

12-16 November  
Russia, Moscow  
Skoltech

# Solid state chemistry of battery materials

6th international  
school-conference  
of young scientists.

Three tracks:  
«Computational Methods»,  
«X-ray Diffraction»,  
«Electron Microscopy»

Organizers



**Skoltech** <sup>2</sup>

Sponsors and partners

**RSF** | Russian  
Science  
Foundation  
Project number 17-73-30006

# Committees

## Conference committee



**Keith  
Stevenson**

Conference  
chair

Provost of Skoltech,  
Professor of the  
Center for Energy  
Science and  
Technology



**Evgeny  
Antipov**

Conference  
co-chair

Professor,  
Department of  
Chemistry (MSU) and  
Center for Energy  
Science and  
Technology



**Artem  
Abakumov**

Deputy conference  
chair

Professor, Director  
of the Center for  
Energy Science and  
Technology



**Svetlana  
Lipovskikh**

Conference secretary

Research Scientist,  
Center for Energy  
Science and  
Technology



**Stanislav  
Fedotov**

Organizing  
committee member

Assistant Professor,  
Center for Energy  
Science and  
Technolog



**Alice  
Isaeva**

Organizing  
committee member

Specialist, Center for  
Energy Science and  
Technology

Invited

# Electronic structure of battery materials

**Artem M. Abakumov**<sup>1</sup>

a.abakumov@skoltech.ru

Crystal structure, chemical bonding and electronic structure play pivotal role in the functional properties of the electrode materials for metal-ion batteries. A covalent mixing of the M nd orbitals of the transition metal and oxygen O 2p orbitals within the MO<sub>6</sub> octahedra gives rise to main features of the band structure of the cathode (positive electrode) materials. The molecular orbital diagram of the octahedral MO<sub>6</sub> cluster provides sufficient qualitative insight into understanding the impacts of atomic orbitals on the most important bands near the Fermi level, which largely determine the redox properties of the M<sup>n</sup>/M<sup>(n+1)</sup> pair. Evolution of the band structure of the cathode material upon alkali cation extraction explains observed changes in electric conductivity, M nd-O 2p hybridization and tendency towards oxygen evolution at the end of charge. Electronic configuration of the transition metal cation and covalency/ionicity of the M-O bonding are the primary factors affecting the redox potential of the M<sup>n</sup>/M<sup>(n+1)</sup> pair, which can be tuned through variation of the first and second coordination spheres, by changing the number of ligands in the MOn polyhedra or the nature of the XOn group in the polyanion cathode materials. At certain specific conditions, oxygen might become an active participant of the redox process, which might occur reversibly or irreversibly causing extra capacity or unwanted oxygen evolution. The abovementioned issues will be illustrated using the Li-ion battery oxide and polyanion cathode materials. RSF project 20-43-01012 is acknowledged.

---

<sup>1</sup> Skolkovo Institute of Science and Technology, Nobel str. 3, 121205 Moscow, Russia

# Transmission Electron Microscopy for Material Science

Artem M. Abakumov<sup>1</sup> Maria Kirsanova<sup>1</sup>  
a.abakumov@skoltech.ru, m.kirsanova@skoltech.ru

The design and development of effective materials for metal-ion batteries or any other application is inconceivable without dedicated knowledge on the chemical composition, bulk and local crystal structure, electronic structure and their evolution upon electrochemical testing. Resources of modern transmission electron microscopy (TEM) appear to be one of the most suitable and informative tool to study the abovementioned essential characteristics of the materials. Due to very small electron probe, forming in a scanning transmission electron microscopy (STEM) mode the information on the crystal structure and chemical composition can be retrieved at the most local scale from individual atomic column. Herein, the basic physical principles of TEM and most important constructional elements of transmission electron microscope will be discussed. The most advanced and powerful TEM techniques, including electron diffraction tomography, aberration-corrected high-resolution STEM imaging, phase differential contrast and electron energy loss spectroscopy, will be illustrated with the examples of different materials, including electrode materials for metal-ion batteries.

---

<sup>1</sup> Skolkovo Institute  
of Science and  
Technology, Nobel str.  
3, 121205 Moscow,  
Russia

# Computational modeling of inorganic solids

Aksyonov D.A.<sup>1</sup> d.aksenov@skoltech.ru

One emerging and promising approach for the discovery and improvement of materials is computer modeling. Traditionally, providing a deep understanding of materials' properties, computer modeling helped to rationalize the process of materials development. Nowadays, with the emergence of high throughput screening techniques, computer modeling allows the discovery of completely new materials with the desired properties [1].

In this talk, a history of computational modeling and its role in materials science is shortly presented. The basic principles of modeling and main methods used for modeling inorganic solids are reviewed. An emphasis is made on density functional theory (DFT) - a method that became a must-have tool in materials science studies. We show how DFT is used for predicting numerous properties of functional materials including catalysts for fuel cells, electrode materials for Li-ion batteries, and radiation-resistant materials for thermonuclear reactors. Practical recipes for calculating atomic and electronic structure, thermodynamics, mechanical properties, ionic and electronic conductivity are given. The talk is concluded by discussing the future of computational modeling based on machine-learning and high-throughput approaches [2].

---

#### References:

1. Jain A., Shin Y.; Persson K.A.; // Nat. Rev. Mater. 2016, 1, 15004.
2. Aksyonov D.A.; Fedotov S.S.; Stevenson K.J.; Zhugayevych // A. Comp. Mat. Sci. 2018, 154, 449

<sup>1</sup> Skolkovo Institute of Science and Technology

# Crystal chemistry of electroactive battery materials

**E.V. Antipov**<sup>1</sup>

evgeny.antipov@gmail.com

Li-ion batteries have originally been developed for portable electronic devices, but nowadays new application niches are envisaged in electric vehicles and stationary energy storages. However, to satisfy the needs of these rapidly growing applications, Li-ion batteries require further significant improvement of their properties: capacity and power, cyclability, safety and cost. Cathode is the key part of the Li-ion batteries largely determining their performance. Severe requirements are imposed on a cathode material, which should provide fast reversible intercalation of Li-ions at redox potential close to the upper boundary of electrolyte stability window, possess relatively low molecular weight and exhibit small volume variation upon changing Li-concentration.

First generation of the cathode materials for the Li-ion batteries based on the spinel ( $\text{LiM}_2\text{O}_4$ , M – transition metal) or rock-salt derivatives ( $\text{LiMO}_2$ ) has already been widely commercialized. However, the potential to further improve the performance of these materials is almost exhausted. The compounds, containing lithium and transition metal cations together with different polyanions ( $\text{X}_m\text{O}_n$ )<sup>p-</sup> (X=B, P, S, Si), are now considered as promising cathode materials for the Li-ion batteries. Covalently bonded structural frameworks in these compounds offer long-term structural stability, which is essential for good cyclability and safety. Further advantages are expected from combining different anions (such as  $(\text{XO}_4)^{p-}$  and  $\text{F}^-$ ) in the anion sublattice, with the hope to enhance the specific energy and power of these materials. Various fluoride-phosphates and fluoride-sulphates have been recently discovered, and some of them exhibit attractive electrochemical performance.

An overview of the cathode materials for the Li-ion batteries will be presented with special emphasis on crystallography as a guide towards improved properties important for practical applications.

---

<sup>1</sup>Lomonosov Moscow State University, Moscow, 119991, Russia  
Skolkovo Institute of Science and Technology (Skoltech), Moscow 121205, Russia

# Bond valence methods and their applications

Stanislav S. Fedotov<sup>1</sup> s.fedotov@skoltech.ru

Crystal chemistry undoubtedly plays a crucial role in materials design. Similarly to the human skeleton, which performs major functions of the body being responsible for the physical capabilities, support, longevity and storage of minerals, the crystal structure defines the “health” and key performances of materials. Most of the functional properties such as chemical, thermal and electrochemical stability, ionic conductivity, ion diffusion barriers and volume variation upon de/intercalation, are directly or implicitly dependent on the crystal structure peculiarities. For instance, rigid three-dimensional crystal frameworks typically provide better chemical and electrochemical stability than two-dimensional layered arrangements as well as ionic conductivity normally requires a continuous system of channels available for the migration of a mobile ion.

In this talk, several widely used crystal chemistry tools including geometry and bond valence-based methods, which can be of great importance for search, design and analysis of materials for metal-ion batteries will be highlighted. To get insight on alkali ion diffusion and ionic conductivity in solid electrolytes and electrode materials we will consider convenient open-space metrics and bond-valence (energy) approaches implemented in various crystallography software. Furthermore, we will discuss how different ionic transport parameters including diffusion energy barriers can be obtained within these approaches and compare the results with those of ab initio computational methods such as density functional theory (DFT) and experimental data.

Finally, some hints and useful resources to deal with the crystal structure of energy storage materials from the personal experience will be given with a special focus on its relationships with the electrochemical properties.

## Acknowledgement

This talk is prepared with the support of Russian Science Foundation (grant #20-73-10248).

---

<sup>1</sup> Skolkovo Institute  
of Science and  
Technology



# Operando powder X-ray diffraction

Stanislav S. Fedotov<sup>1</sup>, Ivan A. Trussov<sup>1</sup> s.fedotov@skoltech.ru

X-ray powder diffraction (XPD) is no doubt a powerful tool for characterization of functional materials. To get an insight into material's crystal structure it is generally and mostly implemented in the so-called ex situ regime when no processes occur within the material. However, most of the functional materials including electrode materials for metal-ion batteries undergo structural transformations or evolution during the operation (operando) which in turn give rise to the functional properties and determine the guiding mechanisms they obey.

For instance, during the charge/discharge reaction in an electrode material, multiple physical and chemical processes take place at various scales: cell parameters change, phase transitions, amorphization, defects formation and charge orderings, surface transformations and segregation, which drastically influence electrochemical behavior and require an in-depth understanding to further improve the functionality of batteries.

In this talk, necessary basics, state-of-the-art and current implementation of operando XPD measurements with regards to various functional materials will be given with a particular focus on key processes taking place in battery electrodes in the course of electrochemical cycling exemplified by many case-studies on different electrode materials (Figure 1) [1]. Importantly, recent advancements in operando X-ray and neutron powder diffraction (XPD and NPD) to directly observe and monitor the abovementioned processes will be highlighted and discussed.

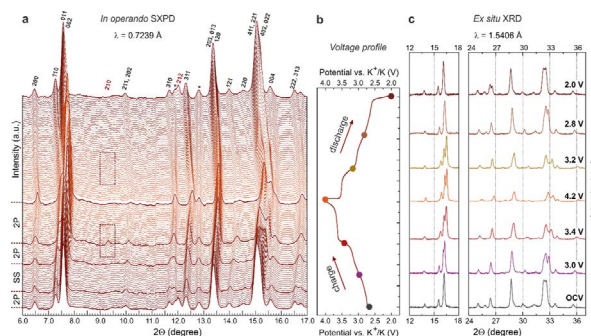


Fig. 1 – a Diffraction patterns of the in operando SXPD of  $\text{KTiPO}_4\text{F}$  in K cell. b Charge-discharge profile. c ex situ XRD patterns of electrodes recovered at various potentials.

## Acknowledgement

This talk is prepared in the framework of joint DFG-RFBR project (# 21-53-12039)

## References:

1. Fedotov, S.S., Luchinin, N.D., Aksyonov, D.A. et al. // Nat. Commun. 2020, 11, 1-11.

# Modelling materials at realistic temperatures and pressures

Sergey V. Levchenko<sup>1</sup> s.levchenko@skoltech.ru

Computational approaches allow us to quantitatively evaluate and predict electronic and atomic structure of materials. However, a typical calculation corresponds to zero temperature (frozen atoms). In practical applications, functional materials operate at finite temperatures and are in contact with a reservoir of atoms or molecules (gas, liquid, or solid). In order to understand the properties of materials at realistic conditions, statistical effects associated with configurational sampling and particle exchange at finite temperatures must consequently be taken into account. In this lecture, we discuss the main concepts behind equilibrium statistical mechanics. We demonstrate how these concepts can be used to predict the behavior of materials at realistic temperatures and pressures within the framework of atomistic thermodynamics. In particular, we introduce and discuss approaches to calculating phase diagrams of bulk materials and surfaces, as well as point defect concentrations. [1].

---

<sup>1</sup> Skolkovo Institute of Science and Technology

#### References:

1. Fedotov, S.S., Luchinin, N.D., Aksyonov, D.A. et al. // Nat. Commun. 2020, 11, 1-11.

# Low temperature electrocatalysis for the generation of green hydrogen and ammonia

Stevenson, K. J.<sup>1</sup> k.stevenson@skoltech.ru

Hydrogen is an important part of the sustainability development goals (SDG) and for reduction in greenhouse gas emissions across major energy sectors (ammonia, steel, ethylene production).[1] In addition to being a feedstock chemical and process gas for many industrial processes, hydrogen is emerging as a fuel alternative for transportation applications including electric ships and aeroplanes. Renewable sources of hydrogen without production of CO<sub>2</sub> (carbon zero H<sub>2</sub> production) are therefore required to increase in capacity and to facilitate the energy transition to meeting emerging (environmental, societal and governance) development agendas.[2] The low-temperature electrolysis of water is currently the most mature method for carbon-free hydrogen generation and is reaching relevant scales to impact the energy landscape. However, costs still need to be reduced to be economical with traditional hydrogen sources. This talk will describe various chemical transformations to facilitate the production of green hydrogen and green ammonia using low temperature electrocatalysts. For instance, the electrooxidation of urea or ammonia continues to attract considerable interest as an alternative to the oxygen evolution reaction (OER) as the anodic reaction in the electrochemical generation of hydrogen due to the lower potential and temperatures required to drive the reaction(s).[3,4]

## References:

1. <https://sdgs.un.org/goals>
2. <https://home.kpmg/uk/en/home/services/environmental-social-governance.html>
3. Forslund, R. P.; Alexander, C. T.; Abakumov, A. M.; Johnston, K. P.; Stevenson, K. J. "Enhanced Electrocatalytic Activities of Nickel-based Ruddlesden-Popper Catalysts for the Oxidation of Urea and Small Alcohols By Active Site Variation," *ACS Catal.* 2019, 9(3), 2664–2673.
4. Forslund, R. P.; Hardin, W. G.; Rong, X; Abakumov, A. M.; Filimonov, D.; Alexander, C. T.; Mefford, J. T.; Iyer, H.; Kolpak, A. M.; Johnston, K. P.; Stevenson, K. J. "Exceptional Electrocatalytic Oxygen Evolution Via Tunable Charge Transfer Interactions in La<sub>0.5</sub>Sr<sub>1.5</sub>Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>4+δ</sub> Ruddlesden-Popper Oxides," *Nature Comm.* 2018, 9(1) 3150.

---

<sup>1</sup> Skolkovo Institute of Science and Technology

# Participants

# Isotopic exchange of oxygen in the gas phase with cobaltites-ferrites of alkaline earth metals replaced by highly charged cations

Akhmadeev A. R.<sup>1</sup>, Eremin V. A.<sup>2</sup>, Khodimchuk A. V.<sup>2</sup>, Voloshin B. V.<sup>2</sup>, Ananyev M. V.<sup>1</sup> [t0lpar@yandex.ru](mailto:t0lpar@yandex.ru)

The complex oxide  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF), having high values of oxygen permeability [1] and electron conductivity [2], is known as one of the most promising oxygen electrode materials for solid oxide electrochemical devices. There is information in the literature about the insufficient stability of BSCF in the operating conditions of solid oxide fuel cells. One of the ways to solve this problem is to dope BSCF with highly charged cations into the cobalt sublattice.

The aim of this work is to study the effect of doping with highly charged cations (Nb, Ta, W, Mo) on the exchange kinetics and oxygen diffusion of oxides based on  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ . The kinetics of the interaction of oxygen in the gas phase with oxides  $Ba_{0.5}Sr_{0.5}Co_{0.725}Fe_{0.125}Ta_{0.15}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.2}Mo_{0.05}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.775}Fe_{0.12}Nb_{0.05}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.78}Fe_{0.2}W_{0.02}O_{3-\delta}$  in the temperature range of 600-850 °C, at the oxygen pressure  $P_{O_2} = 0.057$  kPa. The values of the interphase exchange rates  $r_H$  and the diffusion coefficients  $D$  of oxygen are calculated. The paper discusses the reasons for the observed differences for samples of oxides with different surcharges.

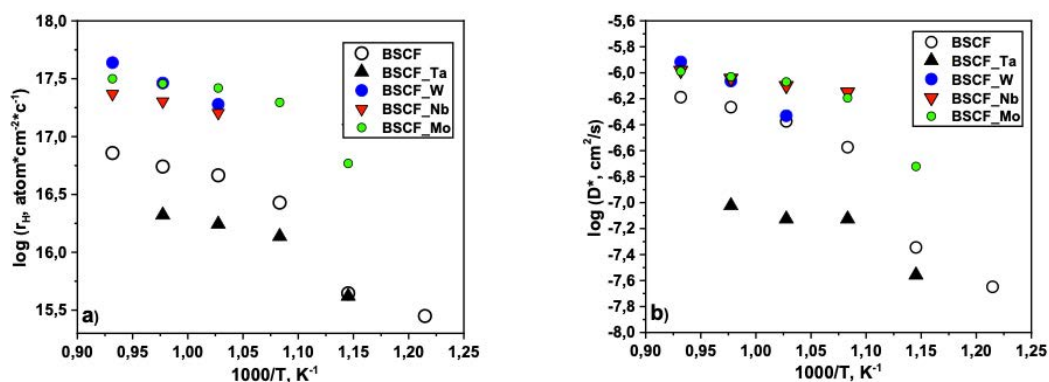


Fig. 1 – temperature dependences of a) the rate of interphase exchange  $r_H$ ; b) the diffusion coefficient  $D^*$  for oxides  $Ba_{0.5}Sr_{0.5}Co_{0.725}Fe_{0.125}Ta_{0.15}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.2}Mo_{0.05}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.775}Fe_{0.12}Nb_{0.05}O_{3-\delta}$ ,  $Ba_{0.5}Sr_{0.5}Co_{0.78}Fe_{0.2}W_{0.02}O_{3-\delta}$  in comparison with the unsubstituted  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ .

References:

1. Kruidhof, H. Influence of order-disorder transitions on oxygen permeability through selected nonstoichiometric perovskite-type oxides // Solid State Ionics. 1993, V. 63-65. p. 816-822.
2. Wei, B. Crystal structure, thermal expansion and electrical conductivity of perovskite oxides  $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$  ( $0.3 \leq x \leq 0.7$ ) // Journal of the European Society. 2006, V. 26. p. 2827-2832.

<sup>1</sup> Ural Federal University, Faculty of Chemistry, Yekaterinburg, Russia  
<sup>2</sup> Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russia  
<sup>3</sup> Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia

# Determination of the characteristics stability of porous silicon structures by the impedance method

Alexandrov Nikita<sup>1</sup>, Andrey Shportenkov<sup>2</sup>, Ekaterina Gosteva<sup>2</sup>, Vitaly Starkov<sup>3</sup>, Vladimir Volkov<sup>3</sup> adelsandrov@mail.ru

Recently, much attention has been paid to research aimed at creating electrodes based on porous silicon (PSi) for various electronic devices and current sources [1]. A significant variety of possible PSi structures [2], as well as the processes of formation of porous layers, significantly affects the electrophysical characteristics of electrodes. In this regard, the relevance of the development of methods that make it possible to assess the influence of the PSi structure feature on the electrical properties of porous layers increases. The paper presents the results of a study by impedance spectroscopy methods of a gradient-porous structure with a variable morphology of a porous silicon layer (GPSi-var structure) [3]. To increase the efficiency of using porous silicon electrodes in the structures of current sources, it is necessary to maximize their electrical conductivity. Optimization of the processes of formation of electrode structures requires determining the relationship of the impedance characteristics with the morphological features of certain porous layers. The impedance was measured using a synchronous amplifier "Zurich MFLI 0-0. 5/5 MHz", the data obtained were presented in the form of a Nyquist diagram. As follows from the results, there is a significant dependence of the impedance value on the measurement frequency. The resistance of the contacts is of the order of 700 ohms, the resistance of the sample is of the order of 6.8 MΩ. capacitance is about 61 nF.

As the results obtained have shown, the used technique allows one to adequately assess the characteristics of the formed porous structures and can be successfully applied to determine the dependences of the resistivity on the modes of formation and modification of porous silicon layers. The Nyquist plot for GPSi-var structure was measured for the first time. At the same time, the non-reproducibility of the characteristics after exposure to air at room temperature was revealed.

The work was supported by the Ministry of Education and Science of the Russian Federation, State task № 075-00920-20-00

## References:

1. Starkov, V.; Sedlovets, D.; Knyazev, M.; Red'kin, A. // Composite electrodes for current sources based on graphene-like films in porous silicon, *Protect. Met. Phys. Chem. Surface* 53 (2017), 85-87, DOI: 10.1134/S2070205116060198.
2. Starkov, V.V. // Preparation, properties and application of porous silicon, *All materials, Encyclopedic reference book*, 2009, pp. 13-21.
3. Starkov, V.V.; Gosteva E.A.; Sedlovets D.M.; Kah. M.O. // Silicon Structures with Variable Morphology of Pores Methods of Obtaining Physical and Optical Properties. *Journal of The Electrochemical Society*, 165 (11) E534-E539 (2018).

---

<sup>1,2</sup> MISIS National University of Science and Technology Moscow, Russia

<sup>3</sup> Russian Academy of Sciences Institute of Microelectronics Technology and High Purity Materials Chernogolovka, Russia

# Development of promising multivalent cathode materials

**Evgeniy I. Frolov<sup>1</sup>, Alexander V. Antonyk<sup>1</sup>, Artem A. Kabanov<sup>1</sup>**  
al.antonyk.2001@mail.ru

The current trends in battery materials science are related to the search for prospective resource-efficient, high-energy-density, and safe post- or beyond-lithium battery chemistries.

Zn-ion batteries attract attention due to the fact that Zn ions has a 2+ charge and, accordingly, a larger theoretical capacity, safety and lower cost than lithium ion batteries (LIBs). We performed a step-by-step search for materials for zinc-ion batteries. We used ToposPro package for Geometric-Topological Screening of the ICSD database and selected the compounds whose structure is suitable for the migration of zinc ions. Next, the Bond Valence Site Energy theory (BVSE, softBV program) and Density Functional Theory (DFT, VASP program) were applied to calculate the migration energy of zinc. As a result, the most interesting cathode materials with high energy storage density and low zinc migration energy were  $\text{ZnCr}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnV}_2\text{O}_4$ ,  $\text{ZnRh}_2\text{O}_4$ ,  $\text{ZnFeCrO}_4$  [1].

The following methods were used for the synthesis of  $\text{ZnM}_2\text{O}_4$  spinels ( $M = \text{Fe}, \text{Cr}, \text{V}$ ): hydrothermal, Pechini, self-propagating high-temperature synthesis in solutions (SHS) [2] and auto-combustion [3]. At the moment, two compounds have been successfully synthesized:  $\text{ZnCr}_2\text{O}_4$  (SHS) and  $\text{ZnFe}_2\text{O}_4$  (auto-combustion).

According to the X-ray diffraction data the best result for  $\text{ZnCr}_2\text{O}_4$  (Fig. 1) was obtained under the following synthesis conditions: initial reagents - zinc and chromium (III) nitrate, synthesis temperature 450 0C; fuel-urea; the ratio of fuel to nitrates is 1.5; additional annealing of the sample after synthesis was carried out for six hours at a temperature of 700 0C. When synthesizing  $\text{ZnFe}_2\text{O}_4$ , the procedure specified in was followed, but the stage of additional annealing of the sample after synthesis had to be selected again due to the presence of noise on the X-ray image, as a result, a clean structure was obtained (Fig. 2) during annealing for one hour at a temperature of 1050 0C.

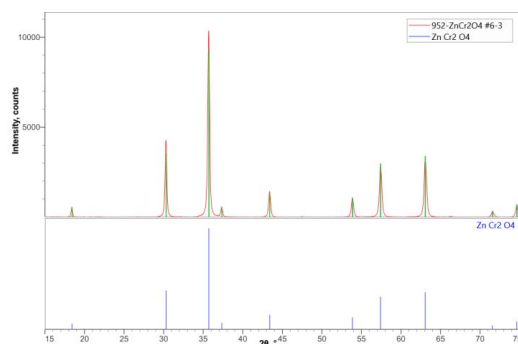


Fig. 1 – X-ray diffraction of the  $\text{ZnCr}_2\text{O}_4$

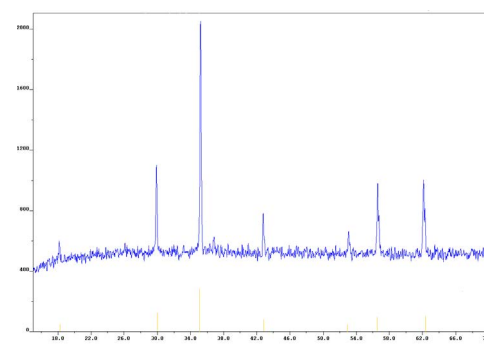


Fig. 2 X-ray diffraction of the  $\text{ZnFe}_2\text{O}_4$

## References:

1. Morkhova, Ye.A.; Rothenberger, M.; Leisegang, T.; Adams, S.; Blatov, V.A.; Kabanov, A.A. // *J. Phys. Chem. C* 2021, 32, 17590–17599
2. Novikov, V.; Firsova, I. // *Modern materials, equipment and technologies* 2017, 14, 93–99
3. Sutka, M.; Mezinskis, G.; Zamovskis, M.; Jakovlevs, D.; Pavlovskaya I. // *Ceramics International* 2013, 39, 8499–8502

<sup>1</sup> Samara State Technical University, Molodogvardeyskaya 244, 443100, Samara, Russia

# Influence of the type of organic sugar-based precursors on the properties of non-graphitizable carbon as an anode material for sodium-ion batteries

Apostolova M.O.<sup>1</sup>, Bobyleva Z.B.<sup>1</sup>, Drozhdin O.A.<sup>2,3</sup>  
hellocolors2@gmail.com

The term "hard carbon" is used to describe carbonaceous materials that do not turn into graphite at temperatures above 3000°C. Hard carbon is a prime candidate for use as an anode in the actively developed sodium-ion battery technology. This material is distinguished by its high capacity, ease of synthesis, and the presence of a large number of precursors. As follows from the literature, sodium ions are able to accumulate on the surface of non-graphitized carbon, as well as to penetrate both the interplanar spacing widened in comparison with graphite and into the closed micropores of the material [1].

As a rule, hard carbon is obtained in the course of multi-stage synthesis, one of the stages of which is caramelization or carbonization of an organic precursor. Important reaction in the caramelization process is dehydration, which leads to the formation of products such as caramelan, caramelen, caramelin [2]. One of the questions that arises in the synthesis of non-graphitizable carbon from various precursors is the effect of the type of precursor and the temperature regime of the first and second stages of synthesis on the electrochemical properties of hard carbon.

In the course of this work, the influence of the precursor and the temperature regime of caramelization on the electrochemical properties of hard carbon as an anode material for sodium-ion batteries was investigated. Several types of monosaccharides and disaccharides were selected as precursors: sucrose, glucose, fructose, lactose. The composition and properties of caramelization intermediates were investigated using scanning electron microscopy, IR spectroscopy, Raman spectroscopy, and thermogravimetric analysis. The electrochemical properties of hard carbons were determined using galvanostatic charge-discharge cycling in a half-cell with metallic sodium. It is shown that the temperature regime of caramelization, as well as the choice of the precursor, largely determine the electrochemical properties of hard carbon.

This work was supported by the Russian Science Foundation grant 17-73-30006.

<sup>1</sup>Department of Material Science, Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>2</sup> Department of Chemistry, Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>3</sup> Skoltech Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str.3, 143026, Moscow, Russia

## References:

1. Xinwei Dou, Ivana Hasa, Damien Saurel, Christoph Vaalma, Liming Wu, Daniel Buchholz, Dominic Bresser, Shinichi Komaba, Stefano Passerini. Hard carbons for sodium-ion batteries: Structure, analysis, sustainability, and electrochemistry, *Materials Today*, Elsevier, Vol. 23. - 2019 - p.87.
2. P. P. Tomasik, M. Pakasinski, S. Wiek. The thermal decomposition of carbohydrates. Part I. The decomposition of mono-, di-, and oligo-saccharides / *Adv. Carbohydr. Chem. Biochem.* - 1989 - Vol. 47 - P. 203.



# DFT study of ion migration barriers in LLZO

**A. Burov<sup>1</sup>, A. Boev<sup>1</sup>, D. Aksyonov<sup>2</sup>,**  
arseniy.burov@skoltech.ru

Li-ion batteries with solid electrolytes have several advantages over conventional ones with liquid electrolytes, such as wide electrochemical windows and good thermal. Simultaneously, batteries with solid-state electrolytes have a high energy density, good resistance against structural fragmentation during the operation cycle, and long cycle life [1]. However, the interfacial construction between garnets and electrodes is challenging, which does not allow us to use them widely at the moment [2]. Understanding the interfacial mechanism of Li-ion transport allows surpassing difficulties that degrade ionic mobility in solid interfaces.

Electrochemical experiments along with diffraction and SEM analysis can provide data on electronic conductivity and some justification why it varies in different phases of the same material [3]. However, they do not reveal the Li-ion transport mechanism. To show particular structural peculiarities and their connection with drastically different electronic conductivities in polymorphic modifications, we suggest utilizing DFT calculations and the nudged elastic band method to find migration barriers.

In this work, we study ion migration barriers in the interface between garnet electrolyte  $\text{Li}_3\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and metallic lithium using DFT calculations. We methodically constructed all available terminations for surfaces with the most important Miller indices of both polymorphic modifications of LLZO – cubic (sg. 142) and tetragonal (sg. 230). The results are consistent with available computational works on this topic. Further, we designed interfaces between the most stable terminations of LLZO and metallic lithium and geometrically optimized them. Finally, we calculated migration barriers for them. The cause of different ionic mobility between two phases and which structural properties reduce it in them are analyzed in the current report.

## References:

1. Liu, Q.; Geng, Z.; Han, C.; Fu, Y.; Li, S.; He, Y.B.; Kang, F.; Li, B. // J. Power Sources 2018, 389, 120–134.
2. Tateyama, Y.; Gao, B.; Jalem, R.; Haruyama, J. // Curr. Opin. Electrochem. 2017, 17, 149–157.
3. Thompson, T.; Wolfenstine, J.; Allen, J.L.; Johannes, M.; Huq, A.; David, I.N.; Sakamoto, J. // J. Mater. Chem. A 2014, 2(33), 13431–13436.

---

<sup>1</sup> Skolkovo Institute of Science and Technology

# The nature of kinetic polarization during sodium intercalation into the structure of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

**Buryak N.S.**<sup>1</sup>, **Nikitina V.A.**<sup>1,2</sup>, **Zakharkin M.V.**<sup>1</sup>, **Levin E.E.**<sup>2</sup>,  
**Antipov E.V.**<sup>1</sup> [nikita.buriak@chemistry.msu.ru](mailto:nikita.buriak@chemistry.msu.ru)

NASICON-structured  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$  is taken in consideration as a cathode for sodium-ion batteries. The material is capable of irreversible de/intercalation of two sodium ions per formula unit in the potential window of 2.5-3.8 V with respect to  $\text{Na}/\text{Na}^+$ . At the same time, the structure remains stable, and the material retains its capacity after multiple charge/discharge cycles, even at high current densities. However, with an increase of the anode potential limit, the de/intercalation mechanism changes simultaneously with a rapid loss of capacitance and an increase of potential hysteresis during continuous cycling [1].

The degradation of the electrochemical characteristics correlates with the low values of the calculated charge transfer rate constant  $K_s$  and the diffusion of sodium ions  $D$  (Fig. 1 a, b). This change can be caused by the appearance of a new amorphous phase at potentials above 3.8 V, which obstruct the intercalation of sodium ions into the structure of the material. This is confirmed by ex situ diffraction studies of electrodes based on  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$  after cycling in various charge-discharge modes (Fig. 1 c, d). A decrease in the capacity during cycling with the limit of the anode potential of 4.1 V is accompanied by an increase in the proportion of the sodium-insufficient phase in the volume of the material. The study was supported by RSF (Grant № 17-73-30006-P).

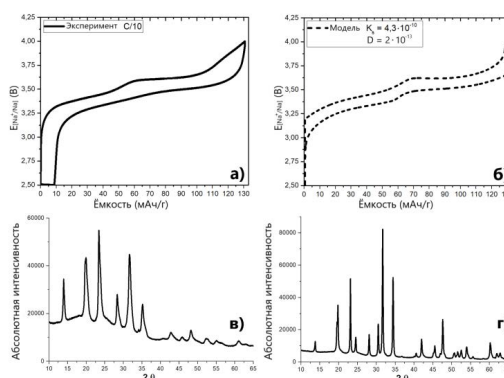


Fig. 1 – galvanostatic curves: a) experimental, b) model; diffractograms: c) the degraded electrode, d) the original electrode.

## References:

1. Zakharkin M. V. et. al. Enhancing  $\text{Na}^+$  Extraction Limit through High Voltage Activation of the NASICON-Type  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$  Cathode // ACS Appl. Energy Mater. 2018. Vol. 1. P. 5842.

<sup>1</sup> Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>2</sup> Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205 Moscow, Russia

# Solvothermal synthesis and electrochemical investigation of $\text{Li}_2\text{MPO}_4\text{F}$ ( $\text{M} = \text{Co}, \text{Fe}$ )

**Iliia R. Cherkashchenko<sup>1</sup>, Maria A. Solovieva<sup>1</sup>,**  
ilyache.msu@gmail.com

Polyanion-type cathode materials attract much attention due to their thermal and electrochemical stability, safety and high operating voltages caused by the inductive effect of  $(\text{XO}_n)^{m-}$  group. An interesting representative of this type of materials is lithium-cobalt (II) fluorophosphates  $\text{Li}_2\text{CoPO}_4\text{F}$  with attractive specific characteristics (redox potential  $>5$  V vs.  $\text{Li}^+/\text{Li}$ ; specific capacity 143 mAh/g per 1 Li atom and theoretical ability to extract more Li on higher potentials) [1,2]. However, electrochemical investigation of this material is limited by electrolytes being unstable at high working potentials. There are two possible ways to overcome this problem. One is partial substitution of cobalt for d-metal with lower working potential (e.g. Fe, Mn). Another way is search for high voltage electrolytes suitable for operation of  $\text{Li}_2(\text{Co},\text{M})\text{PO}_4\text{F}$  fluorophosphates.

Solvothermal route was applied as a method being able to control morphology of obtained samples (with optimal shape and size of particles). To date only one example of solvothermal preparation of  $\text{Li}_2\text{CoPO}_4\text{F}$  is known [3]. We developed a new one-step solvothermal synthesis of  $\text{Li}_2\text{CoPO}_4\text{F}$  using  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  instead of  $\text{Co}(\text{OH})_2$ ; and the application of transition metal sulphates as precursors enabled to carry out partial substitution Co for Fe. Using this technique with addition of a surfactant (carboxymethylcellulose, CMC) we synthesized  $\text{Li}_{2-y}\text{Na}_y\text{Co}_{1-x}\text{Fe}_x\text{PO}_4\text{F}$  (Pnma,  $a = 10.553(3)$  Å,  $b = 6.420(1)$  Å,  $c = 11.007(2)$  Å,  $V = 744.3(4)$  Å<sup>3</sup>) and  $\text{Li}_{2-y}\text{Na}_y\text{CoPO}_4\text{F}$  (Pnma,  $a = 10.478(2)$ ,  $b = 6.388(1)$ ,  $c = 10.909(2)$  Å,  $V = 730.2(3)$  Å<sup>3</sup>) samples. The obtained fluorophosphates were investigated by X-ray powder diffraction and electron microscopy, their elemental composition was confirmed by ICP-OES method.

Electrochemical testing of these samples was carried out in various electrolytes. Based on previous reports [3,4] we varied solvents (sulfolane, propylene carbonate, adiponitrile, diethyl carbonate/fluoroethylene carbonate), salts ( $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ) and their concentrations (1 M to 5 M) upon preparation electrolyte systems. The electrochemical properties of the obtained materials in different electrolytes will be discussed.

This work was supported by Russian Science Foundation under grant #19-73-10078.

## References:

- 1.Okada, S., Ueno, M., Uebou, Y., & Yamaki, J. I. // Journal of power sources, 2005, 146(1-2), 565-569.
- 2.Fedotov, S. S., Kabanov, A. A., Kabanova, N. A., Blatov, V. A., Zhugayevych, A., Abakumov, A. M., Khasanova N. R., Antipov, E. V. // The Journal of Physical Chemistry C, 2017, 121(6), 3194-3202.
- 3.Schoiber, J., Berger, R. J., Bernardi, J., Schubert, M., Yada, C., Miki, H., & Hüsing, N. // Crystal Growth & Design 2016, 9, 4999–5005.
- 4.Ko S., Yamada Y., Yamada A. // Batteries & Supercaps 2020, 9, 910–916. // J. Mater. Chem. A 2014, 2(33), 13431–13436.

<sup>1</sup> Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

# Bipyridine-based Ruthenium Complexes as Redox mediators for Lithium Oxygen Batteries

**Golovnenkova E.K.<sup>1</sup>, Isaev V.V.<sup>1,2</sup>, Zakharchenko T.K.<sup>1,2</sup>**

elizaveta.golovnenkova@chemistry.msu.ru

Lithium-oxygen batteries with aprotic electrolyte are believed to be superior energy storage devices compared to lithium-ion batteries, with their maximum theoretical specific capacity reaching 3500 Wh/kg [1]. They could be widely used in energy storage, if number of significant drawbacks such as overpotential during charge process and low cycle life, could be overcome. Main discharge product of lithium oxygen batteries is lithium peroxide, non-conductive compound that is hard to oxidize electrochemically. Addition of soluble catalyst so called redox mediator (RM) which is capable of converting the process of electrochemical oxidation of lithium peroxide during charge into a chemical one by transfer of an electron using reversible oxidation-reduction reaction can potentially solve those problems [2].

We suggest that bipyridine-based ruthenium (II) complexes presented below (Fig. 1) can act as RM for lithium-oxygen batteries due to specific interactions of ruthenium atomic orbitals with ligands' group orbitals and  $Ru^{3+}/Ru^{2+}$  oxidation-reduction (OR) potential value, which lies above  $Li_2O_2$  oxidation potential and yet below electrolyte decomposition potential.

Huge aromatic bipyridine and imidazole ligands should guarantee low solvation that leads to higher diffusion coefficients and prevent slowing down of the charge process.

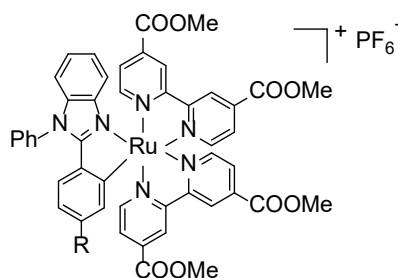


Fig. 1 – Studied Ru(II) complexes structure. R = various functional groups.

Studied complexes were synthesized using cyclometallation reaction [3], their structure was confirmed by  $^1H$  NMR. We showed that bipyridine-based ruthenium (II) complexes can potentially be used as redox mediators for lithium-oxygen batteries because their potentials are in desired range and diffusion coefficients are relatively high. Potential RMs were further analyzed using cyclic voltammetry methods to determine their OR reaction stability, OR potentials and diffusion coefficients in inert and oxygen atmospheres. The resulting compounds formed during cycling  $Li-O_2$  cells with and without RM addition were characterized by X-ray diffraction and Raman spectroscopy.

## References:

1. Ogasawara T.; Debart A.; Holzapfel M.; Novak P.; Bruce P. // *J. Am. Chem. Soc.* 2006, 128, 1390-1393.
2. Lim H.-D.; Lee B.; Zheng Y.; Hong J.; Kim J. // *Nature Energy* 2016, 1, 1-9.
3. Bomben, P. G.; Koivisto B. D.; Berlinguette C. P. // *Inorg. Chem.* 2010, 49, 4960–4971.

<sup>1</sup> Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>2</sup> N.N. Semenov Federal Research Center for Chemical Physics, Kosygina str. 4, 119991 Moscow, Russia

# Optimization of nonaqueous electrolyte composition for reversible sodium electrodeposition

**A. T. Guzhechenko<sup>1</sup>, E. O. Kondratyeva<sup>1</sup>, A.A. Rulev<sup>1</sup>**  
artemguzh@gmail.com

Alkali metal anodes are considered the Holy Grail of negative electrodes in secondary batteries due to their high theoretical specific capacity. However, they tend to exhibit uneven morphology while charging. Alkali metal deposits forming needle-like, dendritic or bushy structures. It leads to large volume change, dead metal formation or even short circuit. [1] Nowadays, sodium-containing secondary batteries are of great interest to the scientific society due to sodium's abundance in nature in comparison to that of lithium. The process of sodium electroplating is investigated in different electrolytes. [2] The most widely used salts are NaPF<sub>6</sub> and NaClO<sub>4</sub> being usually dissolved in such solvents as PC, DME, diglyme, DMC, TEG DME and their combinations. Whilst lithium metal is found to form whiskers during electroplating, sodium deposits with the formation of non-uniform metal structure that varies depending on the electrolyte parameters.

In order to study morphology of sodium deposits and growth mechanism of such metal structures, it is important to identify the factors that affect the deposition-dissolution process and to optimize the electrolyte, according to these factors.

Using galvanostatic cycling, coulombic efficiency of sodium plating-stripping in different electrolytes was measured turning out to be quite low. To thoroughly investigate sodium deposition-dissolution process in different electrolytes, voltammetric cycling (CV) was used. It was showed that deposition proceeds with subsequent dissolution with little to no difference, whether we use perchlorate or hexafluorophosphate salt. However, not all the solvents are appropriate for us: PC and diglyme are considered proper for our needs, DME and EC:DMC combination are worse in terms of passivation, but nevertheless can be used in our experiments, and electrolyte with DOL:DME as solvent combination is absolutely inappropriate for us. Using CV, it was revealed that humidity of electrolyte strongly affects sodium plating-stripping process. Quartz crystal microbalance method was used to characterize mass increment rate of nickel electrode during galvanostatic deposition and to determine the cause of low coulombic efficiency. It was noted, that sodium deposition is exposed to numerous side reactions and morphologic issues during electroplating, and both of them can be the reason of low coulombic efficiency.

The research work is supported by Russian Science Foundation (#20-13-00233).

## References:

- 1.Liu H. et al. Recent advances in understanding dendrite growth on alkali metal anodes // EnergyChem. – 2019. – T. 1. – №. 1. – C. 100003.
- 2.Rodriguez R. et al. In situ optical imaging of sodium electrodeposition: effects of fluoroethylene carbonate // ACS Energy Letters. – 2017. – T. 2. – №. 9. – C. 2051-2057.

---

<sup>1</sup> Department of  
Materials Science,  
Lomonosov Moscow  
State University,  
Leninskie Gory 1-73,  
Moscow 119991,  
Russia

# Electrochemical properties of silylated reduced graphene oxide

**Kislov D.A.<sup>1,2</sup>, Korchun A.V.<sup>1</sup>, Evshchik E. Yu.<sup>1</sup>, Kolmakov V.G.<sup>1</sup>, Dobrovolsky Yu. A.<sup>1,3</sup>**  
Kislov98@yandex.ru

Graphene and silicon are considered promising active anode materials for lithium-ion batteries (LIBs) due to their high specific capacity. In this work, the electrochemical properties of a new active anode material based on silylated reduced graphene oxide were investigated.

The functional groups of graphene oxide readily react with trialkoxysilanes or alkyltrichlorosilanes to provide siloxy linkages (-C-O-Si-) [1]. Using the layer-by-layer deposition method, samples of silylated graphene oxide were obtained. Further, the material was reduced by placing it in hydrazine hydrate vapors. Graphene oxide used in this work was synthesized by the Hummers method.

Electrochemical properties of the new material were studied in model electrochemical half-cells. The active mass consisted of an active material (silylated reduced graphene oxide), an electrically conductive additive (acetylene black, Super P), and a binder (polyvinylidene fluoride, PVDF) in a ratio of 8:1:1. Lithium metal foil on a copper current collector was used as a counter electrode. The 1 m LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) in ratio 1:1 by volume was used as an electrolyte. The material was studied by the cyclic voltammetry method. The material can insert and extract lithium ions and works as anode. Cyclic voltammograms of silylated graphene oxide anodes indicate desirable cyclic performance and reversibility, as shown in Fig. 1.

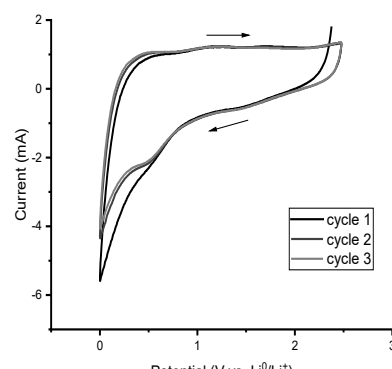


Fig. 1 – Cyclic voltammogram of silylated reduced graphene oxide (sweep rate - 0,5 mV/s)

## References:

1. Dreyer D.R., Todd A.D., Bielawski C.W. // *Chemical Society Reviews* 2014, 43, 5288-5301.

<sup>1</sup> The Institute of Problems of Chemical Physics RAS, Academician Semenov av. 1, 142432, Chernogolovka, Russia

<sup>2</sup> Moscow Institute of Physics and Technology (National Research University), Institutskiy per. 9, 141701, Dolgoprudny, Russia

<sup>3</sup> Platov South-Russian State Polytechnic University (NPI), Prosveshcheniya str. 132, 346428, Novocherkassk, Russia

# Study of the influence of the polymer binder type on the electrochemical characteristics of silicon-containing negative LIB electrodes.

**Kolmakov V.G.<sup>1</sup>, Evshchik E. Yu.<sup>1</sup>, Popov A. V., Dobrovolsky Yu. A.<sup>1,2</sup>**  
hotbrinc@gmail.com

Lithium-ion batteries are one of the most common chemical current sources around the world. However, one of the characteristic disadvantages of this type of battery is its short operating time and fragility. A possible solution to improve stability and energy consumption is to modify the material of the negative electrode.

The negative electrode consists of an active substance, a conductive additive, and a binder. In this work, silicon nanoparticles coated with a SiO<sub>2</sub> layer, obtained by plasma-chemical synthesis, was used as an active substance, since silicon has a theoretical capacity of 4200 mA<sup>\*</sup>h/g. This coin has a second side: during the intercalation of lithium ions, silicon increases in size by 3 times, which leads to the destruction of the negative electrode. This work aim to select the optimal binder to minimize electrode degradation.

In this work were used water-soluble binders such as polyacrylic acid (PAA), polyacrylonitrile (PAN), carboxymethyl cellulose (CMC), and sodium alginate (Na-Alg). The electrode mixture was put on a copper substrate by inkjet printing, then the electrodes were dried under vacuum for 24 hours, 120°C. Pouch cells with lithium as a counter electrode were assembled from electrodes in an argon box, 1M LiPF<sub>6</sub> in an EC:EMC 1:1 solution was used as an electrolyte. The electrochemical characteristics were investigated by galvanic cycling method using a multichannel potentiostat-galvanostat P-20X80 "Elins" in the range 0.01-2V. The test results are presented in Table 1.

Binder	PAA		PAN		CMC		Na-Alg	
	1	10	1	10	1	10	1	10
Discharge capacity, mA <sup>*</sup> h/g	658	1144	709	964	620	1012	735	1127
Coulomb efficiency, %	60	95	57	80	52	84	62	94

Table 1. Dependence of electrochemical characteristics on the type of polymer binder

During the work, the electrochemical characteristics of PAN, PAA, CMC, and Na-Alg samples as binders were studied. It is shown that the largest discharge capacity, which is 735 mA<sup>\*</sup>h/g, in the first cycle has a sample based on Na-Alg. On the tenth cycle, the sample, which includes the PAA, has the highest discharge capacity, the discharge capacity of which is 1144 mA<sup>\*</sup>h/g.

The work was performed in accordance with the state assignments of the Institute of Problems of Chemical Physics of the RAS, No. AAAA-A19-119061890019-5, and Thematic map No. 0089-2019-0007 «Functional materials for chemical power sources».

<sup>1</sup> The Institute of Problems of Chemical Physics RAS, Academician Semenov av. 1, 142432, Chernogolovka, Russia  
<sup>2</sup> Platov South-Russian State Polytechnic University (NPI), Prosveshcheniya str. 132, 346428, Novocherkassk, Russia

# Swelling behavior of lithiated Nafion membrane in aprotic dipolar solvents mixtures.

**Korchun A.V.<sup>1</sup>, Kislov D.A.<sup>1</sup>, Kolmakov V.G.<sup>1</sup>, Evshchik E. Yu.<sup>1</sup>, Dobrovolsky Yu. A.<sup>1,2</sup>** andrei\_korchun@mail.ru

Lithium-ion batteries (LIBs) are the most promising secondary energy sources available today. The high operating voltage of LIBs created a necessity to use organic aprotic dipolar solvents as ethylene carbonate, dimethyl carbonate, etc. Unfortunately, these compounds and salts used to formulate an electrolyte for LIBs are highly flammable and the products produced in a fire are very toxic. Moreover, liquid electrolytes tend to degrade in high temperatures starting from 60°C, which leads to capacity loss. All that cause a big problem utilizing LIBs in harsh conditions and can lead to serious damage to people in case of damage or misuse of LIBs. Therefore, there's a strong need in developing a nonflammable electrolyte, capable of delivering comparable to liquid electrolyte ionic conductivity and electrochemical stability. Commercial Nafion membrane is a suitable candidate to replace liquid electrolyte. Lithiated Nafion provides unipolar Li-ion conductivity at a magnitude of  $10^{-5}$ - $10^{-4}$  S/cm which is close to liquid electrolyte [1], is also electrochemically stable in the potential region 0-5 V vs. Li<sup>+</sup>/Li<sup>0</sup>, and can be swollen in different water based or organic solvents mixtures to obtain desirable properties.

In this work, we investigate the properties of lithiated Nafion swollen in mixtures different dipolar aprotic solvents. The investigated mixture was composed of propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC). Nafion swelling in PC provides better conductivity [2], EC provides the formation of stable solid electrolyte interphase on the negative electrode surface [3] and DMC provides lower operating temperature since it has the lowest freeze point. The swelling degree was determined based on the mass of solvent uptake of the membrane divided by the mass of dry membrane. Three different compositions of solvent were used: PC/EC/DMC as 5/4/1, 2/2/1, 1/1/1 by volume. The swelling behavior was studied at temperatures 25, 35, 45, and 55°C and treatment time from a range of 5 minutes – 96 hours.

It was found that independent from mixture composition the treatment at 55°C resulted in a swelling degree of around 300% for treatment time exceeding 10 minutes. With other temperatures, the highest swelling degree was achieved for 5:4:1 composition in any treatment time.

## References:

1. Flamme B., Garcia G.R., Weil M., Haddad M., Phansavath P., Ratovelomanana-Vidal V., Chagnes A. // Royal Society of Chemistry 2017. 19, 1828–1849
2. Sanginov E.A., Evshchik E.Y.; Kayumov R.R.; Dobrovol'skii Y.A. // Russ. J. Electrochem 2015, 51, 986–990.
3. An S.J., Li J., Daniel C., Mohanty D., Nagpure S., Wood D.L. // Carbon N. Y 2016, 105, 52–76.

---

<sup>1</sup> The Institute of Problems of Chemical Physics RAS, Academician Semenov av. 1, 142432, Chernogolovka, Russia  
<sup>2</sup> Platov South-Russian State Polytechnic University (NPI), Prosveshcheniya str. 132, 346428, Novocherkassk, Russia



# Lithium manganese spinel/ electrolyte interaction at different temperatures

**Koshkina A.A.<sup>1</sup>, Yaroslavtseva T.V.<sup>1</sup>, Bushkova O.V.<sup>1</sup>**

4\_anastasiakoshkina@mail.ru

Nowadays, lithium-ion batteries (LIB) cover the needs of a considerable share of autonomous devices. Therefore, the requirements for the characteristics of such batteries are increasing every year. The main limitations of the LIB's electrochemical parameters are associated with the characteristics of the positive electrode material used in the battery. One of the few commercialized positive electrode materials is lithium manganese spinel  $\text{LiMn}_2\text{O}_4$  (LMO), which is relatively inexpensive, non-toxic, provides high charge/discharge rates, and has good safety indicators [1]. However, one of the limitations of widespread use of this material is its low specific capacity (about 160 mAh/g) and rapid degradation at 40 °C and higher. It is likely caused by side interactions between the electrode and the liquid non-aqueous electrolyte, resulting in the specific capacity of LMO being irreversibly reduced [2]. Therefore, establishing the nature of the ongoing processes would allow it to find effective ways to suppress them.

The chemical interactions between LMO and a standard electrolyte solution of the LP30 type (1M LiPF<sub>6</sub> in an EC/DMS mixture (1: 1), proceeding in the temperature range 25-60 °C, were investigated by a complex of physicochemical methods as impedance spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, electron microscopy, etc. It was shown that even a simple physical contact between LMO and an electrolyte solution leads to soluble and insoluble in the electrolyte interaction products, which forms the primary surface layer. Further formation of the passivating layer growing on the electrode during cycling (cathode electrolyte interface - CEI) occurs with the participation of the primary product layer. Ways to eliminate unwanted processes and stabilize the electrode were discussed.

---

<sup>1</sup> Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Pervomaiskaya St. 91, 620990 Ekaterinburg, Russia

## References:

1. Julien C. M.; Mauger A.; Zaghbi K.; Groult H. // *Inorganics* 2014, 2. 132-154.
2. Li S.; Han Y.; Geng T.; Wang P.; Li W.; Yang L.; Li Z. // *New Journal of Chemistry* 2020, 44. 9540-9545.

# Study of nitrogen-doped reduced graphene oxide as support for fuel cell catalysts

**Kozlova M.V.<sup>1,2</sup>, Pushkareva I.V.<sup>1,2</sup>, Pushkarev A.S.<sup>1,2</sup>**  
kozlova\_mv@outlook.com

Fossil fuels are depleting rapidly, and may not be sufficient enough to meet future energy demands, causing an energy demand-supply gap in the near future, which in turn threatens the energy security of the world. In addition, it is beyond doubt that fossil fuels pollute the environment and cause acid rain, global warming and climate change. The new energy sources include solar energy, wind energy, hydro power, biomass energy, geothermal energy, nuclear energy and hydrogen energy that also include fuel cell technology. Hydrogen energy and fuel cells are the most promising green and clean alternative energy source and energy conversion device respectively. Fuel cells with a polymer electrolyte membrane (PEMFC) because they include such advantages as low operating temperature, high power density, and the most promising are easy scaling up, making PEMFC a promising candidate as the next generation power sources for transportation, stationary, and portable applications [1].

Current ORR cathodes in PEM fuel cells consist of nanostructured Pt-based carbon supported catalysts and proton conductive ionomers. Carbon materials are most suitable for supporting active Pt nanoparticles due to their large specific surface area and relatively high corrosion resistance. The latter is not high enough in case of typical carbon supports-carbon black. These more stable carbon materials like graphene «derivatives» like reduced graphene oxide (RGO) should be considered. The carbon carrier must have such properties as: high specific surface area, high electrical conductivity, developed porous structure, and corrosion resistance. However, due to fewer active sites for the inert graphitized surface of RGO, the efficient utilization of Pt nanoparticles over graphene with an optimized dispersion and size distribution is a key issue still need to be addressed. Nitrogen doping can effectively alter the physicochemical properties of carbon support, including enhancing the electrical conductivity, and strengthening the interaction between Pt nanoparticles and nitrogen doped support, resulting in higher binding energy and stronger attachment [2].

In this study, the possibility of doping carbon materials in a gas discharge plasma in a magnetron-ion sputtering installation was considered, as well as its use as an electrocatalyst carrier in the PEMFC cathode.

---

<sup>1</sup>Moscow Power Engineering Institute (MPEI), Krasnokazarmennaya street, 111250 Moscow, Russia

<sup>2</sup>National Research Center «Kurchatov Institute», Kurchatov square, 123098 Moscow, Russia

## References:

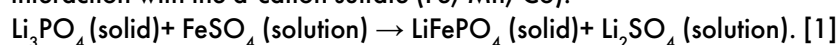
- 1.Daud W.R.W.; Rosli R.E.; Majlana E.H.; Hamid S. A. A.; Mohamed R.; Husaini T. // Renewable Energy 2017, 113, 620–638.
- 2.Sun Q.; Kim S. // Electrochimica Acta 2015, 153, 566–573.

# Development of new synthesis method of cathode materials with the olivine structure from sodium-containing precursors and study of their electrochemical properties

Kurashkina Anna A.<sup>1</sup>, Drozzhin Oleg A.<sup>1,2</sup>, Alekseeva Anastasia M.<sup>1</sup>,  
Antipov Evgeny V.<sup>1,2</sup>.  
anna.kurashkina@chemistry.msu.ru

Lithium iron phosphate  $\text{LiFePO}_4$  with the olivine structure has already established itself as an effective cathode material for lithium-ion batteries. It has a stable structure, which ensures the safety of using this material in unusual conditions and insignificant degradation during long-term cycling. Another advantage is the low toxicity of the material in relation to the environment in comparison with lithium cobaltate  $\text{LiCoO}_2$ . The low cost of the material provides the possibility of its wide use in many spheres of life. However, to further expand the scope of its application, it is necessary to develop cost-effective and efficient methods for its production. Solvothermal synthesis is the one of these methods.

The most common technique for the solvothermal synthesis of cathode materials with the olivine structure includes the stages of lithium phosphate precipitation and its subsequent interaction with the d-cation sulfate (Fe, Mn, Co):



This reaction requires a molar ratio of  $\text{Li}:\text{Fe} = 3:1$ . In this case, lithium sulfate is a waste product and requires further processing, which increases the cost of the method. In the course of the research carried out by our group, it was found [2], it was suggested that the "extra" lithium cations can be replaced by sodium cations, and  $\text{Na}_2\text{SO}_4$  is formed as a by-product.

To prove this hypothesis, a series of hydrothermal syntheses of lithium-iron phosphate was carried out through the interaction of precursors of the composition  $\text{Li}_{3-x}\text{Na}_x\text{PO}_4$  ( $x = 0-2$ ) with iron (II) sulfate  $\text{FeSO}_4$  for 3 and 16 hours at a temperature of 200-205°C. As a result, single-phase samples of the composition  $\text{LiFePO}_4$  with the olivine structure were obtained.

The samples were characterized by powder X-ray diffraction, scanning electron microscopy (SEM), and electrochemical galvanostatic cycling. It is shown that the materials obtained in this way demonstrate attractive electrochemical characteristics, and the proposed technique can be applied in practice.

## References:

1. Qin, Xue; Wang, Jiemin; Xie, Jie; Li, Fangzhi; Wen, Lei; Wang, Xiaohui. // Phys. Chem. 2012, 14, 2669.
2. Patent №2727620, Russia/Drozzhin Oleg A., Alekseeva Anastasia M., Способ получения высокоомощного катодного материала на основе литий-обогащенного фосфата  $\text{Li}_{1+x}\text{Fe}_{1-y}\text{PO}_4$  со структурой оливина для литий-ионных аккумуляторов.

---

<sup>1</sup>Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>2</sup>Skolkovo Institute of Science and Technology, 3 Nobel Str., 143026 Moscow, Russia

# Hard-soft carbon composites as anode materials for sodium-ion batteries

**G.P. Lakienko<sup>1</sup>, Z.V. Bobyleva<sup>1</sup>, O.A. Drozhzin<sup>2,3</sup>**  
bojk25@gmail.com

The key problem in the commercialization of the technology to produce sodium-ion batteries is the search for electrode materials with satisfactory electrochemical characteristics.

Graphite anodes are not suitable for SIB, since sodium ions practically do not intercalate into the interlayer space of graphite. For SIB's anodes, materials based on hard carbon are used, the structure of which contains disordered graphene-like layers [1].

For such anodes to work at high current densities, it is necessary to improve the transport characteristics of the material. One way is to obtain small particles, for example, using hydrothermal synthesis. Another approach to improving the electrochemical characteristics of hard carbon is the creation of a composite based on types of carbon with different morphologies, for example, non-graphitizable and graphitizable carbons. The goal of our work is to optimize the synthesis of hard carbon using hydrothermal synthesis, as well as to obtain and study composites based on non-graphitizable "hard" and graphitizable "soft" carbons as anode materials for sodium-ion batteries [2].

To obtain micron and submicron hard carbon particles, we carbonized D-glucose in a hydrothermal reactor followed by annealing in a furnace in an inert atmosphere. The composites were obtained by mixing in different proportions hard carbon and petroleum pitch, which acted as a source of graphitizable soft carbon, and then annealing the mixture in an inert atmosphere.

Hard carbon anode demonstrated the inner Coulombic efficiency (ICE) of 82% and a discharge capacity of 340 mAh/g in a sodium half-cell. The obtained hard-soft composites showed a noticeable change in electrochemical behavior. The composite showed a capacity of 360 mAh/g comparable to graphite in LIBs and ICE of 79%.

The research was supported by RSF (project No. 17-73-30006).

## References:

- 1.Saurel, D., Orayech, B., Xiao, B., Carriazo, D., Li, X., & Rojo, T. // *Advanced Energy Materials* 2018, 8(17), 1703268.
- 2.Xie, F., Xu, Z., Jensen, A. C., Au, H., Lu, Y., Araullo-Peters, V., ... & Titirici, M. M. // *Advanced Functional Materials* 2019, 29(24), 1901072.

---

<sup>1</sup>Department of Material Science, Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>2</sup>Department of Chemistry, Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

<sup>3</sup>Skoltech Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str.3, 143026, Moscow, Russia

# Synthesis and electrochemical investigation of the mixed phosphate-pyrophosphates $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ( $x = 0.25, 0.5$ ).

Marenko A.P.<sup>1</sup>, Alekseeva A.M.<sup>1</sup>, Drozhzhin O.A.<sup>1,2</sup>, Antipov E.V.<sup>1,2</sup>  
andrei.marenko@chemistry.msu.ru

The mixed polyanionic framework structures, as phosphate-pyrophosphates of sodium and 3d-metals (V, Fe, Co, Mn and Ni), are considered as promising cathode materials for sodium ion batteries due to their superior Na mobility, high operating voltage and thermal stability. The Ni-based cathode material of this family,  $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ , attracts an attention due to its high operating working potential (~5 V vs. Na/Na<sup>+</sup>) and the theoretical capacity of 127 mAh·g<sup>-1</sup> [1]. However, capacity fading of more than 30 % after the 1st cycle hampers the practical application. The substitution in 3d-metal sublattice might enhance the cycling stability due to working potential window shift. This work is devoted to synthesis of Fe-substituted  $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  compounds and to investigation of corresponding electrochemical properties.

The single phase samples of the mixed phosphate-pyrophosphates  $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  ( $x = 0.25, 0.5$ ) have been obtained via conventional solid state synthesis in argon atmosphere. Both compounds are isostructural to  $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  (sp. gr. Pn21a, Z = 4) with corresponding decrease in lattice parameters and volumes:  $a = 18.030(1)$  Å,  $b = 6.5061(1)$  Å,  $c = 10.4814(1)$  Å,  $V = 1229.51(2)$  Å<sup>3</sup> for  $x = 0.25$ ;  $a = 18.0401(2)$  Å,  $b = 6.5235(1)$  Å,  $c = 10.5482(1)$  Å,  $V = 1241.35(3)$  Å<sup>3</sup> for  $x = 0.5$ .

Sodium electrochemical (de)intercalation into  $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  have been investigated by cycling voltammetry and galvanostatic charge-discharge using two-electrode cells assembled in argon-filled glove-box with 1 M solution of NaPF<sub>6</sub> in propylene carbonate as electrolyte and sodium metal anode. Ex situ X-ray powder diffraction and scanning electron microscopy were used for electrodes characterization.

The CV-curves obtained for  $\text{Na}_4\text{Ni}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_2\text{P}_2\text{O}_7$  within the potential range of 2.5-4 V vs. Na/Na<sup>+</sup> revealed three peaks (3.2 V – 3.6 V) with good cycling stability, that is similar to  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  behavior [3], but with higher potentials (3.0 – 3.2 V for the latter). The redox processes correspond to Fe<sup>2+/3+</sup> transition with charge capacity of ~60 mAh·g<sup>-1</sup>. The extension of the potential range up to 5.1 V vs. Na/Na<sup>+</sup> resulted in appearance of three additional peaks (4.1 – 4.6 V), with the potentials lower than ones for pure  $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ . This process, attributed to Ni oxidation, was not reversible.

The work was supported by the Russian Science Foundation (grant No. 17-73-30006) and performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University «The future of the planet and global environmental change».

## References:

1. Kumar P. R.; Yahia H. B.; Belharouak I.; Sougrati M. T.; Passerini S.; Amin R.; Essehli R. // Journal of Solid State Electrochemistry 2020, 24, 17.
2. Wang H., Pan Z., Zhang H., Dong C., Ding Y., Cao Y., Chen Z. // Small Methods 2021, 5, 2100372.

<sup>1</sup>Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia  
<sup>2</sup>Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205 Moscow, Russia

# Improving stability of Ni-rich NMC cathode materials via grain boundaries modification by $\text{Li}_2\text{SO}_4\text{-Li}_3\text{PO}_4$ binder

**Mikheeva M.<sup>1,2</sup>, Orlova E.<sup>2</sup>**

Maria210900@gmail.com

Electric vehicles (EVs) are steadily growing in popularity each year, as public continuously moving towards eco-friendly transportation options. EVs use Li-ion batteries (LIBs) as primary energy source, therefore, prompting researchers to improve their performance, stability, reliability, safety, and cost. Ni-rich NMCs are promising cathode materials for LIBs. They have a high practical capacity over 200 mAh/g and possess high energy density larger than 800 Wh/kg, which allows to accommodate the need for long driving range and fast recharging. In comparison to NMCs with lower amounts of Ni, these materials have lower toxicity and cost less due to Co replacement with Ni. Nevertheless, despite their higher performance, Ni-rich NMCs show a significant decrease in capacity after prolong cycling. Grain boundaries engineering is a common strategy for improving electrochemical properties of cathode materials. As was demonstrated by Savina et al. [1] lithium sulfate binder on the grain boundaries of the material's particles improves ionic conductivity, resulting in enhanced electrochemical properties. Thus, the present work aims at obtaining Ni-rich NMC ( $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ), modified via lithium sulfate-lithium phosphate binder with enhanced ionic conductivity, in order to improve electrochemical properties. We obtained three  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811) samples by co-precipitation synthesis routine by varying concentrations of phosphate, introduced by adding the  $(\text{NH}_4)_2\text{HPO}_4$  solution at the precursor's synthesis step. The performed XRD analysis indicated that all obtained samples possess layered structures (s.g. R-3m) with a minor presence of additional phase. This phase peaks are attributed to the of  $\text{Li}_2\text{SO}_4\text{-Li}_3\text{PO}_4$  solid solution, because they shifted towards lower angles compared to  $\text{Li}_3\text{PO}_4$ , which explained by the substitution of phosphorous with higher ionic radius ( $r(\text{P}^{5+}) = 0.17 \text{ \AA}$ ) by the sulfur with the lower one ( $r(\text{S}^{6+}) = 0.12 \text{ \AA}$ ) [2]. To confirm that the binder is located at grain boundaries of the particles we used electron microscopy methods like EDX-STEM analysis. Obtained phosphorous and sulfur elements distribution maps demonstrated that both sulfur and phosphorous are located at the grain boundaries of materials particles. Furthermore, the prolonged galvanostatic charge/discharge cycling showed that modification of NMC811 by  $\text{Li}_2\text{SO}_4\text{-Li}_3\text{PO}_4$  binder slightly increases the rate capability, and the capacity retention over 200 cycles was significantly elevated from 76% toward 88%.

## References:

1. Savina A.A., Orlova E.D., Morozov A.V., Luchkin S.Y., Abakumov A.M. Sulfate-containing composite based on Ni-rich layered oxide  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  as high-performance cathode material for li-ion batteries. *Nanomaterials*. 2020; 10(12):1-17. doi:10.3390/nano10122381
2. Touboul, M., Sephar, N., Quarton, M. (1990). Electrical conductivity and phase diagram of the system  $\text{Li}_2\text{SO}_4\text{-Li}_3\text{PO}_4$ . *Solid State Ionics*. 1990; 38(3-4), 225–229. doi:10.1016/0167-2738(90)90425-q

<sup>1</sup>D. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russia

<sup>2</sup>Skolkovo Institute of Science and Technology, 143026 Moscow, Russia

# Oxygen ion transport in pure and Li/Cu-doping magnocolumbite

**Morkhova Ye. A.**<sup>1,2,3</sup>, **Koroleva M.S.**<sup>4</sup>, **Egorova A.O.**<sup>5</sup>, **Kabanov A.A.**<sup>2,3</sup>,  
**Blatov V.A.**<sup>1,2</sup> eliztimofeeva@mail.ru

Magnocolumbite belongs to the columbites group with the general formula of  $ANb_2O_6$  (A – Mg, Mn, Fe) [1]. Magnocolumbite is described as a precursor for the synthesis of multilayer ceramic capacitors and for application in microwave devices [2]. From the geometrical point of view,  $MgNb_2O_6$  was selected as potential  $Mg^{2+}$ -ion conductor according to the crystallochemical analysis [3]. However, quantitative calculations performed in this work proved the predominance of oxygen-ionic conductivity with a low migration energy (0.75 eV and 1.44 eV from bond valence site energy and density functional theory methods, respectively).

In order to demonstrate the oxygen conductivity, we synthesized  $MgNb_2O_6$  and investigated the ion conductivity depended on oxygen pressure. Besides, we synthesized the Li- and Cu-substituted compositions with the general formula of  $Mg_{1-x}M_xNb_2O_{6-\delta}$  (M – Li, Cu; x = 0.1; 0.2), performed their structural analysis, investigated optical and electrical properties by impedance spectroscopy method in air and oxygen atmosphere. We showed that the conductivity in the  $MgNb_2O_6$  and Li-doped samples is ionic with oxygen working ions. The conductivity values turned out to be about  $10^{-5}$  S/cm at 700 oC. The Cu-containing structure had mixed ionic-electronic conductivity ( $10^{-3}$  S/cm at 700 oC).

YAM and AAK are grateful to the financial support of RSF project no. 19-73-10026 and the RFBR project no. 20-33-90018. MSK acknowledges RFBR project no. 19-03-00642.

## References:

1. Pagola, S., Carbonio, R. E., Alonso, J. A., & Fernández-Díaz, M. T. // Journal of Solid State Chemistry 1997, 134(1), 76-84.
2. Sreedhar, K., Mitra, A. // Materials research bulletin 1997, 32(12), 1643-1649.
3. Morkhova, E. A., Kabanov, A. A., Blatov, V. A. // Russian Journal of Electrochemistry 2019, 55(8), 762-777.

---

<sup>1</sup>SCTMS, Samara State  
Technical University,  
443110 Samara,  
Russia

<sup>2</sup> SCTMS, Samara  
University, 443011  
Samara, Russia

<sup>3</sup> Institute of Solid  
State Chemistry and  
Mechanochemistry  
SB RAS, 630128  
Novosibirsk, Russia

<sup>4</sup> Institute of Geology,  
Federal Research  
Center Komi Science  
Center, Ural Branch,  
Russian Academy  
of Science 443011  
Samara, Russia

<sup>5</sup> Institute of  
High Temperature  
Electrochemistry,  
Ural Branch, Russian  
Academy of Science,  
620002 Ekaterinburg,  
Russia

# Discharge product formation/ decomposition in magnesium- oxygen cells with an aprotic electrolyte

M.A. Nazarov<sup>1</sup>, Dr. T.K. Zakharchenko<sup>1</sup>

Mikhail.Nazarov@student.msu.ru

Development of Mg-air chemical current sources is an urgent task because they have a high value of the theoretical voltage and capacity, use safe and inexpensive components, and are also able to provide an energy density several times higher than that for the most energy-intensive now lithium-ion batteries.

In a rechargeable Mg-O<sub>2</sub> cell with an aprotic electrolyte during discharge the Mg anode is dissolved, while molecular oxygen is reduced at the cathode simultaneously to form insoluble magnesium compounds - Mg(OH)<sub>2</sub>, MgO, MgO<sub>2</sub> or Mg(O<sub>2</sub>)<sub>2</sub>. [1, 2] The deposition of these products on the electrode blocks the further discharge process, and also significantly hampers the charging process. According to literature data [3], an addition of iodine mediator to the electrolyte, can dissolve the discharge product, but this effect is poorly understood and requires additional research.

The results of the study indicate that in the absence of an iodine mediator, the discharge product of the Mg-O<sub>2</sub> cell is MgO<sub>2</sub>, while MgO and Mg(OH)<sub>2</sub> are absent among the products. In addition, the methods of XPS and CV indicate the possible presence of some superoxide species among the discharge products. According to CV data, elementary stages of O<sub>2</sub> reduction in the 0.1 M Mg(ClO<sub>4</sub>)<sub>2</sub> electrolyte in DMSO are the formation of O<sub>2</sub><sup>-</sup> and MgO<sub>2</sub><sup>+</sup> ions and its subsequent disproportionation to MgO<sub>2</sub>. The fact of dissolution of the supposed discharge products (MgO, MgO<sub>2</sub>) in I<sub>2</sub> solutions in DMSO at room temperature was established by the method of spectrophotometry and XRD. Both reactions were assigned to the first order and the reaction rate constants were calculated.

## References:

- 1.Reinsberg, P.; Bondue, C.; Baltruschat, H. // *Electrochimica Acta*, 2016, 214-221.
- 2.Bhauriyal, P.; Rawat, K. S.; Bhattacharyya, G.; Garg, P.; Pathak, B. // *Chemistry - An Asian Journal*, 2018, 13, 21, 3198-3203.
- 3.Shiga, T.; Hase, Y.; Kato, Y.; Inoue, M.; Takechi, K. // *Chem. Commun.*, 2013, 49, 9152.

---

<sup>1</sup>Lomonosov MSU,  
Leninskie gory GSP-  
1, 119991 Moscow,  
Russia



# Mesoporous nanotubular Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> as an anode for sodium-ion batteries

**A.I. Neumoin<sup>1</sup>, D.P. Opra<sup>2</sup>, S.L. Sinebryukhov<sup>3</sup>, A.A. Sokolov<sup>4</sup>, A.B. Podgorbunsky<sup>5</sup>, S.V. Gnedenkov<sup>8</sup>**  
anton\_neumoin@ich.dvo.ru

In the near future, sodium-ion batteries (SIBs) may become the widespread in grids and homes to store energy on a large scale from renewable resources or to apply as backup power systems. A distinctive attribute of SIBs is the usage of plentiful, relatively cheap, and benign materials (mainly Na and Al). However, to commercialize sodium-ion systems it is necessary to develop materials for SIBs electrodes with adequate specific capacity, energy density, cyclic performance, and safety. Regarding anodes, one of these materials is sodium trititanate (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) possessing a specific capacity of 177 mAh/g and stable cycling (volume expansion during Na<sup>+</sup> intercalation is equals to 6%, while that of graphite successfully used in commercial LIBs achieves 10%).

In the present study, a mesoporous nanostructured Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> with a hierarchical micro/nanoarchitecture has been synthesized. The material was obtained by a treatment of commercial Degussa P25 nanopowder in highly alkaline medium (10 M NaOH solution) using hydrothermal autoclave reactor at a temperature of 130 °C for 36 h. The results of electron microscopic studies have shown that the material demonstrates a complex multi-level structure. At the micron level it is represented by particles of 1-10 μm in diameter exhibiting a roughness surface. At the nano-level, it is clearly observed that these microparticles consist of smaller-scale elements – ultrathin one-dimensional nanotubes with an outer diameter of 6–9 nm and a length of several hundred nanometers. The wall thickness of nanotubes is 3–4 nm. The N<sub>2</sub> adsorption method showed a mesoporous texture for prepared product with a narrow pore size distribution of near 5–6 nm. The total pore volume is reached to 0.5–0.6 cm<sup>3</sup>/g. The specific surface area of product is about 300 m<sup>2</sup>/g. As known, finding the optimum particle shape and size as well as porosity can improve properties of materials making them suitable for different practical applications. The phase composition of the synthesized product is represented by monoclinic Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> with an anatase phase as impurity. According to UV-vis spectroscopy, the material absorbs UV-radiation and has a high reflectance in the region of > 400 nm, which is typical for Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. The band gap of the product is 3.37 eV, which is consistent with the results of theoretical calculations (3.28 eV) and experimental measurements (3.4–3.51 eV). According to electrochemical impedance spectroscopy, the product has a sufficiently high electrical conductivity of at least 4.97 10<sup>-3</sup> S/cm. Preliminary tests in sodium half-cells showed that mesoporous nanotubular Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> demonstrates a promising performance as SIBs anode.

This work was financially supported by the Russian Science Foundation (grant № 19-73-10017).

---

<sup>1</sup>Institute of Chemistry, FEB RAS, 159 100-letiya Vladivostoka Pr., 690022 Vladivostok, Russia

# Synthesis and characterization of graphene nanoribbons as promising electrocatalysts

**Ivan V. Novikov<sup>1</sup>**

novikov.ivan@phystech.edu

To date, carbon materials are actively being studied under the assumption that they can be implicated in many fields: transistors, thermoelectric devices, capacitors and catalysts. Graphene and doped nanotubes are studied in relation to electrochemical processes like oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) as promising and low-cost materials. [1] However, to date there is very few data about study of the narrow graphene nanoribbons (GNRs) as catalysts.

Narrow graphene nanoribbons are represented by three families, based on whether their width can be presented as  $3p$ ,  $3p+1$ , or  $3p+2$ . Within each family, the bandgap decreases monotonically with increase of the GNR width. [2]

We demonstrate chemical vapor deposition (CVD) method [3] for production of atomically precise 3-armchair graphene nanoribbon (3-AGNR) films also known as poly-paraphenylene (PPP) obtained from 4,4"-dibromo-p-terphenyl (DBTP) under low vacuum ( $10^{-3}$  mbar) on common Ni foil. [3] The high quality of produced graphene nanoribbons is confirmed by measuring the Raman fingerprints of 3-AGNRs. The synthesized 3-AGNRs can be dissolved and/or suspended in different solvents like chlorobenzene and toluene. The films synthesized from DBTP precursor molecules via annealing at 250 OC and also samples additionally annealed at 350-400 OC have specific Raman features when excited in ultra violet range. Observed Raman features are in agreement with reported Raman fingerprints of 3-AGNR.

We suppose, that application of GNRs to electrochemistry and reactions with gases like ORR and OER is a necessary step in the study of properties and application of carbon materials.

---

<sup>1</sup>A.M. Prokhorov  
General Physics  
Institute of Russian  
Academy of Sciences,  
38 Vavilov  
Street, Moscow,  
119991, Russia.

## References:

- 1.Zhang, J.; Sun, Y.; Zhu, J.; Gao, Z.; Li, S.; Mu, S.; Huang, Y. // Advanced Science 2018, 5, 1801375.
- 2.Talirz, L.; Ruffieux, P.; Fasel, R. // Advanced materials 2016, 28, 6222-6231.
- 3.Narita, A.; Chen, Z.; Chen, Q.; Müllen, K. // Chemical science 2019, 10, 964-975.

# Single crystal Ni-rich NMC layered cathode material with high tap density

**A. Pavlova<sup>1</sup>, I. Moiseev<sup>1</sup>, A. Savina<sup>1</sup>, A. Abakumov<sup>1</sup>**

Al.Pavlova@skoltech.ru

For the polycrystalline Ni-rich NMCs, the collapsed secondary particle during the electrode pressing process by high pressure could increase the contact area between the cathode and electrolyte. This could give rise to the formation of resistant layer and crack, increasing the charge transfer resistance. Furthermore, during electrochemical cycling, the electrochemically generated microcracks also hinder the lithium ion diffusion, resulting in the capacity drop. By contrast, the morphology of the so-called "single crystalline" (i.e. consisting of the primary single crystal particles with the size  $> 1 \mu\text{m}$ ) cathodes can be stably maintained even after the electrode pressing process and during the battery cycling, allowing for stable electrochemical characteristics. Moreover, single crystals with suitable shape can possibly achieve higher tap and compact electrode density ( $>3.8 \text{ g/cm}^3$  for NMC electrodes) compared to polycrystalline cathode materials.

However, there are drawbacks that limit the commercial use of this material and are being addressed at the moment. In particular, the low tap density and the high cost of the manufacturing process associated with the excess lithium required for the formation of the melt according to the method. Thus, the aim of this work is to obtain single crystal  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  samples with complete replacement of lithium salts as a melt-forming agent with potassium salts.

Powder X-ray diffraction confirmed that material has a highly-ordered hexagonal  $\alpha\text{-NaFeO}_2$  structure with R-3m symmetry without any detectable impurity phase. Rietveld refinement was performed and revealed that the material exhibits a very small percentage of Li/Ni cation mixing ( $\sim 0.5\%$ ), lower than that of a polycrystalline NMC622 analog (Li/Ni mixing  $\sim 3.0\%$ ). According to SEM analysis, the obtained single-crystal NMC622 are of spherical or spherical-like shape. These spherical-like particles have only hexagonal (001) facets, which can be clearly distinguished in the SEM images. The particle morphology is presented as individual crystals with the size ranging from 2 to 8 microns. The tap density of the obtained material reaches record value of  $3.0\text{-}3.1 \text{ g/cm}^3$ . The compact density, measured by pressing the powder of the obtained material into a tablet at a pressure of 3 tons for 30 seconds, is  $3.9\text{-}4.1 \text{ g/cm}^3$ .

The electrochemical properties of the obtained cathode material were evaluated by galvanostatic cycling in the potential range from 2.7 to 4.3 V. Rate capability testing was carried out according to a comprehensive program that includes 6 forming series with different cycling rates (C/10, C/5, C/2, 1C, 2C, 5C) with a duration of 5 cycles each. The initial specific discharge capacity for single-crystal  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  is  $177 \text{ mAhg}^{-1}$  at a rate of C/10,  $171 \text{ mAhg}^{-1}$  at a rate of C/5,  $163 \text{ mAhg}^{-1}$  at C/2, and  $154 \text{ mAhg}^{-1}$  at 1C,  $144 \text{ mAhg}^{-1}$  at 2C and  $125 \text{ mAhg}^{-1}$  at 5C.

The research work is supported by Russian Science Foundation (RSF) (Grand N° 20-13-00233).

---

<sup>1</sup>Skolkovo University of Science and Technology, 121205 Moscow, Russia

# Micro-Raman probing of a single LiFePO<sub>4</sub> particle: method locality and insight into decomposition processes

Alexander A. Ryabin<sup>1</sup>, Dmitry V. Pelegov<sup>1</sup>

ryabin.alexandr.1@yandex.ru

During the last decade, the lithium battery industry is thriving due to steady demand from automobile and energy industries. This maturing phase strongly needs production scale growth and cell price decreasing. Both trends increase the role of quality control tools, especially ones, suitable for industrial applications.

Raman spectroscopy (RS) is one of the most promising candidates for industrial quality control tool due to a relatively low acquisition times, inexpensive equipment, and ability to be built-in production lines. But there is still a gap between chemical and physical aspects of materials characterization.

Despite the abundance of publications focused on solid-state chemistry (material synthesis) and electrochemistry (chemical processes during lithiation and delithiation), there is an obvious lack of research on physics of laser-particle interaction. To correctly interpret the experiment results, it is required to understand from what area the signal is received. However, in the Julien et al. stated about RS probing for popular electrode material LiFePO<sub>4</sub> that "The penetration depth inside LiFePO<sub>4</sub> is unknown, but it should be small" [1].

To define the RS resolution, we switched from common powder characterization to single-particle study. In this work, we examined a series of single LiFePO<sub>4</sub> particles on a Raman-active Si substrate. The ratio of intensity of Si band near 521 cm<sup>-1</sup> to one for major LFP band near 951 cm<sup>-1</sup> was used as a main characteristic parameter.

We showed three main conclusions about peculiarities of laser interaction with particulate microscale LiFePO<sub>4</sub>. First, the probing depth of micro-Raman spectroscopy can greatly exceed instrumental estimation and reach several microns due to the particle morphology. Second, there is a pronounced heterogeneity of local optical properties, conceivably caused by a variation of defect concentration. Third, this heterogeneity results in different pathways and products of laser-induced degradation.

We hope that this work can help to organize relatively non-destructive RS measurements, properly interpret the obtained results, and take another step towards a better understanding of physicochemical processes, induced in microscale particles, regardless of the driving force origin – laser irradiation, heating, or cycling.

## References:

1. Julien, C. M.; Zaghbi, K.; Mauger, A.; Massot, M.; Ait-Salah, A.; Selmane, M.; Gendron, F. // Journal of Applied Physics 2006, 100, 6, 063511.

---

<sup>1</sup>Ural Federal University, 19 Mira str., 620002 Ekaterinburg, Russia

# Application of electron microscopy to study the process of aluminum oxidation by water

**N.S. Shaitura<sup>1</sup>, M.N. Larichev<sup>1</sup>**

tesh-s@yandex.ru

Metallic aluminum is an efficient concentrator of chemical energy that can be easily converted into electrical energy in various ways (aluminum-air battery, fuel cell). In the latter case, the oxidation reaction of aluminum with water is a source of hydrogen, the energy of which is converted into electrical energy in the fuel cell. Solid oxidation products (oxides and hydroxides of aluminum) can be used to reproduce metal at the locations of renewable sources of electrical energy, making the process of using Al renewable. If they are given the desired properties, they can also be used in other high-tech industries. The use of electron microscopy and X-ray diffraction analysis together with the measurement of the kinetics of metal oxidation (the rate of H<sub>2</sub> evolution, the pH of the medium) made it possible to determine the processes that control the kinetics of Al oxidation at each of its stages and to establish (see Fig. 1) the correlation between the parameters of the kinetics and the morphology of solid products formed under various thermal modes of oxidation and various methods of activating the process.

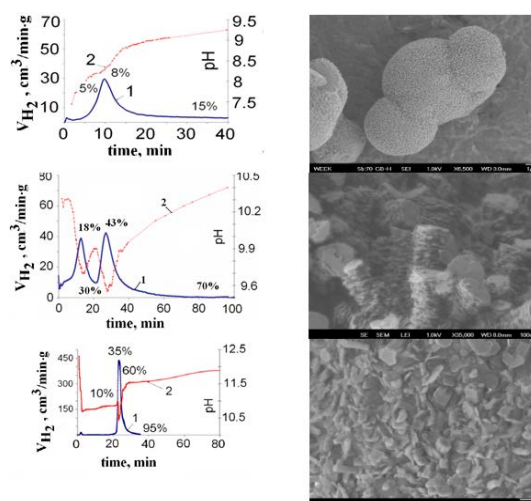


Fig. 1 – Cyclic voltammogram of silylated reduced graphene oxide (sweep rate - 0,5 mV/s)

<sup>1</sup>N.N. Semenov  
Federal Research  
Center for chemical  
physics RAS, Leninskiy  
pr. 38/2, 119991  
Moscow, Russia

# Core-shell structured Ni-rich layered oxides as cathode materials for Li-ion batteries

**Sitnikova L.A.<sup>1</sup>, Dolzhikova E.A.<sup>1, 2</sup>, Savina A.A<sup>1</sup>, Abakumov A.M.<sup>1</sup>**  
 lu-sitnikova1999@yandex.ru, dolzhikova01@list.ru

Layered lithium and transition metals oxides  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  ( $x + y + z = 1$ ) with a nickel content of  $\geq 60\%$ , so-called Ni-rich NMCs, are considered to be the most promising candidates as cathodes for next-generation LIBs due to higher specific capacity (up to 220 mAh/g in the 2.7-4.3 V vs Li/Li<sup>+</sup>), higher energy density (up to 800 Wh/kg) and low cost compared to conventional LiCoO<sub>2</sub>. Nevertheless, Ni-rich NMCs with high Ni content ( $>80\%$ ) are still very limited in terms of practical application due to fast capacity fading upon electrochemical cycling with the extraction of more than 80-90% of lithium, and low thermal and structural stability causing safety problems with battery operation [1]. Various methods have been proposed to solve the mentioned problems. Among them, the protective coatings seem to be an effective approach for the spatial separation of the cathode material and the electrolyte solution, which reduces the reactivity of the electrode surface. One of the approaches for the surface coatings development is to create the so-called "core-shell" structures, where Ni-rich NMCs are selected as the high-capacity core, and more electrochemically and thermally stable NMCs with a high manganese content ( $\geq 50\%$ ) act as the shell. However, the Mn-rich surface is not favored in the industry because Mn cations are known to dissolve into the electrolytes as Mn<sup>2+</sup> cations, which could deposit on graphite and greatly increase the interfacial polarization [2].

In this work, a series of core-shell structured cathode materials with different thicknesses of the shell based on Ni-rich NMC with high Ni content ( $x = 0.95$ ) as a core and Co-rich layered oxides as a shell was prepared via both co-precipitation and microwave-assisted hydrothermal synthesis techniques. The last approach using urea and glycine as complexing agents for preparing of core-shell structure was developed for the first time within this work. First, the core  $\text{LiNi}_{0.95}\text{Mn}_{0.025}\text{Co}_{0.025}\text{O}_2$  with homogeneous distribution of transition metal cations at the nanoscale, uniform particle size distribution and spherical morphology was synthesized via conventional co-precipitation followed by high-temperature annealing with Li source. The obtained material demonstrates a high initial reversible discharge capacity of  $\sim 230$  mAh/g at 0.1C current density and good rate capability, while capacity retention is of about 80% after 100 cycles at 1C. Second, the core-shell structured cathode materials with different thicknesses of the shell were obtained. According to SEM and SEM-EDX cross-sectional mapping, the prepared materials are near spherical particles with the local compositional change from the particle center to the surface consistent with the designed particle structure. The electrochemical performance studies of such materials are in progress.

The research work is supported by Russian Science Foundation (#20-13-00233).

## References:

1. Ding Y, Cano ZP, Yu A, Lu J, Chen Z. Automotive Li-Ion Batteries: Current Status and Future Perspectives. *Electrochem Energy Rev.* 2019;2(1):1-28.
2. Cho Y, Oh P, Cho J. A new type of protective surface layer for high-capacity ni-based cathode materials: Nanoscaled surface pillaring layer. *Nano Lett.* 2013;13(3):1145-1152.

<sup>1</sup>Skolkovo Institute of Science and Technology, Moscow, Russia

<sup>2</sup>D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia

# Development of Synthesis Technology of Initial Components for Growth of IR-Band Optical Crystals Based on Thallium Halides

Soskov O.V.<sup>1</sup>

Thallium halide-based monocrystals offer unique optical properties (transparent in the wavelength range of 0.42-52  $\mu\text{m}$ ), mechanical properties and sufficient chemical resistance. This has led to an interest in these materials for their use in spectroscopy, radiation recording equipment, as well as in a number of special applications. Among demanded fields of application of these crystals, they are manufacturing of volumetric optical elements (windows, lenses, prisms, semitransparent mirrors) for infrared and laser devices (including for operating with radiation of CO- and CO<sub>2</sub>-lasers) and manufacturing of semiconductor elements of ionizing radiation detectors for which crystals of TlBr-TlI (KRS-5) and TlBr compositions are used.

However, some applications of thallium salts are not currently developed and do not require new high-purity crystals. In particular, this problem concerns chloride-containing thallium halides such as TlCl and TlCl-TlBr (KRS-6), previously used in radiators of Cherenkov counters. This has formed a surplus of billets and synthesised components that cannot be recycled due to the high toxicity of thallium, and technologies for their recycling for thallium reuse as well as methods for recovery of initial components from them are lacking.

The aim of this work is to study the recovery of thallium from its chlorinated halides and the choice of optimal method for further use at the plant, providing the maximum yield of metal, and minimum economic and technological costs.

Experimentally tested and optimized processes of thallium reduction by hydrochemical method, electrolysis of aqueous solution, electrolysis of molten thallium chloride and metallothermic method. Comparison of their efficiency showed the advantages of the metallothermic method of thallium recovery, which provided a 96-98% yield, high productivity, as well as sufficient purity of the metal obtained - more than 99.5%. From the thallium obtained by the metallothermy method was synthesized charge system TlI - TlBr, from which after a cycle of purification was grown a single crystal of optical quality KRS-5, which indicates the prospects for further use of this method in production.

---

<sup>1</sup>Skolkovo Institute of Science and Technology, Moscow, Russia

<sup>2</sup>D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia

## References:

1. Ding Y, Cano ZP, Yu A, Lu J, Chen Z. Automotive Li-Ion Batteries: Current Status and Future Perspectives. *Electrochem Energy Rev.* 2019;2(1):1-28.
2. Cho Y, Oh P, Cho J. A new type of protective surface layer for high-capacity ni-based cathode materials: Nanoscaled surface pillaring layer. *Nano Lett.* 2013; 13(3):1145-1152.

# All-solid-state Li-ion batteries based on LLZO electrolyte and Li-rich layered oxide positive electrodes

**Timusheva N.B.<sup>1</sup>, Morozov A.V.<sup>1</sup>, Savina A.A.<sup>1</sup>, Abakumov A.M.<sup>1</sup>**  
Natalia.Timusheva@skoltech.ru

Solid-state lithium-ion batteries (SSBs) are a promising alternative to conventional batteries based on liquid organic electrolytes due to the absence of flammability risks i.e. enhanced safety. In turn,  $\text{Li}_{6.4}\text{Al}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$  (Al-doped LLZO, Al-LLZO) solid electrolyte with cubic garnet-type structure may be considered as a prospective material for high energy density SSBs. It demonstrates both high values of Li-ion conductivity and chemical stability to metallic lithium as well as a uniquely wide electrochemical stability window. As a result, high energy density electrode materials, such as lithium metal or Li-rich layered transition metal oxides can be used in combination with Al-LLZO.

Nevertheless, although being in great promise, the implementation of Li-rich layered cathodes in SSBs has not been reported yet. Thus, this work is aimed at establishing the possibility of Li-rich layered oxide usage as high energy density cathode in Al-LLZO SSBs. As the first step, the conditions of Al-LLZO synthesis and thin electrolyte pellets preparation were optimized. A series of cubic Al-doped LLZO with the nominal composition of  $\text{Li}_{6.4}\text{Al}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$  were prepared via solid-state route. The targeted synthesis characteristics include the amount of plasticizer and Li precursor excess, ball-milling time, temperature and sintering time, pressing load. As a result, membranes of Al-LLZO 10 mm in diameter and with a thickness of 0.3 mm with suitable mechanical stability were obtained. According to powder X-ray diffraction data, all membranes adopt cubic garnet structure, while tetragonal modification of LLZO was found to be either absent or present as a very minor admixture, which is important due to its much lower Li-ion conductivity. The surface and cross-section structure of the pellets were also characterized by SEM. The Li-ion conductivity reaching  $10^{-6}$  S/cm was measured for all the membranes by EIS.

As the second step, the functional layer of  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  was coated on the surface of Al-LLZO membranes using screen printing and annealed at different temperatures varying from 700 to 900°C. The resistance of the cathode-electrolyte interface measured by EIS was established to increase with the annealing temperature indicating the formation of the additional insulating layer.

Further work will be devoted to the investigation of the interbedded phase as well as enhancing the Li-ion conductivity of Al-LLZO membranes.

This work is supported by the Russian Foundation of Basic Research (grant № 20-33-90241)

---

<sup>1</sup>Skolkovo Institute of Science and Technology, Moscow, Russia



# Development of PEDOT-coated $V_2O_5$ -based cathode material for zinc-ion batteries

Volkov F.S.<sup>1</sup>, Eliseeva S.N.<sup>1</sup>

Sokkorat@gmail.com

Among the various candidates of the new type of metal-ions batteries as an alternative power sources, rechargeable aqueous zinc-ion batteries (AZIB) has received much attention last decade due to their safety and cost-effectiveness. Vanadium(V) oxide is regarded as a promising cathode material for rechargeable aqueous zinc-ion batteries (AZIBs) due to its layered structure with enlarged interlayer distance providing high specific capacity via reversible intercalation of  $Zn^{2+}$  ions [1]. However, despite the recent progress, the issues of unsatisfying capacity, rate capability and cycling stability of  $V_2O_5$ -based materials have not been resolved.

One of the approaches to improve the electrochemical performance of  $V_2O_5$ -based electrodes is to form the composites with different conducting polymers, e.g., polyaniline [1], and poly(3,4-ethylenedioxythiophene) (PEDOT) [2] which provide high conductivity and structural stability of electrodes.

Vanadium oxide coated by poly(3,4-ethylenedioxythiophene) ( $V_2O_5@PEDOT$ ) was successfully synthesized by chemical oxidation of EDOT.  $V_2O_5@PEDOT$  was characterized by energy dispersive X-ray and thermogravimetric analyses to evaluate the amount of PEDOT on the oxide surface and by scanning electron microscopy. Electrode materials were prepared by mixing of  $V_2O_5$  and  $V_2O_5/PEDOT$  (70 wt.%) with carbon black (20 wt.%) and polyvinylidene fluoride (10 wt.%) dissolved in N-methylpyrrolidone. The resulting viscous slurry was cast on the titan foil, dried under vacuum and pressed. Coin cells CR 2032 were assembled vs. Zn foil as anode with 3 M  $ZnSO_4$  as electrolyte. Comparative study of electrochemical properties of  $V_2O_5$  and  $V_2O_5@PEDOT$  electrodes was performed by cyclic voltammetry and galvanostatic charge/discharge in a potential range 0.3 – 1.4 V vs.  $Zn/Zn^{2+}$ .

Here we report on the preparation of  $V_2O_5$  coated by PEDOT and comparison of electrochemical performance of  $V_2O_5/PEDOT$ -based cathode materials with those made of pristine  $V_2O_5$ . The proposed PEDOT-containing electrodes showed an excellent specific capacity ( $380 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at  $0.1 \text{ A}\cdot\text{g}^{-1}$ ) and improved C-rate capability, maintaining their functionality during long-term cycling.

Acknowledgements: The financial support from RFBR (grant № 21-53-53012) is gratefully acknowledged. The authors would like to thank the Research Park of Saint Petersburg State University: 1) the Center for X-ray Diffraction Methods, 2) the Interdisciplinary Center for Nanotechnology, the Center for Thermogravimetric and Calorimetric Research.

## References:

1. Chen, K. Li, K.S. Hui, J. Zhang, Regulation of Lamellar Structure of Vanadium Oxide via Polyaniline Intercalation for High-Performance Aqueous Zinc-Ion Battery, *Adv. Funct. Mater.* 30 (2020) 1–11. <https://doi.org/10.1002/adfm.202003890>.
2. D. Xu, H. Wang, F. Li, Z. Guan, R. Wang, B. He, Y. Gong, X. Hu, Conformal Conducting Polymer Shells on  $V_2O_5$  Nanosheet Arrays as a High-Rate and Stable Zinc-Ion Battery Cathode, *Adv. Mater. Interfaces.* 6 (2019) 1–8. <https://doi.org/10.1002/admi.201801506>.

---

<sup>1</sup>Saint Petersburg State University, Saint Petersburg, Russia Student

# Membranes with sulfonylimide groups solvated by aprotic solvents as gel-polymer electrolytes for lithium-ion batteries

Voropaeva Daria<sup>1</sup>

voropaeva@igic.ras.ru

Studying new materials for lithium-ion batteries is one of the essential tasks nowadays. Moving away from widely used liquid and toward alternative electrolytes can provide greater safety, better stability, and more convenient battery geometry. One of the most promising electrolytes is gel-polymer electrolytes containing functional cation exchange groups solvated by low-molecular-weight aprotic solvents. The advantage of this type of electrolytes is the absence of counterion transport during battery operation, thus preventing dendrite formation and increasing battery capacity [1]. To create such electrolytes, membranes based on SEBS polymer (a copolymer of polyethylene, polybutylene, and polystyrene) containing functional sulfonic groups  $-\text{SO}_3^-\text{Li}^+$  as well as sulfonylimide groups  $-\text{[SO}_2\text{N-SO}_2\text{X]Li}^+$  ( $\text{X}=\text{CCl}_3$ ,  $\text{CF}_3$ ,  $\text{Ph}$ ,  $p\text{-NO}_2\text{Ph}$ ,  $p\text{-CF}_3\text{Ph}$ , and  $p\text{-CH}_3\text{Ph}$ ) were synthesized in this work.

The membranes were obtained according to the procedure described in [2]. To obtain gel-polymer electrolytes, SSEBS and SSEBS-X membranes were placed in individual solvents: propylene carbonate (PC), N,N-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMFA); and mixtures containing an equal volume of components: ethylene carbonate (EC)-PC, EC-DMA, EC-DMSO, EC-DMFA, PC-DMA, PC-DMSO, PC-DMFA, DMA-DMSO, DMA-DMFA, DMSO-DMFA. The membranes were soaked in these solvents over activated molecular sieves  $3\text{\AA}$  for 1 day.

According to the IR spectra in the case of the mixture of EC-PC, the content of individual components in the membrane does not differ from the initial solvent composition for all investigated membranes. In the case of solvation with mixtures containing carbonates (EC or PC) and solvents DMA or DMFA, organic carbonates solvate the membrane less effectively, and the average volume ratio of carbonate/DMA or DMFA is 4:6 for all membranes examined, regardless of the type of functional groups and anti-injection. When solvated by the DMA-DMFA mixture, the volume ratio of the first component to the second component in the membrane is also 4:6. The solvation ability of the studied solvents in polystyrene-based membranes decreases in the following series:  $\text{DMSO} > \text{DMF} > \text{DMA} > \text{EC} \sim \text{PC}$ . It was further shown that the ionic conductivity of the polymers containing  $[\text{R-SO}_2\text{X}]^-\text{Li}^+$  groups in contact with aprotic solvent mixtures decreases along the sequence  $\text{R-SO}_2\text{N}^-\text{SO}_2\text{CF}_3 > \text{R-SO}_2\text{N}^-\text{SO}_2\text{CCl}_3 > \text{R-SO}_2\text{N}^-\text{SO}_2\text{PhNO}_2 > \text{R-SO}_2\text{N}^-\text{SO}_2\text{PhCF}_3 > \text{R-SO}_2\text{N}^-\text{SO}_2\text{Ph} > \text{R-SO}_3^-$ . The maximum ionic conductivity was for trifluorosulfonylimide based membrane, which is 1 mS/cm at room temperature in contact with the EC-DMA mixture.

## References:

1. Deng K., Zeng Q., Wang D., Liu Z., Qiu Z., Zhang Y., Xiao M., Meng Y. Single-ion conducting gel polymer electrolytes: design, preparation and application // *J. Mater. Chem. A* 2020, 8, 1557–77.
2. Voropaeva D., Golubenko D., Merkel A., Yaroslavtsev A. Membranes with novel highly-delocalized sulfonylimide anions for lithium-ion batteries // *J. Membr. Sci.* 2020, 601, Art. No 117918.

<sup>1</sup>Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky Avenue, 119991 Moscow, Russia

# Search of zinc-containing solid electrolytes

**Yudova O.A., Morkhova Ye.A., Kabanov A.A.**

ol.yudova2000@mail.ru

During the last decades, increasing attention has attracted to the solid ion-conducting materials with high ionic conductivity: solid ion conductors. Solid ion conductors are widely used in batteries and fuel cells. Currently, lithium-ion batteries are most widely used, and sodium-ion batteries are very close to commercialization. However, the development of new batteries containing high-valence working ions is promising. Such batteries are safer and theoretically have a higher volumetric energy density than lithium-ion batteries [1]. In this work, an extensive search was carried out for cathode materials and solid electrolytes for zinc-ion batteries. Among metal-ion batteries with bivalent working cations, zinc-ion batteries seem promising due to low cost of raw materials, electrochemical reversibility of Zn and its stability in aqueous electrolytes.

Our theoretical search based on the following main steps: geometric-topological analysis [2], modeling by the BVSE method and calculations within the density functional theory. As a result, the most promising zinc-ion solid electrolytes were selected -  $\text{ZnP}_2\text{O}_6$  and  $\text{Zn}_3\text{O}(\text{SO}_4)_2$ . The size of their conduction channels is sufficient for the diffusion of zinc cations (Figure 1): from 1.65079 to 2.27854 Å for  $\text{ZnP}_2\text{O}_6$  and from 1.66841 to 2.19440 Å for  $\text{Zn}_3\text{O}(\text{SO}_4)_2$ . Both materials have a wide bandgaps: 4.716 eV for  $\text{ZnP}_2\text{O}_6$  and 3.364 eV for  $\text{Zn}_3\text{O}(\text{SO}_4)_2$ .

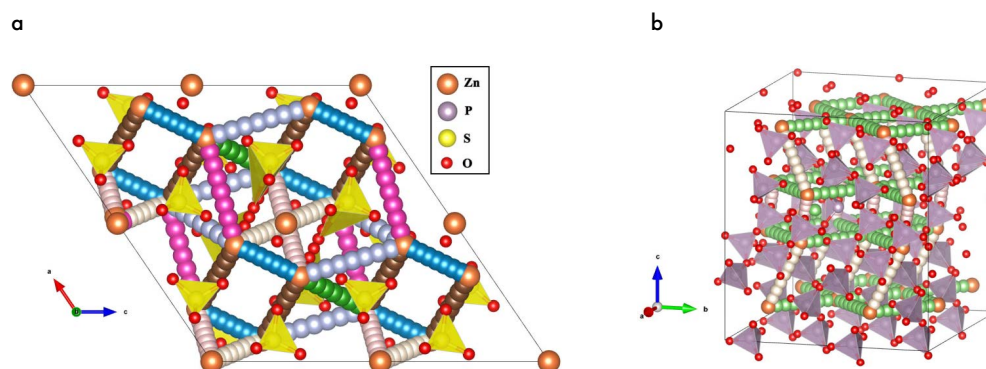


Fig. 1 – Migration maps and structure of  $\text{Zn}_2\text{S}_2\text{O}_7$  (a) and  $\text{ZnP}_2\text{O}_6$  (b) compounds.

## References:

- 1.Morkhova, Ye.A.; Rothenberger, M.; Leisegang, T.; Adams, S.; Blatov, V.A.; Kabanov, A.A. // J. Phys. Chem. C 2021, 125, 32, 17590–17599.
- 2.Blatov, V.A.; Shevchenko, A.P.; Proserpio, D.M. // Crystal Growth and Design 2014, 14, 7, 3576-3586.

<sup>1</sup>Samara State Technical University, Molodogvardeyskaya St. 244, 443100 Samara, Russia