9–13
November
2023

8th International School-Conference
of Young Scientists 2023

Crystallography and Crystal Chemistry of Energy Materials

Book
of Abstracts

Content

Proton Transport in Doped Layered Perovskites Based on $BaLn_nIn_nO_{3n+1}$

Abakumova E.V. [1,2], Bedarkova A.O. [1,2], Davletbaev K. [1,2], Tarasova N.A. [1,2], Animitsa I.E. [1,2]

[1] Institute of High Temperature Electrochemistry, UBRAS, Academic 20, 620066, Yekaterinburg, Russia
[2] Ural Federal University, Mira 19, 620000, Yekaterinburg, Russia

e.v.abakumova@urfu.ru

Hydrogen energy is one of the demanded branches of alternative energy today. Its active development requires the creation of high efficiency devices, including solid oxide fuel cells. Their usage makes hydrogen to be applied as a secondary energy carrier. One of the main components of such devices is a proton-conducting electrolyte. The development of this class of materials involves the study of compounds with various types of crystal structure, including block-layer structures. Promising proton conductors belonging to this class of compounds are doped complex oxides based on $BaLn_2In_2O_7$. The crystal structure of $BaLa_2In_2O_7$ consists of alternating salt layers containing lanthanum atoms (coordination number is 9) and oxygen, and perovskite blocks, each one contains two layers of $[InO_6]$ octahedra. Barium atoms are located in the interoctahedral space in perovskite blocks and are characterized by a coordination number of 12.

In this work, doped complex oxides based on $BaLn_2In_2O_7$ are obtained for the first time, and their structure, hydration processes, and transport properties are studied. The samples were synthesized by the solid phase method. X-ray diffraction confirmed the single-phase nature of the obtained samples. The ability for dissociative absorption of water molecules from the gas phase was confirmed by the method of synchronous thermal analysis in combination with mass spectrometry. The electrical properties of the obtained samples were studied by impedance spectroscopy. The studies were carried out in atmospheres with different partial pressures of oxygen and water vapor to isolate the contributions of partial conductivities (oxygen-ion, electron, and proton). It has been

established that doping leads to an increase in electrical conductivity by ~ 1 order of magnitude; in humid air at temperatures below 400 °C, the conductivity is ~95-98% proton.

Effect of ball milling parameters on the morphological and structural properties of LiFePO$_4$ cathode materials

Abanina A.V. [1], Styuf E.A. [1], Abakumov A.M. [1]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Moscow, Russia

A.Abanina@skoltech.ru

The tap density of electrode materials plays a pivotal role in determining their performance in energy storage systems. In the realm of lithium iron phosphate (LFP), a prominent cathode material for lithium-ion batteries, tap density directly influences electrode packing density, porosity, and consequently, overall electrochemical performance [1]. The ball size used during the milling process significantly influences the characteristics of lithium iron phosphate (LFP) electrode materials due to its impact on particle size reduction, homogenization, and structural properties [2]. The size of milling balls directly affects the mechanical forces exerted on the material being milled, leading to a range of effects that influence LFP's characteristics. Smaller milling balls tend to impart higher levels of energy during collisions with the LFP particles, resulting in more effective particle size reduction. Finer particles offer larger surface areas, which can enhance electrode performance by facilitating faster ion and electron transport. The energy input from milling balls influences not only particle size but also the crystallinity and defect structure of LFP.

Utilizing a systematic approach, we conducted a series of experiments involving varying sizes of milling balls and time of milling during the preparation of LFP. LiFePO$_4$/C was prepared by a mechano-chemical activation, spray-drying, and further annealing process.

All the starting materials were put into a ceramic cylindrical container with zirconia balls (ball-to-powder weight ratio of 8:1) and ground in a planetary ball mill for 2–6 h. The mixture was initially spray-dried and then calcined at 750°C. Three ball milling ways were tried, i.e., ball milling with 0.5, 1, and 3 mm zirconia balls. The structures of the samples were characterized by X-ray powder diffraction. The morphologies of the samples were observed by transmission electron microscopy. The particulate morphologies of the synthesized $LiFePO_4/C$ were also examined by a scanning electronic microscope. The tap density was measured on the Quantachrome Autotap device. During the study, it was determined that the optimal size of zirconium balls is 1 mm (tap density is 1.54 g/cm^3). When using balls with a diameter of 0.5 and 3 mm, the tap density of the material decreased. Smaller balls with higher energy impacts can lead to more intense collisions between particles, potentially causing particle agglomeration or sticking. Agglomerated particles might not pack as effectively, resulting in lower tap density (tap density is 1.28 g/cm^3). In the case of balls with a diameter of 3 mm, they are disproportionately large relative to the agglomerates that need to be crushed (tap density is 1.36 g/cm^3).

References:

1. Wang, X.; Wen, L.; Zheng, Y.; Liu, H.; Liang, G. // *Ionics* 2019, 25, 4589–4596
2. Zhang, D.; Cai, R.; Zhou, Y.; Shao, Z.; Liao, X.Z.; Ma, Z.F. // *Electrochimica Acta* 2010, 55, 2653–2661

The role of nitrogen heteroatoms in the lithiation process of doped MoS$_2$

Alekseev V.A. [1], Bulusheva L.G. [1]

[1] NIIC SB RAS 3, Acad. Lavrentiev Ave., 630090, Novosibirsk, Russia

valexev01@gmail.com

Molybdenum disulfide (MoS$_2$) is a promising anode material due to its layered structure and high theoretical capacity of 670 mAm·h·g^{-1}. However, due to the low electrical conductivity and poor reversibility of the conversion reaction, pure MoS$_2$ requires modification, the simplest of which is doping. Nitrogen atom can act as an impurity atom from available precursors and is suitable for MoS$_2$ doping according to existing methods [1, 2]. Several experimental works showed that the presence of nitrogen heteroatoms leads to enhanced electrochemical capacity in MoS$_2$ [2], as well as in MoS$_2$ based composites [3]. However, there is no possibility to reveal the effect of nitrogen atoms from general electrochemical measurements of the obtained material. The aim of the present work is to model the lithiation process of N doped MoS$_2$ and to distinguish the role of nitrogen in the observed enhancement independently of other possible structural features.

The quantum chemical approach is suitable for this investigation because it allows to model the properties of distinct structures with desired structural features. For the DFT calcula-tions, we used the plane-wave based package Quantum Espresso. The DFT calculations were accompanied by ab initio Car Parrinello molecular dynamics simulations to verify the dynam-ical stability of the MoS$_2$ models considered. During our investigation MoS$_2$ models with 0, 4.2, 12.5 at. % nitrogen concentratons were constructed as 4×4×1 supercells. For each of the doping ratios considered, ten supercells with different relative nitrogen heteroatom distributions were optimised, and structures with the lowest total energies were considered to be the most favourable. We then compared the be-haviour of pristine and nitrogen-doped MoS$_2$ during lithiation. Nitrogen-doped MoS$_2$ showed

no significant preference for concentrating Li ions compared to pristine MoS_2, which shows that the increase in capacity is not due to a higher concentration of Li atoms around the nitro-gen active sites. In addition, AIMD simulations of model structures were performed, which showed that 12.5 at.% doped MoS_2 starts to decompose at lower Li concentrations compared to pristine and 4.2 at.% doped MoS_2. In summary, it was showed that concentrating of lithium atoms around nitrogen active sites can not explain increase in capacity. It has also been shown that doping MoS_2 at high concentrations can lead to premature decomposition of the material. Thus, it is most likely that the role of nitrogen in the lithiation process is mainly to increase the electrical conductivity, which consequently increases the columic efficiency of the material.

References:

1. Azcatl, A. et al. Covalent Nitrogen Doping and Compressive Strain in MoS_2 by Remote N2 Plasma Exposure.// Nano Letters. 2016. V. 16. №. 9. P. 5437–5443.
2. Liu Q. [и др.]. The origin of the enhanced performance of nitrogen-doped MoS_2 in lithium ion batteries // Nanotechnology. 2016. № 17 (27).
3. Lim, H., Kim, H., Kim, S. O. & Choi, W. Self-assembled N-doped MoS_2/carbon spheres by naturally occurring acid-catalyzed reaction for improved sodium-ion batteries. Chemical Engineering Journal 387, 124144 (2020).

Comprehensive theoretical search for new materials with the perovskite structure type for solid oxide fuel cells

Antonyuk A.V. [1], Morkhova Ye.A. [1], Kabanov A.A. [1]

[1] SCTMS, Samara State Technical University, 443110 Samara, Russia

al.antonyk.2001@mail.ru

The $LnMO_3$ perovskites (Ln is any lanthanides, M is a metal with oxidation state +3) are promising materials for solid oxide fuel cells (SOFC) [1]. Such perovskites do not contain alkaline earth metals, the presence of which leads to the degradation of ceramics due to carbonization of the materials. Also particular attention is paid to the search for oxygen-ionic conductors among ternary and quaternary compounds containing large cations, specifically lanthanides, thus providing exclusively oxygen-ionic conductivity and stability in a reducing atmosphere [2]. Here we investigated the oxygen-ionic conductivity in the $LnMO_3$ compounds with rhombohedral and cubic symmetries (totally, 474 entries from the Inorganic Crystal Structure Database, version 2023/1). We used automated methods of crystal chemistry for the analysis of ion migration pathways, including the geometrical-topological (GT) analysis [3] and the bond valence site energy (BVSE) method [4]. GT analysis reveals 372 structures with oxygen migration channels, which is a prerequisite for ionic conductivity. As is known, the ionic conductivity is higher in those structures in which the ionicity degree of the Ln-O and M-O bonds is the lowest [5]. We calculated the ionicity degree (I, %) for each structure and selected 55 most promising compounds with I < 60%. These structures were further processed by the BVSE method to evaluate the oxygen migration energy (E_m, eV). As a result, 35 out of 55 structures had Em of less than 1 eV. For these most promising structures, we additionally calculated the band gap (E_g, eV) within density function theory calculation in the VASP package [6]. Thus, we have roughly divided the resulting structures into solid electrolytes (E_g >3.0 eV – 5 compounds) and electrodes (E_g <3.0 eV – 30 compounds).

References:

1. Lybye, D.; Poulsen, F.W.; Mogensen, M. // *Solid State Ionics* 2000, 128, 91–103.
2. Ishihara, T.; Kilner, J. A.; Honda, M.; Takita, Y. // *J. Am. Chem. Soc.* 1997, 119(11), 2747-2748.
3. Blatov, V.A.; Ilyushin, G.D.; Blatova, O.A.; Anurova, N.A.; Ivanov-Schits, A.K.; Dem'yanets, L.N. // *Acta Crystallogr. Sect. B* 2006, 62, 1010–1018.
4. Adams, S.; Rao, R. P. // *Bond Valences* 2014, 129-159.
5. Morkhova, Y. A.; Orlova, E.I.; Kabanov, A.A.; Sorokin, T.A.; Egorova, A.V.; Gilev, A.R.; Kharitonova, E.P.; Lyskov, N.V.; Voronkova, V.I.; Kabanova, N.A. // *Solid State Ionics* 2023.
6. Kresse, G.; Furthmüller, J. // *Phys. Rev. B.* 1996, 54, 11169–11186.

Synthesis and characterization of catalysts with the structure of perovskites and Ruddlesden-Popper for the electrochemical oxidation of carbamide

Atoian Edita [1], Pavel Sinitsyn [1], Vitaly Kuznetsov [2]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Moscow 121205, Russian Federation;
[2] Mendeleev University of Chemical Technology of Russia, Moscow 125047, Russian Federation

edita.atoian@skoltech.ru

The purpose of this work was to choose the most efficient method for the synthesis of catalysts with the structure of perovskites and Ruddlesden-Popper from the ones presented to date. The literature review presents the characteristics of the structure, properties, and various methods for the synthesis of perovskites and Ruddlesden-Popper phases.
Target single-phase products, namely $LaNiO_3$, La_2NiO_4, $LaSrNi_{0.5}Co_{0.5}O_4$, $LaSrNiO_4$, $LaSrCo_{0.5}Fe_{0.5}O_4$, were obtained using the ultrasonic spray pyrolysis method, which showed the highest efficiency, exactly with the accuracy of solid-phase synthesis and sol-gel. Quantitative and qualitative analysis of all obtained phases, carried out using X-ray diffraction analysis, namely the method of powder X-ray diffraction.

ABSTRACTS OF PARTICIPANTS

The structure was refined using the Jana2006 program using the Rietveld and LeBaile methods.
In the section "Chapter 2" all the experimental methods used in this work are discussed in detail.

References:

1. Wolfram, T. Electronic and Optical Properties of d-band Perovskites. / T. Wolfram, S. Ellialtioğlu; Cambridge University Press. – New York: 2006. – 364 P. – ISBN-10 : 0521850533.
2. Beznosikov, B. V. Perovskite-like crystals of the Ruddlesden-Popper series / B. V. Beznosikov, K. S. Aleksandrov // Crystallography Reports. – 2000. – Vol. 45, №5. – P. 792–798.
3. Zheng, Y.-S. Electronic Origin of Oxygen Transport Behavior in La-Based Perovskites: A Density Functional Theory Study / Y.-S. Zheng, M. Zhang, Q. Li, Y.-A. Zhu, Z.-J. Sui, D. Chen, X.-G. Zhou // The Journal of Physical Chemistry C. – 2019. – Vol. 123, №1. – P. 275–290.

Effect of doping with calcium on the oxygen conductivity of $Nd_{14}W_4O_{33}$

Baldin E. D. [1], Shlyakhtina A. V. [1], Lyskov N. V. [2,3], Vorobieva G. A. [1]

[1] N.N. Semenov Federal Research Center for Chemical Physics RAS, 119991 Moscow, Russia
[2] Federal Research Center of Problems of Chemical Physics and Medical Chemistry RAS, 142432 Chernogolovka, Russia
[3] Faculty of Physics, National Research University "Higher School of Economics", 105066 Moscow, Russia

baldin.ed16@physics.msu.ru   baldin@chph.ras.ru

The R_2O_3–WO_3 systems (R=Ln, Y) are abundant in compounds potentially applicable as materials for hydrogen energy. The most outstanding of these is the family of $La_{6-x}WO_{12-\delta}$ solid solutions based on La_6WO_{12}, which have a high proton conductivity and can be used as solid electrolytes for fuel cells or membranes for hydrogen separation. Additionally,

the predominant oxygen-ionic conductivity was found in compounds $Ln_2W_3O_{12}$ (Ln = La, Sm, Eu, Gd) having a structure of the defective scheelite type.

Until recently, the properties of tungstates $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb) have remained unexplored. McCarthy et al. [1] were the first to attempt solving the structure of $Ln_{14}W_4O_{33}$ in the 1970s. He noticed that heavy REE tungstates (Ln = Er-Lu) crystallize in a simple rhombohedral cell, while tungstates of lighter and larger REE (Ln = Nd-Dy) have a much more complex structure. The diffraction patterns of $Ln_{14}W_4O_{33}$ (Ln = Nd–Dy) contained only 4 unsplit reflections. In 1996, a Swedish team made an attempt to describe the structure of $Gd_{14}W_4O_{33}$ using a body-centered monoclinic unit cell model, but later research showed that this model was not valid [2]. Currently, the structure of $Ln_{14}W_4O_{33}$ with large rare-earth cations is still unresolved to the best of our knowledge. The conductivity of $Nd_{14}W_4O_{33}$ was measured for the first time in [3]. It was found to be a stable oxygen-ion conductor with a conductivity of $\sigma = 4 \times 10^{-4}$ S/cm at temperatures up to 700°C. At higher temperatures, it had an additional electronic contribution to the conductivity. This work focuses on investigating the effect of heterovalent doping with calcium on the conductivity and structural features of Nd14W4O33.

References:

1. McCarthy, G.J.; Fischer, R.D.; Jonson, G.G.; Gooden, C.E. // *Journal of Solid State Chemistry* 1972, 364, 397–410.
2. Nilsson, M.; Grins, J.; Käll, P.-O.; Svensson, G. // *Journal of Alloys and Compounds.* 1996, 240,60–69. https://doi.org/10.1016/0925-8388(96)02325-0.
3. Shlyakhtina, A.V.; Baldin, E.D.; Vorobieva, G.A.; Kolbanev, I.V.; Stolbov, D.N.; Kasyanova, A.V.; Lyskov, N.V. // *International Journal of Hydrogen Energy* 2023, 48, 22671–22684, doi:10.1016/j.ijhydene.2023.03.259.

Structure and properties of $K_2Mn[Fe(CN)_6]$ cathode material synthesized via ion-exchange of cubic ammonium Prussian Blue for potassium-ion batteries

Batkova Y.O., Morozova P.A., Fedotov S.S.

Skolkovo Institute of Science and Technology, 121205 Moscow, Russia

Yana.Batkova@skoltech.ru

Batteries are one of the most powerful tools for autonomous efficient energy storage. Among all types of batteries, lithium-ion batteries (LIBs) are popular devices in portable electronics and electric vehicles. However, the price of lithium components has been increasing incessantly, which initiates a search of cheap, abundant, and effective system for energy accumulation. Potassium-ion batteries (PIBs) are considered as a promising alternative for stationary energy storage technology. The family of compounds, also called Prussian Blue Analogues (PBAs) with formula $K_2M_1[Fe(CN)_6] \bullet zH_2O$ (KMiF) attracts many attention as a perspective positive material for potassium-ion batteries. However, a formation of defects that occurring in the structure during synthesis obstacle the development these materials [1]. The use of some reagents can prevent the appearance of these defects [2], but an additional step increases the final cost of the production technology. Therefore, improved synthesis method is needed both to keep low cost and decrease the defectiveness of the crystal structure. The use of an ammonium cation can allow obtaining a defect-free crystal structure together with the highest symmetry due to NH_4^+ yields a less number of water molecules in the first solvation shell than K^+ in aqueous solutions [3]. Therefore, the less ion-water interaction, the less water insertion into the structure. Taking it into account, we obtained $(NH_4)_xMn[Fe(CN)6] \bullet zH_2O$ (NH₄MF) by a co-precipitation method from $Na_4Fe(CN)_6$ and $(NH_4)_2SO_4$ solutions, and followed by a dropwise added $MnSO_4$ solution prepared in citric acid buffer. After that, $K_3C_6H_5O_7$ was dropped into the solution to get a final compound $K_xMn[Fe(CN)_6] \bullet zH_2O$ (KMF) for PIBs. We refined the crystal structures of the phases by XRPD using the Rietveld method. The NH₄MF phase was crystallized in the cubic symmetry of the space group Fm$\bar{3}$m. After the ionic exchange of ammonium for potassium ions,

the KMF phase transforms to the monoclinic symmetry with the space group P21/n. Occupation of potassium atoms in the unit cell of KMF was refined and the composition corresponds to $K_{1.92}Mn_{0.98}[Fe(CN)_6] \bullet zH_2O$ that has a close value to the theoretical one. KMF delivers an initial discharge capacity of 131 mAh g^{-1} at C/10 rate and saves the capacity of 75 mAh g^{-1} at 1C. Thus, the cathode material $K_{1.92}Mn_{0.98}[Fe(CN)_6] \bullet zH_2O$ was obtained through the formation of an intermediate product of ammonium Prussian Blue. Obtaining a cubic phase prevents water defects implementation while synthesis, and forms the compound with a high potassium content without the use of expensive reagents. Thus, we used the synthesis method by obtaining an intermediate precursor, which contributes to obtaining a defect-free structure and development of cathode materials technology for PIBs.

References:

1. Fiore, M.; Wheeler, S.; Hurlbutt, K.; Capone, I.; Fawdon, J.; Ruffo, R.; Pasta, M. // *Chemistry of Materials* 2020, 32(18), 7653-7661.
2. Deng, L.; Qu, J.; Niu, X.; Liu, J.; Zhang, J.; Hong, Y.; Feng, M.; Wang, J.; Hu, M.; Zeng, L.; et al. // *Nature communications* 2021, 12(1), 2167.
3. Aydin, F.; Zhan, C.; Ritt, C.; Epsztein, R.; Elimelech, M.; Schwegler, E.; Pham, T. A. // *Physical Chemistry Chemical Physics* 2020, 22(4), 2540-2548.

The modeling of CeO_2(100)/Cu nanocomposite's interfacial perimeter

Evgeny N. Cherkovskiy [1]

[1] Federal Scientific Research Center "Crystallography and Photonics" of Russian Academy of Sciences, Leninskiy prospekt, 59, 119333 Moscow, Russia

ev.cherkovskiy@gmail.com

Nowadays, one of the most important directions of technological development is the engineering of systems that operate with alternative energy sources—for example, fuel cells with a proton-exchange membrane, that allows to use redox reactions of hydrogen to produce electricity. One of the cheapest and most efficient ways to increase the performance of such elements consists in adding nanocatalysts to their composition. Composites of that kind normally consist of transition metal oxides nanoparticles coated with noble metals in the form of mono—, biatomic layers or clusters [1].

The visualization of such nanomaterials' interfacial perimeter is a very challenging problem, so the methods of quantum mechanical modeling turn to be quite handy to solve it. In this work, the research was carried out using Quantum Espresso software [2, 3], the material to model was CeO_2/Cu composite. The crystal plane (100) was chosen as the cerium dioxide plane on which the copper layer was modeled, for it is the least studied plane of those whose filling with copper atoms significantly determine the catalytic properties [4]. In the process of consistent calculations, stable configurations of the copper—ceria interface perimeter were established. The formation energies of oxygen and copper vacancies in the modeled structures were calculated. The contribution of copper atoms, oxygen and copper vacancies to the compression of the surface layer of cerium dioxide was estimated, and a tendency of the copper—ceria distance to increase in the presence of oxygen vacancies was established.

In addition to the stable structures that were calculated, the nonstable character of some other configurations of the copper-cerium interface for the CeO_2(100) plane has been established.

References:

1. Shanghong Zeng, Kewei Liu, Lu Zhang, Bin Qin, Tianjia Chen, Yueling Yin, Haiquan Su. Deactivation analyses of CeO_2/CuO catalysts in the preferential oxidation of carbon monoxide // *Journal of Power Sources* 2014, 261, 46–54.
2. P. Giannozzi et al. // *J. Phys.:Condens. Matter* 2009, 21, 395502.
3. P. Giannozzi et al. // *J. Phys.:Condens. Matter* 2017, 29, 465901.
4. Yan Zhou, Aling Chen, Jing Ning, Wenjie Shen. Electronic and geometric structure of the copper-ceria interface on Cu/CeO_2 catalysts // *Chinese Journal of Catalysis* 2020, 41, 928–937.

Influence of pre-synthesis on LAGP properties

Markov V.A. [1,2], Lebedeva M.A [1], Chernyavsky V.A. [1], Maksimov M.U. [1]

[1] Peter the Great St. Petersburg Polytechnic University, 195251 St. Petersburg, Russia
[2] Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, 199034, St. Petersburg, Russia

vlad.djxdr@gmail.com

Among oxide systems, polycrystalline structures of the NASICON type are one of the most promising candidates for the role of a solid electrolyte. The most promising systems are $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) and $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) [1,2] these systems have high chemical and electrochemical stability, high mechanical strength.
In this work, a new technique has been developed that allows to reduce the temperature and time of synthesis of LAGP by the traditional method from 1400 C to 1230 C, from 1-2 hours to 45 minutes, and also makes it possible to use conventional Al_2O_3 crucibles and muffle furnaces instead of expensive high-temperature ones. The specific conductivity of LAGP samples obtained by this method is $5.2 * 10^{-4}$ Cm/cm. To study the electrochemical characteristics, LAGP

samples were tested in symmetrical Li|LAGP|Li cells. The average overvoltage at a current density of 200 µA/ cm^2 was 0.09 V; 400 µA/ cm2 – 0.27 V.
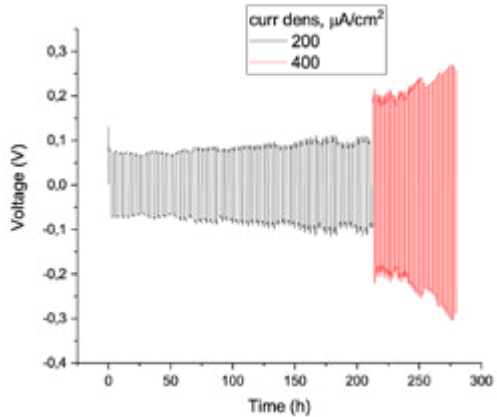
Figure 1. Chronopotential curves of the test sample.

References:

1. Kosova N. V. et al. Lithium conductivity and lithium diffusion in NASICON-type $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ (x=∈0; 0.3) prepared by mechanical activation // *Ionics* (Kiel). 2008. Vol. 14, № 4. P. 303–311.
2. Zhao E. et al. Facile synthesis and performance of NASICON $Li_{1+x}AlxGe_{2-x}(PO_4)_3$ electrolytes for all solid state lithium-ion battery // *Solid State Ion.* Elsevier B.V., 2020. Vol. 356.

Microstructural features of Ni-rich layered oxides with different transition metals distribution through the particles as cathode materials for Li-ion batteries

Dikhtyar Yu.Yu. [1], Savina A.A. [1]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel Str. 3, 121205 Moscow, Russia

yurydikhtyar@gmail.com

Over the last decade, the production of electric-powered transport has increased in an attempt to reduce human impact on the environment. The energy source in electric vehicles is traditionally Li-ion batteries (LIBs) due to their high specific energy density. The positive electrode (cathode) is known to play key role in determining both final cost and performance of LIBs. Currently, layered oxides of Li and transition metals $LiNi_xMn_yCo_z$ (NMCxyz, x+y+z = 1) with high Ni content, so-called Ni-rich NMCs, have become one of the preferred cathode materials for advanced LIBs due to their high reversible electrochemical capacity (up to 220 mAh/g), energy density (up to 800 Wh/kg) and low cost [1]. Improving the performance characteristics by doping the structure with different ions has been widely investigated [2]. Therefore, it is of interest to develop chemical approaches for directed microstructure design. In this work, the influence of different variants of cation distribution through the spherical-like particles on their microstructural features of Ni-rich layered oxides is investigated. The layered oxide $LiNi_{0.75}Mn_{0.25}O_2$ was chosen as a model system. First, three samples $Ni_{0.75}Mn_{0.25}(OH)_2$ were obtained by co-precipitation technique: the mixed hydroxide with a uniform cation distribution (1), with gradient concentration structure (2), and a core-shell structure (3, core – $Ni(OH)_2$, shell – $Mn(OH)_2$). The precursors were further mixed with Li source and annealed in oxygen flow. The obtained polycrystalline samples were investigated by powder X-ray diffraction (PXRD), scanning and transmission electron microscopy (SEM, TEM). Research results can be used for further improving of LIBs industry in Russian Federation.

References:

1. Abakumov, A.M.; Fedotov, S.S.; Antipov E.V.; Tarascon J.-M. // *Nat. Commun.* 2020, 11, 4976
2. Ko, G..; Jeong, S.; Park, S.; Lee, J.; Kim, S.; Shin, Y.; Kim W.; Kwon K. // *Energy Storage Mater.*, 2023, 60, 102840

Ni-rich layered oxides with core-shell structure as positive electrodes for next generation Li-ion batteries

Dolzhikova E.A. [1], Sitnikova L.A. [1], Savina A.A. [1], Abakumov A.M. [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205, Moscow, Russia

Ekaterina.Dolzhikova@skoltech.ru

Layered lithium and transition metals oxides $LiNi_xMn_yCo_zO_2$ (x + y + z = 1) with high nickel content (x>0.6) demonstrate high electrochemical capacity (~220-240 mAh/g at 2.7-4.3 V vs. Li/Li^+) and high energy density (800-900 Wh/kg) and are considered to be the most promising candidates as cathode materials for next generation Li-ion batteries (LIBs). However, due to low cycling life and low thermal stability, these materials are limited in practical application in LIBs [1]. One of the promising approaches to solve the mentioned problems is development of core-shell structured NMCs, where Ni-rich NMC as high-capacity sources act as the core, while more stable layered oxides are chosen as the shell [2-3]. In this work, a series of core−shell structured cathode materials $Li[(Ni)_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})x]O_2$ and $Li[(Ni_{0.95}Co_{0.025}Mn_{0.025})_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})_x]O_2$ with different thickness (x = 0.1, 0.2) of the shell were prepared via co-precipitation synthesis technique. Based on the powder X-ray analysis, all samples are single-phase without foreign impurities. According to SEM and EDX analysis, 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 of the $Li[(Ni)_{1-x}(Ni_{0.6}Mn_{0.2})_x]O_2$ and

$Li[(Ni_{0.95}Co_{0.025}Mn_{0.025})_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})_x]O_2$ (x = 0, 0.1, 0.2) was evaluated via prolonged galvanostatic cycling test. Thus, capacity retention increased by 20% for core-shell structured Ni-rich NMCs compared to unmodified samples.

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. Sun, Yang-Kook, et al. "Synthesis and characterization of Li $[(Ni_{0.8}Co_{0.1}Mn_{0.1})_{0.8}(Ni_{0.5}Mn_{0.5})_{0.2}]O_2$ with the microscale core−shell structure as the positive electrode material for lithium batteries." Journal of the American Chemical Society 127.38 (2005): 13411-13418.
3. Sun, Yang-Kook, et al. "High-energy cathode material for long-life and safe lithium batteries." Nature materials 8.4 (2009): 320-324.

Tortuosity in sodium-vanadium phosphate cathodes as a performance limiting factor

Dyakonov A.K. [1], Zakharkin M.V. [1], Nikitina V.A. [2,1]

[1] M. V. Lomonosov Moscow State University, Leninskie gory GSP-1, 11991 Moscow, Russia
[2] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel Str. 3, 143026 Moscow, Russia

andrei.diakonov@chemistry.msu.ru

Nowadays metal-ion batteries (MIB) have become a crucial part of energy sources. However, one of the main challenges for battery R&D is to achieve higher power with minimal capacity losses and higher active material loading. With the increase of the current density, kinetic obstacles arise, which hampers battery performance. Many studies treat the rate limitations at the particle

level, analyzing the rates of solid-state diffusion, interfacial charge transfer and other microscopic events. However, under certain conditions, such as high current densities or low temperatures, other types of limitations prevail. The electrodes used in metal-ion batteries are porous composites, consisting of active material particles, conductive additive and a binder. For such objects, the major sources of rate limitations are diffusional losses in pores, filled with the electrolyte solution, and ohmic losses, due to low electronic conductivity of the composites [1]. Our study is focused on minimizing kinetic hinderances in MIB cathodes on the electrode level.

To characterize the porous structure quantitatively, the values of porosity and tortuosity are used, which are the fraction of empty space in the composite and the ratio of the real ion path in the electrode to the electrode thickness, respectively. While the porosity could be easily evaluated from the electrode volume and composite material density, tortuosity of a composite electrode is non-isotropic and can hardly be accurately calculated [2]. Here we propose a method for experimental electrode tortuosity evaluation using electrochemical impedance spectroscopy in symmetric two-electrode setup. Sodium-vanadium phosphate ($Na_3V_2(PO_4)_3$) [3] has been chosen as a model material for this study, as it demonstrates high theoretical capacity of 118 mAh/g for two Na^+-ions deintercalation per formula unit and superior capacity retention.

To test this method, we prepared electrodes with close porosity values, but different mass loading: 2, 9, 18 mg/cm². We concluded that the obtained tortuosity values do not depend on mass loading, which validates our approach.

As a continuation of this study, we attempted to prepare electrode with different architectures containing channel-like pores to minimize the tortuosity values and improve the rate capability [4]. Tortuosity values and high-rate performance were compared between samples with reduced tortuosity and samples with randomly distributed pores to draw conclusions about the effect of electrode architecture on battery performance.

References:

1. Heubner, C.; Nikolowski, K.; Reuber, S.; Schneider, M.; Wolter, M.; Michaelis, A. // *Batter. Supercaps.* 2021, 4, 268–285.
2. Ebner, M.; Wood, V.; Chung, D.D.-W.W.; García, R.E; // Adv. Energy Mater. 2014, 4, 1301278.
3. Zhu, Y.; Xu, H.; Ma; J., Chen; P., Chen, Y. // *J. Solid State Chem.* 2023, 317, 123669.
4. Zhang, X.; Ju, Z.; Housel, L.M.; Wang, L.; Zhu, Y.; Singh, G.; Sadique, N.; Takeuchi, K.J.; Takeuchi, E.S.; Marschilok, A.C.; Yu, G. // *Nano Lett.* 2019, 19, 8255–8261.

Facile and Scalable Liquid Metal Driven Synthesis of the Hollow Metallic Nanoparticles

Falchevskaya A., Leonchuk S., Vinogradov V.

ITMO University, Lomonosov street 9, 191002 Saint Petersburg, Russia

falchevskaya@scamt-itmo.ru

Liquid metals (Ga, GaIn, GaInSn) are a class of materials with both metallic and fluid properties. In the last decade, this material has penetrated almost all aspects of materials science, namely in the fields of biomedicine, optics, catalysis, and flexible electronics. Even in the context of nanoscience, liquid metals have proven themselves as tools for a wide variety of purposes. It should be noted that micro- and nanoparticles can be obtained from liquid gallium by simply dispersing a drop of metal in an ultrasonic bath, which attracted experimenters to its use. This approach favorably distinguishes them from other nanoparticles obtained by other, more laborious methods. Recently, more and more attention in various fields of science has been paid to transition metals. This is due to their commercial availability, great variety and wide range of properties, which in some cases exceed those for precious metals (gold, silver, platinum, palladium). To impart additional properties (for example, optical or catalytic), as well as to enhance them, many nanoparticles are converted into hollow nanocapsules,

which can be easily doped with various substances. At the same time, when it comes only to metal nanocapsules, the methods for their preparation are severely limited. In our study, we were able to obtain a library of hollow particles using a galvanic displacement reaction using liquid gallium nanoparticles as a "template". The method is simple and versatile (gallium can be replaced by more than 20 different metals). It can be controlled in terms of size, degree of substitution (ratio of metals) and surface morphology of the capsules [1]. In addition, we experimentally demonstrated laser color and brightness tuning for monolithic and hollow microcapsules made of liquid metals and their alloys in the entire visible range, demonstrating this effect for the first time on metal nanostructures [2]. Research has continued in several directions. The first of these is related to the expansion of the basic technology to non-aqueous media. Thus, it was possible to obtain highly crystalline germanium capsules, which cannot be done in aqueous media due to strong hydrolysis [3]. The second one has moved to the macroscale and is aimed at obtaining flexible electronics, including the methods of additive technologies. Such materials are planned to be used in the fields of energy and flexible electronics.

References:

1. Falchevskaya, A. S.; Prilepskii, A. Y.; Tsvetikova, S. A.; Koshel, E. I.; Vinogradov, V. V. Facile Synthesis of a Library of Hollow Metallic Particles through the Galvanic Replacement of Liquid Gallium. Chem. Mater. 2021, 33 (5), 1571–1580.
2. Falchevskaya, A. S.; Kulachenkov, N. K.; Bachinin, S. V.; Milichko, V. A.; Vinogradov, V. V. Single Particle Color Switching by Laser-Induced Deformation of Liquid Metal-Derived Microcapsules. J. Phys. Chem. Lett. 2021, 12 (32), 7738–7744.
3. Sharova, E. A., Falchevskaya, A. S., Leonchuk, S. S., Redkov, A., Nikolaev, V., & Vinogradov, V. V. (2023). Liquid metal-mediated fabrication of metalloid nanoarchitectures. Chemical Communications. 2023

Transport properties and structure of $SrHf_{1-x}R_xO_{3-\delta}$ (R = Y, Yb, Sc)

N.M. Filatov [1], S.A. Belyakov [1], L.A. Dunushkina [1]

[1] The Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russia

nmfilatow@yandex.ru

Currently, there exists an increasing interest in electrochemical energy, including the development of solid oxide fuel cells and electrolyzers, due to the aggravation of the global environmental and energy crises and necessity to switch to efficient and clean methods of generation, storage and transferring energy. Accordingly, the development of new solid electrolytes, which are the basis for electrochemical devices, is among the urgent tasks of mankind. Electrolytes based on hafnates of alkaline earth elements are poorly studied in comparison with to cerates and zirconates of alkaline earth elements [1,2],. However, they are known to have high chemical stability. W. Yang et al. [3] reported that hafnates of alkaline earth elements have higher ionic conductivity than zirconates. In addition, in the article [4] it was shown that hafnates are more thermally and chemically stable than cerates and zirconates. From the above it follows that strontium hafnates can find practical application in high-temperature electrochemical devices, therefore, the study of this class of substances is promising and relevant.

The samples of $SrHf_{1-x}R_xO_{3-\delta}$ (x = 0, 0.05, 0.10, 0.15; R= Y, Yb, Sc) were prepared by conventional high temperature solid-state reaction method. The phase characterization of the obtained samples was performed by X-ray diffraction method. The electrical conductivity of the samples was measured using a four-probe DC technique in the temperature range of 400–900 °C in dry and wet atmosphere. Additionally, the conductivity versus oxygen partial pressure, pO_2, was measured in a temperature range of 600–800 °C. We showed that at high temperatures (>750°C), the conductivities measured in dry and humid air are similar, while as the temperature decreases,

the conductivity in wet air exceeds the "dry" conductivity, which is typical for proton-conducting oxides.

The conductivity activation energy decreases with an increase in dopant concentration in both dry and wet air conductivity of samples increased with increasing of dopant concentration. In addition, we have found that the highest conductivity is given by doping strontium hafnates with scandium.

References:

1. Kim J.H., Kang Y.M.. Byun M.S., Hwang K.T. // *Thin Solid Films* 2011, 520, 3, 1015-1021.
2. Huang W., Li Y., Lu H., Ding Y., Liu Y. // *Ceram. Int.*, 2021, *47*, 34568–34574.
3. Yang W., Han C., Li Y., Zhou H., Liu S., Wang L., He Z., Dai L. // *Int. J. Hydrog. Energy.* 2021, 46, 35678-35691.
4. Yang W., Wang L., Li Y., Zhou H., He Z., Han C., Dai L.. // *Ceram. Int.*, 2021, *47*, 9273-9286.

Layered Ammonia Polyuranates: Structural Peculiarities

Evgeny Gerber [1], Anna Krot [1], Iurii Nevolin [1,2]

[1] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31/4, Leninsky pr., 119071 Moscow, Russia
[2] Lomonosov Moscow State University, Department of Chemistry, Leninskie gory GSP-1, 119991 Moscow, Russia

chem.gerber@gmail.com

One of the crucial steps of nuclear fuel cycle is a fabrication of fuel pellets. In case of UO_2 fuel, enriched UF6 is hydrolyzed and subsequently reacted with ammonia, forming the ammonia polyuranates $xUO_3 \cdot yNH_3 \cdot zH_2O$. Though properties of ammonium polyuranates have been actively investigated previously [1,2], neither the chemical composition, nor structure of such compounds have not been uniquely determined. It is still debated, whether $xUO_3 \cdot yNH_3 \cdot zH_2O$ are compounds of individual

phases with certain stoichiometry or a homogeneous system in which ratio of $UO_3/NH_3/H_2O$ can be varied continuously. The advancement of the characterization techniques, including synchrotron-based methods of X-ray diffraction (XRD) and neutron diffraction makes it possible to investigate structure of ammonium uranates even though only polycrystalline samples can be synthetically obtained. Technical achievements unsurprisingly resumed scientific interest to this problem[3, 4].

Here we showed the results of structural characterization of ammonia uranate system. All samples were synthesized by adding ammonia aqueous solution to solid UO_3 with various ratio of UO_3/NH_3. The precipitates were washed and investigated with a bunch of methods, including XRD, TEM, elemental analysis, infrared, Raman and EXAFS spectroscopies.

Table 1. Results of the structure solution for ammonium polyuranates.

	$3UO_3 \cdot NH_3 \cdot 5H_2O$	$2UO_3 \cdot NH_3 \cdot 3H_2O$
Space group	Pnnn	I212121
Formula units	6	6
a, Å	12.229(1)	12.175(1)
b, Å	15.012(1)	14.421(1)
c, Å	7.1327(8)	7.0691(7)
Rwp	0.0366	0.0498

It was found, that stoichiometry and synthesis time have a significant effect on the product properties, resulting in monophasic or polyphasic samples. The chemical composition of monophasic samples have been revealed and found to be $3UO_3 \cdot NH_3 \cdot 5H_2O$ and $2UO_3 \cdot NH_3 \cdot 3H_2O$. All samples possess a layer structure similar to uranium oxohydroxide (schoepite), with interlayer water partially substituted with NH^{4+}. Diffraction data was used for structure solution,

additional crystallographic information was obtained (Table 1).

References:

1. Cordfunke, E.H.P. // *J. Inorg. Nucl. Chem.* 1962, 24, 303-307.
2. Stuart, W.I.; Whateley, T.L. // *J. Phys. Chem. Lett.* 2016, 7, 3240–3245.
3. Schreinemachers, C.; Leinders, G.; Modolo, G.; Verwerft, M.; Binnemans, K.; Cardinaels, T. // *Nucl. Eng. Technol.* 2020, 52, 1013-1021.
4. Leinders, G.; Acevedo, B.; Jutier, F.; Colak, G.; Verwerft, M. // *Inorg. Chem.* 2023, 62, 9807-9817.

Single crystal Ni-rich layered cathode materials for LIBs with reduced cation disordering

E. Ivanova [1], A. Pavlova [1], I. Moiseev [1], A. Savina [1], A. Abakumov [1]

[1] Skolkovo University of Science and Technology, 121205 Moscow, Russia

El.Ivanova@skoltech.ru

The electromechanical capacity fade of polycrystalline cathode materials with the general formula $LiNi_xCo_yMn_zO_2$ (x+y+z=1, so-called NMCs) is known to cause by the destruction of secondary agglomerates along the intergranular boundaries of primary particles during lithium (de)intercalation. In contrast, the so-called "single crystal" cathodes are characterized by long cycling life due to the absence of an intergranular boundary and microcrack growth along those. It is necessary to note the direct proportional relationship between the nickel content in NMCs and the number of defects that affect the cyclic stability of the material and capacity retention. The standard temperature annealing of single-crystal NMCs is around 900 °C. Due to such extremely conditions ultra-high Ni-rich NMCs exhibit a large number of anti-site defects in the layered structure. For such a reason, the aim of this work is to investigate the influence of synthesis temperature on the formation of anti-site disordering for single crystal Ni-rich NMC with ultra-high Ni content ($LiNi_{0.95}Mn_{0.025}Co_{0.025}O_2$, SC-NMC95). A series of single crystal SC-NMC95 materials were obtained at different temperature (750-900 °C). According to powder X-ray diffraction analysis, a highly ordered hexagonal structure with α-NaFeO$_2$ structural type (*R*-3*m* space group) was confirmed for all samples. The unit cell parameters and degree of Li^+/Ni^{2+} disordering, occurred from partial exchange of the Li^+ (r_{IV} = 0.76 Å) and Ni^{2+} (r_{IV} = 0.69 Å) cations between the Li (3b) and Ni (3a) sites were calculated for all obtained samples via Rietveld refinement. The degree of Li^+/Ni^{2+} disordering is found to reduce with decreasing temperature annealing (from 4% (900 °C) to 0.1% (750 °C)). However, the particle growth is also reduced and the average size particles

does not exceed 3 µm. The results of galvanostatic cycling with potential limitation show that the obtained material with the lowest anti0site disordering demonstrates specific discharge capacity of 218 mAh/g at 0.1C (2.7-4.3 V vs. Li/Li$^+$).

Iron and manganese-based mixed phosphates as cathode materials for sodium-ion batteries

Jablanovic A. [1,2], Zakharkin M.V. [2], Drozhzhin O.A. [2], Antipov E.V. [1,2]

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

anastasija.jablanovic@skoltech.ru

Nowadays an increasing demand for electricity leads to necessity of the efficient energy storage systems production. Sodium-ion batteries (SIBs) present a promising candidate for this purpose due to the low cost, high gravimetric capacity and safety of these systems. The key task in the commercialization of SIBs is the development of materials, in particular cathode materials, for production of batteries with desired electrochemical characteristics.
Polyanionic compounds present one of the most promising classes of cathode materials for SIBs. Among such systems, mixed phosphates are of particular interest. Mixed phosphates present a class of compounds with a framework composed of phosphate (PO_4^{3-}) and pyrophosphate ($P_2O_7^{4-}$) groups linking cations of transition metals. The interest in these compounds is caused by relatively high values of their operating potential, as well as the possibility of achieving larger values of specific capacity compared to phosphates and pyrophosphates [1]. One of the possible ways to optimize the electrochemical characteristics of mixed phosphate cathode materials for SIBs is synthesis of solid solutions by substituting transition metals in these compounds [2].

The aim of this work is obtaining single-phase solid solutions of mixed phosphates with composition $Na_4M_3(PO_4)_2P_2O_7$ (where M = Fe, Mn), as well as study of the effect of composition on the electrochemical characteristics of cathode materials for SIBs. Synthesis was carried out by two methods: the sol-gel method and solid-state method. As a result, a range of substituted compounds $Na_4Fe_{3-x}Mn_x(PO_4)_2P_2O_7$ was obtained. The samples obtained by solid-state synthesis were characterized by a higher content of the target phase $Na_4Fe_{3-x}Mn_x(PO_4)_2P_2O_7$ compared to the sol-gel method. In a range of obtained solid solutions, linear changes in the unit cell parameters were observed. The effect of the duration, temperature and atmosphere of annealing on the phase composition of the resulting compounds was shown. Cathode materials for sodium-ion batteries were obtained on the basis of the synthesized compounds. The presence of additional electrochemical activity in the potential range of 3.6 – 4.1 V (vs Na^+/Na) was shown by the use of galvanostatic cycling for a number of substituted compounds.

Thus, the possibility of obtaining a range of solid solutions $Na_4Fe_{3-x}Mn_x(PO_4)_2P_2O_7$ (x = 0.15 – 2.75) has been demonstrated in the work and the effect of the manganese content in the solid solution on the electrochemical activity of this compound has been shown.

References:

1. Wu H. et al. Advances in Vanadium-Redoxed Polyanions for High-Voltage Sodium-Ion Batteries // *Batteries. MDPI AG*, 2023. Vol. 9, № 1. P. 56.
2. Kim H. et al. Highly stable iron-and manganese-based cathodes for long-lasting sodium rechargeable batteries // *Chemistry of Materials.* – 2016. – T. 28. – №. 20. –7241-7249.

Cation and anion diffusion in minerals: crystallochemical and DFT modeling

N.A. Kabanova [1]

[1] Samara State Technical University, Molodogvardeyskaya Str. 244, Samara 443100, Russia

weterrster@gmail.com

Despite the ever-increasing number of new synthetic compounds, modern materials science cannot developing without the study of natural objects. In this paper, we present the results of a study of the migration paths of cations and anions for minerals: murmanite, gurimite, badalovite, lintisite, sergeismirnovite carried out using modern methods of theoretical modeling (Voronoi method[1], tiling method[1], BVSE[2], DFT[3]). The geometric-topological method implemented to ToposPro package [1] is successfully applied to the analysis of empty space in the crystalline structures of inorganic materials[3]. For murmanite crystal structure $Na_2Ti_2(Si_2O_7)O_2 \cdot 2H_2O$ the 2D map of Na^+-migration (Fig.1) was obtained.
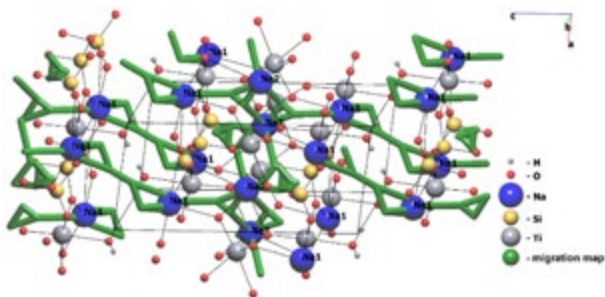
Fig. 1. 2D migration map of Na^+-ion diffusion for crystal structure of murmanite obtained by means GT-analysis.

Figure 2 shows the isosurface of sodium cation migration in the murmanite structure obtained by means BVSE calculations. The energy profile shows that the transition from the Na1 to Na2 position has a barrier above 1 eV.
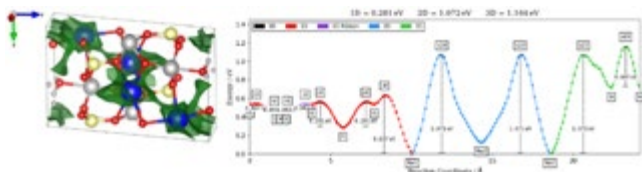
Fig. 2. 2D isosurfaces of the Na⁺-ion diffusion and corresponding energy profile of the activation barriers for murmanite structure calculated by means BVSE approach.

The results obtained using theoretical modeling were compared with experimental data. The correlations found will form the basis of future work on the search and design of new promising ion-conducting and ion-exchange materials.

References:

1. Blatov, V. A., Shevchenko, A. P., Proserpio, D. M. // *Cryst. Growth Des.* 2014., 14, 3576
2. S. Adams et al // *Chem. Mater.* 2021. V. 33. 625–641.
3. G. Kresse, J. Furthmüller, // *Phys. Rev. B.* 1996. V. 54. P. 11169–11186.

Optimization of the method for obtaining cathode materials based on layered oxides in the form of single-crystal particles for lithium-ion batteries

Yu. A. Klychevskikh [1], E. D. Ivanova [1], A. D. Pavlova [1], I. A. Moiseev [1], A. A. Savina [1], A. M. Abakumov [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205 Moscow, Russia

Yuliya.Klychevskikh@skoltech.ru

Ni-rich layered oxides $LiNi_xCo_yMn_zO_2$ ($x \geq 0.6$, $x + y + z = 1$) attract significant attention as cathode materials due to their high specific capacity, high operating voltage and reasonable cost [1]. However, such materials suffer from strong anisotropic lattice distortion during the charge-discharge process which leads to microcracks formation [2]. Obtaining single crystal particles allows to overcome the issue of intergranular cracking providing better performance of the material. Particle size as well as particle morphology affects the performance of the material: smaller particle sizes provide shorter lithium diffusion passage and it has been demonstrated that single-crystal Ni-rich NMC with a particle size of 2-5 μm are sufficient to supress intergranular cracking [3]. To obtain the desired properties and decrease the amount of Li/Ni exchange defects synthesis parameters can be varied. In the present study the influence of synthesis parameters such as flux composition and flux amount and precursor on the properties of NMC95 ($LiNi_{0.95}Co_{0.025}Mn_{0.025}O_2$, space group $R\text{-}3m$) material was investigated. Increase in initial concentration of NH_4OH from 1.0 M to 2.0 M during co-precipitation of precursor lead to increase in particle sizes of corresponding NMC95 samples as well as the number of defects (Ni in 3a site goes up from 3.34(7) to 4.78(5) %). The increase in flux amount from 0.4375 mol to 1.75 mol has similar effect on particle size distribution and the number of defects of corresponding samples. The amount of K-source in the flux was varied to demonstrate that with its increase from 10 to 20 % average particle size decreases while the number of defects lowers (from 4.04(7) to 3.34(7) %). Precursor with initial concentration of NH_4OH 1.0 M, 0.875 mol of flux of 80% LiOH, 20% K-salt proved to be the acceptable parameters to obtain NMC95

material at this stage. For the next stage of the research temperature of the first annealing is going to be optimized simultaneously with nflux and electrochemical performance of synthesized materials will be studied. The research was founded by Skoltech Translational Research & Innovation Program project 4-STRIP-5011_STRIP23-Abakumov.

References:

1. Wang, J. Y.; Guo, S. N.; Wang, X.; Gu, L.; Su, D. // *Journal of Electrochemistry* 2022, 28(2), 2108431.
2. Qian, G.; Zhang, Y.; Li, L.; Zhang, R.; Xu, J.; Cheng, Z., Xie S.; Wang H. et al. // *Energy Storage Materials* 2020, 27, 140-149.
3. Ryu, H. H.; Namkoong, B.; Kim, J. H.; Belharouak, I.; Yoon, C. S.; Sun, Y. K. // *ACS Energy Letters* 2021, 6(8), 2726-2734.

Investigation of the Mechanisms of Polaron Conduction in Cathode Materials of Na and K-Ion Batteries

Kovaleva Olga [1], Aksyonov Dmitry [1]

[1] Skoltech Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, 143026 Moscow, Russia

Olga.Kovaleva@skoltech.ru

Nowadays, the increasing demand for energy storage materials has resulted in extensive research on new electrode materials for metal-ion batteries. Na- and K-ion batteries are cheaper than Li-ion and can help mitigate the risks associated with lithium production concentrated in a few countries, as Na is one of the most abundant elements on Earth. However, Na-based materials may exhibit poor electronic conductivity, e.g. in the case of hexacyanoferrate (HCF) cathodes [1]. Therefore, it is important to investigate electron transport as it influences the battery rate performance. According to experimental results the rate performance of $KTiOPO_4$-type based (KTP) cathode materials

($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) is several orders of magnitude higher than that of hexacyanoferrate based (HCF) materials ($Na_2Fe_2(CN)_6$) [2, 3]. The physical reason for this difference remains unclear. Our hypothesis is that it is derived from the different transport of small polarons in this types of materials. Using Density Functional Theory (DFT) and linear interpolation scheme [4], we perform a computational study of small polarons and calculate polaron migration barriers and formation energies. Our study is focused on hole and electron polarons for intercalated ($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) and deintercalated structures (VPO_4F, $TiPO_4F$), respectively.

We showed that in KTP materials for non-equivalent transition metal sites within one structure the formation energies can differ up to 0.25 eV, leading to an increase in polaron migration barriers. For more symmetric octahedra the polaron localization is more preferable, while polaron formation energies are strongly affected by F displacement. Polaron migration barriers are increasing in the following order: $KVPO_4F$ < $NaVPO_4F$ < VPO_4F < $KTiPO_4F$ < $TiPO_4F$, meaning that the conductivity is decreasing in this row. For $KVPO_4F$ we have obtained the smallest migration barrier of 0.18 eV, which is even smaller than for $LiFePO_4$ [4]. Preliminary results for $Na_2Fe_2(CN)_6$ indicate that the difference in formation energies is greater than any migration barrier in KTP materials. This implies that the migration barriers should be even bigger, resulting in a decrease in conductivity in this material.

References:

1. Tennakone K., Dharmaratne W. G. D. // *Journal of Physics C: Solid State Physics.* 1983, 16, 5633.
2. Fedotov S. S. et al. // *Nature communications.* 2020, 11, 1484.
3. Shraer S. D. et al. // *Nature Communications.* 2022, 13, 4097.
4. Maxisch T., Zhou F., Ceder G. // *Physical review B.* 2006, 73, 104301.

NaK-78 Alloy as a Versatile Reagent for Porous Metalloid-Based Materials Synthesis

Leonchuk S.S. [1], Vinogradov V.V. [1]

[1] ITMO University, International Institute "Solution Chemistry of Advanced Materials and Technologies" (SCAMT), Saint Petersburg 191002, Russian Federation

leonchuk@scamt-itmo.ru

Liquid Ga-based metals have become exceedingly popular in materials synthesis and composites fabrication. The most recent advances in this field of materials chemistry are related with the production of metalloid-based materials using liquid metal emulsions as sacrificial reactive templates [1]. These materials with hollow morphology and controllable porosity are crucial for modern energy storage devices development. Particularly in Li- and Na-ion batteries such micro- and nanostructured materials allow to get over the volume expansion effect. Meanwhile, Ga-based liquid metals are quite limited reagents, which do not allow to synthesize silicon- or carbon-based materials due to the weak reduction potential. In this context, another liquid metal — sodium-potassium eutectic alloy (NaK-78), which possesses stronger reduction properties and can act as a reagent for metalloid-based materials synthesis — can reveal new facile synthetic methods [2]. Moreover, already developed NaK-assisted methods for the synthesis of mesoporous carbon, silicon and germanium promise to be a versatile and highly effective ways to produce materials for anodes in Li- and Na-ion batteries [3-5].

Synthesis of hollow silicon-, germanium-, tin-, and antimony-based microspheres was performed using the emulsion of liquid NaK-78 with ~ 5 μm particle size obtained through the sonication of NaK-78 in organic solvents: 1,2-dimethoxyethane (DME), m-xylene, and n-hexane. $SiCl_4$, $GeCl_4$, $SnCl_4$, and $SbCl_5$ were used as precursors. Concentration regimes of the reagents were varied from 0.010 to 0.025 to 0.050 M precursor solution. Obtained metalloid-based powders were characterized using XRD phase analysis, SEM particle morphology and size distribution analysis, EDX elemental analysis, nitrogen surface area and pore size analysis.

It was shown, that the proposed method allows to produce metalloid-based microspheres with porous shell structure. Crystallite size of by-products (KCl and NaCl) was calculated from XRD data and used as an evaluation parameter for macro- and mesopores size (~ 50 nm). Meanwhile, BJH and NLDFT calculations show mesopore structure of the resulted materials. All the synthesized samples are represented by amorphous metalloids as predominant phases. Increase in reagents concentrations leads to a higher reaction yield up to 30 %. Nature of the solvent plays a key role in the presented synthetic approach. DME allows to produce almost any metalloid-based material (including silicon) even at the room temperature, while hexane and xylene do not. The method is also scalable to other systems.

References:

1. Sharova E.A.; Falchevskaya A.S.; Leonchuk S.S.; Redkov A.V.; Nikolaev V.; Vinogradov V.V. // *Chem. Commun.* 2023, Advance Article.
2. Leonchuk S.S.; Falchevskaya A.S.; Nikolaev V.; Vinogradov V.V. // *J. Mater. Chem. A.* 2022, 10, 22955–22976.
3. Tang D.; Hu S.; Dai F.; Yi R.; Gordin M.L.; Chen S.; Song J.; Wang D. // *ACS Appl. Mater. Interfaces* 2016, 8, 11, 6779–6783.
4. Dai F.; Zai J.; Yi R.; Gordin M.L.; Sohn H.; Chen S.; Wang D. Nat. Commun. 2014, 5, 3605.
5. Tang D.; Yu H.; Zhao J.; Liu W.; Zhang W.; Miao S.; Qiao Z.-A.; Song J.; Zhao Z. // *J. Colloid and Interface Sci.* 2020, 561, 494–500.

HTiNbO$_5$ as anode material for LIB's: synthesis and mechanism of Li$^+$ electrochemical intercalation

Marenko A.P. [1], Alekseeva A.M. [1], Drozhzhin O.A. [1], Antipov E.V. [1,2]

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

marenko.andrey@mail.ru

Mixed oxides of titanium and niobium (TNO) are considered as safe anode materials for lithium-ion batteries (LIB's) with long cycling life. Such benefits are associated by both structural stability and relatively high working potentials of Ti(IV)/Ti(III) and Nb(V)/Nb(IV) redox couples (1.3 – 1.6 V vs. Li/Li$^+$) preventing SEI formation [1]. An additional attention has been attracted to HTiNbO$_5$ as the unique proton-containing anode material providing reversible capacity of ~120 mAh • g^{-1} after 50 cycles [2]. However, no detailed studying of Li$^+$ (de)intercalation in HTiNbO$_5$ can be found up to date. This work is devoted to synthesis and investigation of HTiNbO$_5$ as an anode material for LIB's.

In HTiNbO$_5$ structure [3] (sp. gr. Pnma, Z = 4, a = 6.531(1) Å, b = 3.7756(5) Å, c = 16.733(6) Å, V = 412.6(2) Å3) [(Ti,Nb)O$_6$] octahedra are sharing edges forming zig-zag ribbons (M$_2$O$_6$)∞ (M = Ti, Nb) connected in layers by common vertices. The stability of the described lamellar structure is ensured by the presence of strong O−H-O bonds between adjacent layers.

The single phase sample of HTiNbO$_5$ was obtained using preliminary synthesized sample of KTiNbO$_5$ via ion exchange process in 1 M aqueous solution of HNO$_3$. Applying scanning electron microscopy average particle size of 10 – 20 μm was defined. The electrochemical lithium (de)intercalation in HTiNbO$_5$ was investigated by a galvanostatic charge-discharge at 12 mA • g^{-1} rate using two-electrode cells assembled in argon-filled glove-box with 1 M solution LiPF$_6$ in EC/DEC as electrolyte and a lithium metal anode. Phase and structural transformations upon (de)intercalation of Li$^+$ were studied by operando and ex situ X-ray powder diffraction (PXRD).

Within the potential range of 1 – 3 V vs. Li/Li$^+$ the material exhibited stable cycling with one plateau at ~2 V. At the same time, from the first to the second cycle, the increase in the capacity was observed from 150 mAh • g^{-1} to 170 mAh • g^{-1}. From the second cycle, the reversible capacity exceeded 170 mAh • g^{-1} (after 10 cycles) which was the best achieved value for this material and corresponded to the reversible intercalation of 1.4 Li$^+$ per f.u. PXRD investigation revealed the irreversible two-phase transition during the first cycle. As a result, a new phase isostructural to LiTiNbO$_5$ [4] was formed. From the second cycle (de)lihitation proceeded via a solid solution mechanism with volume change smaller than ~6%.

References:

1. Han J.-T., Huang Y.-H., Goodenough J.B. // *Chemistry of Materials.* 2011, 23, 2027;
2. Colin J.F., Pralong V., Hervieu M., Caignaert V., Raveau B. // *Journal of Materials Chemistry.* 2008, 18, 3121;
3. Rebbah H., Pannetier J., Raveau B. // *Journal of Solid State Chemistry.* 1982, 41, 57.
4. Colin J.F., Pralong V., Caignaert V., Hervieu M., Raveau B. // *Inorganic Chemistry.* 2006, 45, 7217.

Ball-milling as a Tool For Grain Boundaries Engineering in Garnet-Type $Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ Solid Electrolyte

Markopolskii R. [1], Timusheva N. [1], Morozov A. [1], Savina A. [1], Abakumov A. [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

Roman.Markopolskii@skoltech.ru

All solid-state batteries (ASSBs) based on ceramic solid electrolytes are deemed to be a promising alternatives to the conventional liquid organic electrolyte due to potentially high specific gravimetric and volumetric energy density and higher safety [1]. One of the main features of ASSBs is the ability to accommodate Li-metal as an anode which results in a boost of specific energy density. However, one of the problems limiting the development of ASSB is a Li dendrite formation and growth upon cycling that inevitably causes short circuit. Solid-state electrolytes are usually polycrystalline ceramic materials which contain numerous grain boundaries. It is known that Li dendrite propagation takes place along the grain boundaries, hindering electrochemical behavior of solid electrolyte [2]. Therefore, it is important to establish the correlation between the microstructural features of solid-state electrolytes and their electrochemical performance which will contribute to the development of the all-solid-state battery with high energy density and extended cycle life.

That is why this work was focused on studying the influence of synthesis parameters on the microstructural organization of cubic garnet-type $Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ (Ga-LLZO) solid electrolyte. Ga-LLZO was chosen among different types of solid-state electrolytes because of high Li-ion conductivity ($\sim 10^{-3}$ - 10^{-4} S/cm at 25 °C), wide electrochemical stability window (0.05–5 V vs. Li/Li$^+$) and chemical stability against metallic Li [3]. We obtained single-phase Ga-LLZO electrolyte pellets with high relative density of > 90% by conventional solid-state synthesis with the implementation of ball-milling technique and isostatic pressing. The investigation was focused on different parameters of mechanoactivation and grinding step through ball-milling (e.g. solvent

media, grinding duration, Ga-LLZO powder to grinding balls mass ratio) and their impact on the microstructural organization of the solid electrolyte. The wide range of variable parameters of the ball-milling step provided an understanding how grinding conditions affect Ga-LLZO solid-state electrolyte grain structure. Further work will be dedicated to the investigation of the correlation between solid-state electrolyte microstructure and electrochemical properties.

References:

1. Yun-Chae Jung, Seul-Ki Kim, Moon-Sung Kim, Jeong-Hye Lee, Man-Seok Han, Duck-Hyun Kim, Woo-Cheol Shin, Makoto Ue, Dong-Won Kim // *Journal of Power Sources* 2015, 293, 675–683.
2. Milan E.R., Pasta M. // *Materials Futures* 2023, 2, 1, 0–17.
3. Shaojie Chen, Jingxuan Zhang, Lu Nie, Xiangchen Hu, Yuanqi Huang, Yi Yu, and Wei Liu// *Advanced Materials* 2021, 33, 1, 1–10.

Ni-rich NMC composite cathode materials containing $Li_2SO_{4-}Li_3PO_4$ solid electrolyte for Li-ion batteries

Mikheeva M. [1], Orlova E. [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

Maria.Mikheeva@skoltech.ru

Development of high-energy-density cathode materials for Li-ion batteries is a highly relevant field of study as a world moves towards more environmentally sustainable energy sources. Ni-rich NMC811 composite layered oxides are one of the most promising cathode materials with their high practical capacity of over 200 mAh/g and high energy density larger than 800 Wh/kg. However, Ni-rich NMCs have several drawbacks such as significant capacity drop over

prolonged cycling, that prevents them from widespread application. There are several strategies that are used to enhance the performance of Ni-rich NMC cathode materials, one of them – grain boundaries engineering with a Li-conductive solid electrolytes. It allows to improve mechanical properties of cathode materials and enhance Li-ion transportation between particles in agglomerate. Thus, the present work aims at obtaining composite cathode materials based on the Ni-rich NMC ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$), modified via $Li_2SO_{4-}Li_3PO_4$ solid electrolyte system, with enhanced electrochemical properties.

Modified cathode materials based on $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) were synthesized via co-precipitation method with $(NH_4)_2HPO_4$ as a phosphorus source. Five samples were obtained with various concentrations of added $(NH_4)_2HPO_4$. According to XRD analysis, all synthesized materials possess well-crystalline layered structure (s.g. R-3m) with a minor presence of additional phase isostructural to γ-Li_3PO_4. Peaks of this additional phase were shifted towards the smaller angles which suggests formation of a $Li_2SO_{4-}Li_3PO_4$ solid solution. SAED pattern, acquired from the additional phase, also corresponds to γ-Li_3PO_{4-} like phase. Results of HAADF-STEM and EDX-STEM and EELS elemental mapping showed that sulfur and phosphorus are simultaneously segregated on grain boundaries and intergranular contacts, which speaks in favor of solid solution formation instead of two separate phases. Effect of this modification on morphology and electrochemical performance was also investigated. BET analysis showed that sample, containing the largest amount of solid solution (2.18 mol. %) has the smallest surface area of 1.15 m²/g, while primary particles size remains the same of approximately 220-230 nm, indicating that solid electrolyte binder "closes" gaps between primary particles, preventing penetration of electrolyte into agglomerates. Electrochemical impedance spectra, which contain additional semi-circle, attributed to the resistance of solid electrolyte on grain boundaries, demonstrate decrease in charge transfer resistance with rise of solid electrolyte binder content. Due to the prolonged galvanostatic charge/discharge cycling in the 2.7-4.3 V vs. Li/Li⁺ potential range at different current densities from 0.1C to 1C (1C=200 mAh), it was established that composite

cathode materials based on the NMC811 and $Li_{2+x}S_{1-x}P_xO_4$ possess slightly increased rate capability, compared to the one, modified by Li_2SO_4 [1], and significantly enhanced stability as the capacity retention over 300 cycles at 1C elevated from 68% to 81%.

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 $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ as high-performance cathode material for Li-ion batteries. Nanomaterials. 2020; 10(12): 1-17. doi: 10.3390/nano10122381

NiO-SiO$_2$ defect structure investigation by PDF analysis and XRD simulation of 1D disordered crystal statistical models

M.D. Mikhnenko [1], S.V. Cherepanova [1], E.Yu. Gerasimov [1], V.P. Pakharukova [1], R.G. Kukushkin [1], O.A. Bulavchenko [1]

[1] Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5, Novosibirsk, Russia, 630090

m.mikhnenko@catalysis.ru

At present, the search for various energy sources based on renewable natural resources is being actively pursued in order to replace dwindling fossil reserves. One of these sources can be fuel synthesized via the processing of biomass obtained by fast pyrolysis. Ni-containing catalysts are promising candidates for processing such biomass. Another promising process is the NH_3 decomposition, which can be also used at power plants to use excess of the power produced in order to decrease idle time. To improve the textural characteristics of NiO-based catalysts and to change the activity and selectivity various additives are often used, which also influence the phase composition and structure of the catalyst. It was shown that using of Si as a modifier stabilizes

nanosized particles and provides high activity [1]. In the course of this work, the structural features of NiO-based nanostructured catalysts were investigated. The peculiarity of the systems under study was the stabilization of the oxide in highly dispersed form due to the introduction of silicon additives. X-ray diffraction of the catalyst differed from the "classical" X-ray diffraction of bulk nickel oxide and was characterized by certain features – different broadening of diffraction reflections – whose interpretation by standard methods did not give satisfactory results. Therefore, the catalyst was investigated by a set of diffraction techniques such as atomic pair distribution function calculation (PDF) and X-ray diffraction simulations by the Debye method. The data for the PDF calculation were obtained at the shared research center "Siberian Synchrotron and Terahertz Radiation Center" (SRC SSTRC) [2]. The following structural models were considered: (1) particle shape effect using cube, sphere, plate, and filament as examples, (2) different models of silicon embedding into nickel oxide structure. It was shown that inclusion of tetrahedral SiO_2 layers between octahedral NiO layers occurs. The results of transmission electron microscopy also confirmed this hypothesis and showed that the silicon is evenly distributed on the nickel oxide particles, the crystallites have a plate-like shape with a thickness of 1.5 nm and a width of 3 nm [3]. Stabilization mechanism of nanoparticles was also investigated using high temperature treatment. The results of TEM, XPS and XRD shows that decomposition of the initial state is occurring with the formation of pure NiO particles with Ni_2SiO_4 spinel layers. Thus, the suggestion that the Si aggregates to form spinel-type particles occurs and the evidence of Si-O-Ni interaction was obtained.

References:

1. Bykova M. V. et al. Guaiacol hydrodeoxygenation in the presence of Ni-containing catalysts // *Catalysis in industry* 2011, 3, 15-22.
2. Piminov PA, Baranov GN, Bogomyagkov AV, et al. // *Phys Procedia* 2016, 84: 19–26.

3. Mikhnenko, M.D.; Cherepanova, S.V.; Gerasimov, E.Y.; Pochtar, A.A.; Alekseeva, M.V.; Kukushkin, R.G.; Yakovlev, V.A.; Bulavchenko, O.A. // *Inorganics* 2023, 11, 97.

High-throughput crystallochemical search for promising Na⁺-ionic conducting chalcogenides

Morkhova Ye.A. [1], Antonyk A.V. [1], Kabanov A.A. [1]

[1] SCTMS, Samara State Technical University, 443110 Samara, Russia

eliztimofeeva@mail.ru

At present, lithium-ion batteries (LIB) are the most common, the production of which is facing the depletion of lithium resources. Sodium-ion batteries (SIB) are considered as a possible replacement for LIB due to the use of cheaper materials, safety and applicability for large-scale energy storage systems [1]. In the current work, the search for new promising sodium-conducting materials for SIB was carried out among chalcogenides using high-throughput theoretical screening for the first time. Chalcogen-containing compounds should have higher ionic conductivity than oxide counterparts due to the lower ionicity degree of the Na—X bond (X=S, Se, Te). From the Inorganic Crystal Structure Database (version 2023/1), all ternary and quaternary sodium-containing chalcogenides were selected, except for structures in which the working ions and environmental anions were partially replaced by other ions (703 compounds). The structures, in which sodium ion conduction channels were available, were determined as possible ionic conductors (231 structures with 1D, 2D or 3D migration maps of Na⁺-ions) using geometrical-topological analysis in the ToposPro software [2]. After literature analysis and the removal of duplicate structures, 167 new potential sodium ionic conductors were found. Further, calculations of the migration energy (E_m, eV) of Na⁺-ions were carried out by the bond valence site energy method in the softBV program package for each structure [3]. As a result, promising structures with

$E_m < 0.5$ eV were revealed (for example: Na_5InTe_4 – 0.42 eV for 2D migration, Na_4SSe – 0.27 eV, Na_4SeTe – 0.28 eV for 3D). The ionic conductivity at 298 K was calculated by the kinetic Monte-Carlo method in the soft BV program [3] in all structures in which $E_m \leq 0.5$ eV.

References:

1. Gilankar, A.; Mitra, A.; Singh, J.; Das, S.; Majumder, S. B. // *J. Alloys Compd.* 2021, 851, 156813.
2. Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. // *Cryst. Growth Des.* 2014, 14(7), 3576-3586.
3. Chen, H.; Wong, L. L.; Adams, S. // *Acta Crystallogr. Sect. B: Struct. Sci.* 2019, 75(1), 18-33.

Lignin-based hard carbon as anode material for metal-ion batteries

Tatyana Motovilo [1], Grigorii Lakienko [2,3], Zoya Bobyleva [2], Oleg Drozhzhin [2]

1 Lomonosov Moscow State University, Faculty of Materials Science, Moscow, Russia
2 Lomonosov Moscow State University, Faculty of Chemistry, Moscow, Russia
3 Skoltech Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str.3, 143026, Moscow, Russia

tmotovilo@inbox.ru

The need to create cheap and environmentally friendly ways to store energy is growing every year. Lithium-ion batteries (LIBs) are already used as such systems, and sodium-ion batteries (SIBs), which are a promising alternative to LIBs, also can be used in near future. Among the various anode materials for metal-ion batteries, hard carbon (non-graphitizable carbon) attracts great attention [1] due to one of the electrochemical performance. As a sourse of hard carbon, secondary biomass can be used. For example, lignin is the main component of wood along with cellulose and hemicellulose [2]. It is a relatively inexpensive precursor

with a high carbon content (about 60%). This work is devoted to the synthesis of hard carbon from of lignin-based source, in particular to the search for optimal synthesis conditions to improve the performance of lithium and sodium-ion batteries.

Commercial sodium lignosulfonate, which is formed in large quantities as waste in the pulp and paper industry, was used as the precursor. Hard carbon was obtained by several ways. The first synthesis included the following stages: replacement of sodium ions with H^+ using a cation exchange resin, followed by high temperature annealing of the resulting product in an inert atmosphere at 1300 °C. Another series of samples was additionally heat-treated at 200 °C in air. In addition, direct annealing of the initial sodium lignosulfonate was used. The obtained materials have a low specific surface area in the range of 1-10 m². Hard carbon based on sodium lignosulfonate demonstrated an initial Coulombic efficiency of 74% and a discharge capacity of ~220 mAh/g at a current density of C/10 (25 mA/g) in a lithium-ion half-cell, while in a sodium-ion half-cell the discharge capacity reached 250 mAh/g, and the initial Coulombic efficiency 85%. Also, hard carbon was charged below 0 V ref. Li^+/Li, and in this case the reversible capacity was 450 mAh/g with a Coulombic efficiency of 95%. Hard carbon showed high capacity at high current densities 1C (250 mA/g) – 290 mAh/g, 5C – 275 mAh/g, 10C – 255 mAh/g in a sodium-ion half-cell. Pretreatment of sodium lignosulfonate reduced specific surface area of hard carbon, which has a positive effect on the electrochemical characteristics of the material.

References:

1. Jin J. et al. Lignin-based electrospun carbon nanofibrous webs as free-standing and binder-free electrodes for sodium ion batteries // *Journal of Power Sources.* – 2014. – T. 272. – C. 800-807.
2. Wu L. et al. Apple-biowaste-derived hard carbon as a powerful anode material for Na-ion batteries // *ChemElectroChem.* – 2016. – T. 3. – №. 2. – C. 292-298.

Nanotubular $Na_2Ti_3O_7$@α-Fe_2O_3 Hybrid Materials for Sodium-ion Batteries

Neumoin A.I., Opra D.P., Sinebryukhov S.L., Mayorov V.Yu., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, 690022 Vladivostok, Russia

anton_neumoin@ich.dvo.ru

Recently, intercalation-type materials whose electrochemical activity is based on the redox Ti^{4+}/Ti^{3+} couple attract an attention for sodium-ion batteries (SIBs) electrodes. Such as $NaTiOPO_4$, $Na_2Ti_6O_{13}$, $Na_2Ti_3O_7$. This is due to the stability of their crystal lattice upon insertion and extraction of Na^+ ions (e.g. volumetric changes in $Na_2Ti_3O_7$ lattice are approximately 6%), relatively ease of preparation, availability of the resource base, and nontoxicity. Among other titanium-containing materials, sodium trititanate has some advantages, such as moderate specific capacity (177 mA • h/g), suitable (can be used as SIBs anode) electrode potential (~0.3 V vs. Na/Na^+), and fast ionic transport. However $Na_2Ti_3O_7$, which is a semiconductor with wide band gap (~3.3 eV), has low electrical conductivity limiting its power characteristics as a SIBs anode. In addition, at low current densities $Na_2Ti_3O_7$ is inferior in terms of specific capacity to hard carbon (about 300 mA • h/g). In recent years, efforts have been made to improve the electrical conductivity of $Na_2Ti_3O_7$ by creating compositions with carbon materials (amorphous carbon, graphene) or doping with various elements (e.g. Nb, F some lanthanoids: La, Ce, Nd, Sm, Gd, Er, Yb). Much attention is also paid to the creation of ways to increase the storage capacity of sodium trititanate due to hybridization with high-capacity substances (e.g. P, MoS_2, Fe_3O_4). The aim of this work was to develop a method for obtaining a hybrid nanomaterial based on $Na_2Ti_3O_7$ and Fe_2O_3 as high-capacity phase (theoretical specific capacity is 1007 mA • h/g). In this way a series of materials were obtained during one-stage process via simultaneous treatment in a hydrothermal reactor-autoclave of titanium dioxide and iron trichloride in different ratio in a strongly alkaline medium. The synthesized samples are consisted of macroscopic agglomerates formed by nanotubes

with an outer and inner diameter of 7–10 and 3.5–4 nm, respectively. The composition of materials is represented by $Na_2Ti_3O_7$ and α-Fe_2O_3, coexisted in nanotubes. The obtained materials have a mesopo rous structure with a pore size distribution in a narrow range (7–10 nm) and a specific surface area equal to 195–215 m^2/g. The total specific volume of the porous space is 0.45–0.60 cm^3/g. A tendency to increase the optical activity of synthesized materials with an increase in impurity content, especially in the visible region, was recorded. A decrease in the band gap from ~3.3 eV to 2.9 eV, which is caused by the presence of heterojunctions between $Na_2Ti_3O_7$ and α-Fe_2O_3 phases. The synthesized hybrids are expected to be promising for battery applications as SIBs anodes due to increased storage capacity (because of presence an high-capacity α-Fe_2O_3 phase) and improved power characteristics (due to decrease in the band gap energy).

Nanomaterials with Hierarchical Structure based on Cu-Doped $Na_2Ti_3O_7$ for Anodes of Sodium-Ion Batteries

Opra D.P., Zheleznov V.V., Sinebryukhov S.L., Sokolov A.A., Ustinov A.Yu., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, 690022 Vladivostok, Russia

dp.opra@ich.dvo.ru

Recently, the interest to titanates of homologous series $A_2Ti_nO2_{n+1}$ (where A = Li, Na, K) with layered and tunnel crystal framework constructing by zigzag octahedral TiO_6 layers with common edges and alkali metal ions in the interlayer space has increased. This, along with chemical stability and non-toxicity, is explained by their practically valuable properties, includiung photocatalytic, sensor, thermal, biological, electrophysical, electrochemical, etc. Among all other substances of this class, at present, attention is significantly focused on the titanates of $Na_2O–TiO_2$ system, namely $Na_2Ti_3O_7$, due to the surge in research dedicated

to sodium-ion batteries (SIBs). This is due to the fact that $Na_2Ti_3O_7$ is able to reversibly electrochemically intercalate up to two Na^+ ions per formula unit with a specific capacity of 177 mA h/g by a two-phase mechanism ($Na_2Ti_3O_7 \leftrightarrow Na_4Ti_3O_7$) at a potential of 0.2–0.3 V vs. Na/Na+ with small volume changes in the lattice (6%). The disadvantage of $Na_2Ti_3O_7$ is low electronic conductivity due to its semiconducting nature. Doping with impurity elements is an effective way to tune the electronic properties of semiconductor.

In view of this background, herein copper-doped $Na_2Ti_3O_7$ has been fabricated using the hydrothermal route. According to electron microscopy studies the material is formed by clusters of three-dimensional flower-like microstructures ("microflowers") composed of tubular (outer diameter 30–40 nm, wall thickness 2–3 nm, length several hundred nanometers) and sheet-like (several nanometers thick) nanoparticles. It was recorded by XPS that copper in the sample is in a divalent state. The ESR analysis shows that copper ions are located in different positions within the $Na_2Ti_3O_7$ crystal lattice: substituting for octahedral Ti^{4+} and interlayer Na^+ ions. According to UV–Vis spectrophotometric analysis Cu-doped $Na_2Ti_3O_7$ demonstrates a red spectral shift and an optical activity in the visible and near infrared spectral ranges. The band gap of $Na_2Ti_3O_7$ doped with copper decreases from ~3.5 to ~2.4 eV. When used in SIBs, Cu-doped $Na_2Ti_3O_7$ has a capacity of about 116, 97, 84, and 73 mA • h/g at 1C, 2C, 3C, and 4C, respectively. For undoped $Na_2Ti_3O_7$ these values were lower: around 102, 73, 44, and 28 mA • h/g. At low current densities of 0.1C and 0.5C, the both analyzed materials have similar capacities. The improved electrochemical activity of $Na_2Ti_3O_7$ doped with copper is explained by its improved transport properties.

K$_5$R(MoO$_4$)$_4$ phosphors with the palmierite-related structure

Posokhova S.M. [1], Morozov V.A. [1]

[1] Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

posohovasm@gmail.com

K$_5$R(MoO$_4$)$_4$ (R= rare earth elements (REE), Bi, Y) molybdenum oxides with the palmierite-type (K$_2$Pb(SO$_4$)$_2$, sp.gr. $R\bar{3}m$, z = 3) structure are known for all REE. The crystal chemical formula of K$_5$R(MoO$_4$)$_4$ compounds can be represented as M1$^{[6+6]}$K2$_2^{[9+1]}$(MO$_4$)$_2$ (M1= K$_{0.5}$R$_{0.5}$). Depending on the combinations and ordering of K+ and R3+ cations in K$_5$R(MoO4)4, the initial R m palmierite-type structure may undergo various distortions. The coordination number of the M1 and M2 sites may change. A decrease of symmetry to monoclinic or triclinic has been observed for some of them. The distortion of the palmierite-type structure is mainly associated with a rotation of the MoO$_4$ tetrahedra. The flexibility of the tetrahedra in the palmierite-type structure promotes the formation of coordination polyhedra characteristic of a given R^{3+}cation. A decrease in the REE radius leads to a sequential decrease in the coordination numbers (CN) for R^{3+} within the range of CN = 6-12.
It was revealed that some K$_5$R(MoO$_4$)$_4$ compounds have a (3+1)D incommensurately modulated structure. The use of (3+n)D approach allows to obtain accurate crystal chemical data describing the subtle relationships between the composition, structure and properties of phases. For example, in the K$_5$Yb(MoO$_4$)$_4$ palmierite-related structure Yb^{3+} and K$^+$ ordering depends on preparation conditions and three polymorphic modifications were found: γ-, β- and α-modification [1]. Crystal structure study revealed that occupancy of M1 positions by Yb^{3+} and K$^+$ in the ([(K$_{0.5}$Yb$_{0.5}$)1Mo$_2$O$_8$]-layer is ordered (periodic in γ-phase and aperiodic in β-phase) and randomly distributed for α-phase.
Our latest studies have shown that K$_5$Eu(MoO$_4$)$_4$ [2], β- K$_5$Eu(MoO$_4$)$_4$ [3] and β-K$_5$Yb$_{0.3}$Eu$_{0.7}$(MoO$_4$)$_4$ [4] structures are also (3+1)D incommensurately modulated and described with the superspace group C2/m(0β0)00. The occupancy factor of K1 and R1 (Yb$_{0.3}$Eu$_{0.7}$) sites

in the β-$K_5Yb_{0.3}Eu_{0.7}(MoO_4)_4$ is modulated as a step-like crenel) function in contrast to the β-$K_5Tb(MoO_4)_4$ structure where the occupancy factor of K1 and Tb sites is modulated as two complementary waves assuming an absence of K/Tb ordering. Thus, the aperiodic ordering of K1 and R1 in M1 positions along ab direction is observed for the β-$K_5Yb_{0.3}Eu_{0.7}(MoO_4)_4$ as well as for the β-$K_5Yb(MoO_4)_4$ palmierite-related structure.

References:

1. Morozov V. A., Lazoryak B. I., Lebedev O.I., Amelinckx S., Van Tendeloo G., Structure of three polymorphs of the complex oxide $K_5Yb(MoO_4)_4$. // *J. Solid. State Chem.* 2003. V. 176. P. 76-87.
2. Posokhova S.M., Morozov V.A., Deyneko D.V., Redkin B.S., Spassky D.A., Nagirnyi V., Belik A.A., Hadermann J., Pavlova E.T., Lazoryak B.I. // *CrystEngComm,* 2023, 25, 835-847.
3. Posokhova S.M., Morozov V.A., Deyneko D.V., Nikiforov I.V., Redkin B.S., Spassky D.A., Belik A.A., Pavlova E.T., Lazoryak B.I. // *Inorganic Chemistry,* 2022, 61, 20, 7910-7921.
4. Posokhova S.M., Morozov V.A., Zonov E.M., Deyneko D.V., Spassky D.A., Fedyunin F.D., Belik A.A., Pavlova E.T., Vasin A.A., Lazoryak B.I. // *CrystEngComm,* 2023, 25, 4822-4833.

Catalytical activity of higher tungsten boride from the first principles

Aleksandra D. Radina, Alexander G. Kvashnin

Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

a.radina@skoltech.ru

Nowadays the most widely used catalysts for organic synthesis mainly made of noble and rare earth metals that significantly increases the cost of many products. Moreover, 80% of catalyst used in domestic industry including oil and chemical production are imported and it can cause problems in the present political situation. Obviously, the new class of materials for the catalysts is needed. Suggested alternative to the pricey catalysts is the transition metals borides [1], [2]. Along with the cobalt, molybdenum, nickel, and vanadium borides, tungsten borides were studied as potential catalysts for hydrogen evolution reaction (HER) and CO_2 reduction, then, their usage as the catalysts for organic synthesis was proposed.

Moreover, the catalytic activity of transition metal borides increases with the boron stoichiometric content [3], [4]. Hence, the higher tungsten boride (WB_{5-x}) is the most promising one beyond the other tungsten borides. Here we performed the comprehensive study of surfaces of WB_{5-x} using density functional theory. We studied the surface energies of WB_{5-x} slabs with (001), (010), (100), (110), (101), (111), (130), and (201) crystallographic orientations. All the calculations were performed by using density functional theory (DFT) as implemented in VASP package. Python Wulffpack to make Wulff construction and find the equilibrium morphology of higher tungsten boride single crystal. It was shown that boron terminated (010) and (001) surfaces and tungsten terminated (101) surface are the most stable.

Then, by using a the first-principles evolutionary algorithm as implemented in the USPEX code in its adaptation for surfaces, it was founded that there are no stable reconstructions of the (010) and (101) surfaces. As WB_{5-x} has also proposed as the alternative to the catalysts for an automotive motor, the adsorption of the different atmosphere gases (CO, CO_2, H_2, N_2,

O_2, NO, NO_2, H_2O, NH_3, SO_2) on its stable surfaces was investigated. It was shown that at the (010) surface the lowest adsorption energies have the NO, CO and H_2 molecules. On the contrary, WB_{5-x} surface doesn't adsorb SO_2 gas. On (101) surface O_2, NH_3 and NO_2 have the lowest adsorption energies.

Obtained results allows us to possess higher tungsten boride as a perspective catalyst for many different reactions. Furthermore, the experimental work to prove data obtained is already started.

References:

1. Dorri, M. M.; Thörnberg, J.; Hellgren, N.; Palisaitis, J.; Petruhins, A.; Klimashin, F. F.; Hultman, L.; Petrov, I.; Persson, O. A.; Rosen, J. // *Scripta Materialia,* 2021, 200, 113915
2. Zhao, W.; Xu, D.; Chen, Y.; Cheng, J.; You, C.; Wang, X.; Dong, S.; Tao, Q.; Zhu, P. // *Catalysts,* 2022, 12, 222.
3. Gupta S., Patel M. K., Miotello A., Patel N. // *Advanced Functional Materials,* 2020, 30, 1906481.
4. Li, Q.; Wang, L.; Ai, X.; Chen, H.; Zou, L.; Li, G. D.; Zou, X. // *Chem. Commun.,* 2020, 90, 13983– 13986.

Morphology control investigation of single-crystal Ni-rich NMC obtained via flux technique

M.Z. Ratkovich, A.D. Pavlova, I.A. Moiseev, A.A. Savina, A.M. Abakumov

The world market of cathode materials for energy storage elements has been intensively developing recently. Despite a wide variety of different materials are presented, $LiNi_xMn_yCo_zO_2$ (x>0.6) with a high nickel content (so-called Ni-rich NMCs) layered oxides are encouraging candidates for the role of high-energy cathode materials and occupy a leading position in the market. Ni-rich NMC has a number of advantages, such as increased discharge specific capacity (up to 230 mAh/g), high energy density (up to 800 Whkg⁻¹), reduced content of expensive and toxic cobalt oxide. However, due to the polycrystalline morphology there

are some disadvantages, including low cyclic and thermal stability, low tap density.

One of the promising approaches to solve such problems is the development of cathode materials in the form of single crystal (SC-NMC) particles with the average size >1-6 μm. SC-NMC materials demonstrate reduced surface reactivity towards electrolyte, lower stress concentration and increased resistance to mechanical cracking. It causes more stable electrochemical characteristics during battery cycling in comparison with polycrystalline particles of the same composition. By influencing the morphology of the particles, it become possible to achieve not only the above advantages, but also physicochemical characteristics such as high tap density, which will allow the production of more compact batteries with high energy density.

A series of samples with the general formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ were obtained using different ratio of lithium and potassium sources as flux at the stage of high-temperature annealing of the material. The physicochemical properties such as particle size distribution by dynamic light scattering technique, tap density, morphology and electrochemical properties by galvanostatic cycling with potential limitation of the obtained SC-NMCs were studied.

Using powder X-ray diffraction (PXRD) was confirmed obtained samples are single-phase with a layered structure (pr. gr. *R-3m*). Low concentration of anti-site defects in 3b lithium site for obtained samples was showed by Rietveld refinement. It was found that the use of inert potassium salt as a flux formation agent leads to the formation of particles with the shape of truncated octahedrons with smoothed edges and vertexes.

The optimum ratio of lithium hydroxide and potassium sulphate was found as 4:1 respectively, where the particles crystallize with spherical-like shape with a dominant (003) surface according to literature data and scanning electron microscopy (SEM) analysis.

Optimization of electrolyte solutions and the morphology of hard carbon anode materials for sodium-ion full-cells

Safiullina A.R. [1], Bobyleva Z.V. [2], Drozhzhin O.A. [3]

[1,2,3] Lomonosov Moscow State University, 119991, Leninskiye Gory, building 1, structure 3, Moscow, Russia

alls25.11.03@gmail.com

Sodium-ion batteries are a promising alternative to lithium-ion batteries. The development of sodium-ion batteries requires the search for suitable cathode and anode materials. In addition, electrolytes are essential for the proper functioning of any battery technology. Hence, a great attention on battery research is to identify the most appropriate formulation so as to minimize interface reactions and enhance both cell performances and safety aspects.

Electrolyte is a key component used for charge transfer between the anode and cathode. The main requirements for electrolytes are high conductivity, low cost, chemical and thermal stability. The aim of the research is to study electrolyte systems that meet these conditions. The studies were carried out in full cells, since this model is close to battery prototypes. In addition to the electrolyte, the morphology of the anode material, the composition of the cathode material, and the mass ratio of the cathode and anode materials should be studied.

In this work, the electrochemical properties of full cells in different electrolyte's solutions were studied. Electrolytes with organic carbonates as solvents and different concentrations of the NaPF6 salt were prepared. We used non-graphitizable or hard carbon as anode materials and NASICON-type $Na_3V_2(PO_4)_3$ as cathode material. Full cells were studied by galvanostatic cycling, and discharge capacity, Coulombic efficiency, cycling stability were determined. The electrolytes were also studied by cycling voltammetry with idle electrodes in half cells and Raman spectroscopy.

The morphology of non-graphitizable carbon affects the capacity and cyclability of the full cell. The full cell has a higher capacity in case with monolithic-like non-graphitizable carbon [2]. However, the microspherical hard carbon which was obtained through hydrothermal carbonization, has the better cycling stability.

The full cell consisting of monolithic-like hard carbon, $Na_3V_2(PO_4)_3$, and 1 M $NaPF_6$ in EC:DEC (1:1) demonstrated a discharge capacity of 60 mAh/g at the 700th cycle [3]. The electrolytes based on 1 M $NaPF_6$ in two-components (EC:DEC 1:1) and three-component solvent's system (EC:PC:DEC 1:1:2) are suitable for the best cycling of full cells and battery prototypes.

References:

1. Lu Y. et al. Electrolyte and interface engineering for solid-state sodium batteries // *Joule.* – 2018. – T. 2. – №. 9. – C. 1747-1770.
2. Bobyleva Z. V. et al. Caramelization as a Key Stage for the Preparation of Monolithic Hard Carbon with Advanced Performance in Sodium-Ion Batteries // *ACS Applied Energy Materials.* – 2022. – T. 6. – №. 1. – C. 181-190.
3. Hirsh H. S. et al. Role of electrolyte in stabilizing hard carbon as an anode for rechargeable sodium-ion batteries with long cycle life // *Energy Storage Materials.* – 2021. – T. 42. – C. 78-87.

Ultra-high Ni content layered transition metal oxides in the form of single crystal particles of high energy density as the cathode material for lithium-ion batteries

Sergeant A. [1], A.D. Pavlova [1], A.A. Savina [1], A.M. Abakumov [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

aubreylsergeant@yandex.ru

Lithium-ion batteries (LIBs) are one of the hottest topics in today's materials science and chemistry landscape. They are incredibly important to the modern way of life; they provide power to things like electric transportation, handheld electronic devices, and even toys. The major limiting element in LIB innovation is the cathode. By smart design of the cathode, the price and performance of the battery as a whole can be impacted most significantly. Recent studies have been done on particular cathode materials known as layered Ni-rich mixed transition metal oxides with the common formula $LiNi_xCo_yMn_zO_2$, where $x > 0.6$ (Ni-rich NMC). These materials have proven to be a cheaper and safer alternative than the previous commercialized $LiCoO_2$ cathode material. The crystal microstructure of this new material can be synthesized in two different analogues, as secondary agglomerates known as polycrystals and as single crystal (SC) particles. Though the polycrystalline cathode materials being investigated have showed much promise, they also have a large downfall – microcracking. Microcracking occurs over prolonged cycling and contributes to decay of cycling stability. This results in poor energy performance and poor capacity for the overall battery. It occurs due to the accumulation of electrochemical and mechanical stress within the cathode during charging and discharging. Microcracking occurs along the grain boundaries of primary particles as these regions of misalignment disrupt the paths of force vectors through the agglomerate.

The SC analogues of these materials have shown much greater resistance to microcracking due to the absence of grain boundaries. Forces moving through the crystals do not run into boundaries and are therefore more effectively dissipated without as much damage to the material structure. This results in better electrochemical and mechanical stability than observed

in the polycrystalline analogue. SCs also have the advantage of higher energy density compared to polycrystalline analogues. SCs with spherical-like morphology fill space in a more ordered way and therefore results in increased tap density of the material. Aside from the interesting advantages of SC cathode materials, they are not without disadvantages. The main concerns being poor rate capability at a high current density. This is to say that microcracks will still form in the single crystal material when cycled at a high current. Defects are also observed in these crystals and can contribute to poor performance. To correct these issues, novel synthesis approaches will be taken to involve inclusions and dopants into the crystal structure. Inclusions such as non-isostructural materials, specifically transition metal oxides, are to be used to increase the structural stability of the material over long cycling. They will do this by acting as a bolster, buttressing the structure and making it more rigid. This will help decrease collapse of ion transport pathways and thereby improve cycling stability. Dopants such as Al^{3+}, Mg^{2+}, Ti^{4+}, and Zr^{4+} are being considered for the purpose of reducing the quantity of anti-structure disordering. Pushing the boundaries of what is known from Ni-rich NMC cathode materials, a new material known as layered ultra-high Ni content NMC ($LiNi_xCo_yMn_zO_2$, where $x > 0.9$) with above modifications are to be synthesized. The purpose of this material being to make the new generation of lithium-ion batteries safer, longer lasting, and more cost effective.

Effect of FeCo Hollow Magnetic NPs on the Oxygen Evolution Reaction

Ilia D. Shabalkin [1], Pavel V. Krivoshapkin [1]

[1] ITMO University, Leninskie gory GSP-1, 191002 Saint-Petersburg, Russia

shabalkin@scamt-itmo.ru

Alkaline water electrolysis is widely recognized as an efficient and reliable producing method of pure hydrogen and is considered the one of the best choices for mass decarbonization. However, the sluggish kinetics of the oxygen evolution reaction (OER) for water splitting still holds back the widespread adoption of this technology. Oxides based on Ru and Ir are highly active OER catalysts, however, the high cost does not allow to talk about widespread implementation.
An alternative to noble catalysts can be NPs based on transition metals (Fe, Ni, Co). The high surface area, chemical composition and nanoscale make such materials attractive for electrocatalytic applications. Among others, FeCo has one of the highest saturation magnetizations among oxides and transition metal alloys. This makes it possible to regard FeCo magnetic NPs as an effective agent for the spin polarization of intermediate radicals to increase the current density and selectivity of electrochemical reactions.
FeCo NPs were obtained by the co-reduction of Fe and Co salts with sodium borohydride (Fig. 1a). Then, using a flame gun, it was calcinated to obtain a hollow structure and increase crystallinity (Fig. 1b). The average particle size was 18 and 19 nm before and after firing, respectively.
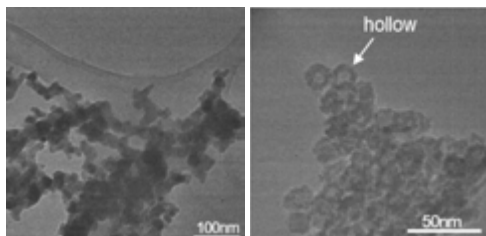

Fig. 1. TEM image of FeCo NPs a) after synthesis, b) after calcination.

We turned our attention to alkaline water electrolysis to investigate the response of a bare Ni–foam anode and Ni-foam covered with 30 mg hollow FeCo in a liquid electrolyte (KOH; 1 M) cell equipped with a platinum mesh cathode and an Ag/AgCl 3.5M KCl reference electrode. As a result, we obtained CV curves that showed a significant increase in current density for Ni-foam covered with hollow magnetic nanoparticles (Fig. 2).
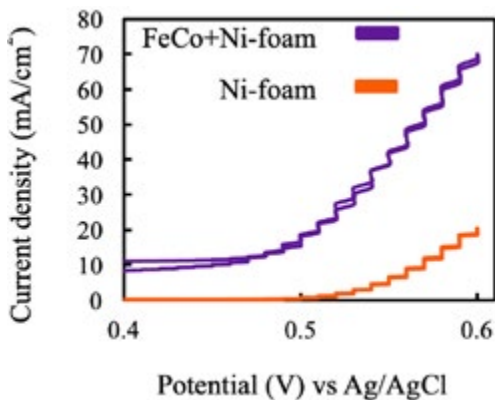

Fig. 2. CV curves for bare Ni-foam and Ni-foam covered with FeCo hollow magnetic NPs

TiO$_2$(B)/ reduced graphene oxide composite materials for lithium-ion batteries

Sokolov A.A., Opra D.P., Podgorbunsky A.B., Sinebryukhov S.L., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, 690022 Vladivostok, Russia

aa.sokolov@ich.dvo.ru

TiO$_2$(B) is one of the promising anode materials for lithium-ion batteries due to the convenience of its crystal structure to transportation and storage of Li+ ions. Unfortunately, the usage of TiO$_2$(B) is hindered by the wide band gap (3.0–3.2 eV) resulting in low electronic conductivity (~10–12 S cm−1). One of the ways to solve this problem

is the creation of composites with conductive materials, mainly carbon.

Within the scopes of present work, composite materials based on $TiO_2(B)$ and reduced graphene oxide ($TiO_2(B)/rGO$) have been synthesized. The composites were obtained by mechanochemical synthesis of $TiO_2(B)$ and rGO in a ratio of 90:10 (wt%) in an isopropanol at a rotation speed of 1200 rpm and a duration of 120 min. According to the X-ray diffraction data, the transformation of the metastable $TiO_2(B)$ phase into anatase and rutile as a result of mechanochemical treatment does not occur under these conditions. The Raman spectrum of the $TiO_2(B)/rGO$ sample exhibits D and G peaks associated with reduced graphene oxide (ID/IG ~ 1.00). Based on the data of thermogravimetric studies in the range up to 700 °C, the weight loss of $TiO_2(B)/rGO$ composite amounted to about 10.5 wt%. According to spectrophotometric studies, the composite has improved optical activity in the visible range of the spectrum compared to pure $TiO_2(B)$, which is due to the presence of reduced graphene oxide. A narrowing of the band gap by ~0.1 eV was registered for $TiO_2(B)/rGO$, which is probably due to carbon doping of $TiO_2(B)$ as a result of mechanochemical treatment. According to experiments in lithium half-cells with a $TiO_2(B)/rGO$ electrode prepared without conductive additives, the following specific capacities were achieved: 243.5, 225.5, 203, 173, 143, and 78.5 mAh g−1 at current densities of 33.5, 67, 167.5, 335, 770, and 1675 mA g^{-1}, respectively. Hence, the drop in capacity of $TiO_2(B)/rGO$ electrode at 167.5, 335, 770, and 1675 mA g^{-1} was about 20, 29.5, 41.5, and 67.5%, respectively. On the other hand, in case of electrode based on pure $TiO_2(B)$ containing a carbon black (13 wt%), these values are 43, 58.5, and 69% at 150, 300, and 700 mA g^{-1}, respectively. These data indicate a decrease in capacity drop with increasing load for the composite as compared to pure $TiO_2(B)$.

Synthesis and structure of Zn_2EDTA metal-organic framework

Alena A. Starodubtseva [1*], Ivan A. Trussov [1,2]

[1] Center of Phisico-Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, Almaty, 010000, Kazakhstan
[2] Skoltech Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, 121205, Russian Federation

alena.a.rubanova@gmail.com

Metal-organic frameworks (MOFs) have gained significant attention in materials science due to their unique properties, such as high surface area, porosity, and tunable electrochemical characteristics. Among various MOFs, Zn-EDTA compounds have shown potential for electrochemical applications. This paper presents the discovery and investigation of a new anhydrous Zn_2(EDTA) MOF and its electrochemical performance as an electrode material for batteries. The study systematically explores the influence of pH and stoichiometric ratio on the formation of Zn_2(EDTA) and Zn_2(EDTA)(H_2O) MOFs using X-ray phase analysis. The anhydrous Zn_2(EDTA) compound is synthesized, offering advantages over the hydrated form in terms of stability and electrochemical activity. The structure of Zn_2(EDTA) is characterized, revealing a 3D network of channels suitable for interstitial ionic mobility. Thermogravimetric analysis (TGA) is used to study the thermal behavior of Zn_2(EDTA), showing two weight loss steps attributed to water and carbon dioxide elimination during decomposition. Electrochemical measurements using cyclic voltammetry in alkaline and neutral electrolytes demonstrate the electrochemical activity of Zn_2(EDTA) as an anode material for batteries. The results suggest that the electrochemical process in both electrolytes involves the reversible stripping/deposition of zinc ions. The anhydrous Zn_2(EDTA) MOF exhibits higher peak current intensities and more positive potentials compared to the hydrated form. The study provides valuable insights for the synthesis and control of Zn_2(EDTA) MOF, enhancing its potential application in electrochemical devices. Further exploration of its properties and applications is warranted based on these promising results.

Effect of biomass pretreatment on electrochemical properties of hard carbon for sodium-ion batteries

Y.V. Sultanova [1], **Z.V. Bobyleva** [1], **O.A. Drozhzhin** [1], **E.V. Antipov** [1,2]

[1] **Department of Chemistry, Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia**
[2] **Skoltech Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str.3, 143026, Moscow, Russia**

yana.sultanova2016@yandex.ru

Hard carbon (HC) is the most perspective anode material for sodium-ion batteries [1]. The material possesses high capacity and stable cycling, ease of synthesis, and a large selection of precursors. Biomass (plants [2], by-products and bio- waste [3]) can serve as promising source of HC. The use of bio-waste for energy purposes is one of the solutions for sustainable development of our planet. However, biomass-based carbon materials demonstrate unsatisfactory electrochemical characteristics. To improve electrochemical properties, various synthetic approaches are being considered, including biomass pretreatment. The aim of this study is to investigate the influence of pretreatment biomass on the electrochemical properties of HC.

The sources of carbon were bio-waste from the oil and fat industry, and microcrystalline cellulose for the comparison of characteristics. The study considered pre-treatment methods of the raw material in air at different temperature ranges, followed by annealing in an inert atmosphere at a temperature of 1300°C. In addition, some samples from were washed with hydrochloric acid solution to remove inorganic impurities.

Among the samples based on sunflower cake, the sample obtained by two-stage synthesis with a pre-carbonization temperature of 150°C and subsequent annealing at 1300°C demonstrated the highest discharge capacity (222 mAh/g). As the pre-treatment temperature increased to 250°C, the capacity of non-graphitizable carbon samples significantly decreased, down to 9 mAh/g, which can be explained by the increased content of inorganic impurities in the material. Materials based on another bio-waste from the oil and fat industry, husk, demonstrated improved electrochemical characteristics

(248 mAh/g and coulombic efficiency 85%). It is important to note, that cellulose-based materials had the best electrochemical characteristics (discharge capacity 287 mAh/g and Coulombic efficiency over 90%). We demonstrated, that the pretreatment step is a necessary stage for the production of hard carbon with advanced electrochemical characteristics. The stage of pretreatment of biomass must necessarily include the stage of washing with an acid solution. We showed effect of inorganic impurities on the electrochemical properties of the materials. These data are important for the further development of approaches to using biomass as a source of carbon materials for sodium-ion batteries.

References:

1. Dou X. et al. Hard carbons for sodium-ion batteries: Structure, analysis, sustainability, and electrochemistry // *Materials Today.* – 2019. – T. 23. – C. 87-104.
2. Yu P. et al. Recent progress in plant-derived hard carbon anode materials for sodium-ion batteries: a review // *Rare Metals.* – 2020. – T. 39. – C. 1019-1033.
3. Wu L. et al. Apple-biowaste-derived hard carbon as a powerful anode material for Na-ion batteries // *ChemElectroChem.* – 2016. – T. 3. – №. 2. – C. 292-298.

Pre-synthesis for LAGP obtaining

Pavel Vishniakov, Maxim Maximov [*]

Peter the Great Saint-Petersburg Polytechnic University, 195251 Saint Petersburg, Russia

*: maximspbstu@mail.ru

One of the main problems of lithium-conducting materials of NASICON-type structure, in particular LAGP, is their relatively low electrical conductivity in comparison with sulfide solid state electrolytes [1]. One of the possible ways to increase ionic conductivity is to optimize the synthesis method for obtaining a better ratio of crystalline, amorphous and side phases [2]. The traditional melt-quenching synthesis method implies high temperatures about 1400° C and has problems with non-stoichiometry of the composition, high-cost crucible, non-homogeneity of the charge [3]. The method can be optimized by introducing a preliminary synthesis to obtain an intermediate phase with a lower melting point and greater homogeneity. Therefore, the article considers the effect of the preliminary synthesis on temperature of LAGP synthesis, conducting and phase composition.

Lithium carbonate ($LiCO_3$), Aluminum oxide (Al_2O_3) and germanium oxide (GeO_2) were used as Li, Al and Ge precursors, respectively. Precursors were added to boiling orthophosphoric acid (H_3PO_4) until the precipitate completely disappeared and phosphates were obtained. After the solution was mixed and kept at a constant temperature. Further, the synthesis of solid electrolytes was carried out in corundum crucibles at 1230 °C for 45 minutes. The production of the glass-forming melt was carried out on a metal plate heated to 80 °C. Then the resulting glass cylinder was placed in an oven at 420 °C for 2 hours for crystallization. Thermal effects were determined by differential thermal analysis (DTA) method. The electrical and diffusion characteristics of studied solid electrolytes were determined by impedance spectroscopy. Phase and chemical composition were studied by XRD and EDX. As a result, the melt-quenching technique improvement allowed to reduce the synthesis temperature from 1400 °C

to 1230 °C and the time from 1.5-2 hours to 45 minutes. In addition, the conductivity of the samples was 5,2 10^{-4} S • cm^{-1} (25 °C) and the interface of the structure remains stable for more than 200h (200 uA/cm²).

References:

1. Manthiram, A., Yu, X. & Wang, S. // *Nat Rev Mater* 2017, 2, 16103.
2. Xiaoxiong X., Zhaoyin W., Xiangwei W., Xuelin Y., and Zhonghua G. // *J. Am. Ceram. Soc.* 2007, 90[9], 2802–2806
3. S.V. Pershina, B.D. Antonov, A.S. Farlenkov, E.G. Vovkotrub // *J. Alloys Compd.* 2020, 835, 155281.

Crystal structure of fluorinated bis(benzofuro) benzenes as promising materials for organic optoelectronics

Zargarova L.V. [1], Skolyapova A.D. [1], Tarakanovskaya D.O. [1], Komarov V.Y. [2], Mostovich E.A. [1]

[1] Novosibirsk State University, 630090, Novosibirsk, Russia
[2] Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Novosibirsk, Russia

leilazargarova@gmail.com

Fluorinated polyaromatic and heteroaromatic systems can possess high charge mobility, high photoluminescence quantum yield, stability in air, flexibility and waveguide effect. Therefore, they are promising materials for organic optoelectronics.

Benzannelated furans, such as bis(benzofuro)-benzenes, successfully combine many of the aforementioned properties. Therefore, they were chosen as the object of the present study. It is extremely important to study the features and patterns of crystal packing of these compounds, since they have critical influence on the target properties (charge carrier mobility and luminescence efficiency). Intramolecular and

intermolecular interactions in crystals can be finely tuned by varying the side substituents. We synthesized a series of derivatives with different substituents at the central ring (Fig. 1) in order to study structure-property correlations.
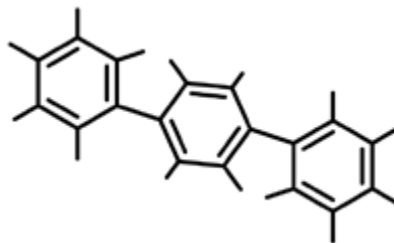

Fig. 1. Target compounds.

Single crystals were obtained by the method of physical vapor transport for X=H and X=Br and by the method of slow vapor diffusion from CH_2Cl_2/Hexane mixture for X=NO_2. According to X-Ray data analysis both X=H and X=Br show similar disorder motifs. However, in case of X=H the alternative orientation occurs with a frequency of about 50%, and in case of X=Br - 5%. Crystals of both of these compounds show π-π stacked dimers, whereas only short contacts between the molecules can be observed for X=NO_2. Oxygen atoms of the NO_2-group are out of the molecule plane and creates steric hindrance.

Ultra-long phosphorescence at 77K τ_{Phos}(77K)=0.842 s was detected for the X=H. The quantum yield of photoluminescence was found to be greater than 90%. Theoretical mobility of charge carriers was calculated. It turned out to be maximal and amounted to 0.22 $cm^2V^{-1}s^{-1}$ in the direction of the predominant crystal growth. Other interesting properties of these crystals are their flexibility and the presence of waveguide effect. We also discovered the possibility of existence of polymorphs during crystallization from different solvents. All of the above makes this compound and its crystals extremely promising for organic electronics.
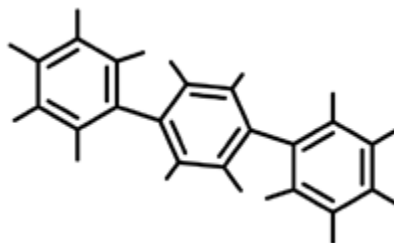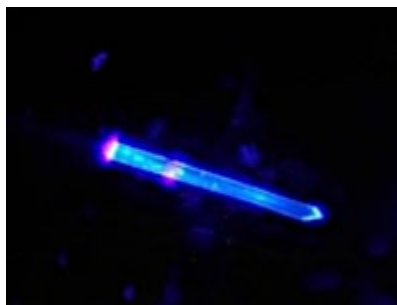
Fig. 2. The appearance of the crystal, where X — H.

Molybdenum-Doped HardCarbon for Next-Generation Electrochemical Power Sources

Zaytsev N.I., Zheleznov V.V., Opra D.P., Saenko N.S., Sokolov A.A., Mayorov V.Y., Ustinov A.Y., Kuryavy V.G., Shlyk D.H., Polyakova N.V., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, 690022 Vladivostok, Russia

zaitcev.ni@ich.dvo.ru

In the last decade, sodium-ion batteries (SIBs) have been seen as a promising replacement for lithium-ion batteries in autonomous power supply sources. For development in a number of industries, e.g. in the automotive industry or stationary energy storagesystems, cheap and high-energy batteries are needed.The cost of raw materials required for the production of LIBs, in particular lithium carbonate,

is 110 times more than the cost of sodium carbonate. Since sodium is one of the most common elements on the planet, its content in the earth's crust is 2.64%, while lithium is only 0.005%. At the same time, the inability to reversibly insertion Na^+ ions into graphite raised the question of finding alternative substances available for use as a SIBs anode. In recent years, a consensus has been found in this regard in the form of the so-called hardcarbon, the capacity of which at low current densities varies near 300 mAh/g. The peculiarity of hard carbon is that it can be produced from a wide range of carbon-containing raw materials. So much work has been devoted to obtaining hard carbon materials from biomass. However, such options, although showing promisingresults, often lead to a significant increase in the cost of the technology (due to the need to introduce additional stages of biomass processing for purification and standardization) and low yield of the final product. One promising wayis the synthesis of hard carbon using commercially available raw materials such as carbon paper or fibre, an approach that is easy to scale and highly repeatable in terms of material characteristics. It is therefore relevant to obtain hard carbon from common commercial viscose fibre as a raw material. In addition, modification of carbon raw materials with various metals, as it is known, can result in lower carbonization temperature, which is important from the point of view of energy consumption in the production of hard carbon materials, the synthesis of which is usually carried out at high temperatures (1300-1400 °C).

In the present work, a method of obtaining new functional materials for SIBs anodes based on hard carbon by carbonization (at different temperatures of 630-1050 °C) of chemically modified (molybdenum-doped) technical viscose yarn is proposed. The relationship between electrochemical parameters of such materials and their structural, morphological, textural characteristics has been revealed. It is shown that the reversible electrochemical activity of the considered carbon materials is in direct dependence on the obtaining temperature. At the same time, achievement of conditions for the appearance of local ordering of graphite-like layers with the formation of domain structures is observed in the considered series

of materials at the annealing temperature of 1050 °C, which is lower than the generally recognized values for hard carbons. This can be explained by the fact that in the presence of molybdenum the thermally-induced structural rearrangement of the carbon framework proceeds more efficiently. Among others, the sample obtained at 1050 °C shows the best electrochemical performance and good cycling with a capacity of 290 mAh/g at 25 mA/g.