



Ladies and Gentlemen,

It is my great pleasure to welcome you in the thirteenth issue of Bulletin of Polish Hydrogen and Fuel Cell Association that is completely dedicated to the 7th Polish Forum Smart Energy Conversion and Storage in Ogrodzieniec, which is held from September 4th to 6th, 2022.

The Forum is a biennial event, however due to covid-19 pandemic and the need for social distancing, it, similar to thousands of scientific events, has had to be postponed.

The conference is co-organized by Polish Hydrogen and Fuel Cells Association (hydrogen.edu.pl) and AGH University of Science and Technology. The history of the Forums began in 2005, with the first conference covering a relatively narrow issues of fuel cells and hydrogen technologies. After 17 years of collecting experience and constantly expanding the formula of the Forums, this year's scope includes: hydrogen production and storage, fuel cells, Li-ion and Na-ion batteries, supercapacitors and thermoelectrics. All these topics are highly important for modern energy conversion and storage. Albeit different, they are based on the similar mass and charge transport mechanisms, related to ionic and electronic defect structure. This brought the idea of gathering of high-level specialists, including theoreticians, in this field.

Further progress in the field of modern energy conversion and storage technologies depends on a development of the scientific basis of manufacturing of functional materials, which relies on comprehensive studies of their structural, transport, catalytic, thermal and mechanical properties, aiming to describe the relationship between crystal structure, chemical composition, electronic properties and the catalytic efficiency of the electrochemical

processes occurring in the electrochemical devices.

An analysis of current technological solutions shows that there is still a gap between current capabilities of fuel cells and practical needs of the hydrogen energy technology. Problems with wide commercialization of fuel cells is associated with strenuous implementation of technology, which is based on technologically immature materials.

Among many aspects of the hydrogen-based economy, the key to success is solution of fundamental issues of the used materials. There is a particular place for technology of nanomaterials and studies of the catalytic processes. Understanding on the atomic-level the fundamental processes involved in the catalysis, shall trigger correlated progress in all fields of modern energy technologies.

The grain size dependent on defect formation energy and space charge effects are significantly influencing the transport properties. Elucidation of the grain boundaries impact on defects and transport properties will enable designing of materials with tailored properties. An extra difficulty, slowing down the progress in science and technology of nanomaterials, is related to the stability of nanomaterials and reproducibility of their properties, because, as it was observed in thin films, unique microstructure may provide unique properties.

I hope that this year's conference will be an excellent place for discussion in the field of materials and technologies for modern energy, and also a good school for young scientists, beginning their careers. I would like to thank you, the participants, who contribute to make this meeting successful, wishing you an exciting and enjoyable time.

A handwritten signature in black ink, appearing to read 'Molenda'.

Prof. Janina Molenda
Chairman of 7th Polish Forum
Smart Energy Conversion and Storage
President of Polish Hydrogen
And Fuel Cell Association

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INVITED LECTURES

Hydrogen energy transition

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Currently, hydrogen's contribution to gross domestic products GDP compared to oil is very low, the situation will change over the coming years, increasing the dependence on hydrogen energy and reducing dependence on oil derivatives, especially in vehicles. The impact on local economy will be as follows:

1. Diversity of income sources.
2. Increase the GDP.
3. Increase career opportunities.
4. Minimize harmful emissions to public health and thus reduce therapeutic expenses.
5. Improve air quality.

The steady increase of carbon dioxide in the atmosphere leads to a gradual increase in temperature which leads to what is known as global warming. This phenomenon causes many environmental problems, including desertification, rising of ocean temperatures and sea level. Thus, this requires the pursuit for alternative energy sources that can reduce the CO₂ emissions in the atmosphere, so the perfect alternative to produce clean energy is hydrogen. Accordingly, this will increase the global dependence on hydrogen in the coming years as an alternative energy source in order to reduce the environmental impact of fossil fuel-based energy and this will have an impact on global economy as follows:

1. Contribute to solving the problem of climate change and global warming, which is affecting the climate and costing many countries economically.
2. Continue in the global energy market as a competitor and source of clean energy.
3. Contribute to the transfer and localization of technology and exchange of experiences among the countries of the world, which allows to build strong global partnerships in the field of clean energy and technologies.
4. There is increasing demand for hydrogen globally and entering the global energy market will contribute to global economic growth and stability of global markets.

Hydrogen technologies can be used in several sectors of the energy systems, such as transport, industry, building, and power sectors. They can be also linked to different energy systems including energy transmission and distribution such as fuel cells and electrolyzers which convert hydrogen to power (e.g. electricity and heat). They can utilize in numerous applications in power sectors. The development of fuel cells and electrolyzers technologies will reduce cost of

the fuel cells electrolyzers and cost of efficient generation of hydrogen.

The lecture covers such topics as hydrogen as an energy carriers, the hydrogen society and the challenges of the transport sector. Production and storage of hydrogen will be presented. Deeper knowledge of hydrogen gas from sun and water will be also covered. Short and long term applications will be discussed.

NOTES

Oxygen electrode materials for reversible solid oxide cells based on Cu-containing complex perovskites

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Keywords: Cu-based perovskites, oxygen electrodes; reversible Solid Oxide Cells

INTRODUCTION

Reversible Solid Oxide Cells (rSOC) can work utilizing chemical energy of the fuel (e.g. hydrogen) and oxidizer to generate electricity and heat, but also may operate in the reversed mode, generating H₂ with the available surplus electrical energy. Numerous and strict requirements concerning transport, electrocatalytic and thermomechanical properties need to be fulfilled by the successful oxygen electrode material to be used in rSOCs. So far, perovskite-type and perovskite-related oxides are among the best candidates for such application, but it is known that high electrocatalytic activity in the oxygen reduction reaction (ORR) does not always mean that the electrode shall manifest similar high efficiency for the oxygen evolution reaction (OER) [1, 2].

Currently, Co-based perovskites are usually adopted for preparation of the oxygen electrodes, but cobalt is known to be toxic, expensive, as well as its resources are limited. In this work we show the development of Cu-containing compounds from the RE_{1-x}A_xTM_{1-y}Cu_yO_{3-δ} (RE: selected rare-earth elements, A: selected alkaline-earth metals, TM: selected 3d metals) group is feasible for usage as oxygen electrodes in rSOCs. It is possible to partially or fully eliminate cobalt, and maintain the desired physicochemical properties at the same time.

EXPERIMENTAL

A modified sol-gel method followed by the auto-combustion was utilized to manufacture different perovskite-type RE_{1-x}A_xTM_{1-y}Cu_yO_{3-δ} oxides. Obtained materials were systematically characterized in terms of the phase composition, crystal structure at room temperature and high temperatures, oxygen content and its evolution with temperature, electrical conductivity, as well as in terms of the electrocatalytic properties in the constructed laboratory-scale rSOCs.

RESULTS AND DISCUSSION

In the present work several groups of mixed ionic-electronic conductors are discussed, all showing the crystal structure beyond that of simple perovskites. The A-site layered RE(Ba,Sr)Co_{2-y}TM_yO_{5+δ} (RE: selected rare-earth cations; TM: Mn, Fe, Cu, etc.) double perovskites are of interest, as they may exhibit very high mixed conductivity and high electrocatalytic activity for higher Co content. However, usage of toxic

and expensive cobalt is also linked with the high thermal expansion, as well insufficient stability in relation to several candidate solid electrolytes.

As the alternative, copper-based RE_{1-x}(Ba,Sr)_xCuO_{3-δ} oxides can be considered [3, 4]. Depending on the composition, the materials may either exhibit RE-(Ba,Sr) cation-ordered or cation-disordered sublattice, as well as the ordered or disordered oxygen sublattice. These compounds show limited thermal expansion, acceptable transport properties, and allow to obtain functional oxygen electrodes. Low electrode polarization values could be obtained with Co-free electrodes, below 0.1 Ω cm² at 650 °C, which enabled to achieve power density outputs for the cells exceeding 250 mWcm⁻² at the same temperature.

CONCLUSIONS

It is documented that the Cu-based complex perovskites may exhibit attractive set of the physicochemical properties, enabling for their utilization to manufacture efficient oxygen electrodes for rSOCs.

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NOTES

Properties of multicomponent oxides based on proton-conducting barium zirconate

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Keywords: proton conductors, high-entropy oxides

INTRODUCTION

High proton conductivity requires a high concentration and mobility of protonic defects. A typical strategy of optimisation of proton-conducting materials is to modify a host material forming a crystal structure of high symmetry, e.g. ABO₃ perovskite, in a way allowing for a high concentration of mobile proton defects. That is usually performed via substitutions of the B-cation, which in proton-conducting perovskite is at the +4 valence state, with acceptor-type cations at the +3 valence state. The effectiveness of this strategy is limited by the solubility of substituents, strain introduced to the crystal lattice and interactions between defects. On the other hand, the recent emergence of a new class of materials, that is high-entropy oxides has opened up novel, exciting possibilities for studying new ways of tailoring the functional properties of proton conductors. In this work, selected properties of multicomponent perovskites in which A=Ba while the B-site is occupied by at least 5 different cations are presented and discussed. In particular, structural, thermogravimetric, and charge transport properties are presented. Special attention was focused on the properties related to proton conduction, since oxides having several B-site cations among which various acceptor-type constituents are present, these oxides may be considered very promising proton conductors.

EXPERIMENTAL

The oxides were synthesized by a high-temperature solid-state route. The phase composition and crystal structure were studied by X-ray diffraction (XRD) at room and elevated temperatures (HT-XRD). Measurements were conducted using CuK α radiation using a Philips diffractometer. For high-temperature measurements Anton Paar HTK 1200N was used. To investigate water incorporation into the sample, thermogravimetric (TG) experiments were performed (Netzsch STA 449). Electrical properties of the high-entropy oxides were studied by electrical impedance spectroscopy (EIS) using Gamry 3000 potentiostat. For selected samples, the conductivity relaxation experiments were performed. Based on the ECR experiments performed in the 300-600 °C temperature range diffusion coefficient, D, and surface exchange coefficient, k were estimated.

RESULTS AND DISCUSSION

XRD analysis showed that the high-entropy perovskite oxides crystallize in Pm-3m space-group. High-temperature XRD studies showed that the unit cell parameter of a previously hydrated materials increases in a non-monotonic way which is connected to water release from the structure. Thermogravimetric studies confirmed that most of the weight change in the vicinity of 200-400 °C originates from water release. The amount of incorporated water in the humidified atmosphere was comparable to well-known acceptor-doped barium zirconates. Both the results of HT-XRD and thermogravimetric analysis indicated slow kinetics of dehydration. Based on the electrical conductivity measurements in dry and H₂O-/D₂O-containing synthetic air, the total, bulk and grain boundary conductivity, proton and deuterium conductivity and activation energies were determined. The observed isotopic effect is evidence of the presence of proton conduction proceeding via the Grotthuss mechanism [1]. In some cases, it was found that the potential barrier heights and the space layer thicknesses are significantly lower than those observed for typical polycrystalline doped barium zirconates.

CONCLUSIONS

Concluding, the properties of proton-conducting high entropy perovskites are reported. All studied oxides formed cubic perovskites with unit cell parameters related to the average B-cation radii following the Vegard rule. We confirmed that high entropy oxides based on barium zirconate exhibit proton conductivity. In all studied oxides, the formation of protonic defects was observed. Moreover, the conductivity in the humidified atmosphere was higher than in dry air as well as it showed typical of proton conductors isotope effect.

ACKNOWLEDGMENT

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NOTES

New combinations in materials for reversible solid oxide cells

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Keywords: hydrogen, synthetic fuels, RSOC materials

INTRODUCTION

A world based on renewable energy will need an enormous capability of energy conversion and storage, because most of the renewable energy will be produced as electricity from the most abundant, but intermittent, renewable energy sources: electricity from solar cells and wind energy. Storage of some of the renewable electricity is necessary to compensate for the intermittency of these energy sources. A reversible solid oxide electrolysis/fuel cell (SOEC/SOFC or just RSOC) can convert electricity into fuel (called power-to-fuel, PtF) or into other chemicals (PtX), and convert fuel back into electricity again. State-of-the-art (SoA) SOEC can electrolyze a mixture of H₂O and CO₂ into H₂ and CO (syngas) with high efficiency in the temperature range between 650 – 850°C [1,2]. Further, syngas may be transformed to CO₂-neutral hydrocarbon fuels using already available catalytic processes. Hydrocarbons will be much needed for heavy transport (airplanes, ships, long distance trucks) as well as for iron and cement production. Syngas is important for chemical industry.

R&D efforts are these years trying to lower the RSOC operation temperature down to 400 – 550°C. This work is predominantly R&D of materials because it is the materials (including structure such as porosity and particle size) that mainly limit cell performance. For example, such low temperature will facilitate application of metals for cell support and stack that are significantly less expensive but stronger than the materials used today. Also SOEC below 550 °C will be able to convert electricity directly into CO₂-neutral hydrocarbon fuels (PtF), which probably will be competitive with fossil fuels. This presentation will contain some concrete examples of R&D leading towards such improvement of RSOC.

NEW RSOC MATERIALS COMBINATIONS

Fig. 1 shows a typical SoA RSOC with specified materials. This is used as background for the discussion of how we may change to a new combination of materials in RSOCs.

The composite LSC-CGO oxygen electrode is an excellent fully reversible electrode above 650 °C, but cobalt is carcinogenic. At 500°C, Pr₆O₁₁ and other Pr-compounds combined with O²⁻-conducting CGO backbone seem to perform even better than LSC-CGO, and Pr₆O₁₁ based oxygen electrode catalysts

may thus replace Co-containing perovskite like LSC in the future.

The classical Ni-YSZ cermet fuel electrode does not have sufficient durability at high electrolysis current densities above ca. 1 A cm⁻². At such load it seems now clear that a Ni-CGO cermet is more durable.

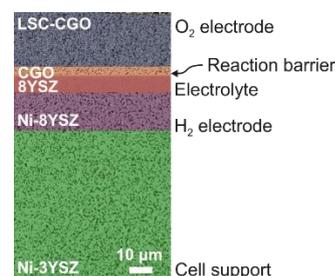


Fig. 1. Artificially colored SEM micrograph of cross-section of a DTU RSOC. The cell support is ca. 350 μm, *i.e.* not in accordance with the scale bar. YSZ is yttria stabilized zirconia. CGO is Ce_{0.9}Gd_{0.1}O_{1.95}, a good O²⁻ ion conductor and a barrier against chemical reaction between YSZ and LSC ((La_{0.6}Sr_{0.4})_{0.98}CoO₃).

With respect to the electrolyte, a main problem is the relatively low O²⁻-conductivity of YSZ. It may be substituted by Zr_{0.79}Sc_{0.20}Ce_{0.01}O_{1.90} (10Sc1CeSZ) which has a significantly higher conductivity than 8YSZ. For both polycrystalline 10Sc1CeSZ and CGO, the grain boundaries have much higher resistance than the bulk crystals. Thus, methods for decreasing the grain boundary resistance should be further developed.

The Ni-YSZ cell support is relatively expensive. It is the ceramic YSZ component that gives the mechanical strength, but the ceramic YSZ is to some extent fragile. Exchanging the Ni-YSZ support with ferritic stainless steel, stable below 550°C, is a clear improvement, everything else being equal.

This way it should be possible to put together a better low temperature RSOC. Data about mentioned materials can be found in [2,3] and references therein.

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NOTES

Symmetric solid oxide fuel cells with high-performance cobalt-free Fe- and W-contained electrodes

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Keywords: Tungsten doped SrFeO_{3-δ} perovskites, redox stable electrode materials, quasi-symmetrical Solid Oxide Cells

INTRODUCTION

The energy generation by combustion of fossil fuels brings many severe environmental problems and the depletion of these traditional fuels urgently requires the development of new alternative clean and green energy. Solid Oxide Fuel Cells (SOFCs) are among the most promising technologies for the production of electricity and heat from traditional and renewable energy sources. The symmetrical SOFCs (S-SOFC) with the same electrode, are very promising, due to reduced cell components, simplified manufacturing process and alleviated chemical stability problems, consequently decreasing production costs and ensuring a long-term stable operation. S-SOFCs can also address carbon deposition and sulfur poisoning problems by simply reversing the gas flows (oxidizing the deposited product). In addition, S-SOFC facilitates a reversible operation between fuel cell and electrolysis mode. To be economically competitive, the commercial application of S-SOFCs and SOFCs will require lowering the temperature to a low temperature range while still maintaining a high-power output [1-3]. Therefore, new redox stable electrode materials with enhanced electrocatalytic properties are indispensable for boosting the performance of S-SOFCs.

RESULTS AND DISCUSSION

In this work, Fe and W contained Sr₂Fe_{2-x}W_xO_{6-δ} oxides (x = 0.1 to 1.0) have been successfully synthesized, and the maximum doping level of tungsten in Sr₂Fe_{2-x}W_xO_{6-δ} compounds was determined which is limited to x = 1.0. The substitution of tungsten in Sr₂Fe_{2-x}W_xO_{6-δ} oxides significantly affects the synthesis condition and crystal structure of compounds. B-site rock salt-type ordered double perovskites Sr₂Fe_{2-x}W_xO_{6-δ} (x = 0.6 to 1.0) with *P21/n* space group can only be synthesized in reducing condition, while simple perovskites Sr₂Fe_{2-x}W_xO_{6-δ} (x = 0.1-0.5) with *Pm-3m* space group can be easily obtained in air. In this study, the synthesized single-phase Sr₂Fe_{2-x}W_xO_{6-δ} (x = 0.1-0.5) perovskites have been systematically investigated as redox-stable electrode materials for boosting the performance of symmetrical SOFCs. Phase composition, crystal structure, oxygen content, transport properties, chemical compatibility towards mostly used electrolytes and chemical stability of

proposed materials under reducing/oxidizing atmospheres were studied. It has been found that Sr₂Fe_{2-x}W_xO_{6-δ} oxides are compatible with classical electrolytes (8YSZ, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-d} and Ce_{0.8}Gd_{0.2}O_{1.9}). Quasi-symmetrical SOFCs were constructed based on selected electrode materials, and very excellent electrochemical performance was recorded (Fig. 1).

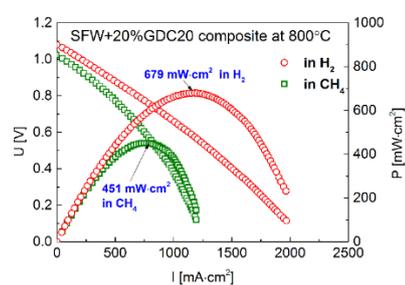


Fig. 1. Voltage and power density of quasi-symmetrical SOFCs in wet H₂ and CH₄.

CONCLUSIONS

Structural properties, oxygen nonstoichiometry, transport properties data were measured for Sr₂Fe_{2-x}W_xO_{6-δ} perovskites (x = 0.1 to 1.0) perovskites. Among all the investigated materials, Sr₂Fe_{1.8}W_{0.2}O_{6-δ}-based symmetrical cell shows the lowest stable electrode polarization with R_p=0.06 Ω cm² at 800 °C for 100 h in air, while Sr₂Fe_{1.6}W_{0.4}O_{6-δ}-based symmetrical cell has the best value in 5 vol.% H₂ in argon with R_p=0.5 Ω cm² at 800 °C for 100 h. Excellent performance was recorded for the constructed quasi-symmetrical SOFCs based on the above selected electrode materials, with 679 mWcm⁻² at 800°C in wet H₂ and 451 mW cm⁻² at 800°C in wet CH₄.

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Self-shearing reactive milling as a new method of synthesis of solid state hydrogen storage materials

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Keywords: hydrogen storage, reactive milling, ball milling, solid state hydrogen storage, metal hydrides

INTRODUCTION

Reactive milling (or grinding) is a process that is carried out with the use of popular ball mills (mainly planetary), and its purpose is not only to refine and mill the input material but also to cause its reaction - usually with gas (e.g. hydrogen) filling the working cylinder. Often this method is used to synthesize binary and ternary metal hydrides, as well as complex hydrides, which are considered as materials for hydrogen and heat storage. This process, known for many decades, is very easy to apply and brings extremely good results, which is why it is very popular and used in hundreds of laboratories around the world. In the classically used version, the reaction is usually carried out with cylinders made of a material with high abrasion resistance and grinding media in the form of steel or ceramic spheres for grinding the batch material. The fact that this technology can be used to synthesize materials under non-equilibrium conditions is attributed to the presence of significant stresses and local overheating at the interface of the colliding spheres and the fact that the batch material is "trapped" between them, which is subjected to extreme stress and strain. Unfortunately, defects in the material that are the "side effects" of the process cause that when materials are ground for hydrogen storage, they do not reach their maximum capacity - mostly due to mechanical disordering. In recent experiments [1,2], it was found that some of the solid-state hydrogen storage materials can react with hydrogen in the reactive milling process, even if grinding media are not used. Moreover, it turned out that the products formed as a result of such a reaction (the case of FeTi) are characterized by a significantly higher capacity (hydrogen content) precisely due to the lack of the disordering effect of the material. This process was called self-shearing reactive (SSRM) milling and allowed activation (first hydrogen absorption) by the FeTi alloy, which typically requires cyclical heating and cooling in a hydrogen atmosphere to become active. Here we present the effective SSRM on the examples of FeTi and NiTi alloys.

EXPERIMENTAL

FeTi and NiTi alloys were processed in a planetary ball mill under hydrogen pressure without the grinding media. With the use of custom-designed and made vials, pressure drop was wirelessly

monitored and used to calculate the absorption of hydrogen during the process. Obtained powders were characterized in terms of the morphology of the particles, surface area, phase composition, and decomposition temperature (where applicable).

RESULTS AND DISCUSSION

It was found that both FeTi and NiTi alloys absorbed hydrogen amounts close to theoretical without any activation prior to the process. The SSRM process was found to be effective for even as low as 150rpm rotational velocities of the cylinder. It was found that absorption of the hydrogen, once started, proceeds even without further movement of the milling vial. For NiTi alloy cross-sections of the hydrogenated particles revealed a small amount of the internal cracks caused by the interaction with hydrogen, however, for smaller rotational speeds, particles remained coherent, despite the full hydrogenation. In opposition to that, FeTi powder after hydrogenation changed its appearance and formed a spongy structure composed of nanometric particles.

CONCLUSIONS

SSRM process was found to be extremely effective in the hydrogenation of AB-type alloys (namely FeTi and NiTi), likely due to the formation of a clean surface of the particles under hydrogen. Lack of mechanical disordering during the process (low energy conditions) allowed for obtaining almost full hydrogen capacity, which is a great improvement as compared to reactive milling with grinding media.

ACKNOWLEDGMENT

This work is supported by National Science Center, Poland, with grant 2021/43/B/ST5/01299.

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NOTES

Arrangement effect of the hydrogen storage material in tank on rate of heat exchange with environment

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Keywords: hydrogen storage, LaNi₅, graphite.

INTRODUCTION

Hydrogen is seen as one of the important energy carriers of this century and is indicated as a fuel of future]. Research problem of physical properties of metal hydrides is strongly connected with very actual topical issues of hydrogen storage. Hydrogen is the most plentiful and ubiquitous substance in the universe. Hydrogen can be used in the fuel (hydrogen) cell – device that converts the chemical energy from a fuel (hydrogen) into electricity through a chemical reaction with oxygen or another oxidizing agent. Fuel cell can work practically non-stop, as long as hydrogen is supplied and emits only heat and water vapour. Problem is in efficient storage and delivery of hydrogen. Currently, hydrogen is stored mainly as a high pressure (up to 80 MPa) gas and as a liquid. Besides these “classical” methods, the physisorption on materials with a high specific area, hydrogen intercalation in metals and complex hydrides, and storage of hydrogen based on metals and water are intensively investigated.

Especially interesting are metallic hydrides of intermetallic compounds. Their advantages are high efficiency of sorption/desorption process, acceptable temperatures and pressures for mobile applications. Disadvantage is high weight of material (not higher than 3 wt % at RT). That is why this kind of hydrides is used usually in heavy mobiles and laboratories. The preparation of a hydrogen storage tank based on chemisorption in metallic hydrides is not obvious. Intermetallic compounds during saturation with hydrogen significantly increase their volume, even by 30% [1,2]. Moreover, these materials heat up considerably during hydrogen absorption, and cool down during desorption. The decrepitation material is observed [2]. These phenomena mean that the intermetallic compounds placed in the tank should have good thermal contact and easily exchange heat with the environment.

EXPERIMENTAL

The work presents a design of a test tank in which commercial LaNi_{4.8}Sn_{0.2} (*abb.* LNS) was used with graphite in various arrangements of its filling and the diagram of the measuring system is shown in Fig.1. The reactor (2) (with a capacity of approx. 200 ccm) with LNS (1) was immersed in an insulated vessel (4) with water (3). The temperature of the water and the hydrogenation material was continuously measured by thermocouples (5-8) and recorded using a

computer. The aim of the experiment was to investigate the arrangement of LNS in which the removal/introduction of heat from/to the material will be the fastest.

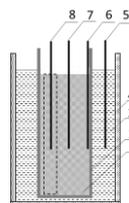


Fig. 1. Scheme of the measuring system. Details in the text.

RESULTS AND DISCUSSION

The presentation will show the results of the LNS heating and cooling curves as a function of time in various variants, which included a loose and compressed layer of LNS, a loose and compressed layer of LNS mechanically mixed with graphite, and LNS placed in special copper jackets. The latter solution is also advantageous in terms of the ease and speed of hydrogen permeation during absorption/desorption from the material along the entire reactor. Newton curves of heating and cooling were fitted to the determined curves. The calculated extreme values of the system constant k differ almost fourfold for the system with a loose material layer and placed in copper jackets.

CONCLUSIONS

The measurement system, although relatively simple, quite well simulates the real operating conditions of the intermetallic compound hydrogenation reactor. The obtained results indicate that the use of graphite as an admixture of the hydrogen storage material increases the ability to remove heat exchange heat, and the use of copper jackets further improves this ability, and may also contribute to faster and uniform supply and removal of hydrogen from the material. The obtained results may be useful in designing tanks with larger capacity.

ACKNOWLEDGMENT

This work was supported by: BIOSTRATEG2/297310/13/NCBR/2016 (NCBiR) and Research program 04-4-1121-015/2020(Poland-JINR Dubna).

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NOTES

How polarons and bismuth's lone pairs control diffusion in sodium bismuth titanate - an ab initio study

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Keywords: oxygen, fuel cells, DFT, ab initio, NBT

INTRODUCTION

Solid electrolytes with high oxide ion conductivity have drawn significant attention as they find applications in a wide range of electrochemical devices, like oxygen sensors, oxygen pumps and solid oxide fuel cells [1]. Recently, ceramic compounds based on the perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) became the focus of that attention due to their high Curie temperature (~ 325 °C), large remnant polarization ($38 \mu\text{C}\cdot\text{cm}^{-2}$) and exceptionally fast oxygen ion conduction. Interestingly, NBT shows high ionic conductivity only if the molar ratio between Na and Bi atoms is above one, called Type I. Below this value, called Type II, a sudden drop of conductivity is observed. Despite significant scientific effort in explaining this phenomenon, a satisfactory explanation has proved elusive.

EXPERIMENTAL

In this project we employ the state of the art Density Functional Theory, using the Strongly Constrained and Appropriately Normed functional (SCAN) [2] together with the Dudarev approach of on-site Coulombic interaction [3] to model the oxide ion dynamics in the NBT electrolyte. We perform a series of molecular dynamics (MD) simulations at 1127K at the gamma point, obtaining a series of 50ps trajectories with various initial positions of cations and oxide vacancies. For the electronic structure calculations we performed thousands of single-point calculations based on the ionic positions of MD runs.

RESULTS AND DISCUSSION

Performed simulations prove that even though there is a clear increase in the diffusion coefficient in Type 1 comparing to Type 2 of the NBT, there is no visible structural difference between those types. Interestingly, obtained results show that the diffusion process is present only in bismuth-rich areas. Furthermore, an investigation of the oxide ion vacancies revealed that for Type I NBT they form stable clusters, that serve as centres of ionic mobility, while for Type 2, those vacancies maintain much greater separation. Finally, we show how this unique behaviour is correlated with the presence of small

polarons near the vacancies, as it is shown in Figure 1, and how the local electronic structure affects ionic mobility.

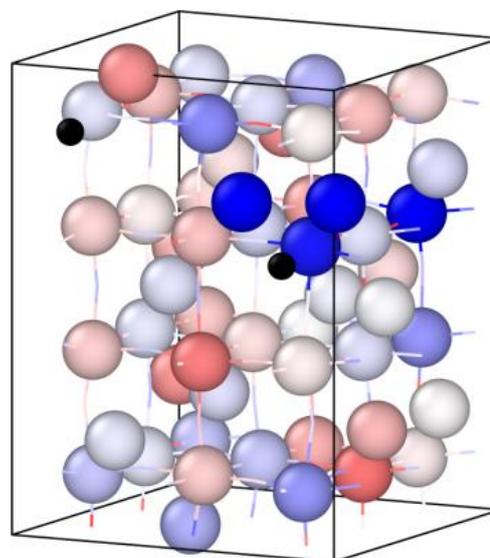


Fig. 1 Small polarons formed around the vacancy (black). Blue and red colour represent the negative and positive charge of cations respectively.

ACKNOWLEDGMENT

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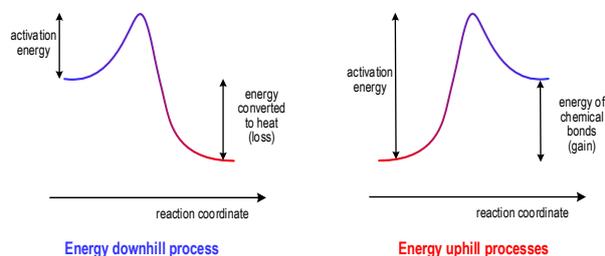
Solar to chemical energy conversion – what is the potential of photocatalysis?

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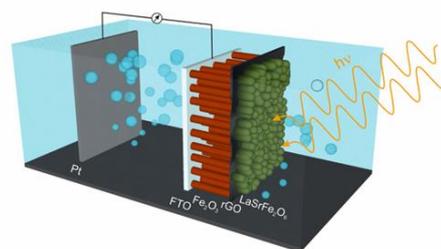
Keywords: photocatalysis, solar fuels

A fundamental difference between photocatalytic oxidation of pollutants and photocatalytic production of solar fuels should be perceived. Similarly to combustion, oxidation of pollutants is an exergonic process, while water splitting or carbon dioxide reduction are endergonic reactions. In energy downhill processes absorbed light is utilized to overcome the activation energy of elemental steps, e.g., activation of oxygen or C-H bond. The role of photons is therefore to “ignite” the energy downhill reaction. Production of hydrogen from water, or methanol from CO₂, are, however, highly endergonic reactions. Photocatalytic production of solar fuels is a process of solar quantum energy conversion to the energy of chemical bonds. In such processes photons can be considered as reagents. This differentiation is crucial to understand a theoretical limit of quantum efficiencies available in these types of processes. In the energy uphill reactions the energy gain (the energy of chemical bonds) originates from the energy of photons. One absorbed photon can generate one e⁻/h⁺ pair which can be used in single elemental reduction/oxidation reactions. Therefore, the limit of the overall quantum efficiency, defined as the number of e⁻/h⁺ redox steps divided by the number of absorbed photons, amounts 1. In the energy downhill reaction the energy evolved in the process can be dissipated as heat (and lost) or can be used to accelerate next elemental, catalytic steps. Taking this into account one can expect the overall quantum efficiency might exceed the unity. In order to facilitate it appropriate catalytic and redox conditions should be provided.^{1,2} A possibility of such reactions will be illustrated and discussed.



Solar to hydrogen conversion efficacy (STH) is the major descriptor of photoelectrochemical activity of electrodes in water splitting. The progress in increasing of STH to the DOE's expected level (25%) using an integrated system of photovoltaic/photoelectrochemical tandem design is promising but so far failed due to the inefficient photoanodes. The heterojunction architecture has been reported as the key design of enhancing STH,

which has presented its own limitations. In this case, the reduced rate of charge transportation at the interface of semiconductors building the heterojunction architecture is the primary constraining factor. To address this issue, we have designed a double-oxide perovskite LaSrFe_{2-x}Co_xO₆ (x = 0 (LSFF) and 1 (LSFC)). The presence of Sr²⁺ ions at the A-sites creates charge deficiency, which affects the B-sites and drive part of the iron/cobalt atoms at the B-sites to compensate it for by changing their oxidation number. This phenomenon alters the number of electrons holding by the B-sites, which results in a decrease in the work-function of the Co-containing perovskite, due to the increased ratio of Co⁴⁺/Co³⁺. The density of electronic states (DOS) reveals the presence of different states in LSFC compared to LSFF. Then a heterojunction of nanorod-Fe₂O₃@rGO@LaSrFe_{2-x}Co_xO₆ system was constructed. The designed architecture based on nanorod iron oxide (absorber), reduced graphene oxide (hole transfer mediator) and double oxide perovskites (water oxidation catalysts) is a promising approach to efficient, cost-effective and durable PEC systems. In the presentation the role of all components of the system will be discussed. In addition, general differences between hydrogen generation and carbon dioxide reduction will be addressed.



ACKNOWLEDGMENTS

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NOTES

Advanced semiconducting heterostructures for photoelectrochemical water splitting

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Keywords: semiconductors, heterostructures, water splitting, hydrogen

INTRODUCTION

Environmentally friendly light-activated processes based on heterogeneous photocatalysis cover many research areas related to both prevention and elimination of adverse phenomena. One of the ways to avoid them is through the usage of renewable energy sources, especially by decomposition of water through the conversion of solar energy into chemical energy of hydrogen. Such an application requires photoactive semiconductors to be in direct contact with the reaction medium and light. There are several semiconductors that can act as photocatalysts in the water splitting process. The criteria they must meet are as follows: appropriate band structure, low recombination rate, high mobility of charge carriers and their long diffusion path, resistance to photo(electro)corrosion, and low cost. Considering this, the choice turns out to be much limited and reduced to a narrow group of broadband semiconductors, requiring, however, modification of the electron structure in the direction of broadening the spectral range of absorbed light while maintaining their advantages. Therefore, it seems promising to move from the microscale to the nanoscale and form a heterostructure consisting of two semiconductors that differ in the band structure.

The aim of the studies was to obtain semiconductor heterostructures such as TiO₂@MoS₂, @Cu₂O or @CdS with designed architecture for efficient production of hydrogen in the photoelectrochemical water splitting process.

EXPERIMENTAL

Titanium dioxide in the form of nanomaterials was prepared via various methods based on titanium oxidation according to the procedure described in our previous paper [1]. Selected narrow band-gap semiconductors were deposited on the surface of TiO₂ to form a heterostructure by the SILAR or electrochemical deposition process [2-4]. Standard experimental methods were used for the characterization of TiO₂-based heterostructures, such as: XRD, Raman spectroscopy, and SEM. Spectrophotometry was used to determine the optical properties and, in conjunction with work function and impedance spectroscopy measurements, the electronic. The photoactivity of the heterostructures toward water splitting was determined by photoelectrochemical studies. The three-electrode photoelectrochemical cell (PEC), in which semiconductor heterostructures act as photoanodes, was used to register the current in the dark and under the illumination of white light.

RESULTS AND DISCUSSION

XRD and Raman spectroscopy studies showed that both the SILAR method chosen for CdS deposition and the electrochemical deposition method chosen for MoS₂ and Cu₂O on the TiO₂ surface are effective. SEM analysis showed that the size of the deposited semiconductors is on the nanoscale, ranging from few nanometer CdS particles through several hundred nanometer Cu₂O to discontinuous few nanometer MoS₂ layer. All heterostructures were found to be active in water splitting by the photoelectrochemical process. After 10 h of the process, the amount of H₂ obtained for TiO₂@CdS was 11.32 mmol/cm², 17.73 mmol/cm² for TiO₂@Cu₂O and was more than twice as low as TiO₂@MoS₂ for which 30.64 mmol/cm² was calculated.

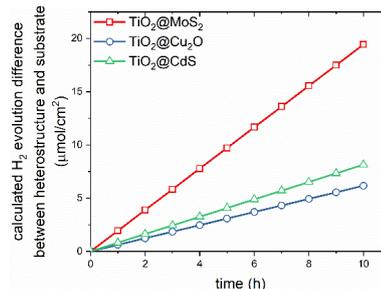


Fig. 1. Hydrogen evolution difference of TiO₂-based heterostructures.

CONCLUSIONS

The use of SILAR and the electrochemical deposition method allows us to obtain photoactive TiO₂-based heterostructures under white light. TiO₂@MoS₂ allowed the generation of more than twice the amount of hydrogen at the same time compared to TiO₂@CdS and TiO₂@Cu₂O.

ACKNOWLEDGMENT

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NOTES

Laser induced hydrogen generation from water by using graphene foam as photocatalyst

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Keywords: hydrogen generation, laser induced dissociation

ABSTRACT

The hydrogen generation by irradiation with CW infrared laser diode of graphene scaffold immersed in alcohol and water solutions is reported. The efficiency of hydrogen production increased exponentially with laser power. It is shown that the process was extremely efficient when the issue of white light emission induced by laser irradiation of graphene foam had took a place. The emission of white light following the multiphoton ionization was assisted by ejection of hot electrons. A generation of hydrogen was found to be extremely high in saline. The mechanism of laser induced dissociation of solvent molecules is discussed.

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NOTES

Carbon quantum dot catalytic electrodes for the oxygen reduction reaction

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Keywords: oxygen reduction reaction

The oxygen reduction reaction (ORR) is of great importance for various energy storage and conversion technologies, including fuel cells and metal-air batteries. The ORR suffers from slow kinetics especially in acidic conditions, due to the difficulty of O=O double bond dissociation, and expensive and rare metal electrocatalysts, such as Pt or Pd, are necessary. In alkaline conditions, the oxygen reduction is easier and non-noble metals or even carbonaceous materials can be used as electrocatalyst. The four-electron process can be written:



In our recent work, we have studied heteroatom-doped carbon quantum dots (CQD) as electrocatalyst on functionalized carbon paper and in presence of anion exchange ionomer (AEI), acting as binder and improving the hydroxide ion transport from the catalytic sites. According to the equation 1, the electrocatalytic reaction occurs at the triple phase boundary between the oxygen gas in pores, the doped CQD catalyst and the hydroxide-ion conducting AEI.

Our work includes the advanced synthesis of doped CQD by three methods - pyrolysis, microwave irradiation, hydrothermal process [1] – and the study of the electrocatalytic properties of N-doped CQD [2] and various co-doped CQD, including B-N, Si-N and S-N. The best electrocatalytic properties are observed with B-N codoped samples [3]. The influence of the AEI binder on the electrocatalytic performance is also investigated. The electrocatalytic properties are related to the defects of the CQD and the presence of various dopant atoms.

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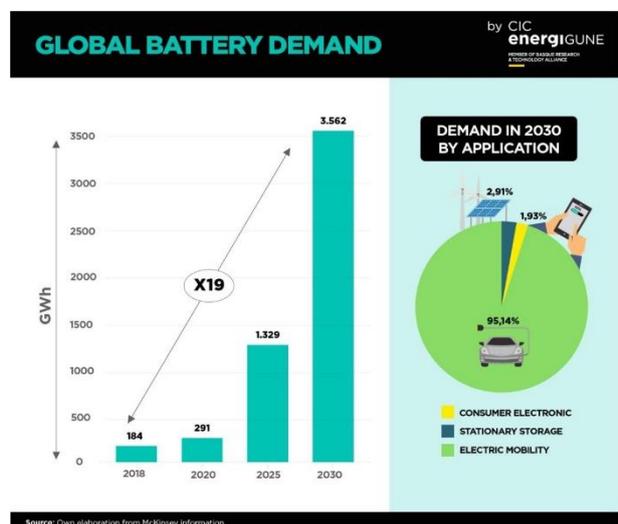
Sustainable Li-ion energy storage systems for green transformation

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Keywords: Li-ion batteries, green transformation, value chain, raw materials

The latest market analysis and forecast of worldwide demand for energy storage systems reveal the Li-ion battery market size worth \$182 billion by 2030 with a demand >3,5 TWh/year.[1, 2, 3] The market size value in 2021 was \$42 billion and is expected to increase at a compound annual growth rate (CAGR) of 18.1% from 2022 to 2030. The very fast growth rate, apart to increasing consumption of rechargeable batteries in consumer electronics, will be mainly driven by emerging market of electric vehicles (EV) but growing renewable energy sector as well.



at process projecting according to green chemistry rules. The sustainability of Li-ion batteries technology is required at any level of value chain, from raw materials to recycling, and with respect to carbon footprint to achieve green transformation targets.[4] Upon green transformation an access to Li-ion batteries supply/production will be strategic for any economy and required for energy efficiency and energetic safety. Thus, securing a supply of raw materials for batteries production will be a key factor together with developing new chemistries of active materials for Li-ion systems (i.e. cobalt-free, low-nickel or nickel-free, high-manganese) but also Na-ion systems should be taken into consideration.

In the paper the sustainability aspects of Li-ion active material systems (*State-of-the-Art* commercial materials and as well as new materials), battery production processes and value chain will be discussed in terms of fast-growing market, raw materials supply shortage and geopolitical energy situation.

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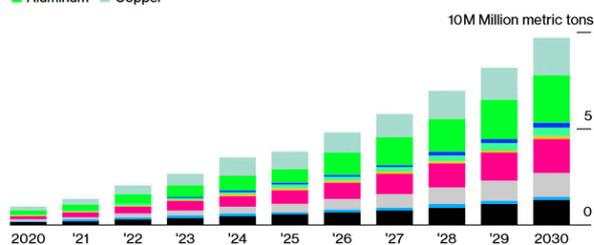
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This is crucial for green transformation and decarbonization of energy sector. Huge demand for Li-ion batteries production strongly affects existing raw materials market, especially for key metals (Li, Co, Ni) and graphite, what results in price increase and supply shortage disturbing whole value chain.

Battery Boom

Rising EV demand supercharges demand forecasts for a group of metals

■ Lithium ■ Cobalt ■ Nickel ■ Graphite ■ Manganese ■ Iron ■ Phosphorus
■ Aluminum ■ Copper



BloombergNEF
All metals expressed in metric tons of contained metal, except lithium is in lithium carbonate equivalent.

On the other hand, for fast scaled-up technologies a sustainability is a challenge and should be implemented

NOTES

Binary salt mixture – novel approach to design electrolytes for Lithium-ion batteries

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Keywords: binary salt electrolytes, lithium-ion batteries

INTRODUCTION

The stability of electrode - electrolyte interfaces is a crucial issue for the long-time performance and safety of lithium-ion batteries. To this end formation and dynamics of Solid Electrolyte Interface (SEI) on the anode side and Cathode Electrolyte Interface (CEI) on the cathode side has been widely studied. Various procedures have been used to form robust and effective interface layers including the use of SEI, CEI forming additives or templating artificial interfacial layers. Currently the concept of use of binary conducting salt mixture one of which can act as an effective moisture or (and) HF scavenger has been developed as well. To this end, Hückel type salts were used as second salt component to commercially available electrolytes. Although the interfacial studies of the effect of binary salts have been explored, there is no information how the addition of the second salt component affects bulk properties of the resulting electrolyte. This presentation aims to shed a light on this issues and couple them with the interfacial characteristics.

EXPERIMENTAL

Three different Hückel type salts, namely LiTDI, LiPDI and LiHDI have been synthesized and used as salt additives to LiPF₆-based electrolyte with the variety of solvent combinations. The conductivity of electrolytes has been studied by Electrochemical Impedance Spectroscopy. Additionally, spectroscopic studies comprising FTIR and FT Raman techniques were undertaken. The mobility of anions for single and binary salt mixture was measured by PFG NMR spectroscopy. Finally, galvanostatic cycling performance of the cathode||Li half cells containing considered electrolyte formulations has been evaluated.

RESULTS AND DISCUSSION

As expected, the conductivity of binary salt electrolytes differs considerably from the single salt analogues. The size of Hückel type anion and type of the solvent are crucial for the conductivity values and their changes with temperature and electrolyte formulation. The most important finding is the change in anion mobility once used in binary salt mixtures compared to single salt electrolytes. The addition of Hückel type salt leads to an increase in PF₆⁻ anion mobility whereas the mobility of Hückel type anion is reduced. The later depends on anion size and its concentration.

Spectroscopic studies indicated that solvation of Li⁺ cation also changes in binary systems compared to single ones.

CONCLUSIONS

It has been shown that not only interfacial but also bulk properties of the liquid electrolytes for lithium-ion batteries can be affected by the addition of the second salt component leading to the formulation of binary salt electrolytes. The crucial findings coming from the present work are changes in electrolyte conductivity coupled with affecting of anion mobility of cation solvation. In the future studies, we aim to find out whether these conclusions can be generalized to other type of binary salt electrolytes.

ACKNOWLEDGEMENTS

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NOTES

Novel insertion concepts for hybrid capacitors

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Keywords: hybrid capacitors, redox-active electrolyte, carbon materials,

INTRODUCTION

Constantly, the world is looking for the perfect energy storage and conversion system. Two energy storage technologies are currently the most popular - electric double-layer capacitors (EDLCs) and lithium-ion batteries (LIBs). On the one hand, EDLCs cannot (and is not obliged to) compete with Li-based technology in terms of energy density; this feature is quite often sought as the reason for the limited commercialization of EDLCs. On the other hand, LIBs have shorter lifespan and lower power values comparing to EDLCs. Therefore, it seems reasonable to merge both technologies into one compact device, called a hybrid lithium-ion capacitor (LIC). The hybridization of energy storage mechanisms allows for acquiring higher energy density values than EDLCs while maintaining high specific power and a great number of charge/discharge cycles. The major problem occurring during LICs assembling is the pre-lithiation stage. Auxiliary metallic lithium electrode is one of the solutions – in fact, this approach was encouraging; however, after the pre-lithiation process, the metallic lithium electrode should be entirely utilized or removed and become replaced by a carbon electrode. This raises technical and safety issues because the exchange requires an inert environment. Another approach uses composite materials as positive electrodes, allowing full intercalation of lithium into graphite structure.

Nonetheless, after the pre-lithiation process, the dead mass of the composite stays in the system and deteriorates the efficiency [1]. A different method of pre-lithiation using lithium from electrolyte was presented by Béguin et al. [2]. In this approach, the main problem identified was the consumption of lithium ions from the electrolyte and the diminished electrolytic conductivity of the solution.

EXPERIMENTAL

In our work, we propose another concept that allows for full intercalation of the negative electrode without an auxiliary electrode or less-conductive composite on the positive side. In principle, the redox-active lithium salt dissolved in 1 mol·L⁻¹ LiPF₆ in EC:DMC electrolyte served as a charge-balancer. Thus, additional Li⁺ in the redox agent structure made the Li⁺ concentration in the electrolyte non-affected. Full electrochemical tests, including cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy, constant

power discharge were carried out. In further studies, optimal LIC operating conditions, i.e., voltage (2.2 – 4.2 V) and current density (0.2 A·g⁻¹), were determined. The system has also been compared with commercial products.

CONCLUSIONS

Both, redox and non-redox processes occurring on both electrodes were identified. The capacitor's cycle life and the effect of the addition of inorganic salt on the conductivity were also investigated. Furthermore, detailed analysis has been conducted using operando mass spectrometry coupled with gas chromatography, SEM/EDS, Raman and FTIR spectroscopy.

ACKNOWLEDGMENT

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NOTES

Design of functionalized separators for practical application in Lithium-metal batteries

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Keywords: Lithium metal batteries; Functionalization; composite separator; dendrite-free Li deposition

INTRODUCTION

Rechargeable lithium metal batteries (LMBs) are regarded as one of the most favored choices for next-generation energy storage systems. However, practical application of metallic Li as anode in LMBs is still hindered by some annoying issues such as lithium dendrites formation, low Coulombic efficiency and safety concerns arising therefrom. To solve these concerns, the modification of separators is one of the most promising strategy, which can well regulate the lithium ions deposition/stripping behavior and inhibit the lithium dendrites formation due to their direct contact with the lithium anode. Some ceramic coating materials such as Al_2O_3 , $\text{Mg}(\text{OH})_2$, and LLZTO have been developed and employed as functional layer of separators in the published works. Although these ceramics coating could mechanically inhibit the dendrites formation, the coating layers are inevitably thick and heavy because of their high density with relatively large interface resistance. Therefore, how to construct a lightweight composite separator that can efficiently regulate the lithium deposition/stripping behavior through a simple and scalable manufacturing process is still a big challenge for high-energy lithium metal batteries.

EXPERIMENTAL

The PP or PE membrane were firstly soaked in an oxidizing solution which contains 4 m H_2SO_4 and 0.05 m KMnO_4 at 30 °C for 6 h to achieve a hydrophilic surface. After that, the PP or PE membrane were rinsed thoroughly with DI water and dried at 45 °C in the oven. The TV layer was composed of TA, VS_4 , and rGO with feeding weight ratio of 15:15:75 for achieving a stable functional layer. First, Ta and VS_4 with molar ratio of 1:10 were first grinded together in ethyl alcohol. After the solvent has completely evaporated, GO solution with a few microliters of hydrazine hydrate was added into the powder mixture followed by ball-milling for more than 12 h to obtain fine slurry. Then the slurry was coated directly on the commercial a thin PE separator (12 μm) or PP separator (25 μm) and dried at 45 °C for 24 h in a vacuum oven.

RESULTS AND DISCUSSION

The as constructed multifunctional separator with bilateral coating layer is prepared via facially casting tannin acid (Ta) and VS_4 on commercial polypropylene (PP) separator using rGO binder. The functional layer is lightweight with mass loading of only 0.16 mg cm^{-2} and

thickness of ~ 1.5 μm , showing targeted electrocatalytic effects towards the sulfur species conversion and can regulate uniform Li stripping and deposition for 1400 h. Accordingly, the full LMBs with sulfur cathode and TaVG-PP separator deliver a stable cycling performance for more than 1200 cycles with a low capacity decay rate of 0.03% and realize favorable area capacity of 3 mA h cm^{-2} for over 400 cycles. The soft packaged LMB with a capacity of 160 mA h can stably cycle about 50 times with Coulombic efficiency of > 98.6%. The bifunctional layer with good mechano-properties could also maintain the overall thermal stability of the batteries even at 130 °C, which guarantees the safety of LMBs in practical application.

CONCLUSIONS

In summary, a simple and multifunctional separator with uniform bilateral functional layers on the commercial polyolefin separator (PP or PE separator) to stabilize the Li anode is proposed successfully. The designed functional layer composed of organic acid, metal sulfide and rGO is lightweight and shows a desirable electrolyte wetting ability. More importantly, the functional layer could effectively redistribute the Li ion flux and endow fast Li ion deposition transportation, enabling a dendrite-free Li anode. Consequently, LMBs with sulfur cathode and the functionalized separator could deliver a high capacity up to 3 mAh cm^{-2} for more than 100 cycles. Additionally, the functionalized separator showed wide compatibility in other types of LMBs (such as with LFP cathode or Li-rich ternary material) and delivered stable cycling performance and high Coulombic efficiency. The simple and cost-effective modification strategy as well as outstanding ions regulation and dendrites inhibition capabilities makes the designed separator has great potential in practical LMBs application.

ACKNOWLEDGMENT

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NOTES

High-resolution X-ray imaging of microcracks in battery electrodes

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Keywords: battery electrode, microcrack, 3D imaging

INTRODUCTION

The long-term performance of batteries depends strongly on the 3D morphology of electrode materials. Morphological changes, i.e. particle fracture and surface deterioration, are among the most prominent sources of electrode degradation. A profound understanding of the fracture mechanics of electrode materials in micro- and nanoscale dimensions requires advanced experimental techniques that allow to study kinetic processes. Experiments that monitor the material's behavior during charge/discharge cycles of a battery require the use of techniques and tools for *in-situ* and *operando* studies. In particular, an experimental setup is needed for microcrack formation and growth during charge/discharge cycling of the battery cell and for simultaneous imaging of microcracks in battery materials at the micro- and nanoscale. X-ray imaging techniques have the particular advantage of allowing a non-destructive 3D imaging of the interior of opaque materials, which is a necessary prerequisite for the study of kinetic processes in materials and systems.

The potential of X-ray microscopy and nano X-ray computed tomography (XCT) for battery research has been reported in several studies at synchrotron beamlines. However, a systematic materials development requires an experimental setup next to the materials synthesis and a 24/7 tool access. Therefore, we are demonstrating the capabilities of laboratory X-ray microscopy and nano-XCT with focusing X-ray lenses to image the morphology of 3D-structured materials for battery electrodes with sub-100nm resolution.

EXPERIMENTAL

X-ray computed tomography (XCT), characterized by a sample thickness / resolution value of $\sim 10^3$, provides non-destructive characterization capabilities across a range of length scales, observing features with sizes down to several 10 nanometers. Since *in-situ* or *operando* 3D imaging of the morphology of materials for battery electrodes and the study of the kinetics of defect evolution require a nondestructive technique with high spatial resolution, lens-based X-ray microscopy and nano-XCT are the techniques of choice.

A miniaturized test setup for 3D-structured systems and materials - a thoroughly designed, X-ray-transparent electrochemical cell in a laboratory X-ray microscope - provides a unique capability for high-resolution 3D imaging of microcracks while cycling the battery cell. Nano-XCT is suitable to image microcracks in advanced materials for battery electrodes with sub-100nm resolution nondestructively.

Here we demonstrate a laboratory *operando* nano-XCT characterization of a novel $\text{Na}_{0.9}\text{Fe}_{0.45}\text{Ti}_{1.55}\text{O}_4$ sodium iron titanate (NFTO) cathode material. A custom-built electrochemical cell was integrated into the nano-XCT tool (Xradia nanoXCT-100), allowing the X-rays to pass through the sample at a wide range of angles, enabling limited-angle XCT to study the evolution of the 3D morphology of the cathode material. It is observed that the probability of the formation and growth of microcracks increases with particle size and density. The microcrack growth is already visible at the first charge and first discharge. Further charging/discharging for five cycles and 30 cycles results in the separation of the large solid particles into smaller ones. The semi-quantitative investigation of the crack width growth in different projection planes indicates that the microcrack growth is similar in all three Cartesian directions [1].

CONCLUSIONS

The impact of the morphology on the degradation of battery materials, particularly the size- and density-dependence of the fracture behavior of the particles, is revealed based on a semi-quantitative analysis of the formation and propagation of microcracks in particles. Our work provides conclusions for the mechanical robustness of battery cells, and it opens new perspectives for screening of novel cathode materials. We demonstrated that laboratory X-ray microscopy and nano-XCT tools can be applied in *operando* mode to nondestructively image the 3D morphology and defect evolution in electrode materials. Profound understanding of kinetic processes in battery materials opens the way for the development of design concepts for novel engineered material systems considering their local properties.

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NOTES

Interplay of electron structure and entropy improving energy conversion in thermoelectrics and ion batteries

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Keywords: electronic structure, chemical disorder, thermoelectrics, ion battery, density of states, electromotive force

INTRODUCTION

It is well-known that crystalline materials exhibiting specific physical properties may convert various forms of energy due to eg. thermoelectric or electrochemical phenomena. The efficiency of such effects is partly related to specific electronic properties that are responsible for transport, magnetic or electrochemical behaviours. In order to optimize the performance of such materials more profound and reliable description of quantum mechanisms responsible for observed physical behaviors is required, which in turn demands first principles electronic structure calculations to allow for modeling of selected physical properties. Although Li-ion battery materials are still considered to be the most promising energy converter due to their excellent electrochemical parameters, many efforts have been recently undertaken to find alternative cathode materials conducting for instance Na ions.

RESULTS AND DISCUSSION

In the first part of this work, our recent results of electronic structure calculations as well as modeling of electron transport properties in selected thermoelectric materials as silicides, half-Heusler alloys or some minerals [1-4], are discussed. We focus mostly on the effect of unusual electronic structure features (e.g. band convergence or interplay between nonparabolic dispersion relations, strong anisotropy of transport properties and entropy induced multivalley bands), by intentional doping, spin-orbit interactions on thermoelectric performance, optimized by proper adjustment of carrier concentration and temperature.

In the second part, electronic structure features of Li-/Na-ion battery materials is presented. The results of electronic structure calculations of operating and potential materials for Li- and Na-ion battery systems, based essentially on AMO_2 compounds ($A=Li, Na$ and $M=Mn, Fe, Co, Ni$) and their alloys, are discussed. Noteworthy, theoretical results obtained using the Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) allowed to interpret the step-like vs. continuous-like character of the discharge curve in terms of some correlations between electronic structure and electrochemical properties in selected Na- and Li-ion cathode materials, respectively as well as to study a novel variant of the well-known cathode material $Li_xCo_{1-y-z}Ni_yMn_zO_2$ [5]. Chemical disorder such as Li vacancy defects and Co/Ni/Mn alloying was accounted for the KKR-CPA calculations, which resulted

in specific evolution of density of states in the whole range of Li contents and alloy compositions. It was predicted that electronic structure might exhibit semiconducting-like, half-metallic-like or metallic-like properties depending on Li content as well as relative concentrations of transition metal elements (Co, Ni and Mn). Moreover, the spin-polarised KKR-CPA computations resulted in magnetic moment onset, which markedly affect the overall DOS shape near E_F [6]. Recently, the KKR-CPA method has been successfully employed to study particular behaviors in the high-entropy oxides for Na-ion cathode with high configuration entropy and some desirable correlations between the variation of Fermi energy along density of states with Li/Na content in highly disordered ion-battery materials were found [7,8].

In summary, unusual electronic structure features appearing in thermoelectric (band convergence, spin-orbit coupling, multi-valley character) and ion-battery (step-like vs. continuous-like character of discharge curve) evidently determine their performance.

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NOTES

High-efficient Thermoelectric Modules For Conversion of Low-Parametrical Heat Into Electricity

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Keywords: energy conversion, thermoelectric modules

INTRODUCTION

Waste heat recovery is one of the most promising ways to improve the energy efficiency of numerous technological processes and energetic devices and can lead to a significant global reduction in fuel consumption and CO₂ emission. Thermoelectric devices are currently at the top of the most advanced waste heat recovery technologies. Because thermoelectric generators TEGs are made in solid-state technology they are much simpler in construction than analogous mechanical systems. They have no moving parts, and as a result, they are silent, robust, and highly reliable.

The team from the Thermoelectric Research Laboratory works on the development of technology for the production of a new class of thermoelectric converters with enhanced efficiency of energy conversion, cheaper in production and more environmentally friendly than commercial modules. For this aim, the novel strategies for the achievement of a high average thermoelectric figure of merit ZT_{aver} based on advanced electronic structure and phonon engineering were applied.

RESULTS AND DISCUSSION

Typical commercial TE modules are constructed using uniform semiconductors with carrier concentration optimized for assumed temperatures of heat sink T_c and heat source T_h . To enhance the efficiency in thermoelectric conversion, the concepts of segmented (i.e. composed of different thermoelectric materials) or functionally graded materials FGTM, with carrier concentration adjusted to the temperature gradient, are used. In our projects, we developed a new concept of Double Tuned Functionally Graded Thermoelectric Material (DT-FGTM) which was experimentally tested on PbTe and Bi₂Te₃ solid solutions. Our approach assumes the simultaneous tuning of two electronic parameters e.g. the bandgap E_g and the Fermi level E_F to gain a high averaged figure of merit ZT_{ave} over the operational temperature range. Additionally, we propose to utilize resonance effects in PbTe and adjust E_F with selected donor and acceptor impurities. We have proved that within the developed DT-FGTM approach the high efficiency in energy conversion, at least ~15 % can be achieved [1-2].

Another approach within this theory concerns the composites made of at least two semiconductors/metals with Attuned Electronic Structure and Mismatched Phonon Structure AES-MPS [3]. In particular, a composite consisting of Mn and Sb co-doped GeTe as a matrix and WC as a dispersed phase was prepared, and its

structural and TE properties were investigated. The simultaneous effect of enhanced thermoelectric power factor and reduced phonon thermal conductivity results in an extraordinarily high figure of merit ZT of 1.93 at 773K. We have tried to implement the above concepts on new classes of materials from a group of tetrahedrites and argyrodites [4-6] composed of environmentally friendly elements. The best materials were selected for the construction of prototypical thermoelectric converters designed for the conversion of low-parametrical heat. The TE modules were applied in the laboratory thermoelectric generator for the recovery of heat from exhaust gases of automotive engines. The determined power density exceeds 5 kW/m² which makes these elements attractive for practical applications.

CONCLUSIONS

The first prototypical thermoelectric converters have been fabricated using new technology developed at AGH UST. Manufactured TE modules are characterized by excellent operational parameters with relatively low production costs.

ACKNOWLEDGMENT

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NOTES

YOUNG SCIENTISTS FORUM

How engineering of the electronic structure of zinc sulfide may change its photocatalytic properties

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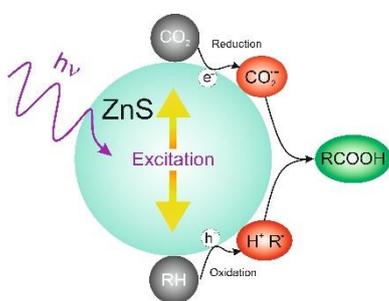
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Keywords: photocatalysis, zinc sulfide, electronic structure

INTRODUCTION

Photocatalytic transformation of carbon dioxide into valuable chemicals (including carbon monoxide, methanol and formic acid) is a very attractive field of research. The most difficult challenge is to activate the highly stable molecule of carbon dioxide and therefore to increase efficiency of the overall reaction. Due to the fact that the photocatalytic carbon dioxide reduction still suffers insufficient efficiency, it motivates researchers to improve the photocatalysts and the reaction conditions.



Zinc sulfide can be considered as a valuable photocatalyst in different reactions. Its most interesting property is a high energy of the conduction band (CB) edge, which is advantageous in the hydrogen evolution [1,2] and CO₂ reduction processes [3,4]. However, zinc sulfide is a well-known green light emitter, therefore electron is losing a part of its energy before the emission process (band gap energy is estimated on 3.5 eV, while energy of maximum emission intensity is merely 2.4 eV). It is well-known that the relaxation process of electron from the conduction band to electronic states beneath CB is a much faster process than the interfacial electron transfer between ZnS and reagents. Therefore, recognition of the whole electronic structure is crucial to understand the real reductive properties of semiconductors. Moreover, the ability to control it might be a key to enhance the desired photocatalytic activity. In this study we checked how engineering of the electronic structure of our materials may influence its spectroscopic and photocatalytic properties.

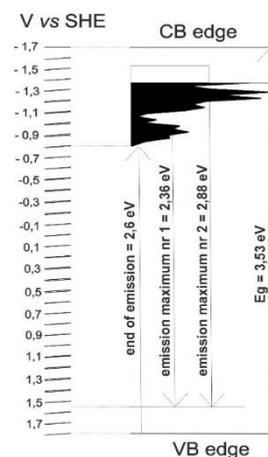
EXPERIMENTAL

Zinc sulfide materials were prepared according to the method described by Baran et al. [5]. Synthesis modifications were performed with the use of different zinc to sulfur ratios (1:0.66; 1:1; 1:1.33; 1:1.5). Moreover, the material with Zn:S ratio 1:1 was additionally synthesized under oxygen atmosphere and modified with the use of oxygen plasma treatment.

Materials were characterized with the use of X-ray diffraction, DRS, photoluminescence measurements and spectroelectrochemical methods. Their photoactivity was tested in photocurrent measurements and tests of photocatalytic reduction of water and carbon dioxide.

RESULTS

Presented results show a significant difference between materials with different Zn:S ratios. We present the exemplary model which concludes spectroscopic and photocatalytic properties of the studied materials.



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NOTES

Tin-iron oxide as CO₂ reduction photocatalyst

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Keywords: carbon dioxide reduction, photocatalysis

INTRODUCTION

Nowadays many people consider the rising environmental and energy concerns and seek to alleviate them with photocatalysts capable of reducing CO₂ which is a greenhouse gas into value added chemicals or so called solar fuels using the supply of energy from our Sun, thus solving two problems at once. However, many well know photocatalytic materials exhibit too wide band gaps limiting the absorbed spectra to ultraviolet range which forms only a small fraction of solar radiation, or have to low reductive properties due to not sufficiently high level of the conduction band. These shortcomings can be alleviated by combining two materials, one being oxidative photocatalyst and one reductive photocatalyst forming so called Z-scheme [1-3]. In such a system at the expense of absorption of two photons of lower energy (visible range which is the main component of solar spectrum) electrons, at low enough potentials to reduce CO₂, can be obtained along with holes which can oxidize a hole scavenger (for example water) to return the system to its ground state [3]. Such a system could be realized with for example tin-iron oxide which is a semiconductor with the reported high energy of the conduction band [1], sufficient for CO₂ reduction, with an oxidation photocatalyst. This presentation concerns other tin-iron oxides (SFO) photocatalytic CO₂ reduction properties both alone and in combination with other materials, their synthesis compared to methods presented in literature, and how the products morphology and structure are influenced by pH in wet methods syntheses.

EXPERIMENTAL

Photocatalytic tests were performed in glass test tubes with silicone septum caps. A photocatalytic material was spread onto the inserted glass plate; deionized and argon purged water was placed as a moisture reservoir. The reactor was filled with argon and CO₂ gas mixture. Irradiation was carried out with a xenon lamp through a water filter. Gas sampling was performed using a gas-tight syringe through the septum and the samples were immediately analyzed using GC. In order to eliminate interference of the reaction environment and to verify that products originated from the photoreduction of CO₂, three blank experiments were carried out. One was done without adding photocatalyst, the second one was done without CO₂, and the third one was done in the dark. No products were observed in these three experiments.

RESULTS AND CONCLUSIONS

High dependence of SFO on synthesis conditions was observed. In particular, pH and substrates mixing procedures were found to produce different products. XRD, SEM and DLS measurements reveal differences in crystalline structure, size of crystallites and morphology. XRF, XPS, EDX measurements indicate different composition of obtained material in syntheses made under different conditions.

Several materials (SFO combined with P25) active in photocatalytic CO₂ reduction were obtained (Fig. 1). It was found that P25 and SFO alone are inactive in that process (Fig. 1). Thus the possibility of a Z-Scheme junction between SFO and P25 is taken into consideration [1-3].

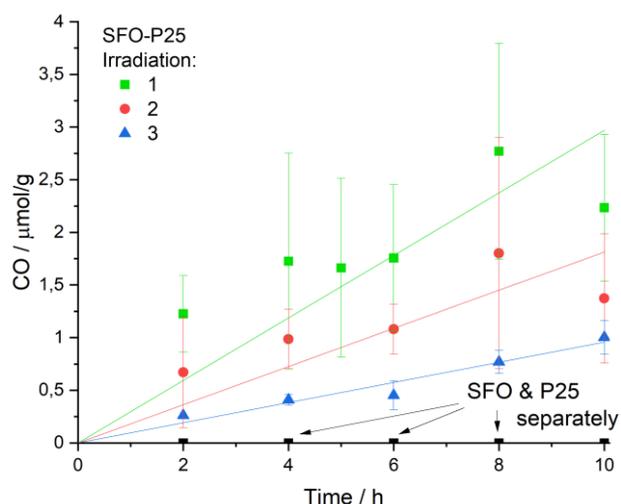


Figure 1. Photocatalytic activity of SFO, P25 and SFO-P25.

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NOTES

Electrodeposition of cobalt (oxy)hydroxide as cocatalyst on TiO₂ nanotubes

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Keywords: water splitting, photoelectrochemical cell, titania nanotubes, cobalt oxyhydroxides

INTRODUCTION

Water electrolysis is one of the cleanest ways to produce highly clean hydrogen by means of exploiting the energy produced by sunlight or wind power. This work aims to create a photoelectrode for efficient photoelectrocatalytic decomposition of water with improved operating parameters of photoelectrochemical cells (PEC). Here we present preliminary results on the design of a hybrid system containing a base photoactive semiconductor, namely a nanostructured material known for its photoactivity in the form of TiO₂ nanotubes, obtained by anodizing pure titanium in a well-known electrolysis process in an electrolyte with ethylene glycol [1]. The electrodeposited titanium dioxide, with a controlled nanostructure modified by cocatalyst, is used in the process of water oxidation. Cobalt oxides and oxy(hydr)ides are known to reduce an overpotential of the oxygen evolution reaction (OER): $4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^-$ [2].

This study aims to produce stable in alkaline solutions photoanode to reduce OER overpotential and preserve high photoactivity of TiO₂NTs by controlling CoO(OH) species amount and morphology using electrochemical methods.

EXPERIMENTAL

Cobalt from the aqueous solution of CoCl₂, NaCl and trisodium citrate was electrochemically deposited onto the crystalline nanotubes (procedure according to Ref. [3]) at different deposition charges. Then, the samples were potentiodynamically fully oxidized in 0.1 M NaOH (pH = 10) solution to stabilize the CV curves (30 cycles). During the electrochemical procedure, cobalt ions were oxidized to a solid nanoprecipitate of CoO(OH) in an alkaline solution, according to the procedure described in Ref. 3. Triple distilled water was used in all studies. Obtained electrodes were tested in an alkaline electrolyte (0.1 M NaOH) towards water molecules oxidation in dark and under illumination using Potentiostat/galvanostat PGStat 30 combined with a solar light source of 100 W/cm². Electrodes were also subjected to SEM, XPS, XRD and UV-Vis studies.

Chemicals used: NH₄F and ethylene glycol were purchased from Chempur (Piekary Śląskie, Poland); were purchased from POCH Gliwice (Gliwice, Poland); NaOH, and methylene blue were purchased from Sigma-Aldrich (St. Louis, USA). Alfa Aesar (Kandel, Germany) provided titanium foil (99.5% metals basis, annealed, thickness 0.25 mm).

RESULTS AND DISCUSSION

Cobalt metal deposits, obtained under potentiostatic control were used for cocatalyst formation in a form of cobalt (oxy)hydroxide. Metal deposition is a crucial stage, as a type of nuclei and crystal growth is controlled by chronoamperometric (CA) pulses. Subsequent dissolution of Co metal to Co²⁺ and further oxidation of Co²⁺ to Co³⁺ brings about a dispersed amount of cocatalyst CoO(OH) on of TiO₂NTs surface. Potentiodynamic polarization in the range from -0.1 to 0.7 V was performed multiply until a constant pattern of CV curves was recorded. Obtained material shows activity typical for redox Co^{II}/Co^{III} couple at E_{p,2} ≈ 0.5V vs. Ag/AgCl electrode and activity of Co^{III}/Co^{IV} above ~1.1 V as expected [3,4].

The photoanode made of TiO₂-NTs covered with a varied amount of cocatalyst was tested in 0.1M NaOH electrolyte in dark and under illumination. The overpotential of water oxidation significantly decreased. The Tafel slope increased up to 550 mV dec⁻¹ (measured above 0.9V) for TiO₂-NTs/CoO(OH) with 31mC/cm² cobalt species mass loading. Moreover, ca. 3-times higher photocurrent density was recorded for this sample. The photocurrent generations for all obtained samples are collected in Table 1.

Table 1. Photocurrent for constant potentials.

	Photocurrent (μAcm ⁻²) for			
	TiO ₂ -NTs	17 mC/cm ²	31m C/cm ²	66 mC/cm ²
at E = 0.3 V	16.4	33.9	57.9	44.1
at E = 0.5 V	16.5	33.1	56.0	46.1

CONCLUSIONS

In summarizing, these results prove that the electrochemical deposition of cobalt (oxy)hydroxides allows obtaining an electrode material with increased photoactivity and reduced overpotential of OER compared to the starting unmodified material TiO₂-NTs.

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NOTES

Structural, electrochemical and thermoelectric studies of multicomponent mixed ionic-electronic conductors

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Keywords: multicomponent oxides; mixed conductors; Seebeck effect; protonic conductivity.

INTRODUCTION

Multicomponent oxides, usually contain five or more elements occupying the same crystallographic position [1]. The lattice distortions influence not only mechanical but also transport properties of these materials. In consequence, the electrical and thermoelectric properties, strongly depend on the structural properties [2-3]. Mixed ionic and electronic conductors conduct both mobile ions (oxygen ions or protonic defects) and electrons/holes. Triple conducting oxides (TCOs) belong to mixed ion-electron conductors however they are characterized by three mobile charge carriers - electrons, protons, and oxygen ions. Cubic perovskites containing both acceptor-type constituents as well as transition metals were shown to be promising triple conducting oxides [4]. The combination of the high configurational entropy and mixed oxygen ionic, protonic, and electronic conductivity of selected high-entropy perovskites may render them interesting electrochemical materials.

EXPERIMENTAL

This work is devoted to the systematic description and understanding of two different groups: Ba(Zr, Hf, Sn, Ti, Ce, Y, Fe, Co, Bi, Zn)O_{3-δ}, (La, Sr, Ca, Y, Ba)(Co, Fe)O_{3-δ} and (La, Nd, Sm, Gd, Ho)(Co, Fe)O₃ oxides with compositions and structures based on the oxides being protonic, oxygen ionic and electronic conductors. The structure and microstructure of these materials are analyzed with X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM). Transport properties are studied both by DC four-wire technique and Electrochemical Impedance Spectroscopy (EIS) as a function of temperature and water vapour or oxygen partial pressures. To provide information about the chemical surface exchange coefficients and chemical diffusion coefficients of water and oxygen, Electrical Conductivity Relaxation (ECR) method is used. The temperature dependence of the Seebeck coefficient and Figure of Merit (ZT) will also be analyzed as a function of pH₂O and pO₂.

RESULTS AND DISCUSSION

All investigated samples have a single-phase cubic perovskite structure. The chemical diffusion studies for chosen Ba(Zr,Hf,Sn,Ti,Ce,Y,Fe,Co,Bi,Zn)O_{3-δ} compositions have shown a change of D_{chem} and K_{chem} parameters both as a function of number of elements in the structure as well as a function of pO₂ and pH₂O. The

preliminary results of electrical conductivity and Seebeck coefficient

as a function of temperature, for BaCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-δ} and BaZr_{0.1}Hf_{0.1}Sn_{0.1}Ti_{0.1}Ce_{0.1}Y_{0.1}Fe_{0.1}Co_{0.1}Bi_{0.1}Zn_{0.1}O_{3-δ} has shown the influence of number of elements and the presence of protonic defects in the sample on the both electrical conductivity and Seebeck coefficient.

CONCLUSIONS

Introducing many elements, where most of them are transition metals, into the B site of perovskite materials simultaneously increase electrical conductivity and induce multiphonon scattering resulting in lowering thermal conductivity. As a result, a high-entropy perovskite tailored in such a way could exhibit high electrical conductivity and the Seebeck coefficient as well as low thermal conductivity which finally result in a high ZT value.

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NOTES

Reversible cation-mediated anionic redox in defect spinel structure for high power batteries

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Keywords: li-ion cells, cathode materials, high-power cathodes

INTRODUCTION

With ever-increasing energy demand, more efforts are dedicated to designing innovative electrode materials providing higher storage capability and power output. As it has been demonstrated recently, the use of mixed cation–anion redox reactions opens up new possibilities for the significant rise of material's capacity and unusual electrochemical characteristics of lithium-ion battery electrodes. Herein, we present a new, spinel-based $\text{Li}_{0.98}\text{K}_{0.01}\text{Mn}_{1.86}\text{Ni}_{0.11}\text{O}_4$ (LKMNO) cathode material that shows unprecedented super-fast mixed cationic/anionic redox reaction. The material is synthesized through a water-based sol–gel route, which results in a cation-deficient nanosized spinel [1, 2, 3]. The product exhibits an extraordinarily high specific capacity in half-cells, along with an excellent rate capability, while maintaining structural stability for hundreds of charge–discharge cycles. Based on electrochemical studies and first-principles modeling we propose a mechanism of swift $2\text{O}^{2-}/\text{O}_2^{n-}$ redox reaction mediated through the TMs oxidation/reduction in the defect spinel structure.

EXPERIMENTAL

LKMNO cathodes were synthesized using sol-gel method. Structure of the material was verified using XRD, TEM and XPS techniques. Composition of the powder product was confirmed using ICP-OES analysis, composition of the electrodes before and after cycling were studied using ICP-LA method. Structural stability of the LKMNO spinel was verified by TG method. Electrochemical methods included in this studies are galvanostatic charge-discharge tests and cyclic voltammetry.

RESULTS AND DISCUSSION

$\text{Li}_{0.98}\text{K}_{0.01}\text{Mn}_{1.86}\text{Ni}_{0.11}\text{O}_4$ shows 170% of stoichiometric spinel theoretical capacity without voltage hysteresis or significant capacity and voltage fading attributed to limitations of reversible anionic redox. The authors' sol–gel-derived defect spinel structure can deliver 250 mAh g^{-1} at 1C and retain 64% of this capacity under a high 50C current rate. The observed electrochemical process shows the reversibility unseen before in mixed cation–anion redox cathode materials for Li-ion systems.

CONCLUSIONS

For the first time, it is shown that defect Fd(-3)m spinel structure, thanks to its flexible oxygen network, can host mixed cationic–anionic redox reactions with remarkable stability and high working safety. This new

cation-mediation of anionic redox is not limited by cation migration which speeds up commonly sluggish $2\text{O}^{2-}/\text{O}_2^{2-}$ reaction that, combined with fast-diffusion spinel structure (3D Li^+ diffusion channels), results in cathode material capable of ultrafast CC charging/discharging. The use of soft chemistry low-temperature synthesis methods, like the sol–gel process, provides conditions for tailored defected structure preparation. These studies open up a new path in exploration for inexpensive and nontoxic high-power cathode materials for sustainable Li-ion batteries. Further modifications of defect spinel system can lead to an even higher energy density in materials with different

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NOTES

Superstructure rearrangement in Li-rich NMC cathodes

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Keywords: Cathode Electrode Interface, Li-rich NMC, cathodes, Li-ion batteries

INTRODUCTION

Li-rich NMC are capable to deliver capacity beyond standard TM redox processes due to ability to additionally utilize the redox reaction of its lattice oxygen. The O redox reactions involve depopulation of the unhybridized O 2p orbitals from the Li–O–Li configurations¹ which, depending on the crystal and electronic structure of the materials may lead to the bonds reorganization and stabilization of the peroxy-like O–O dimers through covalent interactions. The superstructure of the electrode materials was found to have pronounced impact on the mechanism of O redox reactions facilitating formation either O₂ or Oⁿ⁻ species (n<2) depending on the honeycomb and ribbon type ordering of Li within TM layers². Within this study, with intention to contribute to better understanding of the O redox reaction in Li-rich NMC, we present detailed investigation of the structural and electrochemical properties of two compositions Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O₂ and Li(Li_{0.2}Ni_{0.1}Mn_{0.6}Co_{0.1})O₂ with different Li rearrangements within TM layers.

EXPERIMENTAL

The materials Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O₂ and Li(Li_{0.2}Ni_{0.1}Mn_{0.6}Co_{0.1})O₂ were synthesized by co-precipitation method. Obtained precursors were mixed with Li₂CO₃ and annealed in 500°C and 850°C. The crystal structure was characterized by the X-ray diffraction (XRD) method. The microstructure was analysed by scanning electron microscopy. The electrochemical performance of material was investigated in cells with lithium counter electrode via rate capability test and cycling voltammetry. Operando XRD technique coupled with XAS measurement of Mn, Ni L-edge and O K-edge were performed to monitor the crystal structure changes and variations of the electronic environment.

RESULTS AND DISCUSSION

The cathode materials Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O₂ and Li(Li_{0.2}Ni_{0.1}Mn_{0.6}Co_{0.1})O₂ were obtained in C2/m space group. Scanning electron microscopy revealed the presence of spheres (primary and secondary particles). Synthesised materials in Li-ion cells achieve capacity above 150 mAh/g. The detailed XAS investigations of the ex situ O K-edge showed that the for particular compositions we were able to observe during charging repetitively appearing signature coming from, most likely O₂ molecules formed in the materials and rigidly caged within TM vacancy clusters in the materials. According

to the XAS TEY and FY measurements we observed the differences between first and following charge processes on surface and in the bulk, which inform us about composition of the cathode electrode interface (CEI).

CONCLUSIONS

The results confirm synthesis of Li-rich NMC materials Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O₂ and Li(Li_{0.2}Ni_{0.1}Mn_{0.6}Co_{0.1})O₂ with different microstructure. We observe that the O K-edge showed characteristics assigned to the formation of the reduced surface layers, which was associated with the reversible spinel-type structure formation. Moreover, we present that different superstructure rearrangement have influence on reactions on cathode surface and change the cathode electrode interface (CEI)

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NOTES

The layered sodium and potassium oxides as the cathode materials for Na- and K-ion batteries

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Keywords: Na-ion, K-ion, batteries, layered oxides

INTRODUCTION

In the last two decades the fast growing demand for Li-ion batteries (LiBs) powering the electronic devices, cars and smart grids is observed, what is a reason for declining global reserves of Li, and increasing its price. Moreover, the problem with critical elements, such as cancerogenic and expensive cobalt and nickel occurs. The abovementioned issues are the main reasons for searching the alternatives for LiBs. The most promising and similar technologies are sodium-ion [1] and potassium-ion batteries [2] for which the safe cathode and anode materials for them are still being quested. Here we present the results of the studies of sodium and potassium layered oxides with reduced amounts of Ni or Co and based on the ecologically friendly elements.

EXPERIMENTAL

The samples were synthesized using the solid-state method in various temperatures in argon for potassium oxides and in oxygen for sodium oxides, followed by the XRD measurements. The obtained materials were used as an active materials for cathode layer preparation and in the next step, for the CR2032 test cell construction. The cells were charged/discharged under various current rates with different electrolytes. For the Na-ion cells, $\text{Na}_x\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.25}\text{O}_2$ oxide was studied, and for K-ion cells $\text{K}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_2$ family was considered.

RESULTS AND DISCUSSION

All diffraction peaks of obtained materials can be indexed with $P6_3/mmc$ space group characteristic for P2-type layered oxides. The crystal structure consists of MO_6 octahedra sharing edges and corners which form Na/ KO_2 slabs with "ABBA" oxygen stacking. Between these slabs, sodium or potassium ions occupy two prismatic Wyckoff positions: 2b – sharing edges and 2d – sharing faces with Na/ KO_2 octahedra.

The electrochemical tests for $\text{K}|\text{K}^+|\text{K}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_2$ showed the very low specific capacity of the cells without the manganese in the iron sublattice. However, the manganese substitution caused the specific capacity value increase for about $30 \text{ mAh}\cdot\text{g}^{-1}$. Moreover, it can be observed that the charge/discharge curves' shape is strongly dependent on the used electrolyte.

For the $\text{Na}|\text{Na}^+|\text{Na}_x\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.25}\text{O}_2$ cell the electrochemical tests under C/10, C/5, C/2, 1C, 2C and 5C current rates in the voltage regime of 1.5 – 4.2 V. The cell exhibited a stable discharge capacity value of $130 \text{ mAh}\cdot\text{g}^{-1}$ under C/10 current rate and even increasing

the rate to 2C, this stability was still visible and the capacity was about $70 \text{ mAh}\cdot\text{g}^{-1}$.

CONCLUSIONS

The obtained results showed that it is possible to synthesized cathode materials for Na-ion and K-ion batteries with the good cyclic performance. The advantage of these materials is also the ecologically friendly character, because of the lack or decreased amount of the harmful elements, such as cobalt or nickel. Presented materials requires more studies, however they can be treated as potential candidates for cathode materials for Na-ion and K-ion batteries.

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NOTES

Stabilization of crystal structure and electrochemical performance by electrochemically inactive substitutions in Na_xMnO_2

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Keywords: Na-ion batteries, Na_xMnO_2 , electrochemistry

INTRODUCTION

Even though they are considered as a symbol of the green revolution, Li-ion batteries are mostly made of components that consist of difficult to obtain, toxic or expensive raw materials. From this point of view, Na-ion batteries, based on available and non-toxic elements, seem to be a better solution for the future [1,2]. The working mechanism of both Li-ion and Na-ion batteries based on intercalation is similar. Since cathode material's properties have the most significant impact on cell performance, numerous systems are investigated in this role. Among layered oxides, especially Na_xMnO_2 -based cathode material is under consideration due to its high capacity and low-cost elements [3].

Since Na_xMnO_2 has several drawbacks, such as relatively low stability upon cycling, Li^+ , Mg^{2+} and Al^{3+} substitutions were applied in order to investigate their influence on crystal structure and electrochemical properties.

EXPERIMENTAL

Na_xMnO_2 -based cathode materials were obtained via a sol-gel method. Their structural properties were then analyzed by X-ray diffractometry, and the morphology of the samples was examined using scanning electron microscope. The selected samples were used to prepare coin cells, which have undergone electrochemical tests, namely: cyclic voltammetry and cyclic charge/discharge tests. The implemented research methods allowed to study the structural properties and electrochemical performance of investigated compositions as cathode materials.

RESULTS AND DISCUSSION

$\text{Na}_x\text{M}_y\text{Mn}_{1-y}\text{O}_2$ ($\text{M}=\text{Li}^+$, Mg^{2+} , Al^{3+}) crystallized in the hexagonal structure with $\text{P6}_3/\text{mmc}$ or $\text{P6}_3/\text{mcm}$ space group. The morphology of the samples showed grains of few micrometers in size. Both Mg and Li substitutions can lead to exceeding the theoretical capacity during few initial cycles. The capacity retention increases with increasing Mg substitution, however, the capacity values decreases, thus the moderate substitutions with Mg in $\text{Na}_x\text{Mg}_y\text{Mn}_{1-y}\text{O}_2$ (0.1, 0.15, 0.2) seem to be the most favourable.

CONCLUSIONS

The conducted research allowed to obtain cheap and environmentally friendly cathode materials for Na-ion

batteries. The investigation of substitutions with various valence state allowed for better understanding the mechanism of structural and electrochemical processes occurring during intercalation/deintercalation.

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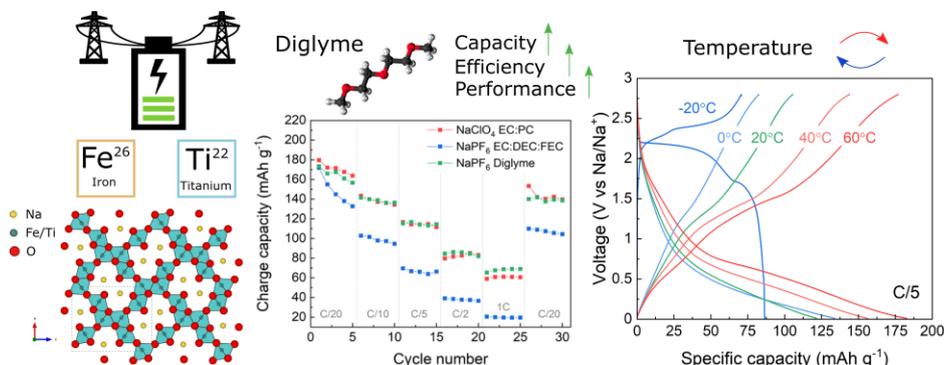
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Electrochemical performance of $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($X = 1; 0.9; 0.8$) anodes prepared via sol-gel method

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Keywords: Na-ion batteries, Anodes, Sol-gel

INTRODUCTION

In the last two years, the demand for Li-ion batteries (LIBs) especially for the e-mobility industry has grown tremendously and soon may surpass current production capabilities. This trend is accompanied by spiking prices of lithium, nickel and cobalt as well as inhibited access to such elements [1]. For such reasons, recently Na-ion technology has grown to be competitive to LIB's in terms of production costs and electrochemical performance. Because the choice of proper anode for Na-ion batteries has not been established yet, we decided to investigate the structural, electrical and electrochemical properties of iron-titanium-based anodes that employ an intercalation mechanism to react with sodium. Here we present the electrochemical behavior of NaFeTiO_4 , $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ low-cost anodes prepared via citrate assisted sol-gel method and compare it with the samples prepared using a high-temperature solid-state route.

EXPERIMENTAL

NaFeTiO_4 , $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ oxides were obtained in two routes [2]: 1) citrate assisted sol-gel method, where the samples were fired at 700°C for 6h or 900°C for 4h and 2) solid-state high-temperature reaction where samples were fired at 900°C for 20h. Structure, composition and morphology were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen absorption isotherms. Electrical conductivity was calculated in impedance spectroscopy (IS) measurements and electronic-band gap was estimated from UV-VIS spectra. Electrochemical performance in CR2032 coin cells was investigated in galvanostatic discharging/ charging experiments in various temperatures. Three different electrolytes were examined to improve coulombic efficiencies.

CONCLUSIONS

Sol-gel synthesis enabled to obtain anode materials characterized by lower grain size and improved morphology leading to enhanced electrochemical

behavior in Na-ion batteries. Impedance spectroscopy and UV-VIS measurements revealed that the electrical conductivities of double tunneled $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ were one order of magnitude higher than those of single tunnel NaFeTiO_4 . Electrical conductivity was dominated mainly by electron and hole carriers, and the activation energy was 0.82 – 0.86 eV. Sodium ion conductivity was recognized to be a limiting factor that may hinder the rate of diffusion. Among the studied materials, $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ possesses the highest charge capacity of 180 mAh g^{-1} during the first cycle at C/20 and can retain 80% of the initial capacity after 30 cycles with an average charging voltage of 1.3 V vs. Na^+/Na . Application of ether-based diglyme, instead of ester-based solvents, resulted in: (1) reduced extent of irreversible reactions during the initial discharge-charge cycle; (2) better performance under higher loads; (3) lower values of charge transfer and SEI resistance. Ex-situ XRD measurements showed that sodium insertion-extraction process is highly reversible and accompanied by minor volume changes in the unit cell. Experiments in temperatures from -20°C to 60 °C reveal that $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ preserve a significant fraction of its capacity: 70 mAh g^{-1} at -20°C and 177 mAh g^{-1} at 60°C. The results prove that $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ is an auspicious material for future low-cost Na-ion batteries.

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POSTERS

Entropy generation minimization in a steam reformer of methane

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Keywords: hydrogen, steam reforming, entropy generation, multicriteria optimization, genetic algorithm

INTRODUCTION

Steam reforming of methane (SMR) is a dominant technology of hydrogen production nowadays and it is predicted that in the near future SMR is likely to remain its major role [1]. However, steam reforming is responsible for severe carbon dioxide emissions (10 t of CO₂ is generated per 1 t of produced H₂ [1]). On the other hand, miniaturized steam reformers of methane can be used as an internal fuel processor for solid oxide fuel cell systems. Miniaturization leads to new problems, for example a carbon deposition on the catalyst, which is a minor problem in a large industrial reactor but can lead to fast catalyst deactivation in a relatively short tube filled with powdered catalyst.

A possible solution for the aforementioned issues lies in increasing the efficiency of hydrogen production during the SMR process. In this work, we show a possibility of efficiency increase by means of the entropy generation minimization (EGM) procedure. Since the rate of the entropy generation is directly associated with the loss of work by the Gouy-Stodola theorem, lowering the entropy generation rate could be a measure of efficiency increase.

METHODOLOGY

The entropy generation rate in a tubular reforming reactor is investigated and optimized numerically. We propose the following workflow:

1. Compute the temperature, species and velocity fields using the computational fluid dynamics method using a well-established in-house numerical code [2, 3].
2. Post-process results to calculate the local entropy generation rates in the reactor.
3. Use a genetic algorithm to optimize the entropy generation field achieving acceptable methane conversion rate (multicriteria optimization) [3].

4. Return to 1 and repeat until convergence.

RESULTS AND DISCUSSION

Figure 1 shows the total entropy generation rate in the reforming reactor in a reference case and in an optimized case. It can be seen that maximum of entropy generation drops about 3 W / K and the profile of entropy generation rate becomes smoother.

CONCLUSIONS

In the presented work numerical computations of entropy minimization generation in the steam methane reformer are shown. The results indicate that it is possible to optimize the entropy field in the reforming reactor, whereas keeping the methane conversion rate at satisfactory high level.

ACKNOWLEDGMENT

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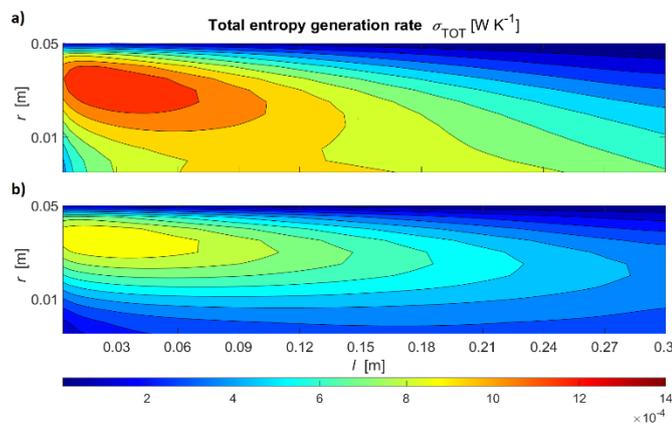


Figure 2. Total entropy generation rate, a) reference case, b) optimized case.

NOTES

Two-station automatic sieverts-type apparatus

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Keywords: hydrogen storage, PCT, sieverts apparatus, solid-state hydrogen storage, metal hydrides.

DESCRIPTION

Precise high-temperature measurement of hydrogen storage characteristics is a matter of high importance. A new concept and prototype of two-station automatic sieverts-type apparatus is shown in this poster. A fully automated device is designed in a way that allows independent parallel measurements of two samples in terms of their hydrogens storage properties in temperature range from ambient to 450°C and pressures from 0.01-10 MPa. The main advantage of this design is its compactness (two devices in one movable cart) and low cost of manufacturing due to properly shared expensive components such as turbomolecular vacuum pumps, pneumatic control components, gas delivery lines, high-quality frame and insulation. The general overview of the machine is shown as well as more detailed views. Exemplary graphs showing its extraordinary temperature stability and basic functions are provided and described.

SCHEMATICS AND OVERVIEW

The schematic of the single module of the system is shown in figure 1. The overview of the system is shown in figure 2.

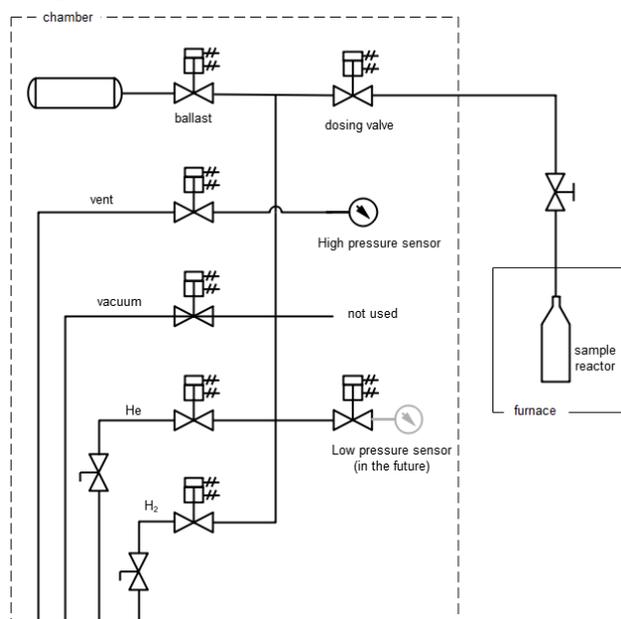


Figure 3. Schematic diagram of single module.



Figure 4. An overview of the two-station system.

ACKNOWLEDGMENT

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NOTES

Graph representation of Solid Oxide Fuel Cell anode's microstructure

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Keywords: fuel cells, solid oxide fuel cells, microstructure, graphs, quantitative analysis

INTRODUCTION

Solid Oxide Fuel Cell's electrodes are characterized by a complex microstructure promoting electrochemical reactions in the possible vast volume of the electrode. Microstructure's performance for each transport process occurring during the fuel cell operation can be related to quantitative morphological properties such as percolation, tortuosity, pore and grain size, porosity, or reaction region area. In order to perform an electrochemical performance simulation, all microstructural parameters must be given. One can generate an artificial microstructure using such methods as cellular automata and thereby attempt to find a theoretically optimal microstructure [1,2]. As there are multiple correlations between those parameters, optimization becomes a challenging task. Analysis of high-fidelity three-dimensional digital material representations is a time-consuming task. Here we show an alternative method for representation and analysis of a microstructure in the form of a weighted graph, which would be independent of the sample's fidelity. The proposed method aims to decrease the computational time needed for analysis and optimization.

METHODOLOGY

The study is based on the three-dimensional digital material representations (DMR) of an anode's microstructure. The DMRs used in the study are obtained either through electron tomography (FIB-SEM) of real microstructures or numerically generated with stochastic algorithms [3]. Each phase is analyzed independently. By repeated morphological erosion of the reconstruction and labeling voxels, connected groups of structures are determined for each erosion iteration. Each time a group disappears, the last voxels represent the coordinates of a node. Nodes are connected with other nodes within the same group if a unique path is within the analyzed phase between them. The path's length is the first weight of the connection between nodes. The second weight represents the necking radius along the path between nodes.

RESULTS AND DISCUSSION

In this study, a graph representation of a pore phase of an anode's microstructure was obtained. The example of the obtained results is presented in Figs 1 and 2. Nodes of the graph are correctly inserted in phase with connections between percolated pores. Future studies will focus on obtaining microstructural parameters from the graph representation.

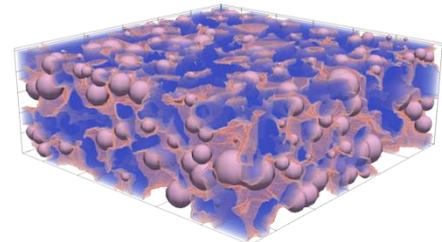


Figure 1 Nodes of the obtained graph for pore phase. Nodes are represented as spheres, with radius equal to the estimated grain size. Blue region with light red surface represents solid phases

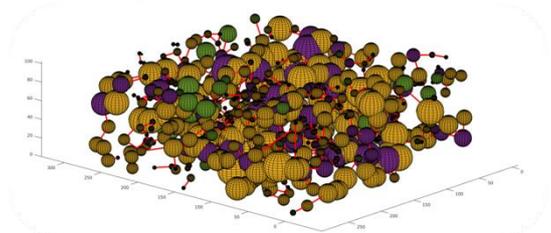


Figure 2 Graph obtained for pore phase with indicated connections between nodes indicated as red lines. Nodes are spheres with size representing estimated pore size, colors change with number of connections

CONCLUSIONS

Solid Oxide Fuel Cell's microstructure can be represented in a form of a graph to simplify the quantitative analysis of microstructure's morphology. We aim to test the faithfulness of the representation based on the comparison between parameters from high-fidelity sample and obtained through graph analysis methods.

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NOTES

Development of new perovskites $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$ as cathode materials for boosting the performance of SOFCs

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Keywords: cathode materials, SOFCs, crystal structure, thermal expansion, transport properties, chemical stability

INTRODUCTION

In the ever changing world, reliable energy sources are required for mankind more than ever in order to be able to achieve the goals of sustainable economic development, improvement of the life quality and social progress. There are growing concerns about environmental issues and uncertainty about the continuity of conventional fossil fuels supply (such as crude oil, natural gas and coal). The development of renewable energy sources (RES) is one of the real ways to reduce greenhouse gas emissions and achieve energy independence. The intermittent nature of obtaining energy from RES (e.g. wind energy, solar energy) requires the technologies capable for efficiently converting and storing energy. SOFC is of the most promising devices for energy conversion and storage [1]. However, the high operating temperature of SOFCs limits the commercial application, which indicates lowering the working temperature of SOFCs while still maintaining a high-power output is very crucial. New electrode materials (especially cathode materials) with enhanced electrocatalytic properties is necessary to boost the performance of SOFCs. Perovskite-structured cathode materials (ABO_3) allow to potentially achieve the goal by A-site and B-site cations modification strategy [2,3].

EXPERIMENTAL

In this work, $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$ materials were synthesized by the sol-gel method. The crystal structure was characterized by XRD and high temperature XRD measurements. The thermal expansion properties were examined by the dilatometry studies. The chemical stability and compatibility of the materials was assessed towards electrolytes. Oxygen non-stoichiometry of materials was determined by the iodometric titration method, and the change of oxygen content as a function of temperature was determined using the TG analysis. The morphology of the considered powders were characterized by the SEM studies. The mass relaxation measurements were applied to evaluate the bulk diffusion coefficient and surface exchange constant. The cathode material with the best desired properties was selected and investigated in constructed SOFCs with electrochemical measurements.

RESULTS AND DISCUSSION

The room-temperature phase of the obtained $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$ ($x = 0-0.1$, $y = 0.25$ and 0.5) materials is

classified to the trigonal system with $R-3c$ space group, and phase transitions from $R-3c$ to simple perovskite $Pm-3m$ have been recorded by HT-XRD studies. The thermal expansion of considered oxides is found to be anisotropic, and the TEC values are very close to the commonly used electrolytes (e.g. $12.7 \times 10^{-6} \text{ K}^{-1}$ for $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{3-\delta}$). Doping with strontium in the A-site significantly increases the oxygen non-stoichiometry. The investigated materials are stable and compatible with GDC-10 and LSGM electrolytes. The cathode materials is applied to construct full anode-supported SOFC, and an excellent power output is recorded with $445 \text{ mW}\cdot\text{cm}^{-2}$ at 650°C in wet hydrogen (Fig. 1).

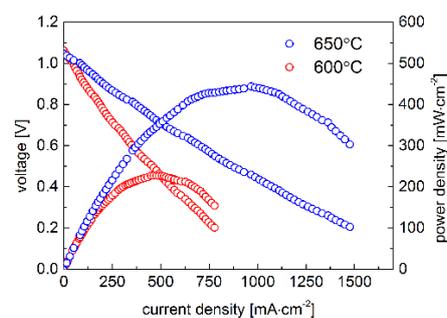


Fig 1. The performance of anode-supported SOFC in H_2 .

CONCLUSIONS

Physicochemical properties including: structural properties, oxygen nonstoichiometry, transport properties, and electrochemical properties of $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$ ($x = 0-0.1$, $y = 0.25$ and 0.5) oxides were characterized. The anode-supported SOFC with selected cathode material $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{3-\delta}$ shows very promising electrochemical performance, with $445 \text{ mW}\cdot\text{cm}^{-2}$ at 650°C in wet hydrogen.

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NOTES

Formation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ oxygen electrode using the spin-coating technique: performance at low temperatures (<600°C)

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Keywords: oxygen electrode, LSC, SOFC

INTRODUCTION

A solid oxide cell is an electrochemical device that converts chemical energy into electricity or can be used to store energy via electrolysis. The SOC consists of 3 basic parts: the hydrogen electrode, electrolyte, and oxygen electrode. The oxygen electrode is responsible for the reduction/oxidation of oxygen from the air. Thanks to the use of bulk ion transport to reduce oxygen to O^{2-} on a large percentage of the electrode surface, the active zone can be expanded and the kinetics improved at temperatures below 800 °C¹⁻³.

LSC ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$) is a well-known mixed ionic-electronic conducting that is used in SOCs. At this point, we would like to present results concerning the electrochemical performance of LSC at temperatures below 600 °C.

EXPERIMENTAL

The LSC cathode was created by calcining the precursor onto the surface of the CGO pellet, constituting the base for the layer, using the spin-coating technique. The precursor was a solution of lanthanum, strontium, and cobalt nitrates in appropriate stoichiometric proportions. The solvents were water with a 10 wt% addition of ethanol. Ethylene glycol and citric acid in a ratio of 1:1 and 1 wt% methocel were also added to the solution. The precursor prepared in this manner was stirred for 24 hrs. The layer was applied by applying 100 ul of the precursor to the surface of the CGO pellet and using the spin-coating technique. A three-stage speed increase of 500 rpm, 1000 rpm, and 3000 rpm was used. The samples were calcinated at various temperatures (600–800 °C) to obtain acceptable conductivity. XRD tests were performed on the powder obtained in the precursor calcination as well as on the layers already on the pellets. The thickness of the layers was estimated from the photos of the sample fractures. Samples with a layer thickness of about 400 nm were subjected to symmetric testing (on both sides of the CGO pellet there was an LSC layer of approximately the same thickness).

RESULTS AND DISCUSSION

The cathode layers in the form of LSC were obtained with thicknesses depending on the number of deposition cycles. For a single cycle, this value is 170 nm, and after each cycle it increases by about 70 nm. The target value was reached after 4 deposition cycles. However, samples with cycles from 1 to 13 were taken and the thicknesses were estimated by photos of the fractures using a SEM microscope. The obtained layers showed excellent continuity throughout the sample. There is a slight edge effect, which is common when using this technique, so

the layer at the edges is slightly thicker than that at the centre of the sample. The calcination of the samples at a temperature of > 600 °C was aimed at creating a crystal structure. Calcination at higher temperatures reduces the ohmic and polarisation resistance of the layer and increases the total conductivity. XRD measurements showed that the LSC structure was formed but also detected the presence of a strontium carbonate impurity, which was tried to be taken out and cleaned up so that pure LSC could be made.

CONCLUSIONS

A uniform cathode layer made of LSC with the possibility of controlling the thickness was obtained. These layers show good impedance properties. It has been shown that increasing the firing temperature allows for better total conductivity and impedance parameters.

ACKNOWLEDGMENT

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NOTES

Sol-gel obtained lithium manganese borate doped with transition metal ions

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Keywords: Li-ion, cathode, sol-gel

INTRODUCTION

One of the promising groups for Li-ion cathode materials are borates. Due to low molar mass of borate group, they exhibit high values of theoretical gravimetric capacity (more than 200 mAh/g). Borate groups may exist in various structural arrangements which enables high diversity of possible compounds. Among borates, there exists lithium manganese borate (LiMnBO_3 , LMB). The compound exhibits high theoretical gravimetric capacity equal to 222 mAh/g and high potential vs. Li/Li^+ equal to 4.1 V. LMB is present in two polymorph forms – monoclinic and hexagonal [1]. Literature results show that one of big challenges is to obtain pure one-phase material.

In this work, LMB and doped LMB were obtained using sol-gel method which allows to obtain materials with uniform doping and high surface area [2]. The main task was to optimize the synthesis process of LMB. Various optimizations like changing pH of sol solution, calcination times and temperatures, amount of dopant – were analysed in light of obtaining a pure-phase material.

EXPERIMENTAL

Vanadium-doped and lanthanum-doped LiMnBO_3 with nominal compositions $\text{LiMn}_{1-2x}\text{V}_x\text{BO}_3$ ($x = 0, 0.025, 0.05$) and $\text{LiMn}_{1-3y/2}\text{La}_y\text{BO}_3$ ($x = 0.025, x = 0.05$) was obtained by metal-citrate sol-gel method. Aqueous solutions of substrates: LiCH_3COO , $\text{Mn}(\text{CH}_3\text{COO})_2$, NH_4VO_3 , $\text{La}(\text{NO}_3)_3$ and H_3BO_3 were added to citric acid solution drop by drop under vigorous stirring. The solution was kept at 60 °C until gel was obtained. The gel was dried under vacuum and calcined at various temperatures in 600-800 °C range.

Thermal events were studied using TA Q600 DTA/TGA analyser. Gel samples were heated up to 1200 °C under argon flow. Phase structure of calcined samples was studied by means of X-ray diffractometry (Phillips Empyrean).

RESULTS AND DISCUSSION

XRD results for optimised materials are shown in Fig. 1. As one can see, no additional peaks related to vanadium nor lanthanum phases can be seen in obtained patterns, which suggests that lanthanum and vanadium were successfully doped in LMB structure.

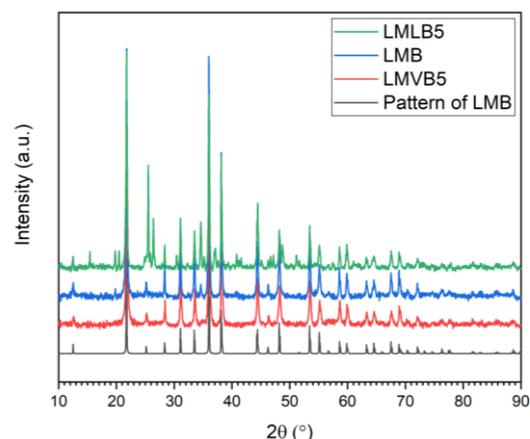


Fig. 1. XRD results for optimised materials. Green, blue and red lines stand for 5 mol. % lanthanum doped, pure and 5 mol % vanadium doped LMB, respectively.

Hexagonal LMB pattern (black) is shown for comparison.

CONCLUSIONS

Pure and doped lithium manganese borate was obtained using simple and facile sol-gel method. The method involved only simple chemicals. As it was shown, by careful optimisation of synthesis parameters, it was possible to obtain pure hexagonal form of LMB, described by higher working voltage.

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NOTES

Structural changes during lithiation and delithiation processes in Li-rich NMC cathodes

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Keywords: Li-ion batteries, cathodes, NMC, operando measurements

INTRODUCTION

The cathode material is the limiting factor for the total capacity and voltage of the Li-ion cells. Current material technologies are based on layered transition metal oxides with the chemical formula $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ (NMC) characterized by varying gravimetric capacities from 150 to 200 mAh/g and potentials relative to lithium from 3.2 to 3.7 V depending on the exact chemical composition. Increasing the capacity with maintaining a high operating voltage is possible by replacing transition metal ions at octahedral positions in MeO_2 layers with lithium ions, forming a Li-rich material¹. The surface of the active material has a crucial impact on Cathode Electrode Interface and consequently on cell parameters². The purpose of this work is to present the lithiation/delithiation mechanism in Li-rich NMC cathodes.

EXPERIMENTAL

The material was synthesized by the co-precipitation method and then annealed at 500 and 850 °C. The crystal structure was characterized by the X-ray diffraction (XRD) method combined with Rietveld refinement and Raman spectroscopy (in comparison with reference samples). The microstructure was analysed by scanning electron microscopy. The electrochemical performance of the material was investigated in cells with a lithium counter electrode via a rate capability test, cycling voltammetry, and electrochemical impedance spectroscopy. The results of the comparison of electrochemical performance for two types of electrolytes, based on LiPF_6 , are presented. Operando X-ray diffraction and Raman spectroscopy measurements were conducted to determine the working mechanism.

RESULTS AND DISCUSSION

The Li-rich NMC ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$) material was obtained in space group C2/m with the spherical shape particles. The observed bands between 300 and 700 cm^{-1} in the Raman spectra correspond to metal-oxygen vibration in Li-rich NMC material. According to the operando Raman measurements, we observed differences between the first and subsequent charge processes, especially for bands between 400 and 600 cm^{-1} , which inform us about the composition of the cathode electrode interface. Operando XRD results confirm reversible crystallographic structure transformation from C2/m to R-3m during lithiation and

delithiation. The work presents cyclic galvanostatic charge/discharge results of cells with stable capacity at around 200 $\text{mA}\cdot\text{g}^{-1}$.

CONCLUSIONS

The results confirm the synthesis of Li-rich NMC materials with sphere microstructure. The application of a broad range of characterization methods, including operando, revealed the structural changes in the electrode depending on the stage of the reaction. The presented results contribute to the development of lithium-ion technology for energy storage.

ACKNOWLEDGMENT

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NOTES

Electrical and structural studies on the $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3\text{-LiAlSiO}_4$ ceramic Li^+ conductor

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Keywords: Li-ion conductor, ceramic, solid electrolyte

INTRODUCTION

Lithium aluminum titanium phosphate (LATP) with NASICON-like structure is considered to be one of the possible promising candidates as a solid electrolyte in all-solid-state batteries due to good thermal and mechanical stability, good chemical stability against moisture in the air and high bulk ionic conductivity of the order of 10^{-3} $\text{S}\cdot\text{cm}^{-1}$ at room temperature. However, the total conductivity of LATP is lower by one order of magnitude because of highly resistive grain boundary phases. Therefore, it is necessary to increase the conductivity of grain boundary region e.g. by introducing additives with good ionic conductivity [1]. For this purpose, the LiAlSiO_4 (LASO) additive was introduced into the LATP matrix. Similar approach has already been applied in our previous works with $(0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3)$ [1] glass and LiF [2] additives as sintering agents, where the enhancement of the total ionic conductivity was also observed.

EXPERIMENTAL

Polycrystalline $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ and LiAlSiO_4 compounds were obtained via a conventional solid-state reaction method. The two components were mixed in several molar ratios varying from 2 to 10wt%, ball-milled, pressed into pellets and sintered. The electrical and structural properties of the LATP-xLASO ceramics were studied applying several different and complementary methods, namely: high temperature X-ray diffractometry (HTXRD), ^6Li , ^{27}Al , ^{29}Si and ^{31}P nuclear magnetic resonance (MAS NMR), scanning electron microscopy (SEM), thermogravimetry (TGA), impedance spectroscopy (IS) and density (Archimedes) methods. The obtained materials were studied not only in a function of LASO content but also in a function of sintering conditions (temperature range 800-1000°C and time range 2-12h).

RESULTS AND DISCUSSION

The experimental data indicate that the addition of LiAlSiO_4 to LATP results in the enhancement of its total ionic conductivity with reference to pristine LATP. The highest value of $\sigma_{\text{tot}} = 2.5 \times 10^{-4}$ $\text{S}\cdot\text{cm}^{-1}$ has been obtained for LATP-0.1LASO material sintered at 1000 °C for 2 h. This study shows that there may be two factors leading to the enhancement of total ionic conductivity in the LATP-xLASO system. The first one refers to the microstructure of the material, which is sensitive to sintering parameters (temperature and/or

sintering time affect the average grain size and the thickness of grain boundary region). The second one, even more significant, is related to the occurrence of another lithium-ion conductor (LiTiPO_5) formed during the sintering process. Moreover, from MAS NMR studies (Figure 1) it can be concluded that a part of Al^{3+} may diffuse into LATP grains and substitute for Ti^{4+} ions, which should affect not only the grain conductivity, but also the grain boundary one.

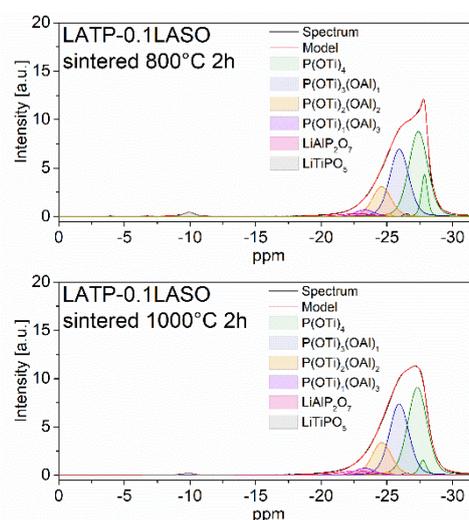


Figure 1 ^{31}P MAS NMR spectra of LATP-0.1LASO sintered at 800 or 1000°C for 2h. The experimental and simulated spectra are displayed as black and red lines, respectively. The simulated spectra is the sum of distinct lineshapes displayed as colored lines.

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NOTES

Impact of Li-excess source on the electrical properties of LiTa₂PO₈ material – a novel solid Lithium-ion conductor

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Keywords: Li-ion conductor, ceramic, solid electrolyte

INTRODUCTION

Among inorganic solid lithium-ion conductors considered for application in all-solid-state batteries, various metal oxide-based compounds have already been studied, e.g., perovskite-type Li_{3x}La_{2/3-x}TiO₃ (LLTO), garnet-type Li₇La₃Zr₂O₁₂ (LLZO), NASICON-structure phosphates Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LTP) and LISICON-type. However, there is still a strong demand for better performing solid electrolytes with high ionic conductivity as well as good thermal, mechanical and chemical stability. Recently, a new compound emerged, lithium tantalum phosphate LiTa₂PO₈ (LTPO), which meets the requirements mentioned above [1]. LTPO has an excellent bulk ionic conductivity of the order of 10⁻³ S·cm⁻¹ at room temperature. However, its total ionic conductivity is one order of magnitude lower because of highly resistive grain boundaries and relatively high porosity [1]. The overall electric properties of this ceramic material strongly depend on processing conditions, e.g., time and temperature of sintering [2]. LTPO requires high sintering temperatures of above 1000°C at which the evaporation of Li₂O becomes highly probable and can be detrimental for its ionic conductivity. In this study, one of possible ways to improve the electrical properties of LTPO is explored. It consists of a modification of the sintering protocol in order to prevent lithium loss, reduce porosity and suppress the formation of unwanted phases.

EXPERIMENTAL

A series of polycrystalline LTPO compounds were prepared using a conventional solid-state reaction method. To compensate for Li⁺ loss at high temperatures, the synthesis procedure was modified by introduction of an excess of lithium (varying from 5 to 15 wt.% with reference to the stoichiometric amount) and by optimization of the sintering conditions (time and temperature).

The electrical and structural properties of the LiTa₂PO₈ ceramics, with excess Li source were studied applying several different and complementary methods, namely: high-temperature X-ray diffractometry (HTXRD), ⁶Li and ³¹P nuclear magnetic resonance (MAS NMR), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetry (TGA), impedance spectroscopy (IS), density (Archimedes) and Hebb-Wanger polarization methods.

RESULTS AND DISCUSSION

The highest value of $\sigma_{tot} = 4.5 \times 10^{-4}$ S·cm⁻¹ has been obtained for LiTa₂PO₈ material sintered at 1025 °C for 8 h. The discrepancy in the values of the total ionic conductivity (Figure 1) may result from the formation of secondary phases at grain boundaries, like LiTa₃O₈. Apart from the formation of the secondary phases, the microstructure of the ceramic material, in particular its porosity seems to play an important role for total ionic conductivity. In this study, the correlations between the sintering conditions, structure, microstructure and electrical properties of the Li-enriched LTPO ceramics will be presented and discussed in detail.

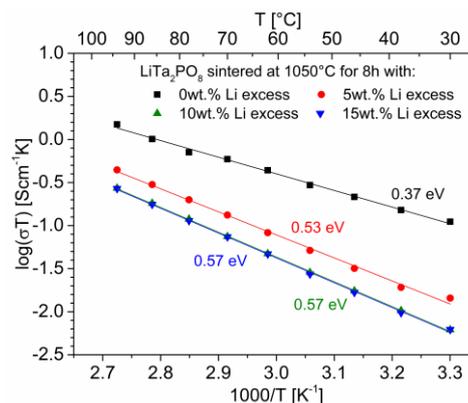


Figure 1. Arrhenius plots of the total ionic conductivity of LiTa₂PO₈ materials sintered at 1050°C with different amount of lithium ions containing substrate.

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NOTES

Na(Mn,Fe,Co,Ni,Cu,M)O₂ (M-Ti, V, Al) six-component oxides – cathode materials for Na-ion batteries

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Keywords: Na-ion battery, transition metal oxides, cathode material, intercalation process, transport properties

We present the results of the structural, transport and electrochemical properties of the Na_xTi_{1/6}Mn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}O₂ high entropy oxide cathode material for Na-ion batteries. The pristine O3-NaTi_{1/6}Mn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}O₂ oxide is found to be semiconductor with low electrical conductivity equal to 1.0·10⁻⁹ S cm⁻¹. The low values of electrical conductivity at RT are accompanied by high activation energy of the conductivity, which is in the range 0.57 - 0.74 eV (depending of the applied method). The XRD in-situ experiments evidence that during sodium de-intercalation O3 phase transforms to P3 phase. Electrochemical tests show that the P3 phase demonstrates much better structural stability and transport properties when compared to O3 phase. The experimental results were supported by the electronic structure calculations (KKR-CPA method). It is found that specific atomic ordering of transition metal atoms in O3 phase may lead to semiconducting state, while P3 phase may be characterised by fully random distribution of atoms with metallic-like state. XAS total-electron yield (TEY) measurements show that Co is the most effective element in charge compensation mechanism of Na_xMn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}Ti_{1/6}O₂ oxide. Electrochemically active are also manganese and nickel. Ti, Fe and Cu are electrochemically inactive. The other results regarding six-component oxides with improved electrochemical properties are also presented.

Acknowledgement:

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NOTES

Surface modifications of the electrolyte as a path to obtain a high-performance Na-ion all-solid-state battery

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Keywords: Na-all-solid-state batteries, solid electrolyte, surface modification

INTRODUCTION

The growing share of renewable energy sources and changes in transport towards the use of electric vehicles require effective balancing of energy demand and supply. This involves the need to store energy. So far, the most effective method of electrochemical energy storage is in Li-ion batteries. However, it seems that this technology is close to reaching its peak. Moreover, some of the materials used in the construction of commercially used Li-ion cells are environmentally unfriendly and difficult to recycle. One of the intensively researched solutions are all-solid-state sodium metal batteries (Na-ASSB), which can potentially be characterized by high energy density and safety. In order for such cells to enter into common use, it is necessary to obtain a dense, well-conductive electrolyte of sodium ions and to solve the problem of high charge transfer resistance through the interface between the electrolyte and the electrodes.

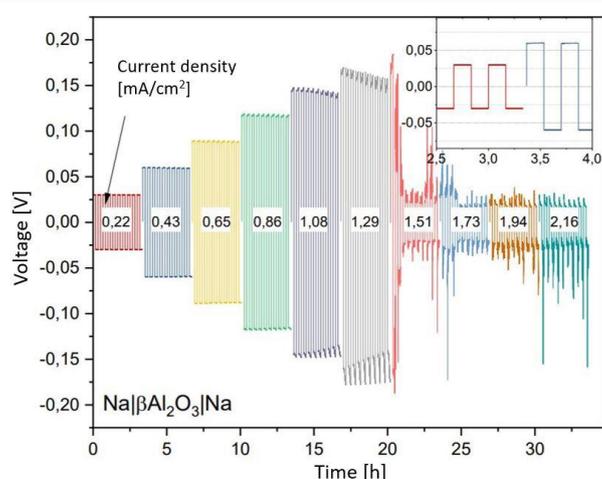
EXPERIMENTAL

As part of this work, two types of electrolytes for Na-ASSB cells were obtained: β - Al_2O_3 and NASICON $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ using solid state reaction. The phase composition of the samples obtained was examined by means of X-ray diffraction and their morphology by scanning electron microscopy. In the next section, the influence of the modification of the electrolyte surface on the contact between the electrolyte and the metallic sodium electrode was investigated. Roughness was controlled by grinding and polishing the electrolyte on various polishing disks. Using the obtained electrolytes, symmetrical cells with sodium metallic electrodes were constructed. The potential necessary to cause a current flow of a certain density was measured. The influence of thermal and chemical modification of the electrolyte surface on the charge transfer resistance and the critical current density at which the cells were short-circuited was investigated. The cells were tested at various temperatures from 0°C to 80°C , in order to investigate the influence of temperature on the electrode/electrolyte charge transfer and the formation of dendrites in the cell.

RESULTS AND DISCUSSION

The research showed a relationship between the roughness of the electrolyte and the operating parameters of a symmetrical cell. This allowed to determine the optimal method of preparing the ceramic electrolyte. Using the XPS method, it was shown that thermal and

chemical modification have an impact on the phase composition of the ceramic surfaces of the sinters. Heating and etching in acid allowed to remove a significant part of surface contamination, thanks to which the load transfer resistance decreased. The figure below shows an example of the measurement results of a $\text{Na}|\beta\text{-Al}_2\text{O}_3|\text{Na}$ symmetric cell.



CONCLUSIONS

Modification of the electrolyte surface can be an effective way to solve the problem of high charge transfer resistance through the electrolyte / electrode interface, and consequently to improve the performance parameters of Na-ASSB cells.

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NOTES

The effect of temperature on sodium dendrite growth in solid state sodium electrolytes

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Keywords: sodium solid state battery, solid electrolyte, dendrites

INTRODUCTION

Room temperature solid-state sodium metal batteries are among prospective electrochemical energy storage technologies reaching beyond the common Li-ion configuration. Due to high energy density related to oxidation of sodium metal and low price, they are well suited for large scale energy storage, e.g. residential or grid scale.

Among various factors critical for operation of such cells are interfacial phenomena occurring at the solid electrolyte – sodium metal interface including contact area, wettability, charge transfer kinetics and sodium plating stripping behavior, including dendritic growth of sodium crystals upon charging.

Recently a bunch of articles have been published regarding understanding mechanism of operation and performance of solid-state sodium metal batteries, however, detailed discussion of the effect of temperature on electrode reaction kinetics and susceptibility to dendrite growth is still missing.

This poster presentation provides insight into electrode polarization, charge transfer resistance, cyclic stability and critical current density for symmetrical sodium metal cells with ceramic solid electrolytes: β -Al₂O₃ and Na₃Zr₂Si₂PO₁₂ NASICON measured as a function of temperature in the 0 – 80°C temperature range using galvanostatic and impedance spectroscopy techniques.

EXPERIMENTAL

β -Al₂O₃ and Na₃Zr₂Si₂PO₁₂ NASICON ceramic electrolyte discs were synthesized using solid-state reaction. Crystal structure and ionic conductivity of the electrolytes were investigated to confirm proper fabrication of the electrolytes. Prior to cell assembly the electrolytes were grinded and polished to a thickness of ca. 0.7 mm and heat treated at 1100°C in argon atmosphere in order to remove surface contaminations. Electrochemical phenomena were investigated in a symmetrical cell configuration Na|solid electrolyte|Na. The cells were assembled in Swagelok-type casings and examined using Biologic VMP3 or Biologic SP-150 in a Binder MK-53 temperature chamber between 0 – 80°C.

RESULTS AND DISCUSSION

Galvanostatic cycling of Na|solid electrolyte|Na symmetrical cells in the current density range between 0.01 and 1 mA/cm² at temperatures between 0 – 80°C allowed to determine electrode polarization and current density that can be reversibly cycled through the electrolyte without short circuit caused by dendrite growth. Impedance characteristics of the cells were modelled using equivalent circuit to determine interfacial charge transfer resistance and further confirm stability of the interface, and current initiating dendrite formation.

CONCLUSIONS

Temperature is one of key parameters governing operation of sodium metal solid state batteries. On the one hand it provides faster electrode reaction kinetics and makes sodium metal to be more plastic and reduces tendency of void formation during sodium stripping, however, on the other hand, it also affects surface energy of the solid electrolyte and can influence dendrite growth at lower current densities finally leading to cell short circuit.

ACKNOWLEDGMENT

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NOTES

Polish Hydrogen and Fuel Cell Association

Polish Hydrogen and Fuel Cell Association was founded in 2004 as a non-profit organization to promote hydrogen as a sustainable energy carrier as well as modern technologies for energy conversion and storage. The Association is a rapidly growing organization, which gathered many scientists (to date 213 members, including 51 professors and 13 supporting members).

Members of the Association are employees of universities and research institutes, as well as directors of state-owned enterprises. Supporting members include universities and research institutes. Association collaborates closely with Polish Technological Platform of Hydrogen and Fuel Cells organizing meetings, schools and preparing national “hydrogen” program. The Association is a member of EHA (European Hydrogen Association) and PATH (Partnership for Advancing the Transition to Hydrogen). Comparing the size and structure of the membership, the Polish Association is one of the largest in Europe, and has significant intellectual potential.

Mission:

- development of collaboration among universities, research institutes and industry,
- support of high-risk projects focused on basic studies of new materials for energy conversion and storage,
- stimulation of educational activities promoting modern technologies for energy conversion and storage.

Activities:

- Annual Bulletin,
- Every 2 years Association is organizing Forum dedicated to fuel cells, hydrogen production and storage Li-ion and Na-ion batteries, supercapacitors, thermoelectrics, solar conversion,
- Every 2 years, interchangeably with Forum, Association is organizing Autumn Schools on energy conversion and storage.

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