2nd International Symposium on Materials for Energy Storage and Conversion

26-28 September 2017, Ortahisar, Cappadocia

Book of Abstracts/Proceedings



^{m}ESC-IS 2017

The Second International Symposium onMaterials for Energy Storage and Conversion

Edited by

Cansu Savaş Uygur and Tayfur Öztürk

26-28 September 2017

Ortahisar-Cappadocia



Participants in mESC-IS2017. The symposium took place from September 26th to 28th in Dilekkaya Hotel,Ortahisar Cappadocia with more than 120 participants. The event coincided with final meeting of HENERGY, an ERAfrica project combining teams from Norway, Turkey, Egypt and South Africa as well as a workshop organized within ENDAM, an initiative on energy storage supported by Ministry of Development, Turkey

Preface

2nd International Symposium on Materials for Energy Storage and Conversion, mESC-IS2017 follows the first organization back in 2015. The symposium, as before, provides a forum for discussion for recent progress made in three major activity areas, namely batteries-supercapacitors, fuel cells-electrolysers and solid state hydrogen storage. It took place from 26th to 28th September 2017 in Dilekkaya Hotel, Ortahisar in a beautiful setting of Cappadocia.

The summer school mESC-ISS is an integral part of this activity that preceded the symposium, i.e. 23rd to 25th September 2017. The school had two bases; one comprised overviews on such topics as batteries, supercapacitors and fuel cells and the other centered on electrochemical and material characterization techniques with emphasis on in-situ experiments. Colleagues who made this school possible would agree that it was well worth their effort. A substantial number of trainees from a variety of institutions in different disciplines, some new or early in their graduate study, some quite experienced, have benefited greatly from this experience.

The symposium comprised a total of 27 plenary presentations, 57 orals in three parallel sessions and 46 contributions in poster sessions. A total of three poster awards were presented on the closing session, the recipients were Aslihan Güler (Sakarya University), Neriman Sinan (Bursa Technical University) and the third poster award was shared by Serkan Sevinç (Gebze Technical University) and Burak Tekin (19 Mayıs University).



Closing session in mESC-IS2017. From left to right: Mykhaylo Lototskyy, Crina Ilea, Hiroshi Inoue, Jasmina Grbovic Novakovic, İnci Eroğlu, Montserrat Casas-Cabanas ,Rezan Demir-Cakan, Vlodymyr Yartys, Tayfur Öztürk, Junxian Zhang, Aslıhan Güler (recipient of the poster award), Şaban Patat, Kadri Aydınol, Hatem Akbulut, Duncan Fagg and Hüseyin Devrim.

We might also add that a fair number of contributions in this event originated from two activities jointly held within the symposium. One was the final year meeting of EU 7 ERAfrica HENERGY Project involving teams from Norway, Turkey, Egypt and South Africa. The other was ENDAM workshop, i.e. Research Center on Energy Materials and Storage Devices, an initiative supported by The Ministry of Development, Turkey.

This event was made possible with generous support of several institutions as well as of the sponsors. We would like to acknowledge TUBITAK-BİDEB for the support provided through the Program 2223B for the symposium and the program 2229 for the summer school. ENDAM workshop was made possible by funds from The Ministry of Development, Turkey which we also gratefully acknowledge.

Many of the papers appearing in this publication either as an abstract or full-length papers have been extended and published in two journals; papers on fuel cell and hydrogen were published as special issue of international Journal of Hydrogen Energy and papers on batteries were published in International Journal of Energy Research. We are grateful to Professor T Nejat Veziroglu and Professor Ibrahim Dinçer for their help in publishing the many of the contributions in this symposium

We are very happy to state that the mESC-IS series continues; the third symposium will take place in September 10th to September 12th 2018 in Belgrade. The fourth one, with the summer school and the symposium, is scheduled for 2019, the precise date and location is to be announced at mesc-its.org.

Tayfur Öztürk
on behalf of mESC-IS 2017 Organizing Committee



Summer School on Materials for Energy Storage and Conversion, mESC-ISS 2017 took place from September 23th to September 25th. A total of 55 participants have taken part in the summer school. The program had two bases; Overviews: Montse Casas-Cabanas (Na-ion Batteries), Dag Noreus (Alkaline Batteries), Mehmet Ali Gulgun (Intermediate Temperature Solid Oxide Fuel Cells) Saim Özkar (Catalysis), Saban Patat (All solid state Li-ion batteries), H.Emrah Unalan(Supercapasitors) and Material/Electrochemical Characterization : M. Kadri Aydınol (How to Make A Battery:Cell Making Processes), Gulfeza Kardas (Electrochemical Techniques), Y.Eren Kalay (Advanced Electron Microscopy), Meltem Sezen (Focus Ion Beam), Burak Ülgüt (Impedance Spectroscopy and its Applications in Energy Storage), Vlodymyr Yartys (Energy Storage Materials probed by In Situ Neutron and Synchrotron Diffraction).

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Characterization Techniques

State of the Art on Electron Microscopy Techniques for the Lithium Detection in Lithium Containing Energy Materials

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Lithium (Li), with its lowest 6.94 g/mole molecular weight and the lowest density (0.53 g/cm^3) within metals is one of the most important choice for the applications where the weight is important. Li alloys of Al, Mg and Zn improves mechanical properties [1-3]. Other areas that Li compounds used are as sintering additive for ceramic materials [4], a solid desiccant material for air conditioning [5] and optical applications [6]. However, the most widely use of Li is for the battery technology used in the mobile equipment and devices such as mobile phones, laptops, EVs and so on. Therefore for these areas, Li detection is very important in order to bring a new understanding to what is happening during production and usage. Not just the detection of Li, but the distribution of Li that is mapping is more important. Therefore, microscopy based techniques are the obvious choice for such investigations.

The detection of light elements like Li and hydrogen has been expected for a long time, but it has been very difficult because of the small atomic radius and also the small interaction with incident electron beam [7]. For the detection of light elements, it is necessary to improve the spatial resolution to below 0.15 nm for lithium and below 0.05 nm for hydrogen [7]. In this sense, the recent development of the spherical aberration corrector is a turning point, since the spatial resolution reaches 0.1 nm by the corrector. Findlay *et al*. [8] reviewed the annular bright field (ABF) scanning transmission electron microscopy (STEM) image formation mechanism based on the S-state channelling model and the imaging condition to obtain lithium atomic columns in several Li ion battery materials.

With TEM based electron energy loss spectrometer (EELS) and precession electron diffraction (PED) techniques Li can be detected [9, 10]. However, due to the high mobility of Li, TEM sample preparation for Li containing samples need an extra care.

Considering scanning electron microscopy (SEM) based techniques, wavelength dispersive x-ray spectrometer (WDS) is not suitable but nowadays, sophisticated energy dispersive x-ray spectrometers (EDS) detectors are able to detect Li. Like PED, electron backscatter diffraction (EBSD) is also capable of showing Li containing phases. But, the main drawback is that the results need to be be supported by microscopy based chemical analysis. Preparing EBSD samples are also difficult.

Soft X-Ray Emission Spectroscopy (SXES) attached to SEM is a useful technique for the detection of Li in addition to investigate the chemical state information including Li [11].

Besides, Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) technique can also detect Li accurately. By combining Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM), ToF-SIMS could give more realistic data and beyond.

The major ion source in FIB-SEM is Gallium (Ga). However, relatively new source used in FIB-SEM is Xenon (Xe) ion source that offers numerous advantages such as low ion contamination, less damage to the surface and larger analysed area. To our knowledge, all ToF-SIMS studies based on detecting Li containing compounds used Ga ion source. Considering the as-mentioned advantages, Xe ion source is expected to be more effective during ToF-SIMS acquisitions.

In this study, state of the art on electron microscopy based techniques for the detection of Li will be reviewed and experimental results obtained from Li detecting systems especially with PED, EELS, EDS techniques will be presented and ToF-SIMS attached to FIB-SEM having Ga and Xe ion sources will be compared for Li containing Al-stabilized $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte produced for all solid lithium ion battery for energy applications.

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Energy Storage Materials probed by In Situ Neutron and Synchrotron Diffraction

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High efficiency and low cost electricity generation when utilizing renewable energy requires utilization of hydrogen based energy storage and conversion systems and rechargeable batteries, which are considered as two complementary alternatives. Efficient hydrogen storage in metal hydrides, both for gaseous hydrogen and electrochemically, in metal hydrides and performance of lithium ion batteries are based on reversible and repeatable intercalation – deintercalation of hydrogen and lithium atoms into the solid storage matrix. It is vitally important to understand not only the mechanism and rate limiting steps of their performance, but, importantly, also of their failure.

In situ diffraction studies of the metal alloys, metal-hydrogen systems and lithium ion batteries were explored as a valuable tool in probing the mechanism of the phase-structural transformations and their kinetics. Two complementary techniques, namely Neutron Powder Diffraction and Synchrotron X-ray diffraction were utilised. In situ studies were performed at variable controllable conditions, at temperatures 20-1000^{o}C, under pressure of hydrogen/deuterium gas reaching 1000 bar / in vacuum, and during electrochemical charge and discharge at controllable rates.

The talk will present a review of our recent studies of the alloys, metal-hydrogen systems, metal hydride battery anode materials and commercial lithium ion batteries containing multiphase layered oxide cathodes. While synchrotron X-ray diffraction data provide high time resolution, high sensitivity in determining formation of the phase constituents, excellent accuracy in yielding the crystallographic characteristics and in probing the microstructural evolution of the constituents formed, neutron scattering studies allow to follow the processes of hydrogen and lithium redistribution on the atomic scale with a time of just 3 minutes being sufficient to assess the transformations in the studied systems.

Particular focus will be on Mg based hydrogen storage materials, including $(La,Nd)_2MgNi_9$-D_2, $LaMg_2Ni_9$-D_2, $MgNi_2D_3$, $MgCo_2$-D_2, and Mg-rich Mg-(La,Mm)-Ni-H_2 systems and on the studies of a (Ni, Mn, Co) Oxides-Based Multicomponent Lithium Ion Batteries

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Vlodymyr A. Yartys

Volodymyr Yartys is professor of materials science and hydrogen technologies at the Institute for Energy Technology and Norwegian University of Science and Technology, Norway. He received his PhD in inorganic chemistry from Lomonosov Moscow State University in 1980 and a Doctor of Sciences in inorganic chemistry from L'viv University in 1995. He then became a professor in inorganic chemistry in 1998. He is working in the fields of materials science of nanomaterials, hydrogen and energy storage with a focus on: (a) Rechargeable Batteries; (b) Hydrogen as an Energy Carrier; (c) Novel Materials for Hydrogen Storage and Battery Applications; (d) Hydrogen storage systems; (e) Use of metal hydrides in energy management. Professor Yartys is the author of 429 publications (210 papers in peer refereed academic journals, 6 patents and three books), and has acted as a project leader in research projects funded by the EU, Norwegian Research Council, Nordic Energy Research, and industry.

Impedance-based, zero-free-parameter modeling of energy atorage systems

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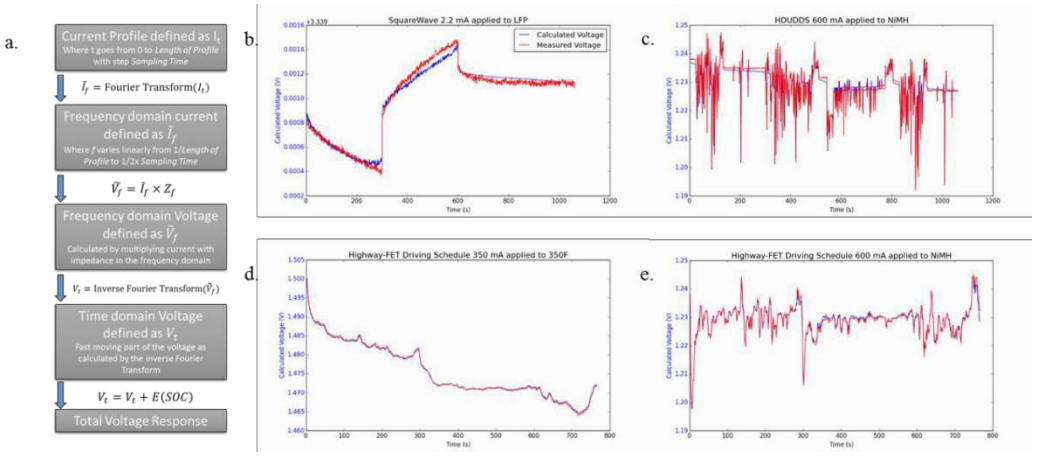
Modeling of energy storage systems are an gaining more importance as batteries and supercapacitors are increasingly finding uses in wildly different fields. In all the applications, being able to accurately model the battery voltage as a function of the applied discharge profile is of great importance. The performance of the selected battery determines the performance of the end-product, in addition to the size and shape.

There are numerous reports in the literature about modeling the voltage response of batteries in response to discharge regimes. Those reports are either compromise accuracy in order to be simple to implement, or at the expense of increased complexity, achieve accuracy. For example, Fan et. al.[1] present a model where the mass transport and kinetics at either electrode is modeled in detail to accurately explain Li ion batteries in high-C rates . In the opposite extreme, Castano et. al.[2] used a simplified Randles cell in order to model a lithium ion system based battery pack. The response captured the battery pack response in broad terms, but missed the fine detail

parameters. The existence of free parameters along with ambiguity of the models used call into question the validity of the models and the predictions.

We will report on a new modeling approach that we developed based on impedance spectroscopy data [3]. In order to use the impedance data to the fullest extent without involving any assumptions or fits, we model the response of the battery in the frequency domain. Instead of modeling the response in the time domain, the discharge profile is transformed into the frequency domain. The frequency domain current thus obtained is multiplied by the impedance at every frequency that constitutes the frequency domain signal of the discharge profile. The result of this multiplication leads to the frequency domain voltage, which is then transformed into the time domain. This voltage, is corrected for the DC voltage dependence on the state-of-charge.

Since we make no assumptions about the details, our method is widely applicable across different energy storage systems. We will demonstrate our model on commercial cells with



In addition to the above stated issues, the biggest problem with either modeling approach is obtaining the parameters that explain the battery reactions and materials. These parameters are either obtained from third party experiments or, more commonly, by fitting of electrochemical impedance spectroscopy data of the batteries and the materials they are made of. These fits by design have to make assumptions about the equivalent circuit that is used to fit the data. Moreover, the results of the fit have to be correlated to fundamental properties about diffusion coefficients or kinetic

$LiFePO_4$ and NiMH chemistries along with a supercapacitor, all with less than 1% error across different amplitudes and various discharge profiles.

[1]Fan G; Pan K; Canova M; Marcicki J; Yang XG; *JECS* **163**(5)A666-A676 (2016)
[2]Castano S; Gauchia L; Voncila E; Sanz J; *Ener. Conv. And Man.*, **92**,396-405(2015)
[3]Ozdemir,E; Uzundal CB; Ulgut B; *JECS* submitted



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Dr.Burak Ülgüt got his PhD in Electrochemistry from Cornell University in 2007. He was a postdoc at the Optoelectronics group in the same university for a year. He then spent 6 years in Gamry Instruments developing various instrumental tools about Electrochemical Impedance Spectroscopy and Spectroelectrochemistry. In 2014 he returned to Turkey to spend a year at Inci Aku as an R&D executive. In the fall of 2015 he joined the Chemistry department of Bilkent University where he is leading a research group working on developing new electrochemical measurement and modeling methodologies mostly geared towards a better understanding of energy storage and conversion systems.

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Coupled Electrochemical and Electrogravimetric Methods for Energy Storage and Conversion

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The need for new materials with improved ions‟ transfer/transport properties continues to be one of the main pressing concerns in energy storage/conversion materials research. In accompanying this search for optimal materials, appropriate characterization tools to assess key parameters of newly developed materials are required. Particularly, the morphology dependent performance, and kinetic or dynamic aspects of ion transfer behaviour of electrode materials is not very well understood. In the literature, the insertion of ions in the electrodes was investigated by in situ and ex situ characterization techniques, including electrochemical and gravimetric methods [1,2]. However, none of these methods alone provides the information on the exact identification of the inserted ionic species, their dynamics of transfer at the interfaces, as well as the role of electrolyte composition and the effect of ions solvation on the charge compensation phenomena.

In spite of its great relevance, fast electrogravimetric methods, i.e. coupling electrochemical impedance spectroscopy (EIS) with quartz crystal microbalance (QCM) (gravimetric impedance) [3-6], have not yet been used for studying transfer and transport phenomena in energy materials (except for the use of QCM along with cyclic voltammetry experiments (EQCM)). This coupled method, so called electrogravimetric impedance differs from classical EQCM and measures the usual electrochemical impedance, $\Delta E/\Delta I$ (ω), and the mass variations of the film under a sinusoidal potential perturbation, $\Delta m/\Delta E$ (ω), simultaneously. This coupling has the ability to detect the contribution of the charged or uncharged species transferred at the electrode/electrolyte interfaces and able to separate/identify the anionic, cationic, and the free solvent contributions during the various faradaic and/or capacitive processes.

As pertinent examples, (i) the charge storage behavior of carbon based materials (Figure 1) [3,4], and metal oxides [5], constituting electrode materials in supercapacitors and pseudocapacitors, respectively and (ii) the H^+ diffusion in polymer electrolyte membranes (PEMs) [6] for fuel cells will be discussed. The EIS and its satellite gravimetric methods can serve as a gravimetric probe to study the ions‟ transfer and transport properties in energy materials and to extract subtleties unreachable with classical tools.

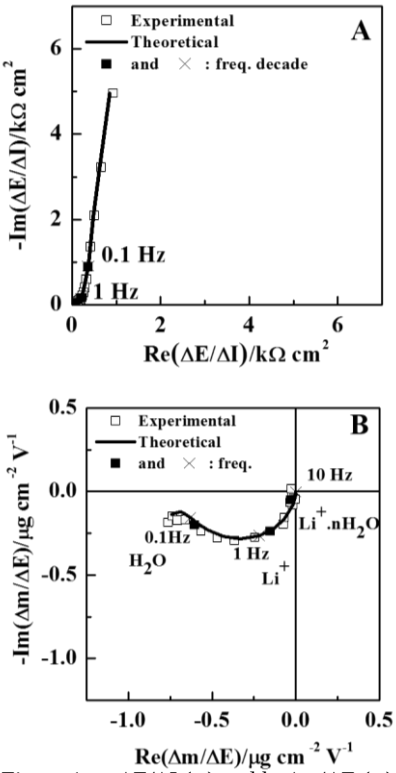


Figure 1. a. $\Delta E/\Delta I$ (ω) and b. $\Delta m/\Delta E$ (ω) of the electrochemically reduced graphene oxide (ERGO) electrodes in 0.5 M LiCl at -0.5 V vs Ag/AgCl.

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Batteries

Investigation of intercalation of multivalent-ions into λ-MnO_2 structure in aqueous electrolytes batteries

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The ultimate in technology, the energy has become one of the basic needs of human beings, such as water and air. Especially, in the last twenty years, the rapid development of portable electronic devices such as mobile phone, computer etc. make the rechargeable batteries attractive. Among the rechargeable batteries, currently, the most widely used and best known type of the rechargeable batteries is Li-ion battery. Moreover, using excessive amount of the lithium with the limited reserve like fossil fuels have the researcher concern. As a result, alternative batteries types have been investigating to fulfill the energy needs for particularly two decades. In this regard, sodium-ion batteries are one of the promising candidate due to having the same electrokinetic structure with Li-ion and one of the abundant elements in the Earth's crust **[1]**. Indeed, although state-of-the- art batteries fulfill the desired expectations over energy needs for the latest technological applications, the new types of rechargeable batteries still need to be developed to push down the price of them.

In the current battery technology, several electroactive materials such as the metal oxides and hydroxides have been investigated to satisfy the energy needs **[2]**. A lot of electrode materials used in the organic batteries are studied in the literature. But, same situation is not said for aqueous batteries. Because, the decomposition potential of water prevents the use of some electrode materials for the batteries with aqueous electrolyte **[3]**. In this respect, MnO_2 material is noteworthy for aqueous rechargeable battery applications due to its low cost, availability, environment-friendly and nontoxicity as well as one of a limited number of materials used **[4]**. MnO_2 is known as α,β, γ and λ forms**[5]**. Among these forms, λ-MnO_2 is preferred to be an electroactive template due to its 3 dimensional spinel structure [6], which make the intercalation process of metal ions easy into λ- MnO_2 structure.

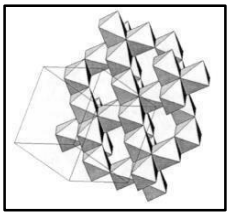


Figure 1. The crystal structure of spinel- λ-MnO_2

The univalent cations based on the Li-ion and sodium-ion intercalation into λ-MnO_2 have been investigated in the related literature. But, the most crucial factor that determines the theoretical capacity of electroactive template in batteries, is the number of transferred electrons. In this regard, recently, multivalent ion batteries have been drawing attentions, due to their high gravimetric capacity and energy density. However, electroactive host material and intercalated-ions must be compatible to each other to obtain reversible capacity and to prevent structural deterioration.

In this work, we have tested the process of multivalent Mg^{+2} ion intercalation into λ-MnO_2 structure in aqueous environment. Electrochemical performance of the operated electroactive template was evaluated through cyclic voltammetry and galvanostatic charge-discharge measurements. Two different Mg containing electrolytes ($MgSO_4$ and $MgCl_2$) have been used during the tests. The electroactive template in 1M $MgCl_2$ and $MgSO_4$ electrolyte delivered approximately 120 $mAhg^{-1}$ and 60 $mAhg^{-1}$, respectively. That is why the aqueous $MgCl_2$ solution exhibits better conductivity than aqueous $MgSO_4$ solution. As a result, λ-MnO_2 has ideal battery behavior in aqueous $MgCl_2$ electrolyte.

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In-situ Investigation of $NaFePO_4$ Electrochemical Conversion From $LiFePO_4$ in Aqueous Electrolyte Batteries

Serkan Sevinç[1], Burak Tekin [2] and Rezan Demir ÇAKAN [3]

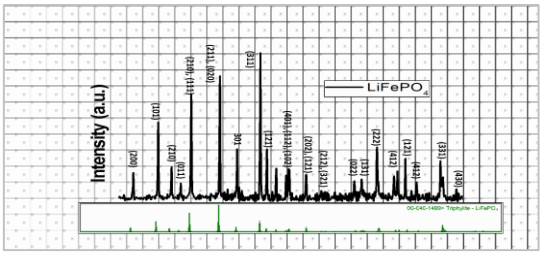
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Demand for the renewable energy has been growing rapidly. Numerous numbers of new wind and solar installations are used over the past few years in order to meet the energy need and reduce global warming emissions. Main issue with those systems is their dependence on weather conditions. Therefore, produced energy must be stored which requires large scale energy storage systems. Although Li-ion batteries have potential to meet the demand, increasing cost of lithium due to the low resources as well as the use of flammable, toxic and expensive organic electrolytes prevent their manufacturing for large scale applications.

Safe, low-cost and clean battery systems manufacturing is aimed with the aqueous electrolyte Na-ion battery systems to overcome the problems in organic batteries. High energy density and high capacity $NaFePO_4$ is used as cathode material. Since this material is not possible to synthesis by chemical methods[1], first of all, $LiFePO_4$ was synthesized by hydrothermal method (1) and then $NaFePO_4$ was obtained by electrochemical displacement of Li-ions with Na-ions in sodium containing aqueous electrolyte. The synthesized $LiFePO_4$ nanoparticles showed no impurity phase in XRD (Figure 1) and with less than 100 nm particles size (Figure 2).



Fiqure 1. XRD pattern of $LiFePO_4$ nanoparticles.

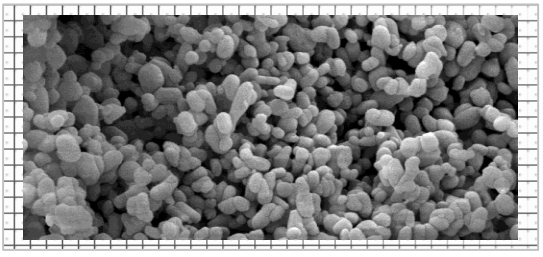
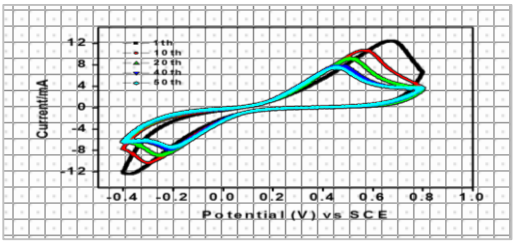


Figure 2. SEM images of $LiFePO_4$

In this study, the cyclic voltammetry of $LiFePO_4$ was investigated with lithium nitrate and sodium nitrate solutions and the intercalation processes of lithium and sodium ions into the host structure were evaluated in the light of the CV peaks in aqueous electrolyte environments. In addition, in-situ electrochemical quartz crystal microbalance (EQCM) and in-situ XRD techniques was performed to prove the lithium // sodium exchange and phase transformation of $LiFePO_4$ to $NaFePO_4$ during galvanostatic charge discharge process in aqueous environment.



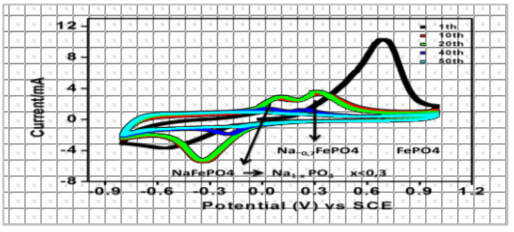


Figure 3. Cyclic voltammetry of LiFePO4 in 1 M $NaNO_3$

In conclusion due to high mass sensivity of EQCM technique we were able observe the lithium and sodium ion exchange and monitor the number of intercalated ions during charge-discharge process and with the use of in situ XRD technique we were able to investigate the phase transformation of $LiFePO_4$ to $FePO_4$ and $FePO_4$ to $NaFePO_4$.

Acknowledgements

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Topics in alkaline batteries: MH-, Fe-, Zn-anodes and Ni-, Air-, MnO_2-cathodes

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Water based electrolytes offers an advantage in high conductivity for ionic species. The Grotthus effect facilitates the making and breaking of O-H bonds promoting electrode reaction kinetics. This in turn reduces the buildup of detrimental gradients in the electrodes as the reactions proceed during both charge and discharge and thus promotes the long time reversibility. This is essential for reaching long cycle life but it will also reduce quality requirements and thus production costs. These benefits have historically made NiFe, NiCd and NiMH but also PbA batteries into large scale industries. The disadvantage is that the cell voltage will be limited by dissociation voltage of water. (Minimum 1.229 Volt but usually somewhat higher due to different over potential reactions at the electrodes) This is, however, significant lower than cell voltage in most Li-battery chemistries and the main reason for the huge capacity advantage of the Li-chemistries leading to their success in portable electronics, where low weight and volume are of outmost importance for the customer.

Much focus has been on cobalt containing cathodes in the Li-batteries as this have so far lead to the highest capacities. Without cobalt the capacity advantage with respect to the aqueous battery chemistries becomes significantly less. Cobalt is, however, a rather sparsely resource in the world. It is usually a byproduct from copper and nickel mining and thus dependent on the world demand for copper and nickel. Also worrying is that 2/3 of the cobalt production comes from the Democratic Republic of Congo.

This talk will suggest how alkaline, water based chemistries can offer large scale and safe battery chemistries. These can more easily be scaled up with respect to available natural resources, to meet an expected very huge demand in future vehicles and electric grids as more and more intermittent solar- and wind power stations are connected to the grid. It will also be discussed how water based systems can offer an opportunity to use gaseous reactions involving H_2 and O_2 to improve battery performance.



Dag Noréus

Dag Noréus is a professor in the Department of Materials and Environmental Chemistry at Stockholm University. He earned his PhD degree in reactor physics in 1982 at the Royal Institute of Technology, Stockholm, Sweden, and completed his postdoc at Daimler-Benz, Metal Hydride Laboratory, Stuttgart, Germany, in 1983. Noréus became a researcher in 1984 and a professor in 2000 in the Department of Structural Chemistry, Stockholm University.

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A method for improving metal hydride surfaces for NiMH cells

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Nickel metal hydride (NiMH) batteries are important power sources in electronic devices as well as hybrid electrical vehicles. NiMH batteries are commonly based on a AB_5 ($LaNi_5$) alloys, where A are an electropositive rare earth elements. B are predominantly Ni, but partly substituted by Co, Mg, Mn and Al to get a proper hydrogen storage performance. The alloy powder surface is partly corroded by the alkaline electrolyte used the batteries. In the initial formation of the NiMH batteries the electropositive rare earth metals form hydroxides and create catalytic active Ni containing nano-particles. These catalytic metallic inclusions embedded in a thin protective layer on the alloy particles improves high-power performance and reduce further corrosion. [1-8]

Previous work has been done to simulate surface reaction paths at the metal hydride alloy by a hot alkaline cooking method.[9,10] Mechanisms of improving activation and high-rate dischargeability of metal hydride alloy has been discussed. However, the method is relatively dangerous and complicated. Here, we present a novel surface treatment method to pre-oxide the AB_5 metal hydride alloy to achieve better performance. The treatment comprises three steps:

1. Gaseous hydrogenation cycling of the alloy powder;
2. Slight oxidizing the obtained hydride alloy powder in air as safety measurement;
3. Continued oxidation in hydrogen peroxide.

This treatment creates a thin catalytic and protective layer on the surface of the metal hydride particles improving performance.

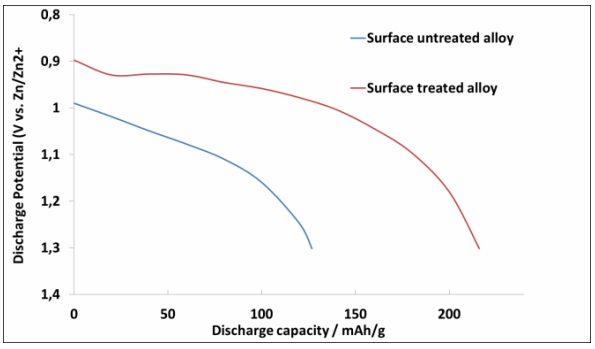


Figure 1.The discharge curves at 2400 mA/g for surface treated and untreated alloy.

Characterizations of surface treated alloys were studied by XRD, SEM and TEM. Half-cell test was used to investigate electrochemical properties. Figure 1 shows the discharge curves at 2400 mA/g before and after surface treatment of an AB_5 material (La20.07 Ce7.31 Pr1.2 Nd3.55 Al1.97 Mn4.57 Co6.24 Ni55.09 Re32.13, numbers are wt%).

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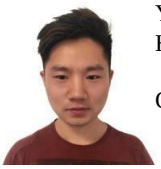
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Surface Modified Magnesium Based Negative Electrode Materials for NiMH Batteries

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Magnesium (Mg)-based hydrogen storage alloys have attracted considerable attention as negative electrode materials for NiMH batteries. This is due to the fact that Mg and Mg alloys if could be hydrided and dehydrided reversibly at room temperature, could yield extremely high discharge capacity, e.g. 1041 mAh/g for Mg_2Ni.

Currently, there are two difficulties with Mg based alloys. The first one is the high stability of Mg and Mg based alloys hydrides, where reversible hydrogenation occurs at elevated temperature [1]. Nanostructuring via ball milling or similar methods yielded alloys of low stability. The $Mg_{50}Ni_{50}$ composition is of particular interest in this respect. The second difficulty is the durability of Mg based alloys in the alkaline environment. Mg rich alloys are subject to corrosion, resulting in a fast decay of discharge capacity.

The current work deals with $Mg_{50}Ni_{50}$ composition and aims to develop an alloy with an improved electrochemical performance and durability as negative electrode material for NiMH batteries

$Mg_{50}Ni_{50}$ alloy in this study was synthesized via ball milling of elemental powders. For this purpose, powders of Mg (Alfa Aesar, 99.8%) and Ni (Alfa Aesar, 99.9%) were mixed in the atomic ratio of 1:1 and milling operation was performed for 5, 10 and 20 hours. The best result was obtained from 20 hours milling in which the resultant powder yielded a mixed structure. Analysis of the XRD spectrum, given in Fig. 1, showed that a broadened peak centered at 41° is mixed with a relatively sharp peak of Mg_2Ni located at 44°.

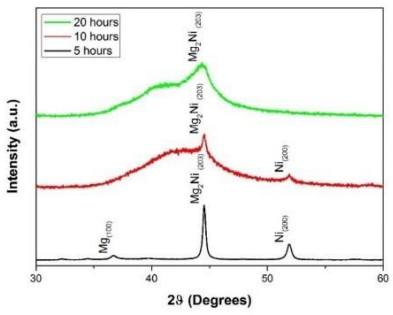


Figure 1. XRD spectrum of the synthesized $Mg_{50}Ni_{50}$ alloy.

Electrode prepared from the milled powders was tested electrochemically and yielded a discharge capacity of 329 mAh/g in the first cycle. There was, however, a fast capacity decay, obviously caused by the corrosion of the alloy, where the value was reduced below 50 mAh/g after 20 cycles.

So as to prevent corrosion, a coating that would be permeable to hydrogen (H^+) but keep hydroxyl (OH^-) away would be desirable. Nafion, a well-known proton conductor can be used to obtain such a protective coating.

To test if nafion coating would affect the performance of the Mg rich alloy, a new electrode was prepared in the same way as the bare electrode, but in the final step was coated with nafion via dip coating. Cyclic discharge curve obtained with nafion coated electrode is included in Fig. 2. It should be noted that there is a capacity increase with nafion coating, 498 mAh/g, as opposed to 387 mAh/g with bare electrode. There is still capacity decay but this is not as much as that in bare electrode. After 20 cycle the capacity was reduced to 338 mAh/g, which is approximately 66% of the initial capacity.

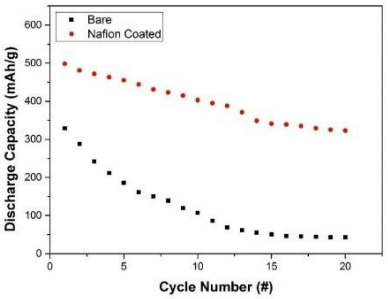


Figure 2. Electrochemical discharge capacities of bare and Nafion coated $Mg_{50}Ni_{50}$ electrodes.

In order to understand how nafion coating affects the capacity and the stability of the alloy, the same coating procedure was applied to A_2B_7 alloy. The results are discussed with regard to possible origin of capacity increase observed in alloys [2].

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A novel inorganic additive for vanadium redox flow battery

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A vanadium redox battery (VRB) system is a kind of new-generation energy storage system which was discovered and employed for the first time in the University of New South Wales [1, 2]. The VRB system has vanadium ions at different oxidation states in sulfuric acid solutions inside of both cells [3]. The main component of VRB system are electrolyte, electrode and membrane [4]. The performance and capacity of a battery system is associated with the concentration of sulfuric acid and vanadium [5]. Some organic and inorganic additives can be used to improve the capacity and stability of electrolyte [6-8].

In this study, fumed silica (SiO_2) was used as additive for positive electrolyte of a VRB to improve the capacity of battery. In this concept, cyclic voltammetric (CV) and electrochemical impedance spectroscpic (EIS) analysis were performed. Anodic and cathodic peak currents and capacities were determined in cyclc voltammetry. Solution resistance (Rs), charge transfer resistance (Rct) and Warburg impedance parameters were investigated in EIS analysis. Morphologic changes of electrodes were also determined by scanning electron microscopic analysis.

Figure 1 shows the cyclic voltammograms of additive including positive electrolyte solutions. Anodic and cathodic peak current increased up to wt% 0.02 of additives. Then, they starte to decreased. Optimum amount of additive was determined as wt% 0.02 of fumed silica.

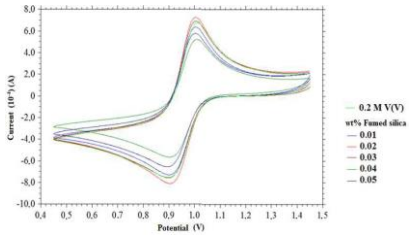


Figure 1. Cyclic voltammograms of additive including electrolytes.

Figure 2 shows the EIS spectra of electrolyte consisting of different amount of additive. Charge transfer resistance was the lowest in the solution consisting wt% 0.02 of fumed silica, as excepted. Solution resistance increased with the increasing amount of additive since the mobility of ions decreased in the solution.

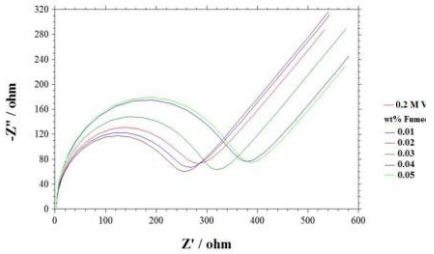


Figure 2. EIS spectra of additive including electrolytes.

SEM pictures of pencil graphite electrode (PGE) which were used in cyclic voltammteric analysis were given in Figure 3. The change of the surface PGE (Fig. 3a) can be seen easily in Figure 3b.

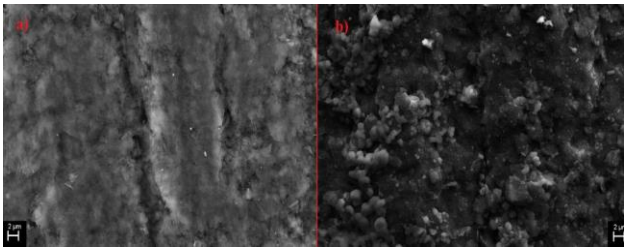


Figure 3. SEM pictures of a pure PGE b PGE after 5 voltammetric cycles in fumed silica including electrolye system.

This work was supported by TUBİTAK with the 114Z774. M. Gençten and H. Gürsu thank to TUBİTAK-BİDEB.

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The effects of boroxide on the electrochemical behaviors of a VRB

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Renewable energy sources have a great potential for sustainable energy in the future [1]. Since the production of energy depends on sunlight and wind in some of these sources, storage of this energy becomes an important issue [2, 3]. A vanadium redox battery system is a good alternative for conventional batteries, such as lead-acid, Li-ion, Ni-Cd, and NiMH, because of the following advantages: high-energy efficiency (up to 80%), simple control and monitoring system, long cyclic life, high safety, relatively low maintenance cost, flexible design, and environmentally friendly [4-6].

The vanadium redox flow batterty, has vanadium ions at different oxidation states in sulfuric acid solutions inside of both cells, was discovered and used for the first time in the University of New South Wales [5-7]. The concentration of vanadium and sulfuric acid mainly effects capacity of a VRB [8]. Some kind of additives in the electrolyte, which can be organic and inorganic, can improvede capacity of battery [9, 10].

In this study, the effects of boroxide (B_2O_3) on the electrochemical behaviors of positive electrolyte of a VRB were investigated by cyclic voltammteric and electrochemical impedance spectroscopic analysis. The morphologic chances on the pencil graphite electrode (PGE) during the cyclic voltammetric analysis were determined by scanning electron microscopic analysis. Figure 1 shows the cyclic voltammograms of additive including positive electrolyte system. When the amount of was wt% 0.04, the anodic and cathodic peak currents and capacities were the highest. This amount was the optimum for the additive.

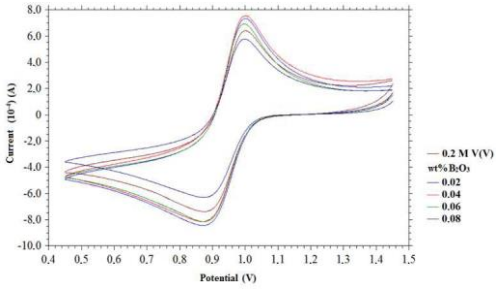


Figure 1. Cyclic voltammograms of additive including electrolytes.

Figure 2 shows the EIS spectra of additive including positive electrolyte system. When the amount of was wt% 0.04, charge transfer resistance was the lowest. The redox reaction occurs easir in this electrolyte composition than those of other solutions. Solution resistance increased with increasing amount of additive. The result may be caused dcreased mobility of ions in the solution by increasing amount of additive.

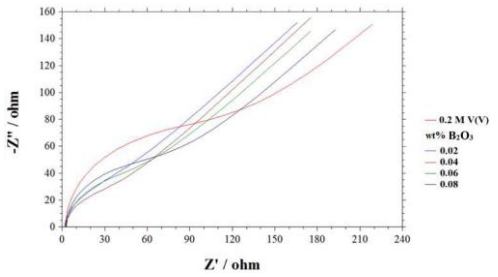


Figure 2. EIS spectra of additive including electrolytes.

Figure 3 shows the SEM pictures of pure PGE and PGE (after 5 voltammetric cyclics). The surface of PGE changed radically with voltammetric analysis in the additive including positive electrolyte solution of a VRB.

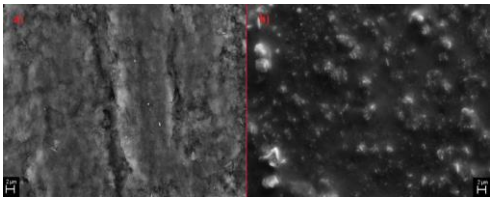


Figure 3. SEM pictures of a pure PGE b PGE after 5 voltammetric cycles in B_2O_3 including electrolye system.

This work was supported by TUBİTAK with the 114Z774. M. Gençten and H. Gürsu thank to TUBİTAK-BİDEB.

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Electrochemical investigation the effects of an organic solvent on a VRB

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A vanadium redox battery (VRB) is a new generation energy storage system. The system was discovered and used for the first time in the University of New South Wales [1-3]. A VRB system basically consists of electrolyte, electrode and membrane [1-3]. The battery system has sulfuric acid and vanadium ions at different oxidation states inside of both cells for electrolyte component [4]. The redox reactions of V(IV)/V(V) (Eq.1) and V(II)/V(III) (Eq.2) occur in positive electrolyte (catholyte) and negative electrolyte (anolyte) solutions on the electrode surface, respectively [5]. The capacity of a VRB system is mainly related with the concentration of sulfuric acid and vanadium species [6]. Besides, some additives also play an important role on the battery performance [7, 8]. Acetonitrile was used as solvent of some vanadium slats by Shinkle et al. (2013), however this solvent could become an useful additive for positive electrolyte of a VRB [9].

$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^{+} + 2H^{+} + e^{-} \quad E^{\circ} = 1.00\ V \ \text{vs. NHE} \qquad (1)$$

$$V^{3+} + e^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \quad E^{\circ} = -0.26\ V \ \text{vs. NHE} \qquad (2)$$

In this study, acetonitrile was used as additive for the positive electrolyte component of a VRB. Cyclic voltammetry and electrochemical impedance spectroscopy were performed for electrochemical charecterizaton of electrolyte system. Morphological charecterization of used electrodes were carried out by SEM analysis. Figure 1 shows the cyclic voltammograms of acetonitrile including positive electrolyte systems. When v/v% 1.0 of asetonitrile was added in the system, anodic and cathodic peak current and capacities increased radically.

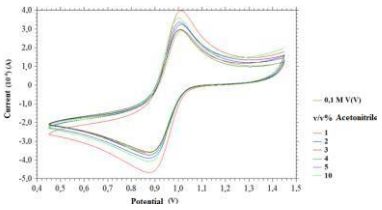


Figure 1. Cyclic voltammograms of additive including electrolytes.

Figure 2 shows the EIS spectra of the electrolyte consisting different amount of acetonitrile. When the amount of additive was v/v% 1, charge transfer resistance was the lowest. The redox reaction probably occurred easired modifided surface of electrodes in the electrolyte consisting optimum amount of additive. Solution resistance showed a regular incresed due to higher concetration of organic solvent.

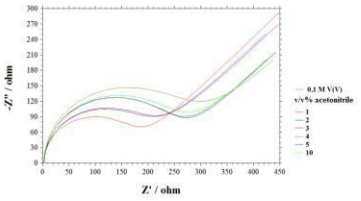


Figure 2. EIS spectra of additive including electrolytes.

SEM pictures of electrodes were given in Fig. 3. The morphology of used electrode in cyclic voltammetric analysis changed radicaly. The surface probably modified by additive particles.

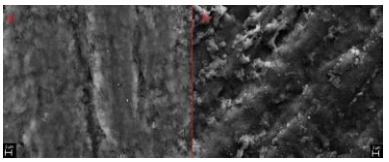


Figure 3. SEM pictures of **a** pure PGE **b** PGE after 5 voltammetric cycles in acetonitrile including electrolye system.

This work was supported by TUBİTAK with the 114Z774. M. Gençten and H. Gürsu thank to TUBİTAK-BİDEB.

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Investigation of over oxidized graphite based electrodes for vanadium redox battery

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Renewable energy sources have great potential for sustainable energy production around the world. Production and storage of this energy become an important issue. Vanadium redox battery (VRB), consisting of vanadium ions at different oxidation statement in sulfuric acid solutions inside of both cell, is new generation energy storage system which was discovered and employed in University of New South Wales (UNSW) for the first time [1-3]. VRB has been a great significance due to its high discharge capacity, fast response time, long cycle life and high energy conversion efficiency. Electrolytes, membrane and electrodes are the main components of VRB systems [4].

Many carbon based materials have been used for the vanadium redox battery electrodes. Although these materials have the advantages such as wide operation potential range, high surface area, corrosion resistance in the acid solution, low cost and etc., these materials showed bad electrochemical activity towards to the redox couples [5]. So, developing new carbon based electrodes with high electrochemical activity for VRB become an important issue.

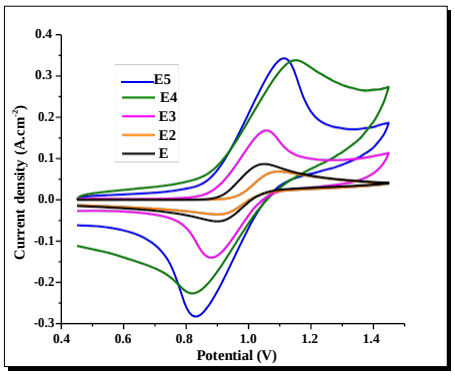


Figure 1. Cyclic voltammetric behaviors of E and E1-E5 (prepared over a different acids) in positive electrolyte of VRB

In this study, over oxidized graphite based electrodes were prepared in different acid solution, and were used as electrodes for the positive electrolyte of vanadium redox battery. In this concept, cyclic voltammetric (CV) method was used to electrochemical synthesized and characterization of these electrodes for positive electrolyte of VRB. Anodic and cathodic peak currents and capacities were investigated by cyclic voltammetric analysis. Anodic and cathodic peak current and capacities were increased when modified electrodes were used. E5 electrode has showed the best performance as a positive electrode in a vanadium redox battery (Figure 1).

Morphological characterization of synthesized electrodes were carried out by SEM analysis (Figure 2).

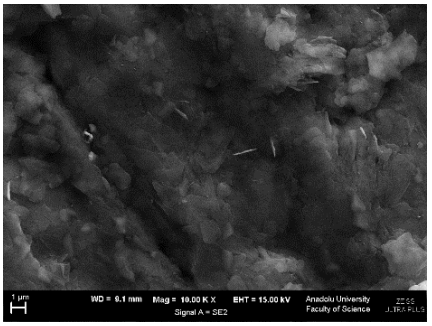


Figure 2. SEM picture of over oxidized graphite based electrode (E5)

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Electrochemically modified graphite based electrodes at constant potential for positive electrolyte of vanadium redox battery

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Redox flow batteries are one of the most influential electrochemical energy storage systems because of their flexible design, uncoupled energy and power capacities, high safety, quick response, low maintenance cost, long life cycle and high energy efficiency [1-6]. Among the various types of RFBs, all-vanadium redox flow batteries have taken a considerable attention since they use the same element as active species of the positive electrolyte and negative electrolyte [7]. This property of the battery significantly minimizes the problem of active component crossover contamination across the ion exchange membrane [8]. Electrolytes, membrane and electrodes are the main components of VRB systems [9].

Most of studies about electrode component of VRB focused on the positive electrolyte. In electrode part, graphite based electrodes are typical VRB electrode materials because of their wide range of operating potentials, corrosion resistance in the acidic solution, good electrical conductivity, high mechanical and chemical stability, porous three-dimensional network structure, and low cost [10]. At this point, developing of new graphite based electrodes with high sensitive and electrochemical activity become an important issue.

In presented study, over oxidized graphite electrodes (E1-E3) obtained in acid solution at constant potential were used as electrodes for the vanadium redox battery. In this concept, environmentally friend, novel, time-efficient and single step method was employed to improve the electrochemical activity of graphite based electrodes for positive electrolyte of vanadium redox flow battery.

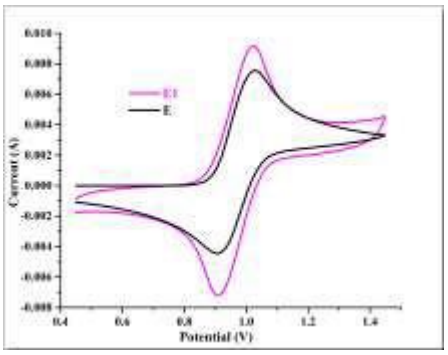


Figure 1. Cyclic voltammetric behaviors of E and E1 in positive electrolyte of VRB

The electrochemical properties of the electrodes were investigated by cyclic voltammteric (Figure 1) and electrochemical impedance spectroscopic analysis in the positive electrolyte of a VRB. The morphologic changes on the surface of electrodes were determined by scanning electron microscopic analysis (Figure 2).

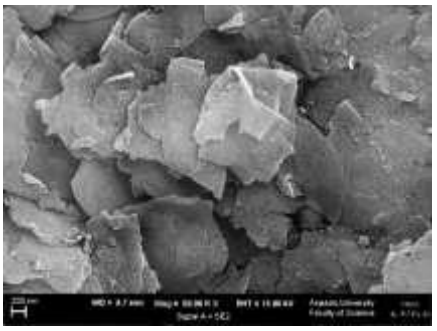


Figure 2. SEM pictures of modified graphite based electrode (E1)

When the modified electrode (E1) was used as positive electrode in a VRB, the anodic and cathodic peak currents and capacities were the highest. It exhibits the highest electrochemical activity for the VO^{2+}/VO_2^+ couple in all the electrodes.

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Synthesis of polypyrrole modified graphite based electrodes for vanadium redox battery

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Energy explained the capacity of work ability of objects and system, is an important need for the human life. The improving technology and developing new devices allow to increasing the need of energy day to day. In recent decades, the vanadium redox flow battery has received great attention as one of the efficient energy storage technologies due to its various advantages such as a long cycle life, high efficiency, flexible design, high reliability, low maintenance costs, and environmentalist [1]. Carbon materials are used the typical electrode materials for VRB. For example, the carbon felt, carbon paper and graphite based electrode are widely used in VRB because they maintain notable advantages such as a high specific surface area, wide operation potential range, stability, and low cost. However, the poor kinetics and reversibility of the carbon based materials negatively effects of their applications in a VRB [2].

The main aim of this study, improving the new graphite based electrodes for positive (anodic) electrolyte solutions of VRB system. In this concept, polypyrrole modified graphite based electrodes (E1-E2) were prepared and used as positive electrodes for the vanadium redox battery. The electrodes were investigated by cyclic voltammetric (Figure 1) and electrochemical impedance spectroscopic analysis in the positive electrolyte of a VRB.

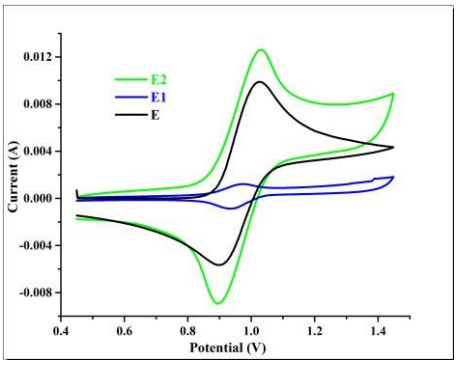


Figure 1. Cyclic voltammetric behaviors of E and E1-E2 in positive electrolyte of VRB

Morphological characterization of synthesized electrodes were carried out by SEM analysis (Figure 2). The best performance was determined in polypyrrole modified E2 electrode. When E2 was used in the system as positive electrode, anodic and cathodic peak current and capacities increased.

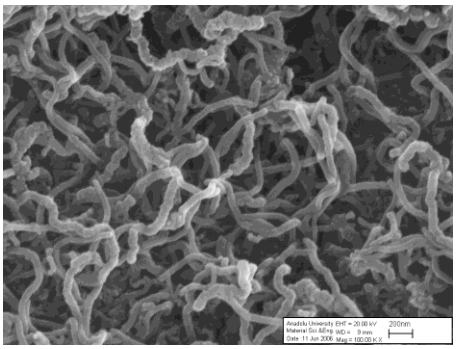


Figure 2. SEM pictures of polypyrrole modified graphite based electrode (E2)

This work was supported by Yildiz Technical University Scientific Research Projects Coordination with the 2014-01-02-DOP06. H. Gürsu and M. Gençten thank to TUBİTAK-BİDEB.

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Hürmüs GÜRSU

High energy electrode materials for rechargeable Na-ion batteries

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In the ongoing quest to improve energy storage systems, Na-ion batteries (NIBs) have recently attracted renewed scientific interest. Over the last few decades, Li-ion batteries (LIBs) have dominated the market for portable applications as offer the highest gravimetric capacity. However, the expansion of the rechargeable battery market towards large-scale grid storage now makes sodium chemistry an attractive alternative to LIBs in terms of cost, safety, and sustainability.[1]

Our recent research regarding low cost and environmentally friendly electrode materials for Na-ion batteries will be reviewed, with selected examples related to different families of materials. Several relevant aspects will be thoroughly discussed such as: i) reaction mechanisms both form an experimental and theoretical point of view (figure 1),[2-4] ii) strategies to increase the operation voltage in cathode materials,[5] iii) choice of preparation routes and its impact in the final cost and performance of the material,[6] iv) SEI (Solid Electrolyte Interface) and SPI (Solid Permeable Interface) layer formation and stability[7,8] and v) the possible use of aqueous electrolyte.[9,10]

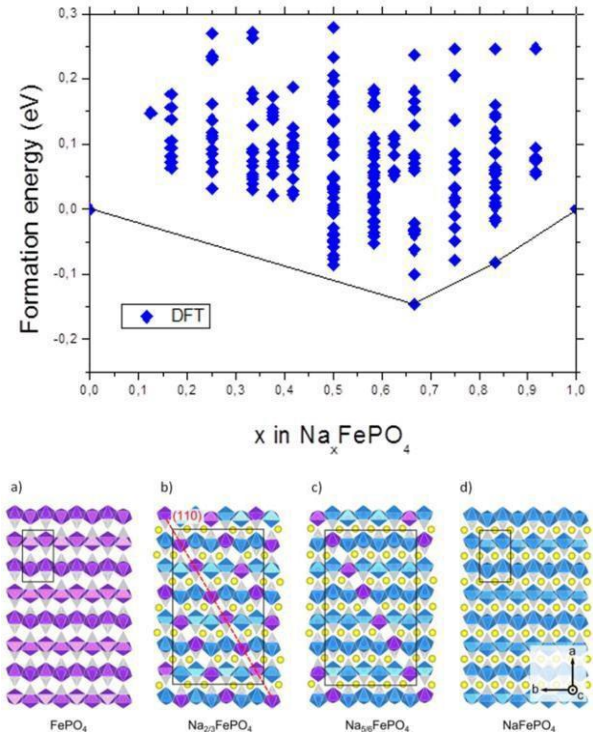


Figure 1. Calculated formation energies per formula unit as a function of Na content in Na_xFePO_4 structures with different Na/vacancy arrangements (top) and optimized geometries of the most stable structures for: (a) $FePO_4$, (b) $Na_{2/3}FePO_4$, (c) $Na_{5/6}FePO_4$ and (d) $NaFePO_4$ (bottom).

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High Performance Layered O3-$NaM_x^1M_y^{32}M_z^4$ M_k^5 M_l^6 M_m O_2 Cathode Materials for Sodium-Ion Batteries

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Sodium ion batteries have attracted great interest in portable electronics, electric vehicles and grid-scale energy storage because of the cheap and abundant of sodium resources. Sodium- based layered transition metal oxides with O3-type layered framework (Na_xMO_2 M=Ti, Cr, Mn, Fe, Co and Ni) have been considered as one of the most promising cathode materials for sodium ion batteries because of high specific capacity, low cost and facile preparation methods. However, they suffer from O3-P3 phase transition, leading to capacity decay and low reversible capacity. In this study, the capacity retention and rate performance of layered O3-Na_xMO_2 cathode materials are significantly improved by substituting some of transition metal ions, M, with other metal ions such as Ti, Mn, Fe, Ni, Ca and Mg to obtain $NaM_x^1M_y^2M_z^3M_k^4M_l^5M_m^6O_2$ (where M^1, M^2, M^3, M^4, M^5 and M^6= Ti, Mn, Fe, Co, Ni, Ca, Mg and $0 \le x,y,z,k,l,m \le 0.5$).

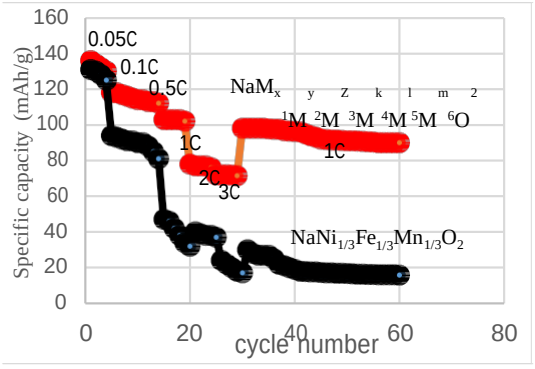


Figure 1. Cycling performance of $NaMx^{11}My^{2,2}MzM^{4}k^{4}Ml^{5}Mm^{6}O_2$ cathode at 241 $mA\ g^{-1}$

The synthesized $NaM_x^1M_y^2M_z^3M_k^4M_l^5M_m^6O_2$ cathode materials showed a high capacity of 100 mAh g^{-1} at a current density of 241 mA g^{-1}, high rate performance and good capacity retention of 93% after 60 charge/discharge cycles at a current density of 241 mA g^{-1}

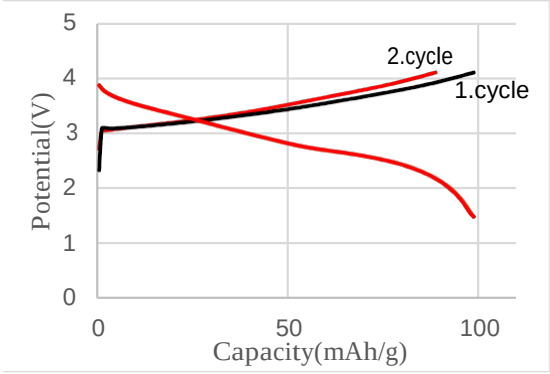


Figure 2. Galvanostatic charge/discharge voltage profile of $NaM_x^1M_y^2M_z^3M_k^4M_l^5M_m^6O_2$ cathode at 241 mA g^{-1}

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Adjusting interlayer distance in graphite as anode material for Na-ion batteries

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Abstract

A study was carried out to produce graphitic material suitable as anode material for Na-ion batteries using RF thermal plasma processing of methane together with hydrogen. . The precursors in use were methane and hydrogen .Experiments were carried out in different proportions of methane and hydrogen flow rates, The study shows that with the conditions of processing used in the present study, graphitic material obtained from methane only has already interlayer distance suitable as anode material. The study also shows that further increase in the inerlayer disatnce of graphite is posssible at least up to a value of 0.3792 by co-feeding the methane with hydrogen, when fed into the reactor with similar proportions.

1.Introduction

Graphite is a common electrode material in batteries due to its layered structure which permits easy insertation of ions inbetween the layers.Thus, graphite is commonly used as anode material in Li ion batteries where extremely small size of Li ion makes its transport easy in and out of the layered structure.

Recently, concerns about limited resources of lithium, together with the demands to increase the energy density further led researchers to look for alternative battery systems. Na-ion batteries is one such alternative which has attracted considerable interest in recent years. Na ion, however, is very much larger than Li ion and graphite in the usual form used in Li-ion batteries is not suitable as anode material for Na- ion batteries. Recent studies (e.g. 1) showed that an interlayer distance of at least 0.37 nm would be needed in graphite so as to make it suitable for Na ion intercalation. This value, considering that the graphite normally has an interlayer distance of 0.34 nm is larger by 0.03 nm .

The interlayer distance in graphite can be adjusted via hydrogen ion bombardement of graphite [2], or processing via a two step process first oxidation then followed by a partial reduction [3]. In this context, the study of Guo et al.[4]is quite interesting in which using graphite electrode as carbon source and feeding hydrogen gas in direct current arc discharge they have obtained few layers of graphene where the interlayer distance was also affected.This study showed that the interlayer spacing of graphene sheet did change depending on the the hydrogen pressure in the reactor.

In this study, we explore the possibilty of adjusting the interlayer distance in graphite in R.F. thermal plasma. The precursors in use were methane and hydrogen co-fed to an RF plasma torch operated at 25 kW.

2. Experimental Procedure

Precursors used in this study were methane and hydrogen with the purity of 99.995%. Methane and hydrogen were fed into Ar as carrier gas with a flow rate of 5 slpm. Experiments were carried out in different flow rates of methane and hydrogen.These were in units of slpm varied from CH4:H2= 2.0:0.0, to 2.0:1.0. Operating parameters of the thermal plasma is given in Table 1. The resulting product was collected in a special conical collector housing a suitable filter.

Samples were examined with X-ray diffraction (XRD) using Cu Kα radiation. Where needed XRD pattern was refined by Rietveld analysis using the software MAUD [5]. Morphology of powders were examined using field emission scanning electron microscope (FESEM). Powders were also examined with TEM to observe detailed morphology of the sample.

3. Results and Discussion

Experiments were carried out in different proportions of methane and hydrogen. These were in units of slpm , CH4:H2= 2.0:0.0, 2.0:0.1 and 2.0:1.0.

First, methane without the use of hydrogen was fed to the reactor yielding a carbonecous material. Fig.1 shows a typical SEM image obtained from this material. XRD pattern recorded from this powder is given in Fig.2. The pattern comprises 4 peaks with positions compatible with the so-called graphite. The peak close to 28 degree is related to the



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Si contamination which comes from the previous experiments.

Table 1. Operating parameters of the thermal plasma process

Parameter	Values
Central gas (Ar) /slpm	15
Sheath gas (Ar and H2)/slpm	60 / 6
Quenching gas (N2)/ slpm	150
Plasma Power (kW)	25
Chamber pressure (bar)	0.97

With the addition of hydrogen, the first sign of the change was the increased volume of the resulting powder, i.e. for the same duration of processing, the resulting powder was more volumonus that that with methane only production . Fig. 1.b shows a SEM image of the powder obtained with CH4:H2=2.0:1.0 Here the majority of the structure is in the form of small particles, but such particles co-exist with large flakes. The size of these flaky graphite is around 5 μm.

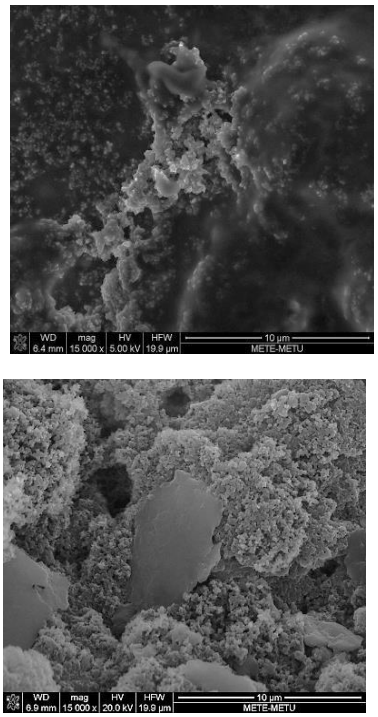


Figure 1. SEM micrograph of graphitic powder obtained with a) CH4:H2= 2.0:0.0 and b) CH4:H2= 2.0:1.0 slpm.

TEM micrographs of this powder together with other powders are given in Fig. 3. Here Fig. 3(a) refers to CH4:H2=2.0:0.0. Here the structure comprises particles that are typically 50-100 nm in size. The structure with CH4:H2=2.0:0.1 was little affected. Drastic change occur in CH4:H2=2.0:1..0.Here, the granular structure which was present in the earlier samples are absent. Instead there is flaky material which is quite thin considering the appearance.

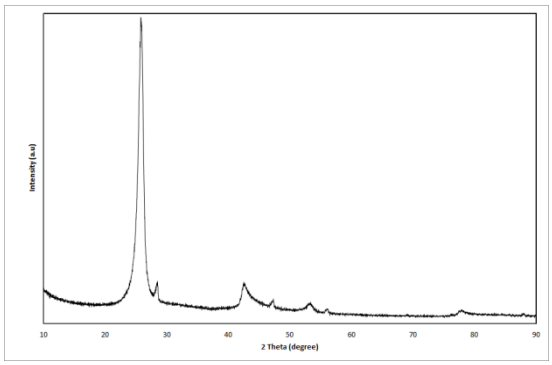
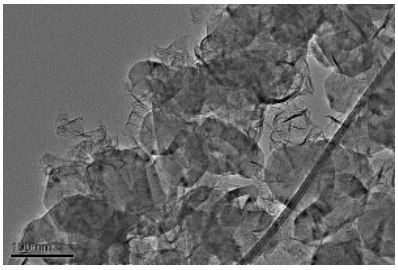


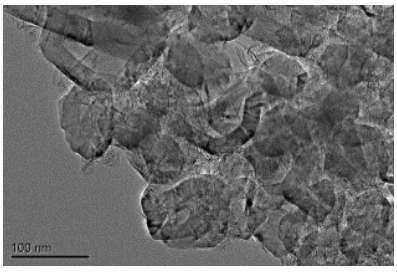
Fig.2. XRD pattern of methane only production

A typical example of XRD pattern obtained from powders with co-feeding of hydrogen is given in Fig. 4. The pattern is differs from the one given in Fig.2 in that there is dominant peak arising from (200) planes. This is an expected result since if graphite is in the form of thin layers as was depicted in TEM micrograph, they would be expected to align during handling resulting a preffered orientation. More importantly the peak positions seem to have altered implying a change in the lattice spacing.

a)



b)



c)

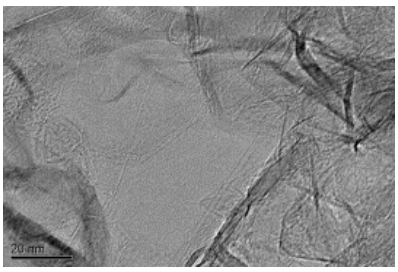


Fig 3 TEM images of the samples obtained at different , CH4:H2 ratios (a) 2.0:0.0,(b) 2.0:0.1,and (c) 2.0:1.0

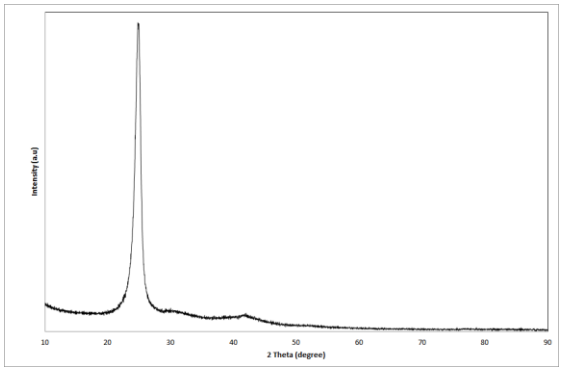


Fig.4. XRD pattern of CH4:H2= 2.0:1.0

Table 2 Interlayer distance as a function of CH4:H2 ratio.

	2.0:0.0	2.0:0.1	2.0:1.0
I(100)/I(002)	0.132	0.130	0.048
d(002)	0.3704	0.3744	0.3792

Table 2 gives the result of calculations carried out on XRD pattern. Included in the table are the the intensity ratio of I(100)/I(002) and the lattice spacing determined for d(002), the first may be taken as a measure of the flakiness of the powder and the latter is the interlayer distance in the graphite.

It should be noted that the I(100)/I(002) decreases with increased proportion of hydrogen. This implies that graphite rather than coming together as "granular" particles tend to take up flaky morphologhy. Currently the work is in progress to determine the average thickness of these flakes.

A more striking result of Table 1 is that the interlayer distance even with pure methane is larger than that of graphite nornally used as anode material in Li-ion batteries. The interlayer distance of such anode materials are normally d = 0.3354 nm [6]. This should be compared with the current value of 0.3704 nm. This value close to the targeted value for Na-ion batteries.

Even if the value of 0.3704 is not suffciently large, Table 1 shows that even larger spacings can be obtained by adding hydrogen to methane.

Cuurently work is in progress so as to determine the limits of adjustments that would be possible in graphite via plasma processing of methane. The currently the maximum value seems to be 0.3792. But it will be checked if higher values would be possible by increasing the proportion of hydrogen.

4. Conclusions

A study was carried out to produce graphitic material suitable as anode material for Na-ion batteries using RF thermal plasma processing of methane together with hydrogen . The study shows that with the conditions of processing used in the present study, graphitic material obtained from methane only has already interlayer distance suitable as anode material. The study also shows that further increase in the inerlayer disatnce of graphite is posssible at least up to a value of 0.3792 by co-feeding the methane with hydrogen, when fed into the reactor with similar proportions.

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Synthesis of carbohydrates-derived carbonaceous electrode materials and their Na-ion battery performances

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Development of the energy systems that make efficient use of energy in the world, safely store existing renewable energy and most importantly, environmental friendly, low cost, high power and efficiency systems are at the forefront of the topics that have been working for many years.

Sodium ion based batteries have been developed in which the lithium element is expensive and the earth reserves are consumed so that the sodium element is used which has close physical and chemical properties also cheaper and more abundant than lithium element.

Hydrothermal carbonization method (HTC) was introduced where generation of carbonaceous materials can be achieved from biomass or carbohydrates that allowing the production of high carbon yielding. Use of nitrogen containing carbonaceous materials such as chitosan and glucosamine directly allows the preparation of nitrogen doped carbon materials with improved high electrical conductivity performance range because of nitrogen atom into the graphitic structure contributes further electron carriers in the conduction band. In addition this, oxygen group including precursors such as furfural was used that to produce sphere carbon (1-3).

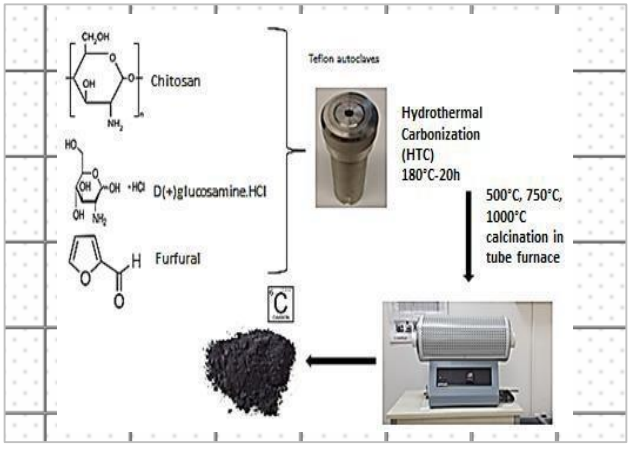


Figure 1. Schematic illustration of hydrotermal carbonization

In this study, carbonosous anode materials derived from chitosan, glucosamine and furfural were synthesized by HTC method under 180°C for 20h and their structural and electrochemical characterization were tested. Na-ion storage capacities of the electrodes have been performed on 1 M $NaClO_4$ in EC:PC electrolytes at C/10 rate and in the voltage range of 0.005-2V (vs Na/Na^+).

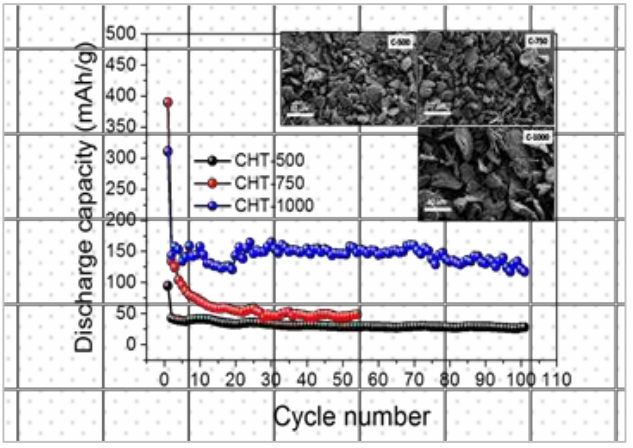


Figure 2. CHT-500, CHT-750, CHT-1000 discharge capacity vs. number of cycle

Discharge capacities of chitosan prepared with CMC binder increase as calcination temperature increases from 500ºC to 1000ºC. The best electrochemical performances of chitosan was obtained with 1000ºC as calcination temperature.

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Acknowlegdements

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Li-S Batteries Beyond the Hype: Future for Electrical Vehicles?

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Li-S batteries are considered as next-generation energy storage option to current Li-ion batteries readily available at the marketplace. Especially last 10 years, the field has been absolutely progressing and great performances have been accomplished at the laboratory scale in terms of cycling. In contrast, comparing energy density achievements and ranking them between the different approaches are frustrating due to the diversity in reporting data. Likewise, the specific energy density calculations flooded in the literature mainly disregards the amount of electrolyte used, the weight of the electrochemically inactive components of the cells (i.e. current collectors, separator, packaging foil, tabs etc.) to be able to understand the development of the system[1].

Herein, the gaps between the pouch and coin cells will be discussed and the fast capacity fading mechanism of a Li-S pouch cell will be unveiled. To do so, a 3 Ah Li-S pouch cell (9.3 cm x 6 cm dimensions consisting of 7 layers of cathode and 8 layers of anode) was manufactured after careful investigation of each cell parameter with the coin cell measurements (Figure 1)[2].

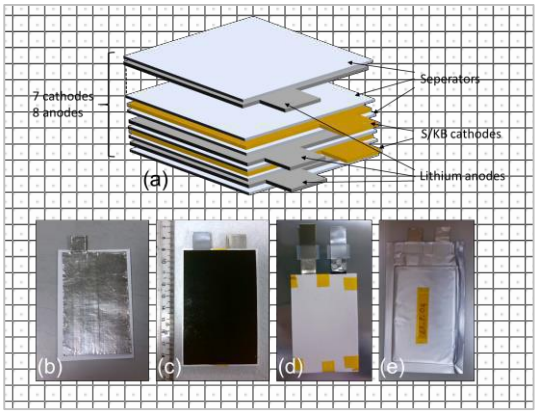


Figure 1. Pouch cell production steps. a) 7 cathodes and 8 anodes were used to produce the cell stack, b) anode electrodes punched from lithium foil c) slightly larger separators placed between punched anode and cathode electrodes d) aluminum tab welded to the cathodes and a stainless steel tab bonded to the anodes e) the stack placed inside an aluminum soft packaging film and sealed with hot press

Although, to date, current Li-S batteries announced around 250 Wh/kg energy densities with 80 cycles, manufacturing steps and details were not shared with the public due to the trade secret formula and process. In this presentation, every details of a proper functioning Li-S pouch cell will be described and further questioned the Li-S battery technology if it is a hype or reality as a next generation storage system.

After cautious determination of the impacts of each parameter, it was observed that besides the common and known issues at the laboratory scale cells, the pouch cell brings additional difficulties to the system which are mostly linked with each other. Having faced all these issues, at the first cycle 120 Wh/kg gravimetric energy density was achieved with a 3 Ah Li-S pouch cell which is still far from the projected values (500 Wh/kg). One of the immense reasons to have this low energy density is directly linked with the necessity of the high electrolyte amount.

As a whole, although relatively low energy density with fast capacity fading were observed with the first prototype Li-S pouch cell, practical realization of the system is crucial since there is still a huge gap between the laboratory scale cells and the reality. Anyhow, we do hope that the Li-S battery option still has a potential to fulfill the future requirements at low cost once all these challenging issues are addressed.

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Electrochemical Performance Model for the Lithium-Sulfur Battery Based on Cathode Design Parameters

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Lithium-Sulfur (Li-S) batteries have gained major attention as a beyond Li-ion chemistry due to their high theoretical specific energy [1]. Despite the attractive characteristics, Li-S batteries are suffering from limited cycle life and low capacity retention [1,2]. Due to the complexity of the Li-S chemistry, cathode design has a key effect on the electrochemical performance of the cell. Carbon to sulfur and electrolyte to sulfur ratios in the cathode are two of these critical design parameters that have a significant effect not only on the electrochemical performance of the cell but also on the systems-level properties [1,2].

In this study, the effect of carbon to sulfur and electrolyte to sulfur ratio in the cathode on the electrochemical performance of a Li-S cell is modeled. For this end, a one- dimensional, concentration-independent electrochemical model for a Li-S cell is proposed based on a previous model [1]. The Li-S cell modeled is disposed of the lithium-metal anode, a porous separator and the porous sulfur-carbon cathode filled with an organic electrolyte. The model predicts the current-voltage relationship for an isothermal, constant- current discharge of the Li-S cell. In the electrochemical model, Li deposition kinetics in the anode is described with the Butler-Volmer kinetics. Ohmic overpotential due to the transport of Li^+ through the porous separator is also taken into account using the Ohm"s Law. The cathode is defined with the porous electrode model by Newman and Tobias [3]. The complex sulfur redox mechanism at the cathode is simplified into a single reaction; thus, the cathode kinetics is treated with a single kinetic model parameter, cathode exchange current density ($i_{0,PE}$).

Due to the insulating nature of sulfur, Li-S cathodes typically require high carbon content [1,2]. Higher carbon to sulfur ratios enhance both the electronic conductivity and the electrochemically active surface area in the cathode. However, a recent techno-economic analysis of the Li-S battery predicts that systems-level energy density decreases significantly at high carbon to sulfur ratios [1]. Consequently, carbon to sulfur ratio is one of the most critical design parameters in the cathode that has a significant effect on both cell- and systems-level performance [1,2]. Therefore, the effect of carbon to sulfur ratio in the cathode on the electrochemical performance of a Li-S cell is investigated using the proposed model and presented in Figure 1. Electrochemical performance of the Li-S cell is discussed through the predicted cell voltages at 60% DOD corresponding to the lower plateau voltage. Figure 1 shows that for carbon to sulfur ratios below 1, there is a significant increase in the cell voltage with increasing carbon amount. However, at higher C:S ratios, the enhancement in the cathode kinetics is less significant.

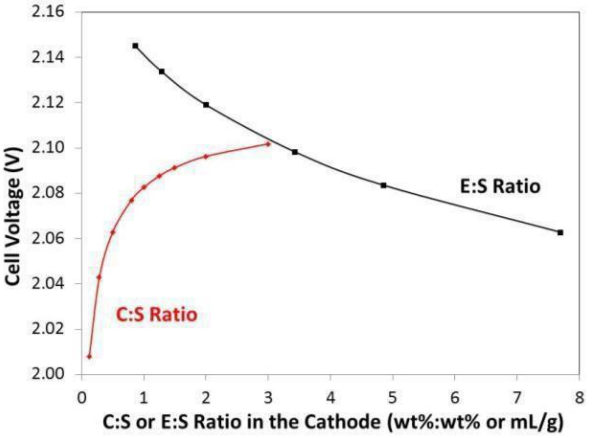


Figure 1. The effect of carbon to sulfur and electrolyte to sulfur ratio in the cathode on the calculated cell voltage at 60% DOD of the Li-S cell for a current density of 1 mA/cm^2.

Electrolyte to sulfur ratio in the cathode is another design parameter in the Li-S cell affecting both the cell- and systems-level performance [1,2]. Li-S cells usually require high electrolyte amount for good capacity retention and improved cyclability [1,2]. However, as the electrolyte amount in the cell increases, the systems-level energy density decreases significantly [1]. Figure 1 presents the effect of electrolyte to sulfur ratio on the cell performance. The model predicts a decrease in the cell voltage with increasing E:S ratio, which is unexpected considering the previous studies [2]. This suggests that kinetic model parameter depends significantly on the E:S ratio; therefore $i_{0,PE}$ should be defined as a function of the electrolyte amount in the model.

Acknowledgments
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The Enhancement of Electrochemical Properties By Using Bacterial Cellulose Interlayers In Li-S Batteries

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Lithium sulfur batteries are considered to be the most suitable candidates for advanced energy storage systems because of their 5 times greater energy density than commercially available Li-ion batteries. Having a high theoretical capacity (1675 mAh / g), the sulfur is abundant in nature, cheap and not harmful to the environment, making it attractive. Practical applications are hampered by a variety of issues such as high volume expansion during discharge and safety issues related to the use of Li-metal anode. Li_2S, the final discharge product instead of sulfur; has a high theoretical capacity (1166 mAh/g) and is a promising cathode candidate because it can be matched with non-lithium anode materials, such as Sn and Si. But the fact that the ionic and electrical conductivity is too low makes the Li_2S work difficult, because of the need for about 1V activation energy in the first charge cycle.

In our work, LiS, which we synthesize, was ball-milled with carbon to increase conductivity. A metal oxide containing (SnO_2) free-standing bacterial cellulose paper was used as an interlayer between the cathode and the anode to protect the lithium surface from soluble polysulfides. In the case of samples without protective layer, a very rapid capacity decrease was observed, while the as-developed bacterial cellulose interlayer could significantly enhance the cycling performance of the Li-S battery.

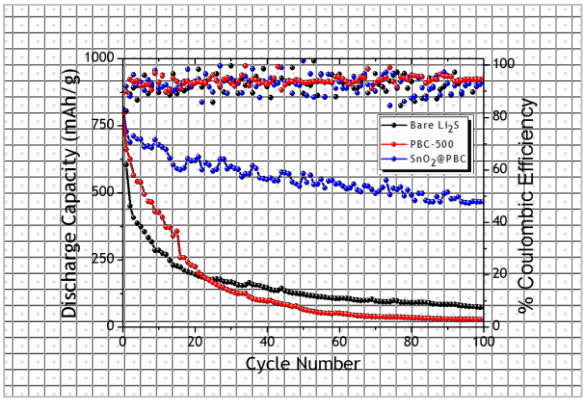


Figure 1. Cycling Performance

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Application of Interlayers as Polysulfide Adsorbers in Lithium-Sulfur (Li-S) Batteries

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Lithium-ion (Li-ion) batteries conquer the marketplace of mobile applications since 1991. However, the use Li-ion batteries is becoming challenging especially for large-scale applications because of their relatively low energy density. Lithium-Sulfur (Li-S) batteries offer theoretically five-fold increase in energy density compared with present Li-ion technologies. However, their utilization in practice is hindered by several issues linked with; (I) insulating nature of sulfur, (II) dissolution of polysulfides in organic solvents, (III) shuttle effect of these dissolved polysulfides and thus occurrence of fast capacity fading, (IV) huge volume expansion (%80) with the formation of Li_2S at the end of discharge, (V) dendrite formation on lithium (Li).

There are several methods in literature to boost the electrochemical performance and prevent capacity fade seen in Li-S batteries. At first, infusion of sulfur into porous carbon materials was tried to solve the insulating problem of sulfur. The other approaches are polymer coating on cathode material[1] and adding co-salts to electrolyte to form a protective layer on anode material[2]. Currently, one of the most famous approach is using interlayers between anode and cathode to hinder the shuttle effect. Up to now, carbon-based[3], graphene-based[4] and Nafion[5] interlayers were used for this aim.

In this work, we used carbon based interlayers (such as carbonized bacterial cellulose, graphene coated separator, carbon nanofiber,.. etc.) that adsorb polysulfides and decelerate their migration to anode side. These interlayers can act as both secondary current collector and polysulfide adsorber. By using of this layer, both higher discharge capacity and Coulombic Efficiency were obtained which is additionally not detrimental to the energy density of the cell contrary to the solid state interlayer counterparts (One of the results shown in Figure 1).

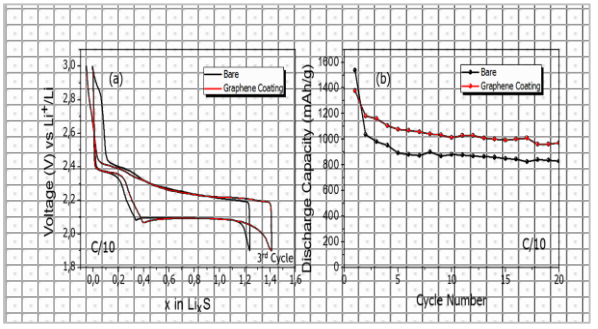


Figure 1. (a) Third charge-discharge profile of the cells without any coating (Bare separator) and with Graphene coated separator, (b) Discharge capacities as a function of cycle number for the cells without any coating (Bare separator), with Graphene coated separator.

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Nanocarbon Composite Electrodes: Synthesis and Application for Li-Ion Batteries

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Electrochemical energy storage has become a critical technology for a variety of applications, including grid storage, electric vehicles, and portable electronic devices. Metal based anodes (Si, Ge, Sn, Al, Sb, etc.) have much higher Li storage capacity than the intercalation-type graphite anode that is currently used in Li-ion batteries (LIBs). Among all the metal based anodes, Si has the highest specific capacity. Si is considered as a promising anode material for rechargeable LIB, owing to its high theoretical specific capacity (about 4200 $mAhg^{-1}$), high abundance in the earth's crust and its environmentally friendly nature. A further benefit is that mass production of elemental Si is already a mature technology in the semiconductor industry. Despite these advantages, graphite anodes still dominate the marketplace due to the fact that alloy anodes have two major challenges that have prevented their widespread use. However, the practical implementation of metal (M) and metal oxide (MO) anodes is still blocked due to three major problems [1]: poor cycle-life results from pulverization during the huge volumetric fluctuations (>300 %), drastic irreversible capacity loss and low coulombic efficiency, the solid electrolyte interphase (SEI) breaks as the nanostructure shrinks during delithiation. This results in the exposure of the fresh silicon surface to the electrolyte and the reformation of the SEI, resulting in the SEI growing thicker with each charge/discharge cycle [2].

The critical issue of fabricating high specific capacity, high rate capability, and long cycle life LIB device is the advanced nano architectured design and flexible electrode materials with good mechanical deformations. Nanocomposite structures are pivotal for the progresses in electrode materials due to their manageable surface-area, stunted mass and charge-diffusion span, and volume change acclimatization during charging/discharging. CNTs, CNFs and Graphene with their special structures provide excellent conductivity, mechanical flexibility and significantly large surface-area, are considered ideal additives to enrich chemistry of electrodes [3].

In order to prevent these challenges, most common and effective strategy to adopt nanoscale materials with various morphologies, including nanoparticles and, nanowires, nanotubes and hollow spheres. Compared to bulk active materials, such nanostructured Si is able to accommodate elevated mechanical stress, resulting in prolonged cycling stability. Optimization of metal and metal oxide electrodes can be achieved by incorporating nano structures with various conductive matrixes, such as graphene and, carbon nanotubes, and carbon and to form core-shell and yolk-shell nanocomposites. The introduction of such a carbon architectures play a key role in alleviating the agglomeration of nano structured active materials [4].

In this review, we summarized the recent progresses on developments of nanocarbon based and/or nanocarbon supported (CNT, CNF, Graphene etc.) negative and positive electrodes for high performance Li-ion batteries. The synthesis techniques of the 1-D, 2-D and 3-D electrodes has been discussed for special hierarchical structures and free standing electrodes. Special concentration has been made on the nano carbon supported silicon and tin negative materials, layered and spinel type of positive electrodes. The main research activities of Sakarya University electrochemical energy storage group has also summarized. The synthesis techniques of Si and Sn active materials and their nanocomposite structures were reviewed. One of the example of this is given with Figure 1 for the yolk-shell structures Si-C rGO reinforced negatives electrodes.

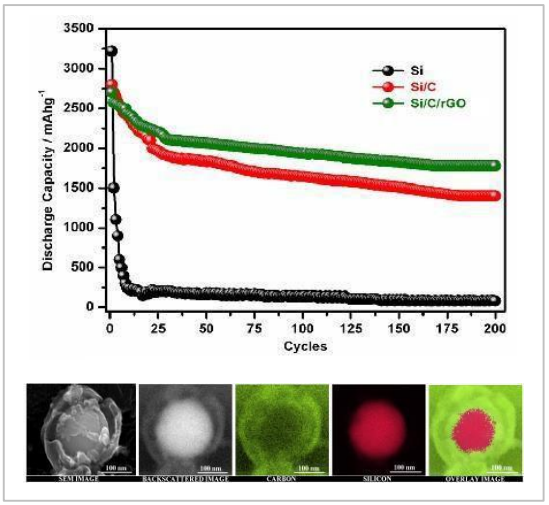


Figure 1. Discharge capacity and FESEM dot mapping of the yolk-shell Si-carbon nanocomposites.

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Hydrides as negative electrode material of Li-ion batteries

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Lithium-ion batteries are today largely used as energy storage systems for mobile electronics and electrical vehicles. However, insertion compounds that are currently used in this technology reach intrinsic limitations. Improved battery performances are expected from novel reaction schemes or new technologies, such as conversion reactions or metal-air batteries. In this context, Metal Hydrides (MH_x) have been proposed as potential candidates for negative electrode in Li-ion batteries [1].

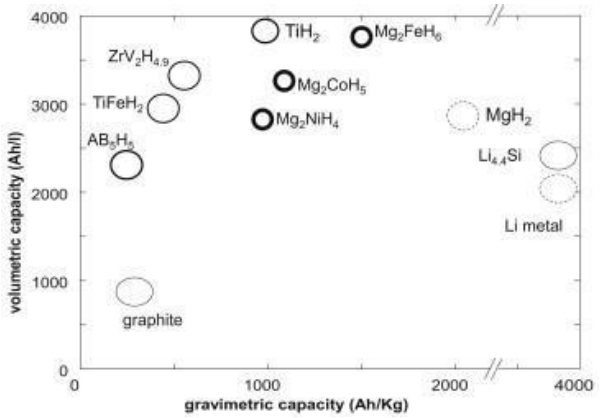


Figure 1. Gravimetric and volumetric capacities of some hydrides compared with those of graphite and other negative electrodes materials [2].

Metal hydrides (MH_x) operate through the conversion reaction: $MH_x + x\ e^- + x\ Li^+ \rightleftharpoons M + x\ LiH$. They offer high capacity, suitable potential and low polarization. However, reaction kinetics and cycle-life need to be improved for practical applications. During the conversion reaction, the metal hydride disproportionates into metallic species and LiH which should be reformed during electrochemical cycling. Therefore, fast enough mass-transport of solid species has to be attained at room temperature which is only possible by using finely dispersed nanostructured hydrides.

Several families of nanocristallin hydrides (MgH_2, TiH_2, Mg_2TmH_x, *Tm* = Fe, Co and Ni)[3-5] have been synthetized by mechanochemistry of the elements under hydrogen gas. During electrochemical lithiation, all these hydrides fully react with lithium at low potentials (< 0.7 vs. $Li^+/Li°$) and provide capacities over 1000 mAh/g. However, reversibility at room temperature is poor. To solve this issue, better understanding of the limiting reaction mechanisms in these systems is required.

In this context, we have recently focused our efforts on the study of MgH_2-TiH_2 nanocomposites, whose hydride phases exhibit synergic effect for hydrogen storage [6]. Their properties as negative electrodes of Li-ion batteries both in terms of reversible capacity and cycle-life have been investigated [7]. The influence of the relative MgH_2 to TiH_2 molar ratio will be discussed and interpretation of the limiting reaction mechanisms will be proposed.

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The Effect of Porosities on the Electrochemical Properties of ZnO Anode Materials with MicNo® Morphology

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Li-ion rechargeable batteries are one of the energy storage options especially for high-energy density required applications such as EVs. The working principle of Li-ion rechargeable battery is based on the movement of Li atoms between anode and cathode during cycling [1].

Graphite with 372 mAh/g theoretical capacity is currently widely used anode material in commercial Li-ion batteries. However, in spite of its abundance, relatively low theoretical capacity inhibits graphite to implement on high-energy density Li-ion batteries [2].

Transition metal oxide (TMO) based anode materials attract more interest nowadays since their outstanding theoretical capacities, stability on environmental conditions and low cost that make TMOs feasable in high energy density battery applications. Considering that, with its 978 mAh/g specific capacity, ZnO stands forward among TMOs. However, their drammatical capacity fading, cycling stability and poor electronic conductivity were main drawbacks that scientists have been trying to get over. Approximately 228 % of volume expansion during cycling processes was the reason underlying most of the problems given above [3].

Many approaches were tried until now for the purpose of compensating such volume expansion. Flower-like morphologies [4, 5] nanoflakes [3], nanorod and/or nanotubes [6], sponge-like [7], free-standing nanocomposites [8] and porous structures [9,10]. Recently, a new morphology called MicNo was developed by Entekno Materials Ltd. (www.enteknomaterials.com) MicNo is a designed, micron sized platelet shape particles that are composed of primary nano particles. MicNo morphology also contains ordered porosities in 3D network that will be considered as an option to accommodate volume expansions. In this study, electrochemical properties of ZnO with MicNo morphology were assessed. The capacity fade and retention after 7 cycles will be evaluated. By comparing with commercial ZnO, the effect of MicNo morphology will also be reported.

Appropriate amount of PVdF as a binder were dissolved in N-Methyl Pyrollidone (NMP) solvent. Electrode slurries were prepared by mixing active material and PVdF with a composition of 80:10:10 in planetary ball mill. As-prepared slurries were tape-casted on to Cu foil and dried overnight in a vacuum oven at 80 ℃. After that, electrodes were punched to a circular shape with a 16 mm diameter. Pouch-type half-cells were assembled with Li foil (Alfa Aesar) as a counter electrode. The electrolyte used in this study were 1M $LiPF_6$ in EC:DMC (1:1) purchased from Sigma-Aldrich. The charge-discharge curves were obtained between 0.02 – 3.00 V from BasyTec multichannel battery cycler with indicated charge/discharge rates. Cyclic Voltammetry (CV) measurements were also conducted by BasyTec multichannel battery cycler with 0.02 – 3.00 V with a scan rate of 0.01 mV/s. All potential values were presented versus Li/Li^+ reference.

Figure 1 shows the comparison of charge and discharge capacities of commercial ZnO provided from Sigma-Aldrich and MicNo for the first six cycles at a charge & discharge rate of 50 mA/g.

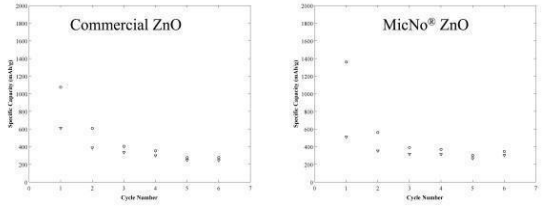


Figure 1. Charge & Discharge capacities of Commercial and MicNo ZnO for the first six cycles

In Figure 1, 240 mAh/g discharge capacity retention was observed from commercial ZnO after six cycles,. However, 300 mAh/g discharge capacity was preserved with using MicNo ZnO stating that 25 % discharge capacity retention increment after six cycles by using MicNo morphology ZnO particles.

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Effect of Different Binders on Cyclic Performance of Si/C Anodes for Secondary Lithium-Ion Batteries

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Abstract

Silicon is a strong anode material alternative to graphite in terms of its high energy and power capacity. On the other hand, the insertion of lithium atoms per silicon atom has some cons. The full lithiation of silicon results in a 400 % increase in volume. This drastic volume change causes diffusion-induced stress, which may lead to fragmentation, disintegration due to fractures and bonding problems of the current collectors with active materials, which lead to significant losses in capacity, and hence, poor cycle performance. Blending with elastomeric binders is one of the many approaches that has been proposed to overcome this problem of silicon based anode materials. In this study, electrodes were prepared using three commercial binder materials; polyvinylidene fluoride (PVDF), LA132 (polyacrylic latex) and PSBR100 (Modified Styrene-Butadiene Copolymer). LA 132 gave the best result. It yielded the highest first discharge capacity with the value of 3050 mAh.g^{-1} and even after 75 cycles, its capacity was around 210 mAh.g^{-1}. On the other hand, commercially used PVDF could stand only for three cycles.

1.Introduction

Current Li-ion battery technologies outperform most other commercially manufactured batteries, such as Ni-MH and NiCd based batteries. Their statistics are proof. Their safety, power, cycle life, zonal temperature performances are indeed superior. However the optimization of the design of electrode makes their usage for portable applications more feasible [1, 2]. Therefore, the need in the development of lithium ion batteries with better characteristics rises day by day. As the electrode materials play the key role in a battery, in order to increase the electrochemical performance, designing better electrode materials is the main task.

For the past few decades, Li-alloying reactions with metallic or semi-metallic elements (e.g., Sn, Sb, Al, Si, Ge, Pb, P, As, Bi, Au, In, Ga, Zn, Cd, Ag, Mg and their alloys) and various compounds have been investigated. Even though these alloying materials can provide a better specific capacity than graphite, they usually lack in irreversible capacity at the first cycle and unimpressive cycling life because of significant damages stemming from huge volume changes during cycling. That is why materials to manufacture anode alloys with high capacities (with respect to graphite) are still studied. But many have been unsuccessful to create commercially feasible products due to failed capacity retention after cycling or due to phase transformations and/or huge volume expansion related electrode cracking and pulverization problems after repeated Li alloying–dealloying. In other words, the more the host anode material accommodates Li, the worse the mechanical degradation issues and hence, the larger the volume expansion and with perpetual cycling [3, 4].

Silicon anodes have received lots of interest because of the fact that a single atom of silicon can accommodate 4.4 lithium atoms, forming $Li_{22}Si_5$. As a result, silicon has the highest theoretical capacity (4200 mAh.g^{-1}) of any alloying element and attractive operating voltage (~0.3V vs versus Li/Li$^+$). This means that silicon anodes could possibly have over ten times the gravimetric capacity with respect to graphite based anodes.

On the other hand, the insertion of 4.4 lithium atoms per silicon atom has some cons. The full lithiation of silicon results in a 400 % increase in volume from cubic silicon (20.0 Å^3 per silicon atom) to cubic $Li_{22}Si_5$ (82.4 Å^3 per silicon atom) [5]. This drastic volume change causes diffusion-induced stress, which may lead to fragmentation, disintegration due to fractures and bonding problems of the current collectors with active materials. It also damages the solid-electrolyte interface (SEI) which protects electrodes from further deterioration. The degradation and loss of electrical conductivity lead to significant losses in capacity and hence, poor cycle performance [6]. Many approaches have been proposed to overcome these problems of silicon based anode materials. The general strategies of creating silicon-based anode materials with good cycle performance can be categorized as follows: (i) controlling the structure and morphology (e.g.



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Burcu Miser

minimization of particle size or creating a hollow nanostructure which has a small volume to limit the volumetric expansion), (ii) active or inactive matrix compositing (also prevents aggregation), (iii) blending with various binders (e.g. elastomeric binders which expands during lithiation and shrinks during delithiation process), (iv) controlling of the cycling voltage window, (v) use of different salts such as LiFSI and introduction of electrolyte additives, such as vinylene carbonate (VC) to form a more stable SEI [7, 8].

The fundamental effects of binders in lithium-ion batteries involve binding the electrode materials on the current collector and ensuring good electrical contact between the active materials and the conductive agents [9]. Polyvinylidene fluoride (PVDF), LA132 (polyacrylic latex) and SBR (Modified Styrene-Butadiene Copolymer), Carboxymethyl cellulose (CMC) are some of the examples of different binders used for lithium ion batteries. SBR has a strong adhesion property and dispersion ability as an aqueous binder. LA 132 is a new alternative to commercial binders because it is aqueous and does not need addition of thickeners like CMC and organic solvents such as NMP, besides; production process is simple, safe, and environmentally friendly. Besides, less binder is required during this process. Additionally, some recent studies showed that NMC cathode with LA132 binder exhibited a much higher specific capacity than cathodes made up with PVDF and CMC [10].

2.Experimental

The chosen silicon powder for this study was produced by RF induction thermal plasma technique. It was used to produce carbon encapsulated silicon nanoparticles (Si/C). The average particle size was 82 nm and thickness of surrounding carbon layer was 7-10 nm. The surface area of the powders were 7.7 $m^2.g^{-1}$. There is 33 wt% SiC phase which is electrochemically inert. Figure 1 shows the TEM image of the encapsulated silicon particle.

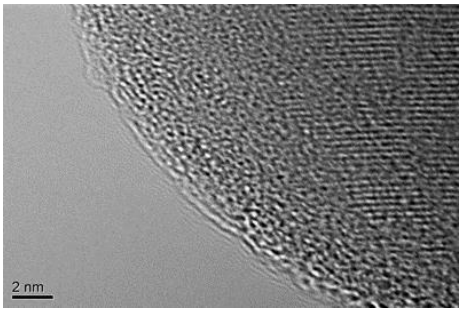


Fig. 1. TEM image of Si/C nanoparticle produced via RF induction thermal plasma.

Galvanostatic tests and Electrochemical Impedance Spectroscopy (EIS) were applied to the cells. As anode, lithium foil was used for all the cells. For cathode preparation, powders were mixed with selected binders. Silicon, binder and carbon black with the ratio of 70:20:10 was mixed. Anode slurry was coated on copper foil by using Doctor Blade technique. Thickness of the wet coating was adjusted to 200 µm. The coated sheets were dried at 80°C for a few hours and then pressed under 0.02MPa pressure. The discs with a diameter of 18 mm were cut from the previously produced electrodes were further dried in vacuum at 80°C for overnight. During the assembly process, as separator a glass microfiber filter was utilized. The electrolyte was 1 M of $LiPF_6$ in a 50:50 EC:DEC solution. Potentiostatic EIS was applied between the 10 mHz and 100 kHz frequency ranges, at the open circuit potential (OCV) of the cells. The AC amplitude was ±5 $mV.s^{-1}$. EIS was applied at the discharged state at the end of activation procedure.

3.Results and Discussions

As the aim of this study is to investigate the effect of three selected binders on cyclic performance of a Si/C composite powder, tests began with cycle tests. To see the change in the performance, the cells were cycled for 75 times. Charge-discharge tests were conducted between 0.05 to 1.2 V. To calculate the capacity, only the weight of silicon powder was considered as active material. The results of the capacity test is shown in Figure 2.

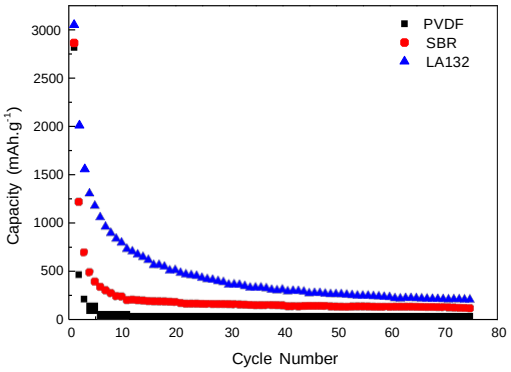


Fig. 2. The discharge capacity comparison of Si/C powder blended with various binders upon cycling.

It can be seen that the discharge capacities of three electrodes decrease gradually with the increasing cycle numbers. the highest capacity was achieved with LA 132 binder for all the cycles. The worst performance belongs to PVDF binder. It did not show better electrochemical results compared to other two. The highest first discharge capacity was 2800 $mAh.g^{-1}$.Unfortunately, it did not give a good confinement result as expected. Capacity retention of the powders was poor and after the second cycling capacities dropped under 300 $mAh.g^{-1}$ which means the battery was failed. As the flexibility of PVDF is lower than needed to compansate volume change of Silicon anodes, this failure was expected. What is remarkable in here is that the success of the LA 132, the capacity of 3050 $mAh.g^{-1}$ came close to full lithiation. It resulted in a higher first discharge capacity and continued to so till the end of the test. On the other hand, capacity fade still exists. It dropped under 500 $mAh.g^{-1}$ after 20 cycles, however, after 70 cycles it still has a capacity of 200 $mAh.g^{-1}$.

Before begginning to the cycle tests, impedances were measured. At this stage, all the samples showed similar behavior which explains the similar first discharge capacities. Figure 3, shows the impedance spectra comparisons of three binders before cycling.

Lastly, impedance values after 20 cycles were studied. According to this study, the highest impedance value got measured on PVDF binder, while LA 132 had the lowest value. The high impedance in the PVDFis probably from the

hindrance of charge transfer due to cracking and shedding of the electrode.

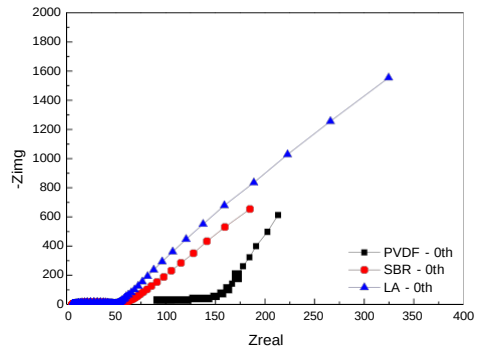


Fig. 3. Impedance spectra comparisons of three binders before cycling.

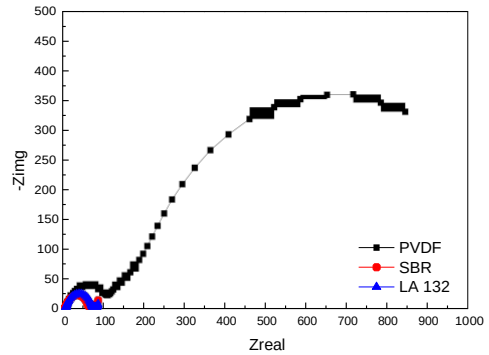


Fig. 4. Impedance spectra comparisons of three binders after 20 cycles.

4.Conclusions

Blending with elastomeric binders is one of the major approaches that has been proposed to overcome volume expansion problem of silicon based anode materials. With the prolonged cycle performance LA 132 gave the best result. It yielded the highest first discharge capacity with the value of 3050 mAh.g^{-1} and even after 75 cycles, its capacity was around 210 mAh.g^{-1}, whereas, commercially used PVDF could stand only for three cycles.

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Binder-free ZnO-SnO_2-rGO Nanocomposite Paper Anodes for Li-ion Batteries

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Lithium-ion batteries (LIBs) are being used for the whole new classes of portable electronic products, including laptop computers, cellular phones, and portable music players. Furthermore, LIBs have been used in prototype and pre-commercial plug-in electric vehicles (EVs) and hybrid electric vehicles (HEVs). Employed the active materials for Li storage are very important on the performances of LIBs. Electrode materials should reversibly accommodate a large amount of Li and fast ionic/electronic transfer in the cell to provide high specific capacity and current density [1].

Metal oxides such as SnO_2 and ZnO have been intensively investigated as promising anode materials for LIBs due to their high theoretical capacities of 1490 mAh g^{-1} and 978 $mAhg^{-1}$, respectively. However, they suffer from poor cycling performance and low rate capacity because of a large volume change and serious aggregation during cycling processes. Much effort has been devoted to the development of SnO_2 and ZnO based materials due to their high theoretical specific lithium storage capacities and low lithium-ion intercalation potential to overcome these problems [2]. To improve the capacity of anode and prevent huge volume change hybrid and composite structures are developed using graphene and other carbon derivative nanostructures [3].

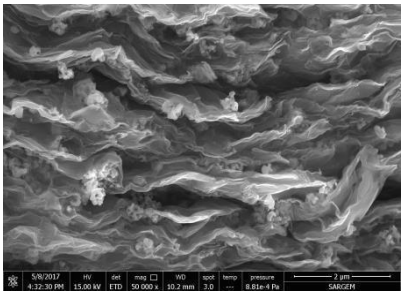


Fig. 1. FESEM image of free-standing ZnO-SnO_2-rGO nanocomposite from cross section of the paper.

In this work, ZnO-SnO_2-reduced graphene oxide (rGO) nanocomposite was produced as a binder-free, flexible free-standing paper anode for Li-ion batteries. For the production of ZnO-SnO_2/rGO nanocomposite, firstly, graphite oxide was produced via Hummers method from graphite and to obtain its aqueous suspension, it was ultrasonicated for 1 hour in water. Then, ZnO and SnO_2 nanoparticles synthesized by sol-gel method were added in 50 mL aqueous graphite oxide suspension and ultrasonicated for 1 hour again. This suspension was vacuum filtrated and produced free-standing anode paper after reduction in hydrazine solution. As can be seen from Fig. 1, which presents FESEM micrograph of ZnO-SnO_2-rGO cross section image, the ZnO-SnO_2 nanoparticles are regularly sandwiched between layers of rGO.

ZnO-SnO_2-rGO nanocomposite anodes were characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectrometer (EDS), and X-ray diffraction (XRD) analyses. CR2016 cells were assembled in a glove box (MBraun-Labstar). The cells were charged and discharged at 25 °C between fixed voltage limits at a constant current density on a BST8-MA MTI model battery tester to search electrochemical energy storage performance of the anode.

The results indicate that this ternary composite structure shows higher capacity retention compared with other binary composites due to the benefits resulting from the combining advantages of SnO_2 and ZnO, as well as the existence of the graphene which can make a contribution to the large-current charge/discharge capacity because of its extraordinary electronic transport properties, large surface area, and high electrocatalytic activities [2,3].

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Carbon Encapsulation and Encapsulated Si Particles for Energy Storage

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Low conductivity of most active materials used in energy storage may be remedied by a variety of methods. The use of additives to improve conductivity is very common, but the same may also be achieved by carbon encapsulation. Carbon coating of active materials either in amorphous or crystalline form not only improves the conductivity, but it also help maintain the stability of the structure by preventing agglomeration. This is particularly important with nanosize active materials which tend to agglomerate due to their small size. Almost all active materials are subject to volume changes during charge-discharge cycling. Carbon coating can usefully be employed to produce confined structures to limit the detrimental effects of volume changes.

There are a number of methods for carbon coating of active materials. Although this can be achieved via solution based methods (e.g. Si, Liu *et al*. 2012), the same may also be achieved via a gas phase synthesis. In the latter metal and carbon may be co-fed into a thermal plasma where they are evaporated and condensed into carbon and metal particles from the gas phase. In this way, particles are encapsulated with carbon by exsolution of carbon particles trapped in the metal particles or encapsulating carbon layers may be formed via direct condensation of carbon atoms onto the particle surface.

In this study, wide range of metals were examined for their encapsulation behaviour using a spark discharge process where graphite electrode and methane was used as a carbon source. This forms the first stage of the current work. Next, of the metals studied, silicon was selected for further study where the process of encapsulation was carried out with thermal plasma. The last phase of this work is electrochemical characterization of carbon encapsulated silicon particles. A brief summary of each stage is presented below.

So as to identify mechanism of encapsulation, metals W, V, Ti, Si, Cu Mg and Sn (Fig.1) were studied in a spark discharge generator where they are used as negative electrode against carbon electrode in an atmosphere of steady flow of argon enriched with methane. The study showed that metals or their carbides are successfully encapsulated with carbon except for Mg and Sn. The latter metals which have low melting point produced nanoparticles embedded in a graphitic matrix. The study showed that melting point of the element is the most critical parameter dictating the formation of composite structure. High melting point metals or their carbides are successfully encapsulated yielding a core-shell structure. The metals with medium melting points, e.g. Cu form a partially filled core-shell structure, as a fraction of space inside the shell is empty. Low melting point metals do not form a core-shell structure but metals condensing after the condensation of carbon produce nanoparticles embedded in a carbonaceous matrix.

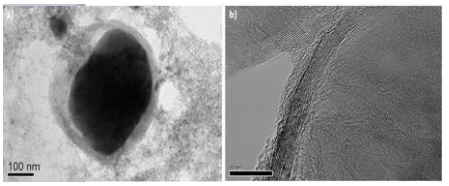


Figure 1. TEM images of carbon encapsulated particles a) Cu obtained with a spark discharge generator b) Particle produced with thermal plasma

Of the nanopowders examined Si was selected for further study. Since the quantity of powders with spark discharge was extremely low, new experiments were carried out with thermal plasma. Tekna 30 kW system was used for this purpose. Si was maintained into the torch with a vibratory powder feeder and methane was the carbon source fed into the Si carrier gas. XRD pattern of the resulting powder in given in Fig.2(a). The powder is made up of Si, SiC and graphite. A TEM image of a particle is given in Fig. 1(b). Fig. 2(b) shows cyclic discharge capacity of the composite powder obtained with thermal plasma. Initially very high capacity of around 2227 mAh/g was reduced down to 300 mAh/g which means that carbon encapsulation did not provide a sufficient protection for the active material.

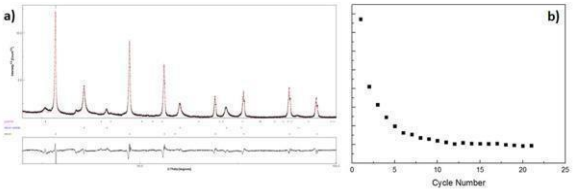


Figure 2.a) Rietveld refined XRD pattern and b) Discharge capacity versus cycle number in composite powder produced via thermal plasma.

Currently experiments are in progress where coating process is modified; Silicon nanoparticles are produced first and then carbon coated downstream, this for the purpose of minimizing or eliminating SiC formation .

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Fe_2O_3/rGO Nanocomposite Free-Standing Anodes for Li-ion Batteries

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Li-ion batteries are currently used in many devices such as portable electronics, laptop computers and cellular phones because of their higher energy density compared to other battery types [1]. Additionally, for electric vehicles and hybrid electric vehicles, Li-ion batteries are becoming a key-enabling technology [2]. To meet the increasing demand for higher energy density batteries, it is important to improve durable, nontoxic, and inexpensive electrode materials which have high charge/discharge rate and a high reversible capacity. In this context, as anode materials, transition metal oxides (Co_3O_4,MoO_3, and Fe_2O_3) are capable of Li^+ alloying/dealloying more than 6 Li^+ per formula, causing significantly larger reversible capacity than that of commercial graphite anode [3]. Among these metal oxide anode materials used for commercial applications, Fe_2O_3 has a great potential because of its high capacity (1005 $mAhg^{-1}$), low cost and low toxicity [4]. During cycling of Li^+ intercalation/deintercalation, transition metal oxides mostly break into small metal clusters, which induces volume expansion and destruction of the anode structure upon charge-discharge cycling. Hence, especially at high rates, capacity loss and poor electrical conductivity is observed with cycling [3]. In order to overcome these obstacles, the conducting carbon matrices have been suggested to absorb the volume expansion and to develop the structural stability of the anode materials [5]. Recently, among various carbonaceous nanostructures, graphene is expected to be an excellent buffer material for Li-ion battery anodes because of its superior electrical conductivity, ultrathin thickness, high surface/volume ratio, chemical stability and flexibility [6].

In this work, free-standing Fe_2O_3/reduced graphene oxide (rGO) nanocomposite anodes were produced for CR2016 Li-ion cells. Fe_2O_3 nanopowders were synthesized from $FeCl_3.6H_2O$ precursor via sol-gel method. 1:1 (w/w) ratio of Fe_2O_3 nanopowder and graphite oxide produced by modified Hummer"s method were ultrasonicated for 2 hours and then vacuum filtration was applied through PVDF membrane. After that, Fe_2O_3/Graphene Oxide paper was peeled off from the membrane and reduced in diluted hydrazine solution to produce flexible, free-standing Fe_2O_3/rGO nanocomposite anode.

Produced Fe_2O_3/ rGO nanocomposites were characterized by Field Emission Scanning Electron Microscopy (FESEM), and X-ray diffraction (XRD) analyses. Optical properties of Fe_2O_3/rGO nanocomposite anodes were investigated via Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. CR2016 cells were assembled in a glove box (MBraun-Labstar). The cells were charged and discharged at 25 ℃ between fixed voltage limits at a constant current density on a BST8-MA MTI model battery tester to investigate electrochemical performance of the anodes.

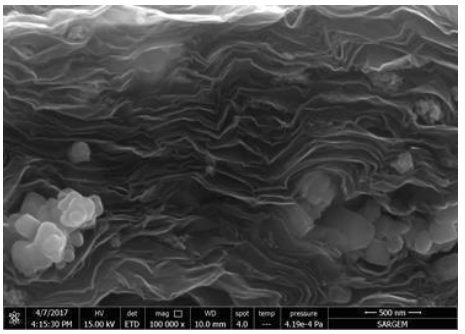


Figure 1. FESEM image of free-standing Fe_2O_3/rGO nanocomposite from cross section of the paper.

Figure 1 represents FESEM micrograph of Fe_2O_3/ rGO cross section image. Well-ordered Fe_2O_3 nanoparticles can be seen among rGO layers of nanocomposite structure. And this free-standing Fe_2O_3/ rGO nanocomposite anode structure has provided high discharge capacity and capacity retention.

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Graphene Assisted Core Shell Sn@C Hybrid Nano Composites Anode Electrodes for Li-Ion Batteries

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In recent years, many studies on lithium ion batteries (LIBs) have been made in order to obtain high energy density, high safety, low cost, and long life cycle [1]. It is well known that the performance of LIBs is mostly rely on anode and cathode electrode materials. The new generation high capacity cathode and anode electrodes are still demanded by an extensive market for high capacity LIBs with higher energy densities and improved cycle life properties. Graphite based anodes are used as an intercalation host for lithium to form LiC_6, which corresponds to a charge capacity of 372 mAh g^{-1} in a traditional LIBs. However, literature studies indicate that extensive experimental have been proposed to increase the anode's electrochemical capacity. Surface modifications with carbon or alloying of lithium with metals such as Si, Sn and Al were also proposed. As an intercalative anode electrode, tin seems to be particularly attractive since it easily and reversibly alloys with Li atoms at potentials <1.1 V versus Li [2-4].

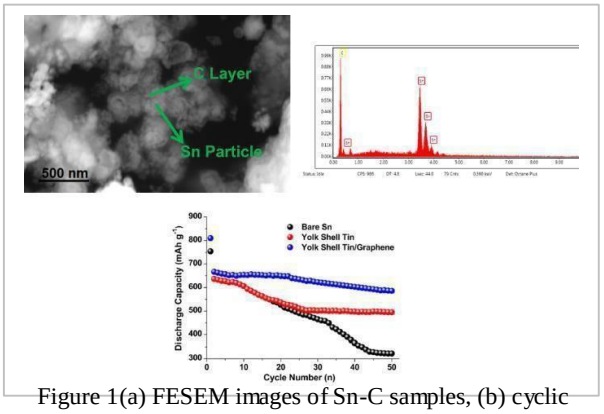


Figure 1(a) FESEM images of Sn-C samples, (b) cyclic performance of Sn, Sn-C and Sn-C/graphene freestanding electrodes.

In this study, multilayer graphene oxide was obtained by graphite flakes via modified Hummers method. Thereafter, the solutions were prepared in different ratios added graphene oxide by ultrasonication. Sn nanopowder was synthesised via chemical reduction method within the graphene oxide solutions and graphene oxide was chemically reduced with the Sn intermetallic nanopowders. The effect of carbon and graphene reinforcing on the electrochemical properties are investigated.

In this study, a unique "Yolk-Shell" structure reinforced with graphene is optimized by facile synthesizing methods. Tin nanoparticles as "Yolk" part of the structure were synthesized via chemical reduction techniques using tin (II) chloride as the precursor. The surfaces of the as-synthesized nano tin particles were subjected to SiO_2 sacrificial layer by sol-gel techniques followed by a microwave hydrothermal carburization in order to obtain the "Shell" structure as shown in Fig. 1(a). The obtained hybrid composite structure was then treated with hydrofluoric acid in order to remove the SiO_2 sacrificial layer and the tin/C yolk shell structure is obtained. In order to increase the electrochemical efficiency of the nanocomposites were reinforced with graphene through facile vacuum filtration techniques. The resulting yolk-shell tin/Graphene hybrid anode thus exhibited superior Li-ion performance with high reversible capacity, excellent cycleability, and good rate capability. This improved performance could be attributed to the formation of 2D graphene framework decorated with well-dispersed yolk shell tin nanocrystals, thus inducing fast diffusion of Li ions as also shown in Fig. 1(b).

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CNT-Graphene Based Hybrid Architectures for ZnO Nanocomposite Anodes

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Lithium-ion batteries have a high reversible capacity, long cycle life, low cost and environmentally friendly properties. Due to these properties of Li-ion cells, they have attracted considerable attention in science and industry fields [1,2]. ZnO is useful in electronics and optoelectronic devices because of its excellent electrical and optical properties. It is a semiconductor, has a wide optical band gap of 3.37 eV and high electrochemical activity [3,4]. Therefore, ZnO nanomaterials have widespread applications in electrode active materials such as Ni-MH cells, lithium cells, solar cells, and fuel cells [5]. For lithium-ion batteries, ZnO is an attractive anode material as a potential substitute for the conventional graphite anode, since the theoretical capacity (978 mAh g^{-1}) has been estimated to be superior to that of graphite (372 mAh g^{-1}) [6]. However, this structure has some disadvantages such as huge volume expansion during Li^+ insertion/extraction cycles and the quick aggregation of zinc particles, so it causes severe capacity fading of the anode [7]. To overcome these problems, several methods have been applied by using CNT and graphene [8,9].

In this study, we have performed a different approach to prevent pulverization of the anodes and subsequent electrical detachment of active materials, which formed by volume expansion. CNT and reduced graphene oxide (rGO) improve the performance of batteries due to their unique structures. They are considered as buffer material to prevent mechanical disintegration of anode material during the battery applications. So, we have used them as hybrid structure to utilize their synergistic effects. Fig. 1 shows this hybrid structure consisting of CNT, rGO and ZnO nanoparticles with FESEM image.

As a result, ZnO-CNT-rGO hybrid nanocomposite materials were produced as free-standing anode for CR2016 Li-ion cell. ZnO was synthesized by sol-gel method, graphene oxide (GO) was obtained by modified Hummer"s method and CNTs was functionalized with HNO_3-H_2SO_4 acid mixture. To produce ZnO-CNT-rGO buckypaper anode, 1:0.5:1 weihgt ratio of ZnO, CNT and GO was ultrasonicated and vacuum filtrated on PVDF membrane. After reduction of the structure, produced ZnO-CNT-rGO anodes were characterized by field-emission scanning electron microscopy (FESEM), energy dispersive x-ray spectrometer (EDS), and x-ray diffraction (XRD). Electrochemical behaviour was also performed to determine discharge capacities on a BST8-MA MTI at a constant current density.

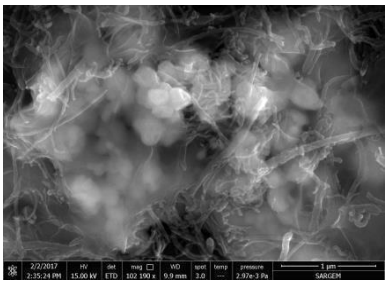


Fig. 1. FESEM image of ZnO-CNT-rGO hybrid nanocomposite structure.

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Development and Characterization of Tungstates and Molybdates for Li-ion Batteries

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Lithium-ion batteries are important for energy storage in a wide variety of applications including consumer electronics, transportation and large-scale energy production [1]. Metal tungstates and molybdates (Metals: Fe, Ni, Co, Mn, Zn, Mg) are two important families of inorganic materials and have found many applications in various fields. [2]. But, their use in energy storage applications is very limited. The tungstates and molybdates in the wolframite structure adapt monoclinic crystal structure and crystallize in P2/c (no.13) and C2/m (no.12) space group, respectively. Both structures have tunnels along certain crystal directions This crystal feature offers a high diffusivity path for ion transport and space for intercalation. Such physical features are among important requirements in Li-ion battery development [3].

More than 10 different ABO_4 type powder samples (A: Cd, Co, Fe, Mg, Mn, Ni, Zn and B: W/Mo) were produced by sol-gel method. These materials were $CdWO_4$, $CoWO_4$, $FeWO_4$, $MgWO_4$, $MnWO_4$, $NiWO_4$, $ZnWO_4$ and $CoMoO_4$, $FeMoO_4$, $MgMoO_4$, $MnMoO_4$, $NiMoO_4$. Calcination temperature range is 750 – 850 °C and duration changes from 2 to 6 hours. The structures of the powders were investigated with X-Ray Diffraction and Scanning Electron Microscopy.

These materials were used as active material against metallic lithium in a battery cell and the cells were characterized by using galvanostatic charge-discharge tests and electrochemical impedance spectroscopy. Figure 1 shows XRD spectrum of $CoWO_4$ and SEM image of $MnMoO_4$. Figure 2. shows the discharge capacity of molybdates at different discharge current. All compounds have shown quite high capacity at the initial discharge stage. Molybdates generally have higher capacity than the tungstates. During cycling, however, capacity decreases drastically. $MnMoO_4$ and $FeWO_4$ showed the highest capacity initially among molybdates and tungstates which are 1350 and 950 mAh/g, respectively. Cobalt, manganese and nickel tungstates suffer from capacity drop. According to the results of EIS, the cell impedance of molybdates was found to be lower than that of tungstates. Molybdates and tungstates in wolframite structure yield high capacity at low voltage values, which makes them a suitable anode material for lithium ion batteries. Further research is needed to understand the lithium insertion mechanisms underlying and amorphization of the compounds.

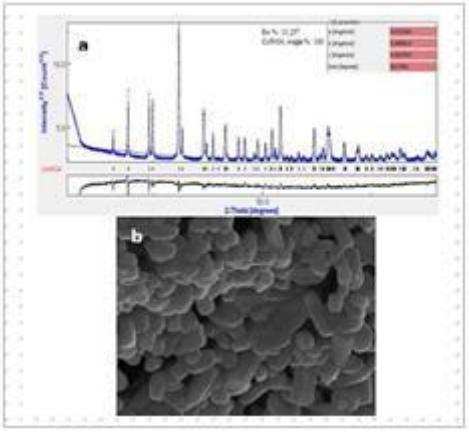


Figure 1. (a) XRD pattern of $CoWO_4$ at 800 °C for 2 hours, (b) SEM image of $MnMoO_4$ at 800 °C, 2 hours.

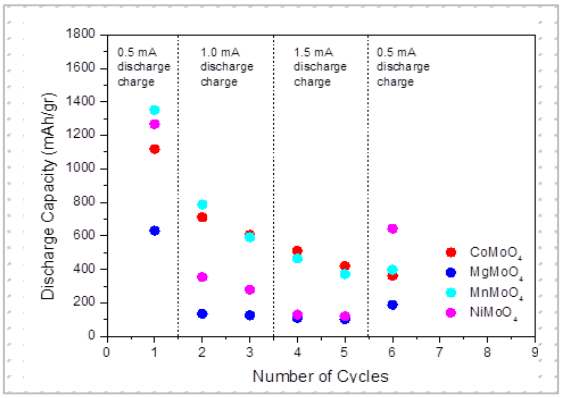


Figure 2. The discharge capacity graph of molybdates.

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Electrochemical Properties of Surface Processed Silicon Micro Particles for Secondary Lithium-Ion Battery Anodes

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Abstract

In this study, the aim was to process the surface of micron sized raw silicon powder via metal-assisted chemical etching method for next generation lithium ion batteries. Raw silicon powder (%99.99 purity, -325 mesh) was converted into surface processed anode material by using this method and its electrochemical performance was tested. For this purpose, cycle life and impedance of the cells were determined. After the production, the surface area was increased from 2.4 to 7.1 $m^2.g^{-1}$. Surface processed silicon powder yielded the higher first discharge capacity with the value of 3200 $mAh.g^{-1}$ and, raw silicon had 2300 $mAh.g^{-1}$. The capacity of surface processed Si fell under 1000 $mAh.g^{-1}$ after 5 cycles, whereas it was 3 cycles for raw silicon. After eight cycles, capacity retention increased for the surface processed Si. After 20 cycles, it still had a capacity of 200 $mAh.g^{-1}$.

1.Introduction

Amongst anode materials, silicon has the highest capacity (at room temperature its capacity is around 3600 $mAh.g^{-1}$ for $Li_{15}Si_4$ phase), whereas; the commonly used graphite has only a capacity of 372 $mAh.g^{-1}$. Although this property of silicon makes it a worthwhile subject, there are some technical issues which make it difficult for commercial use.

Metal-assisted chemical etching method has become a popular method for producing high surface area structures (e.g. nanowires, nanotubes, nanoparticles, porous structuring). It is an easy to apply, cheap, and powerful semiconductor etching technique with relatively precise control of orientation the nanowire creation, size (nano vs microscale), shape and density [1]. Still, there is lack of proper control on the manufactured features such as shape, size, etc. Because the etching conditions, such as the concentration of oxidant in etchant, etching temperature, and time, alter the morphology [1]. Metal assisted chemical etching involves three fundamental agents: (1) a dissolving oxidant for silicon (hydrogen peroxide (H_2O_2)), (2) a proper complexing agent that removes native silicon oxide surface and dissolves ionic silicon (hydrofluoric acid (HF)), and (3) a transition metal that locally enhances silicon dissolution in the vicinity of the metal (silver (Ag)) [2]. Using a two-step approach, Ge et al. produced porous silicon nanoparticles, combining controlled boron doping and metal assisted chemical etching. They assigned porous silicon nanoparticles as lithium-ion battery anode material, with capacities around 1400 $mAh.g^{-1}$ at a discharge current rate of 1 $A.g^{-1}$ and a stable operation up to 200 cycle was achieved. [3]. Bang et al. also worked on a similar experimental method. A low-cost, bulk silicon powder was employed to produce a multi-dimensional silicon structure composed of porous nano-wires and micro-sized cores. These anodes showed a high reversible charge capacity of 2400 $mAh.g^{-1}$ with an initial coulombic efficiency of 91% and stable cycling performance [4].

In this study, the aim was to process the surface of micron sized raw silicon powder via metal-assisted chemical etching method for next generation lithium ion batteries. Raw silicon powder was converted into surface processed anode material by using this method and its electrochemical performance was tested. For this purpose, cycle life and impedance of the cells were determined.

2.Experimental

Two-step metal assisted chemical etching method was applied to raw silicon powder (%99.99 purity, -325 mesh). Names and properties of the used materials are as follows: Silver nitrate ($AgNO_3$, 99+%, Alfa Aeser, Germany), hydrofluoric acid (HF, 38-40%, extra pure, Merck KGaA., Germany), hydrogen



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peroxide (H_2O_2, 30% stabilized, Merck KGaA., Germany), nitric acid (HNO_3, 65%, Merck KGaA., USA).

Before the etching, silicon powder is always washed with 10% hydrofluoric acid at 50 ºC for ten minutes to remove silicon oxide from the surface of the powder. Then, Si powder was immersed in an $AgNO_3$ and HF containing solution for a controlled time to deposit Ag nanoparticles onto the Si surfaces. Subsequently, powder is washed with deionized (DI) water to remove silver salts. Silver deposited Si powder, then, was immersed into the etching solution, which contains HF and H_2O_2 as oxidizing agents. After etching Ag was removed in concentrated nitric acid. After removal of Ag, powder is washed with DI water and dried at 70 ºC. By controlling the amounts of $AgNO_3$, HF, oxidizing agents, dwelling time and temperatures, different types of structures were obtained during experimental studies.

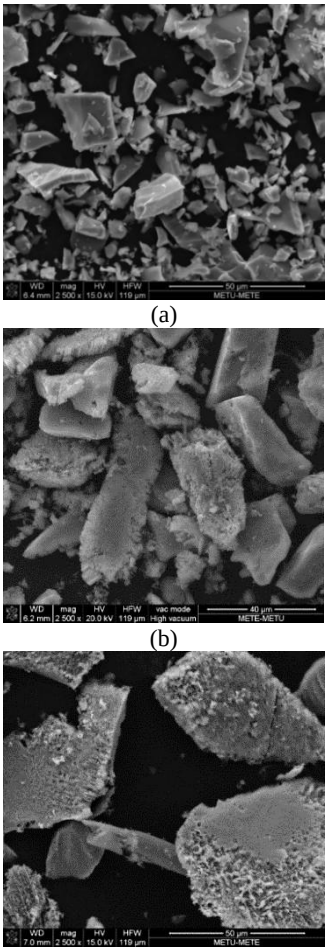
To clearly understand the morphology of each produced silicon powder, observation using a field emission type scanning electron microscope (FE-SEM, Nova NanoSEM 430, FEI) was made. Focused Ion Beam technique were also used to see porosity and columnar structures. Brunauer–Emmett–Teller method was used to identify the surface area of all the powders. To understand the morphology of the selected powder deeply, characterization by Transmission Electron microscopy (Jeol JEM-2100F UHR/HRP Transmission Electron Microscope (200 kV)) was done.

Galvanostatic tests and Electrochemical Impedance Spectroscopy (EIS) were applied to the cells. As anode, lithium foil was used for all the cells. For cathode preparation, powders were mixed with LA132 aqueous binder. Silicon, binder and carbon black with the ratio of 75:20:5 was mixed. Anode slurry was coated on copper foil by using Doctor Blade technique. Thickness of the wet coating was adjusted to 200 µm. The coated sheets were dried at 80°C for a few hours and then pressed under 0.02 MPa pressure. The discs with a diameter of 18 mm were cut from the previously produced electrodes were further dried in vacuum at 80°C for overnight. During the assembly process, as separator a glass microfiber filter was utilized. The used electrolyte was 1 M of $LiPF_6$ in a 50:50 EC:DEC solution. Potentiostatic EIS was applied between the 10 mHz and 100 kHz frequency ranges, at the open circuit potential (OCV) of the cells. The AC amplitude was ±5 $mV.s^{-1}$. EIS was applied at the discharged state at the end of activation procedure.

3.Results and Discussions

Production of Surface Processed Si powder. The main purpose of this study was to determine the proper experimental parameters of two-step metal assisted chemical etching. In the beginning, each step's conditions were specified.

Experiments began with the silver deposition step. The effect of $AgNO_3$(mol)/Si(mol) ratio was investigated. At each experiment, only one variable was changed. Other parameters were kept constant for all solutions. A standardized etching solution was used for all experiments. Three different ratio were studied, 0.01, 0.1 and 0.2. Figure 1 shows the SEM images of these samples. Etching could not be obtained on all the particles when ratio was as low as 0.01. When ratio is increased to 0.2, homogeneity of porous structure on particles disappeared, probably due to the dendritic growth of Ag particles on each other instead of Si. The best results in terms of porosity and wire generation were obtained with 0.1 mol ratio. However, there were too much abrasion loss which counter balanced surface increase.



(a) (b) (c)

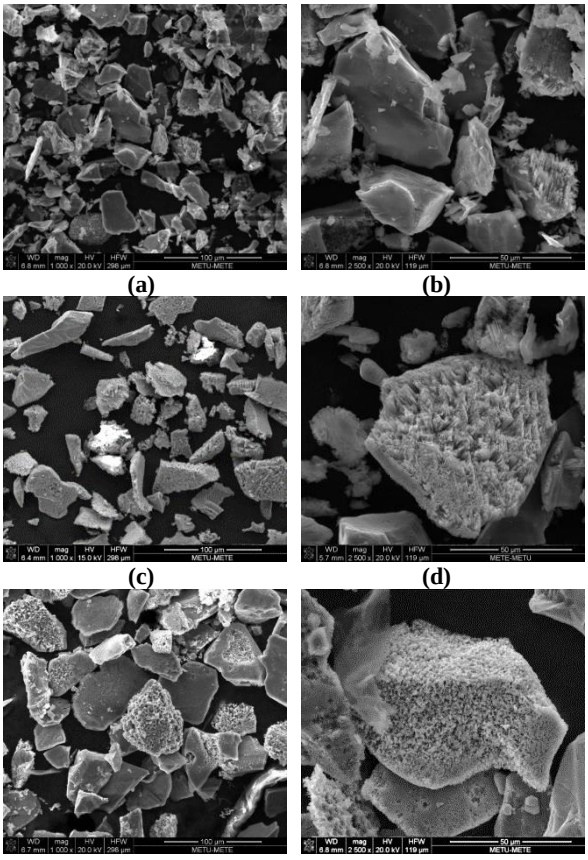
Fig. 1. SEM images of the samples which show the effect of AgNO3(mol)/Si(mol), (a, b) 0.01, (c, d) 0.1, (e, f) 0.2, at x1000 magnifications

After determining the optimal test parameters and values, experiments were continued with etching step. Table 1 shows the variables of etching step. Values, which were used as constant, are pointed out in bold.

Table 1 Experimental details of etching step

Variables of etching step:	Test Values:
H_2O_2 (ml)	0.5, **1.5**, 2
HF (M)	**5**
Temperature (ºC)	**50ºC**
Time (minute)	**60**, 300

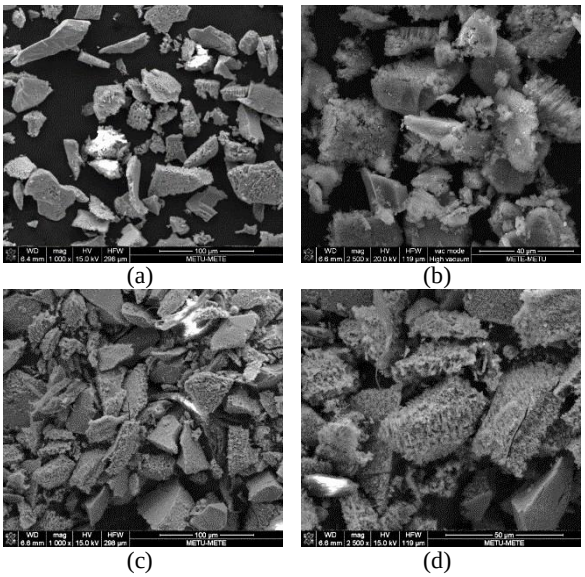
The first investigated parameter was H_2O_2 concentration. 0.5 ml was not enough to generate a porous structure. On the other hand, when the 1.5 and 2 ml volume were tested, the porosity of the silicon became obvious and an improved structure was formed around silicon particles. In the case of 1.5 ml, wires with the length of 3-5 µm were clearly seen in the SEM. 2 ml case also produced a porous structure, but, with larger pore sizes. Because, increasing the H_2O_2 volume can lead to high etching rate. Figure 2 a-f shows the SEM images of these experiments.



(a) (b) (c) (d) (e) (f)

Fig. 2. SEM images of the samples which show the effect of H_2O_2, (a, b) 0.5ml, (c, d) 1.5ml, (e, f) 2ml, at x1000 and x2500 magnifications.

Another factor having a direct influence on the structure is the etching duration. . Figure 3 shows the SEM images of the samples. Prolonging etching duration improves the surface properties, but also decreases the amount of usable powder dramatically.



(a) (b) (c) (d)

Fig. 3. SEM images of the samples which show the effect of time, (a, b) 60 minute, (c, d) 300 minute, at x1000 and x2500 magnifications.

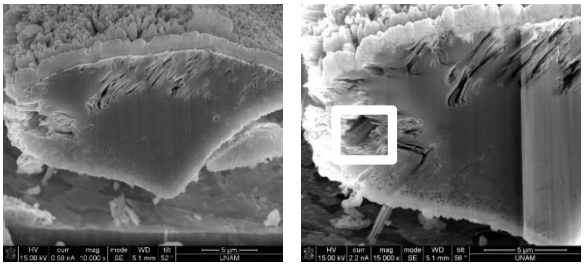
According to these SEM images, results of etching step on the production of mSi were summarized in Table 2.

Table 2 Decided parameters for electrode production

Silver deposition step	
Name of the variable	**Selected Values**
$AgNO_3$ (M)	0.02
HF (M)	5
$AgNO_3$(mol)/Si(mol)	0.1
Time (min)	5
Temperature (ºC)	Room temperature

Etching step	
Name of the variable	**Selected Values**
H_2O_2 (M)	0.02
HF (M)	5
Time (min)	60
Te mpe ra tur e (º C)	50

Before electrochemical tests, detailed characterization were done in order to understand the structure. The most important aspect of anode material production for this study is to increase the surface area of the as-received silicon powder. Surface area of surface processed Si was measured as 7.135 $m^2.g^{-1}$ which is three times larger than that of as-received powder (2.4 $m^2.g^{-1}$). To see the formation of pores, focused ion beam (FIB) technique was used and cross-sectional SEM images of the particles were taken (Fig. 4). Cross-sectional observations verified that porous structures are not homogeneous throughout the structure and the open pores are up to 3-4 μm deep. At image (b), inner wire formations are visible.



(a) (b)

Fig. 4. Cross sectional SEM images of surface processed Si obtained from the FIB process, (a) 10000x, (b) 15000x – it shows the columnar structure.

To investigate the existence of columnar structure, etched powder were dispersed in ethanol and ultra-sonication was applied for 10 minutes. After that, the suspension was rested for a couple of minutes and then a drop of the suspension was transferred onto a copper grid. The images of the detached wires are in Figure 5. EDS analysis were done on all the wires to make sure that they were silicon. Images show that the average diameter of the wires is smaller than 100 nm and their lengths vary. The longest tube height measured is 3 micron.

Particle size distribution analysis was done to these samples, because an important factor of lowered surface area could be due to the abrasion of smaller sized particles after etching (all SEM images). Particle size distribution verified that during etching most of the particles under 10-micron range vanished and average particle size increased up to 26 μm.

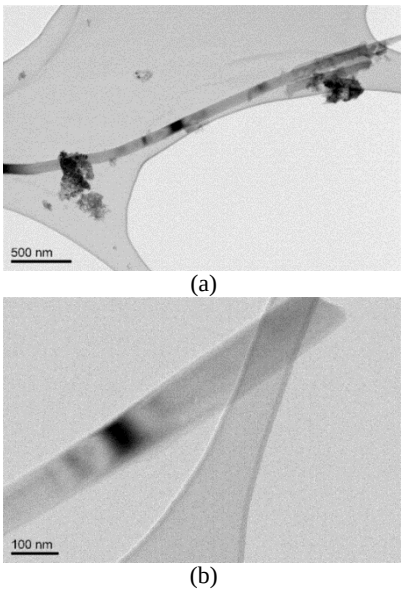


Fig. 5. TEM images showing the wires that were cut off from etched silicon particles.

Electrochemical Performances of Surface Processed Si powder. As the aim of this study is to improve the cyclic performance of a readily available powder, tests began with cycle tests. To gauge the change in the performance, as-received powder was also tested with a rate of 0.2 $mA.cm^{-2}$ during cycling. The cells were cycled for 20 times. Charge-discharge tests were conducted between 0.05 to 1.2 V. To calculate the capacity, only the weight of silicon powder was considered as active material. The results of the first test is shown in Figure 6.

The capacity graph shows that the highest capacity was achieved with the surface processed Si powder for all the cycles. The capacity of surface processed Si fell under 1000 $mAh.g^{-1}$ after 5 cycles, whereas it was 3 cycles for as-received powder. The capacity of the as-received silicon dropped under 100 $mAh.g^{-1}$ after 10 cycles, which means the battery was failed. As the particle size of as-received Si was bigger while its surface area was smaller than the surface processed Si, this failure was expected. What is remarkable in here is that the success of the etching method, the capacity of 2900 $mAh.g^{-1}$ came close to full lithiation. Without any coating layer, it resulted in a higher first discharge capacity and continued to so till the end of the test. On the other hand, the reversibility of the lithium insertion reaction is either very limited since most of the lithium atoms cannot be extracted during charge or shedding of particles has occurred.

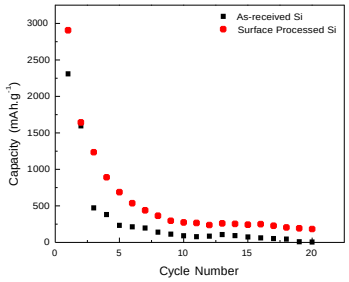


Fig. 6. The discharge capacity comparison of as-received and surface processed Si powders with cycling.

The impedances of the as-received and surface processed silicon powders were also measured and compared. According to this study, surface processed Si had an improvement. This can be attributed to the higher first discharge capacity of the surface processed silicon powder.

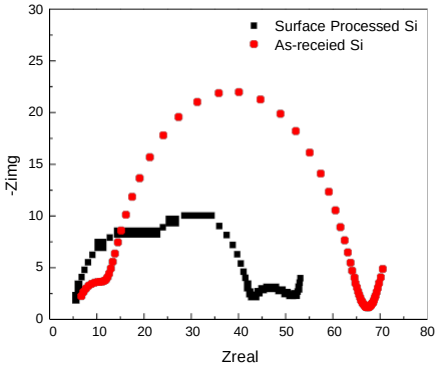


Fig. 7. Impedance spectra comparisons of two powders.

4.Conclusions

Metal assisted chemical etching is a successfully utilized method in order to produce surface processed silicon particles. Our studies confirmed the applicability of the method to powders as well. It produces a high surface to volume ratio structure. Surface area was increased to 7.1 $m^2.g^{-1}$. Surface processed silicon yielded the highest first discharge capacity with the value of 2900 $mAh.g^{-1}$ and even after 20 cycles, its capacity was around 200 $mAh.g^{-1}$ without any coating material. This method could be an alternative to the high-tech, expensive nanomaterial production techniques.

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Graphene Assisted NMC Based Cathode Electrodes with Enhanced Charge Rate and Energy Storage

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There is growing demand in high capacity Lithium ion batteries for consumer electronic devices and now is also being considered for vehicle applications. The cost, safety and performance issues of these batteries are also important. However, these issues in batteries are mostly determined by the cathode electrode materials. Recent studies and industrial applications are mostly focused on alternative electrode materials, which will replace the conventional $LiCoO_2$ electrode due to their high cost and limited electrochemical capacity. $Li(Ni_xMn_xCo_{1-2x})O_2$ based compounds, or named as NMCs, seem to be best candidates due to their low cost and higher capacities. NMC based cathode electrodes where x = 1/3, shows a discharge capacity of 160 mAh/g when cycled up to 4.2 V (4.3 V vs. Li/Li^+) and shows a discharge capacity up to 200 mAh/g when cycled to 4.7 V [1-3].

There are numerous studies for the preparation of NMC based electrodes such as solid state reaction, microwave synthesis, co-precipitation of hydroxides or insoluble salts, cryochemical synthesis, and others. However, these approaches have several drawbacks particularly in long process durations (up to 24 h), high temperature processings (up to 800 ℃), problems in homogeneity and homogenous particle distributions, low electrical conductivity and hence low specific capacity. In this study, a facile and fast synthesizing method is developed in order to obtain high purity $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ electrode materials with high specific capacities. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ electrodes were prepared through sol-gel method using $LiCH_3COO.2H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Co(CH_3COO)_2.4H_2O$ and $Mn(CH_3COO)_2.4H_2O$ reagents as the staring precursors. In a typical process stoichiometric amount of $LiCH_3COO.2H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Co(CH_3COO)_2.4H_2O$ and $Mn(CH_3COO)_2.4H_2O$ were dissolved in quantities corresponding to 0.02 mol of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ in 60 mL of water, containing 0.1 mol of resorcinol, 0.15 mol of formaldehyde and 0.5 m mol of Li_2CO_3. The mixture was heated at 60 ℃ until viscous, then
90 ℃ for 24 h, followed by calcination at 650 ℃ for 6 h to obtain $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. The as-synthesized NMC electrodes were also reinforced with graphene through a facile vacuum filtration technique in order to obtain freestanding electrodes. The electrochemical properties of the NMC and graphene reinforced NMC freestanding electrodes were investigated in detail.

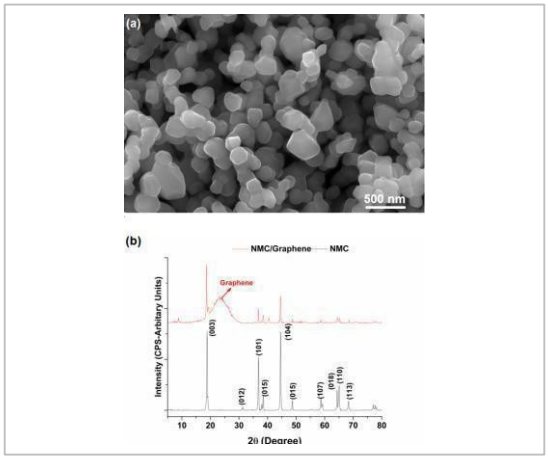


Figure 1 (a). FESEM images of NMC and (b) XRD spectras of the NMC ana graphene reinforced NMC.

In this study, NMC/graphene and NMC/carbon black samples were produced simply by sol-gel process with purity, as shown in Fig. 1. The NMC/carbon black samples were diluted with N-methyl-2-pyrrolidone (NMP) to obtain appropriate viscosity for Doctor Blade coating onto Aluminum foil. The two cathode materials were assembled into full coin cells. All three cells show good rate performance. Replacing carbon black with graphene dramatically improved the rate performance. NMC/graphene cells demonstrated ~145 mAh/g discharge capacity when being discharged at 1C, compared to the ~135 mAh/g from the NMC/carbon black, corresponding to ~7.4% improvement. The improvement was more significant at higher C-rate, such as 17 mAh/g at 5C, and 53 mAh/g for NMC/carbon black and NMC/graphene, respectively, corresponding to more than 200% improvement.

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The effect of lithium amount on electrochemical and structural characteristics of $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ cathode active materials for lithium-ion batteries

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Cathode materials found to be used according to battery criteria such as energy, power, security, cost and performance have not been able to fully meet these criteria until now and it is aimed to provide improvements by alloying [1] and nanotechnology methods [2-4].

In this study, it was aimed to produce $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})\ O_2$ (x = 0.90, 0.95, 1.00, 1.05, 1.10) as cathode-active material by ultrasonic sound assisted processing to be used in the areas where the energy requirement and capacity retention are required. Electrical properties and ionic conductivity, crystal structure and chemical composition, discharge capacity, charge-discharge rate capability and cycle life of the materials produced were characterized using PSA, SEM, EDS, ICP, XRD, CV and EIS methods.

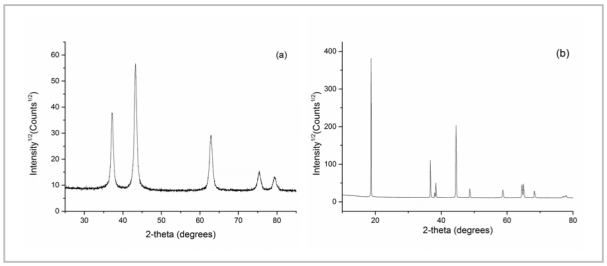


Figure 1. XRD spectrum of (a) cubic NiO phase and (b) layered $Li(NiCoAl)O_2$ phase.

In this regard, pure nickel oxide powder was synthesized with co-precipitation method using ultrasound. Citric acid was used as a chelating agent and pH value was set to 13.5. After pre-calcination at 300 °C for 12 hours, lattice parameter, *a*, of pure cubic NiO phase was obtained 4.181 Å by Rietveld refinement. Lithium carbonate was added by the help of ball mill and calcination was carried out at 800 °C for 24 hours to produce layered $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ where x= 0.90, 0.95, 1.00, 1.05 and 1.10. Figure 1.(a) shows the XRD spectrum of 100 % NiO phase and Figure 1. (b) shows the XRD spectrum of 100 % layered $Li(NiCoAl)O_2$ phase. As can be seen that there is no secondary phase formation. Intensity ratios of the highest two peaks (I_{003}/I_{104}) for all layered samples are larger than 1.33 which gives an information about the absence of cation disorder. These characteristics improve the structural performence. Of all compositions, the largest Li layer spacing and the least degree of cation mixing was seen in the layered 1.05Li-NCA compound.

It can be seen from figure 2. that 1.05Li-NCA compound had superior electrochemical characteristics with a 95 % capacity retention after 22 cycles at 0.12C. Although discharge capacity of this sample was 138 mAh/g, 95 % capacity retention was obtained after 20 cycles.

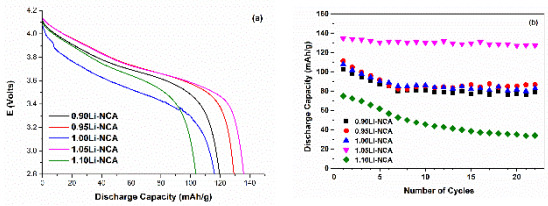


Figure 2. (a) Voltage and (b) charge-discharge profiles of layered $Li_x(NiCoAl)O_2$ compounds.

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Template Synthesis of Nano Structured $LiMn_2O_4$ Cathode Electrodes for High Capacity Li-Ion Batteries

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Recently, $LiMn_2O_4$ (LMO) is thought one of the most attractive cathode metarials for rechargeable Li ion batteries owing to abundant manganese resources, its low cost, fast charging–discharging reactions and no toxicity. However, because of the severe capacity fading due to Mn dissolution into organic electrolyte ($2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$) and Jahn-Teller distortion that results from cubic spinel to tetragonal spinel with a large unit cell expansion, researchers try to increase its cycle stability by employing different approches such as doping the Mn sites with other transition metal element (Co, Cr, Ni, Al, Fe, Mg) and surface coating. One dimensional nanosized structures shows not only less aggregation compared with nanoparticles but also higher rate capability and faster kinetics than micron sized structures because of large surface-to-volume ratio which is increased the contact between active material grains and electrolyte [1,2].

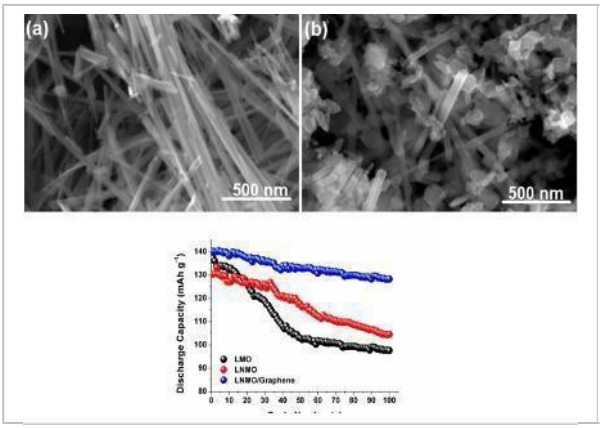


Figure 1(a) As-synthesized α-MnO_2 nanorods, (b) LNMO nanorods (c) cyclic performance of LMO,LNMO and LNMO/graphene freestanding electrodes.

In this study, a synthesis method nanorod LMO, $LiNi_{0.1}Mn_{1.90}O_4$ (LNMO) and LNMO/graphene nanocomposite cathode materials for Li ion batteries are reported. A two facile synthesis processes were applied in synthesizing the nanorod LMO and LNMO cathode electrodes. In the first step, microwave hydrothermal method is employed to obtain 1D α-MnO_2 nano rods. As-synthesized α-MnO_2 nano rods were then used as the starting material in a conventional solid state method in order to obtain LMO and LNMO cathode electrodes in the second step. A graphene based free standing cathodes are also fabricated through a vacuum filtration process. The effect of Ni substitution and graphene reinforcing on the electrochemical properties are investigated.

The morphology of the as-synthesized α-MnO_2 wires, LMO and LMCO nano rods were examined by FESEM and shown in Fig. 1. The FESEM images of the α-MnO_2 sample is shown in Fig. 2(a). The SEM images showed that the growth of the α-MnO_2 nano wires followed initial nuclei formation and continued to grow in unidirection into one–dimensional nanorods with respect to reaction time under uniform high pressure in the vessel. Figure 1(b) shows FESEM image of LMO nano rods obtained at 700 ºC. As can be concluded from Fig. 2(b), the morphology of LNMO has turned to nano rod morphology from nano wire morphology due to the solid state reaction which is performed at relatively high temperatures with long reactions times..

In summary, Ni-doped LMO nano rods with highly crystallinity were synthesized successfully via a solid state method using pre-synthesized α-MnO_2 nano rods as self-templates. A freestanding graphene based cathode electrode with as-synthesized Ni-doped LMO was also prepared by vacuum filtration technique. Graphene based freestanding Ni-doped LMO samples have shown tremendous electrochemical performance as also shown in Fig. 1(c). In addition, Ni-doped LMO freestanding samples maintain the spinel structure and the nano rod morphology with highly crystallinity after 100 electrochemical cycles. The excellent electrochemical cycle performance is contributed to the nano rod morphology, the structure stability derived from inert Ni-doping and graphene reinforcing.

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The Effect of Binders on the Electrochemical Properties of MnO_2 Cathodes

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Nanostructured materials can often produce many benefits, based on their extraordinary properties. Their compositions and modifiable structures make them useful functional materials. Besides this, the rapid development of modern society demands for renewable new energy systems. To meet the requirements of energy applications such as electric vehicles, hybrid electric vehicles, solar and wind electricity generation systems, new-generation cathodes with high reversible capacity and rate performance are required. Due to their high energy density, high voltage, and light weight, lithium ion batteries have become an important energy system. Manganese oxide (MnO_2) possesses high theoretical capacity, low cost, low toxicity and natural abundance; this makes it a useful material for application in lithium ion batteries [1]. Most studies have showed that MnO_2 cathodes are promising material. for Li-ion batteries (LIBs). But there are many factors which effects capacity of (LIBs). One of the effecting factors of battery capacity is the binder of cathode slurry.

Most studies of LIBs have involved the use of carboxymethylcellulose (CMC), poly(vinylidene fluoride) (PVDF) and poly(acrylic acid) (PAA) binders.

In this study, we investigated the binder effect on different types of MnO_2 cathodes. For this research α-MnO_2 nanowires were synthesized via facile and rapid microwave assisted hydrothermal method. As-synthesized α-MnO_2 and commercial MnO_2 cathode slurries were prepared with two different binder systems (*i.* PVDF binders/NMP solvent,*ii.* PAA binders/H_2O solvent) and their electrochemical properties were are studied. The XRD results of assynthesized α-MnO_2 has given in Figure 1.

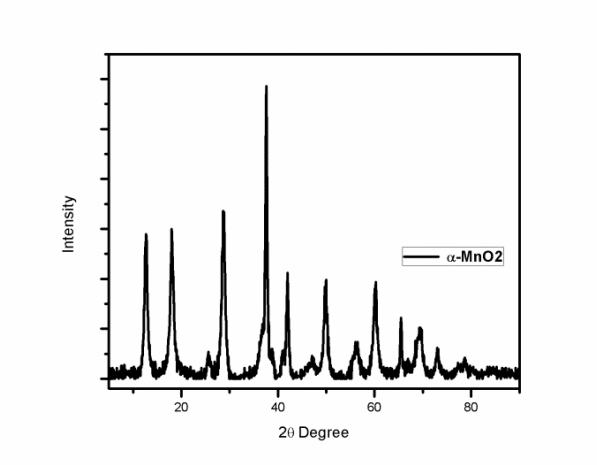


Fig. 1: XRD results of assynthesized α-MnO_2

Surface and cross-sectional morphology of the α-MnO_2 and commercial MnO_2 cathodes were investigated using field emission scanning electron microscopy (FESEM). Structures of the produced α-MnO_2 cathode was characterized using X-ray diffraction (XRD) technique and Raman spectroscopy. The electrochemical studies were performed with pure metallic Li foil anode.

Keywords: Li-ion battery, MnO2, Binder, Cathode.

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Doping of layered $Li(Ni_xMn_yCo_{1-x-y-z}M_z)O_2$ (z=W,Mo) cathode materials for lithium ion batteries

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Abstract

Layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) materials are potential cathodes for lithium ion batteries due to their high capacity, cycle life, rate capability and safety. NMC as a cathode exhibits higher capacity that of close to 200 $mAhg^{-1}$ with enhanced safety whereas well-known cathode, $LiCoO_2$, is limited to perform 50% of its theoretical capacity (140 $mAhg^{-1}$). Furthermore, its actual capacity, cycling stability and the capacity retention does not meet the exact requirements. In this respect, we previously focused on the development of layered $Li(Ni_xMn_yCo_{1-x-y})O_2$ cathode materials with different x and y ratios (x=0.2-0.6, y=0.2-0.6) to improve the properties in question. In the current study, it was also aimed to modify the layered NMC with group VIB elements in the consideration of ionic radius of the dopants. In this study, $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (111), $Li(Ni_{0.2}Mn_{0.2}Co_{0.6})O_2$ (226) and $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ (622) compositions were selected for the further investigation due to outcomes of the previous work. W and Mo (2 wt.%) were used as a doping elements to replace with Co. X-Ray diffraction (XRD) pattern of pristine and doped 111, 226 and 622 cathode materials exhibit good [006]/[102] and [108]/[110] doublets, indicating the layered structure, and good hexagonal ordering.The morphology of the pristine and doped cathode materials were examined by scanning electron microscopy (SEM) and it was clarified that dopants yield respectively finer grain size. The electrochemical cells were cycled at 0.1C and 0.3C rate (1C = 170 $mAhg^{-1}$) in the potential range of 2.7 – 4.2V. It was found that Mo doped NMC-111 performed the highest first discharge capacity of about 139.5 $mAhg^{-1}$, where the lost in its initial capacity was 18.5% after 22 cycles which might be contributed with the higher ordering hexagonal structure with less cation mixing.

1.Introduction

Besides the current usage of Li-ion batteries in power applications, it has been started to be used in electrical vehicles (EV). This kind of application requires more energy than most of the current commercial applications. Therefore, the possible improvements on commercialized products are crucial[1,2]. Considering the available Li-ion technology, $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) is intended as a cathode material to be in place with commercial product. NMC exhibits reasonable capacity and good structural stability with a less safety issue compared to other cathode materials[3]. Despite the favorable properties, NMC cathodes perform poor cycle life at high discharging rates[4]. In this respect, possible cation mixing during the synthesis of NMC is attributed as one of the main problems[5,6]. The dissolution of transition metals at higher cut-off potentials, generally higher than 4.3V[7], self-discharge of NMC-based cells and the side reactions occurring on electrolyte/cathode interface[8] are the other drawbacks of NMC cathodes. It is expected to enhance the structural stability by doping NMC cathodes, which effects the cation mixing arrangement and decreases the phase transition during Li-ion insertion and extraction[9].

Ates et. al, studied Na-doped of Li-rich layered metal oxide cathode material and observed that Na substitution improves the electronic conductivity of the Li-rich NMC cathode compared to undoped NMC. Na substituted NMC provides better rate capability with a lower impedance. Moreover, it is observed that Na substitution impedes the layered to spinel phase transition which is very important for layered cathode materials[10]. Similarly, Wang et. al studied on the substitution of Al and they stated that Al substitution improves the NMC cyclability. This improvement is attributed to formation of less solid electrolyte interface (SEI) layer and the mitigation of layered to spinel conversion[11]. Therefore, modification of layered cathode materials by doping is important to improve electrode performance and to decrease capacity fading[12]. Moreover, substitution of transition metals shows improvements in mitigation of side reactions[13]. Schipper et. al used Mg as a doping element for NMC and observed that the specific capacity increases during the initial 20-30 cycles. Also, the capacity stabilized at about 230 $mAhg^{-1}$ where Mg-doping level is 0.05 for $Li_{1.2}Ni_{0.16}Mn_{0.51}Mg_{0.05}Co_{0.08}O_2$[12]. There are several studies using different doping elements to improve layered cathode materials. In another study, Buyukburc et. al, reported that W doping improves the cyclability, where Mo doping



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In the present work, W and Mo were used as doping elements to check whether they improve the capacity, cycle life and rate capability of selected layered NMC-111, NMC-226 and NMC-622 cathodes. The cathode materials in question were synthesized via spray pyrolysis to improve electrochemical properties.

2. Experimental

$Li(Ni_xMn_yCo_{1-x-y})O_2$ cathode materials were synthesized using aqueous solutions of lithium nitrate ($LiNO_3$), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), manganese (II) nitrate tetrahydrate ($Mn(NO_3).4H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) with certain mole ratio of related compositions. Ammonium metatungstate hydrate ($(NH_4)_6W_{12}O_{39}.xH_2O$) and ammonium molybdate (para) tetrahydrate ($H_{24}Mo_7N_6O_{24}•4H_2O$) were used as doping salts to synthesize doped NMC cathode materials. The total concentration of the solution was 0.5 M with additives of citric acid and ethylene glycol. Solution was nebulized using an ultrasonic nebulizator operating at 1.7 MHz frequency. Droplets were then carried into the quartz tube reactor of 7 cm diameter, inside a three zone tube furnace by pure oxygen as a carrier gas. The flow rate of oxygen was 8.0 l/min and the reactor temperature was maintained at 600 °C. The powders were collected by an electrostatic precipitator at the end of the reactor, then heat treated at 800 °C for 20h. NMC-111, NMC-266 and NMC-622 were synthesized and doped with W and Mo in the range of 1-2 wt.% to replace transition metals with this procedure.

Crystal structure was analyzed by using X-Ray Diffractometer (XRD, Bruker D8 Advance). Phase analysis and lattice parameter of produced cathode materials was determined by Rietveld Analysis by using MAUD software. The morphology of synthesized cathode materials was investigated by scanning electron microscopy (SEM, Nova NanoSEM 430).

For cathode preparation, powders were mixed with polyvinylidene difluoride (PVDF) and carbon black with a ratio of 86:7:7. PVDF was used as a solution after dissolved in N-methyl pyrrolidinone (NMP) and further details are already discussed in our previous work[4]. All cathode samples contain 6 ± 0.05 $mgcm^{-2}$ active materials where a glass fiber sheet with a density of 52 gm^{-2} was used as a separator for cell assembly. 1 M $LiPF_6$ in a 50:50 EC:DEC solution was used as an electrolyte (battery grade LP40, Merck). Open-circuit voltage (OCV), charge-discharge behavior, discharge capacity and cycle life were examined using a potentiostat/galvanostat (Bio-Logic Instruments VMP-300). The electrochemical cells were cycled at different C-rates such as C/18, C/12 and C/4 (1C=170 $mAhg^{-1}$) within a 2.7-4.2 V potential window. Impedance measurements of synthesized cathode materials were performed in the range of 300 kHz to 30 mHz with a 10 mV amplitude.

3. Results and Discussion

NMC-111 samples were studied in order to understand the effect of different heat treatment durations on electrochemical properties. It was observed that relatively better hexagonal ordering with a high crystallinity could be obtained with a heat treatment duration of 20h. Moreover, 20h heat-treated sample showed an improved discharge capacity compared to others, Figure 1. In this respect, 20h was selected as a heat-treatment duration for the rest of the experiments.

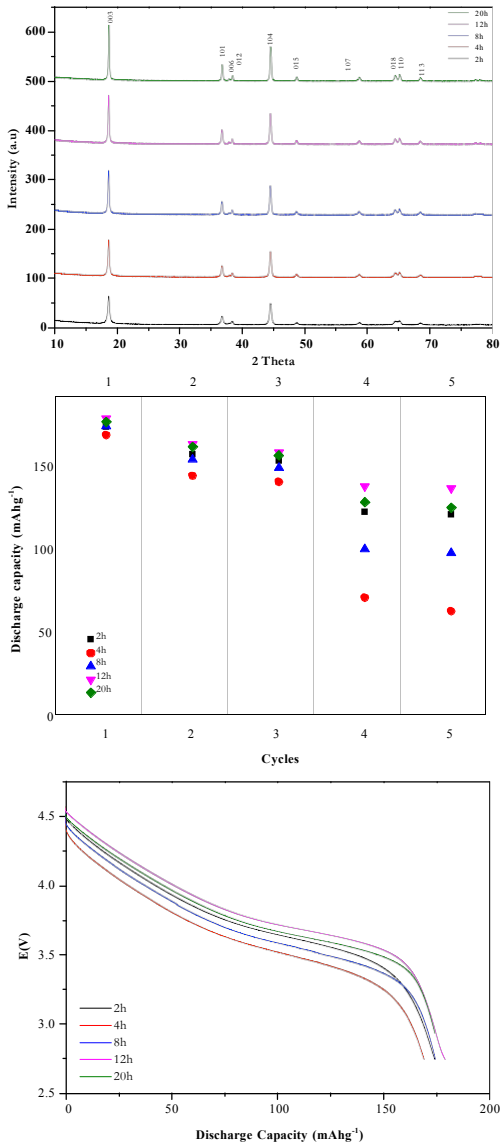


Fig 1. a) XRD patterns, b) discharge capacity-cycle curve and c) voltage profile of NMC layered cathode materials that were heat- treated at different durations up to 20h.

Figure 2 shows that XRD patterns of synthesized NMC-111, NMC-226 and NMC-622, using spray pyrolysis, following the heat-treatment at 800 °C for 20h. Compound formation, crystallinity and phase purity were evaluated, then it was observed that selected 20h heat-treatment results with high crystallization and discharge capacity for all sample

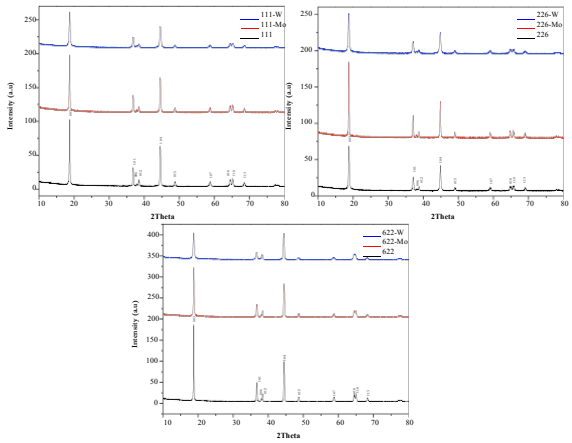


Fig 2. XRD spectra of synthesized NMC-111, NMC-226 and NMC-622 and heat treated at 800 °C for 20h.

XRD patterns show good [006]/[102] and [108]/[110] doublets indicating layered structure and good hexagonal ordering[17]. It is known that the ratio of $I_{[003]}/I_{[104]}$ peak intensity is an important indication to determine ordering characteristics. In the case of higher $I_{[003]}/I_{[104]}$ ratio than 1.2, the cation mixing is relatively less, whereas the ratio lower than 1.2 indicates a considerable extent of cation mixing[16]. High intensity ratio of $I_{[003]}/I_{[104]}$ is an evidence of very low or no cation mixing in the NMC and doped NMC structure. Additionally, it was observed that replacement of Co with doping elements result with formation of secondary phases in a larger extend. An example of XRD pattern belonging NMC-111 is given in Figure 3. It is known that the presence of cobalt decreases the formation of cation mixing during synthesis of NMC cathode materials,[17] which we also observed the same statement in the current study, where $I_{[003]}/I_{[104]}$ ratio is even lower than 1.2.

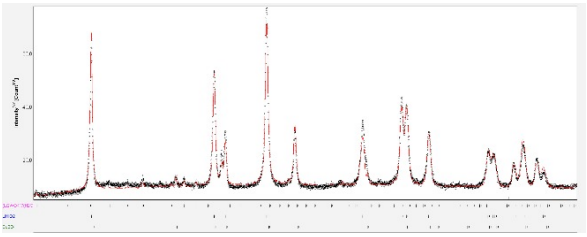


Fig 3. XRD pattern of NMC-111 and the formed secondary phases when dopants substituted with Co.

The refined structure parameters and oxygen positions for specified samples are summarized in Table 1. Lattice parameters *a*, *c* and oxygen position were determined with Rietveld refinement analysis using MAUD 2.76 [18]. In the literature, better electrochemical performance is generally attributed to larger *c* lattice parameter for layered structures.
The morphology of each synthesized cathode material was examined by SEM and typical SEM images are given in Figure 4. The primary particles have a spherical morphology forming aggregates to form larger grains.

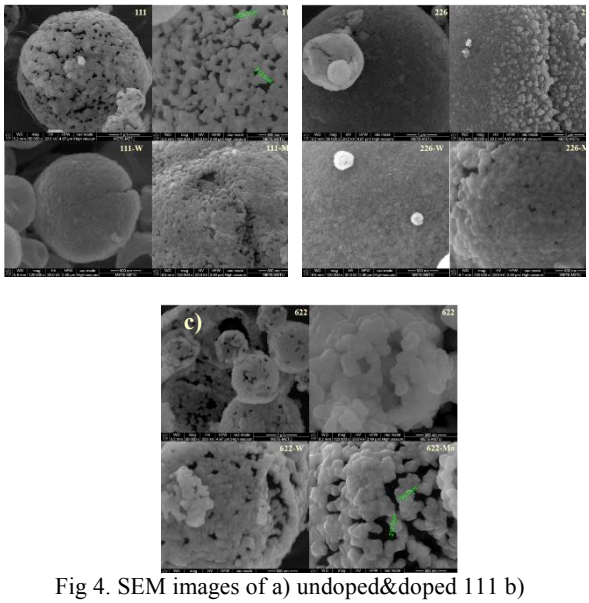


Fig 4. SEM images of a) undoped&doped 111 b) undoped&doped 226, c) undoped&doped 622.

The electrochemical performance of synthesized cathode materials were compared as a manner of undoped NMC, W-doped NMC and Mo-doped NMC. The comparison is given in Figure 5 and 6. The electrochemical cells were cycled at C/18, C/12 and C/4 rates (1C=170 mAhg-1) between 2.7-4.2 volts using potentiostat/galvanostat (Bio-Logic Instruments VMP-300). NMC-111-Mo, NMC-622-W and NMC-226-Mo exhibited capacity of 139.5 mAhg-1, 89 mAhg-1 and 109.5 mAhg-1, respectively as shown in Figure 5. All assembled cells showed similar impedance curve at their initial states. The reason of the capacity fading and impedance rise in NMC-622-W may be attributed with the cation mixing. NMC-111-Mo sample showed relatively better capacity with a lower impedance when it is compared with other samples. Therefore, it can be deduced that cathodes having lower impedance provide relatively better rate capability. The results were also confirmed that W and Mo doping of NMC cathode layered materials show improved capacity when it is compared to our previous study[4].

Table 1. Refined lattice parameters and oxygen positions of layered $Li(Ni_xMn_yCo_{1-x-y})O_2$ cathode materials.

Notation (NMC)	a (Å)	c (Å)	c/a	% Rw	$I_{[003]}/I_{[104]}$	Oxygen Parameter (z)
111	2.864	14.239	4.972	6.768	1.624	0.2582
111-W	2.865	14.253	4.975	5.743	1.603	0.259
111-Mo	2.864	14.246	4.975	7.027	1.608	0.261
622	2.871	14.214	4.950	8.602	1.870	0.2579
622-W	2.875	14.228	4.948	5.874	1.011	0.2585
622-Mo	2.875	14.228	4.948	5.874	1.460	0.2585
226	2.843	14.179	4.987	4.774	1.638	0.2583
226-W	2.844	14.188	4.989	4.503	1.690	0.2874
226-Mo	2.844	14.187	4.988	5.673	1.417	0.2602

a) b)

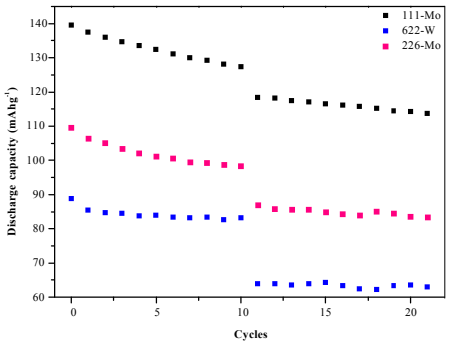


Fig 5. Comparison of charge-discharge tests of 111-Mo, 622-W and 226-Mo.

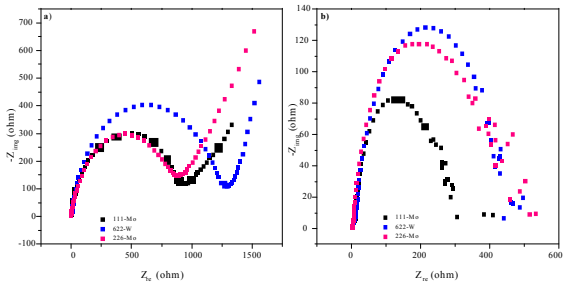


Fig 6. Electrochemical impedance spectroscopy results of NMC samples at 0 % SOC(a) after 1 cycle and (b) after 22 cycles.

The cycling measurements revealed that samples maintain their capacity at around 82%, 71% and 76% for NMC-111-Mo, NMC-622-W and NMC-226-Mo, respectively following 22 charge-discharge cycles, Figure 5. Electrochemical performance of synthesized cathode materials can be related to crystallite size, higher lithium ion kinetics and ordering of cation sites in the layered structure. The calculated gap size in the layered structures were determined very similar. It can be deduced that higher structure ordering with unmixed Li/(Ni-Mn-Co) cations in the layers of the crystal structure is dominantly improves electrochemical performance of samples, rather than particle size or mass transfer.

4. Conclusions

Undoped and doped NMC layered cathode materials were synthesized, having a spherical morphology with a very fine primary particle size, using spray pyrolysis method. The layered crystal structure was obtained following the post heat-treatment at 800 °C for 20h. NMC-111-Mo performed the highest first discharge capacity of about 139.5 mAhg-1, where the lost in its initial capacity was 18.5% after 22 cycles. It was observed that doping elements improve the rate capability and cycle life, however, the electrochemical properties still required to be improved. The current work is a part of comprehensive study where the effect of doping on NMC layered structure is further investigated.

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The Effect of the Li source on the ionic conductivity of $Li_7La_3Zr_2O_{12}$ Solid Electrolytes

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All Solid State Lithium Ion Batteries that contain solid electrolytes are becoming most trendy candidates in the field of energy storage, especially batteries that require high energy density, long cycle life and enhanced safety. However, solid electrolytes" relatively poor ionic conductivity is the main drawback that scientists have been trying to solve [1].

Among other types of solid electrolytes garnet type $Li_7La_3Zr_2O_{12}$ based electrolytes stand forward since their outstanding properties in terms of high chemical stability against Li metal, air and moisture, thermal stability and ionic conductivity [2]. On the other hand, garnet type cubic LLZO stabilization must be achieved during synthesis.

Al is one of the most commonly used cubic phase stabilizer and can create Li vacancies in addition to increasing ionic conductivity [2-4].

Synthesis of LLZO based electrolytes is time-consuming step with relatively slow heating/cooling rate [2]. However, by simply changing precursors, it"s possible to modify synthesis conditions and achieve highly dense ion conducting pellets [5].

In this study, 15 mole % Al contained LLZO electrolytes were synthesized by Solid State Reaction Method. Stoichiometric amounts of $La(OH)_3$, ZrO_2 and $Al(OH)_3$ and different Li sources such as $LiNO_3$, LiOH and Li_2CO_3 powders were mixed in agate mortar grinder (Retsch RM200) for 30 minutes in 2-propanol media. 15 % of excess Li as LiOH was added in order to compensate Li losses during heat treatment. Powders were calcined at 1000°C for 10 hours in a muffle furnace (Nabertherm). After that, powders were ground again for 30 minutes and 1.5 g of calcined powders were isostatically pressed into pellet (15 mm diameter) at 290 MPa. Then, pellets were sintered at 1200 °C for 12 hours in a powder bed containing calcined powders. Alumina crucible was used for all heat treatments. 10 °C/min heating rates were set for all heat treatments.

Crystal structures of pellets were determined by using X-Ray Diffractometer (XRD - Rigaku MiniFlex 600) between 15° - 55° with a scan speed of 1°/min and step size of 0.02° by using Cu K_α. AC Impedance Method were used to measure ionic conductivities of pellets. Pellets were firstly polished up to 2500 grit SiC papers. Then, to obtain a Li-ion blocking electrodes Au-Pd were sputtered on both sides of pellets for 90 seconds. All conductivity measurements were carried out by using Galvanostat/Potentiostat system (Gamry Reference 600) with a minimum current resolution of 20 aA.

XRD measurements after calcination process at 1000 °C and 10 hours showed that three different Li sources resulted in the occurrence of the cubic $Li_7La_3Zr_2O_{12}$ phase. However, the least impurity phases were obtained by using Li_2CO_3 precursor. Furthermore, ionic conductivity results showed that the highest conductivity was obtained as 3.9 x 10^{-6} Scm^{-1} at room temperature when the Li_2CO_3 precursor is used.

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$Li_7La_3Zr_2O_{12}$ fibers as an electrolyte for all-solid-state Li-ion batteries

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Lithium-ion batteries are currently the dominant power source for portable electronic devices because of their high energy density and efficiency. Recently, there is a strong growing interest to develop large-scale Li-ion batteries, particularly for electric vehicles. Developing batteries with high energy density, safe operation, low cost, and long life is vital for successful implementation of Li-ion batteries in automotive industry. All-solid-state Li-ion batteries have been shown to significantly improve volumetric energy density, safety, and cycle life; however, their real-world applications are hindered by the complex and costly manufacturing processes. Recognizing this important need, the main objective of this study is to examine a new scalable and inexpensive technique for fabrication of an electrolyte for all-solid-state batteries.

Conventional Li-ion batteries typically consist of a positive electrode (cathode), a negative electrode (anode), and a liquid organic electrolyte. During charge/discharge cycles Li ions migrate through the liquid electrolyte between the two electrodes. Large-scale Li-ion batteries face many challenges in terms of safety, cost, and cycle life. Many of these challenges are associated with the use flammable liquid organic electrolytes. The liquid electrolyte can leak through the containment walls of the battery and catch on fire. The liquid electrolyte cannot provide a separation between the cathode and anode; therefor, polymeric separators need to be used in order to prevent the battery from a potential short- circuit. The use of flammable organic liquid electrolytes and polymeric separators induce serious safety problems including the risk of fire and explosion. Besides these safety concerns, the complex packaging remarkably increases the manufacturing cost, and lowers the energy density by increasing the weight and volume of the battery packs. In addition, side reactions and poor thermal stability of the liquid electrolyte result in a capacity fade, which shortens the battery cycle life. [1]

In all-solid-state Li-ion batteries, the components are all made up of solid phase. The nonflammability of the solid electrolyte overcomes the safety problem of the conventional Li-ion batteries. Since solid electrolytes neither leak nor vaporize easily, all of the cell components can be directly stacked in one container, instead of multiple containers as in the liquid-containing cells. Therefore, as shown in Figure 1, the battery size reduces, and thus the volumetric energy density significantly improves up to 3 times. Moreover, solid electrolytes physically separate the cathode from the anode, eliminating the need for separators. In addition, solid electrolytes have a wider range of operating potentials (over 5 V) and operating temperatures. They can be paired with certain high-voltage and high-capacity electrodes that are generally difficult to combine with liquid electrolytes. The good examples of these electrodes are lithium metal anodes and sulfur cathodes. Another feature of solid electrolytes is their single-ion conduction that suppresses side reactions and leads to a long battery life. As a result of unity transference number indicating that Li ions are the sole charge carriers, there is no concentration gradient inside the operating cells; thus, the cell over-potential is negligible. Furthermore, the capacity fade caused by the continuous decomposition of the electrode surface in contact with liquid is avoided. [2-4]

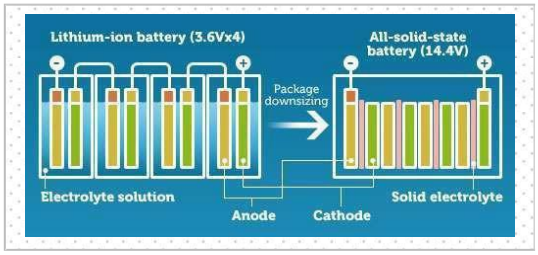


Figure 1. Improved packaging efficiency by direct stacking of the all-solid-state cells instead of using multiple containers in liquid-containing cells (Source: Research Progress: Next Generation Secondary Batteries, http://www.toyota-global.com)

The new methodology proposed in this work uses oxide filaments/fibers instead of a dense thin film electrolyte, allowing: (i) straightforward fabrication without the use of costly thin film production techniques, (ii) minor changes in the existing Li-ion battery production lines, and (iii) better mechanical stability and electrochemical performance. $Li_7La_3Zr_2O_{12}$ (LLZO) fibers as an electrolyte were prepared using the electrospinning technique. The crystallographic phase and morphology of the products was studied by X-ray diffraction (XRD) patterns. The results indicated that the produced electrolyte would be a good alternative of all-solid- state batteries for electric vehicles in terms of battery safety and performance.

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Using Oxide Based Electrolyte Additives in High Performance Li-ion Batteries

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Currently, Li-ion batteries are playing a significant role in portable electronic devices and electric vehicles (EV) because of their high energy and power density properties. Electrolytes, act as a bridge connecting the positive and negative electrodes, have a crucial role affecting the overall electrochemical performance of the cell such as rate, capacity, durability and safety. Various electrolyte additives have been developed and performed in Li-ion batteries in order to improve the electrolyte stability [1,2]. The addition of oxide based additives such as silica (SiO2), copper oxide (CuO), aluminum oxide (Al_2O_3), titania (TiO_2) nanoparticles results in the enhancement of ionic conductivities and thermal stability of the electrolytes [3]. Additionally, boron trioxide (B_2O_3) can be used as a SEI stabilizer to improve lifespan of the battery [4].

Because of high theoretical discharge capacity (978 mAh g^{-1}), zinc oxide based materials have attracted much attention as anode material for Li-ion batteries [5]. During the Li insertion/extraction process, volume expansion of metal oxides takes place and induces cracking and pulverization of the anodes. Hence, metal oxide/graphene nanocomposites are proposed as promising anodes because of the superlative mechanical strength and resilience properties of graphene sheets [6].

In this work, firstly graphite oxide was synthesized from pre-treated graphite powders via modified Hummers" method [7]. The obtained graphite oxide was exfoliated by ultrasonication together ZnO nanopowders. Then, the solution was filtered on PVDF membrane by vacuum filtration technique, the ZnO/Graphene Oxide paper was peeled off from the PVDF membrane and reduced in diluted hydrazine solution. ZnO/reduced graphene oxide (rGO) free-standing paper was obtained and used as anode in CR2016 Li-ion cell. And this ZnO/rGO nanocomposite structure can be seen via FESEM image in Figure 1.

Lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) salt was dissolved in EC:DMC (1:1, w/w) solvent mixture to obtain electrolyte solution including 1 m Li^+ ion. Appropriate amounts of B_2O_3 were added to electrolyte solutions. All the electrolyte preparations were carried out in a glove box in order to protect the solutions from moisture and prevent oxidation of the electrolytes. CR2016 cells were assembled by using these prepared electrolyte solutions, ZnO/rGO nanocomposite anodes and metallic lithium cathodes. Electrochemical tests were performed at room temperature.

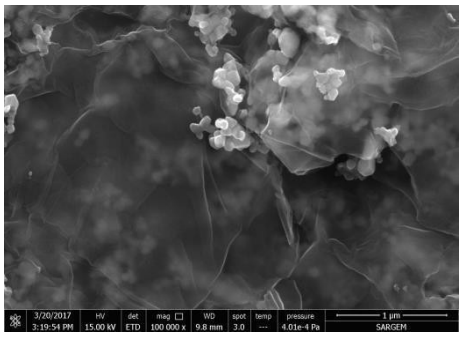


Figure 1. FESEM image of ZnO/rGO nanocomposite structure.

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SPS Sintering of Al stabilized $Li_7La_3Zr_2O_{12}$ Solid Electrolytes

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In recent years, the search for key power and energy storage devices has become necessary owing to the rapid growth in the daily use of devices such as electric vehicles, laptop computers, cellular phones and other portable electronic devices. One of such storage devices that has attracted worldwide attention and has stood the test of time over a decade is All-Solid-State Li-ion Batteries (ASSLIBs). ASSLIBs have been characterized by critical properties needed for today's battery-driven devices. These include; high energy density, portability, cost effective, long cycle life span and environmental friendliness [1]. However, its application in the emerging technologies hindered, because of the safety issues encountered by the use of organic liquid electrolyte including leakage, flammability and toxicity [2]. These problems necessitated the immediate development of an alternative electrolyte that is free from safety issues and ready to replace the liquid type electrolyte. These new materials include; LiPON [3] NASICON [4] perovskite [5] and garnet [6] type Li-ion electrolytes.

Considering the above-mentioned alternatives, $Li_7La_3Zr_2O_{12}$ (LLZO) with garnet structure is an ideal candidate for Li-ion conducting electrolyte as a result of its high ionic conductivity, low grain boundary resistance, good thermal and chemical stability [7]. The garnet structure, which has cubic phase, requires high synthesis temperatures and long sintering times. Furthermore, it's possible to increase ionic conductivity by addition of stabilizers such as Al. Thanks to the Al-Li replacement phenomena reported elsewhere, each mole of Al introduced within LLZO structure could create two moles of vacancies [1].

Lot of methods have been reported in the literature for obtaining cubic phase LLZO [1, 2, 6]. In all of these papers, powder bed sintering is required; the process is time consuming and cost ineffective. Spark Plasma Sintering (SPS) is a fast sintering technique, which uses shorter sintering time and lower temperatures, and have been widely used to obtain dense ceramic bodies. During the process, the sample is acted upon by the DC current and uniaxial pressure. The current passed through the die as source of heat. This heating process make the sample compacted in a shorter time and lower temperatures. As a result of the quick nature of the process, grain growth becomes suppressed [12].

High purity Li_2CO_3 (99.99 %, Merck) was dried at 200 ^oC for 6 hours. 15 % excess Li_2CO_3 was added to compensate the evaporation of lithium during the heating processes. Similarly, La_2O_3 (99.9 % Sigma-Aldrich) and ZrO_2 were calcined at 900 ^oC for 6 hours in order to get rid of hydroxide. Al_2O_3 (30 % mole) was used as Al source for cubic phase stabilization. Stoichiometric quantities of powders were weighed and mixed in agate mortar grinder (Retch, RM200) using 2-propanol. After complete homogenization, the slurry is dried using rotary evaporator and calcined at 1000^oC for 12 hours. To ensure the completeness of reaction, the calcined powdered is re-grinded by using 2-propanol and dried. Six grams of as-prepared LLZO powder was filled into a graphite die and placed between two electrodes with applied pressure of 15 kN. The heating rate is 100^oC/min. Sintering was done at 900^oC to 1250^oC for 3 mins.

Identification of phases of the sintered pellet is carried out using X-ray diffraction (Mini Flex 600) between $2\theta = 10^o$ to 60^o, with a step size of 0.02^o and scan rate 1^o/min. Scanning electron microscopy was used to observe the morphology of the pellet.

In case of measuring the ionic conductivity, a thin film of Au-Pd sputtered on the pellet as lithium-ion blocking electrode. An AC electrochemical impedance method was used in the frequency range from 1 Hz to 1 MHz at room temperature.

The results for different SPS temperatures showed that up to 1200°C, cubic LLZO phase did not observed. However, when the SPS temperature increased to 1250°C, cubic phase started to form according to the XRD results. This is interpreted that tetragonal to cubic phase transformation requires minimum temperature of 1200°C or above at which fully stabilised cubic phase can be obtained by using conventional solid-state methods. The other parameters such as time, heating rate and pressure need to be optimized.

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Understanding the Rapid Capacity Fading of LNMO-LTO Lithium-ion Cells at Elevated Temperature

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The high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has an average operating potential around 4.7 V vs. Li/Li^+ and a gravimetric charge capacity of 146 mAh/g making it a promising high energy density positive electrode for Li-ion batteries. Additionally, the 3-D lithium transport paths available in the spinel structure enables fast diffusion kinetics, making it suitable for power applications [1]. However, the material displays large instability during cycling, especially at elevated temperatures. Therefore, significant research efforts have been undertaken to better understand and improve this electrode material.

Electrolyte ($LiPF_6$ in organic solvents) oxidation and transition metal dissolution are often considered as the main problems [2] for the systems based on this cathode material. These can cause a variety of problems (in different parts of the cell) eventually increasing internal cell resistance, causing active mass loss and decreasing the amount of cyclable lithium. Among these issues, cyclable lithium loss cannot be observed in half cells since lithium metal will provide almost unlimited capacity. Being a promising full cell chemistry for high power applications, there has also been a considerable interest on LNMO full cells with $Li_4Ti_5O_{12}$ (LTO) used as the negative electrode. For this chemistry, for an optimized cell, quite stable cycling for >1000 cycles has been reported at room temperature while fast fading is still present at 55 °C [3]. This difference in performance (RT vs. 55 °C) is beyond most expectations and likely does not follow any Arrhenius-type of trend.

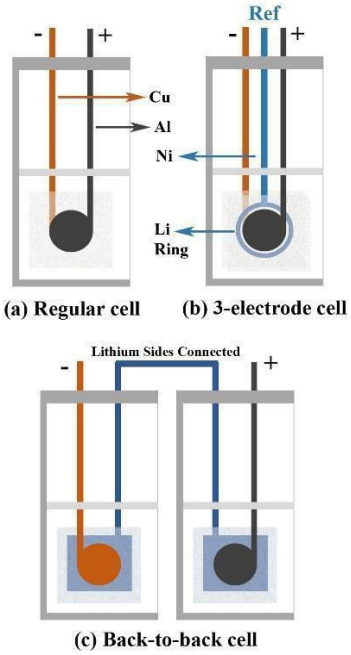


Figure 1. Schematic view of different pouch cells used for cell testing in this study.

In this study, a comprehensive analysis of LNMO-LTO cells has been performed at different temperatures (RT, 40 °C and 55 °C) to understand the underlying reasons behind stable cycling at room temperature and rapid fading at 55 °C. For this purpose, testing was made on regular cells (Figure 1a), 3-electrode cells (Figure 1b) and back-to-back cells [4] (Figure 1c). Electrode interactions (cross-talk) have been shown to exist in the LTO-LNMO systems [5] and back-to-back cells have therefore been used to observe fading under conditions where cross-talk is impossible [4]. Galvanostatic cycling combined with short-duration intermittent current interruptions [6] was performed in order to separately observe changes in internal resistance for LNMO and LTO electrodes in a full cell. Ex-situ characterization of electrodes have also been performed using scanning electron microscop y (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES).

Our findings show how important the electrode interactions can be in full cells, as a decrease in lithium inventory was shown to be the major factor for the observed capacity fading at elevated temperature. In this presentation, the effect of other factors – active mass loss and internal cell resistance – will be discussed together with the consequences of cross-talk.

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The design of a Lithium Ion Full Cell Battery Employing Silicon/Graphene Anode and αMnO$_2$/Graphene Cathode

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Lithium ion batteries have high energy and power density and become essential energy storage devices for mobile phones, laptops and electrical vehicles. Because of the limited capacity of graphite (372 mAhg^{-1}), one active research area is to find new anode material for enhance storage capacity of lithium ion battery. Silicon has the highest known theoretical capacity of 4200 mAhg^{-1} in the anode materials. However, huge volume changes (up to 400%) of Si during the process of lithiation/delithiation can causes crumbling and cracking of the electrode. One effective way is to development of different structured silicon such as nano-rods, nanowire and hollow nanoparticle. However, these studies are still not satisfactory, because of very complicated fabrication procedure and high cost.

Another bottleneck of lithium ion battery is the performance of cathode materials. Manganese dioxide (MnO_2) is one of the most promising metal oxide as lithium ion cathode material because of its high theoretical capacity (308 mAhg^{-1}), environmental friendliness and low cost. However, its volume expansion, aggregation, and low electronic conductance resulting in poor cycle stability extremely limit its potential application. In order to overcome this problem MnO_2 has fabricated in nano size and used with carbon materials to achieve excellent conductivity and large specific surface area.

Graphene is a good candidate for anode and cathode materials due to its excellent properties such as high electrical conductivity, high surface area and good mechanical strength. Two-dimensional graphene served as the transport pathway for electrons/ions and electrochemically active material.
In this study, we developed a lithium ion full cell battery employing Silicon/Graphene anode and αMnO$_2$/Graphene cathode with high specific capacity and excellent cycle performance. For this aim, graphene oxide was prepared from graphite according to the modified Hummers' method. Silicon/Graphene anode material was produced with dispersing selective amounts of silicon into a graphene oxide solution following reduction process to. αMnO$_2$/Graphene cathode material was prepared rapidly by a microwave assisted hydrothermal method.

The surface morphology of the produced electrodes was characterized using Field-emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and Energy dispersive spectroscopy (EDS) was conducted to understand the elemental surface composition of composites. The structures of the composites were characterized using X-ray diffraction (XRD) patterns and Raman spectroscopy. The electrochemical performance of the full cell was investigated by charge/discharge and cyclic voltammetry tests from 0.05V to 4.5V in CR2016 test cells. The resistances of the cell was investigated using ac impedance technique. This study proved that Graphene encapsulated Si anode material with Graphene embedded αMnO$_2$ cathode material give promising results for lithium ion battery applications.

Keywords: Silicon/Graphene anode, αMnO$_2$/Graphene cathode, Li-Ion Full batteries.

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Electrochemical Performance of Au@Pd Core-Shell Nanoparticles decorated Graphene-PEDOT:PSS composite cathode for Li-Air Batteries

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Like lithium oxides, insoluble solids collaps to pores, this prevents the oxygene diffusion. Different aproaches considered to solve this blockage with oxides precipitation. In this end, Preventing lithium oxide blockage at cathode pore is mostly depends on the pore system properties. Increasing mesopore amount and volume makes cathode material very efficient to prevent lithium oxide blockage[1]. In addition, different charge and decharge patways are responsible for achieving over charge potential[2]. According to Bruce[3], during the discharge process, LiO_2 is firstly forms, and this oxide transforms into more stable Li_2O_2 form. During charging, with an one step reaction Li_2O_2 creates O_2. If the Li_2O_2 far from electrode is hard to transfer electrons and it brings about large over potential. Using a redox mediator could be also reach these far dentride type peroxides. Beacause of the very complicated and compex reaction, there is noconsensus about cathode machanism for non-aqueus Li-O_2 batteries(LAB). But, using a metal or metal oxide catalysts at O_2 cathode increases cycle life and efficiency of LABs[4]. All these efforts are improved energy efficiency of LABs from ~50% to %70[5]. Nano-meter sized metals on the cathode material can lead to decreease the charge over-potential and increase the capacity and cyle life of LABs[2].
Because of the limited ores and high price, precious metals (PCMs) are not widely used in Li-O_2 batteries. For all that they are best efficeint catalysts for reactions[6]. Au metals ise highly active for the oxygene reduction reaction (ORR). In spite of that Pd is highly active at the oxygene evolution reaction (OER) in LABs[7].
Herein, we present one pod rapid synthesis of Au@Pd core-shell nanoparticles (NPs) by gallic acid (GA). Au@Pd NPs are decorated into Graphene-PEDOT:PSS multi-functional composite material for an enhanced Li-air-battery air electrode. A electrode containing Au@Pd NP decorated PEDOT:PSS-coated graphene could be prepared without polymeric binders (such as PVDF) avoids side reactions and presents considerable discharge and charge capacity. In this composite, PEDOT:PSS acts as a redox reaction matrix and conducting binder in the air electrode. Moreover, Au@Pd NPs exhibits bifunctional catalytic activity, having responsible for kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in rechargeable Li-O2 cells.

The results shows that, 984 mAh/g specific descharge capacity achieved at 0.1 mA/cm^2 current density in 1 M $LiClO_4$/TEGDME eleytrolyte. In addition, 33 cycle life obtained from this type of LABs.
The present study provides insights into the importance of the using bimallic PGM NPs on the surface of the carbon cathodes.

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Production and Characterization of Ag-based Oxide Catalysts for Zinc-Air Batteries

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Recently, primary and secondary zinc-air batteries have attracted considerable attention due to their high energy density, safety, availability and low cost. Zinc-air batteries consist of zinc anode, porous air electrode, alkali aqueous electrolyte and separator. Zinc-air batteries generate electricity through a redox reaction between zinc and oxygen in air. Oxygen diffuses through the air cathode and reduction of oxygen to hydroxide ion occurs while zinc is oxidized at the negative electrode during discharging.

Zinc-air batteries have higher theoretical energy density due to abundant supply of oxygen from the atmosphere. However, using oxygen reduction and evolution reactions have also negative effects. Poor efficiency of the oxygen reduction and evolution reactions taking place at the cathode limits the use of zinc-air battery in demanding applications. In literature, many studies focus on the development of catalyst materials to improve these reactions. Some catalyst materials such as Pt, Ag, MnO_2, spinel and perovskite oxides are studied to enhance the performance of battery [1-2].

The aim of this study is to produce and characterize a novel bifunctional catalyst material to be used in the cathode. In this regard, Ag based oxide, Ag_2XO_4 (where X= Cr, Mo and W) catalysts were developed for zinc-air batteries. Catalyst materials were produced by precipitation and/or hydrothermal methods. Prior to the application of produced catalysts, structural characterization of catalyst were performed by XRD and SEM. The effect of different catalysts and processing parameters on the oxygen reduction and evolution reactions at the catalyst loaded cathode were investigated by electrochemical characterization techniques.

The ORR and OER activities of catalysts in the aqueous electrolyte (0.1 M KOH) were tested in a three-electrode electrochemical cell using rotating disk electrode (RDE) voltammetry. All these experiments were performed at room temperature using a Hg/HgO (1 M) as a reference electrode. Graphite rod was used as the counter electrode. The working electrode was a glassy carbon electrode (5 mm OD) coated with 10 µl of a solution which was made by mixing catalyst, carbon support (Printex L6) and a solution of 5 wt% Nafion (LIQUionTM solution) in water and isopropanol solution. Catalytic activity of the catalysts were compared with the benchmark α-MnO_2 catalyst.

In this study, Ag_2XO_4 (where X= Cr, Mo and W) powders were synthesized by precipitation and/or hydrothermal methods. The process parameters, such as pH, source of X and additives, were changed to obtain the desired phase having the finest particle size. SEM images of Ag_2CrO_6, Ag_2MoO_6 and Ag_2WO_6 powders are shown in Figure 1.

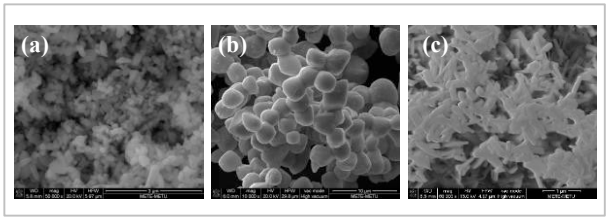


Figure 1. SEM images of: (a) Ag_2CrO_6 (b) Ag_2MoO_6 and (c) Ag_2WO_6 powders synthesized by hydrothermal method.

The linear sweep voltammograms of powders can be seen in Figure 2. All voltammograms showed a well-defined sharp increase in current density at the mixed kinetic and diffusion limited region followed by a plateau at a stable current density in the diffusion-limited region. The onset potential and half wave potential of the oxygen reduction reaction on the Ag_2WO_4 catalyst was slightly more positive compared to the others. The limiting current density of Ag_2WO_4 catalyst was also higher than that of Ag_2CrO_4 and Ag_2MoO_4. The electron transfer number (n) of Ag_2CrO_4 Ag_2MoO_4 and Ag_2WO_4 at 0.5 V was calculated by the help of the Koutecky–Levich (K–L) plots as 3.8, 3.4 and 3.8, respectively.

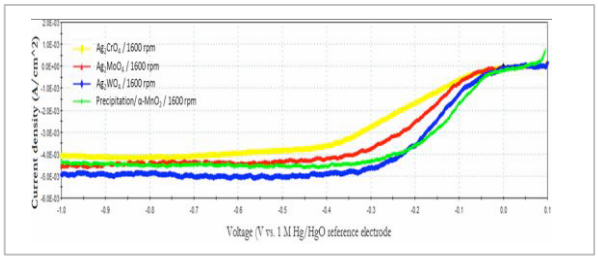


Figure 2. Rotating-disk voltammograms of Ag_2CrO_4 Ag_2MoO_4, Ag_2WO_4 and α-MnO_2 (for ORR) in O_2 saturated 0.1 M KOH with a sweep rate of 5 mV/s at 1600 rpm.

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Supercapacitors

Nickel Oxide Based Materials For Supercapacitor Applications

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Since the invention of capacitor in 1745, very high capacity capacitors that fill the gap between batteries and conventional capacitors could only found widespread use in the beginning of this century. Today these capacitors also named as super capacitors, ultra capacitors or electrochemical capacitors are extensively used in automotive industry, electrical vehicles and also for power quality. Among the two basic types of supercapacitors, electrical double layer capacitors (EDLC) are more widely used. However, for increasing energy density, pseudo capacitors or a combination of EDLC and pseudo capacitors provides more opportunities.

Electroactive nickel oxides have attracted substantial interest as pseudo capacitor electrodes due their high capacity. In this presentation after giving and overview on supercapacitors, production and characterization methods of electroactive nickel oxides will be summarized. Benefits of direct production of these oxides on nickel substrates will be explained and the methods for direct production will be compared. Our recent results on the usage of molten salt oxidation of nickel foams for super capacitor applications will be presented [1].

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Carbon nanotube - polyaniline nanocomposite supercapacitor electrodes

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Supercapacitors have received a lot of attention thanks to their high specific power and moderate energy densities. Their application field spans from electric vehicles, pulse power systems to portable devices [1]. Design of individual supercapacitor devices moreover development of flexible and transparent supercapacitors are the two popular topics in the field. Many studies have been conducted for new design concepts and numerous materials have been tested for improving the efficiency of the devices [2]. Supercapacitor electrodes made from carbon nanotubes are very promising because of their high conductivity, chemical inertness and mechanical stability. Pseudocapacitive materials such as conducting polymers, (i.e. polypyrrole, polyaniline) are utilized to synthesize nanocomposites with carbon nanotubes in order to improve electrochemical properties of the supercapacitor electrodes [3].

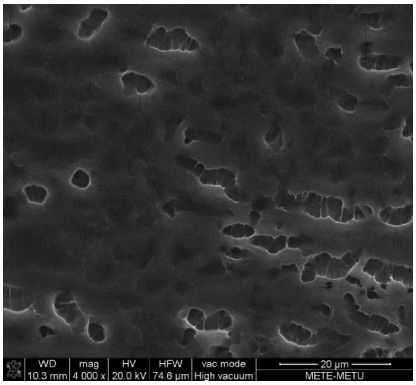


Figure 1. Top view SEM image of produced nanocomposite electrodes

Fabrication and characterization of vertically aligned carbon nanotube (VACNT) - polyaniline (PANI) nanocomposite supercapacitor electrodes on aluminum foils are presented in this work. 5 µm long VACNTs were synthesized using chemical vapor deposition technique, which is followed by the electrodeposition of PANI onto the VACNTs to obtain the nanocomposite electrodes (Figure 1).

Electrochemical characterization of the fabricated nanocomposite electrodes are conducted through cyclic voltammetry, chronopotentiometry, electrochemical impedance spectroscopy in three-electrode configuration and compared to that of control sample fabricated simply by depositing VACNT onto aluminum foils. Gamry Reference 3000 potentiostat/galvanostat instrument was used in electrochemical tests. Platinum plate and the Ag/AgCl electrodes were chosen for the counter and the reference electrodes in three-electrode configuration, respectively. All potentials were relative to the Ag/AgCl electrode and 1 M sodium sulfate (Na_2SO_4) aqueous solution was used as the electrolyte.

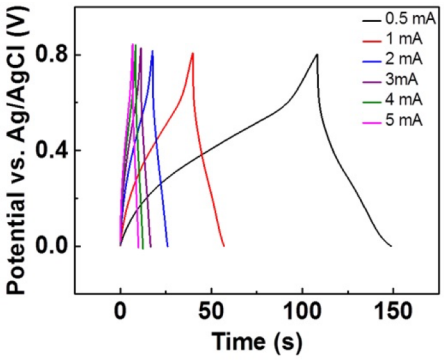


Figure 2. Chronopotentiometry curves of fabricated nanocomposite electrodes

The effect of PANI thickness on the electrochemical properties of the electrodes is also examined. The fabricated nanocomposite supercapacitor electrodes were tested at different current densities from 0.5 to 5 mA, results of which are demonstrated in Figure 2. Fabricated supercapacitor electrodes showed promising performance with notable specific capacitance values of 14 mF cm^{-2} at a current density of 1 mA cm^{-2}.

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One-dimensional $CoMn_2O_4$ nanowire arrays for supercapacitor applications

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The fast-growing market for portable electronic devices and hybrid electric vehicles has highlighted the urgent need to develop portable, efficient and cost-effective energy storage devices. Supercapacitors, known as electrochemical capacitors, are considered to be one of the most promising candidates for next-generation high-performance energy storage devices due to its high power density, fast charging/discharging, long cycling life, high safety, etc. Pseudocapacitive materials, transition metal oxides or hydroxides such as RuO_2, MnO_2, NiO, Co_3O_4, $Ni(OH)_2$, $Co(OH)_2$, etc., have been extensively studied in search of the alternative inexpensive electrode material with high capacitive performance [1]. However, these materials have either low conductivity or poor electrochemical stability, which will largely limit their widespread applications in supercapacitors. Therefore, it remains to be a great challenge to develop new electrode materials with desirable

supercapacitor properties, such as high electrical conductivity, large capacitance, and good electrochemical stability [2].

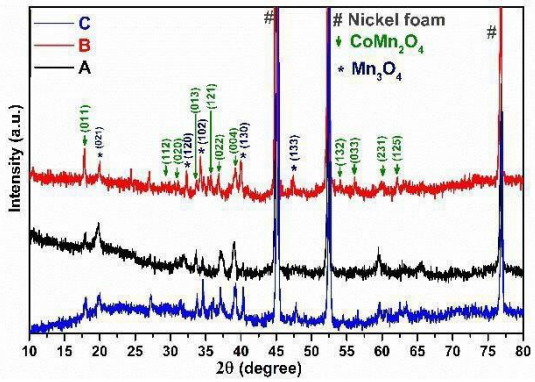


Figure 1. XRD pattern of $CoMn_2O_4$ nanowires. Recently,

micro-/nanostructured mixed transition metal oxides (MTMOs) with a spinel structure (such as AB_2O_4 type) have drawn great attention as promising electrode materials for energy-related applications owing to their high electrochemical performances, low cost and environmental benignity [3]. Among them, $CoMn_2O_4$ is very attractive due to their improved electrochemical performances originating from the complementarity and synergetic effect of Co and Mn in the charge/discharge process.

In this present work, we investigate the electrochemical properties of $CoMn_2O_4$ nanowire array prepared by a facile hydrothermal method coupled with an annealing. The hydrothermal method is one of the most widely used methods to fabricate nanostructured materials, because the size, morphology, and crystal structure of the products can be easily controlled, and the reaction temperatures are also lower than other preparation methods [4]. XRD pattern, SEM images, and CV curves of $CoMn_2O_4$ nanowires are given in figure 1 and 2 respectively.

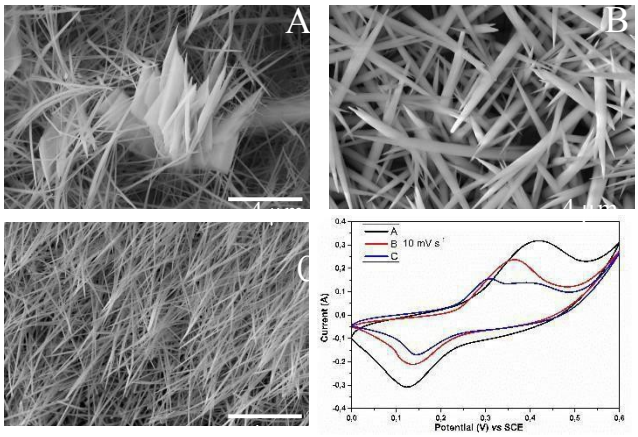


Figure 2. SEM images of A, B and C samples, CV curves of $CoMn_2O_4$ nanowire array electrode for supercapacitor in the potential region of 0 − 0.6 V;

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Nitrogen and oxygen co-doped porous carbons derived from pea protein as electrode materials for high performance supercapacitors

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Abstract

Porous carbons as electrode materials for energy storage devices have attracted extensive interests. Herein, the development of a series of nitrogen and oxygen doped porous carbons by using pea protein as a cost-effective, sustainable and nitrogen-rich precursor is reported. Pea protein derived carbons (PPDCs) were prepared by applying a straightforward and two-step synthetic route including pre-carbonization and KOH-chemical activation. Potassium hydroxide was employed to generate porosity and introduce oxygen functionalities into the framework of carbon. The heteroatoms doping content and porosity parameters were tuned by varying the synthesis temperature and activator to precursor ratio. The carbon obtained under optimal synthetic condition (T=800 °C and KOH/PP=4) featured the highest surface area, total pore volume and N/O-doping level of 3500 m^2 g^{-1}, 1.76 cm^3 g^{-1}, and 2.5/17.9 at%, respectively. PPDC-4-800 as supercapacitor presented a very high specific capacitance (413 F g^{-1} at 1.0 A g^{-1} in 1 M KOH), remarkable cycling stability (92% retention after 20000 cycles) and outstanding rate capability (210 F g^{-1} at 30 A g^{-1}). The cooperative effects of the well-developed porous architecture and surface modification of PPDCs resulted in enhanced electrochemical performances, suggesting their potential for use in energy storage devices.

1. Introduction

Due to the ever-increasing energy consumption of our industrial society, development of cost-effective and high-performance energy storage devices emerges as an absolute necessity. The electrochemical capacitors, also known as supercapacitors or ultracapacitors, are not limited by the electrochemical charge transfer of batteries. Thus, supercapacitors are considered as appealing energy storage devices for portable electronics, hybrid electrical vehicles and medical devices thanks to their rapid charge–discharging rate, long-term cycle life and high power density.[1-3]

Over the last decades, certain nanomaterials including activated carbons,[4] conducting polymers,[5] carbon nanotubes[6] and nanosized metal oxides[7] have been reported as the potential electrode materials for use in energy storage devices. Among these, activated carbons have received considerable attention due to their high surface area, large pore volume, adjustable pore size, physiochemical stability and high electronic conductivity.[1] However, activated carbons suffer from two major drawback. First, activated carbons usually are not accompanied by electrochemically active sites and thus their highly hydrophobic surface limits their capacitive performance in aqueous solutions. This drawback lately has been overcome by modification of the hydrophobic surface of carbon lattice. The incorporation of heteroatoms such as nitrogen, sulfur or oxygen into the carbon framework can significantly enhance their electrochemical properties.[8, 9] Such heteroatoms induce acid/base character to the carbon structure and give rise to the overall capacitance by promoting reversible redox reactions as well as inducing wettability between electrode surface and electrolytes.[8] The second drawback refers to mainly microporous nature of activated carbons. This feature of activated carbons results in a long ion pathway, a large diffusion resistance, a low charge storage capability and a poor capacitance retention at very high discharge rates. This challenge can be addressed if carbons with hierarchical structure of micro-, meso- and macropores are used as electrode materials.[10] The abundant micro-and mesopores are essential for improving the charge storage capability while the macropores are responsible for shortening the ion diffusion length. Hierarchical structures result in a simultaneous improvement of both energy density and power density of capacitor and as such, many research efforts have been devoted to diversifying the pore size distribution of carbon structures.[11]

Carbon materials derived from natural products represent a green and cost-effective pathway toward scalable production.[12] To date, numerous carbon materials with diverse macroscopic morphologies and textural properties have been synthesized by using various biomass sources as precursors. For example, glucose[13], lignin[14] and sugar beets[15] have been successfully transformed to the porous carbons through carbonization/activation process . However, only few reports involve in using commercially available protein powder to synthesize heteroatom-doped porous carbon. [16, 17] Utilizing a pea protein (PP) as a carbon



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Muslum Demir received his Ph.D. in Prof. Ram Gupta's lab at Virginia Commonwealth University (Virginia, USA). He received his B.S. in Chemistry from Cukurova University (Turkey) in 2008 and his M.S. in Chemistry from Rutgers University (USA) in 2013. His doctoral research focused on the development of biomass-derived carbon materials for energy storage and conversion applications. During his doctoral studies, he has published 5 peer-reviewed papers and attended prestigious conferences such as ACS, AICHE and ECS meetings. He is member of AICHE and ECS.

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precursor presents following unique features: (1) cost-efficient yet sustainable (2) high level of initial nitrogen species (3) uniform incorporation of nitrogen into substrate.

Herein, we present a facile and efficient two-step route to prepare a series of highly porous carbon by utilizing natural pea protein as a precursor. The first step involves direct carbonization of pea protein to yield a carbon species with undeveloped texture porosity (bio-char). The second step includes chemical activation of bio-char by using KOH activating agent in order to develop porous structure. The pea protein derived carbons (PPDCs) combine a well-developed hierarchical porous structure with the abundant nitrogen and oxygen surface groups. Textural properties, surface chemistry and electrochemical performance of PPDCs were thoroughly investigated. The optimum carbon with a surface area of 3500 m^2 g^{-1} and N/O contents of 2.5/17.9 at% demonstrate a specific capacitance of 413 F g^{-1} at 1.0 A g^{-1} in 1M KOH aqueous electrolyte with remarkable cycle stability (91.6% after 20000 cycles) and superior rate capability, indicating an ideal electrode materials for supercapacitors.

2. Experimental

2.1. Materials and Methods

Pea protein (NOW Company) was purchased from local nutrition store in Richmond, VA USA. Potassium hydroxide was purchased from Sigma Aldrich and used without further purification. In a typical synthesis process, pea protein powder (1.2 g) was calcinated in a tubular furnace at 500 °C for 1 h under N_2 atmosphere. Carbonaceous material cooled down to ambient temperature to yield a black solid (bio-char). The obtain carbon rich solid was mixed with KOH solution in various mass ratios (KOH/PP of 2, 3 and 4). The mixtures were dried at 80 °C for 24 h, transferred into a tubular furnace, and then annealed at 700, 800 and 900 °C for 2 h under nitrogen flow in a Carbolite (MTF250) tubular furnace. The resulting samples were washed with 10 % HCl solution to remove residual contamination and sufficient water repeatedly until a neutral PH was obtained. Finally, the samples were dried at 80 °C. The pea protein starting material was designated as "PP" and the obtained pea protein derived carbons were denoted as "PPDC-x-y," where the "x" denotes the KOH to PP weight ratio and "y" represents the activation temperature in degree centigrade.

2.2. Characterization Techniques

N_2 (77 K) isotherms were collected on Autosorb-iQ2 volumetric adsorption analyzers (Quantachrome Inc.) using ultrahigh purity N_2 gas. Before adsorption measurements, each sample was degassed under vacuum for at least 12 h at 200 °C. The specific surface area of the samples was measured using the Brunauer−Emmett−Teller (BET) method. The pore size distributions (PSD) were obtained from adsorption branch of N_2 (77 K) isotherms by the QSDFT (quench solid density functional theory) method assuming slit-like geometry on the carbon material kernel. The volume of micropores (V_{Mic}) was estimated by cumulative pore size distribution curves and corresponding volume at pore size of 2 nm. Total pore volume was measured by V-tag method at P/P0= 0.95 as well as cumulative pore size distribution curves. Thermal stability analysis was run on a Perkin thermo-gravimetric analyzer. Operating conditions were settled to a constant heating rate of 5 °C min^{-1} under the N_2 flow with temperature ranging from 20 °C to 1000 °C. Scanning electron microscopy (SEM) images were obtained using a Hitachi SU-70 scanning electron microscope. Samples were prepared by dispersing each specimen onto the surface of a sticky carbon attached to a flat aluminium sample holder. Then the samples were coated with platinum at a pressure of 10^{-5} mbar in a N_2 atmosphere for 60 s prior to SEM imaging. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 spectrometer employing an Al Kα (1486.68 eV) X-ray source equipped with a hemispherical analyzer. Raman spectra were obtained using a Thermo Scientific DXR SmartRaman spectrometer operating at an excitation wavelength of 532 nm.

2.3. Electrode Preparation and Electrochemical Measurements

The working electrodes were fabricated from a mixture of 80 wt.% active electrode material, 10 wt.% carbon black and 10 wt.% binder (PTFE) in ethanol solution. The viscous slurry was casted onto a current collector (nickel foam, 1.5 cm x 3 cm) and dried at 80 °C for 12 h in vacuum. The dried electrode was uniaxially pressed at 5 tons. The geometric area of electrode was 0.32 cm^2. The amount of active material and thickness of electrode were about 1.6 mg and 45 µm thus the measured densities of electrode films are about 1.15 g cm^{-3}. In a three-electrode cell configuration, as-prepared electrodes operated as a working electrode, Pt wire as auxiliary electrode and Ag/AgCl (1M KCl solution) applied to reference electrodes in 1M KOH electrolyte within the potential range of -1.0 to 0.0 V on a CHI 660E electrochemical workstation (CH Instruments Inc.) at room temperature. Additionally, a two-electrode cell testing was conducted in a 2025 coin cell with two nearly identical electrodes and Fisher brand (P8) filter paper as a separator. 1M KOH aqueous solution were examined as electrolytes, within the potential range of 0 to 1.0 V. The EIS data were collected in the frequency range of 0.01 Hz to 500 kHz with a 5 mV AC amplitude. The gravimetric specific capacitance (C_s, F g^{-1}) of the electrodes was calculated from the galvanostatic charge-discharge (GCD) curves according to the equation (1):[18]

$$Cs = I\Delta t/m\Delta V \quad \text{(three-electrode cell)} \quad (1)$$

where I is the discharge current (A), ΔV is discharging voltage m is the mass of the active electrode material (g) and Δt is the discharge time.

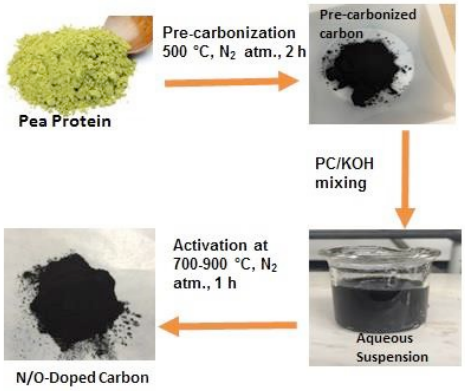


Fig. 1. Schematic for the fabrication of porous carbon materials from pea protein

3. Results and Discussion

3.1. Synthetic Aspects

The synthetic strategy involved two stages of char formation and pore generation. In the first step, the thermally unstable pea protein is converted to a stable carbon species by means of a hydrothermal carbonization. In the next step, chemical activation of the stable bio-char takes place through etching (by redox reactions), gasification (by evolving gaseous species such as H_2O and CO_2) and expansion (by metallic potassium) of the carbon framework as suggested by Kaskel et al.[19] Various mixing ratios of activation agent to bio-char (2,3,4 w:w) are heated up to the high temperatures (700, 800, and 900 °C) in order to afford a series of pea protein derived carbons (PPDCs). The optimization of synthetic condition (temperature and KOH amount) will be performed with respect to the textural properties and heteroatoms (N and O) doping level in the following sections. It is worth noting that the nitrogen incorporation into the carbon lattice is done through the precursor (pea protein possesses about 4.3 wt.% nitrogen). A considerable amount of oxygen groups will also be introduced into the carbon framework from the activating agent (KOH). The pea protein starting material was designated as "PP" and the obtained pea protein derived carbons were denoted as "PPDC-x-y," where the "x" denotes the KOH to PP weight ratio and "y" represents the activation temperature in degree centigrade. Fig. 1 illustrates the entire preparation process for PPDCs.

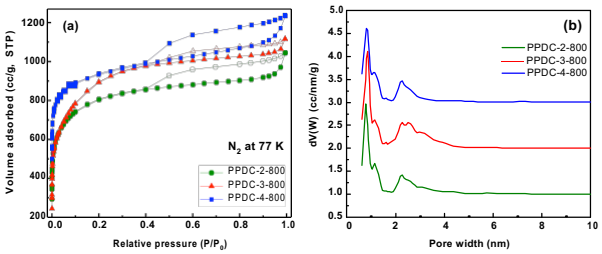


Fig. 2. (a) N_2-77 K isotherms (solid symbols for adsorption and empty symbols for desorption) and (b) Pore size distributions calculated by QSDFT method for PPDC-x-800. (All PSD curves are offset vertically in steps of 1.0 for clarity).

3.2. Textural properties

The N_2 adsorption-desorption isotherms were collected to evaluate the textural properties of PPDCs (Fig. 2a). The values for BET (Brunauer–Emmett–Teller) specific surface area, total pore volume (obtained by both V-tag method at P/P_0=0.95 and cumulative pore size distribution graph) as well as micro- and mesopore volumes are summarized in Table 1.

According to the most recent IUPAC classification,[20] all prepared carbons feature a hybrid of type I(b) and type IV(a) isotherms. The microporous type I(b) isotherms is recognized by a steep uptake at very low pressures (P/P_0 <0.01) while mesoporous type IV(a) is distinguished by gradual decrease at higher pressures (P/P_0 >0.01) as well as a clear hysteresis loop (P/P_0=0.4-1). The BET surface area of carbons prepared at fixed temperature of 800 °C and various KOH to precursor ratios of 2, 3 and 4 were calculated to be 3010, 3325 and 3500 $m^2\ g^{-1}$, respectively. The total pore volume of PPDC-2-800, PPDC-3-800 and PPDC-4-800 were found to be 1.45, 1.63 and 1.76 $cm^3\ g^{-1}$, respectively. The incremental trend of surface area and pore volume is indicative of a more efficient activation process when higher amount of activator is used.[19] To investigate the effect of activation temperature, the textural properties of two carbons synthesized at optimum KOH/PP ratio (4) but various temperatures (700 and 900 °C) were also studied. The results (Table 1) confirmed a drop in surface area and pore volume when the activation temperatures changed to 700 and 900 °C. This can be explained by the insufficient activation of the porous structure at lower temperature (PPDC-4-700) and the collapse of the porous network at higher temperatures (PPDC-4-900).[21] Accordingly, three carbons obtained at constant temperature and different amount of activating agents (PPDC-x-800) will be selected as optimum samples for further discussion. The pore size distribution curves (Fig. 2b) showed all three samples possess pores width maxima, which are mainly center around 0.8, 1 and 2.2 nm. Therefore, a hierarchy of micro and mesopores in the structure of all carbons is present.

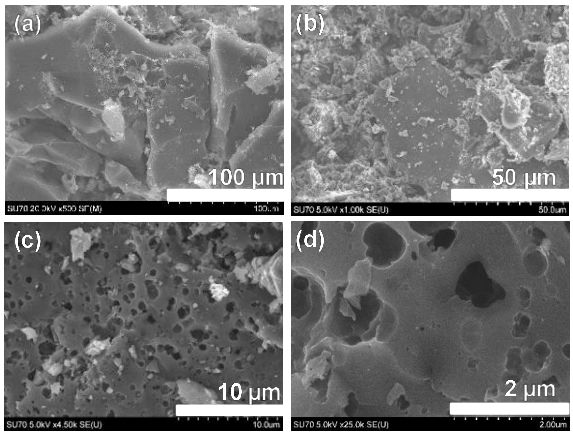


Fig. 3. SEM images of PPDC-4-800 (a,b) the cross-section morphology (c,d) the surface morphology.

Table 1. Textural properties and composition analysis of PPDCs

Sample	SA_{BET} a) [$m^2\ g^{-1}$]	V_{Tot} b) [$cm^3\ g^{-1}$]	$V_{Mic, DFT}$ c) [$cm^3\ g^{-1}$]	$V_{Tot, DFT}$ c) [$cm^3\ g^{-1}$]	$V_{Mes, DFT}$ d) [$cm^3\ g^{-1}$]	C e) [at.%]	N e) [at.%]	O e) [at.%]
PPDC-2-800	3010	1.45	0.85	1.34	0.49	86.8	1.1	12.1
PPDC-3-800	3325	1.63	0.74	1.51	0.77	84.4	1.3	14.3
PPDC-4-800	3500	1.76	1.16	1.64	0.48	79.6	2.5	17.9
PPDC-4-700	2645	1.22	0.71	1.13	0.42	82.2	3.8	14.0
PPDC-4-900	2890	1.34	0.98	1.26	0.30	86.2	1.1	12.7

a) Brunauer–Emmett–Teller (BET) surface area. b) Total pore volume at P/P_0 = 0.95; c) Determined by PSD assuming slit-shaped pores and QSDFT model from adsorption branch of N_2 isotherms d) Obtained by diffraction of total and micropore volume e) Obtained by XPS analysis.

3.3. Structural Characterization

The scanning electron microscopy (SEM) images of carbons at different magnifications are shown in Fig. 3. The cross-section morphologies are mainly consisted of a network of irregularly shaped and distorted layered structures as shown in Fig. 3a-b. The surface morphologies is suggesting the formation of a great deal of curvatures and voids during activation process as depicted in Fig. 3c-d.[22] It is worth noting that these macro scale voids form in the inter-particle spaces and are different from intra-particle micro and meso scale porosity. The porosity obtained in this research work and other KOH activation studies (pore width range of 0.8-5 nm) are not distinguishable by SEM images.

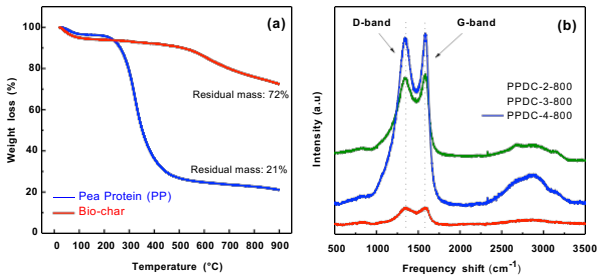


Fig. 4. (a) Thermal analysis for PP and bio-char (b) Raman spectra for PPDCs.

The thermogravimetric analyses (TGA) results of precursor (PP) and bio-char are presented in Fig. 4a. The initial weight loss up to 150 °C is due to the physical adsorption of water in both the samples. The decomposition of PP and bio-char started at around 200 °C but further evolved in different pathways. While a dramatic mass loss (about 70% at 400 °C) was observed for PP, the bio-char showed a gradual decomposition rate even at high temperatures. The residual mass content of the PP and bio-char at 900 °C was found to be 21 and 72 %, respectively, which is suggesting a high production yield for the latter. Raman spectroscopy was carried out to assess the graphitization degree of PPDCs (Fig. 4b). The spectrum features two well-resolved peaks at 1350 (D-band) and 1590 cm^{-1} (G-band). The D-band is ascribed to defects, partially disordered and amorphous structures while the G-band is correlated to sp^2-hybridized graphitic carbon atoms.[23] The ratio of the D-band to the G-band intensities (I_D/I_G is largely accepted as a degree for graphitization of carbon materials. The I_D/I_G values were calculated to be 0.97, 1.02 and 0.98 for PPDC-2-800, PPDC-3-800 and PPDC-4-800, respectively. The nearly identical and close to unity values of I_D to I_G ratio is suggesting the equal degree of graphitization as well as the presence of both ordered and amorphous phases in the structure of all three studied carbons.

X-ray photoelectron spectroscopy (XPS) was performed to evaluate the chemical composition and the nature of different heteroatom functionalities in the structure of PPDCs. The results of XPS survey featured three prominent peaks at 284, 399 and 530 eV, which are correlated to the presence of the C 1s, N 1s, and O 1s, respectively (Fig. 5a). The quantified surface composition (Table 1) showed that in addition to carbon all studied materials contain 1.1-3.8 at.% nitrogen and 12.1-17.9 at.% oxygen heteroatoms as dopants. It should be noted that appreciable amount of oxygen functionalities is usually found in the final structure of carbons, which are prepared under oxidative conditions (such as KOH) even if an oxygen-free precursor is used.[24] The evolution of nitrogen and oxygen moieties was further studied by deconvolution of their 1s core level spectra. The N 1s core level spectra of the optimum PPDC-4-800 (Fig. 5b) indicated the presence of four peaks at 398, 400, 402 and 404 eV, which are characteristic for pyridinic (N-6), pyrrolic/pyridonic (N-5), quaternary (N-Q) and pyridine-N-oxide (N-X) types, respectively. High resolution deconvoluted O 1s spectra of the same sample (Fig. 5c) presented three main contributors at 531, 533 and 535 eV, which are correlated to quinone (O-I), phenol/ether (O-II) and carboxylic groups/water (O-III) moieties, respectively. It can be understood that pyrrolic/pyridonic (N-5) and phenol/ether (O-II) groups are the most abundant nitrogen and oxygen species, respectively. To ensure a fair understanding, a schematic representation of nitrogen and oxygen species on the pore walls of a typical porous carbon along with the corresponding binding energies is provided in Fig. 5d.

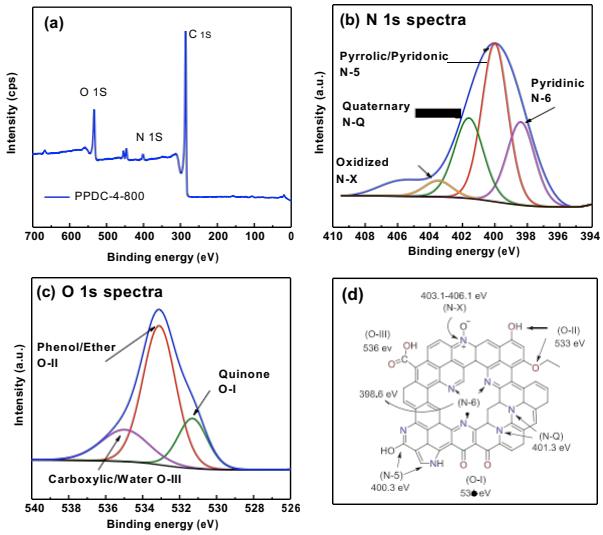
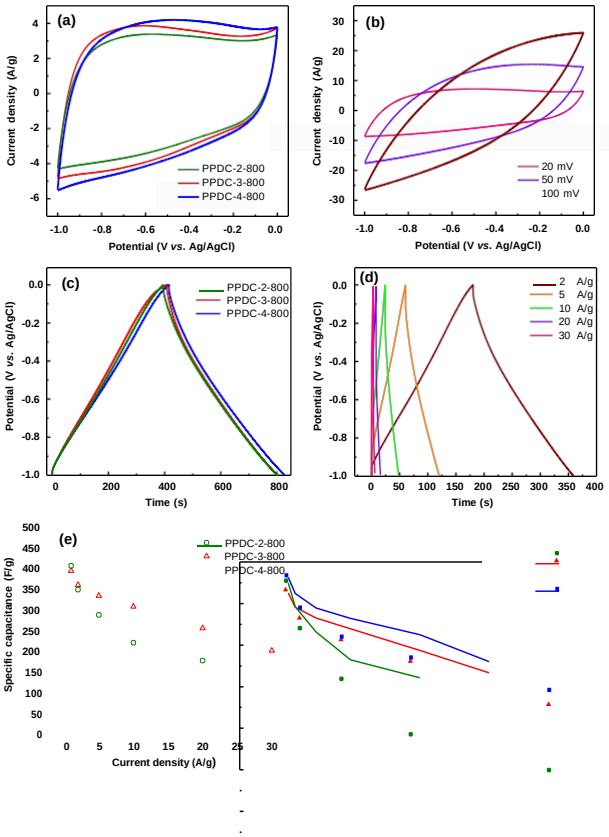


Fig. 5. (a) X-ray photoelectron spectroscopy (XPS) survey spectra of PPDC-4-800 (b) N 1s core-level spectra of PPDC-4-800 (c) O 1s core-level spectra of PPDC-4-800 (d) The schematic representation of nitrogen and oxygen species in a hypothetical porous carbon.

3.4. Capacitive Performance

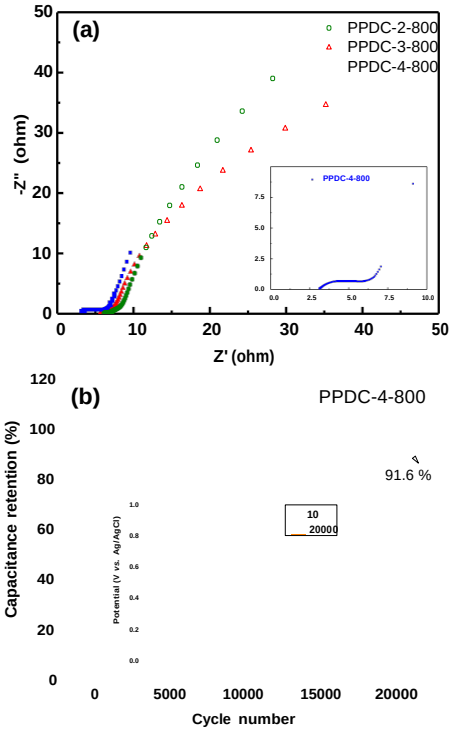
The electrochemical performances of the pea protein derived carbons were investigated in 1 M KOH aqueous electrolyte in a three-electrode cell configuration. The cyclic voltammogram (CV) curves of PPDC-2-800, PPDC-3-800 and PPDC-4-800 at a scan rate of 10 mV s^{-1} and in a three-electrode system are presented Fig. 6a. The impact of nickel substrate on the CV curve (data not shown here) has been disregarded due to its small capacity contribution (less than 0.1 percent). The CV curve of all PPDC electrodes exhibited a rectangular shape, which is characteristic for an ideal double-layer capacitor.[25] It is important to note that a slight diversion from the perfect rectangular shape in the CV curves can be ascribed to the reversible redox reaction.[26] The presence of pseudocapacitance in PPDCs is expected to contribute more positively to the total energy storage alongside the double-layer capacitance. The reversible redox peaks are commonly assigned to the nitrogen and oxygen functional

groups on the surface of carbon electrodes.[27, 28] The more pronounced pseudocapacitance contribution in PPDC-4-800 can be correlated to the highest amount of nitrogen and oxygen as evidenced by XPS results. The CV plots of PPDC-4-800 at various scan rates is also shown in Fig. 6b. The CV curves for PPDC-4-800 retained a rectangular shape without obvious distortion even at a scan rate up to 50 mV s^{-1}, which indicates an excellent capacitive performance of carbon electrodes.[18]



aqueous electrolyte in a three-electrode cell. (a) Cyclic voltammograms at a scan rate of 10 mV s^{-1} for all PPDCs, (b) Cyclic voltammograms of PPDC-4-800 at different scan rates, (c) Galvanostatic charge–discharge curves at a current density of 1 A g^{-1} for all PPDCs, (d) Galvanostatic charge–discharge curves of PPDC-4-800 at different current densities and (e) Specific capacitance versus current density for all PPDCs.

The galvanostatic charge–discharge (GCD) profiles of PPDC-based electrodes within the potential range of -1.0–0.0 V and at a moderate current density of 1 A g^{-1} are depicted in Fig. 5c. The GCD curves of all samples exhibit isosceles triangle shaped curves without any iR drops, which indicates a worthy electrochemical reversibility at tested current load. The specific capacitances of PPDC-based electrodes were calculated by using equation 4 and data obtained from GCD curves. The specific capacitance values at a current density of 1 A g^{-1} were found to be 413, 406 and 394 F g^{-1} for PPDC-4-800, PPDC-3-800 and PPDC-2-800, respectively. These noticeably large capacitance values for PPDCS are originated from collaboration of high surface area, large total pore volume, high amount of nitrogen and oxygen functional groups and suitable graphitization. The largest capacitance of 413 F g^{-1} in PPDC-4-800 is primarily driven by its high surface area and large pore volume by providing more accessibility for the electrolyte ions and facilitating efficient ion transport with lower resistance. Theoretically, micropores larger than 0.6 nm are considered as the most effective size for ion absorption if aqueous solution is used as electrolyte.[29] Hence, PPDC-4-800 has a highest capacity at a low current density in KOH electrolyte thanks to its high micropore volume. Moreover, it is well known that introducing heteroatoms enhances the electrical conductivity of carbon and produces pseudocapacitance effect to improve the total specific capacitance.[30] All studied PPDCs feature noticeable amount of nitrogen and oxygen functionalities on the surface (Table 1) which can contribute to the total capacitance. More specifically, the pyrrolic/pyridonic (N-5) and quinone (O-I) species provide more accessible sites for redox reaction and promotes more pseudocapacitance effect.[31] As it summarized in Table 1, PPDC-4-800 possesses the highest nitrogen and oxygen content, which explains its high specific capacitance. Fig. 6d features the GCD curves of PPDC-4-800 at different current densities. The specific capacitances are calculated from discharge curves to be 374, 339, 314, and 275 F g^{-1} at the current densities of 2, 5, 10, and 20 A g^{-1}, respectively. Even at a relatively high current density of 30 A g^{-1} a considerable specific capacitance of 210 F g^{-1} can be maintained, which is indicative of a good rate capability. The descending trend of specific capacitance upon increasing the current density (Fig. 6e) can be correlated to the ions accumulation within the small pores and/or interaction between electrolyte and surface functional groups/dangling bonds.[32, 33] High capacitance values recorded for pea protein derived carbons outperform the majority of the



biomass-derived carbons reported so far (Table 2).

Fig. 7. (a) Nyquist plots for PPDCs. The inset image shows the data of high frequency range (b) Capacitance retention at the current density of 10 A g^{-1} for PPDC-4-800. The inset image shows charge–discharge curves after 10 and 20000 cycles at 10 A g^{-1}.

Tabel 2. Synthetic strategy, surface area and capacitance values for carbons derived from biomass precursors. (HTC=Hydrothermal Carbonization, CVD=Chemical Vapor Deposition)

Precursor	Synthetic route	Surface area ($m^2\ g^{-1}$)	Capacitance ($F\ g^{-1}$)	Measurements condition	References
Pea protein	HTC/KOH activation	3500	413	1M KOH, 1.0 A g^{-1}	This work
Chicken eggshell	Pyrolysis/KOH activation	221	297	1M KOH, 0.2 A g^{-1}	ref[34]
Celtuce leaves	Pyrolysis/KOH activation	1946	421	2M KOH, 0.5 A g^{-1}	ref[22]
Seaweeds	Pyrolysis	1307	264	1M H_2SO_4, 0.2 A g^{-1}	ref[35]
Yogurt	HTC/KOH activation	1300	225	6M KOH, 2.0 A g^{-1}	ref[17]
Watermelon	HTC	158	281	6M KOH, 0.2 A g^{-1}	ref[36]
Fish scale	Pyrolysis/KOH activation	2273	168	7M KOH, 0.05 A g^{-1}	ref[37]
Gelatin	Pyrolysis/NaOH activation	3012	385	6M KOH, 0.05 A g^{-1}	ref[38]
Microorganism	KOH activation	1578	310	6M KOH, 0.2 A g^{-1}	ref[39]
Glucosamine	HTC/KOH activation	571	220	6M KOH, 0.1 A g^{-1}	ref[40]
Cotton	CVD/ Pyrolysis	1085	207	1M H_2SO_4, 1.0 A g^{-1}	ref[41]
Kelp	Pyrolysis in NH_3	400	440	6M KOH, 0.5 A g^{-1}	ref[42]

The electrochemical impedance spectroscopy (EIS) is a powerful technique to determine the interfacial and electrical characteristics of supercapacitors. The Nyquist plots of PPDC electrodes (Fig. 7a) exhibit straight lines and nearly vertical to the realistic impedance axis at low frequency indicating the outstanding capacitive performance thanks to the rapid ion diffusion and adsorption onto the electrode surface. An intercept at the Z′ axis of high frequency corresponds to the total Ohmic resistance (Rs) including the electrolyte resistance, the intrinsic resistance of the active material, and the electrical contact resistance. [43]Rs values for PPDC-4-800, PPDC-3-800 and PPDC-2-800 are found to be 3.1, 5.6 and 6.1 Ω respectively. The low Rs recorded for PPDC-4-800 is likely due to high level of heteroatoms in the carbon framework. The long cycling durability performance is another key parameter in determining the supercapacitor for certain practical applications. The cycling stability of PPDC-4-800 was carried out under a current density of 10 A g^{-1} as shown in Fig. 7b. The capacitance of PPDC-4-800 remains 91.6% of its original capacitance after 20000 charging–discharging cycles. The excellent cycle life further verified that PPDC-4-800 electrode could be used as long-term energy storage devices.[44]

4. Conclusion

In summary, heteroatom-doped porous carbons with high surface area, hierarchical (micro- and meso-) porous structure and appreciable amounts of N and O functionalities were prepared by a hydrothermal carbonization of pea protein and a subsequent chemical activation. Controlling the amount of KOH to precursor ratio and activation temperature afforded carbons with enhanced textural properties and noticeable level of N/O-doping. The optimal physiochemical properties endowed the resultant carbons specific capacitance values of up to 413 F g^{-1} (at 1.0 A g^{-1} in 1 M KOH). The well-developed porous structure acted as a platform for effective ion transportation, while the N- and O-doped species introduced pseudocapacitance by promoting redox reactions. The superior capacitive response, remarkable rate capability and excellent cycling durability of the carbon products together with sustainability and low-cost of the precursor demonstrate that PPDCs have great potential applications in energy storage technologies.

Acknowledgement

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Effect of Physical Activation on the Capacitive Properties of Chemically Activated Carbons

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Electrical double layer capacitors (EDLC) are electrochemical energy storage devices particularly used for their high power output. The mechanism of energy storage is the electrostatic accumulation of ions at the so called 'double layer'. This nonfaradaic process in EDLC result in high power density, however, their energy densities are typically low compared to that of batteries.[1]

One of the major goals of the studies about EDLC is to increase the energy density. Optimization of electrode materials' properties is an effective way to achieve this purpose. The most important properties of an electrode material are: surface area and conductivity.[2] Carbons, having finely tunable surface area and porosity, are the most widely used electrode materials in EDLC applications. In the present study, activated carbon is produced from biomass precursor (pinus pinea).

The precursor material is chemically activated with $ZnCl_2$ with impregnation ratio of 4 after heat treatment under N_2 at 500 °C (specimen 45). To increase conductivity and also adjust pore size to ion size, another heat treatment at 800 °C under CO_2 is conducted (specimen 45-c). N_2 adsorption experiments show the difference in surface area and porosity before and after the second heat treatment.

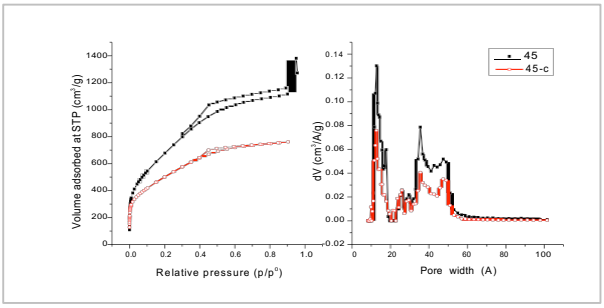


Figure 1. N_2 adsorption isotherms of 800 °C treated (45-c) and untreated (45) activated carbons (left), NLDFT pore size distributions (right).

The effect of CO_2 treatment on porosity is clearly seen in the above figure. Adsorption isotherms are both type 1-4 isotherms according to BDDT classification, indicating microporosity and mesoporosity. However, 45 has a surface area of 1927 m^2/g, while 45-c has 1630 m^2/g according to NLDFT model. This is a result of porosity shrinkage, characteristic of high temperature heat treatment of chemically activated carbons. This shrinkage effect can be also seen on the pore size distribution, especially for mesopores. Even if surface area is considerably decreased by CO_2 treatment, this is not a deteriorating effect for EDLC performance. As pore size gets closer to ion size, porosity is more effectively occupied by ions upon charging.[3]

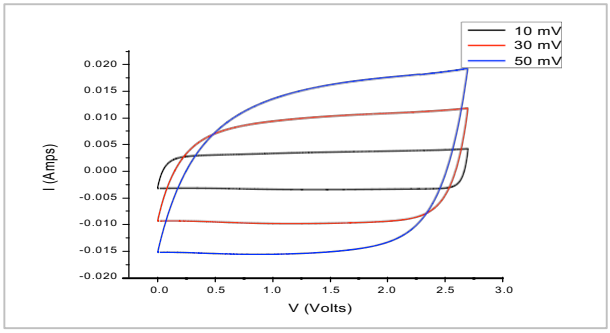


Figure 2. Cyclic voltammetry of 45-c at 10, 30 and 50 mV scan rates.

Using CO_2 treated activated carbon as electrode material, EDLC is constructed in acetonitrile with $TEABF_4$ salt. It has a typical rectangular cyclic voltammetry response at low scan rates, indicating capacitive behavior. As the scan rate is enhanced, it deviates from rectangular shape, with rounded edges, revealing the resistivity of the cell.

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Co_3O_4 nanostructures with high supercapacitive performance

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Development of advanced nanostructured materials which is critical to research in the field of electrochemical energy storage systems has recently gained momentum[1]. This situation involved in portable consumer electronics and hybrid electric vehicles, to industrial scale power and energy management. Research on both high energy density and high power density requirement has lead to an energy storage device[2]. Owing to their capability to deliver high power performance and extremely long cycle life supercapacitors was found to meet this requirement. Supercapacitors can be integrated or replaced batteries in the energy storage system [3].

Researchers are trying to increase the energy storage (i.e. capacitance and working voltage) and life time and simultaneously, decrease the price of these kinds of capacitors. To achieve these targets, transition metal oxides/hydroxides (MnO_2, RuO_2, NiO, Co_3O_4, V_2O_5 $Co(OH)_2$, $Ni(OH)_2$) are extensively investigated as electrode materials for their higher energy density and specific capacitance values than carbon materials due to their faradaic redox reactions [4]. Among them cobalt oxide/hydroxide has maximum theoretical pseudocapacitance of about 3560 F g^{-1} [5].

In this work, we synthesized Co_3O_4 nanostructures on Ni foam by hydrothermal method. XRD pattern, FESEM images, and specific capacitance of Co_3O_4 nanostructures are given in figure 1 and 2 respectively.

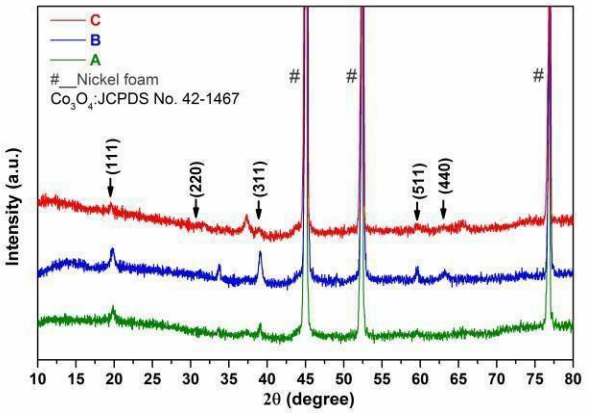


Figure 1. XRD pattern of Co_3O_4 nanostructures.

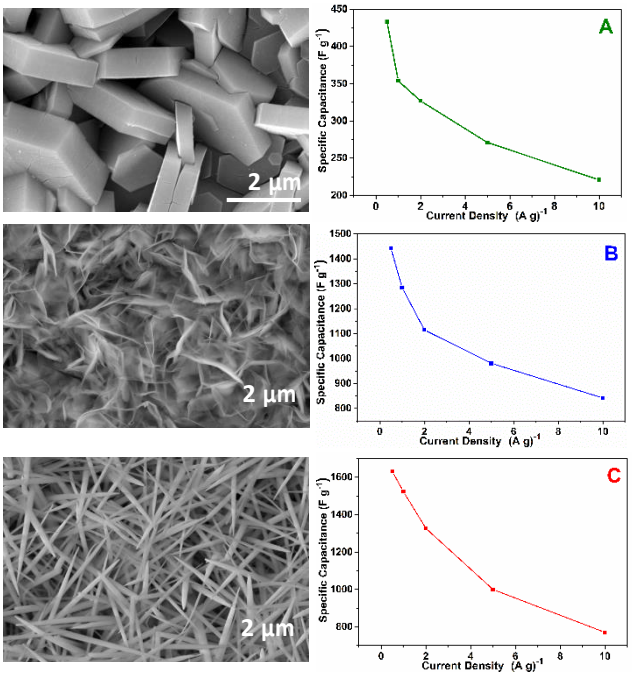


Figure 2. FESEM images and specific capacitances of Co_3O_4 nanostructures.

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Enhanced supercapacitive performance of Fe_3O_4/Carbon nanocomposite in surfactant-added aqueous electrolyte

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Due to their high power density and long-term cycling stability, supercapacitors have become an important electrochemical energy storage device. Hence, they have great potential to be exploited in a broad range of applications, such as smart grids, hybrid electric vehicles and consumer electronics where fast energy uptake or delivery is needed. However, the development of practical supercapacitors is limited by the lack of high energy density nanostructured electrode materials as well as cost-effective and scalable production methods.

Carbon based electric double layer capacitors (EDLCs) provide high power density storage with excellent cycling stability, but their low energy density restricts their practical applications. Instead, pseudocapacitive transition-metal oxides enable superior capacitance and energy density via highly reversible surface redox reactions. However, these reactions often lead to irreversible capacitance losses due to the much quicker degradation of electrode material. Moreover, the low electronic conductivity of metal oxides (causing low power density) compared to EDLC materials and their high manufacturing costs limit their utilization for energy storage applications.

To overcome these limitations, the next generation of high-performance supercapacitors should be able to couple the redox-active pseudocapacitive materials with the porous carbon materials, giving the composite material with the desired combination of properties, i.e., high capacitance, high energy density, good electrical conductivity and long cycling stability.

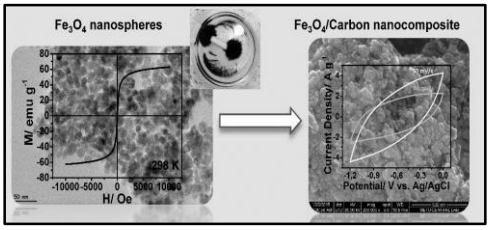


Figure 1. Schematic representation showing magnetic and electrochemical properties of Fe_3O_4 nanospheres and Fe_3O_4/Carbon nanocomposite, respectively.

Magnetite (Fe_3O_4) has been intensively studied as a pseudocapacitive electrode material due to its low cost, eco-friendliness, and natural abundance. In this work, Fe_3O_4 nanospheres were coupled with carbon via the facile and cost-effective route. First, pseudocapacitive Fe_3O_4 nanospheres were synthesized by a scalable chemical co-precipitation technique. Magnetic susceptibility (M vs. H) measurements (Figure 1) reveal that Fe_3O_4 nanospheres are superparamagnetic at room temperature, which makes them also promising for *in vivo* applications in the biomedical field such as imaging and targeted drug delivery [1]. Then the composite material was prepared through hydrothermal carbonization by introducing hazelnut shells as a renewable carbon source and MgAc as a ceramic (MgO) template precursor. Simultaneous templating allows the final composite material to have hierarchical porosity and high specific surface area.

The electrochemical performance of Fe_3O_4/C nanocomposite was studied in a three-electrode test cell. Benefiting from the synergistic effect of Fe_3O_4 and carbon, the resulting nanocomposite electrode showed an improved specific capacitance, rate capability and cycling stability within a large negative potential range (from -1.2 to 0 V vs. Ag/AgCl) in 1M Na_2SO_4 aqueous electrolyte. Moreover, the nanocomposite electrode showed ~20% increase in the specific capacitance when a non-ionic surfactant (Triton X-100) used as an electrolyte additive. Thus, the Fe_3O_4/C nanocomposite is a promising negative electrode material for high energy density asymmetric supercapacitors.

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Single Walled Carbon Nanotube Thin Films Decorated with Cobalt Oxide Nanoflakes for Supercapacitor Electrode

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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.

Metal oxide active materials has attracted much more attention than their carbon counterparts which are commercialized as double-layered supercapacitors in recent years. This is because of their pseudocapacitive behavior; high redox activity and high reversibility. Cobalt oxides (Co_3O_4 and CoO_x) are reported to have such properties, making 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 thin film single walled carbon nanotubes and supercapacitors fabricated by this means with a low-cost route remained elusive.

In this work, single walled-carbon nanotube (SWNT) and cobalt oxide nanocomposite electrodes were prepared as in Fig. 1 and tested. SWNT thin films were fabricated via low-cost vacuum filtration and consecutive stamping method onto glass substrates and cobalt oxides were electrodeposited from a cobalt nitrate solution. Co_3O_4 phase is obtained by annealing the as-prepared electrodeposited specimen. The capacitive behavior of the hybrid supercapacitors was investigated through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. A specific capacitance of 313.9 F/g and 70.5 $mF.cm^{-2}$ was obtained at a scan rate of 1 mV/s for the fabricated nanocomposite electrodes. A detailed analysis on the capacitive behavior will be presented in conjunction with the oxidation states, morphology and structural characterization of the active materials.

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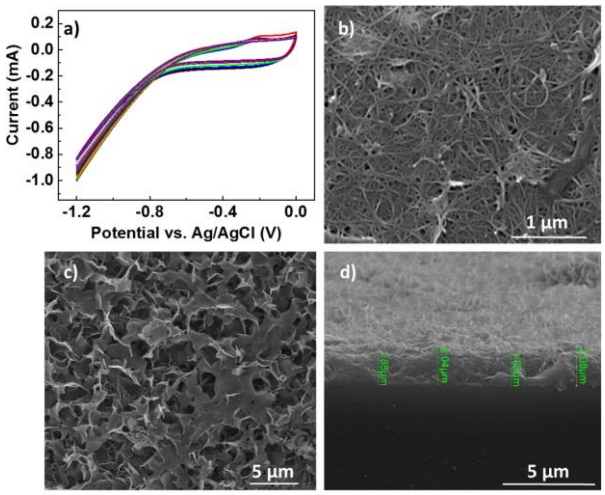


Figure 1 a) CV curves obtained during the deposition of $Co(OH)_2$ on SWNT thin films. Top view SEM images of b) bare SWNT thin film, c) Co_3O_4/SWNT thin film and d) cross-sectional SEM image of Co_3O_4/SWNT thin film.



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Comparing Capacitances of Modified Glassy Carbon Electrodes by Microwave asisted Reduced Graphene Oxide with Metallotphthalocyanines

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Phthalocyanines (Pcs), owing outstanding dye properties and the ability to self-assemble, by means of π-π interactions, into highly ordered arrays can be tuned by careful design of their periphery such as quinoline moiety [1,2]. In this work, quinoline derivative (**1**) of tetra-1-chloro-3,4-dicyano-6-quinolin-8-yloxy substituted novel cobalt(II) and zinc(II) phthalocyanine (CoPc (**2**) and ZnPc (**3**)) complexes were synthesized (Figure 1) and characterized by UV-Vis, FTIR, ^{1}H NMR and Mass Spectroscopies [3].

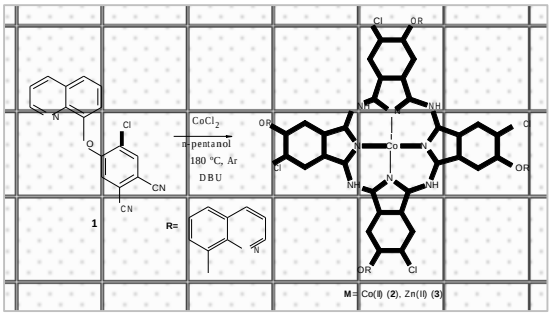


Figure 1. Synthesis of metallophthayanines.

Graphiteoxide (GO) prepared from natural graphite by improved Hummer‟s method is used as the starting material to microwave assisted reduced graphene (MRGO) in Figure 2. CoPc or ZnPc solutions in DMF was added to GO dispersion and the resulting mixture was ultrasonicated. Micro and molecular structure, spectroscopic and elemental properties of GO, ERGO, MRGO, were clarified and characterized by SEM-EDS, FTIR, UV-vis and XRD.

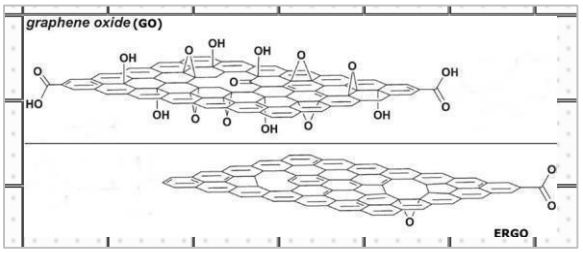


Figure 2. GO and RGO structures.

Cobalt phthalocyanine (CoPc) complex was bonded with GO functional groups in DMF solutions. GO-CoPc hybride solution is first deposited onto the surface of glasy carbon electrode (GCE), and is subsequently dried out to form a GO-CoPc coated GCE. The deoxygenation of GO-CoPc was accomplished via electrochemical reduction technique. Similar procedure were apllied for ZnPc derivative to get GO-ZnPc.

The electrochemical properties of GCE, GO, ERGO, MRGO and GCE/ERGO/CoPc electrodes characterized by cyclic voltammetry (CV) to compare their capacitances. For this, coated GCE is subjected to electrochemical reduction using a standard three-electrode electrochemical system in the presence of 6 M KOH electrolyte to produce ERGO-CoPc or ERGO-ZnPc hybride films on the surface. Electrochemically reduced graphene oxide (ERGO) along with the CoPc or ZnPc will be investigated enhancing capacitance.

The electrodes of CoPc/MRGO or ZnPc/MRGO were also obtained by casting these resulting colloid solutions on a glassy carbon electrode (GCE) for modification. Then, these GO electrodes were reduced via CVs (cyclic voltammetry) for several cycles in the electrolyte solution to prepared CoPc/RGO and ZnPc/ERGO modified electrode for enhanced capacitance[4] and also the metal efect was compared. Mass-specific capacitance of modified GCE electrodes measured by CV.

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Optimization of Graphene Synthesis by Electrochemical Exfoliation of Graphite

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Graphene is the one atom thick allotrope of carbon that is a honeycomb lattice of carbon atoms. Its carbon carbon bond length is 0.142 nm. The graphene sheets interplanar spacing is 0.335 nm. It is very thin and nearly transparent sheet..

Graphene's extraordinary properties make it a suitable candidate for many technological applications such as its use in energy storage, optical electronics and transparent conductors. Since invention of graphene, there has been much research about how to produce it and how to use it efficiently. Currently, there are several routes to produce graphene; mechanical exfoliation, CVD (chemical vapor deposition), SiC thermal decomposition, liquid phase exfoliation, chemical and thermal reduction of graphene oxide. In this study, graphene will be synthesized by electrochemical exfoliation of graphite..

The electrochemical approach has the advantages of being single-step, easy to operate, environmentally friendly (if using ionic liquid electrolytes or aqueous surfactants) and operates at ambient conditions. Highly controllable flakes can be formed without the need for volatile solvents or reducing agents. The process can take several minutes to hours to complete and the reported results are encouraging for the fast-processing of large quantities of graphene flakes. The electrochemical method utilizes a liquid solution (electrolyte) and an electrical current to drive structural expansion (oxidation or reduction), intercalation and exfoliation at a piece of graphite (rod, plate, wire) to produce graphene flakes. The experimental arrangement uses a mono polar, undivided electrolysis cell. The yield, productivity and properties of graphene flakes can be tuned by controlling the electrolysis parameters and electrolytes.

In this project, graphene will be synthesis by electrochemical exfoliation of graphite. Process parameters like electrolyte, electrode, used graphite quality, salts, surfactants, applied voltage, current density, temperature, cell geometry (distance between electrodes) and time will be optimized to produce high quality graphene with high yield.

Both acidic and basic electrolyte were used in past experiments as an aqueous electrolyte and acidic electroyltes yields better results, studies on aprotic electrolytes are going on. Mainly, ions in the electrolyte enter between graphite layers with the aid of the electrical potential and exfoliate them. DC current were applied and it's observed that higher current density results higher yield but lower quality graphene powders.

Structural properties were analyzed by X-ray Diffraction (XRD). Morphological properties were characterized by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

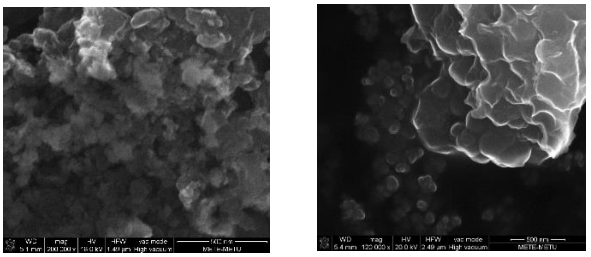


Figure 1: SEM images of graphene powders

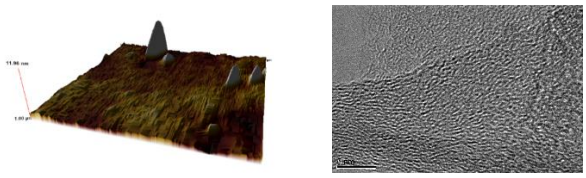


Figure 2: AFM image and TEM image of graphene powders

In AFM images maximum thickness is measured as 12nm and minimum thickness is measured as 3nm (approximately 8-10 layers). Also surface area of powders are calculated as 15 m^2/gr in Brunauer-Emmett-Teller (BET) analysis.

TEM analysis were done on electrochemically exfoliated graphene to observe the number of layers. Raman spectroscopy will be carried out to characterize the defect-activated band information in exfoliated graphene.

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Hydrogen Storage

Ammonia borane as hydrogen storage materials

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The use of hydrogen as an energy carrier is anticipated to facilitate the transition from fossil fuels to the renewable energy sources, on the way towards a sustainable energy future [1]. However, the safe and efficient storage of H_2 is the major obstacle in its wide applications [2]. The most effective and safest way of storing hydrogen is to use solid media such as sorbent materials [3] or hydrides [4]. Chemical hydrides provide a higher energy density for H_2 storage as compared to the gas or liquid H_2 tank systems. Recent reports have shown that B–N adducts need to be considered as hydrogen storage materials because of their high content of hydrogen with multiple nature, the protic N–H and hydridic B–H hydrogen [5]. Among B-N adducts, ammonia borane ($H_3N{\cdot}BH_3$) appears to be an appropriate hydrogen storage materials because of its high hydrogen content of 19.6% wt, high stability under ambient conditions, and nontoxicity [6]. Ammonia borane can be produced by using one of the well established processes [6].

Hydrogen stored in ammonia borane can be released by either thermal dehydrogenation or solvolysis. The former process has some drawbacks: i) it requires long induction time (~3h) and high temperature [7], ii) various by-products, such as ammonia and borazine ($B_3N_3H_6$) can be formed during reaction. The hydrolysis or methanolysis are two practical ways of hydrogen generation from ammonia borane for hydrogen fuel cell applications at ambient temperature. Ammonia borane is relatively stable against hydrolysis in aqueous solution (Eq. 1).

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \quad (1)$$

Therefore, the hydrolytic dehydrogenation of ammonia borane can be achieved at an appreciable rate only in the presence of suitable catalyst at room temperature. Hydrolysis of ammonia borane can be monitored by ^{11}B-NMR whereby NH_3BH_3 exhibits a quartet around δ = -24.0 ppm while borate product (BO_2^-) exhibits a singlet around δ =10.0 ppm [8]. Many transition metal nanoparticles have been tested as catalysts in releasing hydrogen from hydrolysis of ammonia borane. Since the transition metal nanoparticles tend to aggregate causing a momentous loss in activity they need to be stabilized either by stabilizing ligand in solution or by using supporting materials with large surface area in solid state. The results reported in literature will be given together to show that transition metal(0) nanoparticles dispersed in solution or supported on suitable solid materials with large surface area can catalyze the hydrogen generation from ammonia borane at room temperature and ii) how to improve the catalytic activity and durability of transition metal(0) nanoparticles by selecting suitable stabilizer or supporting materials for certain metal. Nanoceria supported rhodium(0) nanoparticles are the most active catalysts providing a turnover frequency of 2010 min^{-1} in hydrogen generation from the hydrolysis of ammonia borane [9].

Similar to the hydrolysis, the methanolysis of ammonia borane can occur in the presence of suitable catalysts releasing 3 equivalent H_2 (Eq. 2).

$$NH_3BH_3 + 4CH_3OH \rightarrow NH_4B(OCH_3)_4 + 3H_2 \quad (2)$$

Compared to the hydrolysis, the above reaction can be initiated even at temperatures below 0 °C, thereby satisfying the applications in cold weather conditions [10]. More importantly, there is no NH_3 release in methanolysis leading to the generation of pure H_2. Various noble and non-noble transition metal(0) nanoparticles have been widely studied for hydrogen generation from the methanolysis of ammonia borane [11]. Rhodium(0) nanoparticles supported on nanoalumina provides the highest turnover frequency (218 min_{-1}) for H_2 generation from the methanolysis of ammonia borane at room temperature [12].

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Vacancies influence on MgH_2 properties

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To study the influence of H-related defects on MgH_2 properties we did bulk and slab density functional theory (DFT) calculations. Slab calculations were used to simulate surface and near-surface effects that are responsible for hydrogen desorption reaction. On the other hand, the bulk calculations of vacant MgH_2 structures were used to study the hydride optical properties. Hydrogen desorption from (110) surface of rutile MgH_2 was calculated by pseudopotentional method as implemented in Abinit code, using Martin Toullier pseudopotentials [1]. Desorption energies for hydrogen atoms (H-vacancy formation energies) were calculated for different surface and near surface vacancy concentrations and configurations and also for diferent distances of H-atoms from the surface (different layers). We did this calulations for pure MgH_2 and MgH_2 doped with boron. Vacancy formation energies are lower in the boron doped system and decline with increasing distance from boron.

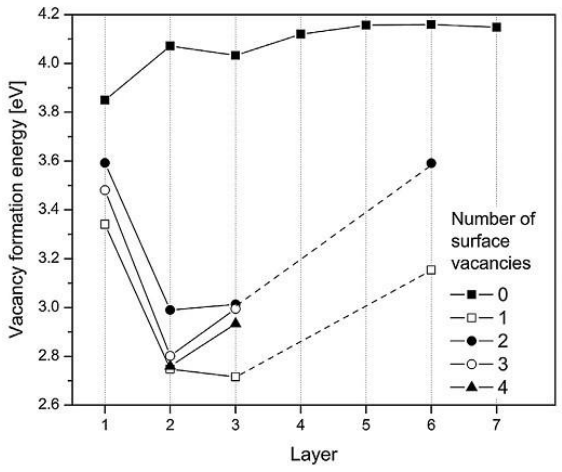


Figure 1. The H-vacancy formation energies in the(110) MgH_2 sub-surface layers as a function of surface coverage with H atoms

The surface hydrogen desorption energy depends on saturation of formed vacancies, but also on their arrangement. For fully populated surface (configuration with 0 surface vacancies) the increase of the H-vacancy formation energy and boron doped hydride, hydrogen desorption energy for going from the surface towards the bulk is almost monotonic, vacancies are already present at the surface. In both un-doped vacant surface strongly depends on vacancies concentration and configuration (Fig 1).

To assess changes in the electronic and optical properties of MgH_2 and derived H-vacant structures, calculations were done using the WIEN2k code [2]. For the purposes of the introduction of hydrogen vacancies and interstitials in sufficiently low concentrations, a stack arrangement of supercells with 2x2x2 and 5x1x1 unit cells was constructed, with initial parameters taken from previously optimized pure MgH_2. In terms of hydrogen vacancy calculations, one H atom was removed, meaning that there was one H vacancy per 32 (3.125 at%) and per 20 (5 at%) H atoms, respectively. The vacancy state contributions to dielectric function are visible as low structures positioned at energies from approximately 2.5 to 6eV for both systems with vacancies. The calculated dielectric functions of the $Mg_{16}H_{31}$ system influence only the short wavelength side of the visible spectrum, up to about 500 nm. The results of the calculations suggest that the hydride colour is highly sensitive to H vacancies and that even at 3.125 at% of H-vacancy concentration, the optical region is affected considerably.This means that the colour changes and partial loss of transparency observed in the MgH_2 thin films during hydrogen desorption [3] can be at least partially explained by the presence, structure, position, and width of the H vacancy (and/or interstitial) level in this material.

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Synthesis and hydrogen storage properties of Mg-V-H thin films

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The main obstacle for use of hydrogen as energy carrier lies in its storage. The solid state storage in form of powders shows promising results regarding desorption temperature and kinetics, but several problems are still to be addressed. Those problems are related to determination of mechanism of sorption and improvement of kinetics. In order to understand the mechanism of desorption, the investigation of thin hydride films is of great importance. Further advantages of thin film hydrides over bulk are:

1) larger surface area – faster (dis)charging rate,

2) pulvarization is slower,

3) pressure and temperature of desorption are lower than in bulk,

4) heat transfer is better in thin films,

5) protective coating could be done on thin films in order to stop poisoning with oxygen and

6) thin films can be easely activated by surface coating [1].

The main drawback of thin film is the mass of stored hydrogen due to the fact that the substrate is massive. Mg thin films [2] seem to be more adequate to obtain detailed information about the influence of thickness, microstructure and surface state on H-absorption/desorption mechanism than others synthesized nanostructures. In order to understand mechanism of desorption we have obtained multilayer Mg-V-H thin films by magnetron sputtering deposition using a KJLC CMS-18 system in the Thin Film Laboratory, Ruđer Bošković Institute. Thickness of Mg layer was tuned in range 10 to 30 nm, while V thickness was kept constant at 1 nm. The deposition was performed for three different deposition temperatures (RT, 150 and 300^{o}C). The films were deposited on glass and Si substrates. Than samples were annealed at 200 ^{o}C in vacuum. To destabilize the Mg-V and thus improve sorption properties, ion irradiation was performed at Facility for modification and analysis of materials with ion beams (FAMA) in Vinča Institute. Samples are homogeneously irradiated using 10 and 20 keV H^{+} ions with ion fluences of 10^{16} ions/cm^2 and 10^{17} ions/cm^2. The hydrogen desorption process was investigated by TPD analysis, at a constant heating rate of 5 K/min, starting from room temperature to 973 K, under starting vacuum of $3\cdot10^{6}$ mbar, utilizing a homemade equipment, with a quadruple mass spectrometer EXTORR XT300. The kinetics parameters were deduced using non-isothermal approach. The phase transformation was characterized by DSC analysis using DSC evo 131. Grazing incidence small angle X-ray scattering (GISAXS) is used to analyse the structure of thin films.

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Review of Thermal Energy Storage using Metal Hydride-based Technology

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Currently half of the EU's total energy demand is consumed by the heating and cooling sector of which only 18% is generated from low carbon or renewable energy sources [1]. Combined heat and power (CHP) or "*cogeneration*" involves the simultaneous production of electricity and thermal energy from the same primary energy source. Combined cooling, heat and power (CCHP), or "*trigeneration*", is similar to CHP but with the added benefit of generating cooling energy which can be utilised for applications including refrigeration and air conditioning [2].

Due to their high efficiencies, reduced maintenance costs, minimal environmental impact and silent operation in comparison to traditional combustion engines, CHP systems based on stationary hydrogen fuel cells (e.g. solid oxide fuel cells) are being developed around the world. Another major advantage of using FC technology with cogeneration or trigeneration is that the only by-products of the electrochemical reaction of hydrogen with oxygen is waste heat, water vapour and (depending on the fuel used) trace amounts of CO_2. A further benefit of this technology is that the waste heat can be reserved utilising a thermal energy storage (TES) medium.

There are three main types of TES processes;

- Sensible heat storage; heating or cooling a solid or liquid storage medium (e.g. water, molten salts, rocks).
- Latent heat storage using a phase change material (e.g. ice, parafin, erytritol).
- Thermo-chemical storage using chemical reactions to store and release thermal energy.

Of the three TES processes, thermo-chemical storage is able to provide the largest storage capacity (up to 250 kWh/t) with temperatures >300°C and efficiencies between 75-100%.

Metal hydrides (MH's) are a safe, efficient and high energy density TES medium. MH's offer long term heat storage and operatate using a wide range of pressures and temperatures.

The reversible reaction of hydrogen with a metal can be expressed as:

$$A_yB_z + x\,H_2 \leftrightarrow A_yB_zH_{2x} + \Delta Q \quad [3]$$

where, A is usually a group IV or rare earth metal forming a stable hydride, B is a transition metal which does not form a stable hydride but allows for a decrease in heat released upon absorption of hydrogen, ΔQ.

Figure. 1 shows the energy density of well studied TES-based MH as a function of operating temperature.

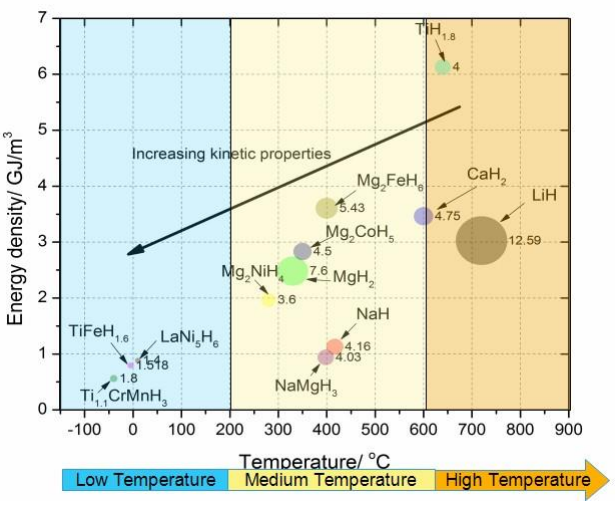


Figure 1. Selected metal hydrides for thermal energy.

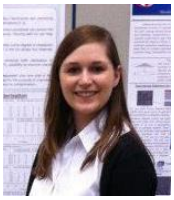
When selecting an appropriate MH for TES there are several factors to consider, including; the heat of reaction, entropy change, reversible capacity, temperature and pressure requirements of the overall system and heat capacity.

The overall aim of this work is to provide a review of the different metal hydrides suitable for TES applications with a focus on energy storage efficiencies and density targets.

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Development of Ti-based AB_2-type Metal Hydrides for Hydrogen Storage and Compression Applications

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Ti-based AB_2-type metal hydrides, which possess C14 Laves and often BCC phases, have been used for a variety of ambient temperature applications, including hydrogen storage and metal hydride hydrogen compressors. A Ti-Zr-Cr-Mn-Ni-Fe alloy (where, Ti and Zr are the A alloy elements and Cr, Mn, Ni, and Fe, the B alloy elements) was recently successfully demonstrated in a fork lift truck operating with a PEM fuel cell and the system for its H_2 refuelling [1]. The selected alloy has a reversible capacity of 1.6 wt% at T=25 °C and P=150 bar and was selected because it provides high enough hydrogen pressures (>10 bar) at temperatures above 0 °C and, at temperatures above 125 °C, most of hydrogen can be desorbed at P >200 bar.

The effects of stoichiometry and alloying elements on the properties of Ti-based AB_2 alloys have been extensively investigated. It has been shown that small changes in composition influence the pressures at which hydrogen is absorbed/desorbed as well as the shape of the plateau slope and usable hydrogen capacity. For example, previous work has shown that an increase in V content decreases plateau pressure whilst increasing the usable capacity and Cr reduces hysteresis and usable hydrogen capacity [2, 3], however, the influence of V and Cr, as well as other constituents has not been fully investigated.

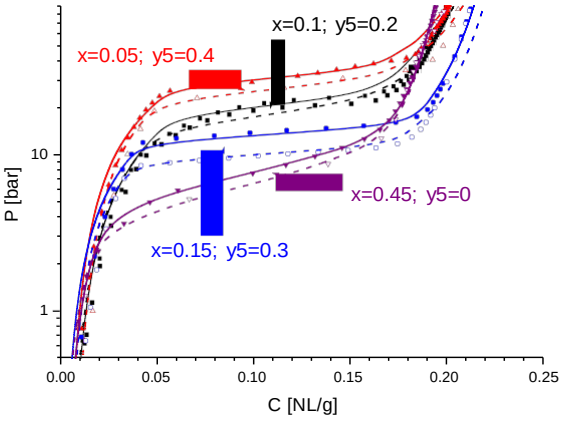


Figure 1. Experimental and calculated [4] PCI's (T=20 °C) of AB_2 alloys with various contents of Zr (x) and V (y5).

The current study is aimed at the development and manufacturing of Ti-based AB_2-type alloys for hydrogen storage and compression applications via induction melting. In the produced alloys the pressure – composition – temperature (PCT) properties are modified by tuning the component composition through varying the Zr content on the A side, along with the content of V and Cr on the B side.

As shown in Figure 1, a range of $Ti_{1-x}Zr_xCr_{y1}Mn_{y2}Ni_{y3}Fe_{y4}V_{y5}$ alloys, where, x=0.05–0.45; y1=0.1–0.4, y2=0.3–1.2, y3=0.2–0.3, y4=0.05–0.5, y5=0–0.6; $\sum_{i=1}^{5} yi$ = 1.8 – 2.5; were prepared by induction melting under an Ar atmosphere. In these alloys and the effects of composition and crystallography on the hydrogen sorption properties were examined using SEM-EDS, XRD and Sievert's-type PCT measurements, which were further processed by a model of phase equilibria in metal–hydrogen systems [4]. In addition to this work, MH production was scaled up from laboratory scale (~50 g) to industrial scale (~10 kg) using a custom built induction furnace.

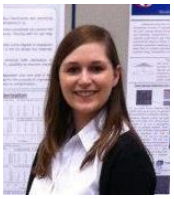
It was found that successful tuning of the hydrogen sorption properties of AB_2-type materials can be achieved by the variation of component composition, specifically relating to the contents of Zr, V and Cr. At a fixed, quite low Zr/(Ti+Zr) ratio (0.05–0.15) the PCT properties of the materials can be adjusted in wide limits by the variation of V content which, in addition, results in an increase in thehydrogen storage capacity.

Further, the results show that induction melting in a ceramic crucible is a suitable and scalable option for the preparation of Ti-based multicomponent AB_2-type hydride forming alloys for hydrogen storage and compression applications. In spite of the "dirty" conditions associated with the interaction of the alloys in the molten state with the crucible material, the alloys prepared by this processing route are characterized by acceptable hydrogen sorption properties, including; reversible hydrogen storage capacities up to 200 NL/kg, tunable hydride stabilities, moderate hysteresis and plateau slope.

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Nb-based Ternary Thin Film Alloys for Hydrogen Separation Membranes

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Abstract

Nb-Pd-Ti ternary system was investigated to determine possible compositions that can be used as a hydrogen separation membrane. Thin films were produced via magnetron sputtering system and then were screened by measurements based on the resistivity. Evaluation based on the resistivity measurement indicated that a small triangular region close to Nb corner react favorably with hydrogen and might therefore be considered as candidates for hydrogen separation.

1.Introduction

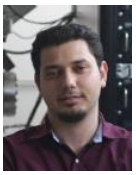
Hydrogen can be industrially produced in a variety of ways such as steam reforming of natural gas, coal gasification or biomass gasification. However, it can be only produced as a component in a gas mixture (CO, CO_2 and H_2S) instead of pure hydrogen [1]. That's why each production method requires an additional purification/separation process. Currently, hydrogen can be purified through one or a combination of three separation processes such as pressure swing adsorption, cryogenic distillation and separation membranes. Hydrogen separation membrane is considered as a promising method due to its ease of operation, low investment requirement and the suitability for the small scale applications [2]. Among the hydrogen separation membranes, metallic membranes are 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 the industrial applications [3]. Therefore, efforts have concentrated on either reducing the Pd content of the membranes or to find new alternatives which are free of Pd [4-6].

Nb and its alloys are particularly attractive due to its orders of magnitude faster hydrogen permeability compared to Pd-based membranes. However, Nb and Nb-based membranes extremely suffer from the hydrogen embrittlement due to their high level of hydrogen solubility [7]. Briefly, the large amount of hydrogen dissolves in the structure and this causes substantial volume expansion in the lattice. In course of hydrogen permeation, contraction-expansion of lattice ends up with the membrane embrittlement under operating conditions [8]. Therefore, the efforts, to produce mechanically durable Nb membranes, have concentrated on reducing the level of hydrogen solubility while maintaining reasonably high permeability. One approach to reduce the hydrogen solubility of Nb is alloying it with other elements having lower hydrogen solubility [9,10]. However, finding an alternative composition or developing a new membrane composition content are not always successful. Besides, this also requires extended coordinated efforts which are time consuming. Therefore, 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 instead of conventional production approaches such as synthesizing one membrane composition at a time and testing it for the permeability.

The current work is concentrated on Nb-based b.c.c. membranes where Nb was alloyed with Pd and Ti elements. The thin film library of Nb-Pd-Ti ternary compositions was produced via a magnetron sputtering deposition system. Thin film membranes were screened due to their hydrogen reactivity with resistivity-based measurements to determine the candidate compositions for the hydrogen separation membranes.

2.Experimental

Nb-Pd-Ti thin film membranes were produced by simultaneous deposition of Nb, Pd and Ti targets (99.95%, Kurt J. Lesker) via magnetron sputtering system. Prior to deposition, a total of 21 glass substrates, with dimensions of 19 mm diameter and ~0.15 mm thickness, were loaded to multiple substrate holder in a triangular geometry and positioned above the sputtering targets in the chamber. Then, chamber evacuated down to $1x10^{-7}$ Torr using a roughing pump assisted turbo molecular pump. The deposition rate of each element was kept equal and constant, 2 Å/sec, to deposit approximately same thickness along the all substrates. The duration of the deposition was around 4h to yield approximately 3 µm thick membranes. In this way, 21 chemically distinct thin film membranes were produced in a single experiment. This procedure was applied twice to obtain two set of membranes having the same compositions. All membranes were annealed in argon for 3h to stabilize their structure. The more detail for the production procedure was described in a previous study [4]. The structure and the elemental composition of the produced thin film membranes were characterized by x-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) techniques. Also, morphology of the membranes was investigated by scanning electron microscope (SEM). Nb-Pd-Ti thin film library were then screened due to their hydrogen reactivity by a four-probe



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resistivity measurement set-up. In the earlier study, it was shown that the resistivity provides a good correlation with pressure-composition isotherms [11, 12, 13] and could be used as a measure of the hydrogen solubility in the particular alloy system. Briefly, during the measurement, membranes were heated up to 450 °C with 5 °C/min heating rate and the change in resistivity was recorded. This procedure was applied to all membranes in argon as well as in hydrogen atmosphere under the same conditions. The resistivity of each membrane was determined and the ratio regarding the argon and hydrogen atmosphere, $\rho H_2/\rho Ar$, was calculated for the desired temperatures. This ratio is considered as a hydrogen reactivity which could also be correlated with the hydrogen solubility.

3.Results and Discussions

The compositional distribution of the deposited thin film membranes is given in Fig. 1. This distribution shows that the large portion of the ternary phase diagram is covered, where the amount of Nb is in the range of 10-76 at.%, with a single deposition. XRD pattern of the selected compositions is shown in Fig. 2. Nb10Pd13Ti77, Nb76Pd13Ti11 and Nb11Pd79Ti10 membranes represents Ti-rich, Nb-rich and Pd-rich compositions where the samples were just above the related sputtering target during the deposition. Nb36Pd28Ti36 compositions is also added into the figure as an example for a membrane, having a similar amount of each element as a component, located in the inner part of the diagram.

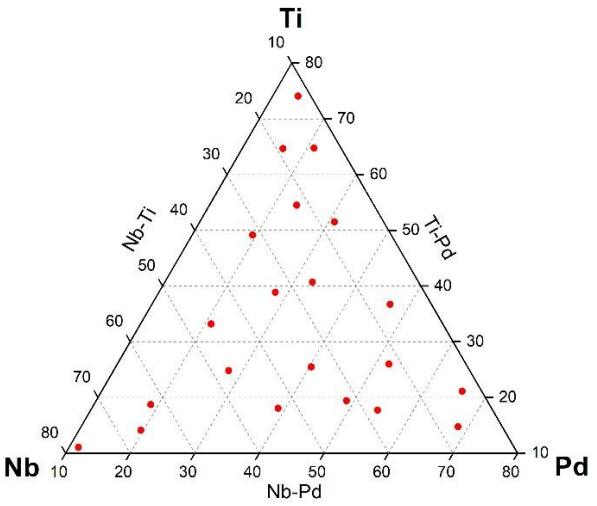


Fig. 1. The compositional distribution of the deposited membranes along the ternary diagram.

Here, XRD patterns indicate that the membranes exhibit single phase structure and they formed solid solutions. The XRD pattern of Nb10Pd13Ti77 matches with b.c.c. β-Ti where Nb76Pd13Ti11 and Nb11Pd79Ti10 matches with b.c.c. Nb and f.c.c. Pd phases, respectively. It should be noted that membranes in question have some deviation in terms of lattice parameter due to the formation of solid solution. Nb10Pd13Ti77 and Nb76Pd13Ti11 have the same structure, b.c.c., with a very similar lattice parameter. Regarding the chemical composition of the membranes, Nb10Pd13Ti77 and Nb76Pd13Ti11 are attributed to β-Ti and Nb, respectively.

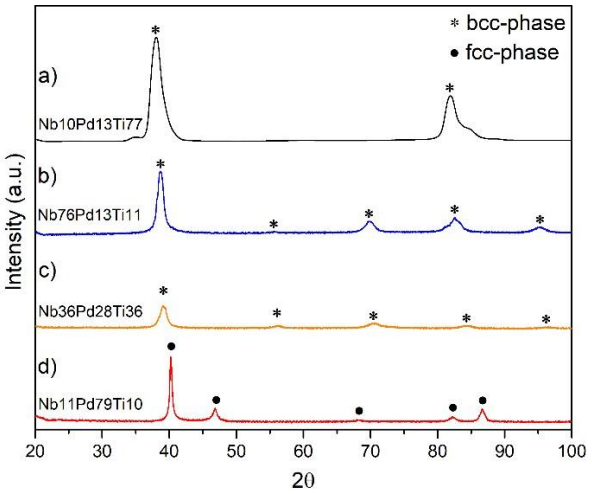


Fig. 2. XRD pattern of selected membrane compositions, a) Nb10Pd13Ti77, b) Nb36Pd28Ti36, c) Nb76Pd13Ti11 and d) Nb11Pd79Ti10.

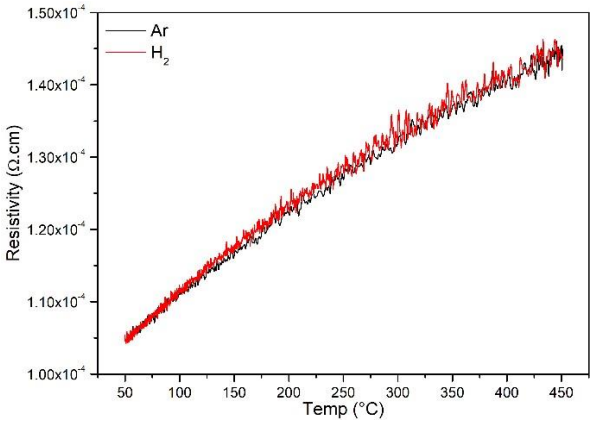
Lattice parameters of thin films, calculated by Rietveld refinement, show that unit cell of Nb10Pd13Ti77, Nb36Pd28Ti36 and Nb76Pd13Ti11, having the same b.c.c. structure, contracted upon alloying. On the other side, Nb11Pd79Ti10 exhibits slightly larger lattice parameter compared to pure f.c.c. Pd which indicate lattice expansion. Additionally, XRD patterns also show that membranes have strong preferential (110) and (111) orientation regard b.c.c. and f.c.c. structures, respectively.

The morphology of the membranes was also examined via SEM. It was observed that the membranes that are close to sputter targets during deposition have relatively finer grain size except Nb76Pd13Ti11. The approximate grain size of Nb10Pd13Ti77 and Nb11Pd79Ti10 membranes are within the range of 60-70 nm and 120-150 nm, respectively. On the other hand, in the case of Nb76Pd13Ti11 that was the closest membrane to Nb sputter gun during the deposition, has relatively larger grain size with a different morphology. The grain shape in Nb76Pd13Ti11 membrane is matching with the tilted columnar grain structure whereas equiaxed grains was observed in Nb10Pd13Ti77 and Nb11Pd79Ti10 membranes. In the case of Nb36Pd28Ti36, the grain morphology is similar to Nb10Pd13Ti77 and Nb11Pd79Ti10 membranes, however the grain size is relatively larger.

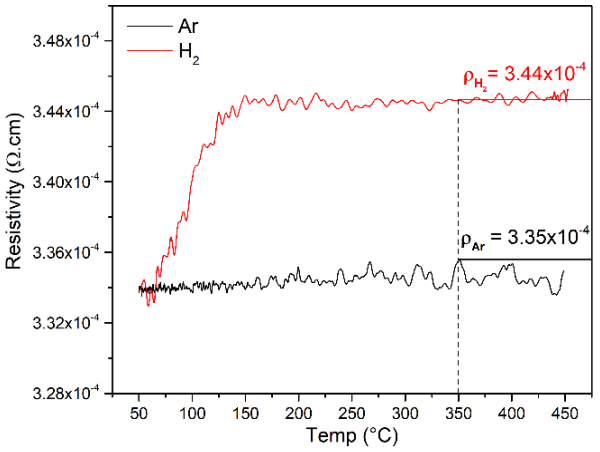
All membranes were screened via resistivity based measurement due to their hydrogen reactivity following the structural and the chemical characterization. In the first step, membranes were heated up to 450 °C in the inert atmosphere, argon, and the resistivity curve recorded as a reference. Then, the same procedure was applied but in hydrogen atmosphere to distinguish the effect of hydrogen. Regarding the hydrogen permeation mechanism through the dense metallic membranes, it is well known that hydrogen molecules split into atomic hydrogen in the first step. Then, hydrogen must dissolve in the membrane and diffuse into the membrane due to the chemical potential gradient. This hydrogen dissolution into the membrane would also affect the electrical properties of the membrane. That's why; introducing hydrogen into the test chamber during the measurement would result with a characteristic change in resistivity depending on the membrane

composition. On the other hand, if the membrane resistivity would be the same in both atmosphere, so $\rho H_2/\rho Ar=1$, this indicates that membrane do not react with hydrogen. It can be related to the lack of hydrogen disassociation or the lack of hydrogen dissolution in the membrane. Either the case indicates that related membrane composition cannot be considered as a separation membrane since each process is very crucial for the separation membranes.

The representative resistivity curves for the membranes that do and do not react with hydrogen is given in Fig. 3. Here, Nb14Pd19Ti67 exhibits the same resistivity change in argon and hydrogen atmosphere upon heating. There is only resistivity increment upon increasing temperature which is a typical metallic behavior. This indicates that hydrogen cannot introduce into the membrane, Fig. 3 a). On the other hand, Nb44Pd29Ti27 exhibits a clear evidence regarding the absorption of hydrogen into the membrane, which causes increase in the resistivity, Fig. 3 b). However, it should be noted that some of highly reactive membrane compositions that are close to Nb corner, e.g. Nb76Pd13Ti11, Nb59Pd25Ti16 and Nb44Pd29Ti27, didn't survive from the resistivity measurement. The membranes in question were suffered from the brittlement following the introduction of hydrogen into the test chamber. This indicates that even though Nb is alloyed with elements having relatively lower hydrogen solubility, some alloys still might have very high hydrogen solubility. The membrane compositions, failed during the resistivity measurement, was tested again with the membranes produced with the second set of deposition. However, Nb76Pd13Ti11 membrane composition didn't survive from any of the resistivity measurement. All membranes were screened with the same methodology and their hydrogen reactivity was calculated for 350 °C and 400 °C which are typical operational temperatures for hydrogen separation process. Hydrogen reactivity of the membranes was gathered as a contour mapping on the ternary diagram. This resistivity based mapping is given in Fig. 4. The membranes that didn't survive from the resistivity measurement are considered as an unreactive membrane since the highly vulnerable compositions cannot be considered as a separation membrane. The membranes that didn't survive and that do not react with hydrogen, $\rho H_2/\rho Ar=1$, are shown in dark brown color in the ternary diagram.



a)



b)

Fig. 3. The representative resistivity curves where a) Nb14Pd19Ti67 do not react with hydrogen and b) Nb44Pd29Ti27 reacts with hydrogen.

Among the membranes that survived the resistivity measurement, the highest reactivity is observed in Nb59Pd25Ti16 with an index of $\rho H_2/\rho Ar=1.068$ at 350 °C. It is followed by Nb44Pd29Ti27 and Nb46Pd36Ti18 with reactivity index of 1.026 and 1.014, respectively. However, it should be noted that Nb59Pd25Ti16 and Nb44Pd29Ti27 compositions were failed on the first resistivity measurement. This indicates that these compositions might also vulnerable to hydrogen embrittlement. It was observed that reactive membranes exhibited lower index at 400 °C which indicates a lower hydrogen solubility with increasing temperature. This also matches with the decreasing solubility of b.c.c. based membranes, e.g. Nb, Ta and V, with increasing temperature. This also causes negative slope in the hydrogen permeability-temperature diagram since the hydrogen solubility is more dominant over diffusivity. The reactivity index of Nb59Pd25Ti16, Nb44Pd29Ti27 and Nb46Pd36Ti18 at 400 °C was calculated 1.056, 1.018 and 1.009, respectively.

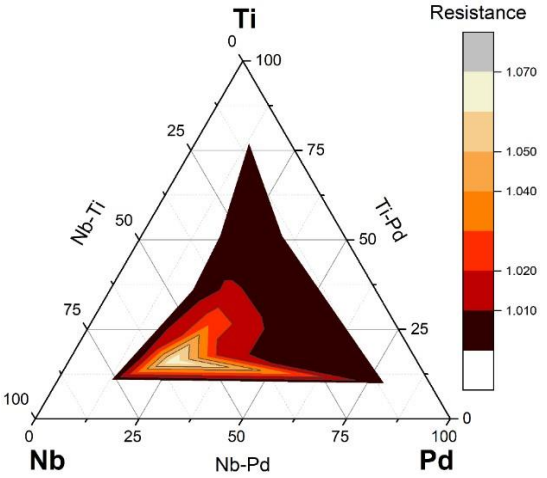


Fig. 4. The resistivity based contour mapping of Nb-Pd-Ti ternary compositions at 350 °C.

The applied methodology indicates that Nb59Pd25Ti16 exhibited promising hydrogen reactivity. The index of Nb59Pd25Ti16 was found as $\rho H_2/\rho Ar=1.068$ at 350 °C and $\rho H_2/\rho Ar=1.056$ at 400 °C which is well above the reactivity of

well-known Pd77Ag23 composition, $\rho H_2/\rho Ar=1.038$ at 350 °C and $\rho H_2/\rho Ar=1.035$ at 400 °C [11]. However, it should be considered that Nb59Pd25Ti16 exhibited an unstable resistance to brittlement since it was failed in one of the resistivity measurement. Therefore, the determined membrane compositions, having promising hydrogen reactivity, require further study. The compositions that are insensitive to hydrogen, so has no potential as a separation membrane, can be eliminated which saves considerable time. In this respect, the current study can be considered as a helpful methodology to narrow down the compositions which are worth for the further investigation.

4.Conclusions

In this study, Nb-Pd-Ti ternary system was investigated to determine possible compositions that can be used as a hydrogen separation membrane. Thin films were produced via magnetron sputtering system and then were screened by measurements based on the resistivity. It was found that the greater portion of the ternary diagram had b.c.c. crystal structure. This covered Nb reach compositions that extended to Ti corner also leaving out regions in Pd corner and the field close to Pd-Ti binary line. Evaluation based on the resistivity measurement indicated that a small triangular region close to Nb corner react favorably with hydrogen and might therefore be considered as candidates for hydrogen separation.

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Fuel Cells and Electrolysers

Protonic Ceramic Electrochemical Cells

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Abstract:

Protonic Ceramic electrochemical cells when operated in fuel cell mode, Fig.1, offer a low-pollution technology to directly convert fuels to electricity with high efficiency when compared to that of combustion engines [1]. Such proton conducting fuel cells, PCFCs, offer the advantage over oxide-ion conducting solid oxide fuel cells of keeping the fuel electrode (anode) undiluted, with the water formation occurring at the air electrode (cathode) side.

Thin electrolyte membranes are preferred for such devices, to reduce the ohmic losses during fuel cell operation [2], with the most common protonic ceramic electrolyte materials being the alkaline earth doped cerates, zirconates and their solid solutions, due to high proton conductivity and low activation energy. Nonetheless, the chemical instability of $BaCeO_3$ in acidic atmospheres and the high sintering temperature and resistive grain boundaries of $BaZrO_3$ are the main problems currently limiting their application [3]. As a compromise, the composition 40% Ce substituted Ba (Zr, Y) $O_{3-\delta}$, lying in the solid solution between the zirconate and cerate materials, has received great recent attention due to improving the chemical stability of the cerate, while maintaining high levels of total protonic conductivity [4][5].

Nonetheless, previous work by the authors [6] highlighted that the performance of thin film PCFC using this electrolyte rapidly becomes limited by the polarisation resistance of the cathode as temperature decreases, with resistance values that far exceed those of ohmic losses associated with the electrolyte.

The present work will provide an overview of the status of protonic ceramic electrochemical devices and will extend discussion to their potential application for the promotion of hydrogenation and dehydrogenation reactions. Such analysis will include a summary of the materials commonly used for cell fabrication and the limitations that currently hinder their more widespread application. Extended reference will be made to the critical selection of electrolyte materials and their relevance for specific applications, as a function of their stabilities and transport properties under different operating regimes.

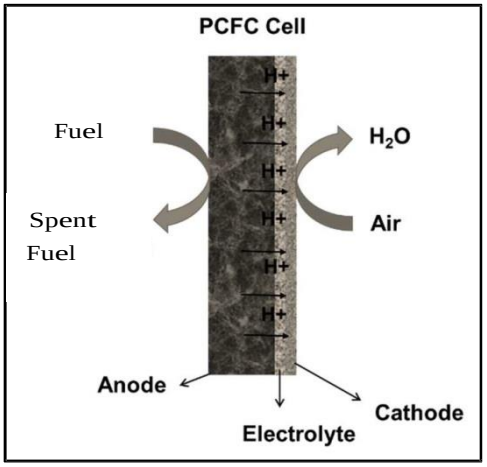


Figure 1: Typical anode supported Protonic Ceramic Fuel Cell

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Acknowledgments

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Fabrication and testing of anode supported Protonic Ceramic Fuel Cells in biogas

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Abstract:

Protonic Ceramic fuel cells (PCFCs) offer a low-pollution technology to directly convert fuels to electricity electrochemically with high efficiency when compared to that of combustion engines [1]. PCFCs also offer the advantage over oxide-ion conducting solid oxide fuel cells of keeping the fuel electrode (anode) undiluted, with the water formation taking place at the air electrode (cathode) side. Thin electrolyte membranes are preferred, to reduce the ohmic losses during the fuel cell test [2], with the most common protonic ceramic electrolyte materials being alkaline earth doped cerates, zirconates and their solid solutions, due to high proton conductivity and low activation energy. Nonetheless, the chemical instability of $BaCeO_3$ in acidic atmospheres and the high sintering temperature and resistive grain boundaries of $BaZrO_3$ are the main problems currently limiting their application in PCFCs [3]. As a compromise, the composition 40% Ce substituted Ba (Zr, Y) $O_{3-\delta}$, lying in the solid solution between the zirconate and cerate materials, has been received great attention due to improving the chemical stability of the cerate, while maintaining high total protonic conductivity [4][5].

In previous work by the authors [6] it was highlighted that the performance of thin film PCFC using this electrolyte rapidly becomes limited by the polarisation resistance of the cathode as temperature decreases, with resistance values that far exceed those of ohmic losses associated with the electrolyte. In the present work, anode (Ni-$BaCe_{(1-x)}Zr_{(x-y)}Y_{(1-x-y)}O_{3-\delta}$) supported thin electrolyte membrane (~6µm thickness) protonic cells were developed by a spin coating technique, with a triple conducting ceramic oxide cathode ($H^+/O^{2-}/e^-$) deposited on the electrolyte/anode assembly, Figure 1. This triple conducting cathode was specifically designed to attempt to combat the high polarisation resistances previously noted, by facilitating charge transfer by extension of three-phase boundary length throughout the cathode bulk.

As well as electrochemical testing in hydrogen, to permit performance comparison of the new cathode to that of the solely O^{2-}/e^- conducting ceramic oxide cathode of our previous publication [6], the current work also extends testing to the use of biogas fuel, an important feedstock from bio-waste consisting mainly of CH_4 and CO_2.

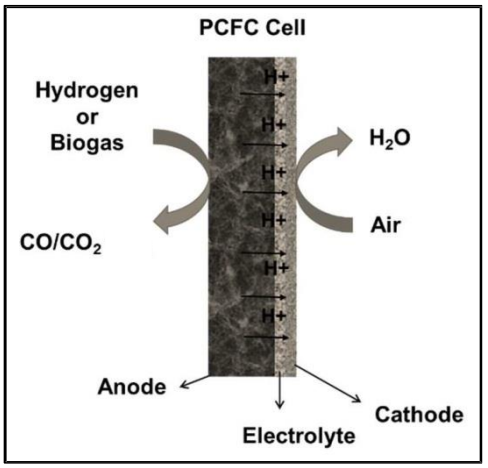


Figure 1: Typical anode supported Protonic Ceramic Fuel Cell

The current work, therefore, will present and discusses the behaviour of the triple conducting cathode, fuel utilization, carbon deposition and overall performance (I-V-P) results, as a function of biogas composition and temperature.

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Anode catalysts for use in direct glycerol fuel cells

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Introduction

Direct alcohol fuel cells (DAFCs) are considered to apply for portable appliances because they have much higher energy density than commercial lithium ion batteries. The complete oxidation of alcohols at the anode produces CO_2, so the use of carbon-neutral alcohols like bioethanol is desirable. Biodiesel fuel (BDF) also attracts attention as a carbon-neutral fuel, and the effective use of the glycerol byproduct, which is also a bioalcohol, is an urgent issue due to the mass production of BDF. The use of glycerol as a fuel for DAFCs will be promising because the anodic oxidation of glycerol is a carbon-neutral process and DAFCs with the glycerol are expected to produce electricity with a low environmental load.

Pd is cheaper than Pt and Au, and Pd-based alloy catalysts are highly active for the electrooxidation of alcohols in alkaline media. We also have reported the PdAg alloys-loaded carbon exhibited higher activity for glycerol oxidation reaction (GOR) and higher tolerance to poisoning species than Pd [1]. The product distribution and reaction mechanism for GOR on them, however, are unclear. In this study we prepared an Ag atomic layer-modified Pd (Ag/Pd) model electrode, and investigated the potential dependence of GOR products by *in situ* infrared reflectance-absorption spectroscopy (IRAS) and quantified the GOR products in potentiostatic electrolysis by liquid chromatography (LC). Based on these results, we will discuss the GOR mechanism.

Experimental

The Ag/Pd model electrode was prepared by underpotential deposition of Cu on a Pd polycrystalline substrate and the following galvanic replacement with Ag. The coverage of Ag on the Pd substrate was evaluated to be 0.66 from the difference in the charges for Cu-upd before and after the Ag modification. Ar-saturated 1 M KOH solutions with and without glycerol were used for electrochemical measurements. *In situ* IRAS and LC were used to qualitatively and quantitatively analyze the GOR products on the Pd and Ag/Pd electrodes in alkaline solution. All electrochemical measurements were performed at room temperature.

Results and Discussion

The cyclic voltammograms of the Pd and Ag/Pd electrodes in an Ar-saturated (1 M KOH + 0.5 M glycerol) solution is shown in Fig. 1. The Ag/Pd electrode had higher oxidation current and more negative onset potential of the oxidation current than the Pd electrode, clearly indicating that the GOR activity was enhanced by the modification of the Ag atomic layer. In addition, the peak potential of the oxidation current for the Ag/Pd electrode was more positive than that for the Pd electrode, and no oxidation peak was observed in the reverse scan, suggesting that the former was superior in tolerance to poisoning species to the latter.

IRAS spectra for the Pt electrode exhibited that the absorption peaks near 1330 and 1580 cm^{-1} assigned to mesoxalate and dihydroxyacetone, respectively, appeared near -0.2 V vs. Hg/HgO and increased at lower potentials, but the absorption peak at 1306 cm^{-1} assigned to oxalate increased at higher potentials. In contrast, IRAS spectra for the Ag/Pd electrode exhibited that the absorption peak assigned to oxalate was observed even near -0.2 V vs Hg/HgO, and increased with potential., suggesting that the C-C bond breaking occurred at more negative potentials for the Ag/Pd electrode.

In the electrostatic electrolysis in an Ar-saturated (1 M KOH + 0.1 M glycerol) solution at -0.1 V vs. Hg/HgO, for the Pd electrode glycelate was mainly obtained, whereas for the Ag/Pd electrode glycolate was the main product. The ratio of C2 products formed by C-C bond breaking of glycerol molecules to C3 products was larger for the Ag/Pd electrode. This also suggests that the C-C bond breaking was accelerated by the Ag modification on Pd.

Acknowledgement

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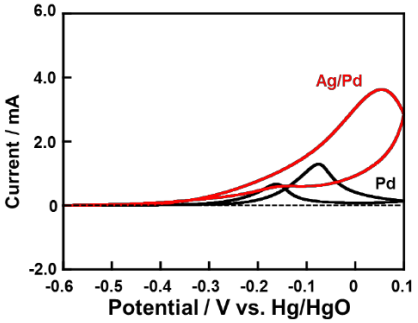


Fig. 1 CVs of Ag/Pd and Pd electrodes in Ar-saturated (1 M KOH + 0.5 M glycerol) solution. Sweep rate : 20 mV s^{-1}.



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Novel Direct Borohydride Fuel Cell Membranes Based on Polybenzimidazole and Sulfonated Polyether-ether-ketone

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Abstract

Direct Borohydride Fuel Cells (DBFC) are one of the most promising liquid fuel cell technologies and the membrane development is one of the keys for its success as for the other FC types. Fluorinated Nafion membranes seems still the first choice for DBFC studies. In this study, an alternative less costly blend membrane formulation and which will have at least similar good properties of Nafion with the experience gained in PEMFC membrane studies. For this purpose, the selected base polymer poly ether-ether-ketone (PEEK) was sulfonated up to high degrees of sulfonation and blended with another base polymer polybenzimidazole (PBI) in different ratios. Basic membrane properties such as degree of sulfonation (DS), water uptake, ionic conductivity, fuel crossover and mechanical strength and glass transition temperature were investigated by H-NMR, electrical impedance spectroscopy (EIS), voltammetry, mechanical tests and DSC. Results showed that the mechanical strength of SPEEK which has a god ionic conductivity value can be improved beyond the value of Nafion 117 without sacrificing too much of the conductivity by blending with the PBI polymer known with its mechanical strength. There is a trade-off between the important properties such as ionic conductivity and mechanical strength at the first sight. First results showed promising results which show that this trade-off could be obtained to give a performance value similar to or better than Nafion in DBFCs. Further studies especially on the single cell performances are needed for developing these blend membranes.

1.Introduction

Fuel cells which are systems directly converting chemical energy into electrical energy electrochemically are the most promising alternative energy converters to overcome pollution, to achieve a distributed energy network and to resolve many problems of the conventional energy converters based on direct combustion with their high efficiency compared to the low Carnot efficiencies of conventional burning systems. Therefore, the fuel cell systems are the center of attention in modern days of scientific and industrial community. However, there are technical problems to be solved in terms of their commercialization such as material performance and durability development as well as their costs. Fuel cells are basically an electrochemical energy conversion devices that converts chemical energy into electrical energy directly as long as the fuel and the oxidant are present, so they may be considered like the contiuous operation based versions of batteries. There are various types of fuel cells classified basically according to their electrolytes of which mostly studies and developed ones being the Proton Exchange Membrane (or Polymer Electrolyte Membrane) Fuel Cell (PEMFC) and Solid Oxide Fuel Cells (SOFC). Some sub-classes having operation and metarials similar to that of PEMFC were also defined according to the fuels used such as direct methanol fuel cells (DMFC) and direct borohydride fuel cells (DBFC). Since pure hydrogen gas is low in energy on volume basis and difficult and costly to produce and store, liquid fuels are eventually becoming better candidates particularly for portable applications.

Direct borohydride fuel cells (DBFCs) have an increasing attention recently as a sub-class of polymer electrolyte fuel cells (PEFC). The reasons behind this attention can be briefly stated as the advantage of the oxidation half-cell potential of sodium borohydride of – 1.24 V over standard hydrogen electrode (SHEs) i.e. a high open circuit potential the high flash point of $NaBH_4$ in alkaline solutions on safe liquid fuel usage, possible use of non-precious metal catalysts because of the ease of the electro-oxidation of BH_4- ion, low fuel crossover to the cathode side, low operational temperature suitable for portable applications, ease of fuel transportation, and finally the high energy density of 9.3 kWh kg^{-1}. [1,2,3]

Half-cell reactions and the overall reaction in the DBFC are given as follows [2]:

Anode Reaction: $NaBH_4 + 8\ OH^- = NaBO_2 + 6\ H_2O + 8\ e^-$ (E^0_{anode} = -1.24 V) (1)

Cathode Reaction: $2\ O_2 + 4\ H_2O + 8\ e^- = 8\ OH^-$ ($E^0_{cathode}$ = 0.40 V) (2)

Overall Net Reaction: $NaBH_4 + 2\ O_2 = NaBO_2 + 2H_2O$ (E^0_{cell} = 1.64 V) (3)

Hydrogen molecules are taken place on the surface of electrode, oxidized electrodes giving maximum eight electrons. At the cathode, the mechanism of oxygen reduction reaction is complicated and it involves generation of H_2O_2 and metal oxide by-product intermediates that decrease the activity of the electro catalysts. DBFC can reach 1.64 V that is approximately 1.3 times compared with the PEMFC and 1.35 times compared with the DMFC.

For electrolyte membranes, the ionic conductivity is the first property that have to be developed. For PEMFC types, proton conductivity is following two mechanisms: Migration of hydrated protons and proton hopping. [4] In DBFC, membrane hydration is essential since proton conductivity depends on the balance of the water content. But, it should be noted that the



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excess water levels may lead to flooding. [5] Increase of the temperature increases of conductivity of membrane whereas very high temperatures can cause dryness. [6,7]

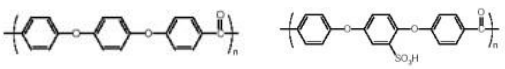
Stability and lifetime of the membranes, are significant and required for commercial fuel cell operations. This has led to the development of membranes with higher durability and lifetime ranging from 500 to 4000 h. according to the applications [8]. The composite and blending approaches may be utilized to obtain a synergistic effect by combining two or more similar or completely different materials (organic-inorganic; or organic-organic). This approach could improve the targeted properties such as ionic conductivity, mechanical stability, chemical stability etc… For example, heteropolyacids are well known solid inorganic materials with their very high conductivities and are one of the candidates for composite membrane ppreparation to increase the conductivity. [9]

Nafion® is still considered as the reference membrane for many low temperature fuel cells today. [4] It is rather durable over 60,000 h in the PEMFC. [8] These membranes have high conductivity and chemical durability. Main ingredient of Nafion®, hydrophobic polytetrafluoroethylene (PTFE), ensure thermal and chemical stability for the membrane as well as termination of hydrophilic sulfonic acid ($-SO_3H$) via the per-fluorinated side chains which secures migration holes for proton transfer. The migration through from anode to cathode occurs with relatively high conductivity of 90-120 mS cm^{-1} at 80 ^{0}C in the relative humidity range of 34-100%. [11] However there are some disadvantages of Nafion which cause the researchers to investigate alternative materials. Basic reasons for fuel cell applications can be listed as:

- High methanol (and other liquid fuels, also ruthenium if used at anode) crossover
- Very high cost (because of the difficulty in production, fluorinated groups)
- Low operation temperature limitation
- High humidification requirements
- Not environmentally friendly production route

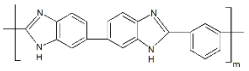
Nafion® membranes are a type of cation exchange membranes (CEM) that was first employed in DBFC by Li et al. [12] and is still employed in a majority of DBFCs. [1, 9,12] The primary mechanism in Nafion® membranes for proton conductivity is via water whenever operated at temperatures below 90^{0}C. [10]. Anion Exchange Membranes (AEM) can also be utilized in DBFCs since the fuel is very alkaline in nature since BH_4^- is a negatively charged ion, it has been suggested that CEMs should be more effective than AEMs to suppress its crossover. Also, CEMs such as Nafion types are commercially available. Nafion 117 has borohydride as low as 8.8×10^{-9} mol/ (cm.s) [7].

Polyether-ether-ketone (PEEK) which is the mostly studied member of the poly (arylene ether ketone) family consists of sequences of ether(-O-) and carbonyl (-CO-) linkages and phenyl rings. Sulfonated form was first used for water electrolysis and then started to be used for for fuel cell applications.



Polyetheretherketone (PEEK) & Sulfonated PEEK (SPEEK)

Its base properties are suitable for aopplications in FCs but it has to become ion conducting before. The easiest way to achieve this is to post-sulfonate PEEK with a suitable sulfonating agent such as conncentrated sulfuric acid. The sulfonated form (SPEEK) has been widely investigated for PEMFCs and good results were obtained, however as Degree of sulfonation (DS) increases the mechanical integrity of the membrane diminishes rapidly because of the excess swelling. Another membrane material being studied especially for high temperature PEMFCs (HT-PEMFC) which are operated at 120-200 ^{0}C because of its very high mechanical strength and the property of the ability to be doped with phosphoric acid to become ion conductive is polybenzimidazole (PBI).



Polybenzimidazole (PBI)

In this study these properties were aimed to be combined for a possible use in DBFcs.

2. Experimental

2.1 Sulfonation Process & Membrane Preparation

6 mm nominal granule size PEEK (*Aldrich) was first* dissolved in concentrated sulfuric acid (95-97%) and left under stirring for sulfonation reaction for 170 h at room temperature.

After the sulfonation the mixture was poured slowly into an ice-cold deionized water under stirring to stop the reaction and the water was exchhanged repetedly to leach the excess acid. SPEEK obtained was dried in an oven and then grinded in a coffe grinder and kept for further characterizations and membrane preparation. PBI solutions were prepared by dissolving certain amounts of PBI in Dimethylacetamide (DMAc) for 12 h. The pristine SPEEK, PBI or blended membranes were prepared by solvent casting method and dried under vacuum in an oven for at least 24 hours. The polymer to acid ratio was always around 10%. The temperature is gradually increased up to 120 ^{0}C. The blends were prepared according to weight percentages, the polymers were separately prepared in DMAc and then combined after having homogenous solutions. The blends were stirred for 1 hour and then poured to petri glasses and dried under vacuum for 24 h to obtain glassy membrane films.

2.2 Characterization Methods:

Degree of Sulfonation (DS) Determination (H-NMR): To assess the properties of SPEEK as an ion conducting electrolyte membrane the determination of DS correctly is improtant, this may be done by several ways but the most reliable one is the one obtained by H-NMR. I this study the SPEEK samples were sent to the cental laboratory of Middle East Technical University (METU) where a high resolution Bruker Biospin Digital 300 MHz NMR Spectrometer was used. Dimethyl sulfoxide (DMSO) was used as the solvent and trimetylsilane (TMS) as the standard. 10-20 mg dried samples were dissolved in 1 ml solvent for the measurement. As the degree of sulfonation (DS) increases intensity of H_E increases.

DS can be calculated from the integration values given in the H-NMR by using the equation below using relative integrated peak areas.

$$\frac{n}{12-2n} = \frac{A_{H_E}}{\sum A_{H_{ARMCO}}} \qquad (0 \le n \le 1)$$

$$DS = n \times 100\%$$

Ionic Conductivity Tests (EIS): A specially designed 4-probe through-plane conductivity cell (Erdes technology) was used and the measurements were made by Gamry Potentiostat/Galvanostat 3000 using AC electrochemical impedance spectroscopy. Test standards, voltage sensivity was 10 mV/s. 4- probe method in the surface direction ionic conductivity has better and more realistic results than other solutions. After obtaining the solution resistance, R, from the high frequency intercept of the real axis, the ionic conductivity was calculated from the equation: conductivity= L/(R.A) where L is the thickness of the membrane and A is the cross sectional area [13]. Measurements were performed at room temperature and 100% relative humidity.

Water Uptake: Membrane masses were recorded at fully humidified and fully dry conditions and the water uptake values were calculated according to the following equation:

$$Water\ Uptake = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

Glass Transition Temperatures: Differential Scanning Calorimeter (DSC) Analysisof the samples were performed with 'Mettler-Toledo DSC 1 Star' system with nitrogen atmosphere and 10 ^{0}C/min rate of heat to determine the glass transition temperatures.

Mechanical Strength: Tensile strengths were measured by 'Instron 3345' with ASTM D882 test (polymeric thin film) standards with 10 mm/min rate.

3. Results and Discussions

DS of the SPEEK prepared by 170 hr room temperature sulfonation was calculated to be 77.5% from the H-NMR spectra shown in Figure 1. This DS value is a high value and it is just below the eater soluble reagion as expected.

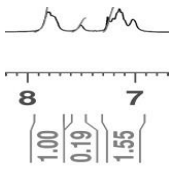


Fig. 1 H-NMR results

Ionic conductivity results were given in Figure 2. As it can be observed from the figure the conductivity of N117 is 0.081 S/cm and the conductivity of SPEEK has a conductivity of 0.073 which is very close to that value. As expected as PBI ratio in the blend increased the conductivity decreased. This is mainly caused because of the interaction of the sulfonic acid groups of SPEEK responsible for the ionic conduction and the basic amine sites of the PBI.

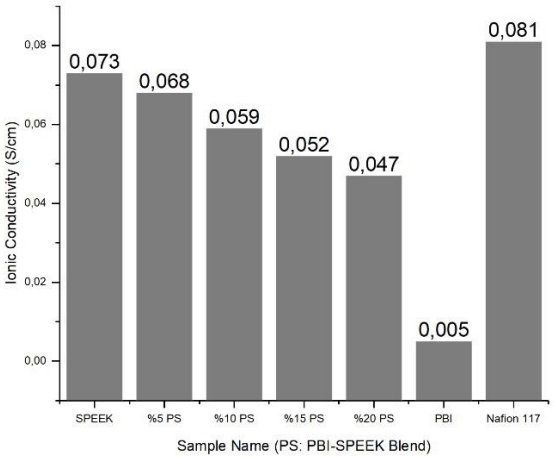


Fig 2. Ionic Conductivity Results

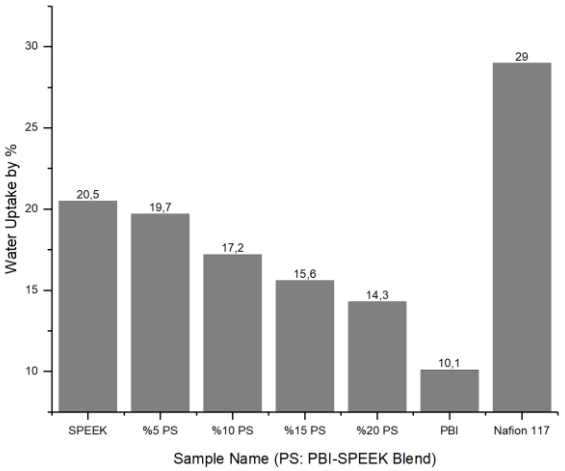


Fig 3. Water Uptake results.

Mechanical strength results in terms of tensile strengths were summarized in Figure 5. The distinct difference between N117 (34 Mpa) and PBI (49 Mpa) can be seen. SPEEK has a very low mechanical strength compared to both with only 17 Mpa value. One of the mahor aims of blending approach is to increase this very low mechanical stability which was caused by a high degree of sulfonation necessary for sufficient ionic conductivity. Since PBI has a very high value a small ratio of PBI blending was expected to carry this low mechanical strength to higher values. From the results it was seen that only 5% PBI resulted 26 Mpa and 15% PBI nearly cathed the value of N117. 20% PBI blend exceeded Nafion's strength.

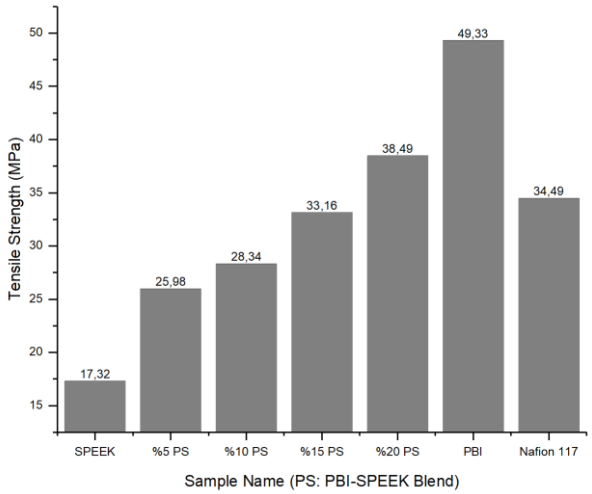


Fig 5. Mechanical Strength Results.

The glass transition temperature (T_g) is an important value for needed polymer properties for specific applications. Below Tg polymer behaves more like "glass", it is more rigid, and above Tg it behaves more elastic basically. In Fuel cell applications a rigid structure is preferred since structural changes with hydration and temperature fluctuations are not wanted. But therefore a Tg above the operation temperature is preferred. As DS increases Tg increases. For example Tg of PEEK is around 15 C and it is 174 C as seen from Figure 6. Tg of PBI (423 C) is very high compared to both SPEEK (DS=77.5) and N117 (140 C). Therefore increasing PBI ratio in the SPEEK/PBI blends were expected to increase Tg and results confirmed this.

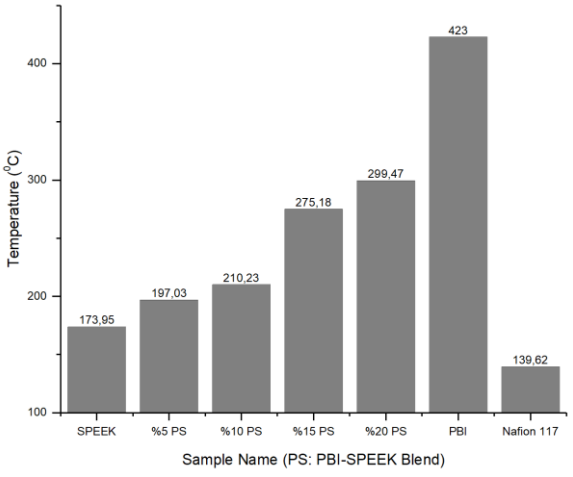


Fig 4. Glass Transition Temperatures-DSC Results.

4. Conlusions

In this study, highly sulfonated SPEEK and PBI polymer blends were fabricated as cast membranes for their potential use in DBFC. For this purpose, preliminary membrane characterizations were performed to determine the degree of sulfonation, ionic conductivity, water uptake, fuel crossover and mechanical strength were performed. Also, two new parameters were defined for the comparison of their potential which are selectivity and modified selectivity. Analysis of all the results of samples showed these SPEEK/PBI blend membranes have the potential to be utilized in DBFC systems but especially fuel permeability, single cell and long term stability tests should be performed for further evaluation.

Acknowledgement

Financial assistance and interest from the Scientific and Technological Research Council of Turkey for 215M255 coded project is gratefully acknowledged.

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CVD graphene as catalyst support for acid electrolytes

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Oxygen reduction in electrochemical processes is the largest contributor of losses and efforts continuing for improved kinetics through material innovation. Platinum (Pt) is considered as best catalyst for oxygen reduction reaction and commonly used. Efforts continue to replace Pt with non-precious metals/alloys to enhance commercial viability of electrochemical processes. Graphene has been utilized for this purpose, but commonly processed with chemical approaches through layer separation from graphite powder. Graphene produced by CVD process requires alternative approaches to obtain suitable materials for heterogeneous nature of gas-liquid catalytic activities. Electrocatalyst that are used in heterogeneous electrochemical systems, i.e. fuel cells, require 3-phase contact with gas and liquid present. If graphene can be produced in 3D form, it will help achieving fast charge transfer and high gas/liquid permeability leading to high catalyst conversion.

CVD process was utilized to grow graphene on metal foam structures that were processed at 850-1000 °C. Ar, N_2, H_2 and CH_4 were used as carrier gases at varying flow rates. Following growth of graphene on metal substrates, base metal support was etched away without destroying graphene structure. The resulting material was a multi-layer self-supporting porous graphene structure (Fig. 1).

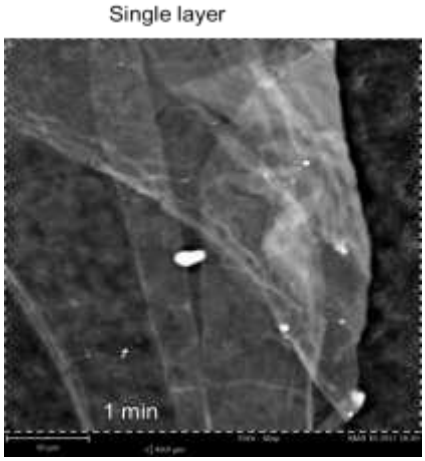


Fig. 1. SEM picture showing graphene layer structure

Raman spectroscopy response showed very defective graphene structure which might be due to presence of impurities in the furnace (Fig. 2). G/2D ratio was larger than 1 indicating multilayer structure formation for growth more than 1 minute.

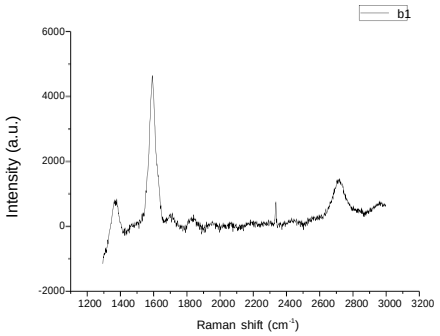


Fig. 2. Raman spectroscopy for graphene grown on copper foil

Electrochemical response of RDE measurements with and without graphene in 0,1M $HClO_4$ electrolyte is presented in Fig. 3. Graphene was contributing catalytic activity by itself.

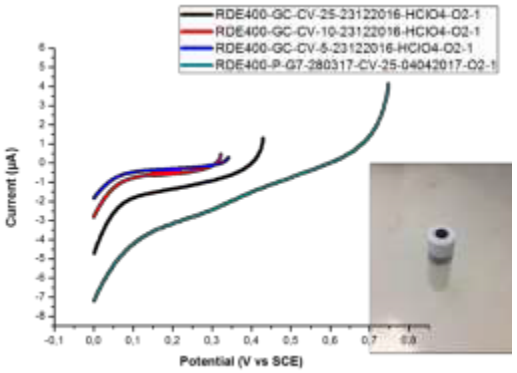


Fig. 3. RDE measurement with and without graphene in 0,1M $HClO_4$ electrolyte

Catalytic performance of newly developed materials in acid electrolytes will be discussed further in detail.

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Preparation of nitrogen doped graphene aerogel and carbon support materials and catalytic activities towards formic acid oxidation

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Direct formic acid fuel cells (DFAFCs) (Figure 1) have attracted significant attention because they are satisfactory power sources for portable devices. A significant interest in the development of direct liquid fuel cell technology is the need for highly active catalysts for formic acid oxidation reaction. The support materials is choosen significantly because of high specific surface area, which is necessary for improving the dispersion of catalytic metals and high conductivity.

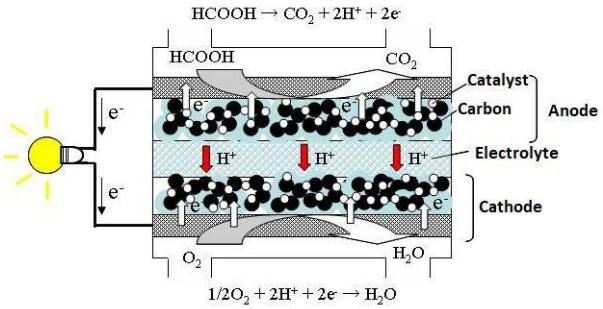


Figure 1. DFAFC schematic representation

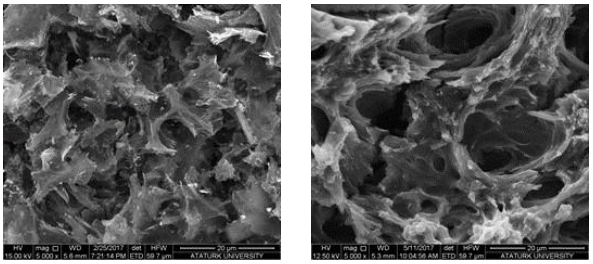
Researchers have widely investigated owing to their high electrical conductivity, large specific surface area, and good chemical stability. Researchers have investigated the N-doped graphene and carbon materials which were used as support for electrocatalyst for improving the catalytic activity [1]. This study includes the synthesis of graphene aerogel (GA), Nitrogen Doped GA and Nitrogen doped carbon black as support materials for Pt nanoparticles in order to use for formic acid oxidation.

***Synthesis of N doped GA*:** N doped GAs were prepared by a facile hydrothermal synthesis. 20 mL of concentrated ammonium hydroxide solution was mixed with 80 mL of the 5 mg mL^{-1} GO precursor solution. Then, the mixture was transferred into a Teflon-lined reactor and sealed in a steel autoclave. The autoclave was heated in an electric oven at 180 °C for 12 h. The nitrogen-doped graphene hydrogel was formed in the reactor. Finally, the N-GA was obtained by freeze-drying the graphene hydrogel for 12 h.

Synthesis of N doped Carbon: In order to obtain N-doped carbon, equal amounts of pre-treated Vulcan XC-72 and melamine as nitrogen source was ground in a mortar for 15 min. Mixture was then heated to 900 °C for 1 h under nitrogen atmosphere and then cooled to room temperature.

Synthesis of Pt/N-GA and Pt/N-Carbon by microwave irradiation technique: N-GA and N-Carbon supported catalysts having 20 wt.% Pt loading were prepared by using microwave irradiation technique. Firstly, required amounts of support materials and 0.05M aqueous solution of H_2PtCl_6 added in 50 ml ethylene glycol and then stirred for 30 min. Then the resulting mixture was reduced for 60s 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.

The morphology of the N-GA and N-Carbon was characterized by a scanning electron microscope (SEM) (Figure 2), The specific surface area of support materials was determined by Brunauer–Emmett–Teller (BET) method through nitrogen adsorption-desorption isotherms. The electrocatalytic activities of the Pt/N-GA and Pt/N-Carbon are evaluated for formic acid oxidation by using electrochemical measurements.



(a) (b)

Figure 2. SEM images of a) Graphene Aerogel b) N-doped Graphene Aerogel

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Improved PEM fuel cell performance with hydrophobic catalyst layers

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Flooding of catalyst layers is one of the major issues, which effects performance of proton exchange membrane (PEM) fuel cells. Generated water on active sites of Platinum (Pt) condenses, while moving along the pores of cathode catalyst layer (cCL). When water generation rate is high, it filled the pores of cathode catalyst layer, and prevents oxidant gas from reaching active sites. This leads lower performances. Effect of hydrophobicity in catalyst layers with respect to conventional catalyst layers on performance has been investigated by comparing the performances of membrane electrode assemblies prepared with 48% Pt/C. Ultrasonic coating technique was used to manufacture highly efficient electrodes.

Power density at 0.45 V increased by the addition of PTFE, from 0.95 to 1.01 W/cm^2 with H_2/O_2 feed

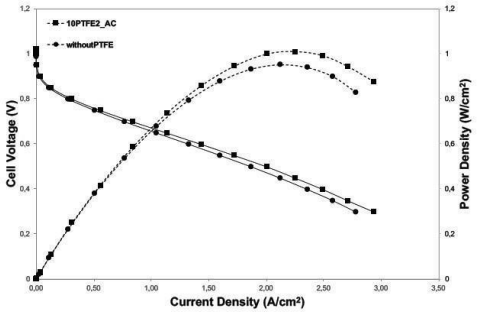


Figure 1. Effect of PTFE addition into conventional catalyst layers with H_2/O_2 feed

Performance of hydrophobic catalyst layers (hCLs) at 0.45V was slightly increased from 0.52 W/cm^2 for convetional catalyst layers to 0.53 W/cm^2 for hydrophobic catalyst layers with H_2/Air feed. Addition of PTFE to catayst layers keeping Pt loading constant, enhanced electrode kinetics. Decreasing Nafion loading from 0.37 mg/cm^2 to 0.25 mg/cm^2 while inclusion of PTFE (0.12 mg/cm^2) to the electrode increased kinetic activity.

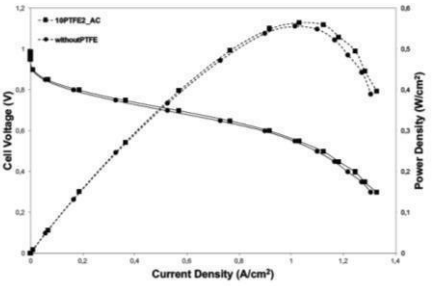


Figure 2. Effect of PTFE addition into conventional catalyst layers with H_2/Air feed

Electrochemical impedance spectroscopy (EIS) results proved that charge transfer resistance decreased with decreasing Nafion loading with PTFE addition. This is attributed to enhanced water management.

Preparation of catalyst ink in two steps diminished PTFE particles occupying active sites, by this way, triple phase boundaries was preserved. Performance of both conventional and hydrophobic catalyst layers decreased by half when oxidant was changed from O_2 to Air, which is similar to our previous studies [1, 2]. This is attributed to reduced partial pressure of oxygen, which lead decreased reaction kinetics.

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Experimental Investigation of CO Tolerance in High Temperature PEM Fuel Cells

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Abstract

In this study, the effect carbon monoxide (CO) poisoning on polybezimidazole (PBI) based high temperature proton exchange membrane fuel cells (HT-PEMFCs) has been investigated in a temperature range from 140ºC to 180ºC. Also dilution effect from CO_2 and N_2 was studied. The effects of CO were studied at various concentrations of CO in hydrogen as the anode feed gas. Polarization curves were measured in order to quantify the cell performance for all conditions. It is proposed that optimal temperature of HT-PEMFC stack is 160º C for the CO level up to 3%. The overall results suggest that the reformate gas with higher CO in the anode gas stream can be fed to the stack directly from the fuel processor.

1.Introduction

Proton exchange membrane fuel cell (PEMFC) is considered as a promising clean energy conversion technology due to the high efficiency, high power density, low emissions and fast start-up. Low temperature (LT) PEMFC using Nafion as the membrane and the temperature is typically limited up to 80ºC. The platinum used as the catalyst to improve the electrochemical reaction has a significant affinity for carbon monoxide (CO) since CO will adsorb onto the platinum surface and poison the platinum electro-catalyst. Therefore, it will reduce the active catalyst sites during the oxidation process. Because of its very low tolerance towards impurities in the fuel, the LT-PEMFC requires pure hydrogen to operate, and this is the main reason for its high operating cost since the production of pure hydrogen is expensive [1-3].

In commercializing the PEMFC technology, researchers and manufacturers need to deal with the drawbacks of the cost and durability. Phosphoric acid-doped PBI membranes are preferred to other membranes for the temperature range in which high temperature (HT) PEMFC operate (140-200ºC). The increased operating temperature in HT-PEMFCs causes enhanced electrode reaction kinetics and increase the tolerance to CO. The reformer system is suitable to be used towards HT-PEMFC since it is able to tolerate impurities,nand most importantly, lower the power production cost [4-6].

In this study CO poisoning effect on HT-PEMFCs was investigated at various concentrations of CO in anode gas stream with different temperatures. Also dilution effect from CO_2 and N_2 was studied. Polarization curves were measured in order to quantify the HT-PEMFC performance for all conditions.

2. Experimental

The PBI based membranes were prepared by a solution casting method according to our previous study [6]. The phosphoric acid doping was carried out by immersing the membranes in phosphoric acid (85 wt. % H_3PO_4) at room temperature for at least 1 week to mintain proton conductivity The acid doping level of the membranes investigated in this study was determined gravimetrically to be approximately 11 H_3PO_4 per polymer repeat unit for PBI enough to provide H_3PO_4 from the membrane to the catalytic layer by diffusion.

For the preparation of the MEAs, non-woven carbon cloth coated with a carbon microporous layer (Freudenberg-H2315C2) was used as the gas diffusion layer. The Pt/C is used as a both anode and cathode catalyst. The catalyst ink was prepared by dispersing catalyst power into a mixture of isopropanol and PVDF dispersion. Before being used, these catalyst inks were ultrasonicated for at least 1 h for homogeneity. The catalyst ink was ultrasonic-sprayed onto the GDL at 80ºC by the Sono-Tek 'Exacta-coat' ultrasonic spray instrument (120 kHz). The catalyst ink was inserted in a syringe pump prior to atomization in the nozzle (Accumist) and sprayed at a flow rate up to 0.5 ml min^{-1}. A catalyst loading of 1.0 mg/cm^2 was used for all MEAs both in the anode and the cathode side. Finally the electrodes were hot pressed onto both sides of the phosphoric acid doped membrane at 150ºC and 172 N/cm^2 for 5 min [7].

The MEAs were tested in a single HT-PEMFC hardware with 50 cm^2 active area. The cell is heated using resistance heaters mounted in the end plates of the cells. The gas flow plates were made of composite graphite and the geometry of the flow channel was the serpentine type.



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The current and voltage of the cell were monitored and logged throughout the operation by the test software. Two pieces of high temperature resistant Viton gaskets were served as sealant between the MEA and graphite plates [8].

Figure 1 shows the flow diagram of the HT-PEMFC test station bench. The test station equipped with a gas handling unit, electronic load (BK Precision, USA), control and data logger computer, was used to test of the HT-PEMFC. A computer-based control and data acquisition system of test station collected and multiplexed the respective signals and fed them into the PC for the overall system control.

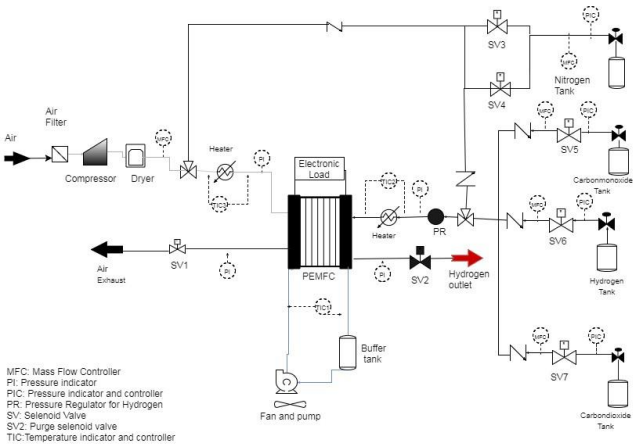


Figure 1. HT-PEMFC test system

3- Result and Dicussion

Figure 2 shows the effect of temperature on PBI and PBI-GO composite membrane based HT-PEMFC performances with pure H_2. The HT-PEMFC test displayed open circuit voltage (OCV) for PBI based MEA approximately 0.96 V, which indicated that membrane possessed low the hydrogen crossover.

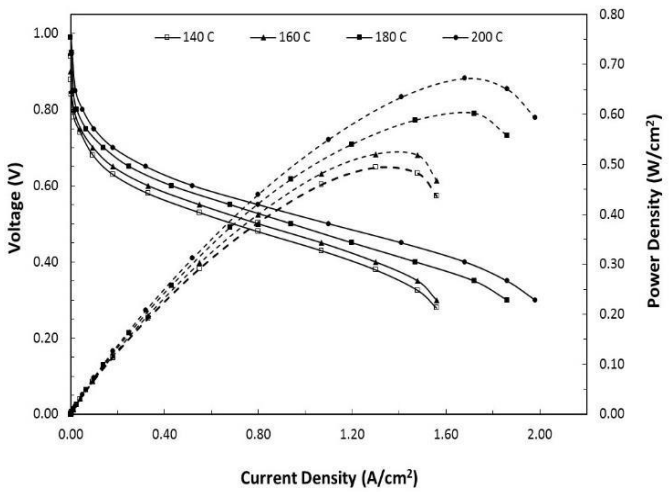


Figure 2. Effect of temperature on HT-PEMFC performance of PBI membrane

At 0.6 V, the current densities are 0.29 A/cm^2, 0.33 A/cm^2, 0.43 A/cm^2 and 0.52 A/cm^2 for 140ºC, 160ºC, 180ºC and 200ºC, respectively. The cell operating at 140ºC exhibited a significant performance loss. The performance loss was more profound at higher current densities. 160ºC working temperature selected was operating temperature. The stack performance is better at higher operating temperatures but the lifetime of the HT-PEMFC will deteriorate.

To simulate poisoning environment, the HT-PEMFC were fed with different concentrations of CO (1 %, 3 % and 5%) in H_2 under same conditions of pure H_2. The concentration of CO in this study is 1-5 % in volume which are in the typical concentration range of CO in the reformate gas derived from hydrocarbon fuel. At 160ºC, effect of different CO contents was studied and it was found that CO up to 3 vol. % can be tolerated in HT-PEMFCs. However, performance loss was appeared for 5 vol. % CO content.

The current density at 0.6 V decreases from The HT-PEMFC voltage loss caused by CO poisoning was found to be lower at higher operating temperatures and lower current densities. Figure 3 shows the effect of CO concentration on HT-PEMFC performance for both membranes. According to HT-PEMFC performance curves of PBI membrane recorded at 160ºC, the current density at 0.6 V decreases from 0.33 A/cm^2 for H_2 to 0.31 A/cm^2 for H_2 containing 1 vol. % CO, to 0.29 A/cm^2 for 3 vol. % CO, and 0.25 A/cm^2 for 5 vol. % CO, respectively.

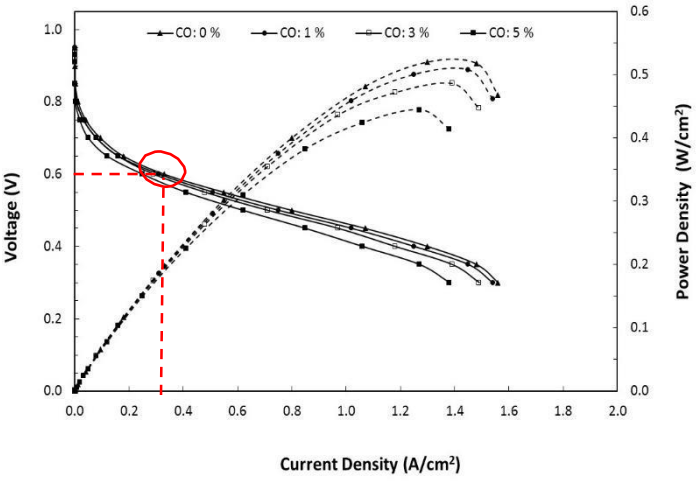


Figure 3. Effect of CO content on HT-PEMFC performance at 160ºC working temperature.

The HT-PEMFC performance loss with the presence of CO is caused by the strong adsorption of CO molecules on the Pt/C catalyst surface and the reduced electrochemical active surface area for hydrogen oxidation reaction.

The Table 1 shows the performance loss of HT-PEMFC using Eq. (1) when CO at various concentrations is present in the reactant gases [9];

$$R_{PL} = \frac{P_{H_2} - P_{CO}}{P_{H_2}} \times 100 \qquad [1]$$

where R_{PL} is the rate of decrease in performance with present CO in H_2; P_{H2} and P_{CO} are the peak powers obtained by using pure H_2 and fuel containing different concentration of CO, respectively. The rate of decrease in performance maximum power density increases from 1.9 % for 1 % CO content to 15.4 % for 5 % CO content, respectively.

Table 1. Performance loss and maximum HT-PEMFC voltage with different concentrations of CO.

CO Content (vol. %)	R_{PL} (%)	Max. Power (W/cm^2)
0	0	0.52
1	1.9	0.51
3	5.8	0.49
5	15.4	0.44

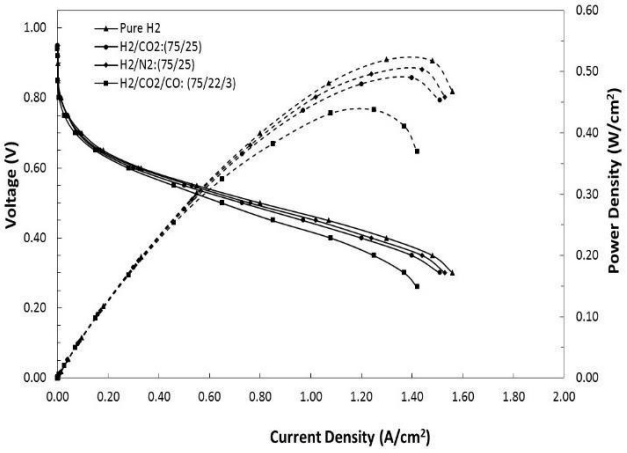


Figure 4. Effect of CO_2, N_2 and CO content on HT-PEMFC performance at 160°C.

Additionally, effect of dilution of hydrogen gas with CO_2 and N_2 was also investigated by polarization studies. Figure 4 displays the effects of anode dilution on the HT-PEMFC performance at 160°C. The total gas flow rate for both pure H_2 and H_2 mixture was kept constant, corresponding to a maximum theoretical current density of 0.33 A/cm^2 for pure H_2 and 0.32 A/cm^2 for hydrogen containing 25% CO_2. It was found that 75 % H_2, 25 % CO_2 gave similar results as pure H_2, which indicates that the hydrogen concentration dilution by 25% CO_2 did not affect the performance at low current densities.

Table 2. OCV, Current density and peak power of pure H_2 and H_2 contains N_2, CO_2 and CO_2-CO.

Gas	OCV	Current Density @ 0.6 V (A/cm^2)	Peak Power (W/cm^2)
H_2	0.95	0.33	0.52
H_2:N_2 (75:25)	0.94	0.32	0.50
H_2:CO_2 (75:25)	0.94	0.32	0.49
H_2:CO_2:CO (75:22:3)	0.935	0.28	0.44

It was found that effect of 25% CO_2 addition had very little effect on performance curve while 25% N_2 addition had almost no effect. The current densities of PBI membrane for the anode feed gas of H_2 including 0 and 25 % N_2 at 0.6 V were 0.330 and 0.320 mA/cm^2, respectively.

Table 2 summarized the OCV, current density and peak power of pure H_2 and H_2 contains N_2, CO_2 and CO_2-CO. The high CO tolerance in HT-PEMFC will make it possible to use the reformate gas directly from the reformer without further CO removal.

4. Conclusion

In this study, the CO poisoning effect on HT-PEMFC was investigated using dry H_2–CO mixtures as a fuel. According to the polarization curves, an increase in temperature has a positive effect on the HT-PEMFC performance. At 160ºC, effect of different CO contents was studied and it was found that CO up to 3 vol. % can be tolerated in HT-PEMFC at 160ºC. However, performance loss was appeared for 5 vol. % CO content. Additionally, effect of dilution of H_2 gas with CO_2 and N_2 was also investigated by performance studies. It was found that effect of 25% CO_2 addition had very little effect on performance curve while 25% N_2 addition had almost no effect.

The overall results suggest that the reformate gas with higher CO in the anode gas stream can be fed to the HT-PEMFC directly from the fuel processor.

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Acknowledgements

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Synthesis of Polypyrrole (PPy) based Porous N-Doped Carbon Nanotubes (N-CNTs) as Catalyst Support for PEM Fuel Cells

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Catalyst support has an important effect on PEM fuel cell performance and durability. Specific surface area, pore size distribution, N, O contents are main parameters for any support material and they change from one to another. Recently, N-doped materials have become popular for catalytic applications. Because, N-containing materials provide more catalytic sites on their surface and have larger surface area [1]. In this study N-doped carbon nanotubes (N-CNTs) were synthesized as catalyst support and polypyrrole (PPy) was used as carbon precursor. It was followed the method of Pan *et. al.* [2] for the synthesis of these CNTs. $FeCl_3$ was also used as an oxidant in the scope of CNT synthesis and it was thought that $FeCl_3$ supplies extra catalytic activity based on high temperature pyrolysis in the course of method [3]. Pt was loaded over the N-CNTs via microwave irradiation method.

Figure 1 shows SEM images of PPy based N-CNTs. As it was seen, it was succeeded to synthesize porous N-CNTs.

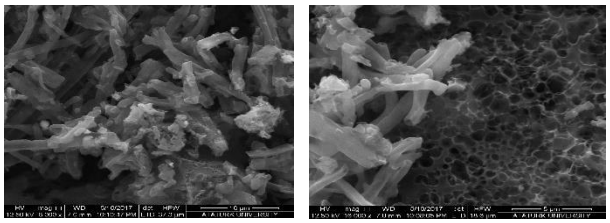


Figure 1. SEM images of N-CNTs

Figure 2. shows XRD pattern of N-CNTs. The characteristic peaks of N-CNTs positioned at 2θ=24° and 42° correspond to the reflections of the (002) and (100) planes, respectively. The XRD pattern shows that amorphous state of N-CNTs.

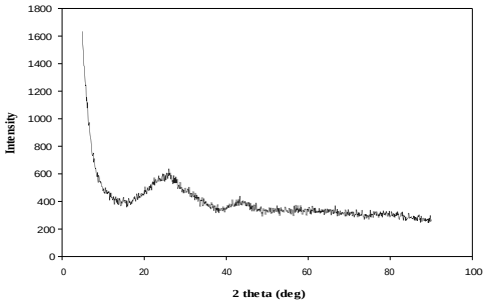


Figure 2. XRD pattern of N- CNTs

Table 1 shows the BET results of the synthesized N-CNTs. It was understood that N-CNTs have substantial surface area with a high micropore volume.

Table 1. Structural Properties of N-CNTs

BET Surface Area (m^2/g)	BJH Total Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	BJH Pore Diameter (nm)
1842.9	0.63	0.6057	2.77

Figure 3 shows PEM fuel cell performance of the fuel cell with N- CNTs supported Pt catalyst. Pt loading on the support was determined as 14 wt. % according to the ICP analysis. At the condition of 70°C cell temperature, it was obtained reasonable performance result such as 234 mA/cm^2 current density at 0.6 V.

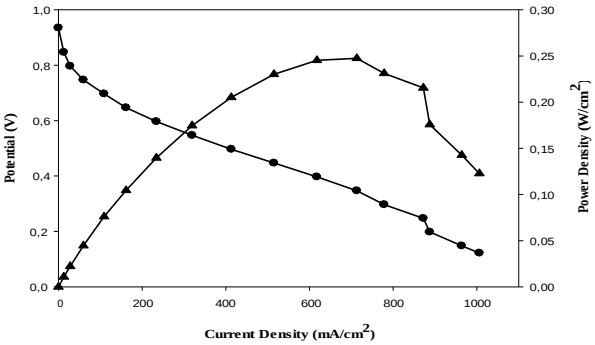


Figure 3. PEM fuel cell performance

In order to obtain higher PEM fuel cell performances it is required to arrange the structural properties of the N-CNTs. Electrical conductivity of the N-CNTs has to be determined for further improvement.

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Chemically Synthesized Reduced Graphene Oxide-Carbon Black based Hybrid Catalysts for PEM Fuel Cells

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One of the most important components of PEMFC is membrane electrode assembly (MEA) in which the supported catalyst materials play a crucial role since electrochemical reactions occur in here and it directly affects the cell performace. Graphene and graphene based hybrid materials shine out in recent years as alternative support materials due to their high specific surface area, good chemical stability and outstanding electrical properties which make them promising candidate for energy conversion and storage applications [1].

In this study, firstly graphene oxide (GO) was synthesized by using the method of Hummers and Offeman [2]. Preoxidized graphite was subjected to oxidation by Hummers method. Then, the reduction of graphene oxides (rGO) was obtained with dimethylformamide (DMF) by using a reflux system (at 150˚C for 6h). Reduced graphene oxide-carbon black (rGO:CB) hybrid composite support materials were prepared by mixing rGO with CB at different percentages as shown in Table 1.

Table 1. Catalysts labeled according to rGO to CB weight ratio (w:w %)

Code	Catalyst	rGO:CB (w:w %)	BET surface area(m^2/g)
H100	Pt/rGO	100:0	41
H90	Pt/rGO:CB	90:10	57
H80	Pt/rGO:CB	80:20	73
H70	Pt/rGO:CB	70:30	87
H60	Pt/rGO:CB	60:40	105
H50	Pt/rGO:CB	50:50	122

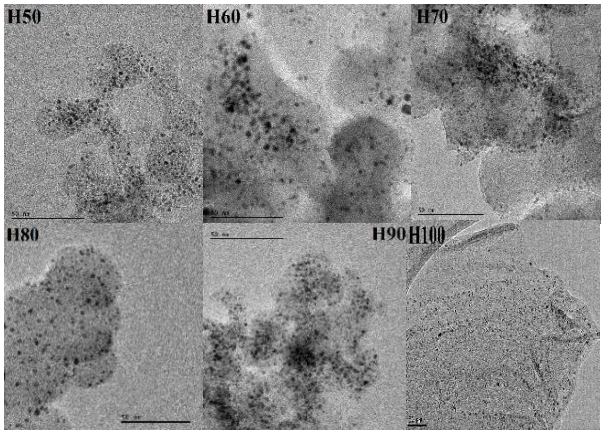


Figure 1. TEM images of catalysts

Pt nanoparticles on hybrid materials were obtained by using supercritical carbon dioxide deposition ($scCO_2$) technique. 1,5-dimethyl platinum cyclooctadiene (Me_2PtCOD) was used as the Pt organometallic precursor. A certain amount of precursor was firstly dissolved in $scCO_2$ (at 35˚C and 12 MPa) and then adsorbed on the hybrid materials. The precursor was decomposed to its metallic form with the heat treatment at 400˚C for 4 h in nitrogen atmosphere. The prepared hybrid supports and hybrid supported Pt catalysts were characterized by using BET, XRD, TEM, TGA, and Cyclic Voltammetry (CV) tests. Surface area of the hybrid materials are given in Table 1. The surface areas of the supports varied in between 41-122 m^2/g. TEM images are given in Figure 1. Figure 1 revealed a homogeneous dispersion of Pt nanoparticles. CV results for the catalysts are shown in Figure 2.

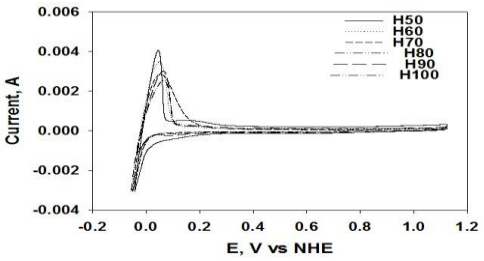


Figure 2. CV results of catalysts in N_2 saturated 0.1 M $HClO_4$ solution at a scan rate of 50 mVs^{-1}

A similar hydrogen electrochemistry is observed for all the catalysts. But the coulombic charge of the hydrogen adsorption/desorption for the H50 catalyst is the biggest when compared to other catalysts which showed the importance of the composition of hybrid material.

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Synthesis and Characterization of Bimetallic Catalysts for PEM Fuel Cells

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Over the past decade, researchers have shown more interest to bimetallic nanomaterials which have desirable prominent catalytic activity, selectivity and stability over monometallic nanomaterials thanks to their new physical and chemical properties which are derived from the synergistic effect between the two different metals and most of the literature reports regarding bimetallic catalysts are related to Pt-Ru, Pt-Pd, while combinations of Pt with other metals have been also reported [1-3].

In this work, we use a commercial graphene nanoplatelets (GNPs) as the support for deposition of bimetallic nanoparticles in supercritical carbon dioxide ($scCO_2$). Thanx to the advantages of $scCO_2$ which results in materials with superior properties compared to the other conventional techniques. In here firstly, Pt and secondary metals (M=Ni, Fe, Cu) on GNPs are obtained by using supercritical carbon dioxide deposition ($scCO_2$) technique as can be seen from Figure 1.

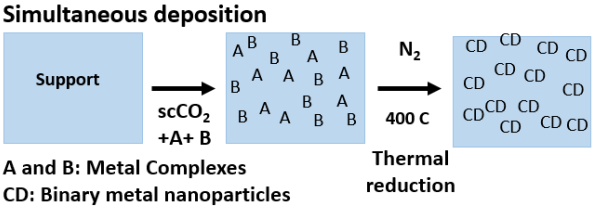


Figure 1. Experimental setup

The prepared bimetallic catalysts are characterized by using XRD, TEM, ICP-MS and PEM fuel cell performance tests.

The Pt and metal loadings over the support are determined by using ICP-MS and the results are given in Table 1. According to the results, highest metal loadings over the support are observed in PtNi/G catalyst.

Table 1. ICP-MS results of catalysts

Catalysts	Pt loading %	M loading %	Total Loading
PtNi/G	25.4	3.4	28.8
PtFe/G	17.5	1.4	18.9
PtCu/G	18.8	3.2	22

PEM fuel cell performance test results are given in Figure 2. Bimetallic catalysts showed different performance as being used either at anode or cathode electrodes. Interestingly, bimetallic catalysts used as anode electrode showed the best performance result.

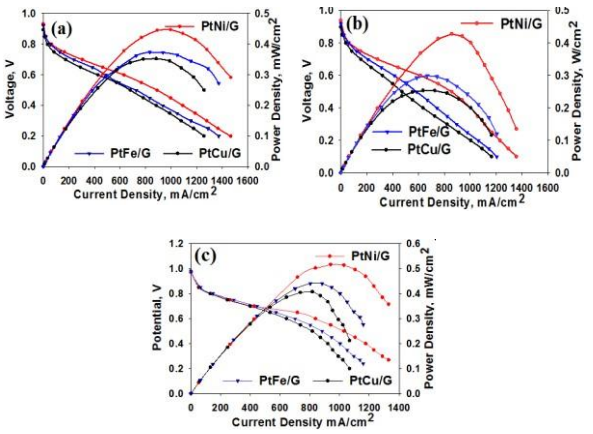


Figure 2. PEM fuel cell performance test results of catalysts (a)Cathode: Bimetallic, Anode: Tanaka 67% (b) Anode and cathode bimetallic (c) Cathode: Tanaka 67%, Anode: Bimetallic

Conclusions

Metal loadings in between 18.9-28.8% are obtained over the GNPs. TEM results showed the homogeneity of the metal nanoparticles. PEM fuel cell performance tests also demonstrate that PtNi/G catalysts have shown more catalytic activity than the other bimetallic catalysts.

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Durability Investigation of Graphene Supported Bimetallic Catalysts for PEM Fuel Cell Applications

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Recent literature studies have shown that graphene plays an important role to achieve high electrochemical performance and durability in difficult PEMFC operating conditions [1]. Alloying of Pt with a second metal is also one of the most common strategies for the improvement of catalyst stability and activity [2]. In particular, the Pt-transition metal alloys have attracted much interest due to their enhanced catalytic activities towards oxygen reduction reaction (ORR) in PEM fuel cells. In some reports carbon supported Pt alloys such as Pt/Fe, Pt/Co, Pt/Mn, Pt/Ti, Pt/Cr for PEM fuel cells showed enhancement of fuel cell performance [2].

In this study, to reduce cost and increase the durability of catalysts for PEM fuel cell applications, we use a commercial graphene nanoplatelets (GNPs) as the support material and four different metals as catalyst. The metals on GNPs were prepared by using supercritical carbon dioxide ($scCO_2$) deposition technique. Bimetallic catalysts were synthesized by using Ni, Fe and Cu metals nearby Pt. In order to simulate the harsh PEM fuel cell operating conditions, the durability of bimetallic catalysts were determined by using cyclic voltammetry (CV) technique via carbon corrosion and potential cycling tests. The CV results and ESA losses of catalysts can be seen at Figure 1 and Table 1. Number of electrons transferred before and after potential holding and cycling are give in Table 2.

Table 1. ESA Losses of catalysts

Catalyst	ESA Loss % (Carbon corrosion)	ESA Loss % (Potantial Cycling)
PtNi/G	6	5
PtFe/G	27	18
PtCu/G	52	49

Table 2. Number of electrons transferred per oxygen molecule for all catalysts

Catalyst	Carbon corrosion n		Potantial Cycling n	
	before	after	before	after
PtNi/G	3.4	3	3.4	3.2
PtFe/G	3	2.5	3	2.8
PtCu/G	2.5	2.1	2.5	2

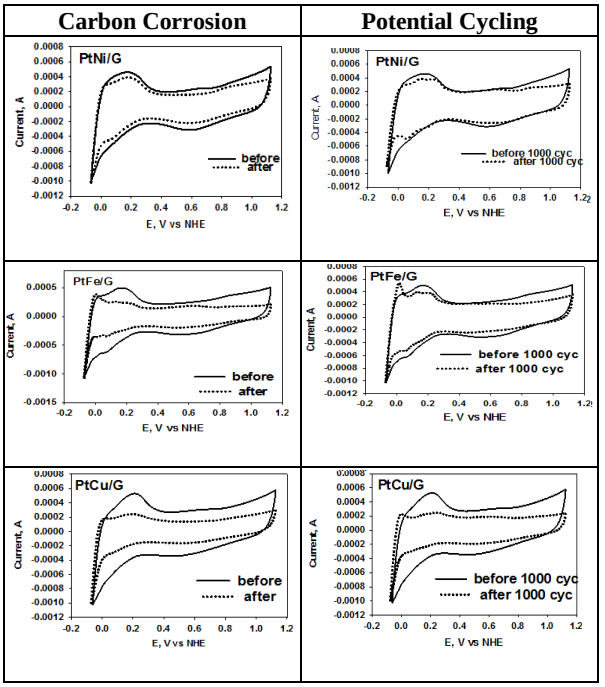


Figure 1. CV results of catalysts which are the record in 0.1 M $HClO_4$.

Conclusions

CV is used to get information on the reaction mechanisms, adsorption processes, kinetics of electron transfer reactions of the materials and quantitative determination of electroactive species adsorbed on the electrodes. PtNi/G catalyst showed highest catalytic activity among the other catalysts.

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Utilization of Different Surface Area Graphenes as Catalyst Support and PDMS Polymer as Catalyst Binder in PEM Fuel Cell

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Catalyst durability affects directly PEM fuel cell performance so catalyst dissolution and agglomeration are undesirable for reliable PEM fuel cell performance. Many investigations have been made to improve different catalyst supports in order to obtain more durable PEM fuel cell catalyst. Graphene is one of these materials and it has been widely studied in the scope of PEM fuel cell components because of its high surface area and mechanical properties. Beside of graphene, N-Doped materials were also commonly investigated in the last years. N-Doped materials both contribute catalytic activity and also provide larger surface area [1]. So, both of these issues still draw interests of researchers.

In this study, two commercial graphenes, Graphene-1 and Graphene-2 having 150 and 750 m^2/g surface area, respectively, were used as catalyst supports for PEM fuel cell. Bare graphenes and also their N-doped equivalents were used as support material. N-Doped graphenes were prepared by heat treatment under inert atmosphere. Melamine was used as nitrogen source and it was mixed with commercial graphenes and heated to 900 °C for 1 h under nitrogen atmosphere. Pt was reduced onto both bare graphenes and N-doped graphenes with a nominal loading of 20 wt. % by microwave irradiation technique. PDMS polymer was used as a binder in the catalyst ink instead of Nafion solution.

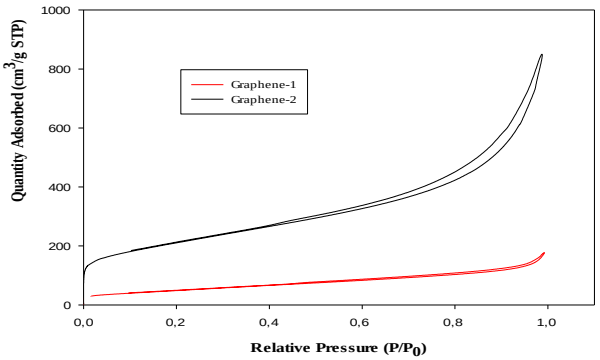


Figure 1. BET Isotherms of Graphene-1 and Graphene-2

Table.1 Structural Properties of Graphene-1 and Graphene-2

Sample	BET Surface Area (m^2/g)	BJH Total Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	BJH Pore Diameter (nm)
Graphene-1	181.1	0.266	0.060	4.46
Graphene-2	745.2	1.217	0.261	5.31

Isotherm profiles in Figure 1 fit Type-II Adsorption Isotherm. This case supports monolayer formation of graphene. Table 1 also shows the properties of two commercial graphenes. Figure 2 shows the PEM fuel cell performances of all catalysts. Graphene-2 provides the higher surface area for the distribution of catalyst particles thus the performances of cells improved with Graphene-2 when compared to the cells with Graphene-1. Both of N-Doped Graphenes fell behind of their bare cases.

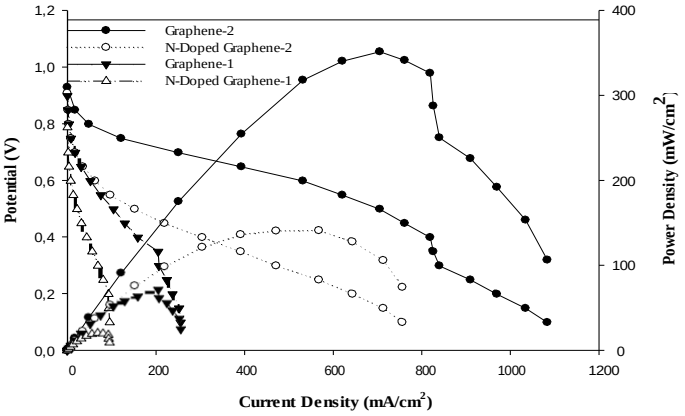


Figure 2. PEM fuel cell performances of the cells

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The effect of nitrogen doping amount on the activity of commercial electrocatalyst used in PEM fuel cells

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Polymer electrolyte membrane fuel cells (PEMFCs) have been studied because of being satisfactory power sources. A significant interest in the development of PEMFC technology is required highly active catalysts for the reduction of oxygen to water. The support materials is choosen significantly because of high specific surface area, which is necessary for improving the dispersion of catalytic metals and high conductivity.

Researchers have widely used several dopant to improve catalytic activity of electrocatalysts. For this aim, nitrogen, phosphorus, sulphur, boron etc. has been used [1]. Nitrogen (N)-doped support materials has been widely researched due to its high electrical conductivity, large specific surface area, and good chemical stability. The N-doped carbon materials which were used as support for electrocatalyst for improving the catalytic activity have been investigated [2]. N-doping of the catalyst resulted in increasing the catalyst performance compared to commercial Pt/C catalyst [3]. This study includes the synthesis of N-doped commercial catalyst and investigation of its fuel cell performance.

In order to prepare N-doped electrocatalysts, equal and quarter amounts of Melamine were mixed with a constant amount of commercial Tanaka catalyst (70% Pt/C) and mixture was then heated to 900 °C under inert atmosphere.

Figure 1 shows the FTIR results for plain and N-doped electrocatalyts. Similar trends were observed for all the electrocatalysts.

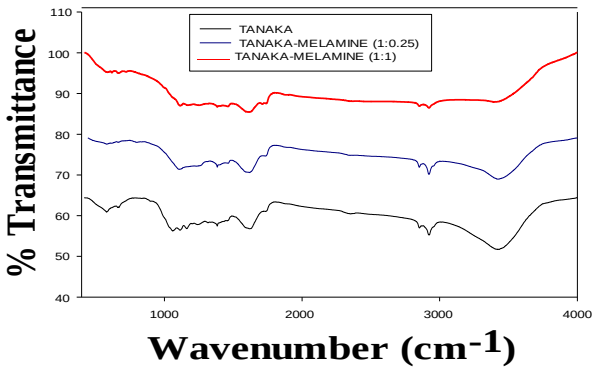


Figure 1. FTIR spectrum of the electrocatalysts

Figure 2 shows PEM fuel cell performances and it was observed that the best performance belongs to Tanaka-Melamine (1:0.25) at lower and medium current densities. The current densities were 343.31 mA/cm^2 for Tanaka-Melamine (1:1), 862.58 mA/cm^2 for Tanaka, 989.34 mA/cm^2 for Tanaka-Melamine (1:0.25) at 0.6 V. there was a significant difference in between the current densities of Tanaka and Tanaka-Melamine (1:0.25). This study showed how important the N doping amount on PEM fuel cell performance.

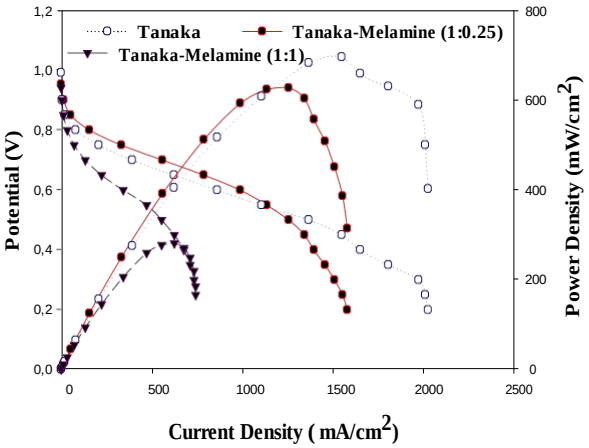


Figure 2. PEM Fuel Cell Performance of Electrocatalysts

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Rapid Microwave Assisted Synthesis of Efficient Hybrid Electrocatalysts for Proton Exchange Membrane Fuel Cell

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Among the other type of fuel cells, polymer electrolyte membrane fuel cell (PEMFC) is one of the most attractive renewable energy sources due to its pollution-free operation in transportation, high effiency, and compact structure [1]. Membrane electrode assembly (MEA), comprises of a proton exchange membrane, gas diffusion electrodes (GDE), is regarded as the heart of the PEM fuel cell. GDE consists of two sublayers: gas diffusion layer (GDL), and catalyst layer (CL). The most significant challenge of PEMFC development arises from the CL because of the complex and heterogeneous structure [2].

In CL, catalyts and catalyst support play essential role for to reduce the cost, improve the durability, and performance of the PEMFC. Platinum (Pt), and Pt containing alloys have been extensively used as catalyst. However, Pt is very expensive and performance of PEMFC strongly depends on its utilization. Moreover, carbon black (CB) has been commonly used catalyst support since it is inexpensive and readily available yet it has various drawbacks (not corrosion resistant, contains deep cracks and mesopores, etc.) cause to decline of activity and performance of the catalyst. Surface area, conductivity, and durability of catalyst support material are also very essential to improve both Pt utilization and PEMFC performance.

Recently, hybrid carbon structures widely have been investigated as alternative catalyst support materials. Two-dimensional (2D) graphene [3] and 1D nanostructures of carbon such as nanotubes (CNTs) and nanofibers (CNFs) [4] have been investigated as catalyst supports, due to their exciting properties such as anisotropy, good electronic conductivity, high surface area and chemical stability.

Here, we reported the development of catalysts for fuel cell reactions based on Pt nanoparticles supported on hybrid carbon support networks comprising highly conducting carbon nanofibers (GANFs), CB (Vulcan-XC-72) and graphene oxide (GO). By means of a rapid and efficient microwave assisted synthesis, Pt nanoparticles were impregnated on various hybrid carbon structures. Hybrid carbon supports provide not only the superior Pt utilization but also better GDE porosity, and conductivity.

Resultant catalysts were investigated by by X-ray Diffraction (XRD), X-Ray photoelectron spectroscopy (XPS) and Transmission Electron Microscopy (TEM) techniques for their structure and morphology The average diameter of the Pt nanoparticles was about 2-3 nm obtained from TEM micrographs (**Figure 1**). Electrocatalytic activity of prepared electrocatalysts towards fuel cell reactions (HOR and ORR) were investigated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The hybrid electrocatalyst was exhibited comparable HOR and ORR catalytic activities by enhanced utilization of Pt. Moreover, gas diffusion electrodes and membrane electrode assemblies are fabricated by using synthesized electrocatalysts and tested in the PEMFC.

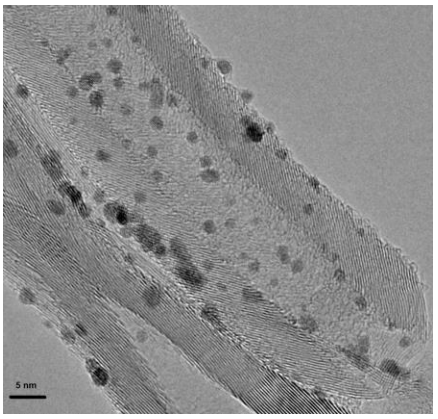


Figure 1. TEM micrograph of Pt/GANFs electrocatalyst.

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Supercritical carbon dioxide deposition as a promising catalyst preparation method for PEM fuel cell electrocatalysts

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PEM fuel cells have a great potential to be used especially in portable and mobile applications because of operating at low temperatures with high power densities. Mostly carbon supported electrocatalysts are used in PEM fuel cells. The structure of the support materials affects the catalyst properties such as the particle size, dispersion, metal–support interaction and the accessibility of the reactants to the active metal. There are several ways to synthesize supported nanoparticles, including impregnation, precipitation, sol-gel, microwave irradiation or microemulsion methods. It is essential to control particle size, distribution, and metal concentration in the composite.

A supercritical fluid (SCF) is a fluid that is heated and compressed above its critical temperature and pressure values (Figure 1). The thermophysical properties of a SCF are intermediate between those of a gas and a liquid and can be adjusted by slight changes in temperature and/or pressure. Among the supercritical fluids, supercritical carbon dioxide ($scCO_2$) (Tc= 31.1°C, Pc=71.8 bar) is particularly attractive for a wide range of applications because it is chemically inert, nontoxic, and environmentally acceptable and leaves no residue in the material. $ScCO_2$ deposition method includes the dissolution of a metallic precursor in $scCO_2$ phase and then 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.

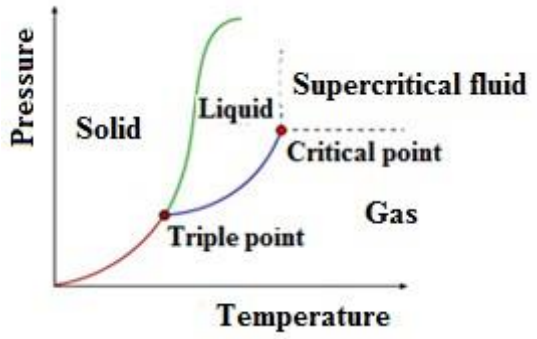


Figure 1. Phase diagram of pure substance

$ScCO_2$ deposition method was used to prepare highly dispersed and small sized either monometalic or bi-metalic nanoparticles over graphene nanoplatelets (GNPs). Figure 2 shows TEM images of supported nanoparticles obtained by using sCO_2 deposition. As can be seen from figure that homogeneous distribution of Pt nanoparticles over GNPs were provided and particle sizes as small as 1.5-2.0 nm were obtained.

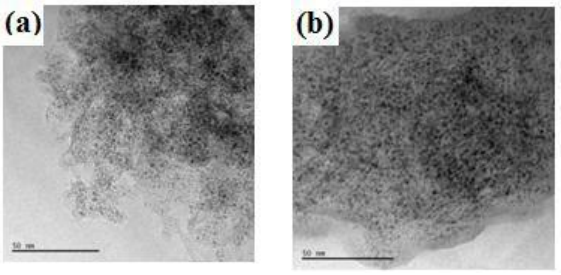


Figure 2. TEM images of (a)-(b) Pt/GNPs.

Supported nanoparticles are very important in chemical industries. In order to control the properties and also get the desired results with the nanoparticles over the support material not only the properties of the support material but also the nanoparticle preparation method play a crucial role.

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Development of Light Weight Stack for UAV Applications

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In this work, a light-weight tactical UAV (unmanned aerial vehicle) is developed by employing a PEM (Proton Exchange Membrane) fuel cell stack. In this context, one small prototype is developed and the performance results are reported. The main purpose is to provide an military advantage for the corresponding operations. If UAV flight time is increase, most military operations will be more successful.

A fuel cell is a device that converts chemical energy into electrical energy directly. PEM fuel cells utilize hydrogen gas (H_2) and oxygen gas (or air) as a fuel and oxidant, respectively. The products of the reaction in the cell are water, electricity, and heat. This is a big improvement over internal combustion engines, coal burning power plants, and nuclear power plants, all of which produce harmful by-products. In the past decades, the negative consequences of fossil fuel usage are exposed. There has been done much research and development lately on fuel cells as a clean energy generation source. Nowadays, some developed countries have been investigating PEM stacks for their UAV, because PEM can provide relatively long operational times with high efficiency compared to standard batteries. Mini unmanned aerial vehicles work with batteries and able to fly approximately for 1-3 hours. When a PEM fuel cell system is included, the flight time can be improved by a factor of 2. There can be found even 26 hours reported flight time achieved by Ion Tiger from Naval Research Laboratory [1]. PEM technology served as a part of NASA"s Project Gemini in the early days of the U.S. pilot space program. Batteries provided spacecraft power in earlier Project Mercury missions, but the lunar flights envisioned for Project Apollo required a longer duration power source. Germany, France and Japan also have started to use PEM systems in their UAVs. [2, 3]

A light weight PEM fuel cell stack (100g) was tested experimentally at different flow field designs, temperatures and relative humidities. The stack consists of 5 cells each having 20 cm^2 active area (Figure 1). The performance of the stack under ambient pressure and 50 °C is given in Figure 2. The stach has approximately 22 Watt power output under 2 – 2.5 volts.



Figure 1: Light weight PEM fuel cell Stack Design

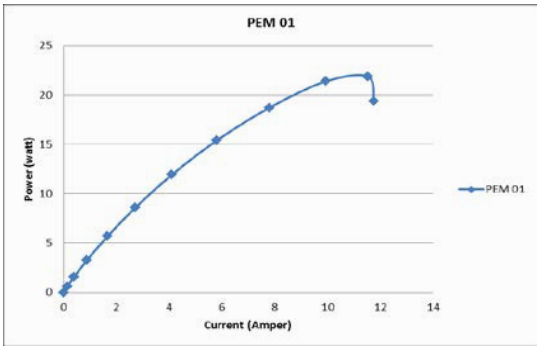


Figure 2: The performance curve of the stack

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Ab initio Electronic Structure Calculations of $LaBO_3$ (B= Cr, Mn and Fe) Perovskites

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Due to their high reaction energy barrier, oxygen reduction and evolution reactions are known to be the limiting reactions which limit the efficiency of metal-air batteries. As the cathode reaction of a metal-air battery is generally a catalytic electrochemical process, the electrocatalyst in the air electrode plays a vital role in determining the electrode performance. Perovskites of the type ABO_3 (A=La, B= transition metal, O=oxygen) are promising catalysts for the aqueous oxygen reduction reaction (ORR). Therefore, as catalyst materials with high electrocatalytic activity, $LaBO_3$ perovskites (B= Mn, Cr, Fe) were selected to gain detailed electronic information. The crucial role of electronic structure of these perovskites in determining the electrochemical reactivity has been well recognized in the field of catalysis. First-principles computational studies, in particular density functional theory (DFT) studies, have made important contributions to such efforts, identifying fundamental correlations between catalytic activity and electronic structure for different types of catalyst materials. Advances in computational catalysis have enabled us to screen different types of catalysts and to predict which catalysts will have more activity for ORR, which prediction helps save time and costs in developing proper catalysts.

In this study, we investigate the structural, electronic and magnetic properties of $LaBO_3$ (B=Cr, Fe, Mn) from first principles using different theoretical schemes including standard DFT and DFT plus Hubbard U (which is used to correct the self-interaction errors in the strongly correlated electronic systems). $LaBO_3$ perovskites are observed in the orthorhombic structure below 750K and above this temperature the structure becomes cubic 1010K. [1] Moreover, in the ground state, the d states of the transition metals of all three compounds $LaCrO_3$, $LaMnO_3$, and $LaFeO_3$ are partially filled and the alignment of the spins causes a finite magnetic moment proportional to the total spin of the electrons at each transition-metal site. For all three compounds, an antiferromagnetic (AFM) ordering of the spin-magnetic moments in the ground state has been reported [2]. Therefore, in order to obtain correct results for these type of perovskites, it is important to study the relative stability between the orthorhombic and cubic phases for different magnetic arrangements.

Figure 1 shows the calculated total denstiy of states (DOS) curve for cubic $LaCrO_3$ with ferromagnetic ordering at Ueff=0 eV (standard DFT), where the Fermi energy is aligned at zero.

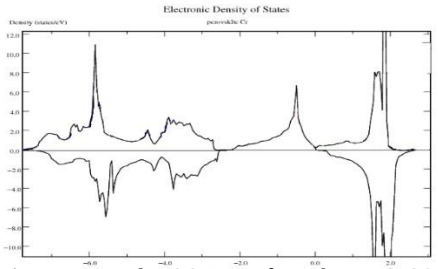


Figure 1. Total DOS curve for cubic LaCrO3 with ferromagnetic ordering at Ueff=0 eV (standard DFT).

According to DOS result, ferromagnetic cubic $LaCrO_3$ bulk structure shows metallic behavior. However, when compared with experimental studies, there was a discrepancy with this result. In addition, total DOS curves for cubic and orthorhombic $LaCrO_3$ with different magnetic ordering at Ueff=0 eV and at the optimal Ueff were calculated. We applied the optimized effective interaction parameter Ueff for the metal atoms in $LaBO_3$ (Ueff = 4, 4, and 3.5 eV for Mn, Fe, and Cr, respectively).[3] The results suggest that the opening of the band gaps in the $LaCrO_3$ calculations depends on the magnetic state, J-T distortion and the Ueff parameter. While no band gaps for the $LaCrO_3$ system is obtained in the pure GGA calculations (at Ueff=0 eV) for cubic FM structure, the J-T distortion can provide band gap opening. In addition, antiferromagnetic ordering can change the band structure and metallic character. To conclude, in order to get the correct experimental ground state for $LaBO_3$ perovskites, it is necessary to take Jahn-Teller distortion, electron-electron correlation and anti-ferromagnetic ordering simultaneously into consideration.

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One Pot Pechini Synthesis of $(La,Sr)CoO_3/(La,Sr)_2CoO_4$ for Cathodes of IT-SOFCs

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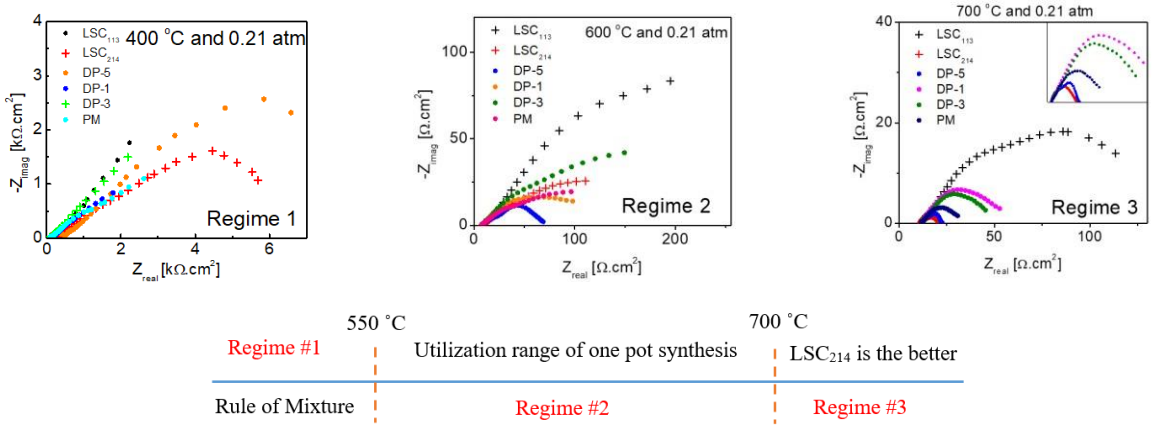
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$LSC_{113/214}$ hetero interface is known to accelerate oxygen reduction kinetics at 300-600 ˚C, which make it a suitable candidate for cathode materials of intermediate temperature (500-700 ˚C) solid oxide fuel cells (IT-SOFCs). In order for this hetero interface to reflect its beneficial effect to cathode operation, it must be the main rate limiting step within cathode processes, which necessitates dense thin film cathode architecture. Accordingly, focus in literature was mainly on variety of sophisticated thin film deposition methods as the way of constructing and finely maximizing hetero interfaces till now. However, thin film architecture suffers not only from thermomechanical incompatibility problem but also from high fabrication cost and difficulties.

On the other hand, as the alternative free from aforementioned problems, conventional porous thick cathodes which are generally fabricated by screen printing and/or tape casting routes are mostly limited by bulk ionic transport of oxygen rather than redox reaction. This situation excludes being limited by direct oxygen reduction reaction (ORR) at any boundary and/or any (hetero) interface and therefore also excludes beneficial effect of $LSC_{113/214}$ hetero interface in principle.

In this work, $LSC_{113/214}$ heterostructures were constructed via low temperature solution based method and making conventional thick porous cathodes limited by oxygen exchange at $LSC_{113/214}$ was targeted. One pot dual phase Pechini synthesis was carried out in pursuit of these. $LSC_{113/214}$ two phase structure thus was successfully synthesized from one single precursors solution without any undesired phase for the first time in literature. Whereas the scale at which phases were mixed was quite coarse in physical mixture of individually synthesized powders, one pot synthesis was found to be capable of yielding finely dispersion of constituent phases. In order to examine the effect of fine scale of structure to final cathode performance of powders, electrochemical impedance spectroscopy (EIS) analyses were carried out at 400-700 ˚C and on symmetric cells containing porous electrodes having thicknesses around 80 µm. Although dual phase synthesis was succeeded as well as fine dispersion of constituent phases, target of making thick cathode redox reaction limited was not achieved.

Recorded EIS responses were discussed as function of temperature and in terms of how consistent the current EIS response with the structural characteristics of cathode pertaining to it.




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GDC based substrates for combinatorial development of Cathode Materials in IT-SOFCs

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Cathode is the limiting material for IT-SOFC. So that, there is a need for the development of new cathode materials with improved performance at intermediate temperature. The combinatorial approach is particularly suitable for identification of suitable cathode materials. This involves a simultaneous deposition of thin film cathodes each with a different composition in a single experiment. These are then screened by a suitable method to determine their performance as cathode materials. Sarı et al. [1], using this approach investigated $(La,Sr)CoO_3$ - $(La,Sr)_2CoO_4$ dual phase system where the best composition was identified in terms of volume fraction of phases. Screening of thin film cathode library may be carried out in several ways. Torunoğlu et al. [2] used symmetrical cells to examine the impedance characteristics of a cell. However, complete cell is necessary to evaluate the electrochemical performance.



Fig. 1 Substrate disc 19 mm in diameter made up of Cu-GDC anode and GDC electrolyte

The aim of this study is to develop suitable materials to be used as substrate in combinatorial thin film deposition of cathodes. The support material should be suitable such as -when the cathode is deposited- to form a complete cell.

For substrate comprising both anode and electrolyte there are a number of alternatives such as; Ni, yttria stabilised zirconia (YSZ), Cu, gadolinium doped ceria (GDC). Ni had been used as an anode for several years. However, pure Ni has a considerable thermal expansion coefficient mismatch with electrolyte material, such as, YSZ, which leads to weakening of its interface with the electrolyte material. Additionally, YSZ reacts with LSC based cathode materials. To prevent reaction between YSZ and the cathode, ceria-based interlayers can be applied as interlayer. However, this increment in the electrolyte thickness reduces the electronic conductivity. While optimizing metal electrodes, cermets (i.e., ceramic–metallic composite e.g., Ni–YSZ) and metal oxides were introduced.

For this purpose, to keep the electrolyte thickness as thin as it can be, the chosen materials are Cu/GDC as anode and GDC as electrolyte. This choice was made because ceria based electrolytes are chosen to prevent undesirable cathode/electrolyte reactions. Also, gadolinium doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$), shows high ionic conductivity at low temperatures.

GDC will be prepared by the thermal plasma synthesis. The precursors will be prepared using a similar method proposed in (Chen and Hwang, 2008 [3]). Gadolinium (III) nitrate hexahydrate, cerium (III) nitrate hexahydrate will be dissolved in the solution of diethylene glycol mono-n-butyl ether and ethyl alcohol at a volume ratio 1:1.

The anode-electrolyte substrates will be fabricated using tape casting. The anode will be prepared from mixtures of CuO powder and GDC powder. Anode slurries will be fabricated from mixtures of Cu/GDC powder, binder, dispersant, and solvent. Hydroxyethyl cellulose, polyvinyl pyrollidon and texanol will be chosen as binder, dispersant and solvent, respectively. The electrolyte slurry will also be prepared with the same method.

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Electrochemical Performance of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ - $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ Composite SOFC Cathodes Fabricated by Electrocatalyst and Electrocatalyst-Ionic Conductor Infiltration

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Solid oxide fuel cells (SOFCs) are regarded as a promising, clean and sustainable energy conversion device. However, SOFCs suffer from high cost, which hinders the commercialization of these devices. [1] This problem can be resolved by enhancing the power density obtained from a single cell using the same materials. It has been reported that the performance of SOFC operating at low/intermediate temperatures is still limited by cathode [2].

Conventional SOFC cathodes are prepared by co-firing method, which, as a result of the high temperatures involved, causes triple phase boundaries (TPBs) to shorten. This leads to high polarization resistance and consequently, a low SOFC performance. As an alternative, infiltration has been proposed in the literature as an effective method to prepare composite cathodes. In general, a liquid solution, typically composed of metal nitrates dissolved in water, is introduced into a previously sintered, porous scaffold structure and the desired oxide phase is obtained by calcination. The main advantage of the infiltration method is that that it allows relatively low calcination temperatures (ca. 400 °C) and minimized reactions between the infiltrated and scaffold phases [3-4].

However, using aqueous nitrate solution for infiltration results in discrete particles, leading to poor current collection and hence, relatively high polarization resistance. To solve this, the use of polymeric precursors, which form interconnected films upon decomposition has been proposed [5]. In addition, it has recently been shown in SOFC anode applications that using the polymeric precursor solutions, nanocomposite thin films consisting of electrocatalyst and ionic conductor phases can be formed on flat substrates. The deposition of a mixture of polymeric precursors of the ionic conductor and the electrocatalyst phases, deposited onto a flat substrate yielded long triple phase boundaries (junctions where the electrocatalyst, ionic conductor and the gas phases (pore) meet and the electrochemical reactions take place) and thus low polarization resistance (6).

In the present work, we propose to infiltrate the polymeric precursor solutions of both the electrocatalyst and the ionic conductor into a porous GDC (Gd Doped Ceria) scaffold to obtain different types of composites with improved electrochemical peformance. The composite microstructure obtained by polymeric precursor infiltration is schematically depicted in Figure 1. Scanning electron microscopy (SEM) is used to investigate the cathode/electrolyte microstructure, while the phase identification was performed by X-ray diffraction (XRD). Electrochemical performance and long term stability of the symmetrical cells were investigated by impedance spectroscopy.

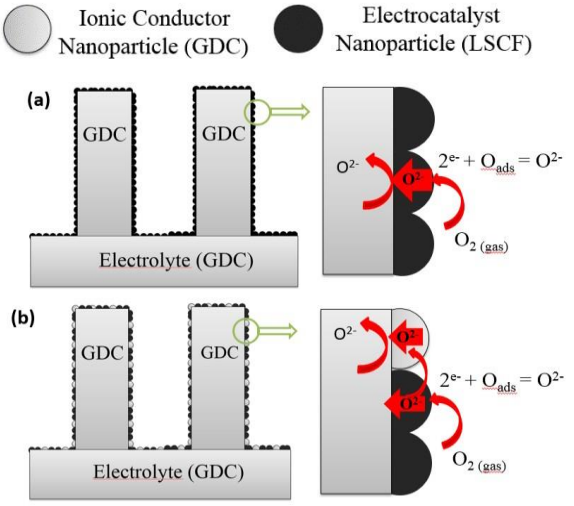


Figure 1. Schematic representation of the microstructure that is obtained as a result of polymeric a)LSCF and b)LSCF-GDC infiltration into porous GDC scaffolds

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Effect of crystal orientation on the aliovalent dopant segregation at the surface of $La_{0.6}Sr_{0.4}CoO_3$

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Perovskite-type oxides with mixed electronic and ionic conductivity (MIEC) have been studied extensively due to their wide range of applications in oxygen permeation membranes, solid oxide electrolysis cells (SOECs) and solid oxide fuel cells (SOFCs). The state-of-the-art cathodes, such as the La-based transition metal perovskites (La,Sr)CoO_3 (LSC), (La,Sr)FeO_3 (LSF), and (La,Sr)MnO_3 (LSM) are attractive due to their high oxygen reduction activity and high oxygen ionic conductivity. However, most MIEC materials belonging to the ABO_3 perovskite family exhibit surface cation segregation under operating conditions. This process can be driven by strain and the electrostatic attraction of aliovalent dopants by surface oxygen vacancies [1]. The dopant segregation towards the oxide surface often leads to the formation of insulating phases that block the electron transfer and oxygen exchange pathways on the cathode surface and thus it hinders the oxygen reduction reaction. This segregation behavior is expected to depend on the surface energy, affected by the atomic arrangements of the perovskite surface [2], and thus, the crystal orientation of the oxide surface might play a key role on the dopant segregation tendency.

The current study systematically investigates the crystal orientation effect on the dopant segregation behavior of LSC with complementary surface-sensitive analytical techniques. A polycrystalline LSC pellet was produced and then annealed at 800 °C in air for several hours (2h, 5h and 10h) to induce the surface cation segregation. The correlation between the crystal orientation and the segregation tendency was investigated via scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) techniques. In this respect, the formation of segregated particles on the grains were examined in terms of both the number of particles and the respective area coverage. In the analysis, 120x140 μm^2 surface area, having approximately 200 grains, was investigated grain by grain to examine the segregated particles on the surface and then the orientation of each grain was confirmed by EBSD.

The results show statistically that the orientations close to <001> are more prone to cation segregation than the orientations close to <101> and <111>. The distribution of the area coverage fraction of the three main crystallographic orientations is given Figure 1. This orientation dependency indicates that the exposed facet has a significant impact on the cation segregation. The LSC surfaces were also investigated with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) before and after annealing procedures to reveal the chemical state and the electrical structure of the segregated particles for each condition.

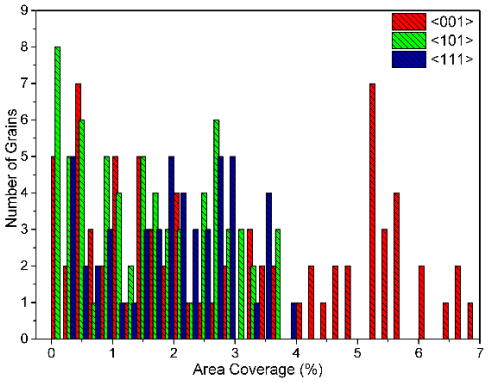


Figure 1. The histogram illastrating the number of grains exhibiting a certain area coverage of segregated particles for different crystallographic orientations.

The present study provides insights into the importance of the atomic arrangements on the surface stability and the cation segregation tendency of LSC cathode material.

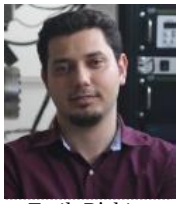
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Characterization of cation segregation in La 0.8Sr 0.2Co O 3-δ / (La 0.5Sr 0.5)2CoO4 heterostructure

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LSC based cathodes, especially composite structures are good candidates for IT-SOFC. The important problem associated with these cathodes is thermally activated degradation caused by Sr segregation as in either elemental or oxide form. At temperatures above 400ºC negatively charged Sr ions start to diffuse towards positively charged oxygen vacancies [1]. As a result, they block oxygen vacancies and reduces cathodic kinetics rapidly. The effect of Sr segregation is more pronounced at higher operating temperatures. Thus, electrochemical performance is distorted by up to two orders of magnitude loss in ORR kinetics [1]. Therefore, it is required to solve Sr segregation problem of LSC based cathodes, to take the advantage of their high electrochemical activity.

In this study, chemical and electrochemical stability of LSC-113/LSC-214 heterostructured cathode was investigated. Additionally, it was aimed to find suitable conditions where the effect of Sr segregation was minimized. Recently, it was shown that simultaneous deposition of LSC-113 and LSC-214 phases resulted in an additional order of magnitude enhancement in the electrochemical performance of the cathode system especially at temperatures around 600ºC [3]. For the observation and comparison of Sr segregation processes in separately and simultaneously deposited samples, specially designed bilayer and co-sputtered samples were produced with the help of magnetron sputtering technique, Fig. 1.

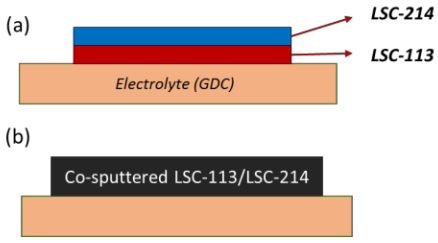


Figure 1. Schematic representation of bilayer and co-sputtered cathode films prepared to observe Sr segregation.

A comparative investigation carried out for Sr segregation in bilayer and co-sputtered composite structures with the help of transmission electron microscopy (TEM). In Fig. 2.(a) and (b), it is clearly shown that the strontium segregation is eliminated in co-sputtered LSC-113/LSC-214 when it is compared with the LSC-113/LSC-214 bilayer cathode after annealing 10 days at 700ºC.

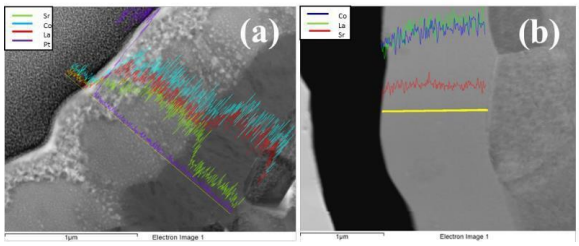


Figure 2. (a) STEM image of layered LSC 113/214 cathode after annealing 10 days at 700ºC, (b) STEM image of co-sputtered LSC 113/214 cathode after annealing 10 days at 700ºC.

The stability of enhanced electrochemical performance of simultaneously deposited composite cathodes were tested with the help sequential EIS analysis, Fig. 3.

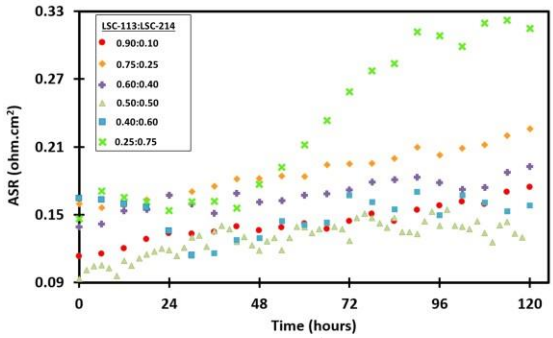


Figure 3. Sequential EIS responses of co-sputtered samples with different LSC-113/LSC-214 volume fractions.

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Preparation of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ / $(La_{0.5}Sr_{0.5})_2CoO_4$ Sputtering Targets Using Deformable Compaction Die

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For voluminous processing of ceramics, it is customary to carry out an extensive preliminary work to determine the fabrication parameters. Once these are determined, a die of suitable dimension is prepared and the powders are compacted and sintered under carefully controlled conditions. In the case of sputter targets, the use of hot-press greatly simplifies this process as it ensures controlled densification with proper dimensional control [1]. Where the hot-press is not available, it is necessary to revert to the conventional practice of compaction and sintering which require, as pointed above, a lengthy preliminary work. This is quite demanding especially for a low volume production.

Sputter targets, especially for research purposes, of necessity, is of low volume, but with stringent requirements. First, they should have high relative densities (better than 0.90) as otherwise there would be compositional deviations between the sputtered film and the target [2]. Also, they are expected to have a uniform distribution of grain size so as to suppress the nodule formation which could lead to problems in the deposited films [3].

The current work is a part of an effort to develop an efficient cathode material for solid oxide fuel cell via sputter deposition. In this study, in place of customary rigid die, we propose the use of a deformable die which greatly simplifies the fabrication procedure. The schematic drawing of the compaction procedures are given in Figure 1.

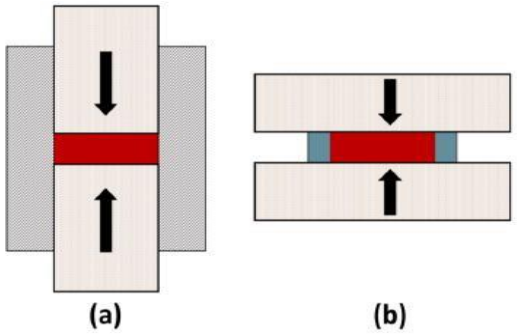


Figure 1. Schematic representation of compaction. a) Conventional approach. b) Compaction with a deformable die. Note that in (b) while powders are compacted, the die is deformed.

In this approach, polytetrafluoroethylene (PTFE) rings are used as compaction die filled with powders, tapped to uniform density. The die is then deformed between parallel platens whereby compacting the powders. The method relies on the fact that the pressing leads to almost no change in the internal diameter of the ring. This approach was illustrated with the fabrication of 2 inch La0.8Sr0.2CoO3-δ (LSC-113) target where the deformable die was dimensioned by preliminary experiments on PTFE rings of small diameter. Sputter targets of sintered density greater than 0.95 and dimensions within the tolerances of the sputter gun were successfully fabricated. It is proposed that the approach may also be applicable to flat products of irregular shape, as high friction in tapped particulate media makes the lateral flow difficult, confining the compaction mainly to axial direction.

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Combinatorial Development of Thin Film $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ / $(La_{0.5}Sr_{0.5})_2CoO_4$ Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells

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A concept of combined cooling, heating and power system requires SOFC/SOEC that succesfully operate at intermediate temperature (1). For IT-SOF/EC, new cathode materials are currently under development. These include perovskite based oxides that have mixed ionic and electronic conductivity; LSF, LSC, LSCF, BSCF. Of these, LSC has attracted considerable attention with its attractive low temperature performance [1]. It was shown recently that the kinetics of cathodic processes can be improved dramatically when LSC-113 is combined with R-P (LaxSr1-x)2CoO4 (LSC-214) cobaltites. This enhancement was attributed to the beneficial effect of hetero-interfaces in the composite cathode [2]. Thus, efforts have concentrated in maximizing the interfaces in LSC based composite cathodes [3].

In maximizing the interfacial regions, the volume fraction is an important parameter as well as the structural scale. Therefore, the current study was undertaken to investigate how the cathode performance is affected by phase fractions, while keeping the structure at nanoscale. For this purpose, we adopt a combinatorial approach based on sputter deposition where the volume fraction of LSC-214 varied from 10 vol % to 90 vol %, Fig. 1.

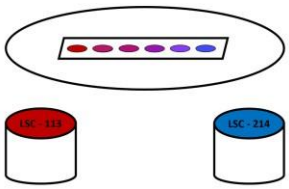


Figure 1. Schematic representation of combinatorial production of LSC-113 / LSC-214 composite cathodes.

Co-sputtered thin films had an extremely refined structure. TEM observations made on samples prepared by FIB showed nanocrystals with sizes that are in the order of 10 nm, Fig. 2.

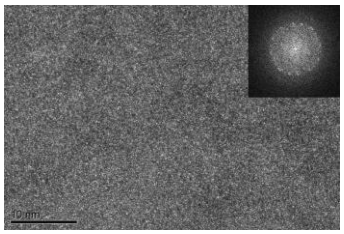


Figure 2. HRTEM image of co-sputtered cathode after annealing at 700ºC for 10 days.

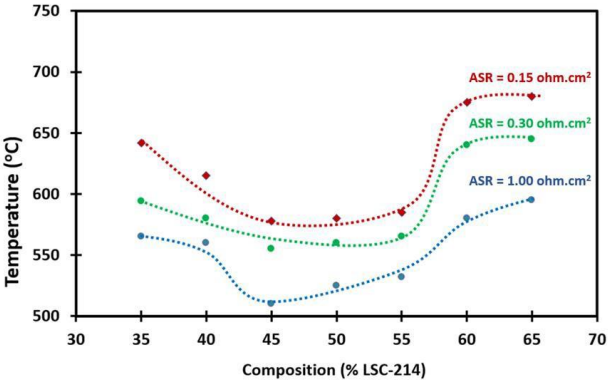


Figure 3. Area specific resistances of combinatorically produced LSC-113/LSC-214 composite cathodes as a function of temperature.

Combinatorically produced cathodes were characterized via electrochemical impedance spectroscopy and performance measurements. The area specific resistance (ASR) values obtained with different compositions are given in Fig. 3. The study shows that the best performance is obtained LSC113:LSC214=0.50:0.50.

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Systems and Applications

Advanced Hydrogen Energy Systems- HENERGY (EU ERAfrica program) – Harvesting energy at high temperatures

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The HENERGY project contributes to the thematic field "Renewable Energies" of the EU ERAfrica FP7 programme and aims to join the best efforts of the European and African scientific communities targeting development of the advanced hydrogen energy systems. The work is collaboration between the leading European and African research institutions: Institute for Energy Technology, Norway (IFE); Hydrogen Storage and Systems, Norway (HSS); Prototech AS, Norway (PRO); University of the Western Cape, South Africa (UWC), Middle East Technical University, Turkey (METU) and Cairo University, Egypt (CU).

The project focuses on the development of novel, integrated with renewable energy sources, high efficiency hydrogen energy systems.

Their advanced performance will be achieved by:

-high gravimetric and volumetric efficiency of the H storage systems;

-development of unitised reversible
Solid Oxide Fuel Cells (SOFC);

-thermal integration of hydrogen store and SOFC;

-modelling and optimisation of the system performance.

Hydrogen stores will accommodate nanocomposites of the hydrides having large reversible gravimetric volumetric H storage capacities of 4-7 wt. % H. Advanced performance of the H storage system was achieved by utilizing a hydrogenated composite material of Mg90Ti10 with 5 wt.% graphite additive as a reversible hydrogen storage material working at 350 °C. Using composite with nanocarbon additive prevented Mg from sintering, allowing long cycle life and providing H storage capacity of 5.6-5.8 wt.
% H. Application of nanocarbon additive also improved the thermal conductivity allowing high rates of hydrogen charge and discharge. Thermal integration between SOFC and composite TiH2/MgH2-based hydrogen storage system is achieved by fine tuning of the operating temperatures via selecting a ratio between MgH_2, TiH_2 and graphite.

SOFC development focuses on the development of robust electrodes and stack design, as well as thermal integration. Mixed oxides La_2O_3-SrO-Co_2O_3 (LSC-113 and LSC-214) are under development for that purpose and are utilised together with optimal engineering of thermal integration between the hydrogen store and fuel cell.

Modelling efforts are focused on the prediction of transient heat and mass transfer and on the dynamic response of the hydride bed. It is important in the design and optimization of the H storage and supply system, and in tailoring the optimum operation parameters of the prototype energy system.

The major focus is on integrating solar heating and electricity from solar energy to achieve harvesting of energy thus allowing efficient operation at high temperatures.



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Volodymyr Yartys is professor of materials science and hydrogen technologies at the Institute for Energy Technology and Norwegian University of Science and Technology, Norway. He received his PhD in inorganic chemistry from Lomonosov Moscow State University in 1980 and a Doctor of Sciences in inorganic chemistry from L'viv University in 1995. He then became a professor in inorganic chemistry in 1998. He is working in the fields of materials science of nanomaterials, hydrogen and energy storage with a focus on: (a) Rechargeable Batteries; (b) Hydrogen as an Energy Carrier; (c) Novel Materials for Hydrogen Storage and Battery Applications; (d) Hydrogen storage systems; (e) Use of metal hydrides in energy management. Professor Yartys is the author of 429 publications (210 papers in peer refereed academic journals, 6 patents and three books), and has acted as a project leader in research projects funded by the EU, Norwegian Research Council, Nordic Energy Research, and industry.

A concept of combined cooling, heating and power system utilising solar power and based on regenerative solid oxide fuel cell and metal hydrides

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Regenerative solid oxide fuel cells (R-SOFC) are able to generate hydrogen through water electrolysis in the electrolyser mode (SOEC) and, conversely, to convert hydrogen fuel to electricity in the fuel cell mode (SOFC). Apart from higher electric efficiency in the fuel cell mode (≥0.65) as compared to other conventional types of fuel cells (~0.5 for alkaline / AFC and Proton Exchange Membrane / PEMFC), SOFC are also characterised by much higher temperature potential of the dissipated heat, exceeding 600 ^{o}C. This makes them promising for various energy systems applications which include heat management, particularly, combined heat and power (CHP) systems.

Metal hydrides (MH) are very suatable for various fuel cell power systems applications. Thermal integration of "low temperature" MH based on AB_5- and AB_2-type intermetallics allows utilisation of up to 40–45% of the heat produced during operation of the AFC or PEMFC, thus improving the overall system efficiency. Other applications also include SOFC, utilising "high-temperature" MH where up to 90% of the released heat is used, thus allowing an efficient control over the temperature and heat flow [1]. "Low temperature" MH when used in addition to that in the SOFC based energy systems can further improve their efficiency and functionality.

In this work, we present a concept of combined cooling, heating and power (CCHP) generation system which uses solar power as a primary energy source and utilises R-SOFC producing hydrogen and generating electricity in the SOEC and SOFC modes, respectively. The system uses "high temperature" MH for the storage of hydrogen and heat, as well as "low temperature" MH for the additional heat management, including hot water supply, residential heating in winter, or cooling / air conditioning during summer.

The system concept is schematically described in Figure 1. Its main components include photovoltaic array (PV), power conditioning system (PCS), R-SOFC, metal hydride hydrogen / heat storage (MHHS), metal hydride hydrogen compressor (MHHC), metal hydride heat pump (MHHP), and heat exchanger / steam generator (HE/SG).

During the day time, PCS distributes electricity generated by PV between the consumer and R-SOFC which operates in the SOEC mode and generates hydrogen at a pressure about 1 bar. During the night time, R-SOFC operates in the SOFC mode and consumes H_2 at P~1 bar generating electricity and

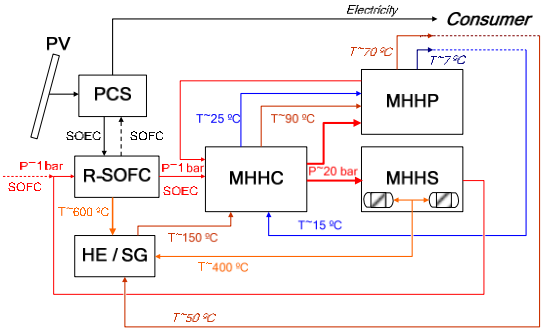


Figure 1. General layout of the CCHP.

heat at T~600 ^{o}C for the customer.

MHHS stores hydrogen and medium-grade (T~400 ^{o}C) heat and includes MH beds based on MgH_2 or Mg_2FeH_6.

MHHC compresses hydrogen from ~1 to ~20 bar. The compression is driven by periodic heating (T~150 ^{o}C) and cooling (T~15 ^{o}C) of MH beds on the basis of AB_5-type intermetallic alloys. MHHC provides supply of higher pressure H_2 to MHHS, as well as operation of compressor-driven MHHP which comprises of MH beds on the basis of AB_2-type intermetallic alloys and provides supply of hot water (T~70 ^{o}C) and coolant (T~7 ^{o}C) to the consumer.

The heat released during operation of SOFC (T~600 ^{o}C) and absorption of the higher-pressure H_2 in MHHS (T~400 ^{o}C) is directed to the HE / SG providing steam (T~150 ^{o}C) for the operation of MHHC. The heat released in the MHHS also assists to the desorption of low-pressure H_2 from the opposite MH bed.

The work presents estimation of energy balances of the system components, as well as heat-and-mass transfer modelling of MH beds in MHHS (MgH_2 and Mg_2FeH_6), MHHC ($LaNi_{5-x}M_x$; M=Sn,Mn,Al) and MHHP (AB_2; A=Ti, Zr; B=Cr,Mn,Ni,V,Fe).

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Trends and Bottlenecks of SOFC Systems

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The Solid Oxide Fuel Cell (SOFC) sytems are regarded as an most efficient systems getting the most out of the fuel used. The technology of SOFC currently accepted as “immature” in approaching the theoretical efficieny figures. In the recent decade noticable progress have been made, but these were not sufficient to make SOFC avaliable at commercial scale.

The small SOFCs are generally designed to be utilized as Combined Heat and Power (CHP) device in the range 1-3 kW. Such a system then will be the essential unit for power and and hot water for domestic usage. Even cooling solutions are planned for domestic purposes. The expected result is the cost savings for home users for electricity and heating. The concequences are less carbon print and decenteralized power generation.

The design of SOFC is such that they will work continuously. So that if surplus of power exists, it is expected to be delivered to the grid. Reverse is also true in that if more power is needed than generated, it will be drawn from the grid. For such an action, code of practice currently applicable in the gird needs to be changed. Actually recent solar cell applications have helped these steps to be taken.

The SOFC composed of stack, reformer, sulphur removal unit and Balance of Plant (BOP) units Figure 1. The research and development are perfomed on the first three units, the majority actually on the first two.

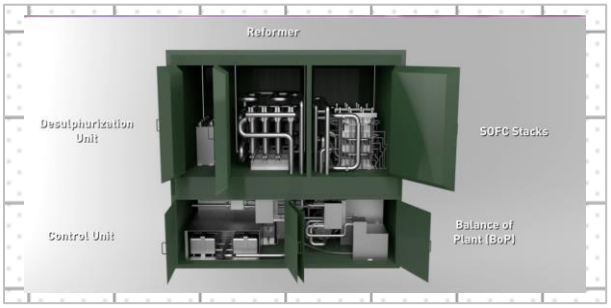


Figure 1. Vestel 5 kW SOFC Prototype.

The stack composed of cells which are regarded as Membrane Electrode Assembly (MEA). The membrane is actually determines the working temperature of SOFC. Anode supported membranes are generaly utilized for SOFC having working temperture of 780-830 ˚C. MEA sealant is generally glass-ceramic especially developed for the operating temperature in question. Nikel Oxide based anode and Lanthanum Strontium Manganite (LSM) or Lanthanum Strontium Cobalt Ferrite (LSCF) based cathode are used. Also various pastes, Nickel and Crofer® based mesh and porous structures are used to collect the current. MEA metallic construction is generally Crofer® although some different options are also avaliable. Steam reforming is the essential reaction that occurs on Nickel based catalyst. Zinc oxide based sulfur removal is generally preferred.

Awareness of SOFC is not at the level it is expected to be. Actually there are very few commercially avaliable systems at the market, though nearly ten claim to be at the market for quite sometime. Current commercial price of such a system (1½ kW) is around €25,000,i.e. ~$16,000/kW. Further €600 is needed for yearly maintanence and a typical contact duration is around 10 years. Now the importance of the awareness is self–evident. Total Cost of Ownership (TOC) is a fact that depends on the number of units manufactured. The cost of a SOFC system will have more acceptable cost tag when some tens of thousands units are manufactured [1]. The expected figure is just below $2000/kW which is nearly 15 times less. When cost analysis done, BOP components take up an important share. Less cost is expected when more units are manifactured. Also new material development can lead the cost reduction. A major cost factor is the high working temperature (~800 ˚C). Lowering this to around 600 ˚C will have enourmous cost benefits.

Expected life time of SOFC unit is at least 15,000 hours. This is also a must and the components have difficulties in fulfilling this requirement. Redox problems on anode, degradation and poisoning of cathode, carbon deposition on catalyst, high water vapor content in the fuel causing membrane microcracks, sealant poisoning from Crofer®, sulfur poisining of MEA are some of the problems in SOFC components that require further research and development. The R&D on these should take into account the scalability in that the laboratory scale results are often not the same when implimented at commercial scale.

[1] R. Scataglini, A. Mayyas, A Total Cost of Ownership Model for Solid Oxide Fuel Cells in Combined Heat and Power and Power-Only Applications, https://energy.gov/, 12 (2015)



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Design and Development of High Temperature PEM Fuel Cell for Airport Ground Handling Operations

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The Eurostars partnership has been established to develop and manufacture a commercial hybrid power system that runs in service vehicles to reduce gas and particulate emissions caused by diesel engines. Hybrid Power System consisting of 5 kW High Temperature PEM Fuel Cell (HT-PEMFC) and battery systems is high technological system that designed to compete with classical systems in terms of cost. TEKSIS has been developing a HT-PEMFC by using MEAs produced by DPS, which will be used in the Hybrid Power System. For this aim, the design of the fuel cell and its components, sealing and cooling systems have been carried out and depending on the design results, the Single and Short Stack were manufactured and tested sequentially.

In this study, the test result of short stack has been evaluated and explained how the results will affect the iterations on designing of complete system. One of the most common problems in HT-PEMFC systems is to be able to produce a system that has the gas and cooling liquid leak-tightness. Special cooling system designs are needed for particular cooling liquids suitable for high temperatures and to safely circulate this liquid in the system without any leakage.

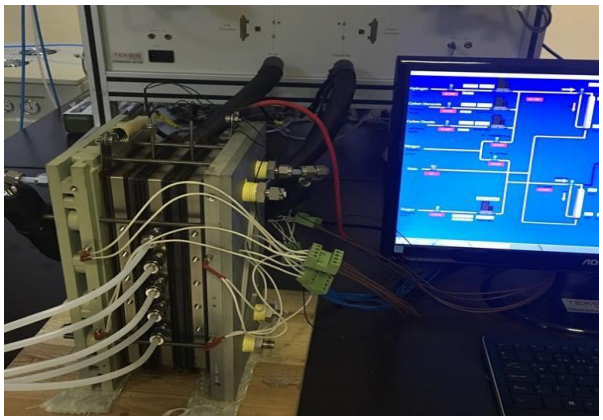


Figure 1. HT-PEMFC stack

Concerning this need and the result of short stack, the first design with the internal cooling manifold system was replaced by cooling capsules in the stack. The cell of short stack was designed and manufactured as similar as the cell of stack in terms of using MEAs with 163.5 cm^2 active area, compression plates, current collectors, gaskets and PBI membranes. Heat transfer oil were recycled through the cooling capsules for heating and cooling during tests. As a result of the tests, maximum power of 500 W was obtained from the stack.

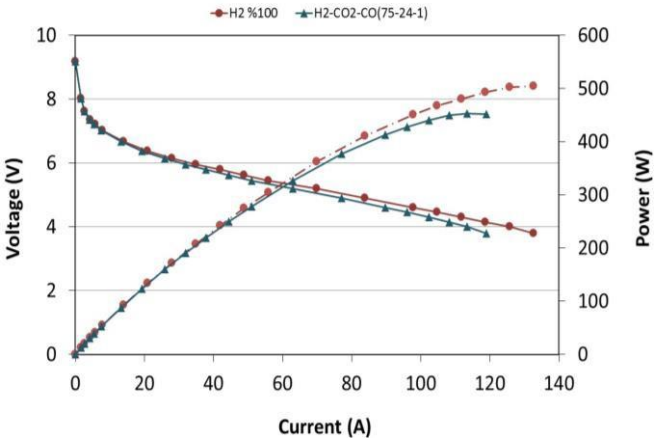


Figure 2. Performance curves of HT-PEMFC stack

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[1] E. Mancusi, et al., Numerical study of two-phase flow patterns in the gas channel of PEM fuel cells with tapered flow field design. Int J Hydrogen Energy, 39, 2261–2273 (2014).

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Clean Highly Efficient Offshore Power with CO_2 Capture (CHEOP-CC)

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Solid Oxide Fuel Cells (SOFC) are the most efficient devices for conversion of chemical energy of hydrocarbon fuels to electricity. A SOFC system has a longer lifetime and provides power at high efficiency, high power density, very low noise and zero emissions.

The Norwegian offshore industry has a world leading environmental standard with efficient resource exploitation and utilisation of best available technology. Still the Norwegian oil and gas activities are responsible for 31% of Norway's total CO_2 emissions, more than any other sector. The majority of electric power is supplied from gas turbines with electric efficiency of 33% with an additional 7% utilised as heat. The leading oil companies have adopted a strong policy to reduce the carbon footprint. Thus, there is a strong need of technology for cost efficient separation of CO_2 to provide zero emission offshore power when connection to shore infrastructure is infeasible.

The underlying idea for the present research project is to realize feasible technology for offshore electric power production from natural gas with carbon capture at high efficiency (60%) and moderate costs. The project will enable replacement of offshore gas turbines with fuel cell based power generation systems with similar footprint and mass as the turbines, but with nearly twice the electrical efficiency and integrated CO_2 capture. The technology will be a game changer for electric power production in general, and for offshore power in particular. Thus, Prototech AS proposed the CHEOP-CC concept, shown in Figure 1, based on different fuel cell technologies namely SOFC and Proton Exchange Membrane Fuel Cells (PEMFC) but also integrating palladium membranes used for hydrogen separation.

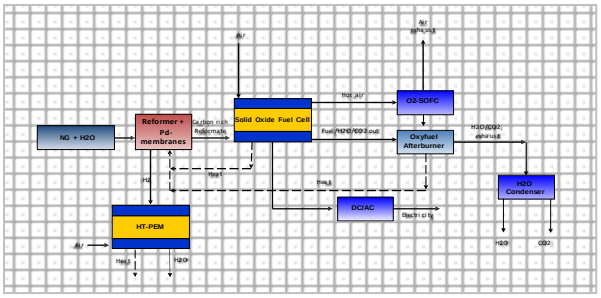


Figure 1. Proposed CHEOP-CC concept

The main objective of the CHEOP-CC concept is to develop a first-of-a-kind demonstrator of a 3.2 MW module which will form the basis for offshore full scale installations, e.g. 8 modules for a 25 MW system. The activity up to demonstration of the 3.2 MW module is planned in three phases, the present project is part of Phase 1.

For all offshore technology the installation is critical for the total cost. The major cost drivers are mass, volume and distance from shore. It is expected that the modularity of the fuel cell systems will simplify the installation and maintenance and the need of additional back-up power which can compensate for the higher basic cost of the new technology. Finally, lower fuel cost and CO_2 tax will strongly reduce the operational cost of the energy supply system.

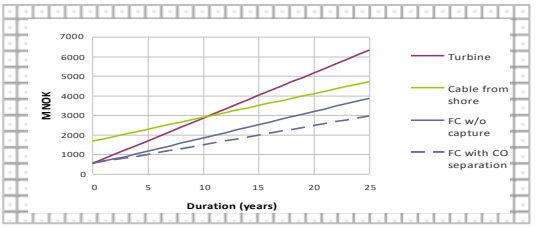


Figure 2. CAPEX and OPEX calculation for power systems to Utsirahøgden outside Norway.

The calculations showed that total manufacture and installation costs of fuel cells compared to turbines are almost identical, but with large saving in fuel cost and CO_2 tax due to the higher efficiency. If the CO_2 can be stored or reused for EOR, even better cost figures can be achieved by including CO_2 separation.

A modular 10kW SOFC stack box was designed, modelled, build and ready for testing at Prototech, see Figure 3. The 10kW box integrates commercial SOFC modules and will demonstrate different key components of the concept optimized for offshore power.

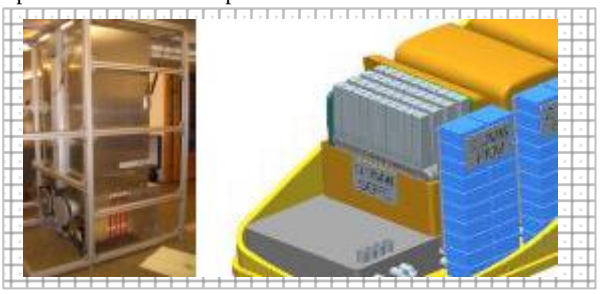


Figure 3. 10kW SOFC stack box

Phase 1 project is funded by Norwegian Research Council and Gassnova, supported by Statoil Petroleum AS, Norske Shell AS, University of Bergen, and has Hydrogen Mem-Tech AS as collaborator.



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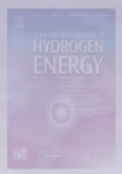
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