_2Ni hydrides directly forming Mg_2NiH_4, whereas Mg_2Cu when hydrided disproportionates into a two-phase structure. A total of ten sorption cycles was applied to the alloys and the resulting size reductions were monitored. The results showed that Mg_2Ni decrepitate quite fast with cycling, the greatest size reduction occurring within the first three cycles. The size reduction in Mg_2Cu, on the other hand, was quite sluggish. This was attributed to the disproportionation of the alloy which involve more extensive diffusion of the metallic species, counteracting some decrepitating effect of cycling due to ensuing particle sintering and growth.

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Electrochemical performance of silver coated $Li_{1.3}Mn_{0.666}Co_{0.167}Ni_{0.167}O_{2.4}$ cathode active material for rechargeable lithium ion batteries

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The active cathode material of LIBs, which acts as the source of lithium ions, determines the energy density of the lithium-ion cells [1]. Among all the reported cathode materials so far, the layered manganese-based lithium metal oxides (Li–Ni–Mn–Co) are attractive cathode materials, because of their lower cost, excellent cycling and thermal stability.[2] In particular,'layeredlayered' $x Li_2MnO_3\cdot(1-x)LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ lithium-rich manganese-based solid solution cathode materials which are comprised of two layered components, are known to deliver a discharge capacity of 200–250 mAh g^{-1} when charged to high potentials, and their capacities are almost twice than that of a conventional Li_xCoO_2 electrode[4].

However,layeredlayered' $x Li_2MnO_3\cdot(1-x)LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ lithium-rich manganese-based solid solution cathode materials still have several performance drawbacks, such as i- Large irreversible capacity loss (20–30%) in the first cycle, ii-Poor rate capacity performance, and iii-Poor cycling stability, especially at high current density[4].

In this study, we first prepared $Li_{1.3}Mn_{0.666}Ni_{0.167}Co_{0.167}O_{2.4}$ (LMNCO) with silver nanocoating which remarkably enhanced the electrochemical performances of LMNCO including cyclic stability and rate capability. The target layered cathode material (LMNCO) was prepared via a novel glycine-nitrate combustion method. The structure, morphology and electrochemical performance of the pristine and silver coated cathodes have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV) and galvantatic charge/discharge.

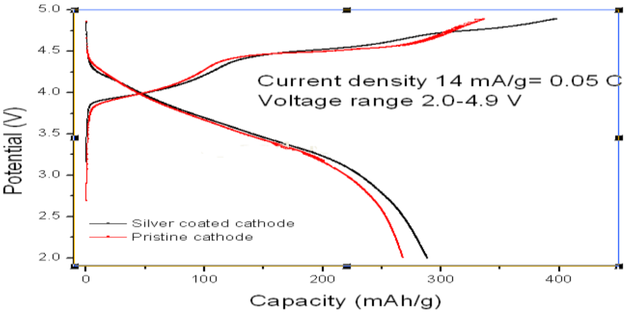

Figure 1. Initial charge-discharge curves of pristine and siver coated cathodes

The initial galvanostatic charge–discharge profiles of the pristine and silver-coated cathode material are shown in Fig.1.It can be obviously observed that the capacity of pristine sample is lower than silver coated one.

Fig. 2. compares the discharge capacity as a function of cycle number for the pristine and silver-coated LMNCO electrode at a constant current density of 0.05C (14 mA g^{-1}), 1C (280 mA g^{-1}) in a potential region between 2.0 and 4.9 V at 25 °C. Distinctly, the electrode coated with silver exhibits much better cyclic performance than the pristine electrode.

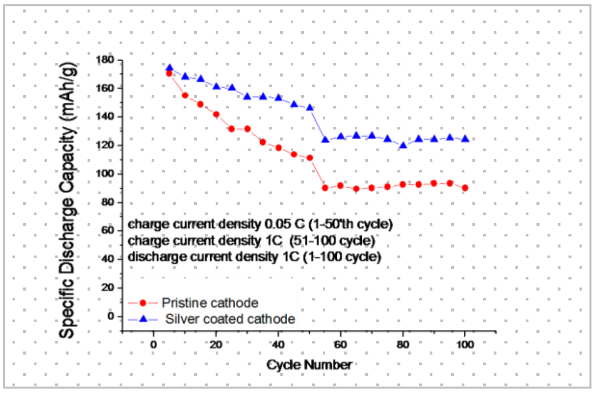

Figure 2. Cyclic performance of the pristine LMNCO and silver -coated LMNCO electrodes during 100 cycles.

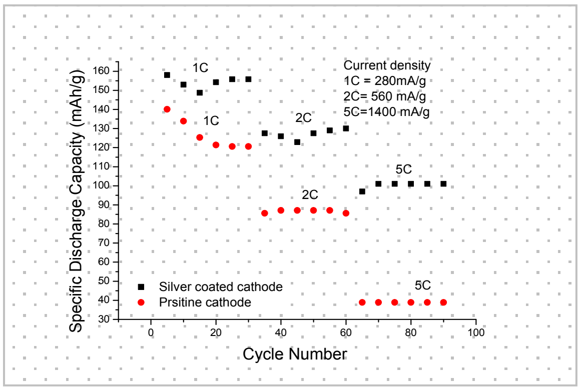

Figure 3. Cycling performance of pristine LMNCO and silver coated LMNCO electrodes.

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Production and Characterization of Silicon Particles with Nanowired Surfaces for Secondary Lithium-Ion Battery Anodes

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The rapid development of electronic devices, hybrid electric and electric vehicles increases the importance of lithium-ion battery systems. Because the potential of lithium batteries to store large amount of energy in a relatively small package is promising [1]. Although there are many research efforts since last decade, the development of lithium-ion batteries is still at the beginning. Particularly, the power density (rate capability), energy density, operating voltage, capacity, cost of materials, cycle life (deep discharge cycles) and safety issues of the lithium ion battery systems have to be optimized [2]. As the electrode materials play the key role in a battery, in order to increase the electrochemical performance and reduce the cost, designing better electrode materials is the main task.

In this research, the aim was to produce a good anode electrode which have high lithium chemical potential, high electronic conductivity, high capacity and good structure stability that can prevent significant structural change after charge/discharge process. Commercial batteries use graphite as anode material because of its low cost, low operation voltage and safety issues compared to the lithium ion itself. The capacity of graphite is 372 mAh g^{-1}. Diverse anodes are studied to solve low capacity problem of graphite [3]. Among other anode materials, silicon is the most promising negative electrode material for its theoretical capacity (4200 mAh g^{-1} for $Li_{22}Si_5$) which is far higher than commercialized carbon anodes. Although many studies have been conducted on silicon anode materials, the pulverization problem of silicon anodes due to high volume change of silicon (%400) during charge/discharge cycles could not be solved yet. With this study, several strategies were demonstrated to fabricate Si electrodes, that can afford high electrochemical performances for applications which require high power and high energy (capacity), using cheaper and easy methods that could be easily scaled up for commercial uses.

In this regard, metal assisted chemical etching technique was chosen to produce Silicon particles with nanowired surfaces. This method requires three fundamental conditions: (1) an oxidant to dissolve silicon (hydrogen peroxide (H_2O_2)), (2) a suitable complexing agent to remove native silicon surface oxide and solubilize ionic silicon (hydrofluoric acid (HF)), and (3) a transition metal that locally enhances silicon dissolution in the vicinity of the metal (silver (Ag)) [4]. In order to produce porous and/or nanowired silicon powder (nanowires on top of Si core), etching parameters were optimized. One and two step etching processes were tried with different parameters in order to obtain different type of structures. Figure 1 shows an example of obtained structure of silicon which consist nanowires on top of silicon core.

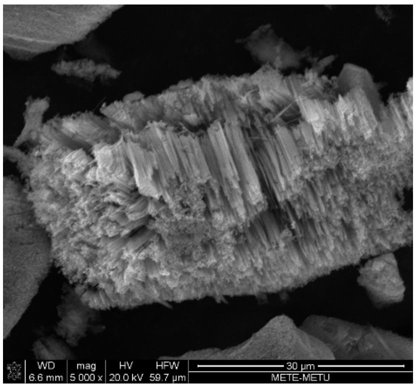

Figure 1. SEM image of produced Silicon particles with nanowired surfaces (nanowires on top of Si core)

After production, galvanostatic measurements were performed to investigate electrochemical performance of these anodes. For this purpose, cycle life, charge-discharge behavior and power density of the cells were measured.

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W doped $LiCoO_2$: Effect of different starting chemicals, doping contents and additional doping elements

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In this study, W doped layered $LiCoO_2$ samples are produced. Also, the effects of different starting chemicals, doping content and additional doping elements are sought. Two different methods, nitrate and hydroxide method, which are named according to the used starting chemicals are applied for producing precursor preparation. The optimum doping content, optimum calcination temperature and the better synthesis method are determined for producing single layered and ordered W doped $LiCoO_2$. It is seen that hydroxide method is superior than nitrate method with respect to producing single phase and ordered layered structure. With hydroxide method, best electrochemical properties are achieved when calcination is applied for 24 hours at 750 °C, doping content is 1 mole% of W and 1 mole% of Mn. When compared with undoped sample, retaining of initial capacity of this doped sample is nearly 2 fold higher. Analysis of structural parameters, measured impedances and calculated Li ion diffusivities suggest that better electrochemical activity in this sample is due to low polarization resistance not because of high solid state Li ion diffusivity but low charge transfer resistance at the interface.

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