mESC-IS2022

6th International Symposium on Materials for Energy Storage and Conversion

5. - 8. 7.2022. Bol, island of Brač, Croatia

BOOK OF ABSTRACTS

Book of Abstracts

WELCOME NOTE

The 6th International Symposium on Materials for Energy Storage and Conversion
(mESC-IS 2022)

The committee would like to welcome you to the 6th International Symposium on Materials for Energy Storage and Conversion (mESC-IS 2022). This event is hosted by Faculty of electrical engineering, mechanical engineering and naval architecture, University of Split, Croatia.
mESC-IS 2022 is held in Bol, island of Brač, Croatia on July 5th to July 8th, 2022, in a hybrid mode.

The 6th International Symposium on Materials for Energy Storage and Conversion (mESC-IS 2022) is a multi-disciplinary international conference aiming to provide a long-term sharing of knowledge and discussions of highly actual issues in the field. The purpose is to bring together people from academic, industry and government organizations to exchange ideas and strengthen cooperation. The symposium will provide a forum for discussion in recent progress made in three major activity areas, namely batteries, solid state hydrogen storage and fuel cells. The symposium will have a fair balance of plenary sessions covering cross-cutting issues and the state-of-the-art reviews and parallel sessions with contributed papers and poster presentation.

On behalf of the committee, we would like to thank the members of the organizational and scientific committees, the reviewers, the session chairs, the authors, and all of you who attend the conference. We wish you four days of interesting and fruitful discussions.

Sincerely Yours,

mESC-IS 2022 Committee

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Increasing the catalytic efficiency of rhodium(0) nanoparticles in hydrolytic dehydrogenation of ammonia borane

Saim Özkar[1]
[1] Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey

Ammonia borane appears to be highly promising solid state hydrogen storage materials. Hydrolysis is the best way of releasing H_2 from ammonia borane in the presence of catalysts (Equation 1).[1]

$$H_3NBH_3(aq) + 2H_2O(l) \rightarrow NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \qquad (1)$$

Transition metal nanoparticles have been tested as catalysts for this hydrolytic dehydrogenation of ammonia borane.[2] Rhodium is one of the most active transition metals providing high activity for hydrogen generation from the hydrolysis of ammonia borane.[3] However, the high price of rhodium and the scarcity of its abundance in the Earth crust hamper its large-scale applications in catalysis. Achieving high catalytic performance with the smallest amount of metal is critical for any catalytic applications of noble metals. While continuous efforts have been devoted to improve the catalytic activity of non-noble metals, an immense challenge is the enhancement of utilization efficiency and catalytic performance, and thus ultimately lowering the cost of precious noble metal catalysts. For example, reducing the particle size of noble metal catalysts from the microregime to nanoregime increases their surface area and thus, the number of active sites.[4] Thus, the use of colloidal rhodium(0) nanoparticles can provide high catalytic activity. However, colloidal nanoparticles are unstable and tend to aggregate to larger particles, which greatly impedes their recyclability and catalytic performance. A proper way of overcoming this instability problem is the immobilization of transition metal nanoparticles on materials with large surface area. The catalytic activity and stability of supported metal nanoparticles depend on the particle size and size distribution, surface area of support, and strength of metal-support interaction. Selecting suitable supports is of paramount importance in obtaining nanoparticles which are stable and still catalytically active.[5] The strength of metal-support interaction turns to be crucial for catalytic activity and stability of nanoparticles on the support surface. Although no mathematical correlation between the catalytic activity and strength of metal-support interaction could be obtained yet, almost all the highly active metal(0) nanocatalysts have high binding energy as determined by XPS analysis. Increasing the lifetime and reusability of nanocatalysts can certainly help to improve the atom efficiency of transition metal nanocatalysts. Lifetime is used as a measure of stability which correlates well to the strength of metal-support interaction relative to metal-metal bond while reusability is mainly determined by the isolability of nanocatalysts for subsequent runs and measures the stability of catalysts. Low reusability is largely caused by material loss during the isolation of catalyst from solution and re-dispersing in a new reaction solution for the succeeding run of catalytic reaction. A recyclability test, which is performed by adding a new batch of ammonia borane to the reactor when the hydrolysis is complete for the subsequent cycle of hydrolysis without isolating the catalyst or removing the reaction solution from the reactor, measures the durability of catalysts. A prolonged recyclability test may also deliver the lifetime of nanocatalysts. A short prelude on the mechanism of catalytic hydrolysis of ammonia borane will give insight to understand and appreciate the reported achievements in enhancing the catalytic performance of rhodium-based catalysts in the hydrolysis of ammonia borane. The progresses in developing highly efficient rhodium(0) nanocatalysts which have been reported to be active catalysts in H_2 generation from the hydrolysis of ammonia borane will be discussed along with the available parameters including temperature, particle size, surface area, the catalyst to substrate ratio, turnover frequency, and the XPS determined binding energy.

It will be shown that the catalytic activity of rhodium-based catalysts can be increased by (i) using the colloidal rhodium(0) nanoparticles, (ii) downsizing the nanoparticles, (iii) supporting the nanoparticles on materials with large surface area, (iv) selecting suitable support which provides favorable metal-support interaction resulting in high stability and long lifetime of rhodium(0) nanocatalysts, (v) making the nanoparticles magnetically separable which enables the recovery of nanocatalysts from the reaction solution. The latter method can facilitate the isolation of nanoparticles from the reaction solution using an exterior magnet and redispersing them in new batch of ammonia borane solution for the successive runs of reusability test. It is noteworthy that the catalytic efficiency of rhodium-based nanocatalysts can be increased by a suitable combination of all these available methods.

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Dr. Özkar graduated from Technical University of Istanbul in 1972, received Ph.D. in inorganic chemistry at Technical University of Munich in 1976 and joined Middle East Technical University in 1979. He spent one year at Max Planck Institute in Mülheim a.d. Ruhr, Germany in 1986, 2 years at University of Toronto in 1988-1990, and now 5 total years at Colorado State University since 2000 starting. He was awarded Science Prize the Scientific and Technological Research Council of Turkey in 1996 and has been member of Turkish Academy of Sciences since 1996. His research interests: metal nanoparticles, catalysis, kinetics, synthesis.
Saim Özkar, e-mail: sozkar@metu.edu.tr tel: +90 538 826 8560

Solving Challenges for Clean Energy Adoption – From a Nano-scale World to Macro-scale Applications

Jasna Jankovic[1]
[1]Materials Science and Engineering Department, Institute for Materials Science and Center for Clean Energy Engineering, University of Connecticut, Storrs, CT, 06269, USA

Governments around the world are showing a renewed, unprecedented interest in clean, renewable energy systems, such as fuel cells, electrolyzers, batteries, wind and solar. International Energy Agency is projecting that renewables will have close to a 30% contribution to electricity generation in 2021. Wind and solar power generation has increased by 17% and 18% respectively from 2020 [1], while the global battery market value of 108.4 billion USD in 2019 is expected to grow at a compound annual growth rate (CAGR) of 14.1% from 2020 to 2027 [2]. An especially increased focus is on hydrogen, a zero-carbon and renewable fuel, accelerating the transition to a global hydrogen economy. World-wide, governments, companies and other organizations are announcing new developments, consortia, infrastructure programs, and financial commitments to propel renewable hydrogen production and use [3-5]. The global hydrogen market value is expected to increase from 130 billion USD in 2020 to 201 billion USD by 2025, at a CAGR of 9.2% [6]. Hydrogen offers a unique chance to decarbonize transportation, power generation, and manufacturing sectors and, thereby, address pollution and climate change challenges.

With these trends in mind, it is a great time to be a researcher in the clean energy sector. Even though these systems are advancing and their applications are expanding, each technology has challenges hindering their widespread adoption. Whether these challenges are related to the efficiency, cost, durability, or public acceptance, they need to be addressed. Starting from the very fundamentals of the materials structure and composition, through advancements in design and fabrication, all the way to the public acceptance and education, this talk will offer an overview of the materials characterization techniques on multiple scales. In particular, the nano-world of fuel cell and battery catalyst materials will be presented, reviewing novel 2D and 3D characterization approaches, understanding of degradation mechanisms, and atomically controlled corrosion protection. The talk will then cover novel fuel cell designs and fabrication methodologies. Finally, an interesting project, focused on development and demonstration of a solar tree to attract interest in Science, Technology, Engineering, Arts and Mathematics (STEAM) and clean energy – the UConn STEAM Tree – will be presented.

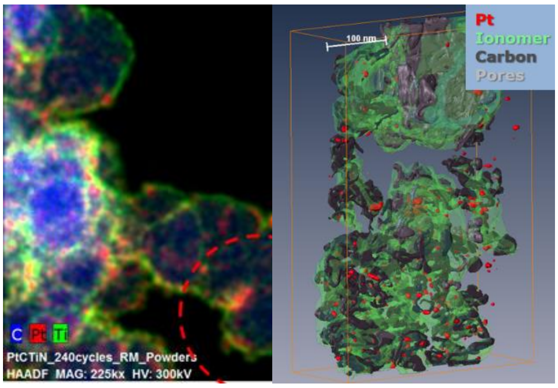

Figure 1. 2D Transmission Electron Microscopy with Energy Dispersive Spectroscopy elemental map and 3D Electron Tomography data set depicting fuel cell nano-world.

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Dr. Jasna Jankovic

Dr. Jasna Jankovic is an Assistant Professor in the Materials Science and Engineering Department at the University of Connecticut (UConn) since 2018. Prior to joining UConn, she worked for 7 years as a Senior Research Scientist at the Automotive Fuel Cell Cooperation in Burnaby, Canada, a joint venture between Ford Motor Company and Daimler. Dr. Jankovic's research focus is in advanced characterization of fuel cells, electrolyzers and batteries using microscopy and spectroscopy techniques, fabrication of novel electrodes for electrochemical devices, as well as Science, Technology, Engineering and Mathematics (STEM) and clean energy education.

Corresponding author: Jasna Jankovic; e-mail: jasna.jankovic@uconn.edu; tel: +1 860 617 8798

Fundamental Aspects of Air Cathode Design for Lithium-air Battery

Yun Wang
Renewable Energy Resources Laboratory, Mechanical and Aerospace Engineering, UC Irvine, CA, 92697-3975, USA

Lithium (Li)-air batteries hold a great promise for high specific energy storage. It has been reported a theoretical value of 3,505 Wh kg^{-1} using non-aqueous electrolytes, which is much closer to those of direct methanol fuel cells (DMFC) (5,524 Wh kg^{-1}) and gasoline engine (11,860 Wh kg^{-1}) than conventional Li-ion batteries [1-8]. Air cathodes, where oxygen reacts with Li ions and electrons with discharge oxide stored in their pore structure, are often considered as the most challenging component in Li-air batteries [3,6]. In non-aqueous electrolytes, typical discharge oxides are insoluble and hence precipitate at local reaction site, raising the oxygen transport resistance in the pore network. Due to their low electric conductivity, their presence causes electrode passivation, as shown in Figure 1.

In this talk, I will describe the fundamental knowledge and analytical equations that were recently developed at the UC Irvine regarding electrode passivation, the spatial variations of key parameters, oxygen profiles, the transport polarization raised by discharge oxide precipitate, and approximate solutions for insoluble Li oxides storage capacity and energy and charge capacities. The variations of cathode quantities, including oxygen content and temperature, are evaluated and related to a single dimensionless parameter — the Damköhler Number (Da). An approximate model is developed to predict discharge voltage loss and oxygen profiles [7], along with validation against experimental data [5]. Air cathode properties, including tortuosity, surface coverage factor [4] and the Da number, and their effects on the cathode's capacity of storing Li oxides are formulated and discussed.

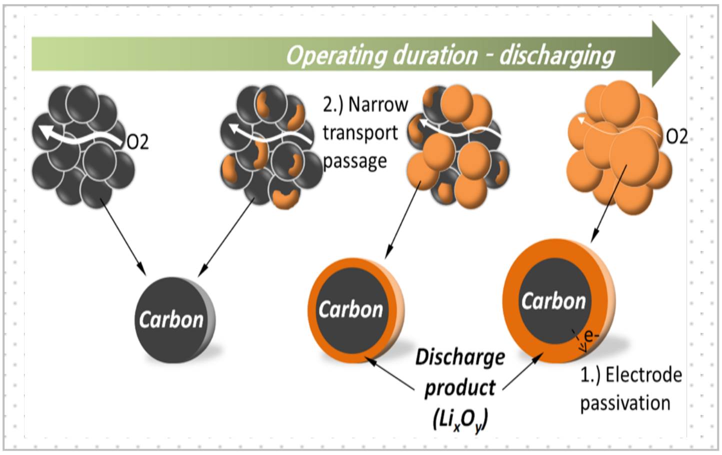

Figure 1. Schematic of the effects of insoluble discharge products on battery performance: 1.) electrode passivation; 2.) raised transport resistance [1,2].

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Yun Wang received his B.S. and M.S. degrees in Mechanics and Engineering Science from Peking University in 1998 and 2001, respectively. He went to the Pennsylvania State University where he earned his Ph.D degree in Mechanical Engineering in 2006. Dr. Wang has produced about 90 publications in PEM fuel cell, Li-air battery, and other energy systems. He has received a number of awards, including the prestigious President's Award and Outstanding Educator Award from Orange County Engineering Council and the 2011-2012 Applied Energy Certificate of Excellence: Most Downloaded Authors. Several of his seminal works are highly cited in major energy/power journals. Dr. Wang served as Track chair/co-chair, session chair/co-chair, conference chair and committee member for many international conferences on power and energy. Dr. Wang received 2018 Reviewer of The Year from the Journal of Electrochemical Energy Conversion and Storage. Dr. Wang is currently Professor at the UC Irvine and ASME and RSC fellows.

Presentating author: Wang, e-mail:yunw@uci.edu tel:01-949-824-6004

Nitrides as potential electrode materials for proton ceramic electrochemical devices.

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

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

The EU Green Deal aims to reduce of CO_2 emissions by the development of new C-neutral technologies for industries and processes[1]. In this respect, ammonia (NH_3) is a key chemical that is produced in vast quantities worldwide as a precursor in a range of products that are vital to society, such as fertilizers and medicines. It also has been proposed as a potential carbon-free fuel, due to its high energy density and the formation of only H_2O and N_2 upon its combustion, [2].

Nevertheless, the current industrial route for ammonia production is the Haber- Bosch process, which synthesises ammonia from nitrogen and hydrogen at high pressures (100-300bar) in the temperature range 300-550ºC [3]. This process has a very high energy consumption, with low equilibrium conversion (10-15%) and produces 300 million metric tons of CO_2 per year due to its reliance on hydrogen produced from natural gas [3].

Thus, new greener concepts for NH_3 production are, therefore, urgently needed.

The current presentation, therefore, will discuss ongoing studies performed in the University of Aveiro, Portugal, where our aim is to eletrochemically synthesise NH_3 directly from H_2O and N_2, with the input of renewable electricity, by the use of a Proton Ceramic Electrolyser Cell (PCEC), Fig.1.

Discussion will highlight the possible use of oxynitride materials as electrocatalytically active electrodes for this process, with focus made on their potential advantages, as well as their limitations and key challenges for successful implementation.

Work will describe, the preparation of these materials, their stability, their compositional tailoring and their processing to form potential electrodes. Here one will clarify the oxy(nitride) nature of these materials and how, such modification of the anion lattice can effect their subsequent properties. Work will further explain possible cation tailoring and how such compositional design can provide tailored electrode materials. From this basis, preliminary results of the performace of these materials as electrodes for NH_3 formation will be presented, Fig.2.

Figure 1. Schematic electrochemical NH_3 production using a PCEC.

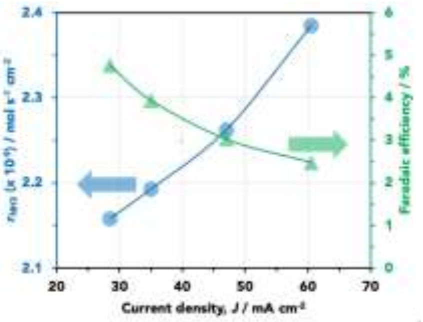

Figure 2. SEM micrographs of BNMO-BCZY composite

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NH_3

Dr. Duncan Fagg is currently employed as a Principal Researcher in the University of Aveiro, Portugal. He obtained his Ph.D. in Chemistry Aberdeen University 1997. He has over 20 years of research experience with previous placements in CICECO Aveiro, Portugal, ICV Autonomous University Madrid, Spain, Dept.Chemical Engineering, Patras Greece, School of Chemistry, St-Andrews University Scotland, and Risø DTU National Laboratory for Sustainable Energy, Roskilde Denmark. He is the author of over 140 international scientific publications in areas covering Solid Oxide Fuel Cells (SOFC), Solid Oxide Electrolyser Cells (SOEC), Oxygen separation membranes, Hydrogen separation membranes, Hydrogen Storage. Presentating author: Duncan Fagg, e-mail: duncan@ua.pt

Gas-phase applications of metal hydrides

Mykhaylo Lototskyy
HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC),
University of the Western Cape (UWC), Bellville, South Africa

Applications of metal hydrides (MHs) utilise a reversible interaction of a hydride-forming metal/alloy, or intermetallic compound with hydrogen. The reversible process of formation/decomposition of the MH involves two mechanisms. The first one (Eq. 1) is the interaction of the parent metal/intermetallic compound with hydrogen gas while the second (Eq. 2) is electrochemical hydrogenation of the metal (or hydride decomposition) in an electrolyte, e.g., aqueous alkaline solution:

$$M\ (s) + x/2\ H_2\ (g) \rightleftarrows MH_x\ (s) + Q; \qquad (1)$$

$$M\ (s) + x/2\ H_2O\ (l) + e^- \rightleftarrows MH_x\ (s) + OH^-\ (l); \qquad (2)$$

where M is hydride-forming metal (intermetallic); Q is heat released during hydride formation or absorbed during its decomposition; the indexes *s*, *g* and *l* correspond to solid, gas and liquid phases, respectively. Both reactions are reversible, so it is possible to change their direction by a small changes of the external conditions (temperature and hydrogen pressure for Eq. 1; electrode potential and temperature for Eq. 2).

Accordingly, the applications of MHs can be generally classified as the gas-phase (Eq. 1) and electrochemical (Eq. 2) ones [1–3]. The latter include NiMH batteries; air – MH batteries and fuel cells and are subject of the separate considerations [4,5].

This presentation overviews the gas-phase applications of the interstitial/metallic hydrides that utilise the following unique features of the hydrogenation/dehydrogenation reaction (Eq. 1):

- Host metal/alloy matrix accommodates H atoms in the interstitial sites;
- Volume density of the accommodated H atoms 1.5–2.0 times exceeds the one for the liquid H_2;
- Fast and reversible hydrogen uptake and release;
- Extremely wide ranges of the operating temperatures (from <0 to >300˚C) and hydrogen pressures (from <1 mbar to >1 kbar) depending on the alloy's composition;
- Significant heat effects, Q, which can vary between <25 and >70 kJ/mol H_2 depending on the alloy's composition;
- 100% selectivity towards H_2;
- Significant volume change of the host metal upon hydrogenation/dehydrogenation (dilatation effects);
- The effects associated with non-equilibrium state of the gas phase when hydrogenation/dehydrogenation reaction takes place, including high catalytic activity of the MH in the hydrogen transfer reactions.

The gas-phase applications of the MHs include but are not limited by the following ones:

- Safe, compact and technologically flexible hydrogen storage;
- Thermally-driven hydrogen compression without moving parts;
- Efficient heat management (refrigeration, heat storage, upgrade and conversion) with a possibility to utilise low-potential heat (T<150˚C);
- Hydrogen separation and purification in 1–2 stages at near-ambient conditions;
- Hydrogen getters and sources of low-pressure hydrogen and its heavy isotopes;
- Powder metallurgy including HDDR and hydride combustion synthesis;
- Various catalytic processes.

Most of the MH applications are very important for energy storage and conversion technologies including hydrogen and fuel cell ones. They allow to combine the processes of compact and safe hydrogen storage and its supply, along with the utilisation of waste heat released during operation of other system components [6].

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Dr. Mykhaylo Lototskyy graduated from the Moscow State University in 1977 and received his PhD degree in 1992 from the Lviv State University. He joined Mechanical Engineering Institute, Kharkov, where he worked on metal hydrides. Following postdoctoral position at the Institute for Energy Technology, Norway, Dr. Lototskyy joined the University of the Western Cape where he is now a Key Programme Manager at HySA Systems Competence Centre hosted by UWC. Dr. Lototskyy's research interest focuses on metal hydrides and nanocomposites, and their gas-phase applications including hydrogen storage and compression.

Presenting author: Mykhaylo Lototskyy, e-mail: mlotoskyy@uwc.ac.za, tel: +27219599314

Multiphysics Simulation of Battery and PEM Fuel Cell Systems – Modelling Challenges and Engineering Applications

Reinhard Tatschl
AVL List GmbH, Hans-List-Platz 1, 8020 Graz, Austria

Legislative challenges, changing customer needs and the opportunities opened-up by electrification are the major driving forces in today's automotive industry. A variety of new powertrain architectures is currently evolving, ranging from various types of hybridization to battery-electric and fuel cell electric vehicles. In hybrid and battery-electric vehicles the electrical energy is directly stored in battery packs composed of a larger number of individual battery cells, today mainly based on Li-Ion technology. In fuel cell electric vehicles adopting PEM fuel cell technology, hydrogen is used as the main energy carrier with the fuel cell converting the chemically bound energy into electricity. By adopting renewable energy sources, such as hydro-, wind- and solar-power providing the electricity for directly charging the batteries and for producing hydrogen via water electrolysis for powering fuel cell electric vehicles, an entirely CO2 emission free mobility is enabled.

The development of the key components of battery-electric vehicles (BEVs) and fuel cell electric vehicles (FCEVs), namely the battery pack and fuel cell system including the related thermal management and hydrogen/air media supply sub-systems for the latter, goes hand in hand with a number of challenges with regards to performance, lifetime and safety aspects. In the case of battery electric vehicles, the development engineers must specifically take care of the proper selection of the battery cell type, the related packaging and thermal conditioning under real-world driving conditions and different charging scenarios. In addition, performance degradation aspects and safety considerations play an important role and need to be addressed in a comprehensive manner. For fuel cell electric vehicles, the proper layout and sizing of the fuel cell stack including the related Balance of Plant (BoP) for handling of the fuel/air media supply, as well as the suitable dimensioning of the cooling system are decisive for the overall system efficiency and achievable lifetime. Finally, the different components and sub-systems need to be integrated into the overall powertrain and vehicle configuration, together with the related control functions to ensure proper operation under all driving scenarios and climatic conditions.

In the above context, scalable multi-physics simulation considerably contributes to supporting the BEV and FCEV development engineers in the different phases of the development process, from concept layout, to detailed component and sub-system development to virtual integration and calibration. Depending on the specific development tasks, different simulation methods and tools are adopted to support the engineers in developing the components and sub-systems to meet the targeted key performance objectives. A clear differentiation can be made between behavioral models, usually neglecting geometrical details and reflecting components or sub-system behavior as a function of time, and geometry resolving methods providing a detailed space- and time-resolved insight into the various mechanical, thermal, electrical and electrochemical processes.

Following a brief overview of selected methods and tools adopted in the different phases of the development process, their application to support typical engineering tasks related to the development and optimization of batteries and fuel cell systems for automotive applications is presented. The application overview of typical battery related development tasks comprises the optimization of performance, efficiency, hazard prevention and lifetime under real-world scenarios. The fuel cell related applications range from detailed anode and cathode flow-field design, membrane-electrode assembly (MEA) component selection, stack media supply and thermal management analysis, to BoP system layout and components sizing, as well as virtual integration and calibration.

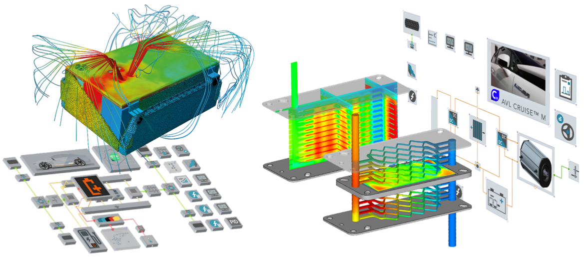

Figure 1. Battery pack venting (left) and PEM fuel cell stack thermal analysis (right)

Reinhard Tatschl is Principal Research and Technology Manager at the business unit Advanced Simulation Technologies of AVL List GmbH in Graz, Austria. After receiving a PhD from Graz University of Technology in 1992 he joined AVL as a CFD development engineer. In 1999 he took over the responsibility for the CFD software development activities, since 2012 he has been holding the current position which comprises initiation and coordination of in-house R&D activities as well as collaborative research and innovation projects with industry and academic partners.

Presentating author: Reinhard Tatschl, e-mail: reinhard.tatschl@avl.com tel: +43 316 787 618

Another way of green H_2 production. SO_2 depolarized electrolysis at high temperature

Justo Lobato[1], Sergio Díaz-Abad[1], Cristina Sáez[1], Imen Fouzai[2] and Manuel A. Rodrigo[1]
[1]Dept. of Chemical Engineering, University of Castilla-La Mancha (UCLM), Ciudad Real, Spain
[2]Res. Unit: Physics, Mathematics and Computer Science, Faculty of Sciences of Gafsa, University of Gafsa, Gafsa, TUNISIA

Hydrogen is back on the crest of the wave, and it seems that this time it is here to stay. Hydrogen has been identified as one of the main figures to reach the *European Green Deal* where hydrogen will play a paramount role for supplying clean, affordable, and secure energy and for a clean and circular economy [1]. The production of green hydrogen is mandatory, and this can be reached using renewable energies coupled with the most well-known process which is the water electrolysis. On the other hand, in a recent study carried out by the Fuel Cells and Hydrogen Joint and Undertaking (FCH-JU) other methodologies were selected as promising routes for green hydrogen production [2]. Among them, the thermochemical cycles for water splitting are very good candidates because membrane is not required for the H_2/O_2 separation, temperature range is moderately high 500-1,800 °C (can be lower in the case of the hybrid sulphur (HyS) cycle, around 900 °C as maximum) and not input electricity is required or is very low in the case of the HyS cycle [3]. The HyS cycle known as Westinghouse cycle is the most well-known hybrid process for thermochemical hydrogen production. The HyS cycle has three steps of which the main one is the electrolysis step, in which hydrogen is generated, which benefits of a very low E_0 = 0.158 V compared to the E_0 = 1.210 V of water electrolysis. The first step is the electrolysis (also called sulfur dioxide depolarized electrolysis, SDE) of water and sulfur dioxide, which produces protons that recombine into hydrogen in the cathode of the electrolyzer and sulfuric acid which, in the second step, is thermally decomposed into water, sulfur dioxide and oxygen. Finally, in the third step, oxygen and sulfur dioxide are separated and then SO_2 is recirculated to the electrolysis step.

With the aim of increasing the overall efficiency of the cycle it has been proposed to increase the operation temperature of the electrochemical step [4]. Thus, new membranes are required, being the PBI based membranes one of the best candidates because of their good properties in High-Temperature Proton Exchange Membrane Fuel Cells [5]. In this work, two different composite PBI based membranes with an organic filler (graphene oxide, GO) and an inorganic filler (TiO_2) have been prepared, characterized and tested in a single 25 cm^2 SO_2 electrolyser for hydrogen production. Furthermore, a novel catalyst deposition technique, as the electrospray is, has been used for the preparation of the electrodes with the goal of reducing the catalyst loading (mg Pt/cm^2). Thus, electrodes with contents below 0.1 mg Pt/cm^2 for this application has been assessed for the first time.

The present study provides insights into the importance of the measurement of hydrogen production in the SDE, how the materials such as advance PBI membranes can improve the system and how the deposition technique can improve the performance of the electrodes with lower Pt content. Operation conditions like the temperature, the cathodic stream or the ratio SO_2/H_2O were some of the parameters evaluated (Fig. 1).

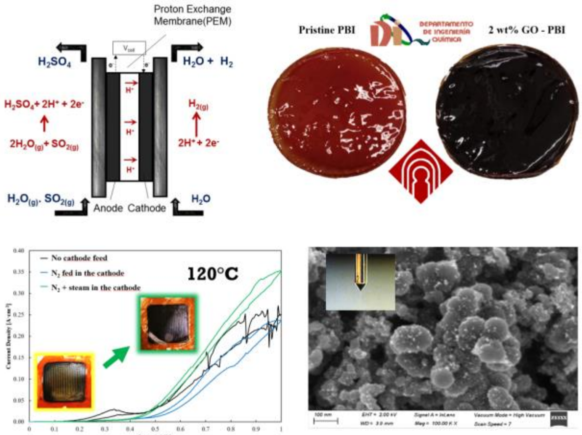

Figure 1. Some results related with the H_2 production through the SDE at temperatures above 100 °C

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Dr. Justo Lobato is full Professor at the Chemical Engineering Department of the University of Castilla-La Mancha, Spain. Currently, he is the Coordinator of the Master in Chemical Engineering and leader of the research line devoted with electrochemical energy storage of the Environmental and Electrochemical Engineering Lab. His research interest covers hydrogen production, PEMFCs, polymeric membranes, electrocatalyst, MFCs, Flow batteries, renewable energy management, LCA,…

Corresponding author: Justo Lobato, e-mail: justo.lobato@uclm.es tel: +34 926 295 300

Mechanisms in Advanced Battery Systems: Theory vs. Experiments

Miran Gaberscek, Sara Drvaric Talian, Joze Moskon, Robert Dominko
National Instititute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Battery cells consist of three main components: negative electrode (anode), positive electrode (cathode) and separator filled with electrolyte that conducts ions between the electrodes. Electrodes in advanced systems usually consist of trillions of nanosized active particles (per 1 cm2 of electrode geometrical surface area) embedded in supporting phases (usually carbon based conductive additive and polymeric binder) and possess significant level of porosity. Depending on the chemical composition of active phase, the reaction/transport mechanisms in such intricate structures may involve a large number of elementary steps (Fig. 1, top) of which more than one can be rate determining – depending on the conditions (state of charge, C-rate, state of health, temperature etc.).

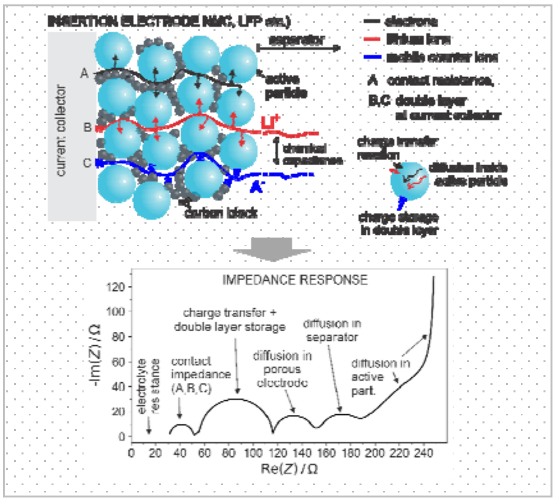

Figure 1. Typical porous electrode model presenting main processes in modern insertion electrode and the mapping of processes to impedance spectrum (adapted from [3]).

We will present and discuss several basic phenomena in selected advanced battery systems, such as lithium ion batteries [1], sulfur batteries containing metallic lithium [2] and magnesium batteries. In order to get insight in the respective battery processes, we will combine the so-called »model experiments« with theoretical modeling.

»Model experiments« differ significantly from the wide-spread »performance experiments« the aim of which is mainly to showcase an improved performance of novel battery materials or novel electrode formulations. Namely, the goal of »model experiments« is primarily to identify the most imporatant contributions in the respective reaction/transport scheme (Fig.1). In order to do so, special electrochemical cells are built (containing planar instead of porous electrodes, using the principle of symmetric cells or three-electrode cells etc.) whereas the electrodes and electrolyte phases may also be appropriately modified (by varying the electrode thickness, porosity etc., varying the electrolyte concentration, viscosity etc.).

As regards the modeling part, we wil mainly (although not exclusively) focus on the application of physics-based transmission line modeling [3] the results of which will directly be verified using dedicated model experiments.

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Dr. Miran Gaberščèk, Professor of Materials Science is Head of Department for Materials Chemistry at the National Institute of Chemistry, Ljubljana, Slovenia. Since 2009 he has also been the Director of Centre of Excellence for Low Carbon Technologies, Ljubljana, Slovenia. Since 2003 he has been affiliated to the University of Ljubljana where he currently holds the position of Full Professor for the field of Materials Science. The primary research field of M. Gaberščèk has been novel electrochemical systems for energy storage and conversion (more specifically: primary and secondary batteries and fuel cells).
Presentating author: Miran Gaberscek, miran.gaberscek@ki.si

Ni-electrodes based aqueous rechargeable batteries continue to improve their performance

Dag Noréus[1] and Weikang Hu[2]
[1] Department of Materials and Environmental Chemistry, Stockholm University, S-106 91 Stockholm, Sweden
[2] Key Laboratory of Advanced Catalytic Materials, Zhejiang Normal University, Zhejiang Jinhua 321004, China.

Since Edison NiFe battery appeared in beginning of last century, it has been followed by a number of rechargeable batteries with other counter electrodes. Valdemar Jungner introduced the NiCd battery in an effort to control the parasitic hydrogen evolution reaction in the Edison battery. The Nickel-hydrogen (NiH_2) battery became a preferable choice in space application due to its long cycle life. The NiMH substituted much of the NiCd market with its better capacity. More recently the NiZn is gaining interest with its lower cost of production and high capacity as reflected in a new European battery project LOLABAT (Long lasting batteries) that aims to bring NiZn back to accelerate the European Energy Transition. https://www.lolabat.eu/

This talk will give a background to the chemistries, review the development and put focus on problems to be solved. These are mainly connected with low conductivity and parasitic side reactions such as oxygen evolution during charging. Additives and the use different phases will be evaluated such as the α-phase $Ni(OH)_2$.[1-3]

Stable α-phase $Ni(OH)_2$ electrodes for alkaline rechargeable NiZn batteries and a higher specific capacitance are reported. The stable α-phase $Ni(OH)_2$ materials were prepared using a wet chemical route by coprecipitation methods that controls solution pH accurately and subsequent hydrothermal treatments at 165℃. The dopants of aluminum and cobalt as well as surface modification by $Co(OH)_2$ were investigated. The influence of synthetic routes and dopants on structure, morphology and electrochemical performance of α-phase nickel hydroxide electrodes were evaluated. Samples were characterized by a variety of methods such as XRD, SEM, TEM, BET, CV, EIS and GCD.

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Dag Noréus 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. He became a professor in 2000 at the Department of Structural Chemistry, Stockholm University. His research interests include x-ray diffraction, elastic and inelastic neutron scattering, and electrochemistry focusing on rechargeable aqueous battery systems

Presentating author: Dag Noréus, e-mail:dag@mmk.su.se tel:+468161253

Hydrogen Based Energy Storage: Status and Recent Developments

Volodymyr A. Yartys

Institute for Energy Technology, P.O. Box 40, NO-2027, Kjeller, Norway

A comprehensive, large scale introduction of hydrogen as an energy carrier and its utilisation in hydrogen energy systems are on the global agenda. The priority for Europe and for the world is to achieve a climate neutrality by implementing zero pollution goals. Development of the hydrogen technologies and production facilities of renewable hydrogen, obtained by using wind and solar energy, is the main trajectory in moving towards these goals. Winning the price competition is a key factor in reaching a success in a broad use of hydrogen as today fossil-based hydrogen is much cheaper compared to both renewable and low-carbon hydrogen. Since every kg of a fossil-based hydrogen produced by steam reforming releases a very significant amount - 8 kg - of CO_2, a cost-efficient carbon dioxide removal process is required to make the production of the fossil-based hydrogen with carbon capture competitive on the market.

The primary focus of R&D of hydrogen storage technologies is in the development of hydrogen storage and supply systems for the stationary, mobile and portable applications requiring a proper use of various alternative hydrogen storage solutions suitable to satisfy the application demands.

The talk will review the available storage options and will focus on use of metal hydrides as safe, convenient and efficient technology to reversibly store and supply purified hydrogen gas. We will present and discuss how establishing and utilizing the structure-properties relationship in the nanostructured hydrides allows to tailor their properties by increasing reversible hydrogen storage capacity, improving kinetics of hydrogen absorption and desorption and by favorably modifying the thermodynamics of the metal-H_2 interactions to suit tailored applications.

An outlook will be presented for the future prospects of the performance improvements of the metal hydrides. An ultimate and a very important goal of the development of the hydrogen storage systems is to achieve energy storage efficiency of 2.2 kWh/kg, as has been suggested by the DoE, USA. Progressing towards the reaching of this goal requires significant advances in hydrogen storage, hydrogen generation and transportation efficiencies, together with a parallel progress in the performance and in lowering of the costs of the fuel cell stacks.

We will focus on considering important classes of hydrogen storage materials. These include:

- Laves type intermetallics of Zr/Ti-based alloys with transition metals;
- Catalysed magnesium hydride-based materials for hydrogen storage and hydrogen generation by hydrolysis process.
- Magnesium substituted alloys of rare earth metals and nickel.

Utilisation of Laves type hydrides benefits from the fact that the crystal lattices of the Zr/Ti-based alloys are very stable towards the cycling in hydrogen gas, withstanding thousands of cycles, and are not prone to the degradation because of the temperatures reaching temperatures, 100-200 °C, and hydrogen pressures up to several hundred bar H_2 while avoiding the disproportionation process. Thus, they are used to build hydrogen storage and compression systems allowing a long cycle and calendar life. Laves type hydrides will continue to be in focus of the research and development of intermetallic hydrides. A great advantage of such hydrides is their operation without a need for the maintenance. What is even more important – is a unique opportunity to finely adjust their hydrogen storage performance because of the presence of the extended homogeneity ranges of the intermetallics allowing to tune equilibrium pressures of hydrogen desorption in a range spanning ten orders of magnitude. Thus, Laves type hydrides fit the requirements for many applications including H_2 getters, materials for hydrogen storage operating at ambient conditions, materials for the efficient compression of hydrogen gas with an output pressure of several hundred bar and anode materials for the metal hydride batteries operating from subzero temperatures (down to –40 °C) and also at extreme heat, at 60-70 °C. Pseudo-binary and more complex multi-element in composition Laves type intermetallics achieve a continuous variation of hydrogen sorption properties, based on an interplay between the stability and crystal structure features of the original alloys. An excellent flatness and high length of the hydrogen absorption plateau pressure can be achieved and optimised based on the intrinsic behaviours of the alloys, including a contribution from elastic and electronic H–H interactions. One promising, yet insufficiently explored feature is in the fact that many Laves type alloys in fact belong to the high entropy materials offering a reversibility of hydrogen storage at convenient for the customer conditions in contrast to the traditional high entropy compositions forming too stable and thus non-reversible hydrides. The fundamentals of Laves phases regarding their structure and properties need to be better understood, even though new important findings have been recently reported. Taking into consideration that rare earth metals belong to the critical raw materials, replacement of their alloys by the Laves phase compounds not containing rare earths will proceed at increasing scale and a future progress in this direction is anticipated.

For Mg based materials we will consider and discuss how changing content of magnesium in alloys and composites allows to tailor and to optimize their hydrogen storage performance as energy storage materials.

Some of the presented in the talk data are described in the reviewer papers [1-9.]

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Prof. V.A. Yartys is a Professor of Materials Science and Hydrogen Technologies and Senior Scientist I at Institute for Energy Technology, Norway. Prof. V.A. Yartys is an international expert in the area of hydrogen-based energy storage. V.A. Yartys published two books and 280 peer reviewed papers which collected more than 8230 citations. He is leading numerous research projects funded by European Commission, NATO Science for Peace Programme, Norwegian Research Council, Nordic Energy Research, industry. Prof. V.A. Yartys is an Editor of Journal of Alloys and Compounds, Elsevier, and a Representative of Norway in the International Society for Electrochemistry. He is also a Member of the Steering Committee of the International Symposia on Metal Hydrogen Systems. https://orcid.org/0000-0003-4207-9127.

E-mail: volodymyr.yartys@ife.no, Tel: +47 454 22 065.

Solar-driven Hydrogen Production via Rationally Designed Heterostructured Photocatalysts

Önder Metin[1], Orhan Altan[1,2] Merve Aksoy[1], and İmren Hatay Patır[3]
[1]Department of Chemistry, College of Sciences, Koç University, 34450 Sarıyer, Sıtanbul, Türkiye.
[2]Department of Nanotechnology and Advance Materials, Institute of Science, Mersin University, 33343, Mersin, Türkiye
[3]Department of Biotechnology, Selçuk University, 42250, Konya, Türkiye

Due to the world's increasing energy demand, global warming, the recent crisis in fossil energy supply due to the pandemic and the war, it is realized one more time that an energy source/carrier reachable in every geopraphy is urgently needed for most countries. Although great advancements have been made in the technology of renewable energy sources, they are not sole remedy for the solution of the current energy and environmental problems due to their intrinsic drawbacks, namely discontinuity and non-availability in all geography. In this respect, hydrogen as the most abundant element in the world is the most promising canditate as energy carrier since it can be produced from numereous sources including water everywhere in the world and generates zero emisson upon its conversion to the energy [1]. Among the hydrogen production technologies without using fossil fuels, photocatalytic hydrogen evolution from water by using solar energy has been regarded as one of the most promising and economic routes [2]. Actually, there is no problem about the hydrogen production, but the safe storage and delivery of the hydrogen is the on-going challenge in the hydrogen-based future, namely "Hydrogen Economy". Among the hydrogen storage technologies, the storage of hydrogen via covalent bond in light-weight compounds such as boron compounds, namely chemical hydrogen storage, is the most promising one. Among the chemical hydrogen storage materials that have been developed so far, ammonia borane (H_3NBH_3) and formic acid (HCOOH) are the most promising ones [3]. However, suitable catalysts required for realising the stored hydrogen from these chemical hydrogen storage materials. Up to date, mostly noble metals have been reported as efficent catalysts for hydrogen generation from ammonia borane and formic acid. However, considering the efficacy, stability, and practicability of the reported catalysts so far, the development of a more efficient, non-toxic, stable, cost-effective, and environmentally friendly catalysts are still required [3]. In this regard, the incorporation of visible-light-driven photocatalysts, allowing the direct conversion of solar energy to chemical energy, in hydrogen generation from ammonia borane and formic acid is one of the most promising approaches to enhance the hydrogen production activity of the traditional transition-metal catalysts [4]. Additionally, the photocatalytic hydrogen generation from water by utilizing solar energy, namely water splitting, has been regarded as one of the most promising and economic routes for hydrogen storage/production/delivery [5]. However, when the current photocatlysts are surveyed, it would be seen that they are mostly inorganic semiconductors suffering from the low visible light absorption, high electron-hole recombination and charge carrier mobility. Therefore, the development of a more efficient, non-toxic, stable, cost-effective, and environmentally friendly photocatalyst is also required for hydrogen evolution from water [6].

With this motivation, our recent research has been focused on the rational design of heterogeneous photocatalysts for hydrogen generation from the chemical hydrogen storage materials (amminia borane and formic acid) and from water splitting under visible light irradiation. In this talk, I will summarize our recent studies on the rationally designed heterojunction photocatalysts comprising the semiconductor two-dimensional (2D) materials (graphitic carbon nitride, black phosphorus, MoS_2, WS_2 and their composites) and the transition metal nanoparticles for hydrogen generation from ammonia borane, formic acid, and water under visible light illumination [6-8].

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Prof. Önder Metin received his Ph.D. from METU, Ankara, Turkey, in 2010. He did post-doctoral studies at Brown University, RI, USA, in 2012-2013. He had worked as Asst/Assoc. Prof. at Atatürk University in 2013-2018. He has been working to Koç University as an Associate Professor since 2018. He has received numerous prestigeous scientific awards and honors given to outstanding young scientists in Turkey. He has published 110+ scientific papers with 7000+ total citations and h-index= 41. He has been a Member of the Board of the Turkish Chemical Society since 2017, and the IUPAC national representative in the field of Inorganic Chemistry since 2018, and an executive board member of Federation of Asian Chemical Societies (FACS) since 2019. Presentating author: Önder Metin, e-mail: ometin@ku.edu.tr, Tel: +90 212 3380942.

Organic electrodes for aqueous electrolyte Zn-ion Batteries

Selin Sariyer[1,2], Nazmiye Kilic[3], Arpita Ghosh[4,5],
Elif Canbaz[1,2], Burcu Unal[1,2] Ozlem Sel[4,5], Serkan Yesilot[3], Rezan Demir-Cakan[1,2]

[1]Department of Chemical Engineering, Gebze Technical University , Kocaeli, Turkey
[2]Institute of Nanotechnology, Gebze Technical University , Kocaeli, Turkey
[3]Department of Chemistry, Gebze Technical University , Kocaeli, Turkey
[4]Chimie du Solide et de l'Energie, UMR 8260, Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France
[5]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France

Aqueous rechargeable batteries have gained prominent attention in terms of safety, high ionic conductivity, cost-effective, environmentally benign. Notably, zinc metal is highly attractive for this battery systems as anode material due to stability and compability with water. Until now, various cathode materials such as manganese-based, vanadium-based, Prussian Blue Analogues and organic electrodes have been developed to effectively and reversible store zinc ions [1, 2]. Among these cathodes, organic electrodes are appealing for aqueous rechargeable zinc ion batteries in the aspects of renewability, natural resource, molecular diversity and flexibility, high capacity and reversiblity as well as sustainability.

In this perspective, organic electrode materials containing quinone and ketone group materials have been implemented in aqueous electrolyte zinc ion battery. Moreover, zinc ions transfer and transport properties were deeply investigated by employing a novel ac-electrogravimerty method and EQCM (electrochemical quartz crystal microbalance) [3].

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Rezan Demir-Cakan is an Associate Professor at the Chemical Engineering Department of Gebze Technical University (GTU) in Turkey. She received her PhD at the Max Planck Institute of Colloids and Interfaces (Germany, 2009), then pursued post-doctoral work at the University of Picardie Jules Verne (France, 2009-2012). Since 2012 she has been leading the battery research laboratory at GTU. Her current research focuses on the synthesis of nanostructured energy materials and their application in the field of rechargeable batteries.

Presentating and author corresponding: R. Demir-Cakan, e-mail: demir-cakan@gtu.edu.tr
tel: +90262605517665

Energy storage in super-activated carbon from agrifood wastes

Chiara Milanese,[1] Ilaria Frosi,[1,2], Alessandro Girella,[1] Simone Puoti, [1] Vittorio Berbenni,[1]
Giacomo Magnani,[3] Daniele Pontiroli,[3] Mauro Riccò,[3] Adele Papetti[2]
[1] Pavia Hydrogen Lab, C.S.G.I. & Chemistry Department, Università di Pavia, Italy;
[2] Pavia FoodLab, Drug Science Department, Università di Pavia, Italy;
[3] Nanocarbon Laboratory, DSMFI, Università di Parma, Italy

The European Union and its member states set up an ambitious plan to become climate-neutral by 2050. For this goal, the Green Deal includes the task of a deep decarbonization of industry and the energy sector by 2030. To contribute to reach climate neutrality, the whole resource cycle of the future - energy carriers and raw materials - has to be based on renewable materials or efficient reuse of resources. Finding ways of closing resource loops and designing processes and materials with their circularity in mind are among the most important tasks for materials development and engineering today. In our groups we are working on solid state hydrogen storage and supercapacitors for energy storage obtaining the storage materials and the electrodes composites from suitable treatments of local agrifood waste.

Recently biochar, the carbon side-product in the pyrolysis/gasification of residual waste biomasses, started to receive a widespread attention in the field of energy-storage, thanks to its hierarchical porous structure inherited from biomass precursors, its excellent chemical and electrochemical stability, high conductivity, high surface area and inexpensiveness. In particular, biochar converted to activated carbon (specific surface area > 1000m^2/g) through a chemical treatment with KOH appears to be a new cost-effective and environmentally-friendly carbon material with great application prospect in the field of energy-storage. We report here on the preparation of novel hierarchically-porous super-activated carbon materials originating from biochar derived by the pyrolysis of agrifood wastes such as rice bran and husk, and melon and pumpkin peels (Figure 1). The chemical activation process proved to be efficient to remove the majority of impurities other than carbon, stabilizing highly porous hierarchical structures with local graphene-like morphology. The porous compounds obtained by rice bran and husk mixtures demonstrated to behave as excellent electrode materials for high-performance symmetric supercapacitors (SCs), reaching interestingly high specific capacitance. On the contrary, the materials obtained by rice bran and the vegetable peels, having specific surface area up to 3000 m^2/g, show a very good hydrogen storage ability, adsorbing up to 4.5 wt % of hydrogen in around 20 seconds at 77K and around 1.5 wt% at room temperature. Work is in progress to optimize the pyrolysis and activation conditions and to improve the performance of the materials by decoration with transition metals.

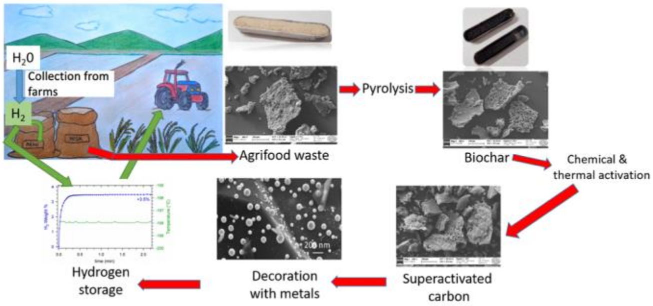

Figure 1. From waste to materials for hydrogen storage.

Chiara Milanese is associate Professor at the Physical Chemistry Section of the Chemistry Department – Pavia University, where she is the scientific coordinator of the Pavia Hydrogen Laboratory. Her main research activities regard the preparation and characterization of innovative materials for solid state hydrogen storage and energy storage and topics linked to circular economy. She is Italian expert of the task 40 "Energy storage and conversion based on hydrogen" activated by IEA and member of the International Hydrogen Carrier Alliance. She is author of 220 papers on materials science topics (h index 33).

Presentating author: Chiara Milanese, e-mail: chiara.milanese@unipv.it tel: +39 0382 987670

Metal hydrides by design – insights from DFT and data science

Katarina Batalović[1], Bojana Paskaš Mamula[1], Jana Radaković[1], Mirjana Medić Ilić[1], Bojana Kuzmanović[1]

[1]CONVINCE - Center of excellence for hydrogen and renewable energy, Laboratory of nuclear and plasma physics,
VINCA Institute of nuclear sciences – national institute of Republic of Serbia, University of Belgrade
P.O.Box 522, 11 000 Belgrade, Serbia

Clean energy solutions rely on various hydride materials, for both hydrogen storage and hydrogen production. In our work, we address the possibility of tuning the properties of the most attractive hydrides: Mg-based hydrides, AlH_3, and $NaBH_4$, by doping.

Density functional theory (DFT) is used to address the stability and electronic structure of the studied doped hydrides. Incorporation of the dopant atoms as substitutional and/or interstitial impurities in the α-AlH_3, β-AlH_3, and MgH_2 is considered[1,2]. Fig.1. presents relaxed supercell of α-AlH_3 doped with Ti, which was demonstrated as one of the best dopants for stabilization of this hydride.

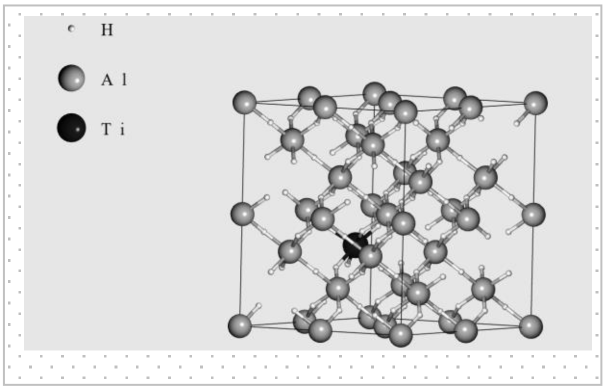

Figure 1. Supercell of Ti-doped α-AlH_3

For the studied AlH_3 polymorphs we found that their stability is determined by the chemical nature of the dopant rather then the crystal structure of the hydride.

In addition to DFT, data science tools offer new perspectives for design in materials science. In this work, we demonstrate an exploratory data science study, done using an unsupervised machine learning approach. Besides results obtained in our DFT studies, we assessed over 500 hydride calculation data found in the NOMAD archive [3] to understand the relevant inner structure of the hydride dataset containing AlH_3, MgH_2, and $NaBH_4$ hydrides.

Finally, we employ artificial neural network models based on the graph neural networks, including MEGNet [4] and our custom-developed model, to predict thermodynamical properties of the doped hydrides based solely on the hydride crystal structure or the crystal structure of the metal/intermetallic compound.

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Dr. Katarina Batalović is an associate research professor at the Vinča Institute. She obtained her Ph.D. in 2013. at the Faculty of physical chemistry, University of Belgrade. Her research interests are theoretical materials chemistry, density functional theory, and machine learning applied to hydrogen energy, energy conversion, and photocatalytic materials.

Presenting author: Katarina Batalović, e-mail: kciric@vin.bg.ac.rs tel: +381113408599

First Principles Investigation of the Substitutional Doping of rare-earth elements and Co in La_4MgNi_{19} Phase

Yuchen Liu[1,2], Djafar Chabane [1,2] Nouredine Fenineche[3] and Omar Elkedim [1,2]
[1] FEMTO-ST Institute, Univ. Bourgogne Franche-Comte, UTBM, CNRS, Belfort, France
[2] FEMTO-ST Institute, FCLAB, Univ. Bourgogne Franche-Comte, CNRS, Belfort, France
[3] ICB-PMDM-LERMPS, UTBM, 90010 Belfort Cedex, France

RE-Mg-Ni alloys, including AB_3, A_2B_7, A_5B_{19} and AB_4 types, have received extensive attention due to their excellent hydrogen storage properties. These alloys are also considered as a potential replacement for commercial $LaNi_5$ hydrogen storage alloys. Among them, A_5B_{19} alloy has excellent hydrogen storage performance, but its poor cycle performance due to its complex structure is a major threshold for its use as a commercial hydrogen storage alloy[1]. Many methods are used to optimize the properties of this alloy, such as element substitution, heat treatment, surface modification, trying unique synthesis methods, etc. Among them, element substitution is the most commonly used method by researchers, such as Pr, Sm, Gd and Nd substituting La, Co substituting Ni, etc. It is noteworthy that most of the literature only shows the nominal change of the chemical composition of the alloy after element substitutions, but does not show the real substitution of atomic lattice positions. First-principal calculations can show which position substitutions are likely to occur, and on this basis some basic performances can be obtained.

This research was carried out in material studio software and calculated using the CASTEP program, a first principles quantum mechanical code based on the density functional theory[2]. It employs a plane wave basis set for valence electrons and pseudopotentials to approximate the potential field of an ionic core (including nuclei and tightly bonded core electrons). Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange and correlation potentials were used for the calculations. An ultrasoft pseudopotential in reciprocal space is used to replace the core electron. An energy change of 5.0×10^{-6} eV/atom, a maximum force of 0.01 eV/Å, a maximum stress of 0.02 GPa, and a maximum displacement of 5.0×10^{-4} Å were set as the convergence bounds in this study. And in this calculation, the enthalpy of formation of a compound is defined as the difference between the total energy of the alloy and the fundamental energy of its constituent elements. The enthalpy of formation can be used to show the thermodynamic changes in the thermodynamics of the constituent elements as they form the alloy of interest, thereby exploring changes in structural stability.

The calculation results show that La_4MgNi_{19} alloy shows the negative enthalpy of formation, indicating the more stable in the thermodynamic. When the substitution of La occurs, among the two sites La(2c) and La(4f), Pr prefer to sub La(4f), Sm, Gd and Nd prefer the La(2c). Meanwhile, Sm, Gd and Pr substituting can stabilize the structure of alloy, but Nd substituting destabilize it. Among them, the substitution of La by Sm is the most promising selection. When Co substituting Ni, a single Co atom occupies the Ni(12k) preferentially among the seven different Ni positions. During this process, the crystal structure will be destabilized.

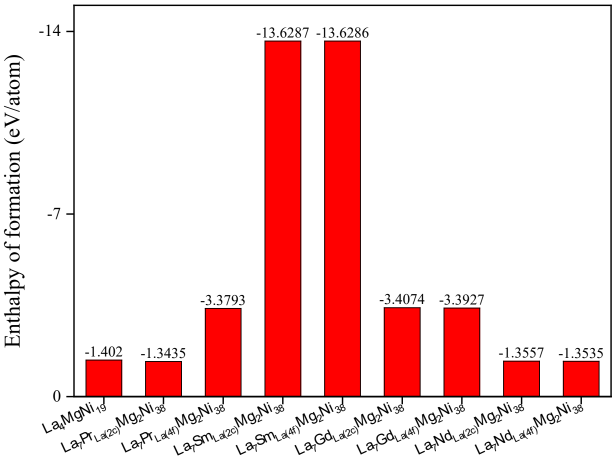

Figure 1. Formation enthalpy of La_4MgNi_{19} base and substitution of La by Pr, Sm, Gd and Nd.

This work can provide theoretical guidance on the element selection in the process of using element substitution to optimize the properties of La_4MgNi_{19} alloy in experiments, and the corresponding thermodynamic principles.

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Acknowledgements

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Yuchen Liu

Dr. Yuchen Liu is with the FEMTO-ST Institute, Univ. Bourgogne Franche-Comte, UTBM, CNRS, Belfort, France. Yuchen Liu obtained his Bachelor's degree in 2017 and Master degree in 2020, both from Northeastern University,China. Now Yuchen Liu is studying for the Ph.D. degree. His research interest covers hydrogen storage materials, intermetallic compounds and mechanical alloying.

Corresponding author: Yuchen Liu, e-mail: yuchen.liu@utbm.fr tel: +33 749 82 88 26

Multi-objective optimization of a metal hydride reactor coupled with phase change materials for fast hydrogen sorption time

Serge Nyallang Nyamsi[1], Mykhaylo Lototskyy[1], Ivan Tolj[2], Sivakumar Pasupathi[1]
[1] HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, Bellville 7535, South Africa
[2]Faculty of Electrical Engineering, Mechanical Engineering, and Naval Architecture, University of Split, R Boskovica 32, 21000 Split, Croatia

In recent years, the interest in H_2 as a fuel has risen dramatically. However, its storage remains the main challenge due to its lightweight. Solid-state H_2 storage inside metal hydrides has been the forefront option due to its high hydrogen storage capacity and safety[1]. However, H_2 storage in metal hydrides (MH) comes with a hefty price for heat management. As a result, for mobile applications, many works are devoted to designing efficient heat exchangers to decrease the hydrogen storage/restore time. Recently, much attention has been turned to innovative passive heat management using phase change materials (PCM)[2]. The results of previous works showed that the hydrogen charging/discharging time from metal hydride reactors (MHR)-PCM systems are still higher than 5 min, target set by the US department of energy (DOE) for mobile applications. Therefore, such MHR-PCM systems fit beautifully in stationary applications where the H_2 charging time is not critical.

In this study, we analyze the performance of MHR-PCM systems using a two-dimensional numerical model. Figure 1 schematically depicts an MHR-PCM for stationary applications. This work aims to investigate the effects of the thermophysical properties of PCM on the H charging and discharging time. Furthermore, the impact of the heat transfer enhancement by inserting extended surfaces such as fins on the system's performance is also analyzed.

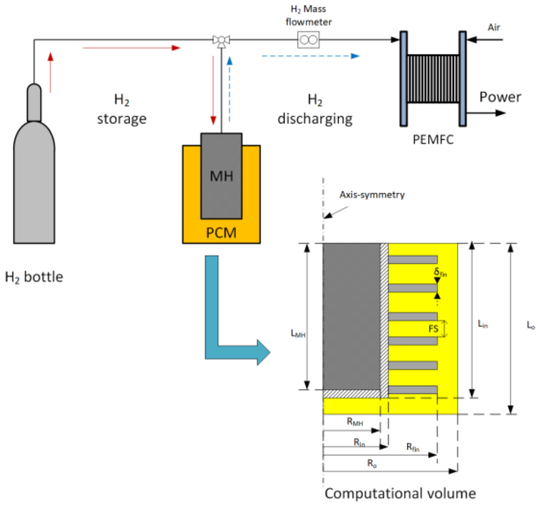

Figure 1: MHR-PCM systems for stationary applications.

The well-known $LaNi_5$ based hydride materials are selected in this work due to their fast kinetics and their readily available thermophysical properties. On the other hand, paraffin-based PCMs are chosen for their highly versatile properties to thermal energy storage applications. Since temperature gradients drive the metal hydride performance, the difference between the MH operating temperature and the heat transfer media should be high. Therefore, the choice of the melting point of PCM should depend on the absorption/desorption temperatures intimately linked to the H_2 ab/desorption pressures through the Van't Hoff equation. The simulations are conducted with absorption and desorption pressures of 10 and 1.5 bar, respectively. The melting point is allowed to vary between 25 and 50 °C.

Figure 2 portrays the H_2 charging/discharging time variation with the PCM's melting/freezing point. As can be seen from the figure, the H charging time t_c and H discharging time t_d have opposite trends. The increasing of the melting point favors the decreasing of t_d, while increases t_c. However, there is an optimum PCM melting point where the overall process time, t_c+t_d is minimum.

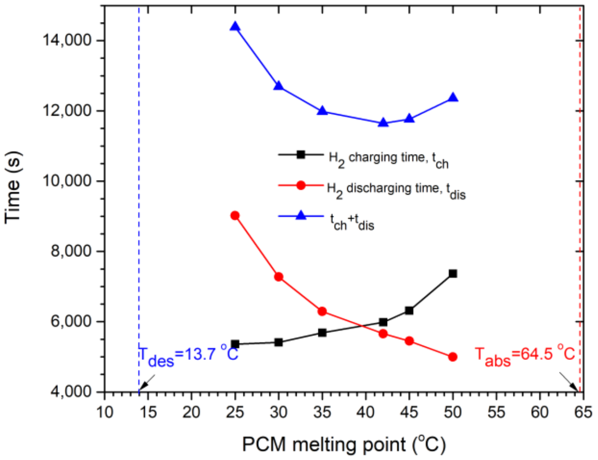

Figure 2: The change of H_2 charging/discharging time with the PCM melting point

This work aims to conduct a multi-objective optimization by simultaneously minimizing tc and td with the properties of PCMs as decision variables.

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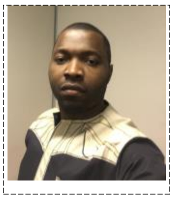

Serge Nyallang

Dr Serge Nyallang Nyamsi completed his Ph.D. degree in power engineering and engineering thermophysics from the school of Energy and Power Engineering, Xian Jiaotong University, China in 2013. He is currently a research fellow at HySA Systems within the South African Institute for Advanced Materials Chemistry (SAIAMC) from the faculty of Natural science, university of the Western Cape. His research interests in energy storage technologies include design and optimization of potential metal hydrides for hydrogen storage and thermal energy storage, heat management and energy efficiency improvement. He also have interest in efficient conversion of renewable energy resources.

Presenting author: Serge Nyallang Nyamsi, e-mail: nyamsiserge@gmail.com , tel: +27 21 959 9310

Hydrogen and fuel cells for mobile applications

Amela Ajanovic[1] and Marlene Sayer [1]
[1]Vienna Univeristy of Technology (TU WIEN), Gusshausstr. 25-27/370-3, 1040 Vienna, Austria

First visions of hydrogen economy according to which hydrogen should be used for almost all energy services was presented already in 1876 by Jules Vernes. However, although this idea is very old one, hydrogen and fuel cell are still mostly seen as an option for the future. The major reasons for this are related to the high costs, lack of infrastructure, low public acceptance and lack of safety standards and regulations.

Over the last decade two very important developments can be noticed. On the one hand, there is rapidly increasing use of the volatile renewable energy sources such as wind or solar energy. With the increasing share of volatile energy sources in the energy system raised also need for additional storage options. Since hydrogen is an energy vector which can be used as energy carrier and energy storage, his role in the energy system is becoming more important. On the other hand, the environmental problems are becoming more and more evident and there is a huge need for the decarbonization of energy system and especially transport system. The transport sector is one of the largest contributors to the increasing greenhouse gas (GHG) emissions. This sector is almost completely based on fossil fuels. Currently, mostly discussed alternatives to fossil fuels are electricity and hydrogen. Battery electric and fuel cell vehicles could significantly reduce local air pollution and depending on the primary energy used for electricity generation and hydrogen production they can more or less contribute to the reduction of GHG emissions.

In this paper major challenges and prospects of hydrogen and fuel cells in mobile applications are analyzed with the focus on economic and environmental aspect, as well as possible sector coupling.

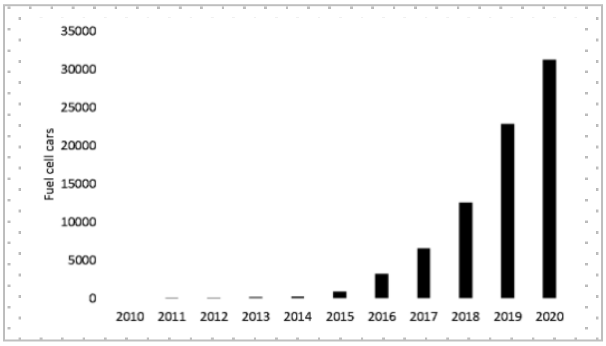

Figure 1. Stock of fuel cell vehicles (data source: [1]).

In contrary to battery electric vehicles which are already relatively well established in the market, the deployment of fuel cell vehicles (FCVs) is still very slow. Figure 1 shows the development of the stock of fuel cell vehicles worldwide. Although, the number of fuel cell vehicles is increasing, there were just about 31 000 FCVs in use in 2020, largely concentrated in four countries. The major reason for slow penetration of fuel cell vehicles are high vehicle purchase prices and very limited infrastructure.

Yet, after the decades of intensive research and investment in hydrogen and fuel cells, their commercialization could be expected in the next years. The fuel cell stack costs should be reduced due to the reduced material use, as well as due to increasing manufacturing volume per year. Moreover, in spite a broad support for battery electric vehicles it is obvious that they are still facing major challenges such are short driving ranges and long charging times. This is especially challenging for large vehicles such as trucks or buses, and FCVs have already good performance in such transport modes.

Additional reason for optimism for the faster deployment of hydrogen and FCVs in the future is the fact that hydrogen is not just an energy carrier which can be used in the transport sector but an energy vector for applications ranging from the small-scale power supply in off-grid modes to large-scale chemical energy exports [2]. Hydrogen has potential to reduce emissions from transport and contribute to the decarbonization of this sector, to contribute to diversification of energy use for mobility, to increase energy supply security, and to increase flexibility in electricity supply and demand serving as an energy storage for the surplus electricity from variable renewable energy sources. Finally, in the long-run, hydrogen has ability to generate different benefits for the whole energy system. However, to enable this very clear policy targets are needed as well as corresponding supporting policy measures.

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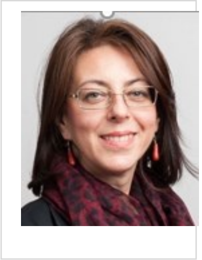

Amela Ajanovic is Associated Professor in Energy Economics at Vienna University of Technology (TU Wien). She is a lecture and faculty member of the postgraduate MSc Program “Renewable Energy Systems”. She holds a master degree in electrical engineering and a PhD in energy economics at TU Wien. Her main research interests are alternative fuels and alternative automotive technologies as well as sustainable energy system and long-term energy scenarios. She has been involved in many national and international research projects, and her work has been published in the leading scientific peer- reviewed international journals.

Presentating author: Amela Ajanovic, e-mail: ajanovic@eeg.tuwien.ac.at tel: + 43 1 58801 370364

Electrochemical study of $CaNi_{4.8}Mg_{0.2}$ anode material used in rechargeable nickel-metal hydride batteries

Imen Karoud[1], Youssef Dabaki[1], Chokri Khaldi[1], Omar ElKedim[2], Nouredine Fenineche[3], and Jilani Lamloumi[1]

[1] Université de Tunis, ENSIT, LR99ES05, 1008 Montfleury, Tunisia.
[2] FEMTO-ST, MN2S, UTBM, UBFC, 90010 Belfort Cedex , France
[3] ICB-PMDM/FR FCLAB, UTBM, UBFC, 90010 Belfort Cedex , France

Abstract:

Ni-MH battery is a rechargeable electrochemical cell with an extended lifetime. This type of battery is widely used because of the following properties: flexible cell size, operational safety, flexible packaging, better thermal properties, low cost charging environmentally friendly and recyclable production materials [1]. It is the third most sold rechargeable battery in the world, after lead acid and alkaline Ni-Cd batteries, and is becoming an important component not only for advanced information and telecommunications systems, but also for the next generation of hybrid (HEVs) or fully electric vehicles (EVs) [2]. In fact, the performance of this type of battery depends not only on the performance of the active materials (the type of hydrogen storage alloys), but also on the production procedure of the negative electrodes, as it affects the charge/discharge properties**.**

In the present work, we studied the electrochemical properties of $CaNi_{4.8}Mg_{0.2}$ alloy used as anode in nickel-metal hybrid batteries.

The $CaNi_{4.8}Mg_{0.2}$ powder is prepared by mechanical milling for 40 h and with ball to powder weight ratio of 8:1 using a Retsch PM400 type ball mill under an argon atmosphere [3].

The metal hydride electrode is prepared using a so-called "latex" technology [4,5]. It is then characterized by different polarisation methods at ambient temperature, such as galvanostatic polarisation and potentiodynamic polarisation, using the electrochemical device Potentiostat-Galvanostat Ec-Lab system (Biologic^{TM})
XRD analysis of $CaNi_{4.8}Mg_{0.2}$ powder indicates the existence of two main phases Ni (face-centred cubic) and $CaNi_5$ (hexagonal). Morphological characterization shows the existence of agglomerates with an average particle size of 19 µm.
The $CaNi_{4.8}Mg_{0.2}$ electrode is activated during the third cycle with a maximum discharge capacity of 30 mAhg^{-1}. After activation, the discharge capacity gradually decreases during long cycling due to the degradation of the active material in the electrode.(Fig1)

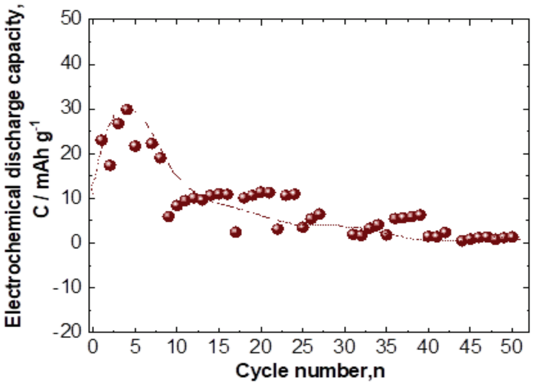

Figure 1. Evolution of the discharge capacity as a function of the number of cycles of the $CaNi_{4.8}Mg_{0.2}$ electrode.

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PhD student Imen karoud is a member of the metal hydride team in the mechanics, materials, and processes laboratory at the high national school of engineering of Tunis. She is obtained her master's degree in physics 2020. Her thesis topic is entitled synthesis and structural, morphological, and electrochemical characterization of hydride alloys used as anode in Ni-MH batteries

Presenting author: Imen Kaorud, e-mail:karaoudimen@gmail.com tel:29889788.

Electrochemical properties of $LaNiO_3$ oxide as a new anode material for nickel–metal hydride accumulators

Ahmed Khedimallah[1], Abbes Kaabi[1], Dabaki Youssef[1], , Chokri Khaldi[1],Omar.El-Kedim[2], NouredineFenineche[3], JilaniLamloumi[1]

[1]Université de Tunis, ENSIT, LR99ES05, Montfleury, 1008 Tunis, Tunisia
[2] FEMTO-ST, MN2S, UTBM, UBFC, 90010 Belfort Cedex , France
[3] ICB-PMDM/FR FCLAB, UTBM, UBFC, 90010 Belfort Cedex , France

Abstract—in this work, we studied the hydrogen storage properties of the perovskite-type oxide $LaNiO_3$ used as a new active material of the negative electrode in a nickel-metal hydride battery. The perovskite-type oxide LaNiO3was synthesized by the sol-gel method, its structure and electrochemical properties are systematically studied. X-ray diffraction analysis (XRD) showed that the perovskite-type oxide $LaNiO_3$ consists of a single phase and crystallizes in the Rhombohedral space group R. Characterisation by the galvanostatic charging/discharging method of the $LaNiO_3$ electrode showed that the activation is fast and requires only two cycles to reach the maximum discharge capacity (118 mAh g^{-1} after two charge/discharge cycles).

Keywords –perovskite $LaNiO_3$ type oxide; Nickel metal-hydride accumulators; Galvanostatic charge and discharge method.

RESULTS AND DISCUSSION

A. Microstructure analysis

The XRD pattern of $LaNiO_3$ is shown in Fig.2. All diffraction lines can be indexed to a perovskite-type structure. The XRD shows the presence of several spokes and that the perovskite-type oxide $LaNiO_3$ consists of a single phase and crystallizes in the Rhombohedral R space group.

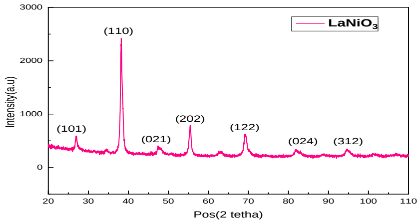

Fig1:XRD pattem LaNiO3 oxide powder

B.Activation capacity and cycliing stability of perovskite-type LaNiO3 oxide.

It can be seen that the perovskite-type oxide $LaNiO_3$ is easily activated after two cycles. Indeed, in a first cycle, the discharge capacity is about 18 mAhg^{-1} while it increases to 118mAh g^{-1} in the second cycle. Fig. 2 shows the evolution of the discharge curves as a function of the discharge capacity during the electrochemical cycling of the perovskite-type oxide $LaNiO_3$ at C/10 rate and at 25°C. It clearly shows that perovskite-type oxide $LaNiO_3$ requires two activation cycles to reach its maximum discharge capacity.

After activation, a sharp drop in discharge capacity is observed. Indeed, the discharge capacity stabilises around 25 mAh g-1 from the fourth cycle and for the rest of the cycles. It should be noted that despite the significant decrease in discharge capacity after activation, good stability and rapid activation are observed.

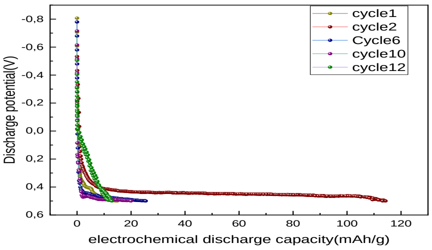

Fig. 2. The evolution of the discharge curves as function of capacity during electrochemical cycling of the $LaNiO_3$ electrode at C/10 rate and at 25°C.

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Khedimallah Ahmed doctoral student at the national school of engineering of Tunis. As part of my master's degree, I carried out my research work in the field of renewable energies, in particular on the concept of the transfer of solar energy into electrical energy at the Energy Research and Technology Centre (CRTEn). Currently, my research work is focused on hydrogen storage and its applications at the Mechanics, Materials and Processes Laboratory (LMMP).

Ahmed Khedimallah, e-mail:ahmedkhdimallah27@gmail.com tel:+21623781502

Vanadium (oxy)nitride: tailoring the catalyst oxidation kinetics and stability by tuning the anion stoichiometry

Laura I.V.Holz[1,2,3], Vanessa C.D.Graça[1], Francisco J.A. Loureiro[1], Sergey M.Mikhalev[1], Diogo Mendes[2] , Adélio Mendes[3], Duncan P.Fagg[1]

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

[2] *Bondalti Chemicals, S.A., Quinta da Indústria, Rua do Amoníaco Português no. 10 Beduído, Estarreja 3860-680, Portugal*

[3] LEPABE - Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Transition metal (oxy)nitrides are fascinating materials due to their good catalytic and electronic properties. Therefore, research on (oxy)nitride materials is an emerging and rapidly growing field with a wide range of potential applications. Vanadium (oxy)nitrides, in particular, have generated high interest due to their wide applicability in heterogeneous catalysis, energy-related research (*e.g.*, supercapacitors), and superconductors. Nonetheless, the ability of (oxy)nitride materials to assume the roles is highly dependent on their chemical stability towards oxidation, which in turn is highly dependent on the N/O ratio in their anionic lattice[1-5].

In this sense, VON compounds were synthesized by ammonolysis route at different temperatures (from 600 to 1000 °C) aiming to clarify the effect of synthesis temperature on the final (oxy)nitride stoichiometry and on its stability towards oxidation. The materials were then fully characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and thermogravimetric studies (TGA). In order to examine the effect of N/O ratio on the material stability, the isoconversion and model-based kinetic methods were applied.

In this work, we observed that the ammonolysis temperature was found to have a strong effect on the N/O ratio of the formed (oxy)nitride, increasing as the synthesis temperature increases. XRD studies revealed unit cell volume expansion with nitrogen incorporation and subsquent release of oxygen from the anionic lattice. These compounds are known to be non-stoichiometric, having the ability to accommodate an excess of anions, while mantaining the rock-salt type structure,[6] and where this type of point defect was shown to be the most thermodynamically favorable for this type of group (V), rock salt structure, nitrides[7]. In line with prior work, one, therefore, explains the defect chemistry of the VON compound, based on the substitution of nitrogen by oxygen in the anionic lattice, accompanied by the creation of cation vacancies[8].

The kinetic studies showed that samples with an increased N/O ratio undergo a more complex oxidation behaviour, where the rate determining steps can be best associated with radial oxygen diffusion / F^n order oxidation and that a higher N/O ratio is beneficial for oxidation resistance (Fig.1).

As such, the current work provides an essential new tool for control of composition in the anion lattice, which can be extended to the synthesis of other (oxy)nitride compounds. The method allows properties tailoring with direct impact on materials stability, offering high relevance to the applicability.

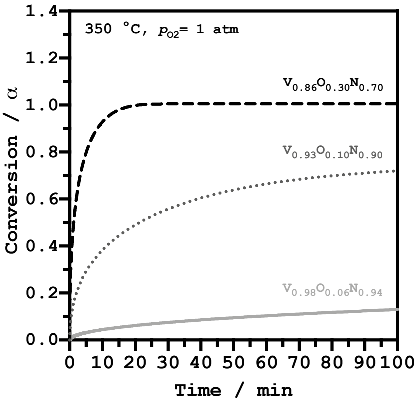

Fig.1 – Conversion of $V_xN_yO_{1-y}$ to V_2O_5: Isothermals prediction of $V_{0.86}O_{0.30}N_{0.70}$, $V_{0.93}O_{0.10}N_{0.90}$ and $V_{0.98}O_{0.06}N_{0.94}$ samples, obtained by the kinetic model based analysis. α=1 represents 100 % of conversion to V_2O_5.

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Laura I.V.Holz is currently enroled in a industrial PhD programme in the frame of Refining, Petrochemical and Chemical Engineering, at University of Aveiro, in close collaboration with Bondalti Chemicals, a Portuguese Company. Her research interest covers nitrides, ceramic oxides and solid oxide fuel/electrolytic cells.

Presentating author: Laura Holz, e-mail: lauraholz@ua.pt

Composites of transition metal dichalcogenides and topological insulators as a new class of catalytic materials

Jelena Rmuš[1], Blaž Belec[2], Igor Milanović[1], Mattia Fanetti[2], Sandra Gardonio[2], Matjaž Valant[2], Sandra Kurko[1]

[1]Department of Physics, Center of excellence for hydrogen and renewable energy (CONVINCE), "Vinča" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike petrovića Alasa 12-14, 11351 Belgrade, Serbia
[2]Materials Research Laboratory, University of Nova Gorica, Vipavska cesta 13, 5000 Nova Gorica, Slovenia

Recently, it was shown that TMD/TI hybrid structures possess extraordinary catalytic performance which can be considered attractive for addressing the current worldwide challenges of energy shortage and environmental pollution [1,2].

Transition metal dichalcogenides (TMDs), as earth-abundant and non-noble metal materials, are attracting a lot of attention as electrocatalysts for hydrogen evolution reaction due to their simple synthesis and excellent electrochemical activity. Molybdenum disulfide (MoS_2) as the typical TMDs, holds great potential for energy storage and catalysis due to its layered structure where catalytically active sites are edges and defects. Conversely, basal planes of MoS_2 are catalytically inert and their performance is largely limited by its poor conductivity and concentration of available active sites. To improve the electrical conductivity of electrocatalysts, composites or hybrid materials of MoS_2 with conductive support such as graphene, carbon nanotubes, conducting polymers, or other transition metal compounds are studied.

Topological insulators (TI) are a new class of materials, possessing bulk band gap but metallic surface states and therefore are expected to be ideal conducting channels for electron transport. Bismuth selenide (Bi_2Se_3) is one of the most promising TI due to a narrow bulk band gap of 0.3 eV and the single Dirac cone dispersed on its surface [3]. Therefore combining such material with the catalytic active but poorly conductive MoS_2 could result in the enhanced electron transfer between the MoS_2 active sites and the electrode.

In this work, different approaches were utilized in preparing TMD/TI catalysts. Initially, both materials were synthesized via the hydrothermal method. Afterwards, mechanical milling and high power sonication were used for producing MoS_2/Bi_2Se_3 composites with various compositions. The morphology and phase distribution in composites were examined by scanning electron microscopy, while the phase composition was determined using X-ray diffraction analysis. The electrochemical activity of prepared catalysts was studied by impedance spectroscopy, linear sweep and cyclic voltammetry in an acidic electrolyte solution (0.5M H_2SO_4) at room temperature. The obtained results show an increment of conductivity in composites and accordingly better activity towards hydrogen evolution reaction as shown in Figure 1.

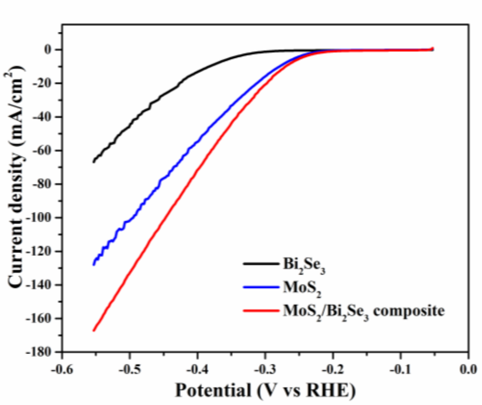

Figure 1. Polarisation curves of MoS_2, Bi_2Se_3 and MoS_2/Bi_2Se_3 composite catalyst

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Jelena Rmuš is PhD student at the Faculty of physical chemistry, University of Belgrade and research assistant at Vinča Institute of Nuclear Sciences in Belgrade, Serbia. Her doctoral research is focused on nanomaterials for hydrogen energy and the application of hydrogen as a renewable energy source, particularly on synthesis and characterization of nano and twodimensional transition metal dichalcogenides.

Presentating author: Jelena Rmuš, e-mail: jelenarmus@vin.bg.ac.rs tel: +381 64 312 47 98

Bifunctional carbon free gas-diffusion electrodes based on composite metal/transition metal oxides for secondary Zn-air batteries

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

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

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

Due to their high electrical conductivity Ni- and Co-based bifunctional electrocatalysts have paid considerable attention over the past decades. These oxide materials have promising activity towards the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) and attract with low cost, availability, and their environmental friendship. The stability of this type oxides in alkaline media have made them the most studied candidates for practical application as an air electrode (gas diffusion electrode, GDE) for electrically rechargeable Zn–air batteries. A wide variety of methods and techniques to achieve controlled morphology of their bifunctionality have been reported. The conventional method for GDEs production is based on the use of a carbon, which serves as the catalyst support. Several types of high-surface carbons with different structures, surface areas and origins have been largely investigated in order to provide an effective flux of oxygen to the catalyst centers during discharge and release of oxygen to the gas side during charge. Unfortunately, the high electrochemical carbon corrosion at charging reduces the stability of the electrode and influences the long-term stability of the battery. Therefore, the recent investigations are focused on the replacement of a carbon-based gas-diffusion electrode with a carbon free electrode, and it is a currently a hot and emerging topic.

In this work we propose a novel concept for a carbon free gas diffusion electrode design, based on well-known fabrication procedure - hot pressing. A mixture of catalyst (Co_3O_4, $NiCo_2O_4$) and different ratios of most commonly applied hydrophobic bonding material, polytetrafluoroethylene (PTFE), were milled and hot pressed onto a stainless-steel mesh (current collector). Additionally, to enhanced the electrical conductivity and thus to increase OER performances, up to 70 wt.% Ni powder, was included. The produced in this way gas diffusion electrodes were examined in a half-cell configuration with 6M KOH electrolyte with stainless steel counter electrode and hydrogen reference electrode at room temperature. Electrochemical tests including volt-ampere characteristics, charge/discharge cycling tests and Impedance measurements were performed and coupled with microstructural observations to evaluate the properties of the present oxygen electrodes in the light of their bifunctionality and stability enhancement. The results were compared with state-of-the-art carbon based GDE - impregnated with PTFE carbon blacks, Ag+Co_3O_4 catalyst, PTFE (Etalon Electrode).

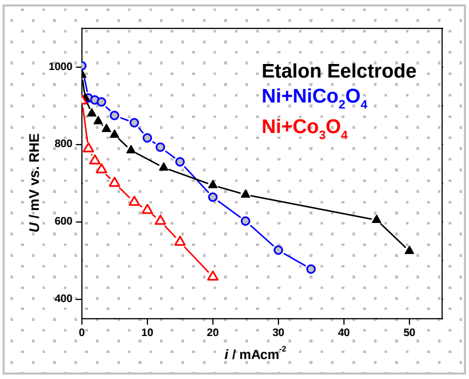

Figure 1. Volt-ampere characteristics of the new carbon free electrodes during discharge.

The electrochemical behavior of the new type gas-diffusion electrodes is presented on Fig.1. Both electrodes, Ni+Co_3O_4 and Ni+$NiCo_2O_4$ show acceptable overpotentials for OER and ORR, and comparatively better mechanical and chemical stability of electrodes consist Ni+$NiCo_2O_4$ (70:30 wt%) was registered.

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Miglena Slavova - Doctor of Chemistry. Lives and works in Sofia, Bulgaria.
Affiliation:
1. Institute of Electrochemistry and Energy Sytems part of the Bulgarian Academy of Sciences; 2. Todor Kableshkov University of Transport.
Presentating author: Miglena Slavova, e-mail: mslavova@iees.bas.bg tel: +359/89735266

Effect of metalic and metal-oxide catalysts on $LiAlH_4$ decomposition

Bojana Babić[1], Milica Prvulović[1], Jelena Rmuš[1], Anđela Mitrović Rajić[1], Sanja Milošević Govedarović[1], Igor Milanović[1], Sandra Kurko[1]

[1]Department of Physics, Center of excellence for hydrogen and renewable energy (CONVINCE), "Vinča" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11351 Belgrade, Serbia

Metal and complex light hydrides are the best fitted materials for hydrogen storage within the concept of hydrogen based economy [1]. They meet the basic application requirements: low-cost, safety and they are environmentally friendly. Beside their benefits, as relatively stable compounds, these materials exhibit also some undesirable properties like sluggish kinetics and high temperature of hydrogen desorption. $LiAlH_4$ has emerged as a potential material for solid-state hydrogen storage because of its high hydrogen gravimetric capacity (10.5 wt%). It decomposes in three steps, according to the reactions [2]:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + H_2 \quad (R1)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \quad (R2)$$

$$3LiH+3Al \rightarrow 3LiAl + 3/2H_2 \quad (R3)$$

The temperature of the first reaction is between 150-175°C, of the second between 180-220°C and the third between 400-420°C. The first two reactions (R1 and R2) are very important from the hydrogen storage point of view: (i) both take place at a reasonable low temperatures and (ii) overall sum of theirs gravimetric hydrogen capacity is 7.8 wt.%, so the reactions (R1) and (R2) are accessible for practical hydrogen storage. However, the slow dehydrogenation kinetics and irreversibility under moderate condition hinder its imminent application.

Particle refinement and catalyst or additive introduction by mechanical milling led to the significant improvement of $LiAlH_4$ hydrogen storage properties [2]. However, during the milling process, the temperature in the milling chamber can significantly increase reaching the temperature of R1 or even R2 leading to the degradation of hydride, change in the hydrogen desorption mechanism (figure 1) and decrease in the hydrogen storage capacity of material [3]. So, in this work the impact of metallic (V, Mn an Cr) and metal oxide (Fe_2O_3 and Nb_2O_5) additives on the $LiAlH_4$ hydrogen desorption properties with the emphasis on the hydride degradation process during milling and a consequent hydrogen desorption reaction mechanism was studied. The aim was to improve the hydrogen desorption kinetics without hydrogen capacity deterioration.

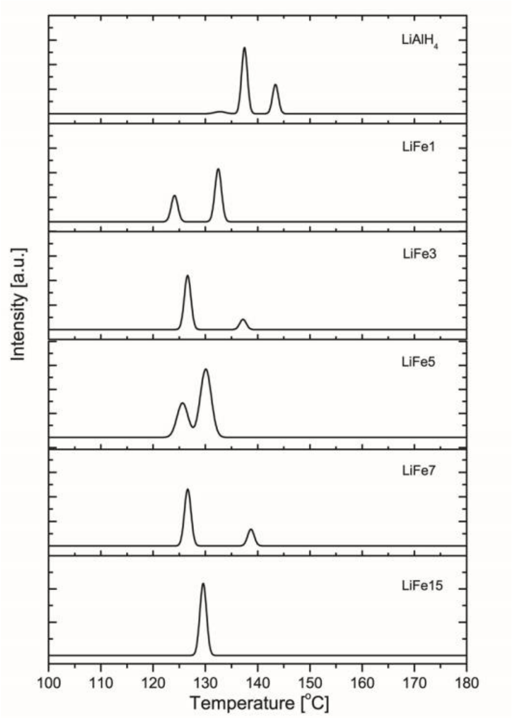

Figure 1. Temperature programmed desorption (TPD) spectra of the: un-milled $LiAlH_4$; and $LiAlH_4$-5wt.%Fe_2O_3 composites milled for 1 min (LiFe1), 3 min (LiFe3), 5 min (LiFe5), 7 min (LiFe7), and 15 min (LiFe15).

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Dr Sandra Kurko is associate research professor at Vinča Institute of Nuclear Sciences in Belgrade, Serbia. She obtained her PhD at the Faculty of physical chemistry, University of Belgrade. Her research is focused on developing materials for hydrogen production and storage. The main interest is to improve the hydrogen sorption properties as well as the catalytic performance of materials by the introduction of defects into the materials structure by mechanochemistry and low energy ion beams irradiation.

Presentating author: Sandra Kurko, e-mail: skumric@vin.bg.ac.rs tel: +381 64 1745 363

Heat discharge performance of metal hydride thermal battery under different heat transfer conditions: An experimental inquisitiveness

Serge Nyallang Nyamsi[1], Mykhaylo Lototskyy[1] Wafeeq Davids[1], Ivan Tolj[2], Sivakumar Pasupathi[1]
[1] HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, Bellville 7535, South Africa
[2]Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, R Boskovica 32, 21000 Split, Croatia

The thermal batteries utilizing metal hydride pairs are gaining tremendous research attention for their applications in thermochemical energy storage. The pair consisting of a high-temperature metal hydride (HTMH; Mg-based hydride) and a low-temperature metal hydride (LTMH: AB2 or AB5 type hydride) is more appealing due to its relatively high energy storage density and medium energy storage efficiency, around 60-70 %[1]. However, the energy storage efficiency can be significantly increased by improving the heat discharge performance of the thermal battery. To accomplish this, heat should be provided to the LTMH bed to increase the operating gas pressure, thereby raising the temperature output from the HTMH. In this work, we experimentally explore the heat discharge performance of the MgH_2/(Ti-Zr)(Mn-Fe-Cr)$_2$-based thermal battery (Figure 1).

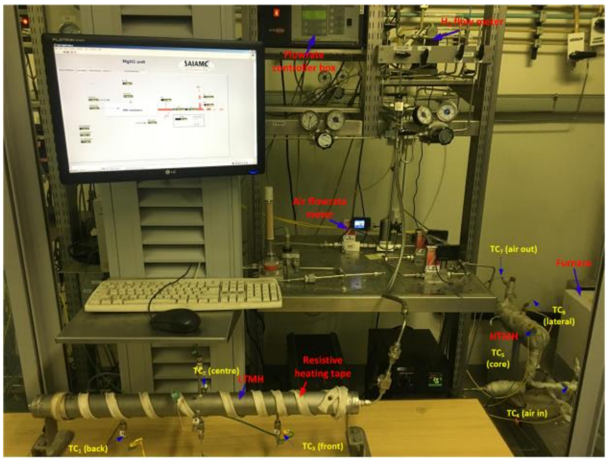
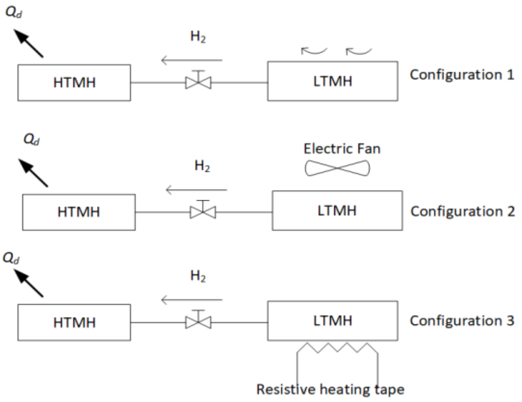


Figure 1. photographic representation of the test rig.

Figure 1 depicts the thermal battery connected to the test rig. Several thermocouples were placed in different locations in the reactors to monitor the local temperature changes during the heat discharge dynamics. Three configurations of the thermal battery were analyzed where the heat transfer conditions on the LTMH bed were varied. These heat transfer conditions include natural convection (config.1), forced convection(config.2), and resistive heating (config.3). Figure 2 summarizes the performance indicators of the thermal battery.

The results showed that when operating the LTMH bed under active heat transfer conditions (forced convection or resistive heating), the thermochemical energy storage density varies between 1500-1820 kJ/kg-Mg with relatively high-temperature lift (heat upgrade) between 47-55 °C. On the other side, the thermal battery discharges heat at relatively high specific power ca. 100-225 W/kg-Mg, which can be benefic to heat-to-work conversion applications.



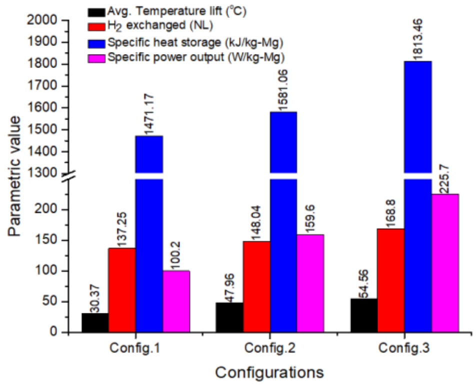


Figure 2: Key performance indicators of the thermal battery during heat discharging process

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Serge Nyallang

Dr Serge Nyallang Nyamsi completed his Ph.D. degree in power engineering and engineering thermophysics from the school of Energy and Power Engineering, Xian Jiaotong University, China in 2013. He is currently a research fellow at HySA Systems within the South African Institute for Advanced Materials Chemistry (SAIAMC) from the faculty of Natural science, university of the Western Cape. His research interests in energy storage technologies include design and optimization of potential metal hydrides for hydrogen storage and thermal energy storage, heat management and energy efficiency improvement. He also have interest in efficient conversion of renewable energy resources.

Presenting author: Serge Nyallang Nyamsi, e-mail: nyamsiserge@gmail.com , tel: +27 21 959 9310

Energy conversion in a city bus with an internal combustion engine in conjunction with a photovoltaic system - a case in southern Europe

Michał Jan Gęca[1], Gojmir Radica[2], Ivan Tolj[2]

[1]Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, PL-20618 Lublin, Poland

[2]Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, Boškovića 31, 21000 Split, Croatia

Electricity consumption in a combustion engine bus is an important energy component in the vehicle's overall energy balance. The total power of onboard electric devices can reach up to 5.6 kW [1]. Electrical systems like audiovisual information equipment, punchers and highlighted information boards make travel more comfortable but also significantly load a city bus electrical installation. An automatic air conditioning (AC) system is an important energy receiver in a city bus., i.e., about 1.9 kW [2]. Electricity is generated by an alternator driven by a combustion engine and means higher fuel consumption. The combustion engine consumes about 8-10 kW to drive alternators, which is, according to operational investigations, approximately 25% [3] of the total fuel consumption of a city bus. The total efficiency of converting chemical energy into electricity onboard ranges from 19% to 21% [4]. Increased fuel consumption for the generation of electricity on board the bus has a negative impact on the emission of toxic components and carbon dioxide. An additional onboard energy source can reduce the production of electricity generated by an alternator powered by an internal combustion engine. At the same time, the bus roof surface allows to place a set of lightweight photovoltaic panels with power from 1 to 1.5 kW. Electricity produced directly from the sun will power the bus's electricity consumers.

The 1.8 kW PV panels installed for research purposes in central Europe, according to preliminary estimates, produce 26% of the electricity that replaces the energy obtained from the fossil fuel-powered alternator. But PV system mounted in a vehicle driving in urban traffic generates about 18% less energy than an identical open-air stationary system [5].

Based on experimental research conducted in Central Europe (Poland), this paper analyzes the impact of photovoltaic panels installed on city buses operating in the latitude of the city of Split in Croatia on reducing fuel consumption. In Poland, the yearly global value of horizontal irradiation GHI is 1,100 kWh/m^2, while for Split it is 1600 kWh/m^2. In addition, the temperature and sunlight profile per year is different for these two different latitudes as shown in the article. The article presents an experimental study of electricity consumption of a city bus with diesel engine equipped with photovoltaic installation. The electricity consumed by the bus and the electricity produced from standard alternators and PV systems were recorded. Figure show the electricity consumption, production by the PV system and the sets of alternators per year. The bus consumed 6,328 kWh of electricity of which 4,499 kWh was produced from alternators powered by an internal combustion engine that consumes diesel fuel, and PV panels located on the roof of the bus produced 1,829 kWh.

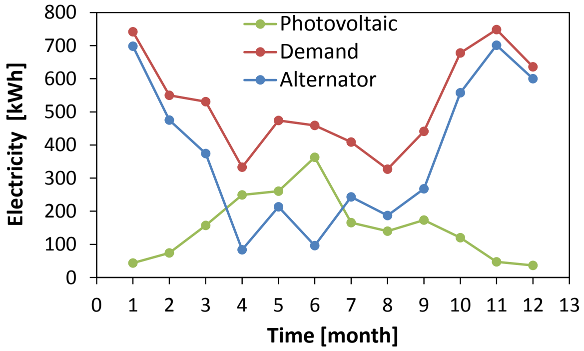

Figure 1. Electricity consumption by the city bus and electricity output per year by the hybrid solar electric system. Blueline – electricity consumption, green line – electricity production by the PV system, red line – electricity production by the set of the alternators.

Mentioned theoretical efficiency of the conversion of chemical energy of fuel into electricity is on average 20%, which means that a liter of fuel (10 kWh) produces 2 kWh of electricity. The theoretical K-factor is 0.5 dm3/kWh. The PV system is able to replace 24% of annual electricity consumption from diesel engine city bus, which at the same time will reduce 3% of fuel consumption and accordingly CO_2 emission. This means that one Split bus will consume less diesel fuel of about 720 dm3 per year. Bus transport in Split have 19 city routes and 6 suburban lines. City bus zones are operated by 170 buses. The next research will include an overall techno-economic analysis of the application of solar panels to the entire fleet of buses.

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Michal Jan Geca received Ph.D. degree in the Faculty of Mechanical Engineering at the Lublin University of Technology, Poland, in 2015. He is a researcher at the Lublin University of Technology for 15 years. His current research interests include data analysis from combustion engines. Also, his research work includes a comparison between solar radiation reaching steady and moving objects. He is an author of more than 50 scientific articles and 2 patents, is involved in many national and European projects including 7 FP UE. All research carried out is directed to practical application and close Business- Science cooperation. He conducts research concerning the photovoltaic technology application in the automotive industry.

Corresponding author: Michal Jan Geca, e-mail: m.geca@pollub.pl, tel.: +48 81 538 4764

High entropy transition metals oxides - applications in electrochemical energy storage

Janina Molenda[1]

[1]AGH University of Science and Technology, Faculty of Energy and Fuels, Department of
Hydrogen Energy, al. Mickiewicza 30, 30-059 Krakow, Poland

The author of this work basing on her own investigations of A_xMO_2 cathode materials (A=Li, Na; M=Ni, Co, Mn, Fe, Ti, Cu) has demonstrated that the electronic structure of these materials plays an important role in the electrochemical intercalation process [1]. The paper reveals correlation between crystal and electronic structure, chemical disorder, transport and electrochemical properties of layered Na_xCoO_{2-y}, $Na_xCo_{1-y}Fe_yO_{2-y}$ and $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ high entropy cathode materials and explains of apparently different character of the discharge/charge curve in those systems. The complex studies, including experimental as well as theoretical parts (electronic structure calculations performed using the Korringa-Kohn-Rostoker method with the coherent potential approximation KKR-CPA to account for chemical disorder), showed a strong correlation between structural, transport and electrochemical properties of these materials.

The battery on the base on the developed high entropy oxides $NaNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ cathode materials are characterized by high potential, high capacity and high rate capability guaranteeing high energy and power densities. The quickly appearing of O3-P3 phase transformation in this oxide leads to metallic conductivity and better kinetics of $Na|Na^+|Na_xMn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}O_2$ cell. By using the structural analysis methods (operando XRD, XAS and Mossbauer spectroscopy) we described the mechanism that governs the sodium deintercalation/intercalation processes in $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ cathode with indicating the valence state of transition metals. Our investigation indicated that only titanium is electrochemically inactive during the cell operation, while Mn, Fe, Co, Ni undergo reduction and oxidation processes [2].

The detailed analysis presented in this work provides a strong proof that the high-entropy $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ oxide with reduced content of cobalt and nickel, might be applicable in sodium batteries technology, especially in terms of large-scale energy storage units.

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Prof. J. Molenda was listed in the prestigious world list of Stanford University of the TOP 2% highest cited scientists. Prof. J.Molenda for many years has been developing materials for Li-ion batteries as well as for a new generation of Na-ion batteries http://home.agh.edu.pl/~molenda).Scientific publications authored by J. Molenda comprise works on the relationship between the nature of chemical bonds, crystal and electronic structures, and the reactivity of solids. The new discipline of science being developed by the author – electronic states engineering – provides an effective method of finding new materials for Li-ion and Na-ion batteries and development of their functional properties.

Presentating author: Janina Molenda, e-mail: molenda@agh.edu.pl tel: +48 12 617 2522

Influence of fin number on paraffin melting and solidification in the longitudinally finned latent thermal energy storage

Mateo Kirinčić, Anica Trp, Kristian Lenić, Josip Batista
University of Rijeka, Faculty of Engineering, Rijeka, Croatia

In order to effectively counter the dependency on fossil fuels and challenges of increased pollution, it is necessary to effectively utilize the energy from renewable sources, primarily solar energy. Though a major energy source, solar energy's main disadvantage is its intermittent nature. Various types of thermal energy storage are used to counter this issue, most commonly sensible (STES) and latent thermal energy storage (LTES). In LTES, the phase change material (PCM) undergoes phase change, storing and releasing additional energy as a result. The heat transfer fluid (HTF) flows through the LTES, providing heat to the PCM during melting, and drawing heat from the PCM during solidification. Organic PCMs (paraffins and fatty acids) are often used due to their stability, small volume change during phase change and large latent heat content. However, their main disadvantage is low thermal conductivity [1]. Various attempts have been made towards enhancing heat transfer between the HTF and the PCM, the most common of which being the implementation of fins on the PCM-side in order to increase the total heat transfer surface area. Various fin shapes and configurations have been reported, such as longitudinal, radial, spiral etc. Among them, longitudinal fins are most widely used [2].

This paper presents a numerical study regarding the influence of the number of fins on heat transfer in the longitudinally finned shell-and-tube type LTES using paraffin as the PCM and water as the HTF. Mathematical model, based on the enthalpy formulation, has been defined for the physical problem of transient forced convection and phase change heat transfer. The existing numerical procedure in the Fluent solver has been expanded with a set of user-defined functions to simulate phase change heat transfer. An experimental shell-and-tube LTES tank, consisting of 19 concentric tubes, with 8 equidistant longitudinal fins on each tube, has been constructed and measurements have been performed to validate the mathematical model and numerical procedure. Numerical calculations have been performed both for melting and solidification to evaluate the influence of fin number (N) on heat transfer. Three LTES configurations have been examined; with 4, 8 and 12 fins and contours of temperature and liquid fraction, as well as total heat stored/released during charging/discharging period and times at which the PCM is fully melted/solidified have been obtained.

The results show that increasing the number of fins significantly increases heat transfer during both melting and solidification processes. Time at which the PCM is fully melted or solidified (shown in Figure 1) significantly reduces with the increase of fin number since heat transfer surface area is increased, which expedites heat transfer. The amount of stored/released heat also increases with the increase in number of fins. However, this increase is only moderate since adding fins reduces the amount of the PCM in LTES which in turn reduces its heat storing capacity.

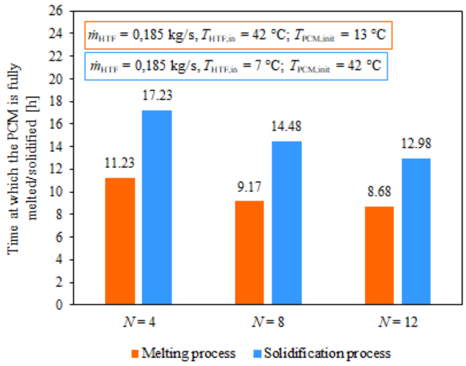

Figure 1. Times at which the PCM is fully melted/solidified for different number of fins

The present study provides insights into the influence of fin number on paraffin melting and solidification processes. While melting/solidification time can be significantly reduced by installing additional fins, adding fins can potentially reduce the amount of stored/released heat.

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Mateo Kirinčić

D. Sc. Mateo Kirinčić is a postdoctoral researcher at the Department of Thermodynamics and Energy Engineering of the University of Rijeka, Faculty of Engineering. He earned a master's degree in mechanical engineering at the Faculty of Engineering in 2015 and attained a doctoral degree in 2021 at the same institution. His research interests include latent thermal energy storage, heat exchangers, renewable energy sources and numerical modeling of heat and mass transfer.

Corresponding author: Mateo Kirinčić, e-mail: mateo.kirincic@riteh.hr, tel: +385 51 651 517

Recent advances and perspectives in diagnostics and degradation of electrochemical hydrogen compressors

Ivan Pivac [1,2], Anamarija Stoilova Pavasović [1,2,3] Frano Barbir [1,2]
[1]FESB, University of Split, R Boskovica 32, 21000 Split, Croatia
[2]Center of Excellence STIM, University of Split, R Boskovica 31, 21000 Split, Croatia
[3]KTF, University of Split, R Boskovica 35, 21000 Split, Croatia

In order for hydrogen to become a widespread energy carrier, its purification and compression are unavoidable industrial processes. Hydrogen is typically required at elevated pressures, depending on its application, in order to increase its density and to reduce its volume. For instance, hydrogen used in industrial processes like ammonia production requires 20 MPa, while the hydrogen refueling stations for automotive applications have to reach up 70 MPa or even higher. Today, the most commonly used hydrogen compressors in the industry are mechanical, pneumatically and electrically – driven, whose disadvantages include vibrations and noise due to their moving parts [1,2]. However, electrochemical hydrogen compression (EHC) systems [3–5], also known as electrochemical hydrogen pumps (as they could be used also for hydrogen recirculation in a fuel cell stacks [6,7]), enable both gas purification and compression for storage with high energy efficiency and pressurization capacity up to 100 MPa in a single stage [8], and they are noiseless due to lack of moving parts. Moreover, from the theoretical point of view, isothermal compression on which is an EHC based is preferable to adiabatic mechanical compression. Actual compression work is usually slightly larger than the one calculated using the adiabatic compression formula owning to additional losses. Therefore, energy consumption is not negligible and have to be considered in the overall chain of hydrogen supply. All of these advantages also impose potential for lower capital costs in the perspective, longer lifetime, and less scheduled or unscheduled maintenance needs. However, the main drawbacks of the EHCs are back-diffusion, which includes permeation of compressed hydrogen from the cathode side across the membrane to the anode side, water management inside an EHC due to fact that proton (H^+) conductivity through the membrane is a function of membrane water content, and ohmic resistance directly related to membrane thickness as well. In addition, the EHCs must promote fast hydrogen oxidation reaction and high poison-tolerance, while their expected operating lifetime should be at least equal or preferably longer than the competition.

In general, the EHCs would only be (economically) competitive to their competing compression technologies provided if they could operate in very intensive conditions: high current densities (above 2 A cm^{-2} or even higher), combined with low cell voltage (likely below 0.5 V) and high differential pressure per cell (likely 5–7 MPa). Reaching these performances would be desirable (if not mandatory), but they could be achieved only if the EHC core materials (the membrane and the electrodes/electrocatalysts, primarily the anode), are optimized [9]. However, optimization is not feasible without proper diagnostics methods applied, which would emphasize the critical issues on the EHC performance (output pressure and efficiency). On the other hand, each of EHC structural components is susceptible to various decay mechanisms that can be associated with different types of performance losses. Therefore, the endurance of EHCs is still considered to be a critical parameter in life-cycle costs and require further exploration with the aim of MEA deterioration recognition during the operation and its deeper understanding considering the degradation mechanisms.

Therefore, a critical overview of the EHC progress and state-of-the-art performance diagnostics, durability testing methods and possible degradation mechanisms that could affect the desired performance is provided here. The review also critically gives current technology shortcomings and challenges, mostly considering the existing testing procedures issues of EHC state-of-health, but also suggests potential development ideas for improvements in perspective.

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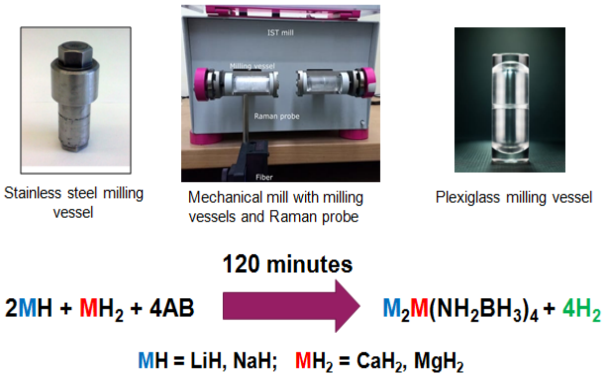
Anamarija Stoilova Pavasovic was born on April 19, 1991 in Split, Croatia. After high school, she enrolled in the Chemical engineering at the Faculty of chemistry and technology (KTF). From January 2018 she has been working as a Research Assistant on the project under Center of excellence STIM, University of Split and joined the research group of Prof. Frano Barbir at the Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture (FESB). From 2018 she also enrolled in postgraduate study of Chemical Engineering in Materials Development and Environmental Protection at KTF.

Presentating author: Anamarija Stoilova Pavasović, e-mail: astoilov@fesb.hr tel: +38521305946

Novel Mg and Ca Containing Bimetallic Amidoboranes - Mechanochemical Study

Igor Milanović[1,2], Nikola Biliškov[2], K. Užarević[2], S. Lukin[2] and I. Halasz[2]
[1]Vinča Institute of Nuclear Sciences−National Institute of the Republic of Serbia,
Centre of Excellence for Hydrogen and Renewable Energy−CONVINCE, 11000 Belgrade, Serbia
[2]Ruđer Bošković Institute, Zagreb, Croatia

Mechanochemistry can be very useful technique for synthesis of bimetallic amidoboranes - very prominent materials for solid state hydrogen storage. By using the mechanical ball milling technique, solventless solid state reaction between ammonia borane (NH_3BH_3, AB), alkali metal hydrides (NaH, LiH) and alkaline earth metal hydrides (CaH_2 and MgH_2) is absolutely possible [1-3]. Exclusively hydrogen and bimetallic amidoboranes could be obtained as final products.
Using the Raman spectroscopy for solid state in-situ monitoring of reaction between ammonia borane and hydrides we firstly synthesized two mixed metal Mg-containing amidoboranes - $M_2Mg(NH_2BH_3)_4$ (M=Li, Na). As a milling equipment we used PMMA (plexiglass) jars and stainless steel balls. Mentioned approach allowed real time observation of key intermediate phases and a straightforward follow-up of the reaction course. Detailed analysis of time-dependent spectra revealed a two-step mechanism through $MNH_2BH_3 \cdot NH_3BH_3$ adducts as key intermediate phases which further reacted with MgH_2, giving $M_2Mg(NH_2BH_3)_4$ as final products [1].
After the success with Mg-containing amidoboranes we have also developed a new green and rapid mechanochemical procedure for the synthesis of Ca-containing alkaline metal amidoboranes [2], $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$, using similar approach – solid state reaction between metal hydrides and ammonia borane. The tandem technique - in-situ X-Ray diffraction with temperature profile measurement was used for monitoring of mechanochemical syntheses. On such a way we revealed how the course of the reactions and their thermal profiles strongly depend on the starting alkali metal hydride. For instance, NaH induced a sudden and dramatic increase in temperature of the reaction mixture, which induced a partial decomposition of thermally labile AB and influenced the yield and composition of reaction products. The changing of milling reactor material from insulating plastics (PMMA) to thermally conductive stainless steel readily amended this issue, most likely through more effective heat dissipation.
In summary, solid state chemical reaction for bimetallic amidoborane synthesis is shown in Figure 1. On such a way we successfully synthetized four new compounds - $Na_2Mg(NH_2BH_3)_4$, $Li_2Mg(NH_2BH_3)_4$, $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$. In all cases, as a products only mixed metal amidoborane and hydrogen gas are obtained, without usage of any solvent. This means that such kind of synthesis is fulfilling all aspects of green synthesis.



Stainless steel milling vessel

Mechanical mill with milling vessels and Raman probe

Plexiglass milling vessel

$$2MH + MH_2 + 4AB \xrightarrow{\text{120 minutes}} M_2M(NH_2BH_3)_4 + 4H_2$$

MH = LiH, NaH; MH_2 = CaH_2, MgH_2

Figure 1. Mechanochemical equipment for synthesis (up) and reaction during the solid state reaction between hydrides and ammonia borane (down).

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Dr. Igor Milanović is working in the Vinča Institute of Nuclear Sciences − National Institute of the Republic of Serbia, University of Belgrade, Serbia. Having graduated from Faculty of Physical Chemistry in University of Belgrade in 2010, Igor Milanović obtained his M.SC in 2011 and Ph.D. in 2015 in the same institution. In period between 2017 and 2019 he attended postdoctoral studies in Ruđer Bošković Institute, Zagreb, Croatia. His research interest covers investigation of hydrogen storage materials and tanks, vacuum techniques in analysis and hydrogen evolution reaction.

Corresponding author: Igor Milanović, e-mail: igorm@vin.bg.ac.rs tel: +381 64 262 79 94

Hydrogen absorption-desorption properties and hydrolysis performance of MgH_2–$Zr_3V_3O_{0.6}H_x$-graphite composites

Ihor Zavaliy[1], Roman Denys[2], Vasyl Berezovets[1] and Volodymyr Yartys[2]
[1] Physico-Mechanical Institute of the NAS of Ukraine. 5, Naukova str., 79060, Lviv, Ukraine.
[2] Institute for Energy Technology, P.O. Box 40, N-2027, Kjeller, Norway

Recently hydrogen generation via hydrolysis of magnesium hydride and its subsequent use to power PEM fuel cells attracts attention [1,2]. Efficient synthesis of magnesium hydride can be achieved by utilizing mechanochemical synthesis when employing various catalysts [3]. In this paper we employed reactive mechanical milling (RMM) in hydrogen for the synthesis of magnesium hydride and prepared its composites utilized for a dual purpose. Effective hydrogen storage and hydrogen generation by hydrolysis has been achieved by utilizing nanostructured magnesium hydride synthesized by the mechanochemical synthesis. Increased yield of the hydrolysis and enhanced reaction rate of MgH_2 interaction with water have been achieved.

MgH_2-based nanocomposites were synthesized by the RMM of magnesium together with 10 wt.% of catalytic additive of $Zr_3V_3O_{0.6}$ suboxide and 3 wt.% graphite. Magnesium powder, single-phase suboxide $Zr_3V_3O_{0.6}$ (homogenized at 1000 °C) and chemically pure graphite were used as the starting components for the synthesis of hydride nanocomposites. We found that the rate of the hydrogenation during the RMM is almost three times higher than in the process of the grinding of pure magnesium without a catalyzing additive. A close to complete saturation of the composite mixture by hydrogen (maximum H content reached was 7.0 wt.% H) occurred after 2 hours of the milling. 3 wt.% of added to the Mg–$Zr_3V_3O_{0.6}$ mixture graphite causes an increased rate of the mechanochemical hydrogenation (<90 min). After desorption of hydrogen from the hydride composite, it was re-hydrogenated at hydrogen pressure of 2 MPa and temperatures between 20 and 350 °C. Even at room temperature the ternary composite slowly absorbed hydrogen, even though it took several hours for a complete saturation. The rate of hydrogen absorption increased in several times with increasing processing temperature. Thus, at 100 °C, Mg–10%$Zr_3V_3O_{0.6}$–3%C composite reached a capacity of 6 wt.% within 40 min from the start of the hydrogenation, whereas at 200 °C the composite was saturated by hydrogen immediately, in just 30 sec. Hydrogen desorption studies from the composites were performed into a system with a constant volume at constant temperatures, when using a Sieverts-type installation. Desorption of hydrogen from the Mg–10% $Zr_3V_3O_{0.6}$–3%C composite at 350 °C at initial pressure of H_2 of 0.17 MPa occurred within 3 min. For all composites, the amount of released hydrogen exceeded 6.0 wt.% H. After 5 cycles of hydrogen absorption-desorption performed at 350 °C, the reversible hydrogen absorption capacity remained unchanged.

To study the effect of carbon on the properties of the composites, the samples after hydrogen desorption at 350 °C into a dynamic vacuum (10^{-3} Pa) were re-hydrogenated under the same conditions. Hydrogen absorption curves for these composites measured at 150 and 200 °C are shown in Fig.1. Both composites were characterized by extremely high rates of hydrogen absorption. However, for the C-free material, absorption almost stopped when the capacity reached 4.3-4.5 wt.% H, while for the C-modified composite a much deeper saturation (6.0-6.5 wt.% H) has been achieved.

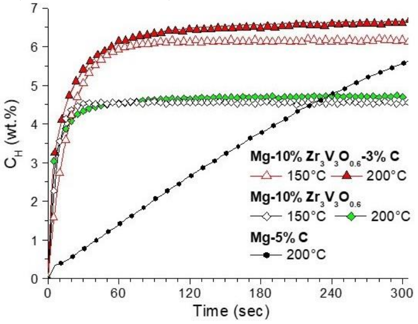

Figure 1. Hydrogen absorption curves by Mg–10% $Zr_3V_3O_{0.6}$ and Mg–10% $Zr_3V_3O_{0.6}$–3%C composites at 2 MPa H_2.

To determine the activation energy (E_a) of hydrogen desorption from the hydride composite Mg-10% –$Zr_3V_3O_{0.6}$–3%C, the thermodesorption spectra of hydrogen evolution at the constant heating rates of 0.5…5 °C/min were studied. For the ternary composite the activation energy calculated using the Kissinger dependencies was found to be 58 kJ/mol and was the smallest for the studied materials. The influence of mechanochemical milling of MgH_2 with the abovementioned additives on the efficiency of hydrolysis generating hydrogen gas in pure water and $MgCl_2$ solutions has been studied [2]. The RMM of Mg mixed with $Zr_3V_3O_{0.6}$ suboxide improves the reaction rate of the hydrolysis and increases hydrogen yield. The use of graphite as an additive further increased the yield of the hydrolysis reaction, from 270 ml/g to 460 ml/g in pure water and from 310 ml/g to 760 ml/g in 0.01 M $MgCl_2$ solution.

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Prof. Ihor Zavaliy is the head of the Dep. of hydrogen technologies and materials of alternative energy, Karpenko Physico-Mechanical Institute of the NAS of Ukraine. He is an expert in: Materials for Hydrogen Storage and Battery Applications(a); Nanomaterials and their properties(b); H-generation systems (c). https://orcid.org/0000-0002-9825-6922.
Corresponding author: Ihor Zavaliy, e-mail: ihor.zavaliy@gmail.com, tel: +38 032 2296833

Optimization of one-dimensional $Ca_3Co_2O_6$ electrodes for Solid Oxide Fuel Cells

Allan J. M. Araújo[1], Klivia P. V. Melo[2], João P. F. Grilo[3],
Daniel A. Macedo[2], Duncan P. Fagg[1], Francisco J. A. Loureiro[1]

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

[2] Materials Science and Engineering Postgraduate Program – PPCEM, Federal University of Paraíba – UFPB, João Pessoa, 58051-900, Brazil

[3] Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, 3810-193, Portugal

A future energy system, based exclusively on renewable sources, relies heavily on technologies capable of converting fuels into electricity with high efficiency. In such a context, solid oxide fuel cells (SOFCs) are of urgent interest [1]. However, one of the main components still requiring optimization is that of the oxygen electrode [1]. In this regard, the two-dimensional $Ca_3Co_4O_9$ (C349) mixed ionic electronic conductor (MIEC) has emerged as an exciting candidate due to its excellent thermal compatibility with typical electrolyte materials and highly favorable surface-exchange kinetics (1.6×10^{-7} cm s^{-1} at 700 °C) [2,3]. Nonetheless, under sufficiently lower oxygen partial pressures (*e.g.*, p_{O2} = ~10^{-4} atm at 700 °C) this material undergoes structural decomposition into the one-dimensional $Ca_3Co_2O_6$ (C326) compound [2,3]. Such a behavior has been shown to be dramatically accentuated towards less oxidizing conditions and high temperatures [2]; factors required for application in typical SOFC environments [1,3].

On the other hand, the direct use of a C326 electrode-based composition has been discarded due to its poor ionic transport compared to C349 [3]. Hence, if such constraint could be addressed, the C326 would be a much more interesting alternative to C349 compounds due to higher stability under the above-described SOFC requirements.

To accommodate such an idea, the processing of screen printed C326 electrodes was optimized in this work. Several symmetrical cells of C326 electrodes, using $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO10) electrolyte substrates, were prepared by varying the sintering temperature of the electrode films (950 °C, 975 °C and 1000 ºC). The polarization resistance (R_p) of the different cells shows a decrease with increasing sintering temperature, achieving the lowest R_p value of 1.1 Ω cm^2 at a measuring temperature of 800 ºC (Figure 1). Such an interesting result was tentatively explained based on a better sintering of the ceramic interfaces and improved connectivity between grains [4]. Furthermore, this factor was also noticed in an electrode composition containing 50 wt.% of CGO10 (Figure 1). The composite electrode shows a R_p value of ~0.7 Ω cm^2 at 800 °C, which can be considered as representative for SOFC electrodes (*i.e.*, 0.5 Ω cm^2, irrespective of the temperature [1]). Hence, this work demonstrates the feasibility of C326/CGO composites as promising cathode materials for SOFC applications.

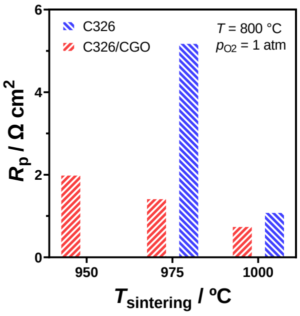

Figure 1. Variation of the total polarization resistance (R_p) of both C326 and C326/CGO composites as a function of sintering temperature.

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Dr. Allan Araújo obtained his PhD in Materials Science and Engineering from the Federal University of Rio Grande do Norte (UFRN/Brazil), focusing on solid-state mixed ionic-electronic conductors (MIECs) for energy conversion applications. Currently, he is working as a post-doctoral researcher in TEMA/University of Aveiro (Portugal). His research interests are especially related to solid-state electrochemistry and modelling of electrode mechanisms (transport processes in the time and frequency domain).

Presenting author: Allan Araújo, e-mail: allan@ua.pt.

Hydrogen storage properties of $LaCrO_3$ perovskite-type oxides: numerical and experimental study

Mohamed Amine Lahlou Nabil[1,2], **Nouredine Fenineche**[1,2*], **Ioana Popa**[3], **Joan Josep Sunyol**[4]
[1]ICB-PMDM, UBFC University, UTBM, Rue du Leupe 90040 Sevenans, France
[2]FR FCLAB, UTBM bât. F, Rue Thierry Mieg, 90010 Belfort Cedex, France
[3]ICB, UMR CNRS 6303, UBFC University, 9 Av. Alain Savary, 21078 Dijon Cedex, France
[4]Dep de Fisica, Universitat de Girona, Campus Montilivi, Girona 17071, Spain
* mohamed.lahlou-nabil@utbm.fr

Introduction

Hydrogen represents a clean source and very important energy vector. Hydrogen has always been the focus of related research because of the high value of its energetic density. Hydrogen is primarily produced using two principal methods: steam reforming and electrolysis. Steam reforming is a high temperature process in which steam reacts with hydrocarbon fuel to produce hydrogen. Moreover, hydrogen can also be produced by reforming hydrocarbon fuels such as natural gas, diesel, renewable liquid fuels and gasified cool or gasified biomass. Electrolysis is a process that split water into hydrogen and oxygen using an electric current. Hydrogen is an efficient way to store and transport energy. Hydrogen is also used for electricity production through a fuel cell which produces electricity by converting chemical energy into electrical energy. Solid hydrogen storage represents an important economic issue and is nowadays a promising technology for fuel cells vehicles since the volumetric hydrogen density of materials is usually higher than 100 Kg/m^3. Therefore, smaller tanks can be used to store large amounts of hydrogen [1–2]. The aim of the present work is to study the hydrogen storage properties of the perovskite-type oxide $LaCrO_3$, as there is no experimental study in the literature on perovskite type oxides materials for hydrogen solid storage, with the exception of the numerical study of Gencer et al [3]. In this study, a double approach is carried out. A numerical approach consists in studying the system $LaCrO_3$ before and after restitution of hydrogen atoms by using ab initio calculations. An experimental approach focuses on the elaboration of the perovskite type oxide, then a structural and morphological characterization is carried out before measuring the storage capacities. Therefore, the present paper presents the perovskite type oxide $LaCrO_3$ as a novel material dedicated for hydrogen storage.

Results and discussions

In order to determine the calcination temperature allowing to obtain a well crystalized oxide, the as-dryed precursor of $LaCrO_3$ was analyzed by thermogravimetry and differential temperature analysis. In order to determine hydrogen storage properties PCT results are shown in figure 1. The three samples of $LaCrO_3$ show almost the same hydrogen sorption and desorption capacities and they all show a hydrogen storage capacity up to 4wt % under 333 K. Thus, each sample has trays one for absorption and the second for desorption. At 303K, the samples tested have the lowest storage capacity. The maximum storage capacity increases from with the increase of temperature. This variation can be explained by the fact that the compound is not tested at its optimum absorption and desorption temperature.

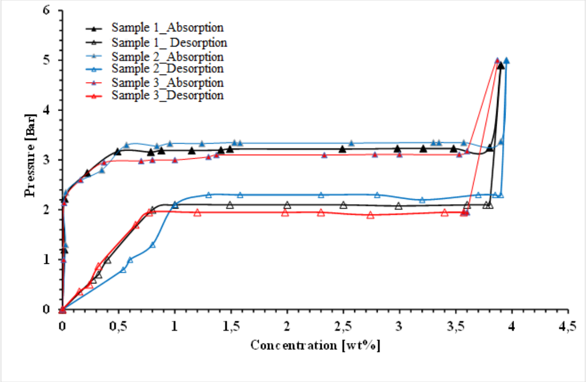

Figure 1: PCT Curves of $LaCrO_3$ at 333K.

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The presenting author obtained his PhD in materials science from the University of Technology of Belfort-Montbéliard in France. Actually, working on hydrogen storage in metallic hydrides for electric vehicles.

Presentating author: Lahlou Nabil Mohamed Amine, e-mail: mohamed.lahlou-nabil@utbm.fr

$Ba_2NiMoO_{6-\delta}$ as a potential electrode for protonic ceramic fuel cells at intermediate temperature (400-600°C).

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

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

Perovskite related materials exhibit several fundamentally interesting chemical and physical properties, which can be combined in a single material, and where these properties can be refined for application as possible electrode materials by compositional modification [1]. For example, their structural and compositional flexibility can allow partial cation substitution on the A or B sites, giving rise to a subclass of the perovskite family, commonly designated as double perovskites ($A_2BB'X_6$) [2]. Double perovskites are gaining special interest as electrocatalysts, due to their good chemical stability, high eletronic conductvity and high electrocatalytic activity for the oxygen evolution, oxygen reduction and hydrogen evolution reactions [3].

In this work we investigate the use of the layered double perovskite $Ba_2NiMoO_{6-\delta}$ (BNMO) as a potential electrode for protonic ceramic fuel cells in the intermediate temperature range (400-600°C). Studies of chemical stability and compatibility, as well electrochemical performance were performed as function of composition, by varying the compositional ratio of $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$(BCZY712)-BNMO in composite electrodes.

Chemical stability results reveal that the BNMO composition maintains its integrity in O_2, N_2 and $10H_2$-N_2, at temperatures below 600°C and is fully compatible with the BCZY712 protonic electrolyte phase at T<1100°C. In contrast, in carbonaceous atmospheres the perovskite BNMO phase is shown to decomposes into barium carbonate ($BaCO_3$) and barium molibdenate ($BaMoO_4$).

To understand the electrochemical behaviour of BNMO and BNMO-BCZY composites, symmetrical cells were prepared and tested, where the electrode materials were deposited on BCZY712 electrolytes by screen printing method and studied using electrochemical impedance spectroscopy in wet O_2 (pH_2O=0.03 atm) in the temperature range 600-400°C. Results reveal that the BNMO-BCZY712 composites can exhibit good electrochemical performance, with the best behaviour offered by the 40vol% BNMO-BZY712 composite composition.

To the best of our knowledge this is the first study of the layered BNMO double perovskite for proton conducting applications. Continued work aims to further improve these electrodes by control of electrode thickness and processing parameters.

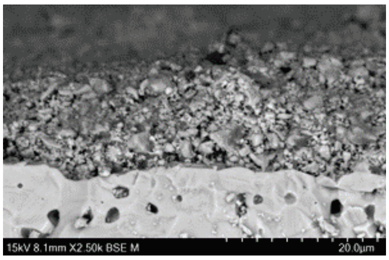

Figure 1. SEM micrograph of BNMO-BCZY712 composite.

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The authors would like to express their gratitude to the Fundação para a Ciência e Tecnologia (FCT) for the following grants/projects: SFRH/BD/130218/2017, PD/BDE/142837/2018, CEECIND/02797/2020, PTDC/CTM-CTM/2156/2020, PTDC/QUI-ELT/3681/2020, POCI-01-0247-FEDER-039926, POCI-01-0145-FEDER-032241, UIDB/00481/2020, UIDP/00481/2020 and also to CENTRO-01-0145-FEDER-022083 – Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). We acknowledge LAQV-REQUIMTE Aveiro (FCT UIDB/50006/2020) and Jorge Saraiva, for kindly carrying out the isostatic pressing of the samples.

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

The crucial role of green hydrogen for heading towards sustainable energy systems

Reinhard Haas [1]and Amela Ajanovic
[1] Energy Economics Group, Vienna University of Technology, 1040 Vienna, Austria

Hydrogen is among the energy carriers most often named for bringing about a sustainable energy system. However, so far in the real energy world hydrogen has been very far away from fulfilling the promises. An argument for the increasing interest in hydrogen in recent years is the rising electricity generation from variable renewable energy sources (VRES) such as solar and wind energy and the accompanying need for long-term storage for surplus electricity. A resulting expectation is that soon high quantities of clean "green" and cheap hydrogen could be provided by these sources world-wide.

Figure1 shows an example for the imbalances between load and electricity generation from variable RES e.g. from wind and photovoltaic systems. The graph shows a hypothetical situation with a high quantity of variable electricity production using monitored hourly data over a summer week for the example of Austria. High volatility in electricity market prices can be noticed. With the increasing electricity generation from VRES also larger quantities of temporarily cheap excess electricity could become available [1]. Hydrogen could be a storage opportunity to meet the challenge of evening out this imbalance.

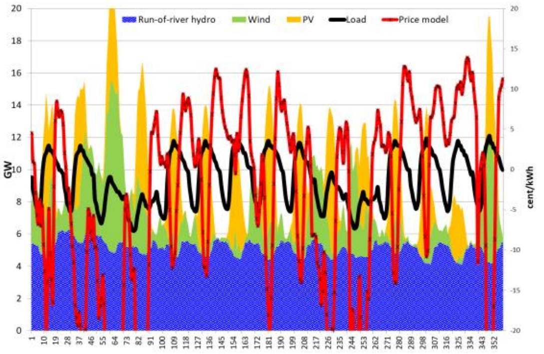

Fig. 1. Example: electricity generation over two summer weeks from variable renewables and load on an hourly base, as well as corresponding wholesale prices

The core objectives of this paper are: (i) to analyze how efficient technical solutions based on hydrogen can be implemented considering whole conversion chains, (ii) how the economics of green hydrogen is today and what are prospects for the future, (iv) to identify the major barriers aside from economics, (v) to analyze and discuss which policy strategies should be implemented to accelerate the use of hydrogen and (vi) to analyze, which hydrogen application should be targeted.

Background. Already in 2003, the European Commission presented a roadmap how an integrated energy system based on hydrogen and fuel cells might look up to 2050 [2].

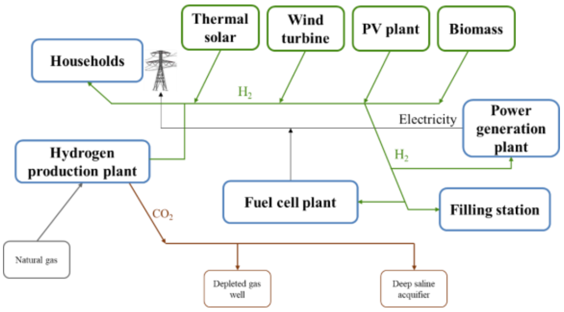

Fig. 2. The vision of a hydrogen-based energy system

However, neither the goals regarding production and dissemination technologies of hydrogen, envisaged in the early 2000s nor the targets regarding fuel cells and hydrogen systems have so far been met. An integrated energy system of the future, based on the EU-roadmap is illustrated in Fig. 2. It shows that a hydrogen-based energy system combines large and small fuel cells for centralized and decentralised heat and electrical power generation. In such a vision hydrogen would be distributed through pipelines. However, none of these hydrogen visions has so far to any extent put into practice.

Today the idea of green hydrogen – produced from electrolysis using electricity from hydro, photovoltaics and wind – is most popular. Yet, the major problem are the high production costs, mainly the investment costs of the electrolyzers. However, due to so-called Technological Learning (TL) especially the electrolyzer costs in future are expected to decrease. This possible TL-effect for electrolyzers is shown in Fig. 3. This Figure shows the possible development of investment costs for small and large hydrogen plants with high and low learning rates. Over the period, from 2020 to 2050, investment costs are expected to decrease by about 30% for both electrolyzer size variants.

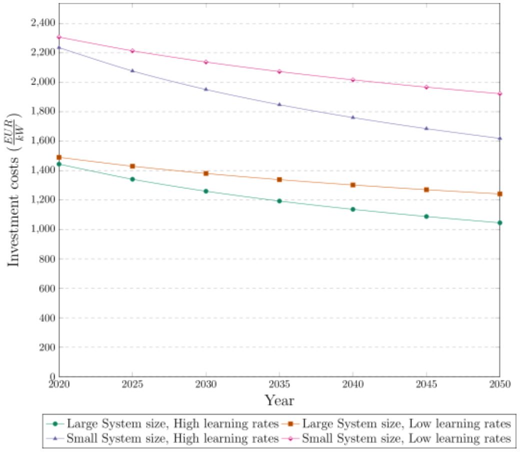

Fig. 3. Perspectives of the development of investment costs of small and large electrolysis plants depending on learning rates

The major conclusions of this analysis are: (i) several technologies for the production of hydrogen exist with the best future prospects for electrolyzers; (ii) re-electrification of hydrogen will be less attractive because of low overall efficiency and high costs; (iii) for reducing hydrogen production costs by electrolysis of high relevance is to increase full-load hours, as well as the full exploitation of economies-of-scale and technological learning; (iv) there is also a broad portfolio of options for hydrogen use in different sectors; (v) Cost reduction of fuel cells due to technological learning is essential for the economic competitiveness of hydrogen; (vi) in the long-term hydrogen use in industry will be increasingly needed. However, also here the development of proper technologies is most crucial.

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$Na(Mn,Fe,Co,Ni,Cu,M)O_2$ (M-Ti, V, Al) six-component oxides – cathode materials for Na-ion batteries

Anna Milewska [1], Wojciech Zajac [1], Janusz Tobola [2] and Janina Molenda [1]

[1] AGH University of Science and Technology, Faculty of Energy and Fuels, Al. Mickiewicza 30, 30-059, Krakow, Poland

[2] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Al. Mickiewicza 30, 30-059, Krakow, Poland

In the last decade, intensive research has been carried out on electrode and electrolyte materials for lithium and sodium batteries belonging to the group of high entropy oxides (HEOs) with increased structural stability, and thus enhanced cyclic performance. This work contains the results of research conducted on O3-type layered six-component

This material was obtained using high-temperature solid state reaction and low-temperature sol-gel methods. In order to determine the mechanism of the electrochemical (de)intercalation in $Na_xMn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}Ti_{1/6}O_2$ XRD *in-situ* measurements and transport properties measurements were performed. When compare to $NaMn_{0.25}Fe_{0.25}Co_{0.25}Ni_{0.25}O_2$ [1] mentioned oxide shows only one O3/P3 phase transition. Based on the conducted electrochemical tests, we analysed the influence of the O3/P3 phase transformation on the battery performance. XAS total-electron yield (TEY) measurements show that only nickel, cobalt and manganese are electrochemically active during charging and discharging of the battery in the 1.5-3.9 V range. Obtained results were supported by the electronic structure calculations (KKR-CPA method), which indicated that elements tend to form clusters. The other results regarding six-component oxides with improved electrochemical properties are also presented.

Acknowledgement:

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Photo of the presenting author

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She graduated from the Faculty of Materials Science and Ceramics of AGH UST. She obtained a PhD degree in the field of material science in 2002 at AGH UST. Employed at the Faculty of Energy and Fuels of AGH UST in the Department of Hydrogen Energy. Scientific activity in the field of: material science in the field of lithium and sodium cells (Li-ion batteries, Na-ion batteries).

Presentating author: Dr. Anna Milewska, e-mail: amilewsk@agh.edu.pl tel: 48 12 617 20 80

Effect of palladium coating on hydrogen storage and hydrogen separation features of high-entropy alloys

Ivan Savvotin[1], Vladislav Zadorozhnyy[2], Elena Berdonosova[1], Mikhail Zadorozhnyy[2],
Korol Artem[2], Semen Klyamkin[1].
[1] Lomonosov Moscow State University, Chemistry Department, Leninskie Gory 1/3, Moscow, 119991 Russia
[2] National University of Science and Technology “MISIS”, Leninsky prospect 4, 119049 Moscow, Russia

Multicomponent alloys with close to the equiatomic component content, crystallizing in the form of solid solutions with a BCC and FCC type structure, the so-called high-entropy alloys (HEAs), attract a great attention due to the combination of unique mechanical, physical and chemical properties. An abnormally high sorption capacity respect to hydrogen was found for this class of alloys [1]. Moreover, group 5 metals (V, Nb, Ta), which are part of many HEAs, have a uniquely high permeability to hydrogen, especially at close to room temperatures [2], which makes them particularly attractive for membrane hydrogen separation. However, the use of HEAs in membranes, especially composite metal-polymer membranes, is significantly hampered due to their tendency for surface passivation. To overcome this problem, it is proposed to spray palladium directly onto the HEA particles during the manufacture of metal-polymer membranes.

In this work, Ti-Zr-Nb-Hf-Ta-V and Ti-V-Zr-Nb-Ta alloys obtained in the form of micro-sized fibers by ion-plasma sputtering were studied [3]. Palladium was applied by vacuum spraying. The interaction of hydrogen with alloys was studied by volumetric method. It is shown that after coating, the temperature of interaction with hydrogen decreases from 400 °C to room temperature without prior high-temperature activation. According to the XR-data, the presence of palladium does not affect the structural parameters of the resulting hydrides. The formation of hydrides is not completely reversible due to the high thermal stability of the hydride phases.

For the preparation of membranes, HEA fibers were subjected to cyclic hydrogenation/dehydrogenation followed by mechanical activation (MA) in a planetary ball mill. Palladium was sprayed onto the resulting metal powder, then mixed with Sabic ® polyethylene granules. The study of transport properties of composite metal-polymer materials was carried out by the barometric method on films with a thickness of about 100 microns obtained by thermal pressuring. The permeability and ideal selectivity of the membranes with respect to H_2, CH_4, CO_2, He, Ar, N_2 were determined based on the measurement results. The dependence of the main functional parameters of the membranes on their composition and processing conditions has been produced.

Acknowledgments

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Ivan Savvotin graduated Chemical Departmen of Lomonosov Moscow State University in 2020 and defended his work on the topic «Composite gas separation membranes based on hydride-forming intermetallic compounds and polymer binders». His research interests are hydride-forming intermetallic materials, high-entropy alloys and composite membranes for hydrogen separation.

Presentating author: Savvotin Ivan, e-mail: 79166550606@mail.ru, tel: +7-916-655-06-06

Floating Ice Platforms: Analysis of Different Methods of Ice Formation

Željko Penga[1], Mišo Jurčević[1], Branko Klarin[1]
[1]Faculty of Electrical Engineering, Mechanical Engineering
and Naval Architecture, University of Split
R. Boškovića 32, 21000 Split, Croatia

Floating ice platforms are nothing new, they have been used since 1973. as a support structure for oil drilling applications in the Canadian Arctic regions [1]. The method for building such platforms was to pump the water onto the existing ice structure to increase the thickness where the oil drilling rig will be located and then installing the rig. The application of floating ice platforms instead of artificial island is economically viable since ice supports large structures with ease due to its massive thickness and results in stable structure even when sea currents are strong and large size of the supporting structure shields the oil drill rig from sea waves. Floating ice platforms are commonly constructed in Arctic regions due to very low surrounding temperatures throughout the year. Due to favourable characteristics of ice platforms as a structural support, as a part of an ongoing research project, the objective is to develop a large floating ice platform with dimensions 70 x 70 x 6 meters, with steel frame, where the water will be poured and solidified to create ice as a supporting internal structure for various applications, e.g. as a floating island. Since ice is characterized by poor thermal conductivity it is necessary to devise economical and efficient cooling strategy to determine which approach would be feasible for large scale applications.

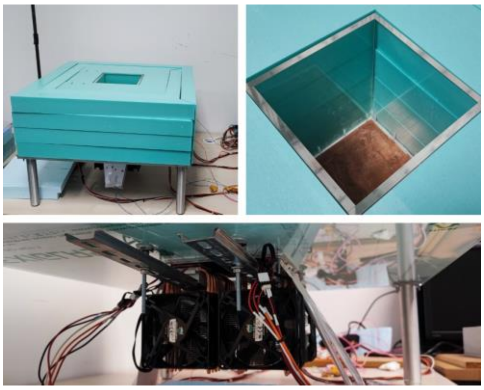

Figure 1. Experimental setup for studying different methods of ice formation

During a previous study [2], cooling system was developed using refrigeration unit and a heat exchanger, and two cooling loops, the outside cooling loop and internal cooling loop. The internal cooling loop used water-glycol mixture which circulated through a closed flow circle with heat exchanger submerged in water. Throughout the experimental investigations it was noted that the entire cooling process was very time consuming and inefficient due to poor thermal conductivity of the ice and polymer heat exchanger pipes. The results of computer simulations showed that the experimental control over boundary conditions was poor, and that precise initial conditions have significant impact on the ice formation and propagation during the experiments, since minor initial discrepancies result in large errors as the time elapses. For this reason, new experimental setup was devised, shown in Fig. 1. The new setup has very precise PID temperature control achieved by using Peltier thermoelements stacked on top of each other, mounted with system for CPU cooling using heat pipe principle. The new system is capable of achieving temperatures below -20 °C in very quick times, and since the bottom of the tank is a copper plate, the experiments can be quickly carried out in only a fraction of time vs. previous study. The new experimental setup will be used to study which method of ice formation will be the most economical and/or time efficient. The following methods will be studied experimentally:

(i) passive and active solidification

(ii) solidification using a slurry mixture

(iii) solidification with sprinkler

To gain better understanding of the solidification process, the processes will be filmed using a camera and temperatures will be recorded using a high number of thermocouples, while the temperature profiles will be precisely controlled using PID regulation. Computer simulations will be developed for the cases which show the best performance and optimization will be carried out. Once the optimal configuration is determined, the system will be upscaled and a large scale module will be developed which will then be implemented in the full-scale ice floating platform.

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Asst. Prof. Željko Penga, PhD is expert in Computational Fluid Dynamics analysis and experimental validation of complex multiphysical processes, such as PEM fuel cells, renewable energy powerplants, chemical processes, etc. He works on a number of national and international projects. He won State Science Award and University Science Award for young researchers in Technical Sciences for years 2019 and 2020, respectively, for his R&D activities, international collaboration with renowned universities and automotive industry, and large number of published research papers in top ranked international journals.

Presentating author: Željko Penga, e-mail: zpenga@fesb.hr tel: +385 91 4305 958

Multi-principal-component alloys produced by pendant drop melt extraction: structure, hydrogen storage and mechanical properties

A. Korol[1], V. Zadorozhnyy[1], M. Zadorozhnyy[1], A. Bazlov[2], E. Berdonosova[2], M. Serov[3],
A. Stepashkin[2], M.Zheleznyi[1], S.Kaloshkin[1] and S. Klyamkin[2]
[1]National University of Science and Technology "MISIS", Leninsky Prosp., 4, 119049 Moscow, Russia
[2]Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia
[3]Moscow Aviation institute (National Research University), 119049 Moscow, Russia

Multi-principal-component (MPC) alloys which include 5 or more elements with concentrations ranging from 5 to 35% are a new class of materials with exceptional mechanical properties. Due to the acquired distortions of the crystal lattice and deformtion at the graind boundaries, they are promising for the formation of hydrides, and therefore, for reversible hydrogen storage [1].

Due to the very high hardness, cast MPC alloys are difficult to convert to a dispersed state, which is required for many hydrogen-related applications, in particular, for hydrogen separating metal-polymer membranes [2]. In this work, a series of MPC alloys were produced by electron beam melting with pendant drop melt extraction (EBM PDME) in order to expolore the effect of production mode on their structure, hydrogen storage performance and mechanical properties. Four single-phase MPC alloys with BCC crystal structure, namely $Ti_{20}Zr_{20}V_{20}Nb_{20}Ta_{20}$, $Ti_{20}Zr_{20}V_{15}Nb_{15}Ta_{15}Hf_{15}$, $Ti_{25}Zr_{25}V_{15}Nb_{15}Ta_{20}$ and $Ti_{20}Zr_{20}V_{20}Nb_{20}Hf_{20}$, were successfully obtained in the shape of fibers with a diameter of about 100 μm (Figure 1). Subsequent hydrogenation led to formation of hydride phases accompanied by BCC to FCC transition with the lattice volume expansion close to 30%. The reveresible hydrogen capacity was of the studied alloys correspond was 1.5–1.7 wt.%. Analysis of physico-mechanical properties showed that the tensile strenght of the pristine MPC alloys reahed 1000 MPa with a relative elongation of 5%. It was also demonstated that the thermal conducitvity values are close to the stainless steels and Ti-based alloys.

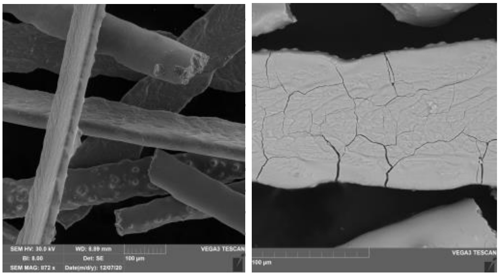

Figure 1. SEM images of MPC alloy obtained by EBM-PDME: (a) before and (b) after hydrogenation.

The revealed features are of interest for the use of alloys as fillers for composite metal-polymer membranes.

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Artem Korol received bachelor’s degree in Materials Science at National University of Science and Technology "MISIS", Moscow, Russia (2020). His thesis was titled Synthesis and investigation of hydride-forming multi-principal-component alloys for reversible hydrogen storage. Korol presented nine oral and poster presentations at scientific conferences. He works now at State Research Center “TsNIIchermet” Moscow, Russia (junior researcher).

Presentating author: Artem Korol, e-mail: artemkorol1998@gmail.com tel: +79803718135

Effect of Hetero-interfaces on Hydrogen Production of LSMA:LCMx (x=Al, Fe, Co) Dual Perovskite Oxides

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

In the last decades, hydrogen has emerged as a potential energy solution in the long term due to its high energy density per mass (120MJ/kg) and being zero carbon emission.. However, hydrogen production is still dependent on the fossil fuels based production which restricts the transition to hydrogen energy utilization in the major fraction.

Thermochemical Water Splitting (TWS) is one of the solar based hydrogen production methods which enable us to produce pure hydrogen. In this method, hydrogen is produced by the dissociation of water at elevated temperature which achieved by the sun’s rays. The materials to be used in TWS determine the solar-to-fuel efficiency. Therefore, it is hence important to develop redox materials used in TWS for high efficient hydrogen production. So far, perovskite oxides has received greatest research interest due to their attractive properties. Especially, Sr and Al doped $LaMnO_3$ perovskite has shown as an ideal redox material for TWS [1]. However, with increasing cycle numbers, it is observed that hydrogen production capasity of $LaSrMnAlO_3$ decreased. Although different doping studies of $LaMnO_3$ perovskites have been tried, the redox capacities and structural stability of perovskite oxides developed by doping could not reach the desired level.

Over the past two decades, hetero-interfaces is one of the most studied materials design parameter due to its contribution to oxygen release and reoxidation reactions and structural stability of materials. In addition, quite different characters can be observed with the hetero-interfaces created between the two component and could have superior features than the main components [2,3].

In this study, $La_{0.6}Sr_{0.4}Mn_{0.4}Al_{0.6}O_3$ (LSMA), $La_{0.6}Ca_{0.4}Mn_{1-x}Al_xO_3$ (LCMA), $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_3$ (LCMF) and $La_{0.6}Ca_{0.4}Mn_{1-x}Co_xO_3$ (LCMC) (x= 0.2 to 0.6) perovskites were produced via the Pechini method. To determine oxygen and hydrogen production capacity of synthesized perovskites, TWS cycles were carried out at 1400 °C for reduction reaction and 800 °C for oxidation reaction. TWS results of each perovskites are shown in Table 1.

Table 1. Thermochemical Water Splitting Results of Synthesized Perovskites

Samples	Total O_2 production (µmol/g)	Total H_2 production (µmol/g)
LSMA6464	215.55	257.18
LCMA6482	226.30	47.99
LCMA6464	271.17	135.58
LCMA6446	203.47	70.06
LCMF6482	345.37	39.09
LCMF6464	392.95	37.21
LCMF6446	212.16	59.51
LCMC6482	291.03	66.97
LCMC6464	354.92	41.64
LCMC6446	372.64	60.04

Hetero-interfaces were created between the LSMA:LCMx dual perovskite oxides. To investigate the effect of hetero-interfaces on hydrogen production, produced dual perovskite were subjected to Termochemical Water Splitting.

Acknowledgements

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Seyfettin Berk SANLI is currently a Master student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. He completed his BS degree at the same university in 2020. He is working at Energy Materials Laboratory and his research areas are hydrogen production, thermochemical water splitting, perovskite oxide materials.
Presentating author: Seyfettin Berk SANLI, e-mail: seyfettinberksanli@posta.mu.edu.tr, tel: +90 539 785 70 48

The effects of boron addition on the grain boundary properties of lithium titanium phosphate as a solid-state electrolyte for Li-ion batteries

Francisco J. A. Loureiro[1,*], Zinaida Shakel[1], Bruno M. G. Melo[2], Vanessa C. D. Graça[1], Laura I. V. Holz[1], Sergey M. Mikhalev[1], Aliaksandr Shaula[1], Duncan P. Fagg[1]

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

[2]I3N, Department of Physics, University of Aveiro, Aveiro 3810-193, Portugal

The adoption of solid-state electrolytes for Li-air batteries has been suggested to prevent damage by atmospheric moisture and oxygen [1,2]. Nowadays, the best commercially available solid Li-electrolyte is that of $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$, which is based on the sodium super ionic conductor (NASICON) structure. However, the presence of a reducible Ti ion limits its electrochemical performance through a concurrent decrease in the ionic conductivity [1,2]. Therefore, in this work, we aimed to improve the design of this family of materials, by tailoring the chemical composition of the lithium titanium phosphate solid electrolyte composition, with a partial substitution of the Ti ion for 20 mol% of boron (B) ($Li_{1+x}Ti_{2-x}B_x(PO_4)_3$). To this end, we compare the structural, microstructural, and electrochemical features of the unmodified ceramic (x = 0, designated as LTP) with the boron-doped composition (x = 0.2, designated as LTBP20).

In terms of structural properties, by *Rietveld* analysis of the X-ray diffraction (XRD) data, we found that the introduction of 20 mol% of B into the LTP structure led to an increase in the lattice parameter with respect to the unmodified sample. This factor was explained by a compensating mechanism with increasing Li^+ concentration in the bulk.

Subsequently, ceramic compacts of both LTP and LTBP samples were made by firing uniaxially pressed samples at 650 °C and 850 °C, respectively. Then, scanning electron microscopy (SEM) was used to characterize the microstructure of the sintered ceramics. The results showed that the LTBP sample had a much more homogenous microstructure, with a lower grain size distribution (~100 nm). Conversely, the pure LTP sample had a non-uniform grain size, with larger grains (~20 μm) surrounded by smaller grains within the submicron range.

From the electrochemical impedance spectroscopy (EIS) results, the bulk conductivity was found to be significantly enhanced in the LTBP sample, in agreement with the higher Li^+-ion concentration determined from the analysis of the XRD patterns. However, for evaluating the grain boundary properties of these samples, due to their inherent dependence on the microstructure, we adopted two well recognized mathematical procedures, capable of circumvent this effect: i) the standard brick layer model (s-BLM) and ii) the *Maxwell–Wagner/Hashin–Shtrikman* (MW-HS) model [3]. The latter was proven to yield more reliable results in the determination of the specific grain boundary conductivity due to its higher accuracy in samples with a nanometric grain size.

With this MW-HS model, the space charge properties of the grain boundary region were then determined (Figure 1), revealing that the level of the depletion of Li^+ charge carriers is less severe in the LTBP20 sample. This important result confirms the enhancement of the conducting properties of this region as a result of B-doping in the LTP structure. Overall, this work provides new insights regarding the electrochemical nature of the grain boundary of NASICON-based solid-state electrolytes, which has been often overlooked in the literature.

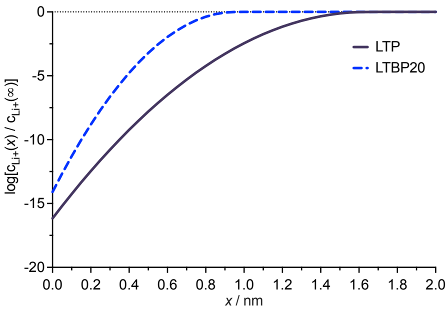

Figure 1. Bulk-normalized concentration profiles of the space-charge layer obtained at 150 °C.

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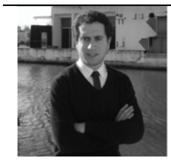

Bio: Dr. Francisco Loureiro is a doctorate researcher working in the Centre for Mechanical Technology and Automation (TEMA) at the University of Aveiro (Portugal). His research interests focus on the study of energy conversion and storage systems, with emphasis in solid-state electrochemistry of ceramic inorganic compounds. **Presenting author:** Dr. Francisco Loureiro, **e-mail:** francisco.loureiro@ua.pt, **tel:** +234 370 830.

Off-design operation of super critical CO2 cycle

Jarosław Milewski, Piotr Lis, Olaf Dybiński and Arkadiusz Szczęśniak
Warsaw University of Technology, Faculty of Power and Aeronautical Engineering, Institute of Heat Engineering

European Union countries are addressing climate change concerns through introducing regulations in the 2030 and 2050 time perspectives. One goal in the 2030 horizon is to boost energy efficiency to 27%. These regulations will lend added impetus to the development of low-carbon economy in individual countries [1]. This positively impacts the development of new technologies like fuel cells [2] which can generate power with ultra high efficiency (60%+[3]) and the search for improvements in classical heat cycle based solutions [4]. Other issues which need to be addressed regard energy storage, especially coupled with unpredictable renewable energy sources [5].

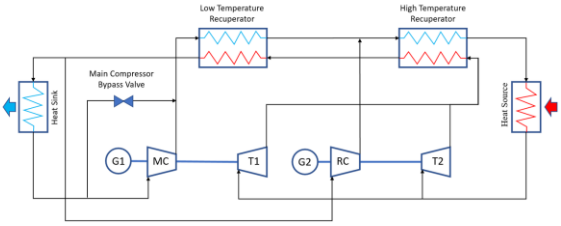

Figure 1: Off design supercritical Brayton cycle

The goal of the simulation was to study the power flexibility of the supercritical CO2 system.. Simulation was prepared based on previous study, all modeling relevant data can be found in previous works.

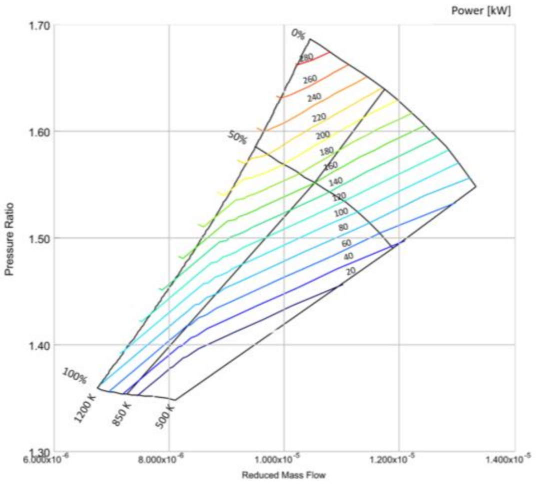

Figure 2: Supercritical system performance map

The map on Fig. ??? represents supercritical CO2 Brayton recompression cycle performance. The X axis corresponds to reduced mass flow rate, the Y axis represents cycle pressure ratio. The horizontal lines tagged with % values represent different main compressor bypass valve opening: 0% - fully closed, 100% - fully open. The vertical lines tagged with K values represent different TIT. The lines inside the map indicate system power output in kW.

Based on available measurement data an off design supercritical Brayton cycle simulation model was prepared. The model represents the recompression Brayton cycle as shown on Fig. ???. The system consists of two turbine-compressor-generator units. The first unit powers the main compressor, the second unit powers the recompressor. Total system power output is the sum of power outputs from each unit.

The article discusses potential and existing applications of the supercritical CO2 cycle. Commercial applications and pilot units are still under development. As there is no field operation data available to date, the authors investigate examplary sCO2 cycle power flexibility based on a simulation model of the laboratory supercritical CO2 unit developed by Sandia National Laboratories. The study shows that small scale sCO2 units like this can be used for waste heat, geothermal or ship propulsion applications.

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Prof. Jaroslaw Milewski is is employed by Warsaw University of Technology, Faculty of Power and Aeronautical Engineering, Institute of Heat Engineering.He is a Head of Power Division at the Institute of Heat Engineering, Editor-in-Chief of Journal of Power Technologies, and a Member of the Editorial Board of Applied Energy.He has experience in fuel cell research (Molten Carbonate Fuel Cells–-MCFC and Solid Oxide Fuel Cell–-SOFC) and other power sources, hybrid systems, advanced power systems (hydrogen-based), and steam/gas turbine power generation systems.

Presentating author: Jarek Milewski, e-mail: jaroslaw.milewski@pw.edu.pl tel:+4822 2345 207

PEMFC based combined cooling and power (CCP) system

Uday Raj Singh[1] and Satya sekhar Bhogilla[1]
[1]Dept. of Mechanical Engineering, IIT Jammu, Jammu, India

With the rapid decline in fossil fuels and the advent of global warming, fuel cells have proven to be a novel platform to combat the ongoing energy crisis. Fuel cells have proven to be one of the most sought-after technologies for their excellent energy conversion efficiency and less harmful effect on the environment [1]. In the present research scenario, fuel cells, mainly PEMFC and Solid oxide fuel cells (SOFC), are integrated with the cooling, heating or power generation systems (CCHP) in order to increase their overall efficiency. However, compared with the SOFC, PEMFC is considered more sought for the CCHP systems due to better efficiency and less noise, among many other advantages [1–4]. Also, the PEMFC is known for its high-power density (300-1000 mW/cm²).

Fuel cell releases a large quantity of heat during their operation. This heat can be utilised in a refrigeration unit with a good heat transfer coefficient, a good medium to recover waste heat. In recent years, many studies have been carried out in the field of Vapor adsorption refrigeration cycle (VADRC) systems. The VADRC systems are driven by low-grade thermal energy as input, and it provides many advantages over other cooling technologies, although the Coefficient of performance (COP) of the VADRC is less compared to the Vapor compression refrigeration cycle (VCRC). Some advantages of VADRC are that it is flexible, causes no harmful effect on the environment, has a low cost of maintenance, no vibrations, and can work on a wide range of heat sources. These are the reasons why this technology is grabbing the attention of researchers worldwide. Many studies have also been performed on the thermal integration of this technology with low-grade heat sources such as solar energy, waste heat from IC engines, geothermal energy, etc. At present, the ways to recover heat from fuel cells is done by incorporating CCHP systems. The CCHP system is mainly used when the waste heat is generated at high ranges of temperatures.

In the present study, a theoretical analysis of the integrated system is performed wherein a VADRC system is incorporated to utilize the heat generated from the PEMFC. The VADRC system operates on the heat generated from the PEMFC at low temperature, which is equal to the working temperature of the VADRC, i.e., around 65-85°C. The heat coming out of the PEMFC will be utilized as input for the generator of VADRC. However, in the present research work, the thermodynamic performance investigation is carried out by varying the operating parameters such as operating temperature, current density and evaporation temperature.

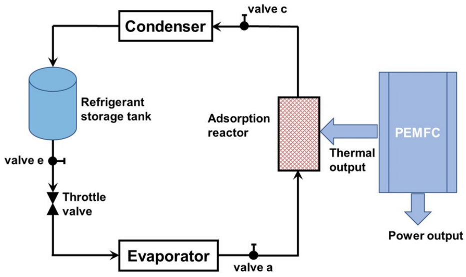

Figure 1. Schematic diagram of the PEM and adsorption cycle

The system in this study consists of a PEMFC fuel cell and an adsorption refrigerator, as shown in Fig. 1. The PEMFC driven adsorption refrigeration system works on an adsorption refrigeration cycle which runs on thermal energy as the only input. In the present system, the thermal input is provided by the by-product heat generated due to the operation of PEMFC. A low-temperature PEMFC is selected for this study which has its operating temperature ranges between (65-85°C) [4]. The results show that the system energy and exergy efficiency decrease as the current density value increases. Maximum system energy and exergy efficiency of 63.01% and 29.88% are achieved. The results also reveal that at a current density of 0.8 A/cm², the system efficiency increases from 61.35% to 63.01% as the PEMFC temperature increases from 65 to 80°C. In addition, maximum energy efficiency of 65.39% was reported at an evaporator temperature of 5°C and a current density of 0.8 A/cm².

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Dr. Bhogilla Satya Sekhar received B.E. (Mechanical Engineering) in 2008 from Andhra University and M. Tech in 2010 with specialization in Fluid & Thermal Science from Mechanical Engineering at IIT Guwahati. Following this, he started PhD at the same Institute, where he was involved in the development of Hydrogen Systems. His areas of interests are Hydrogen Energy, Renewable Energy Systems, Energy Conversion and Storage, Fuel Cells, Sorption Heating and Cooling Systems.

Corresponding author: Dr. Bhogilla Satya Sekhar, e-mail: satya.bhogilla@iitjammu.ac.in tel: +91-7397463653

Effect of catalyst ink composition on the performance of carbon aerogel based Fe-N-C catalyst for the oxygen reduction reaction

Tanja Zierdt[1], Julia Müller-Hülstede[1], Dana Schonvogel[1], Jessica Schettler[2], Marina Schwan[2],
Barbara Milow[2], Peter Wagner[1] and K. Andreas Friedrich[3]
[1] German Aerospace Center (DLR), Institute of Engineering Thermodynamics,
Carl-von-Ossietzky Str. 15, 26129 Oldenburg, Germany
[2] German Aerospace Center (DLR), Institute of Materials Research,
Aerogels and Aerogel Composites, Linder Höhe, 51147 Köln, Germany
[3] German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

The performance of high temperature (HT) polymer electrolyte membrane fuel cell (PEMFC) limited due to adsorption of phosphates, emerging from the phosphoric acid doped polybenzimidazole (PBI) membrane, poisoning the typically used platinum catalyst. Therefore, higher amounts of platinum up to 1 $\mathrm{mg_{Pt}\,cm^{-2}}$ for each the anode and cathode are needed. At this point, precious metal-free Fe-N-C catalysts are a promising and cheaper material for replacing commonly used expensive platinum-group metals in PEMFCs. The reduced costs should help to commercialize HT PEMFC.[1]

However, the application of Fe-N-C catalysts faces two main challenges. The initial performance loss during first hours of HT PEMFC operation of membrane electrode assembly (MEA) containing Fe-N-Cs as cathode catalyst is much higher compared to Pt/C-based MEAs. This originates mainly from carbon corrosion and Fe demetalation [2]. Moreover, the lower volumetric activity of Fe-N-Cs compared to Pt/C demands thicker catalyst layers, which can cause mass transport limitations [2]. These challenges need to be overcome to use Fe-N-C catalysts in the HT PEMFC cathode.

To minimize mass transport limitation and increase the volumetric activity porous carbon aerogels (CA) are a promising candidate for incorporation of Fe-N_x sites. The pore structure of CAs can be tuned during their manufacturing. This allows to build a structure which has an improved electrolyte accessibility to the active sites which was shown to have a impact on activity, determined by rotating ring disk electrode (RRDE) measurement, as reported by Wang et al. [3]. Moreover, Wang et al. identified that the low temperature PEMFC performance is affected by their Fe-N-CA ink compositions, which is used for gas diffusion electrode (GDE) fabrication [3]. Therefore, a systematic analysis of the impact of ink composition on the activity of Fe-N-CAs for HT PEMFC application later will be shown in this study.

The Fe-N-CA catalyst is produced via CA support-based synthesis including impregnation with Fe and N containing precursor, two pyrolysis steps and an acid leaching [4]. Physical characterization of the CA and the Fe-N-CA using transmission electron microscopy (TEM) will provide insights to the carbon and catalyst structure. Furthermore, via N_2-sorption studies the pore structure and surface area are examined. Different catalyst ink suspensions with varied compositions of catalyst material, ethanol or 2-propanol, water and Nafion™ are produced and investigated using RRDE setup to gain insights on activity and selectivity. The experiments are conducted at room temperature in diluted phosphoric acid to investigate the impact of phosphates on the activity. Figure 1 depicts the RRDE setup and ink composition. ORR polarization curves, cyclic voltammograms and impedance spectra are recorded for analysis of catalytic activity, double layer capacity and electrolyte resistance. The results are compared to a commercial Fe-N-C (PMF-0011904, Pajarito Powder) catalyst. The outcomes from electrochemical and physical evaluations will provide insights into the importance of optimizing the catalyst ink for Fe-N-CA material. The results are important for further catalyst ink optimization for Fe-N-CA GDE manufacturing and their investigation under HT PEMFC conditions in a GDE half-cell setup (Figure 1).

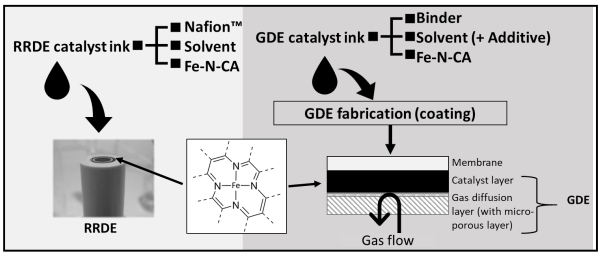

Figure 1. Scheme of ink components for RRDE coating and GDE fabrication.

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Tanja Zierdt currently works as research scientist at the Institute of Engineering Thermodynamics of the DLR in Oldenburg (Germany). She achieved her MSc in Engineering Physics in 2021 at Carl von Ossietzky University of Oldenburg and obtained her BSc in Chemical Engineering in 2018 at University of Applied Science Emden/Leer. Her research interest focuses on PEMFCs, precious-metal free catalysts, electrode manufacturing and the GDE half-cell setup.

Presentating author: Tanja Zierdt, e-mail: tanja.zierdt@dlr.de tel: +49 441 99906-288

The influence of defects on hydrogen sorption from magnesium-based composites and thin films

Tijana Pantić[1], Bojana Paskaš Mamula[1], Kristina Žagar Soderžnik[2], Igor Milanović[1], Nikola Novaković[1], Sanja Milošević Govedarović[1] and Jasmina Grbović Novaković[1]

[1]Department of Physics, Center of excellence for hydrogen and renewable energy (CONVINCE), "Vinča" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike petrovića Alasa 12-14, 11351 Belgrade, Serbia

[2]Department for Nanostructured Materials, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

The kinetics and thermodynamics of hydrogen uptake/release remain the main drawback for the practical application of magnesium hydride (MgH_2) since its high thermal stability. There are possible ways of modification and destabilization of structure in order to improve hydrogen storage characteristics, such as mechanical milling, the presence of additives (metals, metal oxides, non-oxide ceramics, amides, amines, etc.), alloying, ion irradiation. Mechanical milling introduces defects into the material which leads to an improvement in reaction kinetics, especially hydrogen diffusion. Also, the particle size is reduced and the specific surface area of the material is increased, which shortens the desorption path of hydrogen, thereby accelerating the desorption process and reducing the desorption temperature. Ion bombardment introduces vacancies, dislocations, and micro-changes into the material surface layer, increasing the number of nucleation centers. While mechanical milling represents the simple and fast way for structure destabilization, thin films are a great way to monitor the influence of microstructure and/or additives on sorption properties under controlled conditions. They are particularly suitable because of the fact that ion bombardment can be used to control a certain concentration of defects at certain depths by simulation predictions. Milosevic et al. showed that after milling MgH_2 with VO_2, the kinetics of hydrogen sorption were significantly altered due to the presence of a multivalent V ie. VO_2/VH system [1]. During mechanical milling, various additives are added to act as so-called catalysts and/or milling agents, which may produce additional defects, delay agglomeration, and thus improve the sorption properties of MgH_2. Rašković - Lovre and her colleagues investigated the effect of modification of MgH_2 films by Ar^{4+} ions, and it was found that ion bombardment introduced uniformly distributed vacancies in the surface layer of the film [2]. This study aims to investigate the effect of defects in the volume and on the surface of the material. The first part will deal with the influence of defects created in volume, on composites synthesized by mechanical milling at different parameters and different amounts of additives. The second part deals with the study of the influence of surface defects on sorption properties by bombarding thin films with H^- and Xe^{8+} ions.

A series of MgH_2 composites with different weight percent of WO_3 additive (5, 10, and 15 wt.%) is synthesized under different milling conditions in the SPEX 5100 and SPEX 8000M vibration mills. Milling is carried out in an argon atmosphere to avoid hydroxide formation due to the presence of moisture in the air. Microstructural characterization is performed by scanning electron microscopy (SEM), which will examine the change in particle morphology after milling, as well as the distribution of additives in MgH_2. The change in particle size is monitored using a laser method for determining the particle size distribution (PSA). The desorption properties of the composite are tested by differential scanning calorimetry (DSC), temperature-programmed desorption (TPD), and the Sivert hydrogen sorption analysis method (HSA). The desorption process of H_2 from the composite is analyzed by fitting the experimental data using different kinetic models.

Thin films consisting of alternating Mg (30 nm) and V layers (1 nm) with 10 repetitions were synthesized by magnetron sputtering and modified by ion irradiation using H^- and Xe^{8+} ions at FAMA ion source. Time-of-flight elastic recoil detection analysis (TOF-ERDA) shows the concentration of elements in the film, as well as their depth profiles. The microstructure and composition are examined by scanning transmission electron microscopy (STEM) with EDX mapping.

Mechanical milling and the addition of WO_3 introduced the defects into the MgH_2 bulk. The particle size is reduced and there is a decrease in desorption temperature compared to the as-received MgH_2. Composites with a higher amount of additive show faster hydrogen sorption. TOF-ERDA results show that ion-irradiation induced defects improve hydrogen absorption. Surface defects play a major role in sorption reaction as they promote hydrogen dissociation.

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Tijana Pantić is a PhD candidate at the Faculty of Physical Chemistry, University of Belgrade and currently works as a research assistant at Vinča Institute of Nuclear Sciences. Her research is focused on materials for solid state hydrogen storage.

Presentating author: Tijana Pantić, e-mail: tijanap@vin.bg.ac.rs tel: +381 64 802 52 13

Vanadyl phosphate as a host material for aluminium intercalation

Dragana Jugović[1], Miloš Milović[1], Tanja Barudžija[2] and Miodrag Mitrić[2]

[1]Institute of Technical Sciences of SASA, Belgrade, Serbia
[2]„VINČA” Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

The development of safe, durable, cheap, and environmentally friendly batteries is one of the most important challenges of modern electrochemistry. Hence, there is an interest in the investigation of aqueous batteries with multivalent ions such as calcium, magnesium, or aluminium. Furthermore, the use of polyanionic compounds as cathode material can provide multi-electron transport. $VOPO_4{\cdot}2H_2O$ with its layered structure is a particularly interesting and promising material.

The current study is focused on the investigation of $VOPO_4{\cdot}2H_2O$ as cathode material in aluminium aqueous rechargeable cells. According to the literature data, the conventional reflux method is mostly used for the material's synthesis [1]. Here is presented a sonochemical synthesis as a less time- and energy-consuming method, that starts from the mixture of vanadium(V)-oxide, phosphoric acid and water as a reaction media. The synthesis is done within 20 min.

The characterization of the synthesized material includes X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and cyclovoltammetry (CV).

XRD data were used for both the powders' phase identification and crystal structure refinement. The structure of the powder was refined in the tetragonal space group P4/nmmZ (No. 129). Crystal structure refinement was based on the Rietveld full profile method [2]. The structure is characterized by infinite layers of PO_4 tetrahedra linked to VO_6 octahedra by shared oxygen atoms that form 2D sheets in the *ab*-planes; water molecules are located in the interlayer space. The refined cell parameters, $a = b = 6.2136$ Å, $c = 7.4141$ Å, are in good agreement with the literature data. Lattice parameter c is a measure of the interlayer distance, thus varies with water content. The value of the refined c parameter implies that the structure consists two water molecules per formula unit.

The working electrode is prepared from a slurry of sonochemically derived $VOPO_4{\cdot}2H_2O$ as an active material, carbon black, and a binder dispersed in a solvent. Two different binders are used: polyvinylidene fluoride (PVDF), 2.4 wt% solution in N-methyl-2-pyrrolidone or Nafion, 5 wt% solution in a mixture of lower aliphatic alcohols and water. Cyclic voltammetry measurements are done in several electrolytes to probe the intercalation of various cations such as magnesium, calcium, and aluminium. The best results are obtained when the electrode is cycled in 1M $Al(NO_3)_3$ aqueous solution. This probably originates in different ionic radii.

During the process of electrode preparation, structural changes in the powder are noticed. The structural changes were followed step by step through the combined XRD and FTIR analysis. It turns out that the structure is prone to release water molecules even when the powder is mixed with carbon black and also with the addition of a solvent, which could lead to the formation of a bilayered vanadyl phosphate. It was shown that using different solvents has a diverse impact on the structure, and consequently on powders' cyclic performances (Figure 1).

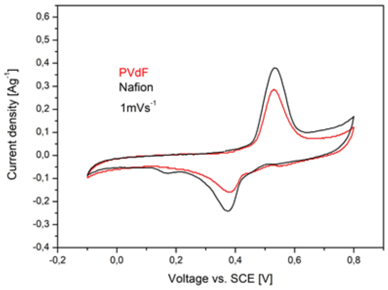

Figure 1. The cyclic voltammograms of $VOPO_4{\cdot}2H_2O$ electrodes prepared with two different binders, PVdF and Nafion.

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Dr Dragana Jugović is a Principal Research Fellow at the Institute of Technical Sciences of SASA.

Her scientific research activity is oriented toward the synthesis and physicochemical characterization of materials that find their application as electrode materials for lithium-ion batteries and other rechargeable batteries. She is especially interested in examining the relationship between the structural and transport properties of the synthesized materials.

Corresponding author: Dragana Jugović, e-mail: dragana.jugovic@itn.sanu.ac.rs tel: +381 64 1177549

Oxidation of Al- and Mg-based materials in aqueous solutions for on-site hydrogen generators

Klyamkin Semen, Sevastyanova Ludmila, Stupnikov Vladimir, and Bulychev Boris
Lomonosov Moscow State University, Chemistry Department, Leninskie Gory 1/3, Moscow, 119991 Russia

Storage and transportation of hydrogen remain the main challenges for the widespread introduction of hydrogen technologies in the energy sector. The low density, flammability and explosiveness of hydrogen require the development of alternatives to conventional storage techniques related to compressed and liquefied gas. As a possible solution for certain application, the use of solid materials capable of generating hydrogen on-demand when interacting with water is suggested. Magnesium and aluminum which can produce up to 0.92 L and 1.24 L per gramm, respectively, are among the most attractive for this purpose due to their low cost, abundance, and recyclability [1].

However, surface oxide layer and the formation of poorly soluble reaction products during hydrolysis dramatically reduce the reaction rate and the hydrogen yield. There are several approaches to overcome these shortcomings:

- Microstructure modification of metallic reagents. High energy ball milling in an inert atmosphere is usually applied to enhance reactivity of magnesium or magnesium hydride because of particle and crystallite size reduction, surface oxide removal, and generation of crystal structure defects. Such pretreatment leads to an increase in the initial reaction rate with water, but does not ensure its completeness [2].

- Alloying with potential catalysts. High-temperature melting as well as mechanochemical processing are used for this purpose. Minor additions of some transition metals to magnesium or Ga, In, Sn, Bi to aluminum change the hydrolysis mechanism by the formation of galvanic pairs and/or destruction of the metal grain structure [3-5].

- The use of aqueous solutions instead of pure water. While the impact of alkaline or acidic solutions is easily explained, the effects of salts with a neutral pH are not so obvious. The most effective salt additives are halides and there are several models describing the mechanism of hydrolysis in their solutions [3, 6].

Here, the combined effect of all three factors (alloying, mechanochemical pre-treatment and adjustment of solution composition) on the process of hydrogen generation during the oxidation of magnesium, magnesium hydride and aluminum by water is considered. The most effective approaches to increasing the rate of hydrogen generation and achieving maximum yield are discussed from the point of view of the reacting metal microstructure and reaction mechanism.

Aknowledgment

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Semen Klyamkin is a professor at the Chemistry Department at Lomonosov Moscow State University. He obtained PhD degree in inorganic chemistry (1987) and Doctor of Sciences in solid state chemistry (2014). His research activity covers hydrogen storage materials, metal hydrides, gas adsorption in porous matrices (MOFs, carbons) with emphasis on high pressures, mechanochemistry, gas separation membranes.

Presentating author: Semen Klyamkin, e-mail: klyamkin@highp.chem.msu.ru, tel: +7-495-9394576
Presentating author: Name Surname, e-mail: tel:

Assessing the Stability of Oxygen Evolution Reaction Electrocatalysts During Accelerated Stress Tests

Matej Zlatar[1], Daniel Escalera-López[1], Hoang Phi Tran[2], Hong Nhan Nong[2], Peter Strasser[2], Serhiy Cherevko[1]

[1]Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich GmbH, Cauerstrasse 1, 91058 Erlangen, Germany

[2]Department of Chemistry, Chemical and Materials Engineering Division, The Electrochemical Energy, Catalysis and Materials Science Laboratory, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

The widespread application of various renewable energy sources is currently challenged by their intermittent availability. One of the most promising solutions is to store excess energy by producing H_2 with proton exchange membrane water electrolyzers (PEMWE). However, sluggish kinetics of anode, oxygen evolution reaction (OER) reaction, and a need for scarce Iridium electrocatalysts, limit the complete commercialization of this technology. Therefore, current research is generally focused on maximizing Ir oxygen evolution reaction (OER) activity while decreasing Ir loading. However, Ir stability under OER operation is an equally important parameter in PEMWE research, often overlooked. For this reason, it is crucial to establish benchmark strategies to estimate the catalyst lifetime by developing well-established test protocols.

So far, the electrocatalyst stability was estimated under constant current mode in the literature even though it is inconsistent with the real operation of PEMWE. To accurately simulate the fluctuating input power of PEMWE, [1] accelerated stress tests (ASTs) were proposed [2], where potential square-wave cycles in three-electrode setups provided more representative degradation rates than those shown in PEMWEs. [3] Even though they are often neglected in the literature, important parameters such as the AST protocol in itself and the backing electrode used are not evaluated and can have significant impacts on the stability metrics obtained. [4, 5]

To evaluate the function of both AST parameters and backing electrodes (Au foil, GC plate, BDD, IrOx Wafer) on the stability of a commercial Ir catalyst (Ir Black, Alfa Aesar), we combined scanning electrochemical flow cell coupled to inductively-coupled plasma mass spectrometry setup. This way, we gained deeper insights from the interplay of lower potential limits (LPLs) and the transient anodic/cathodic dissolution observed during OER benchmarking. We showed that by increasing the LPL, Ir dissolution significantly changed on different substrates. [6] In the case of glassy carbon, gradual passivation yielded lower Ir degradation rates than on Au, whereas Au redeposited at lower LPL values. The results of this work showcase the importance of the careful selection of LPL and backing electrodes in square-wave ASTs, in which LPLs should not exceed <1.23 V_{RHE} to prevent stability underestimations of any Ir-based electrocatalyst.

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Matej Zlatar graduated from a University of Zagreb, Faculty of Chemical Engineering and Technology by obtaining a B.Sc. in 2017, and M.Sc. in 2019. Currently, he is a PhD student at Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, in the group of Electrochemical Energy Conversion, supervised by Dr. Serhiy Cherevko. His research interest covers acidic water electrolysis towards renewable hydrogen production, specifically catalyst support interactions in oxygen evolution reaction electrocatalysis.

Corresponding author: Matej Zlatar, e-mail: m.zlatar@fz-juelich.de tel: +49 (0) 9131 12538 185

Development of TiO_2-based Ternary Photocatalysts for Renewable Hydrogen Production

İhsan Emre Yiğiter[1,2,3], Çağla Ünal[1,2,3], Berke Pişkin[1,2,3] and Fatih Pişkin[1,2,3]
[1]Dept. of Metallurgical and Materials Engineering, Sıtkı Koçman University, Mugla, Turkey
[2]Energy Materials Laboratory, Dept. of Metallurgical and Materials Engineering, Mugla Sıtkı Koçman University, Mugla, Turkey
[3]Hyen Material Technologies Research and Development and Consultancy Inc., Kotekli Mahallesi, Mugla, Turkey

In the modern world, the energy demand rapidly increases day by day. Thus, clean energy technologies have significant importance to overcome environmental pollution. Among these, photocatalytic water splitting possesses a high potential since it can provide hydrogen (H_2) production by efficiently harvesting solar energy. As shown in Figure 1, the photocatalytic water splitting process includes a few steps: i) incident light is absorbed by the semiconductor-based photocatalyst material, ii) the electrons migrate from the valance band (VB) to the conduction band (CB) when the energy of irradiance of light is greater than or equal to the bandgap of semiconductor, iii) photogenerated electron-hole pairs move towards the surface or recombine, iv) adsorption of reactants (H_2O and H^+) and desorption of products (O_2 and H_2), v) reduction and oxidation reactions on the surface of the semiconductor [1].

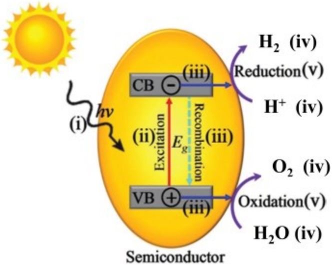

Figure 1. The mechanism of photocatalytic water splitting on the semiconductor-based photocatalyst [1].

Photogenerated electron-hole pairs tend to recombine very rapidly because of Coulomb's force. During recombination, no redox reaction occurs while useless heat energy is released. In this sense, charge separation is essential to prevent electron-hole recombination on the surface of the photocatalyst. A variety of strategies such as doping, metal loading, and heterojunction of photocatalyst have been developed. One of the most effective and flexible strategies is forming of heterojunction. By the approach of heterojunction, an interface between two semiconductor photocatalysts is created via unequal bandstructure to improve charge separation efficiency and photocatalytic activity. Z-scheme systems are one of the heterojunction designs inspired by natural photosynthesis. In the Z-scheme system, one of the photocatalysts behaves as a reduction site while the other one serves as the oxidation site. Thus, the redox reactions in Z-scheme systems occur at a higher potential of CB and VB which results in charge separation and enhanced photocatalytic activity.

Semiconductor photocatalysts must fulfill the requirements to photocatalytically split water [2];

- The VB and CB potential of photocatalyst must be proper for reduction and oxidation reactions. In other words, a more positive VB than 1.23 eV for oxygen evolution and a more negative CB for hydrogen evolution are desired.
- Photocatalyst must be the visible light response to harvest sunlight effectively.
- Chemical stability and photo corrosion resistance are sought to prolong the lifetime of the photocatalyst.
- A higher surface area to increase the number of active sites is necessary.
- Low cost and high abundance.

Titanium dioxide (TiO_2) is one of the most important photocatalysts due to its superior photocatalytic, optical, structural, and electrical properties. TiO_2 has three polymorphs anatase, rutile, and brookite. However, the major drawback of TiO_2 is to possess a wide bandgap, 3.2 eV for higher photoactive anatase, which is UV irradiance response, and this limits the photocatalytic performance in visible light.

Polymeric carbon nitride (g-C_3N_4) is a graphite-like, metal-free, low-cost, non-toxic n-type semiconductor. It is a promising photocatalyst with unique electrical, optical, physical, chemical, and structural properties. Since the bandgap is 2.7 eV, photocatalytic hydrogen production takes place under visible light. However, slow reaction kinetics, recombination, and limited absorption of visible light are disadvantages restricting its use of it as a single photocatalyst.

Cadmium sulfide (CdS) is one of the most prominent visible light responded semiconductors with a bandgap of 2.4 eV. However, this material suffers from rapid recombination of electron-hole pairs and low photo corrosion resistance.

In this study, Z-scheme heterojunction of ternary TiO_2/gC_3N_4/CdS will be systematically synthesized in different fractions by hydrothermal synthesis to reveal their hydrogen evolution profiles. By this approach, it is aimed to avoiding the recombination of photogenerated electron-hole pairs and enhancing photocatalytic activities.

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İhsan Emre Yiğiter is a metallurgy and materials engineer who works on photocatalytic water splitting at Energy Materials Laboratory in the Department of Metallurgy and Material Engineering, Muğla Sıtkı Koçman University and Hyen Material Technologies Research and Development and Consultancy Inc. He earned a B.S. degree from the same department in 2021 where he works, and he is a Master's degree student in the same department. His research interests are in materials for hydrogen production, perovskite oxides, photocatalyst, Li-ion batteries, and Fuel cells.

Presentating author: İhsan Emre Yiğiter e-mail: ihsanemreyigiter@posta.mu.edu.tr tel: +90 554 668 43 46

Prediction and modelling of a proton exchange membrane fuel cells performance during start-up and shut-down operating conditions

Andraž Kravos [1], Ambrož Kregar [1,2] and Tomaž Katrašnik [1,3]
[1]LICeM, Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva 6, 1000 Ljubljana, Slovenia
[2]University of Ljubljana, Faculty of Education, Kardeljeva ploščad 16, Ljubljana, 1000, Slovenia
[3]Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova ulica 19, Ljubljana, 1000, Slovenia

Low temperature proton exchange membrane fuel cells (LT-PEMFC) are one of the promising technologies for achieving zero tank-to-wheel toxic emissions in the automotive and heavy-duty sectors. Even though the progress in the area of PEMFC lifetime, performance and efficiency is undeniable, the degradation phenomena that are inherently linked to the unavoidable operating regimes such as start-up and shut-down (SU-SD) remain a challenging task to address. One of the promising ways besides using new, more durable components, is utilisation of the advance control strategies such as coupled virtual observers with an aim of avoiding detrimental operating conditions and thus achieving optimal transitioning from one operating point to another.

The main challenges in the design of the models for virtual observers are, besides determination of sufficient depth and dimensionality to adequately represent the physical phenomena, the retention of sufficiently high computational speed, parameter identifiability and observability of the model states. Complying with all aforementioned constraints calls for insightful selection of phenomena that most significantly influence performance and degradation of the fuel cell, out of which the gas crossover is one of key factor for establishing the durability of the LT-PEMFC throughout its lifetime, and performance behaviour during SU-SD.

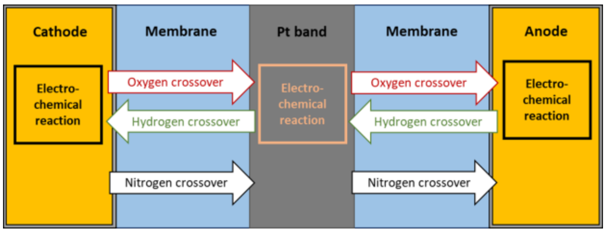

Figure 1. Schematic representation of individual processes modelled by the newly proposed modelling framework.

With an aim of enabling an adequate modelling of the SU-SD operating conditions, while qualifying for use in the observer applications, recently developed thermodynamically consistent electrochemical model [1] is in the scope of this work extended to accommodate the effects of nitrogen, oxygen, and hydrogen crossover, as proposed in [2,3], together with the electrochemical reactions with the dissolved platinum particles that are diffused in the membrane (see Figure 1). Furthermore, the model considers electrochemical reaction of the permeated oxygen with the hydrogen on the anode side, and that of permeated hydrogen with the oxygen on the cathode side, resulting in the changed mixed potential at each electrode and open circuit voltage (OCV) of PEMFC. As a direct result of these extensions of the model, initially presented in [1], the newly devised modelling framework enables not only the appropriate modelling of the OCV and idling at the lower potentials during shut-down but also offers an interface for coupling with enhanced physical modelling of catalyst dissolution, platinum band formation, hydrogen peroxide production and chemical degradation of the membrane that all need to be coupled into unified degradation modelling framework to properly model the entire causal chain of chemical membrane degradation [4].

Results of the newly devised modelling framework that consist of spatially and temporally resolved profiles of species concentrations and potentials were validated on several SD strategies proposed in the scope of experimental study [5]. Validation process showed that the modelling framework achieves good agreement with the experimental data (R^2 of 0.991) while fulfilling the real-time constraint with the average real-time factor of 0.0015 with timestep of 1 ms, thus offering a unique insight into the performance and degradation related phenomena of the PEMFC in the area of system level modelling and models for control applications such as coupled virtual observers.

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Andraž Kravos, PhD candidate (2017-), MSc (2017) in mechanical engineering and BSc (2014) in physics, all at University of Ljubljana. He works at the Faculty of Mechanical Engineering, University of Ljubljana, as a research assistant in the Laboratory for Internal Combustion Engines and Electromobility. His research focuses on development of system level multiscale reduced dimensionality models for fuel cell modelling, diagnostics, and control applications.

Presentating author: Andraž Kravos, e-mail:andraz.kravos@fs.uni-lj.si tel:+386-1-4771-512

Synthesis and electrochemical properties of Ti-Fe-V hydrogen storage alloys prepared by mechanical alloying

[1] Bilel Hosni, [2] Nouredine Fenineche, [1] Omar Elkedim, [3] Chokri Khaldi, [3] Jilani Lamloumi
[1] FEMTO-ST, MN2S/ FC-LAB, UBFC-UTBM, Site de Sévenans, 90010 Belfort Cedex, France
[2] Laboratoire ICB-PMDM/FR/ FC-LAB, UBFC University, UTBM, Site de Sévenans, 90010 Belfort Cedex, France
[3] Université de Tunis, ENSIT, LR99ES05, 1008 Montfleury, Tunisia

Hydrogen is the potential solution for the success of the energy transition of a current system basically based on fossil fuels towards a system friendly to the environment. However, the storage of hydrogen is a big challenge that hinders its practical application in different areas The general formula of metal hydrides is ABn (n=1, 2, 3 or 5), where A is a rare earth or a transition element that has a high affinity for hydrogen and forms stable binary hydrides (La, Ce, Ti, Mg,…). While, B is a transition element that does not interact with hydrogen (Fe, Ni, Mn …) [1-3]

In this study, $TiFe_{0.90}V_{0.10}$ and $TiFe_{0.95-x}V_x$ (x = 0.05, 0.15) with excess in titanium powder samples were synthesized through mechanical alloying (MA) at room temperature under argon atmosphere. The micro-structural and morphological properties of these powder alloys were investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and transmission electron microscopy (TEM). The effects of the substitution of Fe by V and the excess of Ti on the electrochemical properties were studied through the galvanostatic, potentiostatic and potentiodynamic polarization methods.

The XRD and SEM analysis confirm the presence of the amorphous phase for all the samples.

The substitution of iron by vanadium in the TiFe parent alloy increases the number of activation cycles and reduces the maximum discharge capacity. This reduction is more pronounced for the alloy made with stoichiometry $AB_{0.95}$ ($TiFe_{0.90}V_{0.05}$ and $TiFe_{0.80}V_{0.15}$). Indeed, the maximum discharge capacity found is respectively about 63, 100 and 65 mAh g^{-1}, for $TiFe_{0.90}V_{0.05}$, $TiFe_{0.90}V_{0.10}$ and $TiFe_{0.80}V_{0.15}$. These capacity values are still low and are only 44-68% of those of the parent alloy TiFe (147 mAh g^{-1}, 5 activation cycles). During cycling, we found that the substitution of Fe by V improves cycling performance and reversibility. Indeed, the loss in capacity is about 4.8%, 22% and 1.5% and the loss in reversibility is 3.82%, 0.08% and 4.96% for $TiFe_{0.90}V_{0.05}$, $TiFe_{0.90}V_{0.10}$ and $TiFe_{0.80}V_{0.15}$, respectively.

The hydrogen diffusion coefficient, D_H, of $TiFe_{0.90}V_{0.05}$, $TiFe_{0.90}V_{0.10}$ and $TiFe_{0.80}V_{0.15}$ electrodes is estimated to be about 2.57×10^{-12}, 8.65×10^{-12} and 1.06×10^{-12} cm^2 s^{-1} respectively, after the 20th cycle. The $TiFe_{0.90}V_{0.05}$ and $TiFe_{0.80}V_{0.15}$ ($AB_{0.95}$) electrodes show the best values of exchange current density compared to those of $TiFe_{0.90}V_{0.10}$.

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I am a researcher in the laboratory of FEMTO-ST, FC-LAB, France. My researches are based on the solid hydrogen.

e-mail: bilel.hosni@utbm.fr

Development of Novel Binary Ni/Co MOFs for Energy Storage Applications

Ilias Ntoukas, Alexander Roberts, Evangelos Gkanas*
Centre for Advanced Low Carbon Propulsion Systems (C-ALPS)/Clean Growth and Future Mobility, Coventry University, UK,
presenting author, corresponding author*

INTRODUCTION

Advanced energy storage devices are necessary for the next generation of electric vehicles and electronic devices. In addition, such devices will assist towards the utilization of clean energies, like solar and wind to the power grid[1]. Supercapacitors (SCs) are highly potent electrochemical energy storage devices, however in their current form are used as secondary power sources, mainly due to the low energy density. It is out of great importance to practically upgrade their potential[2]. Metal Organic Frameworks (MOFs) are a new type of crystalline porous materials that present some extraordinary properties such as high porosity, large surface area, tuneable pore size and incorporated redox metal centres; thus, they have the potential to replace the current electrode materials[3].

This work is a systematic study towards the development of binary Ni/Co MOFs. Parameters such as the Ni/Co ratio and the metal to organic ratio have been examined and their effects to the structure and properties of the resulted MOFs have been evaluated and identified. The resulted MOFs have been structurally and electrochemically characterised.

EXPERIMENTAL DETAILS

The Ni/Co MOFs have been synthesised by a one-step solvothermal method. $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ have been used as the metallic salts and terephthalic acid (H_2BDC) as the organic ligand. The solvent used was a mixture of N,N-dimethylformamide (DMF) with ethanol (1:1). Various ratios of Ni:Co have been considered (4:1, 3:1, 2:1 and 1:1). The metal to organic ratio was 1:1. The solutions were kept under magnetic stirring for 1h and then were placed in a 200mL stainless steel autoclave and kept to 170°C for 16h. After natural cooling, the precipitate was centrifugated and washed with DMF and ethanol several times.

RESULTS AND DISCUSSION

Figure 1a presents the SEM micrograph of the Ni/Co MOF (Ni:Co – 1:1). The resulted MOF consists of multiple 2D interlayered nanosheets leading to a microflower-like crystalline structure. The micrographs, when the Co content decreased presented a similar pattern.

Figure 1b presents the XRD spectrum for Ni/Co MOF (Ni:Co ratio 1:1). The peaks present sharp and narrow shape indicating that the synthesised sample is crystalline. The peaks at 2θ=8.86°, 14.2°, 15.86° and 17.8° were identified. They correspond to the (200), (001), (201) and (-201) crystalline planes of the $[Ni_2(OH)_2(C_8H_4O_4)]$, respectively[4].

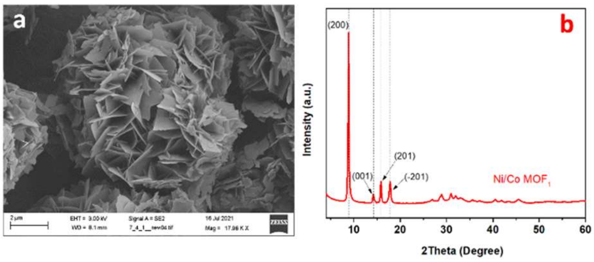

Figure 1. 1a SEM image of Ni/Co-MOF. 1b XRD spectrum of Ni/Co-MOF

Figure 2 presents the CV curves of synthesised Ni/Co-MOF (Ni:Co 4:1) and Ni-MOF. They demonstrate their redox peaks, showing that they possess pseudocapacitive properties. Moreover, Ni/Co-MOF owns a larger area than Ni-MOF, indicating a higher capacity which is attributed to the redox reactions by both nickel and cobalt ions.

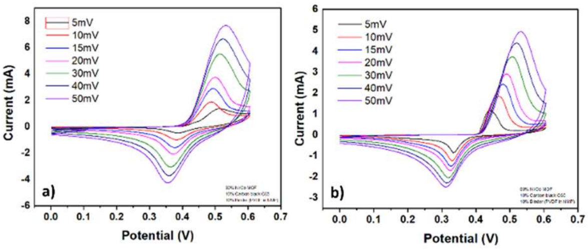

Figure 2. CV curves of Ni/Co-MOF and Ni-MOF

CONCLUSION

Bimetallic Ni/Co-MOFs were successfully synthesised by solvothermal method. The successful incorporation of Co is achieved when it partially replaces Ni while maintaining the desired crystalline structure. The following step is to scale up these materials to fabricate and test electrodes for high power energy storage applications.

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Ilias Ntoukas was born in Greece. He completed his BSc degree in the department of Materials Science at the University of Patras in 2019. His final year project Thesis was in the field of the development of novel processes and materials for hydrogen production with the utilisation of photoelectrochemical cells. Currently, Ilias is undertaking his PhD at the Centre for Advanced Low Carbon Propulsion Systems (C-ALPS), Coventry University where the main focus of his research is towards the development of novel nanostructures and systems for energy storage applications.

Presentating author: Ilias Ntoukas, e-mail: ntoukasi@uni.coventry.ac.uk tel:+447311488772

Nanostructures formed by copper passivation as catalysts for hydrogen generation

Anđela Mitrović Rajić[1], Tijana Pantić[1], Sandra Kurko[1], Jelena Rmuš[1], Anna M. Brudzisz[2], Damian Giziński[2], Jasmina Grbović Novaković[1], Wojciech J. Stępniowski[2]

[1]Vinča Institute of Nuclear Sciences,National Institute of Republlic of Serbia, Centre of Excellence for Reneable and Hydrogen Energy, University of Belgrade, POB 522, Belgrade, Serbia

[2]Institute of Materials Science & Engineering, Military University of Technology, Kaliskiego 2 00908 Warszawa, Poland

Nanostructured oxides formed by copper electrochemical oxidation have found numerous applications in emerging applicastions, like sensing, electrochemical carbon dioxide reduction into hydrocarbons and their derivatives, photocatalysis, or as electrodes in direct methanol fuel cells [1]. Up to now, numerous ways of an electrochemical copper oxidation were tested. Both systemts, 3 electrode with potentiostat and standard 2-electrode with DC power supply were found to form succesfuly nanowires, nanoneedles and nanorods made of copper oxides, like Cu_2O, CuO as well as copper (II) hydroxide, $Cu(OH)_2$ [2]. Numerous electrolytes, like NaOH, KOH, NH_4HCO_3, Na_2CO_3, K_2CO_3 were tested.

In current research, electropolished copper was anodized in 1.0 M NaOH, using potentiostat and 3-electrode system in order to form nanoneedles. The major novelty in the research was application of electrolyte additives, enhancing formation of the nanostructured passive oxide layer. Potassium permanganate, $KMnO_4$ was used as an oxidation booster during anodizing. Application of even 10^{-4} M $KMnO_4$ in 1.0 M NaOH was found to be advantegeous for the nanostructured formation.

Another oxidation booster used to enhance nanostructures formation was H_2O_2 However in this case, rapid gaseous oxygen formation as the eletrolyte was prepared was a problem. In order to avoid it, fresh, concentrated H_2O_2 was being added at various moments of copper anodizing. It was found that the best moment to add the boosting agent was 5 minutes before end of the process. When hydrogen peroxide was added too early, the formed oxide was not uniform – there were local zones where thin, oxide layer tends to delaminate and in extreme situations, pitting corrosion was promoted. The best effects were for 1 hour long copper anodizing when H_2O_2 was added during the last 5 minutes (1 ml of 30% H_2O_2). This provided high uniformity of oxide and dense packaging of the nanoneedles (Fig. 1).

The obtained materials were found to be promising for photoelectrochemical water splitting. Preliminary research reveal that thanks to the composition and morphology of the oxide efficient H_2 generation is possible.

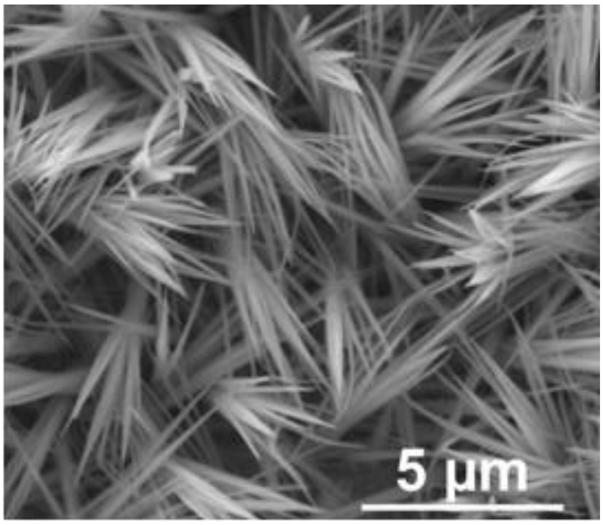

Figure 1. FE-SEM images of CuO_x formed by copper anodizing in 1.0 M NaOH with H_2O_2 as an oxidation booster.

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Anđela Mitrović Rajić is research assistant at Vinča Institute of Nuclear Sciences in Belgrade, Center of excellence for hydrogen and renewable energy (CONVINCE). Her research work is foused on mechanochemical activation of natural materials as well as synthesis by anodization.

Presentating author: Anđela Mitović Rajič; email:andjela.mitrovic@vin.bg.ac.rs; tel:+381631590057

Synthesis of Yttrium doped Barium Zirconate/Cerate electrolyte materials and densification using conventional and cold-sintering processes

Castellani Pablo, NICOLLET Clément, QUAREZ Eric, JOUBERT Olivier and LE GAL LA SALLE Annie

Institut des Matériaux de Nantes Jean-Rouxel (IMN-CNRS- Nantes Université)
2 rue de la houssinière, 44 000 Nantes, FRANCE
Tel: +33-2-40-37-39-39
pablo.castellani@cnrs-imn.fr

Compared to high temperature SOEC usually based on Yttrium stabilized Zirconia electrolytes, intermediate temperature PCEC allows the production of water free hydrogen and a better chemical stability. Proton conducting perovskite specific materials, such as Barium Indates[1], Zirconate or Cerates[2] are nearly commercial electrolytes for such devices.

This study focuses on the synthesis the characterization and the densification of the $BaZr_{1-x}Ce_xY_{0.1}O_{3-\delta}$[3] powder. At intermediate temperature and under humid atmosphere, hydration process allows diffusion of protonic charges. Such electrolyte material combines a low thermal expansion coefficient and a high protonic conductivity. Two specific stoichiometry's have been studied, Cerium rich $BaZr_{\mathbf{0.3}}Ce_{\mathbf{0.6}}Y_{0.1}O_{3-\delta}$ (BZCY361) and Zirconium rich $BaZr_{\mathbf{0.7}}Ce_{\mathbf{0.2}}Y_{0.1}O_{3-\delta}$ (BZCY721). BZCY361 shows at 550°C, a conductivity level of 2.10^{-2} $S.cm^{-1}$. However, despite its high protonic conductivity, the cerium rich phase is not stable at high temperature and is torn apart in presence of carbon dioxide.

$BaZr_{1-x}Ce_xY_{0.1}O_{3-\delta}$ powder has been synthetized by combustion reaction based on nitrate precursors and glycine as organic complexing/fuel agent. The fuel/oxidizer (nitrates) ratio, which is a key parameter[4], has been optimized in order to obtain the best purity and crystallinity. The powder is then milled and calcined. The single-phase electrolyte powder is conventionally shaped into pellets and densified A minimal temperature of 1600°C is necessary to obtained a density of 90-95%. In order to reduce the sintering temperature, an intermediate sintering step called "Cold Sintering Process"[5] (CSP) has been investigated. In this technic, derived from the hydrothermal method, BCZY powder mixed with a small volume of liquid phase (3-30 wt%) is simultaneously pressed (at 50 to 500 MPa) and heated during a short time period (1-60 min) at low temperatures (100-200°C), leading to dense pellets.

In regards to design a complete cell based on this electrolyte, EIS has been performed under hydrogen and air atmosphere. The electrochemical measurements of the samples provided by the different protocols and stoichiometry's have been compared in order to determine the impact of the CSP and stoichiometry parameters on the ionic conductivity of the material.

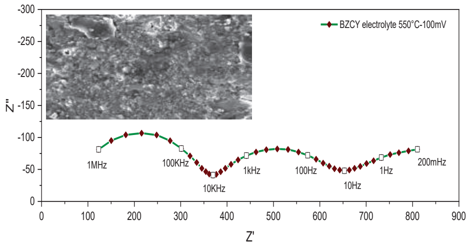

Figure 1. SEM and EIS characterization of the $BaZr_{1-x}Ce_xY_{0.1}O_{3-\delta}$ electrolyte

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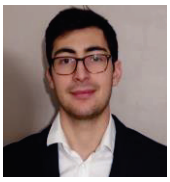

I am Castellani Pablo, second year PhD student in solid state chemistry at the material intitute of Nantes. I am French. I graduated my master degree in materials and energy at the School of Mines de Paris. And I am actually working on the synthesis and characterisation of a protonic conduction electrolysis cell.

Castellani Pablo email: pablo.castellani@cnrs-imn.fr Tel: +33 6 13 24 03 66

Lithium-ion Battery Safety Analysis with Physical Sub-models

Samuel Ogunfuye[1], Hayri Sezer [2] and V'yacheslav Akkerman [1]
[1]Center for Innovation in Gas Research and Utilization, West Virginia University, 1306, Evansdale Drive,
Morgantown,WV,26505, USA
[2]Department of Mechanical Engineering, Georgia Southern Univesity, 1332, Southern Drive,
Statesboro, GA 30458, USA

Ever-increasing explosions occurring globally at a rapid rate and also in diverse situations have re-establish the fact that novel, faster and accurate approaches have to be developed to analyze and possibly curb these explosions and avert future explosions. Experimental endeavors and CFD simulations do require huge time, resources as well a high level of expertise and technicalities. This might delay prompt analysis and the ability to draw concrete conclusions, as such cause setback in recommending safety measures for different situations and conditions. Therefore, robust models which are accurate and fast to give an insight into an explosion, and possibly simulate different conditions easily and quickly are much needed.

Also, this study has a holistic approach towards explosions, by not only considering characterizing the contemporary gaseous explosions in an enclosure at different configurations but extending to lithium-ion batteries explosion prediction and characterizing these explosions. As we move (paradigm shift) towards the renewable energy age, more and more fire explosions from energy storage systems such as Li-ion batteries are on the rise. Which makes computational tools a timely, robust, and versatile tool for predicting these explosions, characterizing them quickly, and accurately, which gives an edge in prompt LIB explosions analysis and gives suggestions on possible solutions, as well as aiding future design considerations and safety analysis..

However, there are limited works and numerical models that have attempted to quantify and characterize the hazards associated with the explosion of gases ejected from LIBs during thermal runaway inside the battery pack enclosure. Therefore, in this work, LIBs explosion hazards are analyzed, and a computational model is developed to study explosion venting scenarios of hazardous gases released from LIBs during battery failure, as well as developing sub-models to characterize LIB failure, explosions and their associated hazards.

It is the hope that this research will aid lithium-ion battery safety analysis, and the results from this research work can be employed in the design of safety vents used in LIB energy storage compartments to mitigate the effect of explosion. Also, the National Fire Protection Association (NFPA) standards are widely used in industry because of their simplified equations. Therefore, the numerical model developed in this work will enable a field engineer who does not have experience with numerical methods or/and the physics of complex explosions to use this code to design a vent for a compartment where an explosion from a LIB failure might occur. In all, this work will greatly support the fire safety research community in terms of lithium-ion battery safety analysis and explosion characterization.

A current Ph.D. student at west virginia university, USA, actively involved in energy and combustion research. A renewable energy generation , next-generation power cycles, and energy systems enthusiast. Having a great passion for design innovation, and building of efficient, effective and safe process.

Presentating author: Samuel Ogunfuye, e-mail: sao0008@mix.wvu.edu tel: +13042769245

Oxygen reduction and oxygen evolution reaction electrocatalysis over Fe_3C decorated wood-derived integral N-doped C cathode used in rechargeable Li-O_2 batteries

Costas Molochas [3], Georgia Balkourani [3], Huagen Liang [1], Zejia Gai [1], Fu Chen [1],
Shengyu Jing [1], Wei Kan [2], Bing Zhao [2], Panagiotis Tsiakaras [3]
[1]China University of Mining and Technology, Xuzhou, 221008, China.
[2] Heilongjiang Provincial Key Laboratory of Surface Active Agent and Auxiliary, Qiqihar University, 161006, China.
[3] Department of Mechanical Engineering, University of Thessaly, Pedion Areos 38834, Greece.
(tsiak@uth.gr)

Cheap and efficient cathode is the premise for the industrialization of Li-O_2 batteries. Herein, an integral Fe_3C decorated wood-derived Fe, N co-doped carbon (N-wdC-MS) was developed via one-step pyrolysis with $FeCl_3$/LiCl impregnated paulownia wood and melamine, serving as the cathode of Li-O_2 battery. This three-dimensional (3D) free-standing cathode inherited the aligned channels of wood, ensuring unimpeded O_2/electrolyte supply.

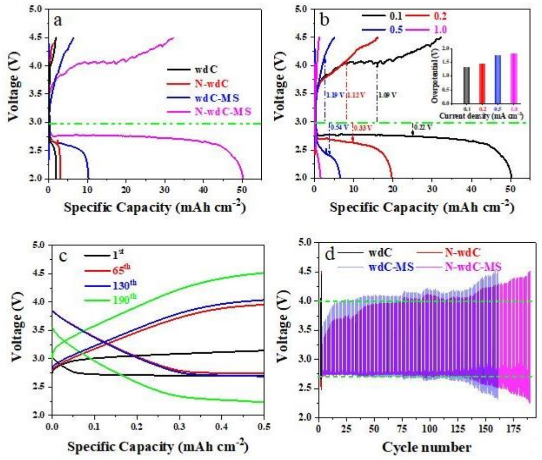

Figure. a) Discharge/charge curves of Li-O_2 batteries with different cathodes at 0.1 mA cm^{-2}. b) Rate performance of Li-O_2 battery with N-wdC-MS. c) Discharge/charge curves of Li-O_2 battery with N-wdC-MS at 0.1 mA cm^{-2} with a limited capacity of 0.5 mAh cm^{-2}. d) The termination voltages of discharge and charge as a function of cycle numbers.

The etching effect of FeCl3/LiCl mixed molten salt created more pore structure for the carbonized wood, contributing to expanded triple-phase boundary. Fe3C@NC aggregates evenly grew on the surface and channels of carbonized wood, which acts as the catalytic sites.

Moreover, in aqueous solution, N-wdC-MS showed excellent oxygen reduction reaction/oxygen evolution reaction (ORR/OER) catalytic activity. With so many advantages, the Li-O2 battery assembled with N-wdC-MS as cathode deliver a superhigh specific capacity of 50.28 mAh cm-2 at 0.1 mA cm-2, and achieve a long cycle-life of 190 times. This low-cost and easily available wood-based electrode provides a new idea for designing and large-scale production for cathode of other Metal-Air/Metal-S batteries.

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Molochas Costas completed his studies in 2019 at the Department of Mechanical Engineering of the University of Thessaly (uth). At the beginning of 2020 he was admitted to the same Department for the preparation of his doctoral dissertation in the laboratory of alternative energy conversion systems (LAECS), with emphasis on the design and development of catalytic materials with high carbon monoxide tolerance for application in fuel cells. Konstantinos Molochas has submitted three publications to peer-reviewed journals and has participate in two world conferences.
Presentating author: Costas Molochas, e-mail:molospao@gmail.com, tel:6985748665

Effect of CO, CO_2, and CH_4 in the hydrogen oxidation kinetics of Pt/C: An electrochemical PEMFC H_2-pump experiment

Costas Molochas [1], Georgia Balkourani [1], Aggeliki Brouzgou [2], Sotiria Kontou [1], Panagiotis Tsiakaras [1]
[1] Laboratory of Alternative Energy Conversion Systems, Department of Mechanical Engineering, School of Engineering, University of Thessaly, 1 Sekeri Str., Pedion Areos, 38834, Volos, Greece
[2] Department of Energy Systems, Faculty of Technology, University of Thessaly, Geopolis, 41500 Larissa, Greece
(tsiak@uth.gr)

The severe degradation of Pt activity towards hydrogen oxidation reaction (HOR) in presence of impurities has been well demonstrated over the past 1-2 decades. However, their effect has not been clearly supported by kinetic data because their evaluation with rotating disk electrode experiments is hindered due to mass transport limitations in the whole range of HOR overpotentials. Herein, we investigate the effect of various concentrations of CO, CO2, and CH4 on the HOR kinetics of a benchmark Pt/C anode catalyst layer via an electrochemical H2-pump experiment.

The effect of the tested impurities on the HOR kinetics are revealed by the change in the exchange current densities and HOR activation energies relative to the case of pure hydrogen supply. First of all, our HOR kinetic results in the absence of impurities are in good agreement with previous works, indicating the validity of the followed experimental procedure. We found that CO2 and CH4 have a minimal impact on the Pt/C HOR kinetics for concentrations up to 40 vol.%, indicating that they have no essential poisonous effect on the catalyst surface due to adsorption. On the other hand, the presence of CO in concentrations above 3 ppm significantly hinders the HOR kinetics of Pt/C, leading to impractical anode overpotentials.

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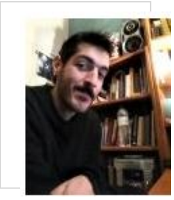
The authors thankfully acknowledge co-financing by European Union & Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (Project code: T1EDK-02442).



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Presentating author: Costas Molochas, e-mail:molospao@gmail.com, tel:6985748665

Studies of the effect of Hf doping on the electrochemical performance of C15 Laves type metal hydride battery anode alloys

Ika Dewi Wijayanti[1] and Volodymyr Yartys [2]
[1] Department of Mechanical Engineering, ITS, Surabaya, Indonesia
[2] Institute for Energy Technology (IFE), Kjeller, Norway

This paper is focused on studying the electrochemical performance of Hf-modified Ti-Zr based AB_2 Laves type metal hydride battery anode alloys with composition $Hf_xZr_{24-x}Ti_{6.5}V_{3.9}Mn_{22.2}Fe_{3.8}Ni_{38}La_{0.3}Sn_{0.3}$ (x=1-4). Earlier we showed that Zr-Ti-based Laves phases crystallize with cubic C15 and hexagonal C14 Laves type structures and that they exhibit excellent electrochemical performance as anode electrodes of the metal hydride batteries also allowing to achieve a good high rate dischargeability (HRD) and easy activation [1-5]. To further improve the performance of the alloys, a substitution of Ti and Zr by Hf is an option to explore. The alloy samples were prepared using the arc melting. The phase composition and the morphology of the alloys were analysed by X-ray diffraction and scanning electron microscopy. Metal-gas interactions and electrochemical capacities were characterized by PCT measurements and by performing the electrochemical tests on the half-cells. MH alloy powder with a particle size in the range of 40–60 μm was selected to perform the electrochemical tests. Electrochemical properties were tested in a three-electrode system using a 9 N KOH solution electrolyte at room temperature. The system consisted of a MH working electrode, a sintered $NiOOH/Ni(OH)_2$ counter electrode, and a Hg/HgO reference electrode.

The studied alloys contained a mixture of the Laves phases of C15 and C14 types. With increase of the Hf content, the abundance of the C14 phase increased. This was followed by the contraction of the unit cell volume of the C14 phases.

In contrast, for the C15 phase, its abundance decreased with the increase of Hf content. Maximum hydrogen storage and discharge capacities reached 1.47 wt.% H and 307 mAh/g, respectively, for the Hf-free Ti-Zr alloys.

An introduction of 1-4 wt.% Hf into the alloy slightly decreased the hydrogen storage and discharge capacities. However, hydrogen diffusion became faster for the Hf-doped alloys with H diffusion coefficient of 4.2E-9 $cm^2.s^{-1}$ obtained for the alloy containing 3 wt.% Hf. This value is significantly higher than that for the Hf-free Ti-Zr alloy, 2.4E-10 $cm^2.s^{-1}$. Effect of Hf is related to the formation of the secondary La-Zr and La-Sn rich phases which remain inert to hydrogen during the adsorption-desorption of hydrogen by the studied alloys but also to the change of the intrinsic properties of the Laves type alloys for which a substituion (Zr/Ti) → Hf causes a facilitation of hydrogen diffusion in the formed hydrides.

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Ika Dewi Wijayanti earned her PhD from the Norwegian University of Science and Technology (NTNU) in collaboration with Institute for Energy Technology (IFE) in 2020. She was working on the development of Nickel Metal Hydride (NiMH) battery anode materials. By combining several methods for preparing anode materials including arc melting, rapid solidification, and annealing, she obtained promising materials with discharge capacity reaching 500 mAh/g. She is currently working as a lecturer and researcher at Institut Teknologi Sepuluh Nopember (ITS) Surabaya, Indonesia.

Presenting author: Ika Dewi Wijayanti; e-mail: dewi@me.its.ac.id; Tel: +62 8211 000 7268.

Towards a digital twin of fuel cell hybrid electric city bus

Jacek Hunicz, Michał Gęca and Paweł Droździel
Lublin University of Technology, Department of Sustainable Transport and Powertrains, Nadbystrzycka 36, 20-618 Lublin, Poland

The complexity of the system presents a challenge to the development of hybrid fuel cell (FC) battery vehicles when striving to minimise both energy consumption and rare materials utilisation. The design process includes the electric drive, sizing of the fuel cell and batteries, fuel storage system and energy management strategies (EMS) [1].

The use of control-oriented grey-box models accelerates the design process and cuts development costs. However, real-time, physics-based models (digital twins) are emerging as they offer better predictive capability and scalability than their mean-value, data-driven counterparts [2].

This study proposes a digital twin model of the FC bus, including vehicle dynamics, powertrain system and onboard energy consumers. The research object is a 12-metre city bus powered by two synchronous electric motors integrated with a rear axle. The energy supply system is based on a li-ion battery pack and proton exchange membrane fuel cell (PEMFC) module, which generates energy from hydrogen stored in metal-polymer tanks under 350 bar pressure. The comprehensive information about the baseline bus configuration can be found in [3].

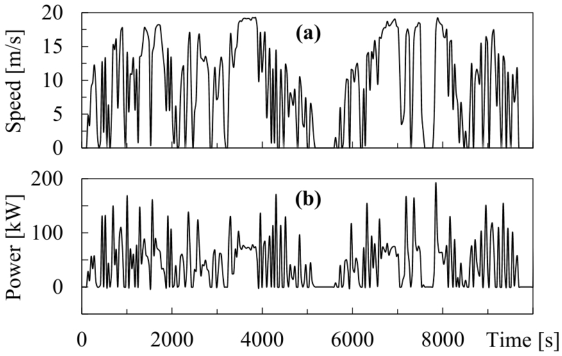

Figure 1. Filtered time-series of measured speed and calculated power on motors during operation

Comprehensive experimental data for model validation were collected during supervised real-world bus service in the intercity mode. Model calibration and validation involved detailed running parameters, overall vehicle fuel consumption and transient electric parameters at various system knots.
Figure 1a shows exemplary time series of speed, which served as input data, whereas Figure 1b shows calculated power demand on propulsion motors. The model validation demonstrated a good agreement with experimental data. The fuel consumption was predicted with lower than 5% error under multiple operating tasks. Notably, the same model with proper calibration was used for the simulation of an ultra-light FC vehicle [4], providing satisfactory results.

The powertrain system simulations included various sizes and types of the components and EMS. Figure 2 shows the exemplary comparison of the battery state of charge (SOC) for two variants of EMS; the typical rule-based control (a) and a proprietary heuristic algorithm (b) aimed at increasing battery life. Without any detailed analysis, Figure 2 indicates that in case (b) the charging/discharging intensity is reduced.

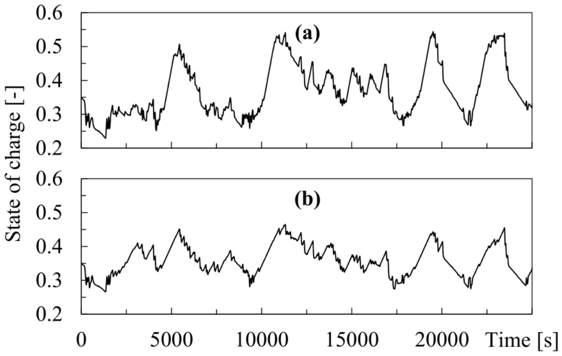

Figure 2. The battery state of charge for two EMS variants.

As a final remark, it should be underlined that the developed model can mimic the operation of a real FC bus with satisfactory accuracy. The model can be implemented to (i) support the sizing of the system components, (ii) EMS testing, and (iv) planning of the charging/refilling infrastructure.

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Jacek Hunicz (PhD, DSc.) is an associate professor and head of Powertrains Laboratory at the Lublin University of Technology, Poland. His track record includes experimental research into low-carbon fuels and electrified powertrains. With 23 years of professional expertise, he is an author of over 50 papers in SCI journals and a grant holder of several projects funded by the National Science Centre. He is a member of the board of the Polish Society of Combustion Engines, a scientific advisor in the field of powertrain R&D to the Polish military company HSW Dęblin and PAK-PCE Polish Hydrogen Bus company.

Presenting author: Jacek Hunicz, e-mail: j.hunicz@pollub.pl, tel: +48 81 5384175

Hydrogen storage properties of MgH_2-M (M=Ni,V,Cr) composties

Zorana Sekulić[1], Jasmina Grbović Novaković[2], Bojana Babić[2], Milica Prvulović[2], Igor Milanović[2], Katarina Tošić[2], Vanja Asanović[2]

[1]Ministry of Capital Investments, The Government of Montenegro, Directorate for Energy and Energy Efficiency,Rimski trg 46, 81 000 Podgorica, Montenegro

[2]Vinča Institute of Nuclear Sciences, National Institute of Republic of Serbia, Centre of Exccellece for Renewable and Hydrogen Energy, University of Belgrade, POB 522, 11000 Belgrade, Serbia

[3]Faculty of Metallurgy and Technology, University of Montenegro, Cetinjski put 2, 81000 Podgorica, Montenegro

The matter of thermodynamic barriers in the decomposition of magnesium hydride is the subject of many scientific studies, primarily through the process of destabilization of the hydride structure [1]. The most commonly used method for hydride destabilization is nanostructuring by mechanical milling which leads to reduction in the particle and crystallite size of the MgH_2 powder. Nanostructuring is often combined with catalyst addition and composite formation [2,3]. Depending on the energy input during the milling process, the typical milling time for magnesium or magnesium hydride ranges from 15 min to 20 h for high-energy mills and from 20 to 150 h for low-energy mills. The most of research is focused on the morphological, structural and thermodynamic effects typical for long milling times, while in this work we have followed the changes taking place under short milling time. The thermal stability of magnesium hydride, is related to structural changes - change of the crystallites and powder particles size. The analysis also considered the changes in activation energy.

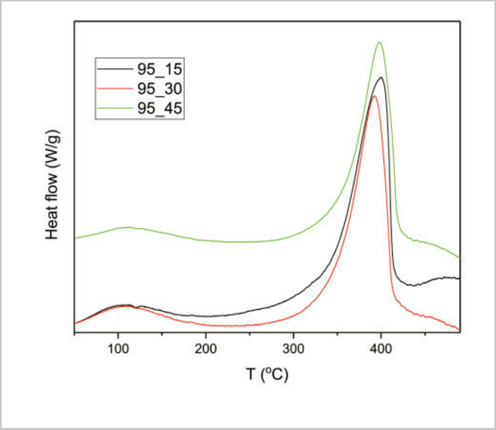

Figure 1. DSC curve for MgH_2-5% V nanocomposites mechanically milled for 15, 30 and 45 minutes.

MgH_2-M composites were prepared by mechanical milling of the as-received MgH_2 powder (Alfa Aesar, 98% purity) with the addition of 2 and 5 wt.% of M (M= V, Ni, Cr). Mechanical milling was performed in s SPEX 5100 Mixer Mill using 8mm diameter milling ball. The vial were loaded with powder and balls up to 40% of the volume in order to leave enough space for efficient milling. Samples were milled for 15, 30 and 45 minutes under the inert atmosphere of argon and ball-to-powder ratio 10:1 Figure 1. shows the differential scanning calorimetry (DSC) curves for MgH_2 samples with the addition of 5 wt.% of V milled for 15, (95_15), 30 (95_30) and 45 (95_45) minutes. The DSC curve of commercial powder MgH_2 shows the sharp symmetric high temperature (HT) maximum which originate from desorption from β – MgH_2 at 454°C. The maximum of very low intensity peak is observed at about 350°C, which is a consequence of surface-bound OH groups. If the sample is exposed to the atmosphere, a third, low - temperature maximum may occur, which originates from OH groups and water. It is observed that with increasing milling time hydrogen release temperature increases, which means that shorter milling times have a better effect on the desorption properties of MgH_2. All three samples show a significantly different desorption profile compared to the commercial sample. The absence of desorption from medium temperatures is clearly visible, but a pronounced low temperature peak (LT) appears at approximately 110 ºC.

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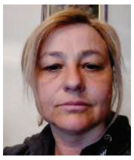

Graduate degree in physical chemistry, **1999**, Magisterium in physical chemistry, **2003,** PhD in physical chemistry **2005**. From **1999** works in Vinča Institute of Nuclear Sciences in Laboratory of physics as principal researcher. **2008** Post doc in ENEA CR Casaccia. President of Serbian Society for Microscopy from **2010-2020. 2009** awarded from International Association of Hydrogen Energy with IJHE outstanding Service Award. Guest Editor: Novel Perspectives on Hydrogen Storage in Solid Media and International Journal of Hydrogen Energy. From **2018** she is the head of Centre of Excellence for Hydrogen and Renewable Energy.

Presentating author: Jasmina Grbović Novaković, e-mails:jasnag@vinca.rs, jasnagn@gmail.com tel:+381641696253

Paper-based laser-induced in situ nano-hybridization of Co_3O_4-rGO as an active bio electrode

Nishchitha N K[1], Pavar Sai Kumar[1], and Sanket Goel[*1]

[1]MEMS, Microfluidics, and Nanoelectronics (MMNE) Lab, Department of Electrical and Electronics Engineering, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India

In situ nano-hybridization provides well-decorated Co_3O_4-rGO electrode in one-step process which significantly increases the specific surface area and sensitivity. Flexible electronic devices developed via *in situ* decoration of reduced graphene oxide (rGO) delivers high performance and reliability. For the first time, this work provides a solution to the tedious, expensive, and time-consuming conventional method.

Herein *in situ* uniform, nano-hybridized Co_3O_4-rGO electrodes were fabricated via simple and user-friendly 450 nm laser dosing on Grade 1 Whatman filter paper through photothermal reduction. Such predominantly available paper was dip-coated uniformly in cobalt chloride ($CoCl_2.6H_2O$) solution and used as a substrate after ensuring proper drying as displayed in Figure 1.

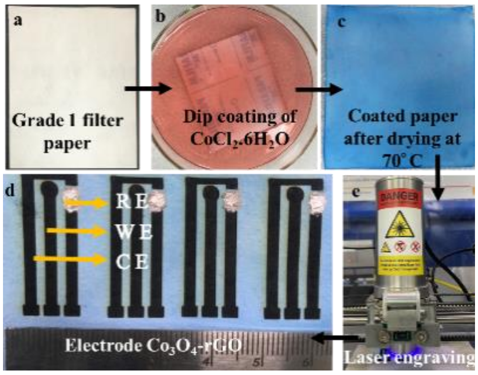

Figure 1. (a, b, c) $CoCl_2.6OH$ coating on the Grade 1 filter paper. (c, d) Laser dosing by 450 nm laser to fabricate *in situ* Co_3O_4-rGO, electrode on paper.

The conductivity of bare rGO was 2423 S/m [1] and interestingly even with the presence of 30 atomic% of oxygen, for an optimized concentration of (Co^{+2}), the conductivity of the Co_3O_4-rGO electrode was found to be 1150 S/m. The specific surface area of *in situ* Co_3O_4-rGO is found greater than the bare rGO [2] and it is highly greater than the specific surface area of nanocomposite synthesized by other reported methods [3],[4]. So it is perceived that Co_3O_4-rGO should lead to achieve better sensory parameters and higher-power output in fuel cell applications [5]. The Brunauer-Emmett-Teller (BET) method was utilized to study the surface area of the developed material. X-ray diffraction analysis (XRD) confirmed the crystallinity of the material [6], and the morphology of the *in situ* modified surface was found to be uniformly distributed as shown in Figure 2, this was visualized by Scanning Electron Microscopy (SEM). The elemental mapping and composition for the different doping concentrations were analyzed by the Energy Dispersive X-Ray Analysis (EDX).

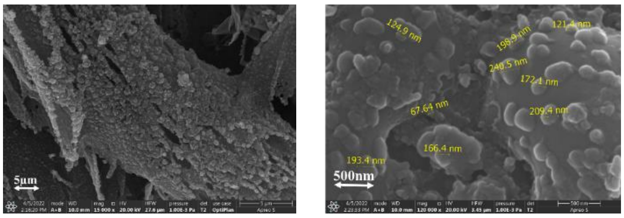

Figure 2. SEM imaging of optimized electrode on paper at 5 µm and 500 nm resolution.

Such rigorous characterizations reveal the potential of the developed *in situ* Co_3O_4-rGO as a bioelectrode for developing flexible devices such as biosensors with higher sensitivity and selectivity, and other energy harvesting applications.

Keywords: *In situ* decoration, Laser-Induced Co_3O_4-rGO, Biosensing applications, Surface modification, uniform growth.

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Nishchitha N K is a Ph.D. candidate with the MEMS, Microfluidics, and Nanoelectronics (MMNE) Lab, BITS Pilani, Hyderabad Campus, India. She obtained her B.E from KVGCE (VTU Belgaum, India) in 2017 and M.Tech from NIE Mysuru, India in 2019. She has done her internship and M.Tech project work at NTU, Taiwan under the 'Research Visiting Program' and worked as a project assistant on perovskite solar cells at Mangalore University, India. Research interest covers Micro / Nanosensors and Energy Harvesters

Presenting author: Nishchitha N K, e-mail: p20210417@hyderabad.bits-pilani.ac.in tel: +919482715986

Modelling and analysis of marine PEM fuel cell hybrid energy system

Tino Vidović[1], Jakov Šimunović[1], Ivan Tolj[1], Gojmir Radica[1]

[1] University in Split, Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, Split, Croatia

Developing more efficient and versatile marine power systems is important due to increasingly stringent emissions regulations. Without further action to reduce greenhouse gas emissions, the contribution of shipping will increase by 150% to 250% by 2050, reaching a share of 12% to 18% of global CO_2 emissions [1]. One way to achieve this is to transform the conventional power system and its energy management strategy into a hybrid system. The hybrid architecture itself is complex and broad enough, but not yet developed far enough for marine applications [2]. The main argument for implementing a more complex system such as hybrid marine power system, is that additional options in energy management bring the operation of each energy source closer to its optimal operating point. This is especially important for internal combustion engines, which operate most of the time in the part-load range, where their efficiency can drop significantly.

Today, the most common alternative energy source system is fuel cell technology with different types of fuel cells, batteries, and supercapacitors as energy storage systems [3] The objective of this research is to size and analyse one of the possible auxiliary power systems, namely a hydrogen PEM cell with its associated components. For this research, the model was developed using the AVL Cruise-M software package (shown in Figure 1).

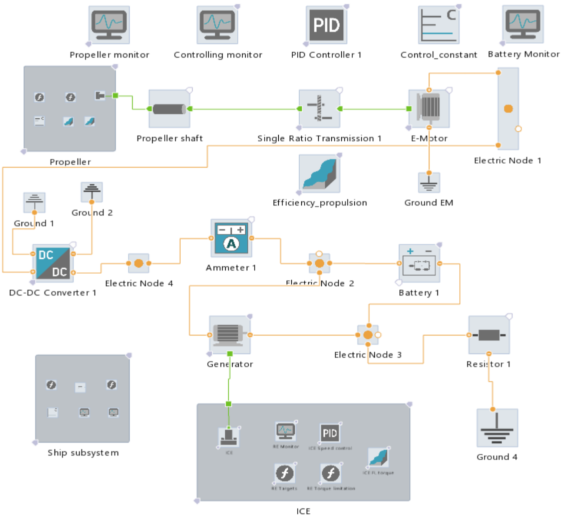

Figure 1. Model developed in Cruise-M

The sizing is done according to the energy demand of the ferry operating on the local line. Fuel cells generate DC energy that is compatible with modern electric and hybrid naval architectures, and can be used in parallel, disconnectable configurations to meet the variable energy needs of the vessels. And, if renewable hydrogen is utilized, fuel cells are a true well-to-wake zero emission power source [4].

By using the hybrid system, the specific fuel consumption on a given route could be reduced by about 5% compared to the case where only a diesel engine is used, and accordingly reduces exhaust emissions.

Acknowledgements

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Mag. ing. mech. Tino Vidović is a doctoral researcher at the Department of mechanical engineering and naval architecture of the University of Split, Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture. He earned a master's degree in mechanical engineering at the same Faculty in 2021.
His research interests include internal combustion engine modelling, hybrid energy systems, energy management optimization.
Presentating author: Tino Vidović, e-mail: tvidov00@fesb.hr tel: +385 99 518 9088

Modifying SPEEK/PBI Blend Membrane with boron nitride for PEM Fuel Cells

Huzaifa Mohammed Adam Harameen, Ramiz Gültekin Akay
Department of Chemical Engineering, Kocaeli University, 41380 Kocaeli, Turkey.

Polyether-ether-ketone (PEEK) is a widely used low cost thermoplastic material. Sulfonated poly(-ether-ketone) (SPEEK) has a relatively high electrical conductivity with low methanol permeability which makes it a competitive alternative ion exchange membrane material for PEM [1]. To overcome the mechanical and thermal stability limitation in SPEEK membranes PBI was introduced to SPEEK membrane Akay RG, et al [2]. In which SPEEK/PBI-10% was found to has the optimum properties. The only limitation of the blind is the low protonic conductivity due to the poor conductivity of PBI. Yet, this limitation can be overcome by sulfonating PBI and or by filling the membrane with a high protonic conductive material or both.

Among all the possible fillers, BN nitride shows an extraordinary physicochemical, electrochemical, thermal, mechanical, and barrier properties, extraordinary physical/chemical stability and high protonic conductivity. properties. Therefore, BN can be introduced to SPEEK/PBI blend to enhance the protonic conductivity remarkably. In addition, it improves the other physicochemical properties. That makes BN the absolute solution for SPEEK/PBI membrane limitation. Moreover, the expected high protonic conductivity, thermal and mechanical stability, and low cost make SPEEK-PBI/BN blend one of the best non-perfluorinated membrane to be used in various application.

Therefore, in study SPEEK/PBI/BN membrane was prepared by simple casting. Firstly, BN was functionalized by adding BN to a 8:1 mixture of H_2SO_4 (95%con) and H2PO4 (85%con). Subsequently, a 15gm of $KMNO_4$ were added to the solution in a very slow rate and left for 24 hrs under stirring. Later on, 15ml of H_2O_2 was added followed by 250ml of deionized water. BN particles were then separated with a centrifugal separator. SPEEK and the functionalized BN were dissolved in DMAs, subsequently followed by adding PBI solution to the mixture and then dried in a vacuum oven (Figure 1).

The proposed membrane showed an attractive IEC compared to SPEEK/PBI membrane. The IEC stays at 2.18 mS/m and didn't change noticeably when the amount of filler increased from 10% up 20% (Figure 2a). Since BN had been treated with H_2SO_4 before it was mixed, the degree of sulfonation increased from 67% to over 80% (Figure 2b). The results from water uptake test were very law, the maximum uptake was 6.3% and it decreases with the higher amount of BN (Figure 2c). The membrane showed poor mechanical stability when the percentage of filler is higher than 10%, however, the mechanical stability for SPEEK/PBI/BN-10% membrane was remarkably high with a tensile stress of 8.61 MPa.

Other tests such as DSC, TG, protonic conductivity, and methanol permeability are going to be measured soon.

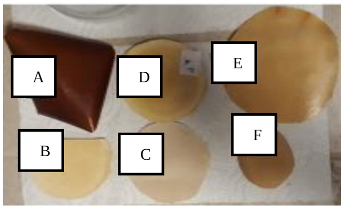

Figure 2: a) PBI, B) SPEEK@PBI/BN-20, C) SPEEK-PBI/BN-15, D) SPEEK-PBI/BN-10, E) SPEEK/PBI 12hrs stirring and ultrasonic , F) SPEEK/PBI 24 stirring

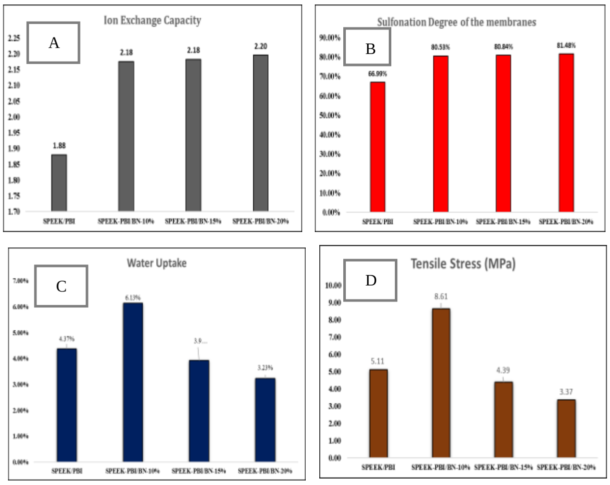

Figure 1: Charactrization of SPEEK/PBI/BN Composite Membrane

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Adam Harameen

Mr.Adam Harameen from the Department of Chemical Engineering, Kocaeli University. Having graduated from University of Khartoum in 2018, Adam Harameen obtained his B.SC in 2018 and currently he is doing his M.SC at Kocaeli university. His research interest covers Chemical plants design, Desalination, Thermal Energy storage, Hydrogen technology, and membranes.

Corresponding author: Adam Harameen, e-mail: hoz2t96@yahoo.com tel: +90 552 613 41 23

Synthesis of Pre-lithiated LixSi Anode Material for Lithium Sulfur Batteries

Muhammed Osman Numan Oğuz,[1,2] Ahmed M. Faris[2,3] Hatem Akbulut,[1,2,4] Mahmud TOKUR[1,2,4]
[1]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Türkiye
[2]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Türkiye
[3]Sakarya University, Institute of Natural Sciences, Nanoscience and Nanoengineering Department, Esentepe Campus, 54050, Sakarya, Türkiye
[4] NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Türkiye

Lithium ion batteries have a high capacity, high energy density, and long cycle life, which have been widely used in consumer electronics, electric vehicles, large power grids, etc. However, current lithium ion batteries have not met the demand of constantly evolving technology. The main reason for this is the limited capacity of transition metal oxides and graphite, which are mostly used in state of the art lithium ion batteries. Without any doubt, lithium metal is one of the most attractive anode materials for lithium ion batteries. [1] Nevertheless, lithium metal is very sensitive to humidity and oxygen and causes safety problems which is an important factor limiting the use of lithium metal in batteries. Besides all of this, commercial lithium-ion batteries have achieved extensive applications in the past years, but the development space is very small due to the high cost and limited theoretical energy density.

Lithium sulfur batteries have been widely researched due to their higher theoretical specific capacity (1675 mAh/g) and theoretical energy density (2600 Wh/kg) compared to the lithium ion batteries. In addition, lithium-sulfur batteries are the most competitive in gravimetric energy density with current technology, rather than volumetric energy density compared to lithium-ion batteries, which makes them suitable energy sources for electric cars, and portable electronic products. Besides, lithium-sulfur batteries have other great features such as rich raw material resources, low cost, and being environmentally friendly [2].

Despite many advantages of lithium-sulfur batteries they also have many challenges that need to be overcome. It is difficult to reach the desired theoretical capacity due to the discharge product of lithium sulfide and poor electrical and ionic conductivity. The volume expansion/contraction during charge-discharge is as high as 80%, which causes loss of active substance and decreases the capacity. Moreover, the shuttle effect occurs as a result of the migration of polysulfides formed during charging [3]. Therefore, the abovementioned problems have limited the commercial development of lithium-sulfur batteries.

In this study, prelithiated silicon alloy anode will be researched to overcome the several problems of lithium metal used in lithium-sulfur batteries. Because prelithiation is a common way to improve the manufacturability and safety of high capacity and high energy density batteries.The surface morphology of the produced electrodes will be characterized using Field-emission scanning electron microscopy (FESEM), and Energy dispersive spectroscopy (EDS) in order to understand the elemental surface composition of composites. The structures of the composites will be characterized using X-ray diffraction (XRD) patterns and Raman spectroscopy. The electrochemical performance of the produced LixSi electrodes will be investigated by charge/discharge and cyclic voltammetry tests from in CR2016 test cells. The resistances of the cells will be investigated using the ac impedance technique (EIS). This study could contribute to improvements in Li-S battery technology.

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

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Muhammed Osman Numan Oğuz

Muhammed Osman Numan Oğuz is a Master's Student at the Department of Metallurgical and Materials Engineering, Sakarya University. From 2017-2021, he was a graduate student in the same department and worked on scientific projects as a Tübitak-Star Scholarship Student in the shadow of the pandemic. His expertise area is in the development of anode materials for Li-S batteries and currently working in an H2020 project.

Corresponding author: Muhammed Osman Numan Oğuz, e-mail: numan.oguz@sakarya.edu.tr, tel: +90 530 558 02 96

Graphene/Lithium Composite Anode for Lithium Based Batteries

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

The quality of life of living things is becoming poor due to unprecedented ecological degradation depending on many factors such as global warming and pollution. One of the most important reasons for this is the irresistible increase in the use of fossil fuels [1]. Therefore, it has become inevitable to find clean and renewable alternatives to these extremely attractive and harmful energy sources [2]. Over the last two decades, scientists have extensively researched batteries as an alternative to fossil fuels. And at this point, the first quarter of this century has been the beginning of an important transition period [3]. In recent years, lithium-ion batteries are widely used in portable, mobile, and stationary applications and their designs are being broadened [4]. With the acceleration of technological developments so fast, the demand for electrochemical energy storage systems grew day by day [5]. Increasing energy density, reducing cost, and improving the electrochemical performance of the existing battery technologies are some of the most important efforts to meet the energy needs of commercial electric vehicles [6]. The energy density of the current lithium-ion batteries is changed between 100–265 Wh/kg depending on the cell chemistry, cell type, and cell shape which are all factors that were chosen for the specific application areas. This performance is still significantly less than that of gasoline. While cell chemistry is responsible for the efficiency of electrochemical reactions, the structure of the cell determines the weight and usage area. Thus, improving both cell chemistry and design is critical to increasing the energy densities of lithium-ion batteries. The aforementioned elements also have a great role in the cost of the cell. The energy sector is trying to reduce the battery costs from \$200/kWh to \$125/kWh and then \$100/kWh, respectively. However, the unfortunate developments, such as the pandemic and war between 2020-2022, that affect the world negatively, have brought along the increase in raw material prices and production costs, and logistics problems. Therefore, in the shadow of these unexpected developments, battery prices do not look to appear to decrease for a long time. In addition, the unpredictable rapid growth of the electric vehicle industry, and the consequent high demand for batteries, made supply difficult and intensified competition in the market. For all these reasons, it has become a necessity to better understand the current battery technology and to approach the aspects that need improvement more modestly.

In this study, Graphene/Lithium anode material will be synthesized and characterized to improve the electrochemical performance of both lithium-ion and lithium-sulfur batteries. One of the most important bottlenecks in the commercialization of lithium-sulfur batteries is using metallic lithium on the anode side. This study is believed to contribute to both the electrochemical performances of commercial (graphite-based) lithium-ion batteries and the scaling up of lithium-sulfur batteries.

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Mahmud Tokur

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

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

Comparison of Argyrodite Li$_6$PS$_5$Cl and Li$_7$P$_3$S$_{11}$-type Sulfide Solid Electrolytes for All-Solid-State Lithium-Sulfur Batteries

Seda EĞRİ[1,2,3], Mustafa Çelik[1,2], Abdulkadir Kızılaslan[1,2], Tuğrul Çetinkaya[1,2,3], Hatem Akbulut[1,2,3], Mahmud TOKUR[1,2,3]
[1]Sakarya University, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54050, Sakarya, Turkey
[2]Sakarya University, Research, Development and Application Center (SARGEM), Esentepe Campus, 54050, Sakarya, Turkey
[3]NESSTEC Energy&Surface Technologies A.S., Technology Development Zones, 54050, Sakarya University, Sakarya, Turkey

Demand for electrochemical energy storage systems has seen exponential growth in recent years. Among them, lithium-ion batteries are presently the foremost engaging alternative for mobile energy storage and power sources thanks to their high energy density [1]. However, the performances of the present battery chemistries have begun to be deficient because of the perpetually increasing demands of the technology market. Lithium-Sulfur (Li-S) batteries are thought of as the foremost appropriate various with their high energy density (2500 Wh/kg). However, despite the benefits of Li–S batteries, like lithium-ion batteries, they're still exhibiting ignitability, toxicity, liquid discharge, and volatilization once victimization organic liquid electrolyte components. Moreover, Li dendrites type throughout during, leading to an indoor short-circuit that results in combustion and even the explosion of the cell. Supported by the renowned normal characteristic of the Li-S battery, numerous soluble polysulfide (Li$_2$S$_x$, $4 < x \leq 8$) intermediates form on the cathodes can dissolve into the organic electrolyte and diffuse through to the Li metal anode, wherever they're reduced to insoluble Li$_2$S and Li$_2$S$_2$, that then accumulate on the Li-surface. The insoluble Li$_2$S and Li$_2$S$_2$ compounds eventually kind lower polysulfide compounds, that square measure then transferred to the cathode and deoxidized before returning to the anode. This reiterative parasitic method generates associate degree unsought "shuttle effect." These issues end in a poor cycle and rate performance, preventing the sensible application of Li–S batteries. One of the foremost spectacular strategies to beat these disadvantages is developing solid-state Li–S batteries and replacing typical organic electrolytes with solid electrolytes, like inorganic and compound ones, that gift several engaging benefits [2]. Solid-state batteries have an excellent potential to eliminate the foremost mentioned issues caused by liquid discharge and volatilization. What is more, they'll stop the danger of combustion and the explosion of organic compounds. Once they are adopted in Li–S batteries, the layers of solid electrolytes will effectively stop the "shuttle effect" as a result soluble polysulfide compounds cannot permeate into them. Therefore, exploring solid-state Li–S batteries will offer a thought to essentially solve some inherent issues and therefore may greatly contribute to the development of safe and high-performance Li–S batteries.

The ideal solid-state electrolyte should have exceptional chemical and electrochemical stability, lower surface resistance, high ionic conduction, and high active material utilization. Among totally different sorts of solid-state electrolytes, sulfide-based solid electrolytes have significantly enticing properties of high ambient ionic conduction and good processability [3]. Even though Li$_7$P$_3$S$_{11}$ (LPS) solid electrolytes have vital benefits, like high lithium-ion conduction, and may simply fabricate to form bulk-type all-solid-state Li batteries [4], however, they also have some challenges as a result of their massive surface resistance with Li, which might limit to get sensible performance all-solid-state battery. Another vital candidate of solid electrolytes is Li-argyrodites Li$_6$PS$_5$X (X=Cl, Br and I) with a high Li-ion conductivities within the vary of 10^{-2} - 10^{-3} S/cm at room temperature and a large electrochemical window up to 7.0 V vs. Li/Li+ [5]. In this study, two of these solid electrolytes (LPS and LPSCl) will be synthesized using the ball milling method and compared in all-solid-state Li-S cells. It is expected that the interface stability of Li6PS5Cl solid electrolyte will be better, and therefore the electrochemical performance of all-solid-state Li-S batteries will be improved contained this electrolyte.

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Seda Eğri

Seda Eğri is a Master's Student at the Department of Metallurgical and Materials Engineering, Sakarya University. From 2016-2021, Her studies focused on the development of Lithium-sulfur solid-state battery systems, and currently working at 120N492, High Energy Density Lithium-Sulfur Batteries for Stationary Applications, ARDEB, UPAG – International Collaboration H2020 project.

Corresponding author: Seda EĞRİ e-mail: seda.egri@ogr.sakarya.edu.tr tel: +90 531 024 96 72

Development of Multi-component lightweight AB alloy for hydrogen storage

[1]Osama Rahall, and [1]Gülhan Çakmak

[1]Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey

Hydrogen generated from the renewable may be stored using different methods, of which the solid-state storage is the most reliable. Among the alternatives, interstitial hydrides are particularly attractive as others (storage in porous media and chemical hydrides) suffer from their drawbacks [Thomas,2007]. The requirements for hydrogen storage materials can vary but the most critical ones are having high absorption capacity, good reversibility, fast sorption kinetics and low-cost. The materials based on light metals are promising to fulfil these requirements. An interesting development within the interstitial hydrides relates to AB alloy with prototype MgNi CsCl structure). Recently, Mg-Co [Zhang, 2005], Mg-Ti [Asano, 2007], Mg-Ni [Shao,2008], Mg-Ni-B [Shao,2009] and Mg-Tm-V (Tm: transition metals) binary and ternary alloys have been successfully achieved with AB structure. In a binary alloy with a composition MgCo, 3 wt % was reported.

The concept of “high entropy alloys” which attracts great attention has modified the alloy design significantly. In this concept, rather than using the classical alloys which are based on a base metal with added alloying elements a new alloy design concept in which the alloying elements are much higher and nearly equimolar. These high entropy alloys are sometimes called multi-component alloys especially if the components are non-equimolar. Preparing Mg-based alloys with some other capable to store hydrogen alloys or metals with high catalytic activity or better anti-corrosion capability is an approach to improve the performance of Mg-based anodes in NiMH batteries.

On the other hand, although the present predominance of Li-ion cells in portable electronics, Ni-MH cells stand in an important position in the market for applications such as hybrid electrical vehicles (HEVs), power tools, and stationary applications. Ni-MH batteries must continuously enhance their performances to remain in their place in the market. The main concerns related to NiMH batteries are i) the specific energy densities, which are determined by the hydrogen storage capacities of the hydride electrodes, ii) their power densities, controlled by the high discharge ability properties of hydride electrodes, and iii) their cycle life, controlled by corrosion/degradation of the hydride electrodes [Santos, 2005]. Preparing Mg-based alloys with some other capable to store hydrogen alloys with high catalytic activity or better anti-corrosion capability is an approach to improve the performance of Mg-based anodes in NiMH batteries.

In the current study, we aimed to develop an AB multi-component alloy to be used both as solid-state storage media and as an anode in a Ni-MH battery. In the study, A is kept as Mg due to its lightweight, high theoretical hydrogen storage capacity and abundance but B -normally Ni- is replaced by equimolar alloying elements of preferably low atomic weight. Thus, we aim for pseudo high entropy alloys in that Mg is still the dominant element. The alloys are produced by arc-melting. Selected alloy compositions initially which are produced by an arc-melter to check whether alloys exhibit single-phase CsCl crystal structure. Alloys that satisfied this criterion will be considered as

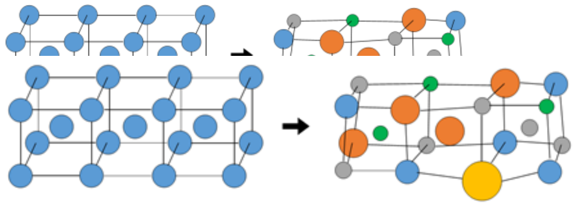

Figure 1. Simple illustration of the effect of multi-component alloying on the lattice distortion of a BCC crystal structure. (Sahlberg et al., 2016)

The selected alloys will be then characterized with respect to their gas-solid storage characteristics as well as with regard to their electrochemical properties for Ni-MH batteries. The structural and chemical analyses will be carried out after each production and hydrogenation stage.

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Osama Amin Ahmad Rahall is currently a Master's student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. He completed his BS degree at the same university in February 2021. He is working at Energy Materials Laboratory and his research areas are solid-state hydrogen storage and Ni-MH batteries.

Presenting author: Osama Amin Ahmad Rahall, e-mail: osama.rahall95@gmail.com tel:+905418139945

Synthesis of expanded graphite for Na-ion Batteries

Gülhan Çakmak[1,3], Tayfur Öztürk[2,3]
[1]Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey
[2]Middle East Technical University, Ankara, Turkey
[3]ENDAM, Center for Energy Storage Materials and Devices, Dept. of Metallurgical and Materials Engineering

The success of graphite as electrode material depends on its structure as well as its morphology. Turbostratic graphite which has irregularities in its structure i.e. layers are randomly oriented with respect to c axis, do not necessarily adversely affect its electrochemical performance [1]. Interlayer distance in graphite is the most crucial parameter as it affects the ease with which the intercalation occurs in and out of graphite. For instance, high rate dischargeability of Li-ion battery is improved when the graphite anode has larger interplanar spacing [2]. This is particularly true for Na-ion batteries where the larger radius of Na requires much larger interlayer distance.

The interlayer distance in graphite normally has a value of 0.334 nm, but this value can vary depending on the synthesis method used. For instance, Wen et al. [3] have synthesized graphite via reduction of graphene oxide which yielded interlayer distance of Lc = 0.43 nm. Wang et al. [4] obtained Lc = 0.369 nm in graphite via nitrogen doping. Tai et al. [5] etched graphite using potassium hydroxide at elevated temperature which yielded the interlayer spacings of 0.358 nm. Gotoh et al. [6] carried out a controlled experiment using hydrogen ion irradiation where they were able to increase the inter- layer spacing from Lc = 0.34 nm to Lc = 0.402 nm. The values of interplanar spacings obtained with thermal plasma processing of hydrocarbons, though have not yet been studied systematically, varies from Lc = 0.338 to 0.416 nm. In a recent work, Zhang et al. [7] have used R.F. plasma and synthesized graphite from methane using hydrogen as additive. In this study with the addition of hydrogen, graphite which would normally occur as sphere like particles was also morphologically modified into sheet like formation. Moreover, the number of layers were drastically reduced which resulted in the formation of the so-called a few layers of graphene (FLG).

In the current work, a systematic study was carried to determine the extent to which the interlayer distance in graphite could be controlled via thermal plasma processing. Here the precursor used was methane, to which hydrogen was added as modifying agent. T he following conclusions can be drawn;- There is a critical fraction of hydrogen, around half of that of methane flow rate, up to which it is possible to control graphite both structurally and morphologically. - Granular graphite obtained with methane only with sizes of typically 100 nm could be modified into a flaky form of up to 10 µm insize. The layers, around 25, making up the granular graphite couldbe reduced in number down to as few as 12 layers in the flaky graphite where the specific surface area can be as high as 300 m2/g.- Current X-ray data combined with data from literature show that it is possible to adjust the interlayer distance of graphite from Lc = 0.334 to 0.369 even up to 0.416 nm with the careful control of hydrogen input.

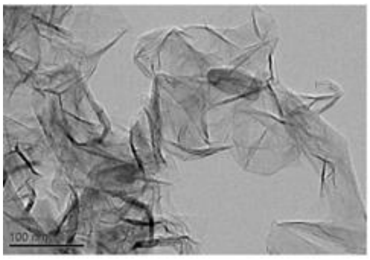

Figure 1. TEM micrograph of graphitic material produced from plasma processing of methane and hydrogen

The significance of the interlayer spacing, and its modification was discussed within the context of use of graphite as anode in rechargeable batteries..

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Gülhan Çakmak is an Assistant professor in Department of Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University. She obtained her B.Sc from Anadolu University in 2002 and her PhD from Middle East Tehnical University in 2011. Her interest covers the processing and properties of hydrogen/energy storage materials.

Corresponding author: Gülhan Çakmak, e-mail:gulhancakmak@mu.edu.tr tel: +90 252 211 5613

Combinatorial Development of Active Materials For Energy Storage and Conversion

Tayfur Öztürk
Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey
ENDAM, The Center for Energy Materials and Storage Devices, METU, Ankara, Turkey
INNOVASCOPE Materials Technologies Ltd. Sti., METUTECH, Ankara, Turkey

Active material development in energy storage and conversion, as in similar development other fields of materials research, have largely followed Edisonian approach of focusing on one material composition at a time. The approach requires a careful pre-consideration in selecting the material composition and the success depends largely on the suitability of the initial choice made for the material. Combinatorial approach is an alternative method whereby a large number of samples each with different compositions are produced simultaneously. They are then screened in a fast manner to single out the material(s) with best performance. The materials selected are then fully characterized as is customary for the conventional method. The combinatorial approach is more efficient in terms both time and effort and yield more fruitful results.

In this work, we describe a sputter deposition system which we specifically designed for combinatorial material development [1]. The system designed could incorporate up to 6 sputter targets 2 inches in diameter plus the central one in 3 inches which would provide the base composition. Above the targets, there is a sample magazine which would allow simultaneous deposition on multitude of substrates each with a different composition

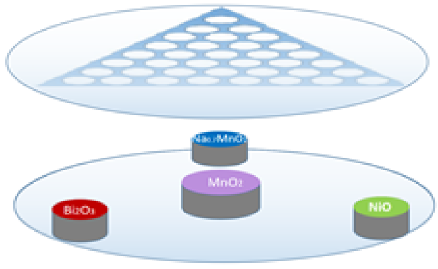
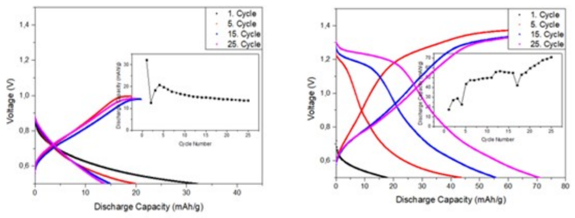


Fig.1 Combinatorial geometry for fabrication of thick film material library for Zn-MnO2 batteries. Three peripherial targets are in triangular geometry, substrates above mimicking the position of the peripherial targets underneath.

So far the system was used in binary, ternary and quaternary configurations. In binary configuration, two sputter targets were used to optimize dual oxide cathode for improved ORR performance for intermediate temperature solid oxide fuel cell (IT-SOFC) with quite impressive results [2]. Similarly, in ternary configuration, the sputter targets were arranged in triangular geometry and a number of alloy system Ag-Ti-Pd, Ag-Ni-Pd, Ag-Mn-Pd and Nb-Ti-Pd were examined to identify potential composition as membranes for hydrogen separation [1,3].

In this presentation, following a brief review of the previous achievement, we concentrate on combinatorial development of cathode material for Zn-MnO2 battery. This is a low cost alkaline battery, with limited rechargeability, mostly used as primary battery. There is, however, considerable interest in recent years on this chemistry to make it truly rechargeable, preferably with two electron exchange ,i.e. $Mn^{4+} \rightarrow Mn^{2+}$.

MnO_2 was therefore modified, with other oxides, namely Bi_2O_3, $Na_{0.7}MnO_2$ and NiO in quartenary configuration. A total of 36 cathodes were deposited on nickel substrate typically 2.5 µm thick, each with a different composition, Fig. 1. Runs were repeated with different power settings, thus cathodes were produced covering a large compositional volume. Thick film cathodes were then screened using a Swagelok cell against metal hydride anode with a relatively narrow voltage window so as to speed up the process.



(a) (b)

Fig. 2 Charge-discharge profiles at selected cycles a) $Bi_{0.06}Na_{0.04}Ni_{0.69}Mn_{0.21}O_x$ and b) $Bi_{0.06}Na_{0.34}Ni_{0.17}Mn_{0.44}O_x$, Insets showing the cyclic discharge capacity

The results showed that thick film cathodes were largely amorphous in as-deposited state but upon charge-discharge cycling, the structure rearranges into crystalline form with a layered δ-MnO_2 structure. Two regions were identified as potential cathodes one region was close to NiO corner, and the other regions had moderately large Na content, Fig. 2 [4,5].

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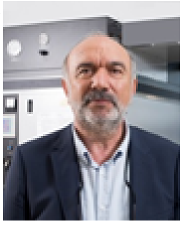


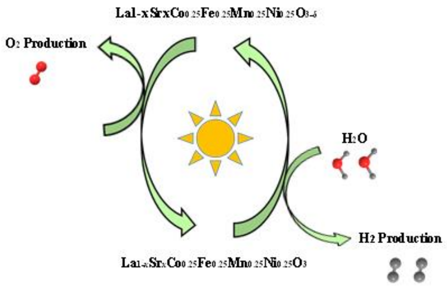
Professor Tayfur Öztürk is the founding chair of International Sympoisum on Materials for Energy Storage and Conversion, mESC-IS, a series of sympósia and summer schools organized since 2015. He earned his Ph.D. in Materials Science at Cambridge University in 1978 and his B.Sc. degree from Istanbul Technical University in 1973. Before joining METU, he worked as a post-doc at Sheffield University and Istanbul Technical University. He is the founding member of ENDAM, the Center for Energy Materials and Storage Devices. His research interest covers nanopowder synthesis, thermal plasma processing and sputter deposition of thin/thick films for combinatorial material chemistry. The emphasis is to develop active materials for hydrogen storage and separation, rechargeable aqueous batteries, and solid oxide fuel cells. e-mail: ozturk@metu.edu.tr

High Entropy Perovskite Oxides for Thermochemical Water Splitting

Ezgi Afyonlu, Serhat Demirpençe, Hakan Yüce,İhsan Emre Yiğiter, Berke Pişkin, Gülhan Çakmak

[1]Dept of Metallurgical and Materials Engineering, Sıtkı Koçman University, Mugla, Turkey

The rapid increase in population and economy and the resulting increasing energy demand are met by fossil fuels, which are not renewable by nature and cannot be used again when they are exhausted[1]. The limitation of fossil fuels and the increasing negative impact of greenhouse gas emissions on the environment are identified as the biggest challenges to energy sources. Therefore, alternative clean, renewable environmentally friendly sources and global decarbonization are needed to reduce climate change and environmental pollution[2]. Hydrogen gas is considered to be one of the most suitable sources for renewable energy, as it is a clean energy source that does not contain carbon. Hydrogen can be generated by many methods such as electrolysis, photolysis, gasification, thermolysis, etc. Thermochemical water splitting is one of these methods. This method uses concentrated solar energy to drive pure redox reactions. One of its most important advantages is that it can produce hydrogen without the need for purification, that is, it does not require catalysis to carry out chemical reactions[3]. The redox materials used in TWS are chosen from perovskites oxides due to their superior structural stability. High entropy oxides are among the oxide groups that have become widespread recently. It provides many advantages with its unique compositions, micro-structures and adjustable features.They are active materials that can be used in TWS reactions, thereby positively affecting the hydrogen production efficiency. In this context, La0.5Sr0.5Mn0.25Fe0.25Co0.25Ni0.25O3 (LSCFMN) based perovskite oxides were studied in this study. LSCFMN powder was synthesized by Sol-gel-based Pechini method. As starting chemicals, nitrates of all of the considered cations were used: La(NO3)3·6H2O, Sr(NO3)2, Co(NO3)2·6H2O, Fe(NO3)3·9H2O, Mn(NO3)2·4H2O and Ni(NO3)2·6H2O. Primarily, the stoichiometric amount of the metal nitrate precursors were dissolved in distilled water, then citric acid and ethylene glycol were added into the solution. The molar ratio of all the cations, citric acid, and ethylene glycol in the mixture was 1:2:4. The solution was heated up to 70°C with continuous stirring by the help of the magnetic stirrer to drive the esterification reactions. The resulting gel was dried at 250°C for 2 hours to remove residual organics and nitrates. The dried gel was calcined at 700°C, 900°C and 1100°C for 6 hour. The resulted structures were characterized with respect to their crystal structure and particle size and candidate materials are selected for using TWS redox reactions



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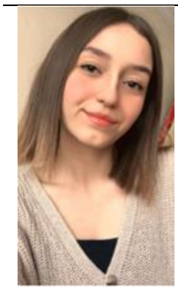

Ezgi Afyonlu is currently an undergraduate student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. She is working at Energy Materials Laboratory and his research areas are hydrogen production, thermochemical water splitting and hydrogen storage in metal hydrides

Presentating author: Ezgi Afyonlu e-mail: ezgiafyonlu@posta.mu.edu.tr tel: +90 553 600 87 35

Development of Dual Perovskite Oxides for Two-Step Thermochemical Water Splitting

Seyfettin Berk Şanlı[1,2], İhsan Emre Yiğiter[1,2], Çağla Ünal[1,2], Ezgi Gümüşoğlu[1,2], Gülhan Çakmak[1,2], Fatih Pişkin[1,2], and Berke Pişkin[1,2*]

[1]Mugla Sıtkı Kocman University, Engineering Faculty, Metallurgical and Materials Engineering Department, Mugla, Turkey

[2]Energy Materials Laboratory, Muğla Sıtkı Koçman University, 48000, Muğla, Turkey

Hydrogen has a very important place in green-energy applications. Thermochemical methods based on solar energy come to the fore in hydrogen production. It is possible to produce hydrogen without the need for purification via the two-step thermochemical water splitting (TWS) method. TWS uses metal oxides as redox materials allowing for the production of pure hydrogen at lower temperatures as compared to thermolysis. Therefore, the thermodynamics and kinetics of redox reactions are the important factors that determine hydrogen production efficiency and are influenced by the structural properties of active materials used in these reactions. For this purpose, perovskite-oxides draw attention to be able to use in TWS reactions due to providing higher structural stability with allowing compositional diversity. In the TWS method, for effective hydrogen production, there is a need for structurally stable metal oxides performing high redox capacity, high reaction kinetics, and high stability during the thermal cycles [1].

It was aimed to improve hydrogen production capacity with the existence of hetero-interfaces as well as preserve stability during the redox cycles. It is known that the production capacity of perovskite oxides in the literature is decreased significantly (40%-80%) in the initial cycles. It is aimed to improve structural stability and stabilize the hydrogen production rate (>80%) of perovskite oxides with the hetero-interface approach.

In this study, the perovskite families were firstly doped with A-site and B-site elements and then the compositions were optimized due to their hydrogen production capacities. For this purpose, a total of 36 perovskite oxides including $La_{1-x}Sr_xMn_yAl_{1-y}O_3$-SLMA (Sr=0.4-0.6, Al=0.4-0.6) and $La_{1-x}Ca_xMn_yAl_{1-y}O_3$-LCMA (Ca=0.4-0.8, Al=0.4-0.8), LCMF (Ca=0.4-0.8, Fe=0.4-0.8) and LCMC (Ca=0.4-0.8, Co=0.4-0.8) compositions were synthesized by Pechine method. These compositions then were evaluated in thermochemical redox reactions (T_{red}=~1400 °C, T_{ox}=~800 °C) and three compositions with the highest hydrogen production were chosen for further studies. Determined hydrogen production for the three highest candidates for each perovskite family were summarized in Table 1.

Table 1. Three highest hydrogen production of selected perovskite oxides

Samples	**Total H_2 production (μmol/g)**
LSMA6464	257.18
LSMA6455	207.86
LSMA6446	204.50
LCMA6482	47.99
LCMA6464	135.58
LCMA6446	70.06
LCMF6482	39.09
LCMF6464	37.21
LCMF6446	59.51
LCMC6482	66.97
LCMC6464	41.64
LCMC6446	60.04

Calcined candidate perovskite powders of **27** different LSMA: LCMA, LSMA: LCMF, and LSMA: LCMC dual perovskite were mixed in the molar ratio of 50:50 by mortar and pestle. The mixture was taken into a metal mold and 1.5 ml of isopropyl alcohol was added. In order to create an equiaxed and porous structure, the slurry-like structure in the mold was molded by a punch. Subsequently, formed monolith structures were exposed to heat treatment to create hetero-interfaces. The composite perovskites produced will also be evaluated in two-step thermochemical redox cycles and then compare to their individual components [2].

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Berke Pişkin is an Assist. Prof. Dr. in the Department of Metallurgical and Materials Engineering at Muğla Sıtkı Koçman University. She earned a BS degree from Anadolu University in 2009, an MS degree from Middle East Techincal University in 2012, and a PhD degree from Middle East Techincal University in 2018.

Corresponding author: Berke Pişkin, e-mail: berkepiskin@mu.edu.tr tel: +90 534 424 20 45

Influence of diverse additives into tap water ice on ice energy storage capacity

Natalia Bodrožić Ćoko[1], Tomislav Lušić[1], Ivan Tolj[2]
[1]Department of Fluid Mechanics, University of FESB , Split, Croatia
[2] Department of Thermodynamics and Thermal Engineering, University of FESB , Split, Croatia

One of the first applications of thermal ice storage occurred in 1930's. The daily production of milk had to be cooled on adequate temperature for storage. The previous processes of cooling milk, had to be carried out with large heat exchangers that worked only few hours in period of day with the peaks of total consumption of electric energy. In 1980's, a few electric power companies in progression had idea to use some form of a thermal storage of energy to equalize the hourly production of electric energy and accordingly reduce the needs to build more power plants. The financial incentives had been offered by these companies to their customers to reduce the energy usage in these peak hours. [1] The price of energy that is used in these hours rapidly increased so many of these companies accepted the financial incentives. Thermal ice storage presents an ingenious solution that allows shifting energy costs from peak period in electricity grid, when costs are high, to non-peak period, when energy costs are affordable (Figure 1.).

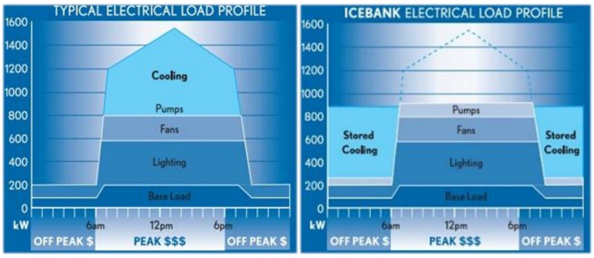

Figure 1. Comparison of two electrical load profiles: (left) typical electrical load with energy peak and (right) electrical load profile while using cold energy storage [2]

To achieve more suitable thermal and mechanical properties of tap water ice, the tap water has been mixed initially with sawdust and sheep wool. Then, the thermal properties measurements of different ice samples were conducted. Three types of ice samples were obtained: ice formed by freezing tap water, ice reinforced by adding 14% sawdust, and ice samples reinforced by adding 15 g of cleaned sheep wool in 215 ml of tap water. Transient Plane Source (TPS) method was used to investigate thermal conductivity, thermal diffusivity, and volumetric specific heat capacity. Samples were conditioned in the freezer to achieve the desired temperature during the measurement. The mentioned properties of sample were measured at 5 points.

Figure 2. Thermal constant measuring device: Hot Disk TPS 500 and Pico Data Logger (left) and samples (right)

This paper presents the experimental results of specific volumetric heat capacity measurements (Figure 3.) obtained for different ice samples and discussion about different additives impact on thermal property behavior. It can be noticed that addition of appropriate material into tap water before freezing can increase the ice energy storage capacity.

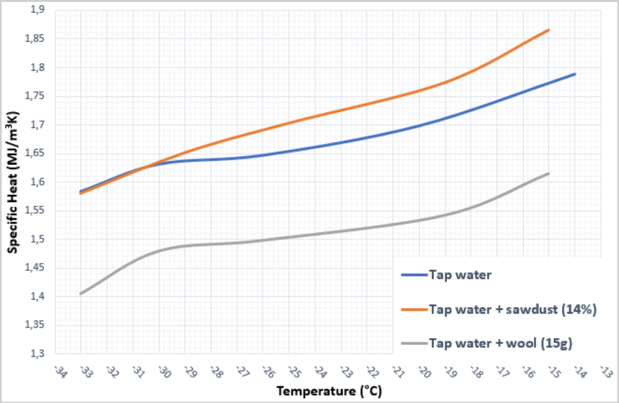

Figure 3. Experimental values of volumetric specific heat capacity for three samples based on tap water ice

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Acknowledgements

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Natalia Bodrožić Ćoko

Natalia Bodrožić Ćoko is phD student at the Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split. She participates in teaching Fluid Mechanics and works as junior researcher research project CEKOM: *Development of a floating ice platform made of artificially frozen water*. Her research interest covers investigation of water properties, renewable energy sources and hydrogen production.

Corresponding author: Natalia Bodrožić Ćoko e-mail: nbodro01@fesb.hr tel: +385 95 874 8545

Oxide-based cathodes for aqueous electrolyte Zn-ion Batteries

Selin Sariyer[1,2], Tutku Mutlu[1,2] and Rezan Demir-Cakan[1,2]
[1]Department of Chemical Engineering, Gebze Technical University , Kocaeli, Turkey
[2]Institute of Nanotechnology, Gebze Technical University , Kocaeli, Turkey

Rechargeable aqueous batteries have become remarkable energy storage option considering their green and reliable, non-toxic, low cost, non-flammable, high ionic conductivity, and easier assembly features compared to organic electrolytes. Notably, zinc metal has been attractive to rechargeable aqueous batteries owing to high abundance, straightforward and large manufacture, high volumetric energy density (5851 mAh cm^{-3}) and theoretical energy capacity (820 mAh g^{-1}), stability, suitable for aqueous electrolyte. The cathode materials, where zinc ions intercalate, are an important component of zinc ions aqueous battery systems (ARZIB), which are especially promising in large-scale energy storage implementation [1]. Up to now, despite many host materials have been developed to accommodate and transport of the divalent charge carriers, various crystal structures of manganese and vanadium-based cathode materials stand out in the aspects of exhibiting different electrochemical behaviours, efficiently and reversibly store zinc ions. Comparing manganese-based electrode with vanadium-based cathode, manganese-based electrodes posses moderate operating voltage, however they display poor cycling stability and energy density [2].

Herein, vanadium-based oxide material was synthesized by microwave-assisted hydrothermal method. The effect of different oxidazing agent, temperature and synthesis time was investigated in order to obtain desirable phase. Further, produced material was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). As seen in the XRD pattern (Figure 1a), vanadium-based electrode material was indexed to the V_2O_5.1.6H_2O structure (JCPDS 00-040-1296) with nanobelt morphology (Figure 1b). Electrochemical performance of the V-based electrode synhesized at 160 ^{o}C in the presence of potassium permanganate oxidazing agent and vanadyl sulfate precursor, was examined in aqueous electrolyte of 3 M Zn(CF_3SO_3)$_2$. Two oxidation (1.01/0.57 vs Zn/Zn^{2+}) and two reduction peaks (0.97/0.50 V vs Zn/Zn^{2+}) were observed in CV curves of electrode as illustrated in Figure 1c. More importantly, very stable cycling performance and high capacity (initial discharge capacity 375 mAh g^{-1} at a current density of 1C) was obtained with a capacity retention of 88% after 200 cycles (Figure 1d). Furthermore, electrochemical performance of synthesized manganese-based electrode was evaluated in a comperative manner [3].

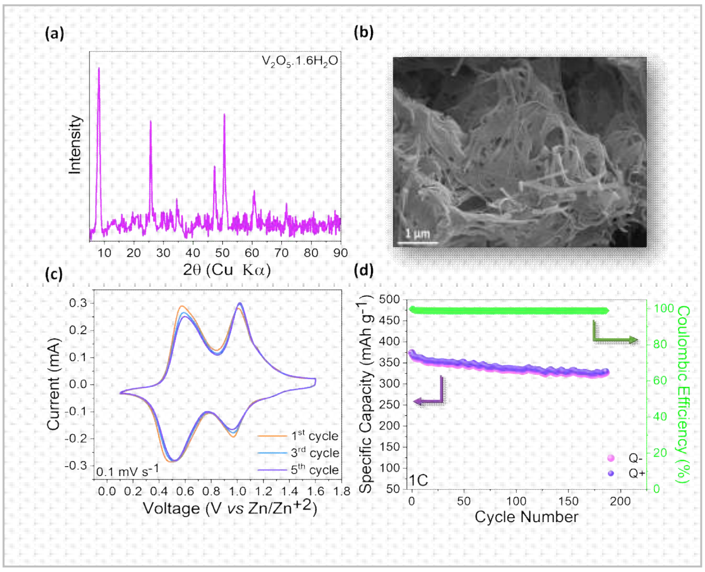

Figure 1. Synthesized vanadium-based material a) XRD pattern, b) SEM image, Elecrochemical performance in 3 M Zn(CF_3SO_3)$_2$ c) CV curves at a scan rate of 0.1 mV s^{-1}, d) Cycling performance at a current density of 1C.

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

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

Development of Aqueous Electrolyte Zinc-Selenium (Zn-Se) Batteries

Elif Canbaz[1], Tutku Mutlu[1], Selin Sarıyer[1], Mert Yalçınöz[1], Burcu Ünal[1] and Rezan Demir-Cakan[1]*

[1] Department of Chemical Engineering, Gebze Technical University, 41400, Gebze, Kocaeli, Turkey.

Rechargeable aqueous zinc metal batteries have attracted great interest because of their high safety, easy assembling and environmental friendliness. To date, several (de)intercalation cathodes have been reported, such as vanadates [1], manganates [2] or prussian blue analogues [3]. Although these cathodes show good cycling stability, relatively low energy densities are achieved. In contrast, cathode materials based on a conversion reaction mechanism can allow high capacity and energy density since they are typically not relied on the framework structure [4]. In this regard, aqueous Zn-metal batteries which are based on the conversion reaction mechanism such as Zn-S and Zn-Se have been recently reported [5, 6].

Herein, a rechargeable aqueous Zn-Se battery was designed by using selenium as cathode coupled with a Zn metal anode. Although selenium was chosen due to several advantages such as high theoretical capacity and high electrical conductivity, Se volume expansion upon reduction and solubility of polyselenides during cycling are the drawback of this system. Thus, firstly Se was encapsulated into porous carbon via melt diffusion method and used diretly as cathode. The impact of electolyte salts ($ZnSO_4$, $ZnCl_2$ and $Zn(CF_3SO_3)_2$ in water) were also investigated. First experimetal results demonstrated that after several cycles Zn anode surface was deteriorated. In order to stabilize Zn anode, different protective surface coatings were used, i.e. CNT, Al_2O_3, Nafion-CNT and Nafion- Al_2O_3. Figure 1 shows the cycling performance of Zn symmetric cells of different Zn surface coatings in which Nafion-Al_2O_3 coated Zn symmetric cell demonstrated the smaller overpotential than that of the others.

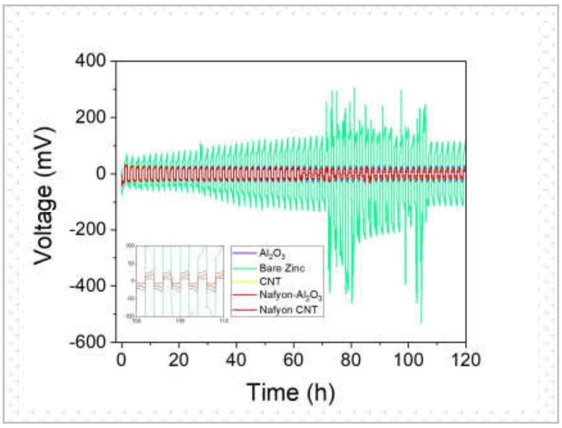

Figure 1. Cycling performance of Zn symmetrical cells in the electrolyte of 2 M $ZnSO_4$ for different coatings.

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Tutku MUTLU graduated from Marmara University, Chemical Engineering Department in 2015. She received her Master Degree from Marmara University, Chemical Engineering Department in 2018. After completing MSc degree, she started her Ph.D. work at Gebze Technical University, Chemical Engineering programme under the supervision of Assoc. Prof. Dr. Rezan Demir-Cakan in 2018. She has been working as Research Assistant at Gebze Technical University, Chemical Engineering Department since 2018.

Presentating author: Tutku MUTLU, e-mail: tutkumutlu@gtu.edu.tr tel: 0537 977 19 97

Development and Characterization of PBI derivatives for HT-PEMFCs

Arzu Göbek[1], Tuncay Kadioglu[4], Ayşe Bayrakçeken Yurtcan[2,3] and R. Gultekin Akay[4]

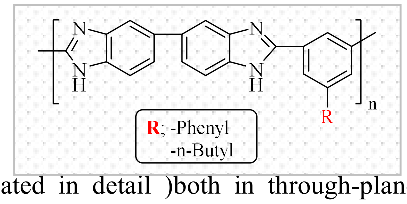
[1]Faculty of Science, Department of Chemistry, Atatürk University, Erzurum 25240, Turkey

[2]Faculty of Engineering, Department of Chemical Engineering, Atatürk University, Erzurum 25240, Turkey

[3]Graduate School of Science, Department of Nanoscience and Nanoengineering, Atatürk University, Erzurum, 25240, Turkey

[4]Dept. of Chemical Engineering, Kocaeli University , Kocaeli, Turkey

One of the most promising Fuel Cell (FC) type is the High Temperature Polymer Electrolyte Membrane FC (HT-PEMFC) due to its high carbonmonoxide (CO) tolerance and theoretical high efficiency. They operate typically at higher temperatures at around 120-200C compared to conventional PEMFCs operating at 60-80 C related with the proton conductivity range for phosphoric acid which is responsible for the proton conductivity. One of the most critical component in the membrane electrode assembly (MEA) is the polymer electrolyte material because of its resistance affecting the total voltage losses (ohmic losses). Therefore the design and development of this material is critical for further development of PEMFC technologies.[1] Most of the researches focused on well characterized perflouro sulfonic acid (PFSA) based PEMs. Because of the difficulty in manufacturing these types have high cost and also limitation of proton conductivity above 80°C due to the dependence to water.[2,3] Until today many different membrane materials have been investigated in the literature including Nafion^{TR} improvements utilizing composite/hybrid approaches for operating at higher temperatures but phosphoric acid doped PBI [2,2-(m-phenilene)-5,5-bibenzimidazole] still seems to be the best alternative. PBI has unique thermal stability and chemical resistance at high operating temperature up to 200 ^{0}C. At these high temperatures, the Pt catalyst is more tolerant to gas contaminants and the electrode kinetics for both anodic and cathodic processes are quicker. It also provides high ionic conductivity without water management have high proton conductivity up to 200°C, have high thermal stability and high fuel cell performance.[4] Considering these advantages, new modified PBI derivatives have been investigated in this study by adding different functional groups to PBI (Figure 1).



investigated in detail)both in through-plane and in-plane) and sufficient proton conductivities were obtained. Proton conductivity behaviour is especially analyzed according to the tempertaure and humidity behaviours for obtainin information on isotropy of the material. HT-PEMFC tests are still going on and will be presented.

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Ramiz Gültekin Akay took his BS degree from the chemical engineering department of Middle East Technical University (METU) in 1998. Took MS and Ph.D degrees in chemical engineering from the same institution in 2001 and 2008 respectively. His Ph.D thesis was on the development of composite membranes for proton exchange membrane fuel cells (PEMFC). After taking Ph.D he started working in chemical engineering department of Kocaeli University where he is still an academic staff and instructor. He has been giving courses in electrochemical technologies and applications in undergraduate level and Fuel Cell Technology & Applications and Electrochemical Characterization Methods in graduate level in chemical engineering department since 2009.

Presentating author: Ramiz Gültekin Akay, e-mail: gultekin.akay@gmail.com tel: 90-533-3152768

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