

Book of Abstracts

presented at the

14th International Symposium on Systems with Fast Ionic Transport



7–9 July 2021

Online

<https://issfit14.si>

Book of Abstracts presented at the 14th International Symposium
on Systems with Fast Ionic Transport

(ISSFIT-14)

Online event, 7 – 9 July 2021

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About the Symposium

The International Symposium on Systems with Fast Ionic Transport is an established conference series with a long tradition that is organized every two to three years for the scientific community working in the interdisciplinary field of charge-transport materials.

The 14th in the series of the symposia, ISSFIT-14 had originally been planned to take place in Rogaška Slatina in Slovenia in the summer of 2020, but unfortunately had to be postponed several times due to the COVID-19 pandemic.

The first online format of the symposium will welcome 11 invited speakers, 15 oral presenters and 34 presenters of e-posters.

Scope and Topics

The symposium will cover a wide range of topics related to solid state electrolytes that include

- Theoretical aspects of fast ionic and charge transport in the bulk and at surfaces/ interfaces
- Experimental methods for systems with fast ionic transport
- Crystalline solid electrolyte materials (synthesis, structure, properties)
- Mixed ionic-electronic conductors
- Polymer conductors and glasses
- Ionic liquids/liquid salts
- Nanostructured materials
- Applications including electrochromic devices, batteries, fuel cells and hydrogen energy systems

International Scientific Committee

- **Isaac Abrahams**, Queen Mary University of London, United Kingdom
- **Bernard Boukamp**, University of Twente, Netherlands
- **Yury A. Dobrovolsky**, Institute of Problems of Chemical Physics RAS, Russia
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- **Maria Gazda**, Gdansk University of Technology, Poland
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- **Ilan Riess**, Technion, Israel
- **Vyacheslav S. Vikhrenko**, Belarusian State Technological University, Belarus

Organizing Committee

- **Miran Gaberšček**, National Institute of Chemistry, Slovenia
- **Urša Petek**, National Institute of Chemistry, Slovenia
- **Matjaž Spreitzer**, Jožef Stefan Institute, Slovenia



Contact Information

<https://issfit14.si>

issfit14@ki.si

Department of Materials Chemistry
National Institute of Chemistry
Hajdrihova 19, SI-1000 Ljubljana, Slovenia



NATIONAL INSTITUTE
OF CHEMISTRY



Symposium Program

7 July 2021, Wednesday

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09:00–09:55	Symposium opening (Chairperson: Miran Gaberšček)
9:00–9:10	Opening Remarks <u>Miran Gaberšček</u> <i>National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia</i>
9:10–09:55	Plenary invited lecture <u>I-01</u> Significance of Fast Ion Transport for Solid State Ionics and Beyond <u>Joachim Maier</u> <i>Max Planck Institute for Solid State Research, Physical Chemistry of Solids, 70569 Stuttgart, Germany</i>
09:55–10:00	Break (5 min)
10:00–11:10	Session 1 (Chairperson: Franciszek Krok)
10:00–10:30	Invited lecture <u>I-02</u> High entropy oxides as mixed conductors <u>Maria Gazda</u> ^a , Daniel Jaworski ^a , Arkadiusz Dawczak ^a , Tadeusz Miruszewski ^a , Wojciech Skubida ^a , Aleksandra Mielewczyk-Gryn ^a , Sebastian Wachowski ^a , Kacper Dzierzgowski ^a , Piotr Winiarz ^a , Iga Szpunar ^a , Jagoda Budnik ^a , Daria Gierszewska ^a <i>^aInstitute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdansk, Poland</i>
10:30–10:50	<u>O-01</u> Direct observation of local mass transport pathways via isotope exchange-atom probe tomography <u>Federico Baiutti</u> ^a , Francesco Chiabrera ^a , David Diercks ^b , Andrea Cavallaro ^c , Ainara Aguadero ^c , Alex Morata ^a , Albert Tarancon ^{a,d} <i>^aCatalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930 Sant Adrià Besos, Spain</i> <i>^bDepartment of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, United States</i> <i>^cDepartment of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom</i> <i>^dICREA, 23 Passeig Lluís Companys, Barcelona 08010, Spain</i>
10:50–11:10	<u>O-02</u> Ion Transport in H₂O-doped and Hydrated LiSCN · x H₂O <u>Markus Joos</u> ^a , Maurice Conrad ^b , Andreas Münchinger ^a , Sebastian Bette ^a , Igor Moudrakovski ^a , Rotraut Merkle ^a , Robert E. Dinnebier ^a , Thomas Schleid ^b , Joachim Maier ^a <i>^aMax Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany</i> <i>^bUniversity of Stuttgart, Institute for Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany</i>
11:10–11:20	Break (10 min)
11:20–12:30	Session 2 (Chairperson: Ilan Riess)
11:20–11:50	Invited lecture <u>I-03</u> DRT based analysis of broadband impedance data

	<p><u>Edvardas Kazakevicius</u>,^a Algimantas Kažionis,^a</p> <p>^a <i>Institute of Applied Electrodynamics and Telecommunications, Faculty of Physics, Vilnius University, Saulėtekio av. 9, LT-10222, Vilnius, Lithuania</i></p>
11:50–12:10	<p><u>O-03</u></p> <p>Catalytic anode materials for direct internal reforming Solid Oxide Fuel Cells (DIR-SOFCs) – Summary of the research project</p> <p><u>B.Bochentyn</u>,^a P. Błaszczak,^a A. Fuerte,^b S.-F. Wang,^c P. Jasiński,^d</p> <p>^a <i>Advanced Materials Center, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12 Poland</i> ^b <i>Energy Depart., Centre for Energy, Environment and Technology, Av. Complutense 40, 28040 Madrid, Spain</i> ^c <i>Department of Material and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei, 106 Taiwan</i> ^d <i>Advanced Materials Center, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12 Poland</i></p>
12:10–12:30	<p><u>O-04</u></p> <p>High temperature co-electrolysis of CO₂/H₂O and direct methanation over Co-impregnated SOEC</p> <p><u>P. Błaszczak</u>,^a S.-F. Wang,^b B. Bochentyn,^a P. Jasiński^c</p> <p>^a <i>Advanced Materials Center, Faculty of Applied Physics and Math., Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland</i> ^b <i>Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei, 106 Taiwan</i> ^c <i>Advanced Materials Center, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland</i></p>
12:30–13:30	Lunch break (60 min)
13:30–14:50	Session 3 (Chairperson: Joachim Maier)
13:30–14:00	<p>Invited lecture</p> <p><u>I-04</u></p> <p>Protonic transport in the Ba_{0.8}Ca_{0.2}NdInO₄ mixed oxide ion conductor</p> <p><u>Stephen Skinner</u></p> <p><i>Department of Materials, Faculty of Engineering, Imperial College London, Exhibition Road, London, SW7 2AZ, UK</i></p>
14:00–14:30	<p>Invited lecture</p> <p><u>I-05</u></p> <p>Dynamical heterogeneity beyond amorphous solids</p> <p><u>Kryński Marcin</u>,^{a,b,c,d} Stephen Elliott,^b Chris E. Mohn,^c Mariana Rossi,^d Wojciech Wróbel^a</p> <p>^a <i>Faculty of Physics, Warsaw University of Technology, Plac Politechniki 1, 00-661 Warszawa, Poland</i> ^b <i>Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW, UK</i> ^c <i>Centre for Earth Evolution and Dynamics, University of Oslo, N-0315 Oslo, Norway</i> ^d <i>MPI for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22765 Hamburg, Germany</i></p>
14:30–14:50	<p><u>O-05</u></p> <p>The electrochemical performance of the infiltrated SrTi_{0.3}Fe_{0.7}O_{3-δ} perovskite oxygen electrode for Solid Oxide Cells</p> <p><u>Aleksander Mroziński</u>,^a Sebastian Molin,^a Jakub Karczewski,^b Piotr Jasiński^a</p> <p>^a <i>Laboratory of Functional Materials, Gdańsk University of Technology, Narutowicza Street, 80-233, Gdańsk, Poland</i> ^b <i>Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza Street, 80-233, Gdańsk, Poland</i></p>



14:50–15:00	Break (10 min)
15:00	Meeting of the International Scientific Committee <i>(Only for members of the Committee)</i>

8 July 2021, Thursday

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09:00–09:50	Session 4 (Chairperson: Stephen Skinner)
09:00–09:30	<p>Invited lecture</p> <p>I-06</p> <p>Point Defect Concentrations in the Monomolecular Surface Layer of Binary Oxides, Dependence on Oxygen Partial Pressure and Acceptor Doping</p> <p><u>Ilan Riess</u></p> <p><i>Physics Department, Technion-IIT, Haifa 3200003, Israel</i></p>
09:30–09:50	<p>O-06</p> <p>Cobaltites with perovskite structure as positrode materials for proton ceramic electrolyzers</p> <p><u>Sebastian Wachowski</u>,^a Iga Szpunar^a, Daria Gierszewska,^a Ragnar Strandbakke,^b Maria Balaguer,^c Maria Gazda,^a Jose M. Serra,^c Truls Norby,^b Aleksandra Mielewczyk-Gryń,^a</p> <p>^a <i>Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland</i> ^b <i>Department of Chemistry, University of Oslo, FERMIo, Gaustadalléen 21, NO-0349 Oslo, Norway</i> ^c <i>Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Av. Naranjos s/n, E-46022 Valencia, Spain</i></p>
09:50–10:00	Break (10 min)
10:00–11:10	Session 5 (Chairperson: Edvardas Kazakevicius)
10:00–10:30	<p>Invited lecture</p> <p>I-07</p> <p>Electro-chemo-mechanical actuation based on rapid diffusion in Gd-doped ceria-based composite</p> <p>Evgeniy Makagon^a, Ellen Wachtel^a, Sidney R. Cohen^b, Anatoly Frenkel^c, <u>Igor Lubomirsky</u>^a</p> <p>^a <i>Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel</i> ^b <i>Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel</i> ^c <i>Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, USA</i></p>
10:30–10:50	<p>O-07</p> <p>A Local View of the Disordered Structure of BIMEVOX Solid Electrolytes for Fuel Cell Applications</p> <p><u>Yajun Yue</u>,^a Isaac Abrahams,^a Stephen Hull,^b Francizsek Krok,^c Marcin Malys^c</p> <p>^a <i>School of Biological and Chemical Sciences, Queen Mary University of London, E1 4NS, U.K.</i> ^b <i>Science and Technology Facilities Council, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.</i> ^c <i>Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw Poland.</i></p>
10:50–11:10	<p>O-08</p> <p>Multifunctional Materials in the ZrO₂ – Nd₂Zr₂O₇ System</p> <p><u>A.V. Shlyvaktina</u>,^a N.V. Lyskov,^b A.N. Shchegolikhin,^c J.C.C. Abrantes,^{d,e} E. Gomez^e</p> <p>^a <i>N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia</i> ^b <i>Institute of Problems of Chemical Physics RAS, Moscow region, Chernogolovka 142432, Russia</i> ^c <i>Emanuel Institute of Biochemical Physics RAS, Moscow, Russia,</i> ^d <i>proMetheus, Instituto Politécnico de Viana do Castelo, 4900-348 Viana do Castelo, Viana do Castelo, Portugal</i> ^e <i>CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal</i></p>
11:10–11:20	Break (10 min)

11:20–12:30	Session 6 (Chairperson: Yury Dobrovolsky)
11:20–11:50	<p>Invited lecture</p> <p><u>I-08</u></p> <p>A Fresh Look at Defect Structure in LISICONS using Reverse Monte Carlo Analysis of Total Neutron Scattering Data</p> <p>Isaac Abrahams^a, Ludan Zhang,^a Stephen Hull,^b Francizsek Krok,^c Marcin Malys^c</p> <p>^a Department of Chemistry, Queen Mary University of London, E1 4NS, U.K. ^b Science and Technology Facilities Council, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K. ^c Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw Poland.</p>
11:50–12:10	<p><u>O-09</u></p> <p>Relaxation dispersion of ionic conductivity of the Mg-doped Na_{0.5}Bi_{0.49}TiO_{3-δ} ceramics studied by impedance spectroscopy</p> <p>M. Malys^a, K. Kwatek^a, A. Dziegielewska^a, M. Krynski^a, W. Wrobel^a, I. Abrahams^b, F. Krok^a</p> <p>^a Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland ^c Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London, London, United Kingdom</p>
12:10–12:30	<p><u>O-10</u></p> <p>Ionic conductivity mechanism in Bi_{1-x}Pr_xO_{1.5} system</p> <p>J. Jamroz^a, W. Wrobel^a, M. Malys^a, I. Abrahams^b, F. Krok^a</p> <p>^a Faculty of Physics, Warsaw University of Technology, Koszykowa75, 00-662 Warszawa, Poland ^b Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London</p>
12:30–13:30	Lunch break (60 min)
13:30–14:30	Poster session 1 (Chairperson: Miran Gaberšček)
13:30–14:00	Poster group 1
	<p><u>P-01</u></p> <p>Properties of vanadium-doped lithium-manganese-borate glass and nanocomposites</p> <p>Agata Jarocka^a, Przemysław P. Michalski^a, Jacek Ryl^b, Tomasz K. Pietrzak^a, Marek Wasiucionek^a, Jerzy E. Garbarczyk^a</p> <p>^a Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland ^b Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland</p>
	<p><u>P-02</u></p> <p>The mechanism of enhanced ionic conductivity in Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃–(0.75Li₂O•0.25B₂O₃) composites</p> <p>K. Kwatek^a, W. Ślubowska^a, C. Ruiz^b, I. Sobrados^b, J. Sanz^b, J.E. Garbarczyk^a, J.L. Nowiński^a</p> <p>^a Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland ^b Instituto de Ciencia de Materiales de Madrid (ICMM CSIC), Madrid, Spain</p>
	<p><u>P-03</u></p> <p>Comprehensive study of lithium-borate glasses and nanomaterials</p> <p>P.P. Michalski^a, A. Jarocka^a, J.Sz. Otrębski^a, O. Lafon^b, J. Trébosc^b, T.K. Pietrzak^a, J.L. Nowiński^a, J.E. Garbarczyk^a</p> <p>^a Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland ^b University of Lille, CNRS, UMR 8181, UCCS-Unité de Catalyse et de Chimie du Solide, F-59000 Lille, France</p>

	<p>P-04</p> <p>Effect of high pressure on the electrical properties of olivine-like glasses</p> <p>Aleksander Szpakiewicz-Szatan^{abc}, Emilia Pawlikowska^c, Tomasz K. Pietrzak^a, Jerzy E. Garbarczyk^a, Sylwester J. Rzoska^c, Michał Boćkowski^c, Justyna Zygmuntowicz^d</p> <p>^a Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662, Warsaw, Poland ^b Doctoral School No. 1, Warsaw University of Technology, Plac Politechniki 1, 00-661 Warsaw, Poland ^c Institute of High Pressure Physics Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland ^d Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507</p>
	<p>P-05</p> <p>Ionic conductivity of Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ doped with lithium perchlorate</p> <p>Artem S. Ulihin^a, Nikolai F. Uvarov^{a,b,c}, Vyacheslav R. Khusnutdinov^a, Tatyana A. Vasileva^{a,b,c}, Kamil S. Rabadanov^d, Malik M. Gafurov^d</p> <p>^a Institute of Solid State Chemistry and Mechanochemistry SB RAS, 630090, Novosibirsk, Russia ^b Novosibirsk State University, 630090, Novosibirsk, Russia ^c Novosibirsk State Technical University, 630071, Novosibirsk, Russia ^d Federal Multiple-Access Centre "Analytical Spectroscopy" DSC RAS, 367025 Makhachkala, Russia</p>
14:00–14:30	Poster group 2
	<p>P-06</p> <p>Temperature dependance of ionic transference numbers and stability of high entropy BIMEVOX (Me=Mg_{0.25}Cu_{0.25}Ni_{0.25}Zn_{0.25})</p> <p>A. Dziegielewska^a, M. Malys^a, W. Wrobel^a, I. Abrahams^b, F. Krok^a</p> <p>^a Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland ^b Department of Chemistry, Queen Mary University of London, Mile End Road London, E1 4NS, U.K.</p>
	<p>P-07</p> <p>Structural and electrical properties of nanocomposites in Bi₂O₃-Al₂O₃-SiO₂ system obtained with fast cooling technique</p> <p>P. Kruk-Fura, T. K. Pietrzak and J. E. Garbarczyk</p> <p>Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75</p>
	<p>P-08</p> <p>Contribution withdrawn</p>
	<p>P-09</p> <p>Transport properties of solid composite electrolytes (1-x)NaNO₂-xAl₂O₃</p> <p>Lina Andrea Rodriguez Rubiano^{a,b}, D.V. Alekseev^{a,c}, Yu. G. Mateyshina^{a,b,c}</p> <p>^a Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Kutateladze 18, Novosibirsk, Russia ^b Novosibirsk State Technical University, Prospekt K. Marksa 20, 630071, Novosibirsk, Russia ^c Novosibirsk State University, Pirogova 2, 630090, Novosibirsk, Russia</p>
	<p>P-10</p> <p>Thermal, structure and transport properties study of composites (C₄H₉)₄NBF₄- Al₂O₃</p> <p>Artem S. Ulihin^a, Nikolay F. Uvarov^{a,b,c}, Konstantin B. Gerasimov^a, Kamil S. Rabadanov^d, Malik M. Gafurov^d</p> <p>^a Institute of Solid State Chemistry and Mechanochemistry SB RAS, 630090, Novosibirsk, Russia ^b Novosibirsk State University, 630090, Novosibirsk, Russia ^c Novosibirsk State Technical University, 630071, Novosibirsk, Russia ^d Federal Multiple-Access Centre "Analytical Spectroscopy" DSC RAS, 367025 Makhachkala, Russia</p>
14:30–14:40	Break (10 min)

14:40–15:40	Poster session 2 (Chairperson: Maria Gazda)
14:40–15:10	Poster group 3
	<p><u>P-11</u> Influence of dopants on the crystallinity and grain size in barium zirconate cerate thin films formed by e-beam vapor deposition</p> <p>Monica Susana Campos Covarrubias¹, Mantas Sriubas¹, Kristina Bockute¹, Piotr Winiarz², Maria Gazda², Giedrius Laukaitis¹.</p> <p>¹Kaunas University of Technology, Physics Department, Studentu str. 50, LT-51368, Kaunas, Lithuania ²Gdansk University of Technology, Faculty of Applied Physics and Mathematics, Narutowicza 11/12, 80-233 Gdansk, Poland</p>
	<p><u>P-12</u> Transport Properties of Proton-Conducting Electrolytes Based on Tin Substituted Barium Zirconate</p> <p>A.V. Kasvanova,^{a,b} J.G. Lyagaeva,^{a,b} D.A. Medvedev^{a,b}</p> <p>^a Institute of High Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, ul. Akademicheskaya 20, 620137 Yekaterinburg, Russia ^b Ural Federal University, ul. Mira 19, 622002 Yekaterinburg, Russia</p>
	<p><u>P-13</u> Synthesis and Cycle Life of Na_{2/3}MnO₂ Cathode for Sodium-Ion Batteries as Function of Electrode Binder</p> <p>Gints Kucinskis, Beate Kruze, Inara Nesterova, Gunars Bajars</p> <p>Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, LV-1063, Riga, Latvia</p>
	<p><u>P-14</u> Sn-doped barium cerates: structural, morphological and conductive properties</p> <p>L. R. Tarutina^{a,b*}, I. A. Zvonareva^{a,b}, G. K. Vdovin^a, J. G. Lyagaeva^{a,b}, D. A. Medvedev^{a,b}</p> <p>^a Institute of High Temperature Electrochemistry, 620137 Yekaterinburg, Russia ^b Ural Federal University, 620002 Yekaterinburg, Russia</p>
	<p><u>P-15</u> Electrical properties and protonic conductivity in yttrium-doped barium cerate-zirconate strained thin films</p> <p>Piotr Winiarz,^a Daniel Jaworski,^a Mirosław Sawczak,^b Monica Susana Campos Covarrubias,^c Mantas Sriubas,^c Kristina Bockute,^c Zivile Rutkuniene,^c Giedrius Laukaitis,^c Maria Gazda^a</p> <p>^a Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland ^b Polish Academy of Sciences, The Szewalski Institute of Fluid-Flow Machinery, 80-231 Gdańsk, Poland ^c Physics Department, Kaunas University of Technology, Studentu str. 50, LT-51368, Kaunas, Lithuania</p>
15:10–15:40	Poster group 4
	<p><u>P-16</u> Conductivity of (Bi₂O₃)_x(Nd₂O₃)_y(WO₃)_z compounds in dry and wet air</p> <p>Elena Kharitonova,^a Ekaterina Orlova,^a Nikolay Gorshkov,^b Vladimir Goffman,^b Valentina Voronkova^a</p> <p>^a M.V. Lomonosov Moscow State University, Leninskie gory, 119991, Moscow, Russia ^b Yuri Gagarin State Technical University of Saratov, 410054, Saratov, Russia</p>
	<p><u>P-17</u> Connectivity and Resistivity Degradation of Ni-YSZ Cermets</p>

A.V. Khrustov,^a M.V. Ananyev,^b D.I. Bronin,^a D.A. Osinkin,^{a,b} D.S. Pavlov,^a N.M. Porotnikova^a

^a Institute of High Temperature Electrochemistry, 20 Akademicheskaya, 620137, Yekaterinburg, Russia

^b Ural Federal University, 19 Mira, 620002, Yekaterinburg, Russia

P-18

The influence of preparation methods on conductivity and crystal structure of $Ce_{1-x}Pr_xO_{2-\delta}$ ($x = 0.1, 0.2$)

M. Leszczyńska,^a K. Kowalski,^a M. Małyś,^a F. Krok,^a I. Abrahams^b

^a Faculty of Physics Warsaw University of Technology, Koszykowa 75, 00-662, Warsaw, Poland

^b Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

P-19

Synthesis and properties of fluorine-substituted $Ce_{0.8}Sm_{0.2}O_{1.9}$

E. Pikalova,^{a,b} L. Ermakova,^c M. Vlasov,^a and D. Shepel^d

^a Institute of High Temperature Electrochemistry UB RAS, 20, Akademicheskaya st., 6200137, Yekaterinburg, Russia

^b Ural Federal University, 19, Mira st., 620002, Yekaterinburg, Russia

^c Institute of Solid State Chemistry UB RAS, 91, Pervomayskaya st., 620990, Yekaterinburg, Russia

^d Federal Research Center for Chemical Physics RAS, 4, Kosygina st., 119991, Moscow, Russia

P-20

Structure, Electrical Conductivity and Magnetism of $Ln_{10}W_2O_{21}$ ($Ln = Sm, Er, Tm, Yb$)

A.V. Shlyakhtina,^a S.N. Savvin,^b A.V. Kasyanova,^{c,d} D.A. Medvedev,^{c,d} I.V. Kolbanev,^a K.N. Denisova,^e I.V. Shchetinin,^f A.N. Vasiliev^{e,g}

^a N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia

^b Institut Laue-Langevin, 71 avenue des Martyrs, 38000, Grenoble, France

^c Institute of High Temperature Electrochemistry, Ural Branch, RAS

^d Ural Federal University, First President of Russia B.N. Yeltsin

^e Lomonosov Moscow State University, Moscow 119991, Russia

^f National University of Science and Technology "MISIS", Moscow 119049, Russia

^g National Research South Ural State University, Chelyabinsk 454080, Russia

9 July 2021, Friday

All times given in [CEST](#). Click on the title to jump to the abstract.

09:00–09:50	Session 7 (Chairperson: Isaac Abrahams)
09:00–09:30	<p>Invited lecture</p> <p>I-09</p> <p>Polymer Membranes Nafion for Metal Ion Batteries</p> <p>Dobrovolsky Yury,^{a,d} Kayumov Ruslan,^a Shmygleva Lyubov,^a Sanginov E.A.,^a Aigul Istomina,^b Olga Reznitskikh,^c Tatyana Yaroslavtseva,^b Tatiana Melnikova,^b Olga Bushkova^b</p> <p>^aThe Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russia ^bThe Institute of Solid-State Chemistry of the Ural Branch of the Russian Academy of Sciences, 620990, Ekaterinburg, Russia ^cI.M. Sechenov First Moscow State Medical University, 119991, Moscow, Russia ^dPlatov South-Russian State Polytechnic University (NPI), 346428, Novocherkassk, Rostov Region, Russia</p>
09:30–09:50	<p>O-11</p> <p>Building of the Glass Models by a self-assembly procedure with Non-constant Force Field Molecular Dynamics</p> <p>Anton Raskovalov,^a Nailiya Saetova^a</p> <p>^a Institute of High Temperature Electrochemistry of UB RAS, Akademicheskaya st., 20, 620137, Yekaterinburg, Russian Federation</p>
09:50–10:00	Break (10 min)
10:00–11:10	Session 8 (Chairperson: Matjaž Spreizer)
10:00–10:30	<p>Invited lecture</p> <p>I-10</p> <p>Towards higher electric conductivity and wider range of thermal stability via nanocrystallization of glasses</p> <p>Tomasz K. Pietrzak, Marek Wasuiczonek and Jerzy E. Garbacz</p> <p>Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland</p>
10:30–10:50	<p>O-12</p> <p>Electrical and structural properties of K₂O-Nb₂O₅-P₂O₅ glasses</p> <p>Marta Razum,^a Luka Pavić,^a Luciana Ghussn,^b Andrea Moguš-Milanković,^a Ana Šantić^a</p> <p>^a Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia ^b Department of Mechanics and Energy, Rio de Janeiro State University (UERJ), Resende, Brazil</p>
10:50–11:10	<p>O-13</p> <p>Towards higher conductivity and better phase purity of alluaudite-type nanocrystallized glass-ceramics for sodium-ion batteries</p> <p>Maciej Nowagiel, Mateusz J. Samsel, Tomasz K. Pietrzak</p> <p>Faculty of Physics, Warsaw University of Technology, Koszykowa 75, PL-00-662 Warsaw, Poland</p>
11:10–11:20	Break (10 min)
11:20–12:30	Session 9 (Chairperson: Igor Lubomirsky)
11:20–11:50	<p>Invited lecture</p> <p>I-11</p> <p>Electrical transport in phosphate glasses containing MoO₃ and WO₃</p>

	<p>Ana Šantić, Andrea Moguš-Milanković <i>Ruđer Bošković Institute, Bijenička cesta 54, 10000, Zagreb, Croatia</i></p>
11:50–12:10	<p>O-14 Fast electronic conduction in tungsten phosphate glass-ceramics Sanja Renka,^a Teodoro Klaser,^b Sanja Burazer,^a Petr Mošner,^c Peter Kalenda,^c Ana Šantić,^a Andrea Moguš-Milanković^a ^a <i>Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia</i> ^b <i>Faculty of Science, University of Zagreb, Bijenička cesta 32, 10000 Zagreb, Croatia</i> ^c <i>Faculty of Chemical Technology, University of Pardubice, Studentska 573, 53210 Pardubice, Czech Republic</i></p>
12:10–12:30	<p>O-15 Effect of Boron Oxide Addition on Electrical Properties of Iron Phosphate Glasses Luka Pavić,^a Stjepko Fazinić,^a Mevlüt Karabulut,^b Andrea Moguš-Milanković,^a Ana Šantić^a ^a <i>Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia</i> ^b <i>Department of Physics, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey</i></p>
12:30–13:30	Lunch break (60 min)
13:30–14:30	Poster session 3 (Chairperson: Jerzy E. Garbarczyk)
13:30–14:00	Poster group 5
	<p>P-21 New high-entropy BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}(Sm, In)_{0.2}O₃ proton conducting perovskites Daniel Jaworski, Wojciech Skubida, Tadeusz Miruszewski, Maria Gazda <i>Gdańsk University of Technology, ul. Narutowicza 11/12, 80-233, Gdańsk, Poland</i></p>
	<p>P-22 Transition Metals High-Entropy Spinel Oxides Prepared by Spray Pyrolysis Technique: Microstructural and Electrical Investigations of Thin Films Bartosz Kamecki^{a,b}, Jakub Karczewski^a, Piotr Jasiński^b, Sebastian Molin^b ^a <i>Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gabriela Naurutowicza 11/12, 80-233, Gdańsk, Poland</i> ^b <i>Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, Gabriela Naurutowicza 11/12, 80-233, Gdańsk, Poland</i></p>
	<p>P-23 3D -printing of ceramic electrode materials Małgorzata Nadolska^a, Joanna Pośpiech^a, Tomasz Sobczyk^a, Marek Chmielewski^a, Iga Szpunar^a, Sebastian Wachowski^a ^a <i>Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology, Gdansk, Poland</i></p>
	<p>P-24 Electrical properties of high-entropy perovskite oxides Wojciech Skubida, Daniel Jaworski, Maria Gazda <i>Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland</i></p>
	<p>P-25</p>

	<p>Ternary composite electrode materials for electrochemical biosensors</p> <p>N.F. Uvarov,^{a,b} A.S. Ulihin,^a A.I. Titkov,^a I.A. Malbakhova,^a T.A. Vasilyeva,^{a,c} O.S. Protazanova,^c V.R. Khusnutdinov,^a D.K. Avdeeva,^d M.M. Yuzhakov^d</p> <p>^a <i>Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, 630090, Russia</i> ^b <i>Novosibirsk State Technical University, Novosibirsk, 630071, Russia</i> ^c <i>Novosibirsk State University, Novosibirsk, 630090, Russia</i> ^d <i>National Research Tomsk Polytechnic University, Tomsk, 634050, Russia</i></p>
14:00–14:30	Poster group 6
	<p>P-26</p> <p>Structure, water uptake and electrical transport properties of BaCe_{0.6}Zr_{0.2}Y_{0.1}Mo_{0.1}O₃ (M = Fe, Pr, Tb) triple conducting oxides</p> <p>J. Budnik,^a T. Miruszewski,^a A. Mielewczyk-Gryń,^a M. Gazda^a</p> <p>^a <i>Gdańsk University of Technology, Narutowicza 11/12, 80-233, Gdańsk, Poland</i></p>
	<p>P-27</p> <p>Interphase phenomena in La₂Mo₂O₉–La₂Mo₃O₁₂ composite oxygen-ionic electrolytes</p> <p>A. Khrustov,^a N. Porotnikova,^a M.V. Ananyev,^b A. Farlenkov,^b A. Khodimchuk,^a D. Pavlov^a</p> <p>^a <i>Institute of High Temperature Electrochemistry, 20 Akademicheskaya, 620137, Yekaterinburg, Russia</i> ^b <i>Ural Federal University, 19 Mira, 620002, Yekaterinburg, Russia</i></p>
	<p>P-28</p> <p>Partial protonic conductivity of BaZr_{0.7}Ce_{0.2}Y_{0.1}O₃ studied by the modified DC Hebb-Wagner polarization method</p> <p>Tadeusz Miruszewski^a, Kacper Dzierzgowski^a, Piotr Winiarz^a, Sebastian Wachowski^a, Aleksandra Mielewczyk-Gryń^a and Maria Gazda^a</p> <p>^a <i>Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland</i></p>
	<p>P-29</p> <p>Properties of Al and Ce co-doped scandia stabilized zirconia</p> <p>Darius Virbukas^a, Mantas Sriubas^a, Nursultan Kainbayev^{a,b}, Kristina Bockute^a, Giedrius Laukaitis^a</p> <p>^a <i>Physics Department, Kaunas University of Technology, Studentu str. 50, LT-51368 Kaunas, Lithuania;</i> ^b <i>Department of Thermal Physics and Technical Physics, Al-Farabi Kazakh National University, 71 Al-Farabi Ave., 050040 Almaty, Kazakhstan</i></p>
14:30–14:40	Break (10 min)
14:40–15:10	Poster session 4 (Chairperson: Miran Gaberšček)
14:40–15:10	Poster group 7
	<p>P-30</p> <p>Structure and transport properties of donor-doped barium strontium cobaltites</p> <p>Arkadiusz Dawczak,^a Tadeusz Miruszewski,^a Wojciech Skubida,^a Kacper Dzierzgowski,^a Sebastian Wachowski,^a Aleksandra Mielewczyk-Gryń,^a Maria Gazda^a</p> <p>^a <i>Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233, Gdansk, Poland.</i></p>
	<p>P-31</p> <p>Exsolution of oxide nanoparticles on Fe- or Lu-doped barium lanthanum cobaltite (BaLaCo₂O_{6-δ}) surface</p>

	<p>D. Gierszewska,^a S. Wachowski,^a I. Szpunar,^a A. Mielewczyk-Gryń,^a M. Gazda^a</p> <p>^a <i>Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233, Gdańsk, Poland</i></p>
	<p>P-32</p> <p>Performance of Pr_{1.95}La_{0.05}CuO₄-Based Cathode in Micro-Tubular Solid Oxide Fuel Cells</p> <p>Nikolay Lyuskov,^{a,b} Marat Galin,^a Ilya Gvozdkov,^b Alexander Sivak,^b Vitaliy Sinitsyn^{a,b}</p> <p>^a <i>Institute of Problems of Chemical Physics RAS, Acad. Semenov av. 1, 142432, Chernogolovka, Russia</i> ^b <i>Inenergy LLC, 2nd Kotlyakovsky lane, 18, 115201, Moscow Russia</i></p>
	<p>P-33</p> <p>Structure, transport features and electrochemistry of layered lanthanum nickelate substituted with rare earth elements</p> <p>V. Tsvinkinberg,^{a,b} V. Sadykov,^{c,d} E. Sadovskaya,^c A. Kolchugin,^a E. Filonova,^b N. Ereemeev,^c N. Pikalova,^{a,b} A. Vylkov,^a I. Baynov,^a E. Pikalova^{a,b}</p> <p>^a <i>Institute of High Temperature Electrochemistry UB RAS, 20, Akademicheskaya str., 620137 Yekaterinburg, Russia</i> ^b <i>Ural Federal University, 19, Mira str., 620002 Yekaterinburg, Russia</i> ^c <i>Federal Research Center Boreskov Institute of Catalysis, Akad. Lavrentieva ave. 5, 630090 Novosibirsk, Russia</i> ^d <i>Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russia</i></p>
	<p>P-34</p> <p>Influence of iron doping on functional properties of Ba_{0.5}La_{0.5}Co_{1-x}Fe_xO_{3-δ}</p> <p>Iga Szpunar¹, Aleksandra Mielewczyk-Gryń¹, Daria Gierszewska¹, Małgorzata Nadolska¹, Ragnar Strandbakke², Maria Balaguer³, Jose M. Serra³, Maria Gazda¹, Sebastian Wachowski¹</p> <p>1. <i>Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland</i> 2. <i>Department of Chemistry, University of Oslo, FERMIØ, Gaustadalléen 21, NO-0349 Oslo, Norway</i> 3. <i>Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Av. Naranjos s/n, E-46022 Valencia, Spain</i></p>
15:10–15:30	Symposium closing
15:10–15:30	<p>Concluding Remarks</p> <p>Miran Gaberšček</p> <p><i>National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia</i></p>

Abstracts

Invited Lectures

Significance of Fast Ion Transport for Solid State Ionics and Beyond

Joachim Maier

Max Planck Institute for Solid State Research, Physical Chemistry of Solids,
70569 Stuttgart, Germany, e-mail: office-maier@fkf.mpg.de

The role of ion transport for solid state science can be hardly overestimated. It is fundamental to all electrochemical devices. Various devices (fuel cells, batteries, sensors etc.) use solid electrolytes. Even if liquid electrolytes are employed, it is usually the electrode as mixed conductor for which ion mobility is indispensable.

Since the point defects are not only the ionic charge carriers in solids but also the fundamental acid-base excitations, they play a paramount role for solid state reactions and heterogeneous catalysis. In typical semiconductor problems they are present as frozen species and are treated as dopants. Here then the preparation kinetics is the crucial. However, at least at interfaces their mobilities may be sufficient for them to be redistributed even under operation conditions.

The contribution discusses the significance of ion-transport for a few selected examples:

- a) Electrodes in Li- and Na-based batteries [1].
- b) Superconductivity at interfaces [2].
- c) Significance for the photo-perovskites [3].

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High entropy oxides as mixed conductors

Maria Gazda,^a Daniel Jaworski^a, Arkadiusz Dawczak^a, Tadeusz Miruszewski^a, Wojciech Skubida^a, Aleksandra Mielewczyk-Gryń^a, Sebastian Wachowski^a, Kacper Dzierzgowski^a, Piotr Winiarz^a, Iga Szpunar^a, Jagoda Budnik^a, Daria Gierszewska^a

^a*Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdansk, Poland*
e-mail: maria.gazda@pg.edu.pl

High entropy oxides (HEO) are a new class of multicomponent oxides stabilized by configurational entropy. High-entropy oxides differ from these containing cations introduced to the host structure as substitutions or dopants which have always been studied, since in HEOs all five cations are equivalent. The research on high entropy oxides commenced in 2015 from the pioneering work of Rost et al. [1] who obtained rock-salt HEO in the system of MgO, CoO, NiO, CuO and ZnO mixed in equimolar ratios. Most of the properties of high entropy oxides, especially their electrical properties, have not been sufficiently studied so far. The first studies on proton conduction in high-entropy perovskites have been published recently [2].

In this work, we present and discuss the electrical properties of selected high-entropy oxides which belong to two groups of proton-conducting oxides. The first group constitutes exemplary perovskites based on barium zirconate, whereas the second one includes modified lanthanum niobates.

Single-phase oxides were prepared using solid-state reaction method. Electrical properties of HEOs were characterized by electrochemical impedance spectroscopy and/or by DC 4-terminal method in different atmospheres. Possible contribution of proton defects, oxygen vacancies and electronic charge carriers to the total conductivity of the oxides is analyzed and discussed.

References

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DRT based analysis of broadband impedance data

Edvardas Kazakevicius,^a Algimantas Kažionis.^a

^a *Institute of Applied Electrodynamics and Telecommunications, Faculty of Physics, Vilnius University, Saulėtekio av. 9, LT-10222, Vilnius, Lithuania*
e-mail: edvardas.kazakevicius@ff.vu.lt

The preparation of the data of electrochemical impedance spectroscopy (EIS) for representation in the form of distribution of relaxation times (DRT) and finding the probability density function (PDF) of relaxation times are considered. Usually, the measurement errors of broadband EIS are not normally distributed and, herewith, cannot be modeled by white Gaussian noise. This circumstance is essential because the DRT method is hugely susceptible to measurement errors. It is shown, that considering the variation of the measurement errors across the frequency range improves the quality of the DRT function. Thus due to a comprehensively optimized problem, the DRT may provide a better resolution of distinct charge relaxation processes than the conventional equivalent circuits. The Python application was written for the calculation of the nonparametric DRT function, and the measured impedance data of solid electrolytes and RC circuits (Fig. 1) were used to illustrate the methodology of the calculation [1].

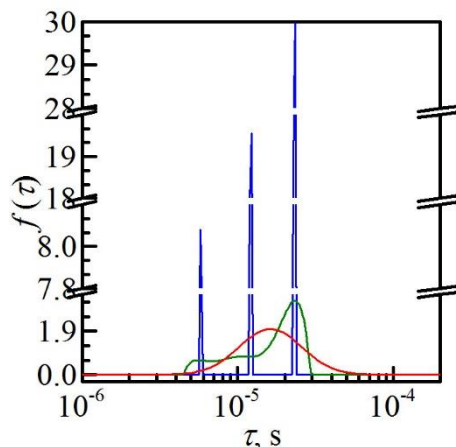


Fig. 1. DRT functions: for triple RC circuit calculated with two values of regularization coefficient (blue, red) and for single Voigt element (green).

The shape of the DRT function of the single distributed relaxation process usually is close to the Gaussian bell curve in a logarithmical time scale. Unfortunately, this kind of PDF hardly ever describes conductive ionic system's spectral characteristics satisfactorily. More complex PDFs with a greater number of independent parameters are discussed.

References

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Protonic transport in the $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{NdInO}_4$ mixed oxide ion conductor

Stephen Skinner

Department of Materials, Faculty of Engineering, Imperial College London, Exhibition Road, London, SW7 2AZ, UK

e-mail: s.skinner@imperial.ac.uk

Materials for low temperature ceramic fuel cells are increasingly sought to enable operation in the 400-600°C temperature window. To address this regime it is clear that a range of ion transport mechanisms are evaluated with the most recent advances being in the area of solid oxide proton conducting ceramics. The majority of studies have focused on the use of BaCeO_3 perovskite based electrolytes, with relatively few studies reporting new proton conductors. Combined with this there has been debate over the existence of triple conductors as electrodes in these devices (oxide, electron, proton). Recently the BaNdInO_4 composition was proposed as a new oxide ion conductor, and in this work we demonstrate that the Ca substituted phase also exhibits significant protonic transport. Our measurements encompass impedance spectroscopy and isotopic labelling studies to conclusively show that this material is a mixed conductor with significant proton mobility.

Dynamical heterogeneity beyond amorphous solids

Kryński Marcin,^{a,b,c,d} Stephen Elliott,^b Chris E. Mohn,^c Mariana Rossi,^d Wojciech Wróbel^a

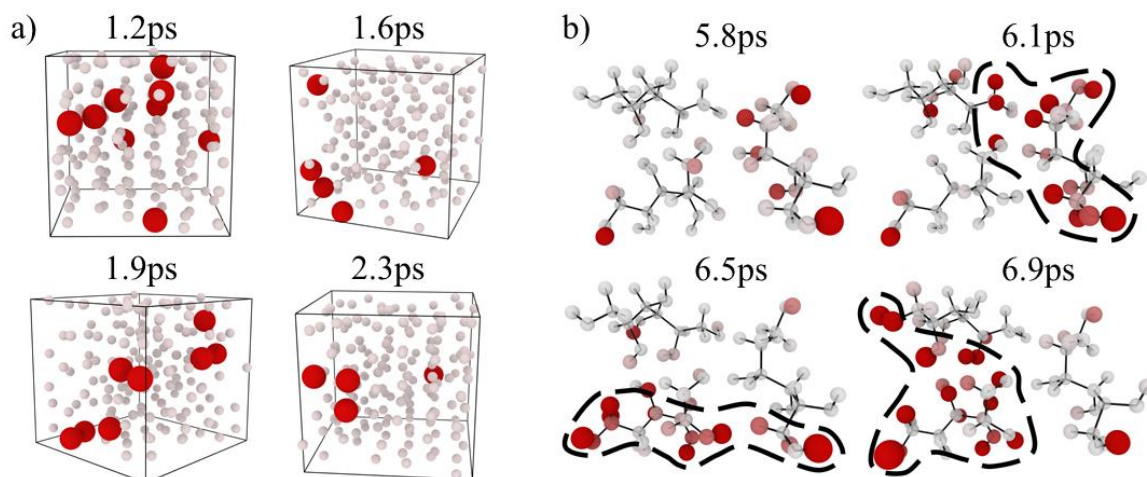
^a Faculty of Physics, Warsaw University of Technology, Plac Politechniki 1, 00-661 Warszawa, Poland

^b Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW, UK

^c Centre for Earth Evolution and Dynamics, University of Oslo, N-0315 Oslo, Norway

^d MPI for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22765 Hamburg, Germany
e-mail: marcin.krynski@pw.edu.pl

Dynamical heterogeneity is a spatiotemporal fluctuation in the local atomic dynamical behavior and it is known to control phase transitions in amorphous solids [1] as well as diffusion and viscosity near biological interfaces [2]. Here we show that this concept can be used to unravel dynamical motifs governing not only the glassy relaxations of molecular solids but also the ionic diffusion process in number of crystalline solid electrolytes. We employ *ab initio* molecular dynamics (AIMD) simulations together with case-tailored data-analysis tools to shed light on: oxide ion trapping in yttrium and niobium doped δ -Bi₂O₃, the collective nature of ionic diffusion in δ -Bi₂O₃ and PbF₂, the cooperative and heterogeneous changes in hydrogen-bond dynamics controlling α - and β -relaxation processes in glassy polyols, and the rapid ionic conductivity change of perovskite Na_{0.5}Bi_{0.5}TiO₃ associated with change in Na/Bi ratio.



Graphical depiction of the dynamical heterogeneity in consecutive steps of AIMD simulations. Red color marks rearranging atoms and white non-rearranging ones, revealing dynamically active clusters. a) δ -Bi₂O₃ at 1033K with only oxide ions displayed, b) three adjacent molecules of amorphous sorbitol at 300K with all atoms displayed.

References

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Acknowledgements

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Point Defect Concentrations in the Monomolecular Surface Layer of Binary Oxides, Dependence on Oxygen Partial Pressure and Acceptor Doping

Ilan Riess

Physics Department, Technion-IIT, Haifa 3200003, Israel

e-mail: riess@technion.ac.il

For allowing analysis of surface reactions on oxides, we here discuss the concentration of point defects in the monomolecular surface layer of binary oxides being undoped or acceptor doped. A full answer would require the knowledge of a significant number of reaction and rate constants, usually unknown. We provide the dependence of the point defect concentration in the surface layer on the oxygen partial pressure, $P(O_2)$, and bulk acceptor concentration A_b [1]. This dependence was recently shown to be sufficient for identifying series of elementary steps in surface reactions [2]. By calibrating the concentration at one value of $\{P(O_2), A_b\}$ the concentration in a wide range of values can be calculated from the known dependence on $P(O_2)$ and A_b .

While the dependence on $P(O_2)$ and A_b of point defects in the bulk of oxides is known the dependence of the concentrations in the surface layer is not known. It is repeatedly assumed, without supporting theoretical justification, that the $\{P(O_2), A_b\}$ dependence in the surface layer is the same as in the bulk. We here relate the $\{P(O_2), A_b\}$ dependence of surface defect concentrations to the known dependence of the bulk one. It turns out that there are only four classes to be considered, determined by the two options of the oxide surface layer being insulating (including semiconducting) or metallic and whether chemisorption is high (dense) or low (dilute). It turns out that the assumption of similar $\{P(O_2), A_b\}$ dependence of the surface and bulk concentrations of point defects is justified in one of these four cases: when the surface is insulating and chemisorption is low. This state is quite common as the surface layer of many oxides is insulating rather than metallic and at elevated temperatures chemisorption is low.

In highly reduced $Sm_{0.2}Ce_{0.8}O_{1.9-x}$ (SDC) the surface becomes metallic while the bulk stays a semiconductor. Applying the present method, the measured surface electron concentration vs $P(O_2)$ reported by Chueh et al.[3] is interpreted.[4] The analysis provides also the α f.c.c. phase boundary of reduced SDC. It is also shown that the surface concentration of the dopant acceptors (Sm) is enhanced by 40% over the corresponding concentration in the bulk.

For detailed analysis under dense chemisorption the knowledge of the nature of the chemisorbed specie is required. This is demonstrated by examples of common chemisorbed oxygen particles, $O_{2,ad}^{\downarrow}$ and O_{ad}^{\downarrow} . The dependence on $\{P(O_2), A_b\}$ of the density of chemisorbed particles is also presented.

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Electro-chemo-mechanical actuation based on rapid diffusion in Gd-doped ceria-based composite

Evgeniy Makagon^a, Ellen Wachtel^a, Sidney R. Cohen^b, Anatoly Frenkel^c, Igor Lubomirsky^a

^a*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel*

^b*Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel*

^c*Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, USA*

e-mail: Igor.Lubomirsky@weizmann.ac.il

The electro-chemo-mechanical (ECM) effect causes dimensional change in a solid due to change in chemical composition induced by a Faradaic electric current. The ECM effect seriously impairs the functioning of batteries or fuel cells, but, as recently suggested, it has the potential for use in actuation [1]. To explore this idea, we propose the following scheme as a basic design for an ECM actuator: electrode1\WB1\solid-electrolyte(SE)\WB2\electrode2, where WB denotes a working-body comprising a mixed ionic-electronic conductor with a large chemical expansion coefficient.

Theoretical analysis of this actuator design indicates: 1. The speed of actuation is limited by the ionic diffusion coefficient in WBs but not in SE, which may reach 10^{-14} cm²/s at room temperature. 2. ECM actuation has several potential advantages: (a) ECM actuators can simultaneously deliver large strain and large stress, which is difficult to achieve with other actuation mechanisms; (b) ECM actuators maintain their state after external voltage is removed; (c) displacement and force generated by an ECM actuator are determined by the amount of charge transferred, which is more readily controlled than electric field-driven devices. 3. The only major shortcoming of ECM actuation is that its energy conversion efficiency cannot exceed a few percent.

To demonstrate the concept, we have constructed a room temperature, nanocrystalline ECM membrane actuator (2mm diameter and $\approx 2\mu\text{m}$ thick) with Gd-doped ceria as SE. We tested two alternative compositions for WB's: (1) metal/(metal oxide) or (2) nanocrystalline ceria/metal composite. Electrical and electromechanical measurements demonstrated that the actuator response with metal/metal oxide WB's is limited by the rate of oxygen diffusion from the solid electrolyte to the metal surface. Actuators with ceria/metal composite WB's provide shorter response time ($\approx 20\text{sec}$) and larger vertical displacement ($>3.5\mu\text{m}$). These findings suggest that ECM may indeed become a valuable actuation mechanism for MEMS applications.

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Acknowledgements

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A Fresh Look at Defect Structure in LISICONS using Reverse Monte Carlo Analysis of Total Neutron Scattering Data

Isaac Abrahams,^a Ludan Zhang,^a Stephen Hull,^b Francizsek Krok,^c Marcin Malys^c

^a Department of Chemistry, Queen Mary University of London, E1 4NS, U.K.

^b Science and Technology Facilities Council, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

^c Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw Poland.
e-mail: i.abrahams@qmul.ac.uk

Over 30 years ago we proposed a defect cluster model for LISICON type systems, but physical evidence for this was limited by the technology of the time. Using reverse Monte Carlo analysis of total neutron scattering data on ⁷Li isotopically enriched samples of the model LISICON system $\text{Li}_{3+x}\text{Ge}_x\text{P}_{1-x}\text{O}_4$, details of the lithium-ion distribution are revealed. A detailed analysis of the defect clustering in $\text{Li}_{3+x}\text{Ge}_x\text{P}_{1-x}\text{O}_4$, has been obtained supported by ⁷Li and ³¹P solid state NMR spectroscopy. Analysis of the partial pair distribution functions Fig. 1 a,b have allowed for the identification of two independent types of defect cluster at low x -values (Fig. 1 c,d), which then cluster together to form larger clusters at higher lithium-ion concentrations. The details of local structure revealed in this study form the basis of a better understanding of conduction mechanisms in this important class of solid electrolytes.

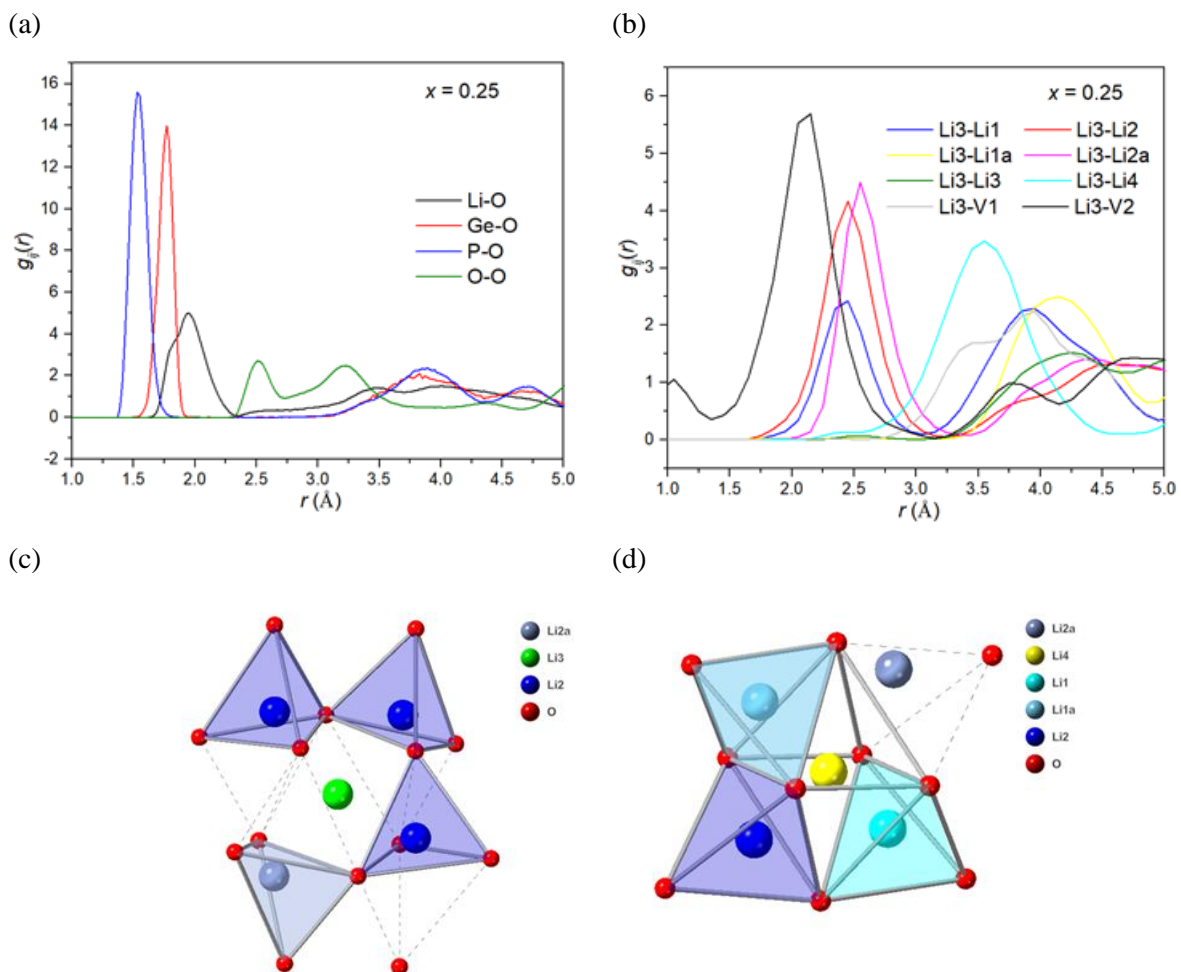


Fig 1. (a) Selected Partial pair correlations, (b) Li-Li site correlations (c) Type I cluster and (d) Type II cluster in $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{O}_4$

Polymer Membranes Nafion for Metal Ion Batteries

Dobrovolsky Yury,^{a,d} Kayumov Ruslan,^a Shmygleva Lyubov,^a Sanginov E.A.,^a
Aigul Istomina,^b Olga Reznitskikh,^c Tatyana Yaroslavtseva,^b Tatiana Melnikova,^b
Olga Bushkova^b

^a*The Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 142432, Chernogolovka,
Moscow Region, Russia*

^b*The Institute of Solid-State Chemistry of the Ural Branch of the Russian Academy of Sciences, 620990,
Ekaterinburg, Russia*

^c*I.M. Sechenov First Moscow State Medical University, 119991, Moscow, Russia*

^d*Platov South-Russian State Polytechnic University (NPI), 346428, Novocherkassk, Rostov Region, Russia*
e-mail: doibr@icp.ac.ru

The search for new materials with high transport properties is relevant for creating more energy-intensive and efficient electrochemical power sources, such as lithium and metal ion batteries. Non-aqueous conducting solid polymer electrolytes are of fundamental and practical interest. In connection with the active development of electrochemical energy sources, much attention is paid to the development of new materials with high ionic conductivity. Among materials with unipolar ionic conductivity, polymer electrolytes based on ionomers containing perfluorinated ionogenic groups ($-\text{CF}_2\text{SO}_3^-$, etc.), one of the weakest coordinating anions providing a high concentration of counterions, have significant prospects in non-aqueous environments. This, in turn, favors ion transport, especially at high electrolyte concentrations.

The growing usage of mixed solvents in electrochemical research has prompted the evaluation of plasticizing mixtures with moderately high dielectric constants. This will increase the unipolar conductivity for the cations of lithium, sodium, potassium, etc.

The analysis of the literature shows that, despite a rather large number of works published on the problem of ion transport and improving the characteristics of polymer membranes of the Nafion type, the issues of the behavior and usage of such membranes in aprotic media and their usage, as well as their properties in salt forms, are poorly understood. The search for regularities in the conductivity of membranes in salt form and in aprotic media is an important task for the problem of the development of solid polymer metal-ion electrochemical devices.

The report will present the results of experimental and calculation methods to study the effect of plasticization with aprotic solvents of acid and salt forms of Nafion- M^+ membranes (where, $\text{M}^+ = \text{H}^+$, Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Ba^{2+} , Mg^{2+} , Sr^{2+}) on their physicochemical and transport properties. These electrolytes were tested in a prototype of flexible thin-film lithium battery.

Acknowledgements

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Towards higher electric conductivity and wider range of thermal stability via nanocrystallization of glasses

Tomasz K. Pietrzak, Marek Wasiucioneck and **Jerzy E. Garbarczyk**

Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland

e-mail: jerzy.garbarczyk@pw.edu.pl

This review lecture will be focused on the earlier and recent studies on nanostructured glass-ceramic materials with substantially improved ionic or electric conductivity or with an extended thermal stability range of highly conducting, high-temperature crystalline phases. Such materials were synthesized by the thermal nanocrystallization of selected electrically conducting oxide glasses. Various nanostructured systems have been described, including glass-ceramics based on ion conductive glasses (silver iodide and bismuth oxide ones) and electronic conductive glasses (vanadate-phosphate and olivine-like ones). Most systems under consideration have been studied with the practical aim of using them as electrode or solid electrolyte materials for rechargeable Li-ion, all-solid batteries, or solid oxide fuel cells. It has been shown that the conductivity enhancement of glass-ceramics is closely correlated with its dual microstructure, consisting of nanocrystallites (5–100 nm) confined in the glassy matrix. The disordered interfacial regions in those materials form “easy conduction” paths. It has also been shown that the glassy matrices may be a suitable environment for phases, which in bulk form are stable at high temperatures, and may exist when confined in nanograins embedded in the glassy matrix even at room temperature.

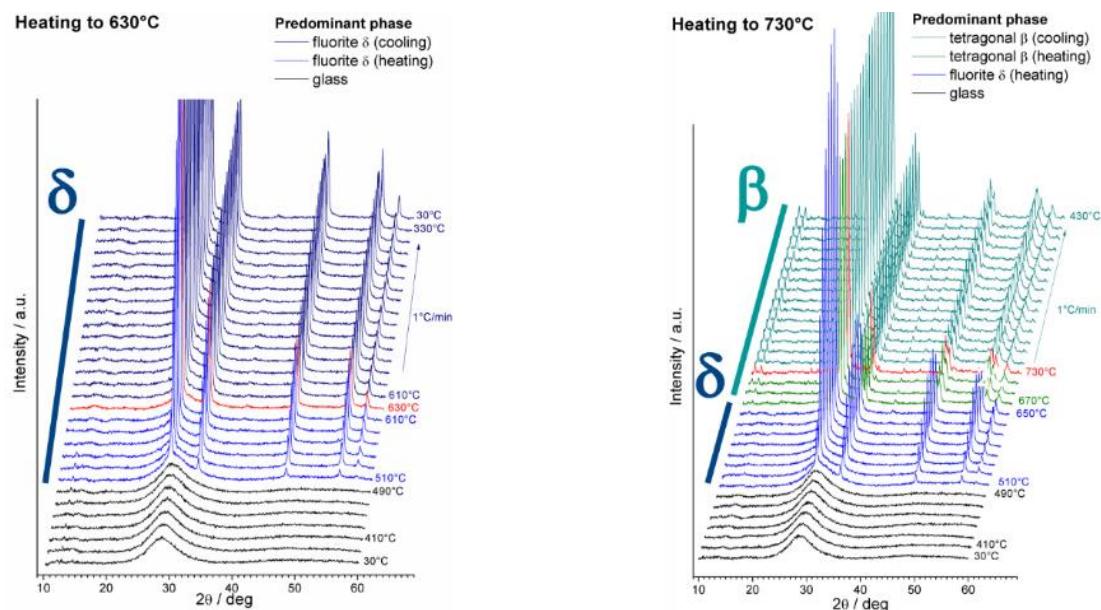


Fig.1. XRD patterns of glasses based on α - Bi_2O_3 transforming into δ and β crystalline phases during heating up to: 630 °C (on the left) and 730 °C (on the right), respectively [1].

Acknowledgements

The studies were partly funded by Materials Technologies project granted by Warsaw University of Technology under the program Excellence Initiative: Research University (ID-UB TechMat-1).

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Electrical transport in phosphate glasses containing MoO₃ and WO₃

Ana Šantić, Andrea Moguš-Milanković

Ruđer Bošković Institute, Bijenička cesta 54, 10000, Zagreb, Croatia
e-mail: asantic@irb.hr

Phosphate glasses containing transition metal oxides such as MoO₃ and WO₃ are well-known for their semiconducting nature with polaronic conduction mechanism. Also, these glasses can accommodate a relatively high amount of alkali and silver oxides which give rise to ionic conductivity. Such a large compositional and preparation variability enables tuning of the types and mechanisms of the electrical conduction and makes these materials attractive for application in modern electrochemical devices.

In this contribution, we discuss various factors that influence electrical transport in these glasses from simple binary WO₃/MoO₃-P₂O₅ systems to complex ones containing variable amounts of alkali/silver oxides. Interestingly, WO₃ and MoO₃ can play very different roles in the electrical conduction in these materials. While polaronic conductivity in MoO₃-P₂O₅ glasses depends strongly on the amount of MoO₃ and fraction of molybdenum ions in different oxidation states, in phosphate glasses containing WO₃ it is governed mainly by the features of the glass structure, in particular clustering of tungsten units which facilitates the transport of polarons. In combination with alkali oxides, WO₃ and MoO₃ can actively contribute to the electrical conductivity via polaronic transport, hence giving rise to the mixed ion-polaron conductivity, Figure 1(a). [1] On the other hand, these oxides can influence the conductivity without introducing the polaronic conduction - by forming mixed phosphate-tungstate and phosphate-molybdate units in the glass network which facilitate the transport of alkali ions in a similar manner to the classical mixed glass-former effect, Figure 1(b). [2]

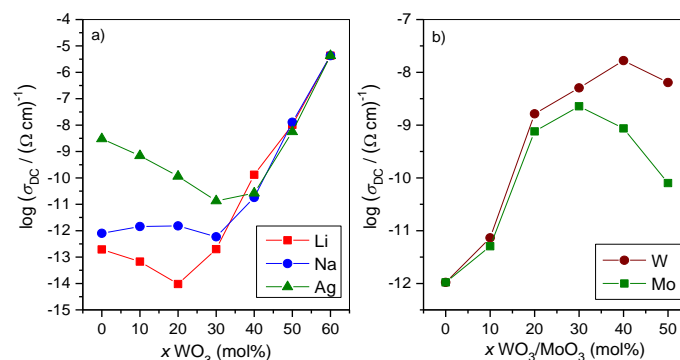


Figure 1. Compositional dependence of DC conductivity at 30 °C for a) $x\text{WO}_3$ -(30-0.5 x)Li₂O/Na₂O/Ag₂O-(30-0.5 x)ZnO-40P₂O₅, $x=0$ -60 mol% and b) 40Na₂O- $x\text{WO}_3$ /MoO₃-(60- x)P₂O₅, $x=0$ -50 mol%, glasses

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Abstracts

Oral Presentations

Direct observation of local mass transport pathways via isotope exchange-atom probe tomography

Federico Baiutti,^a Francesco Chiabrera,^a David Diercks,^b Andrea Cavallaro,^c Ainara Aguadero,^c Alex Morata,^a Albert Tarancon^{a,d}

^a Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930 Sant Adrià Besos, Spain

^b Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, United States

^c Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom

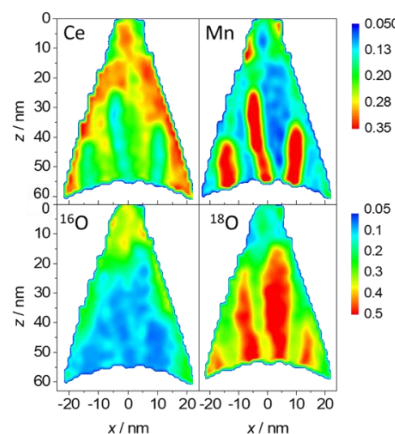
^d ICREA, 23 Passeig Lluís Companys, Barcelona 08010, Spain.

e-mail: fbaiutti@irec.cat

Engineering mass transport properties at interfaces (e.g. heterocontacts and grain boundaries) is a highly potential approach for overcoming the sluggish kinetics of typical functional oxides at intermediate temperatures.¹ Pursuing such a strategy goes hand-in-hand with the development of new tools which are able to capture local transport processes at the nanoscale.

In the present work, we demonstrate the successful application of atom probe tomography coupled with oxygen isotope exchange (IE-APT) for providing direct observation of local fast diffusion pathways in thin film nanostructures. APT is capable of resolving atomic concentrations down to 1 ppm and, most importantly, can provide a 3D map of ionic species (anionic and cationic) with spatial resolution <1 nm both off-plane and in-plane. The use of APT on thin film nanostructures which were previously annealed at high temperature in ¹⁸O-enriched atmosphere allowed to draw a quantitative picture of the preferential mass transport channels in terms of local oxygen concentration, grain size and grain boundary width, which is not directly accessible by typical spectrometry or spectroscopy methods.²

Examples of application of IE-APT for the study of grain boundaries in mixed ionic-electronic conductors and of artificial heterostructures is given, demonstrating the wide applicability and the unique potential of the approach.



2D contour of ¹⁸O-enriched LSM-SDC vertical heterostructure by IE-APT.

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Ion Transport in H₂O-doped and Hydrated LiSCN · x H₂O

Markus Joos^a, Maurice Conrad^b, Andreas Münchinger^a, Sebastian Bette^a, Igor Moudrakovski^a, Rotraut Merkle^a, Robert E. Dinnebier^a, Thomas Schleid^b, Joachim Maier^a

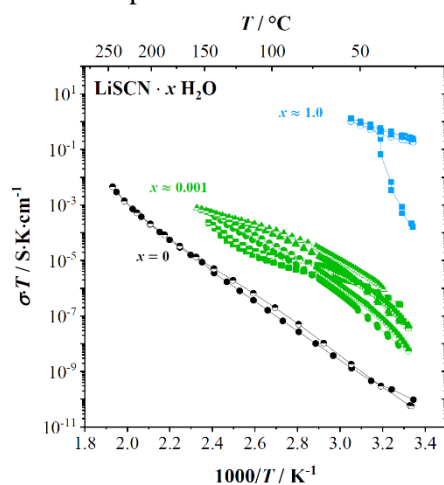
^a Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany

^b University of Stuttgart, Institute for Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

e-mail: m.joos@fkf.mpg.de

Ion conductors play an important role in energy conversion and storage, and hydrated materials are key components in protonic ceramic or polymer membrane fuel/electrolysis cells. In general, hydration can occur in three different mechanisms: (i) dissociative bulk incorporation, (ii) molecular bulk incorporation or (iii) molecular and dissociative surface adsorption. In case of molecular bulk incorporation, it was shown for layered minerals such as vermiculite that the uptake of H₂O increases the mobility of the present cation (e.g. alkaline (earth) or transition metal) by providing a more beneficial potential landscape with decreased migration barriers. The formation of LiI hydrates represents a different case, as the molecular water incorporation leads to a complete structural change and an increase of the concentration of lithium vacancies.^[1]

Anhydrous LiSCN is a poor Li ion conductor with $\sim 10^{-12}$ S/cm at room temperature, yet it shows very interesting aspects regarding the effect of water on ion transport.^[2] Upon the incorporation of only 0.001 mol-equivalents of H₂O (LiSCN · x H₂O, $x \approx 0.001$), the conductivity increases strongly by ~ 3 orders of magnitude. From thermogravimetry and impedance spectroscopy it was concluded that the water effectively dopes LiSCN by forming H₂O_{SCN} defects. The formation of this defect demonstrates the strong preference of Li⁺ for small, hard ligands, such as N of SCN and O of H₂O, over soft ligands such as S in SCN. The positive H₂O_{SCN} defects are charge-compensated by lithium vacancies V_{Li}. At temperatures below 70 °C, these defects associate to (H₂O_{SCN}V_{Li}) and then form free V_{Li} carriers at higher temperatures. With increasing water uptake the monohydrate forms ($x \approx 1$) which shows a high room temperature conductivity of $\sim 10^{-3}$ S/cm. Its crystal structure was solved ab initio from XRPD data and upon heating a phase transition was observed. The well-known dihydrate LiSCN · 2 H₂O has a low melting point of ~ 30 °C and a room temperature conductivity of 0.01 S/cm. For selected compositions, the Li⁺ as well as local SCN⁻ dynamics is studied by NMR. The results are used to construct a phase diagram of LiSCN · x H₂O and elucidate the characteristics of humidity effects on the Li⁺ ion transport. Depending on the degree of hydration, the conductivity can be tuned by up to 9 orders of magnitude which involves pronounced modifications of the defect concentrations as well as defect mobilities.



Measured conductivity of LiSCN · x H₂O for anhydrous ($x = 0$), H₂O-doped ($x \approx 0.001$) LiSCN and its monohydrate ($x \approx 1$).

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Catalytic anode materials for direct internal reforming Solid Oxide Fuel Cells (DIR-SOFCs) – Summary of the research project

B.Bochentyn,^a P. Błaszczak,^a A. Fuerte,^b S.-F. Wang,^c P. Jasiński,^d

^a *Advanced Materials Center, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12 Poland*

^b *Energy Depart., Centre for Energy, Environment and Technology, Av. Complutense 40, 28040 Madrid, Spain*

^c *Department of Material and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei, 106 Taiwan*

^d *Advanced Materials Center, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12 Poland*

e-mail: beata.bochentyn@pg.edu.pl

Ceria-based materials present high mobility of oxygen ions, high oxygen storage capacity (OSC), attractive redox catalytic properties, chemical compatibility with water and carbon dioxide at high temperatures, and sufficient resistance to reduction under relatively low oxygen partial pressures. Moreover, the high oxygen mobility in ceria promotes the mechanism of carbon removal, which in turn should contribute to the stability of the catalysts in hydrocarbon conversion reactions. Therefore, ceria-based compounds were investigated as catalytic materials for SOFC anodes directly fed with biogas to minimize the problem of carbon deposition and sulfur poisoning and therefore to increase a lifetime and efficiency of a commercial SOFC without the usage of an external reformer.

Nanocrystalline ceria doped with various elements (La, Pr, Nd, Sm, Gd, Mn, Fe, Co, Ni, Cu) was fabricated via reverse microemulsion or Pechini method. After initial structural analysis, these materials were deposited in the form of additional catalytic layers on the surface of a Ni-YSZ anode. The electrical properties of the modified SOFCs were examined by a current density-time and current density-voltage dependence measurements in hydrogen (24h) and biogas (at least 100h). Both pure synthetic biogas (CH₄/CO₂ mixture) and with additional contaminants (H₂S, chlorides, siloxanes, etc.) were applied. Simultaneously, an analysis of the catalytic activity of specific anode materials towards internal biogas reforming based on the composition of outlet gases was performed. For this purpose, a method using FTIR for the in-situ quantitative analysis of the outlet gases composition from SOFC was developed. Conversion rates for both CH₄ and CO₂ were calculated as well as yields and selectivities towards CO and H₂ generation. Moreover, a carbon balance was determined. To predict the direction of the particular reforming reactions, a non-equilibrium analysis was performed and a thermodynamic probability of a solid carbon formation was estimated.

It was found that among investigated dopants usage of lanthanides lead to a better long-term stability as well as to a higher resistance to carbon deposition and lower susceptibility to contamination than when ceria was doped with a transition metals. However, doping with Pr results in a mechanical mismatch between SOFC components due to a chemical expansion. Therefore, La, Sm, and Nd elements seem to be the most promising additives for ceria. Moreover, FTIR was found to be a reliable, quantitative method allowing to determine the efficiency of internal reforming, as well as a direction and the contribution of the particular biogas reforming reactions to the DIR-SOFC stability in time.

Basing on the conducted research, it can be stated that the internal reforming of biogas during SOFC operation is a very complex process dependent on the various phenomena taking place simultaneously. Although the role of catalytic layers is undeniable, the whole process is influenced by many factors, such as anode microstructure, gas composition, temperature, external current load, the humidity of gas and many more.

Acknowledgements

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High temperature co-electrolysis of CO₂/H₂O and direct methanation over Co-impregnated SOEC

P. Błaszczak,^a S.-F. Wang,^b B. Bochentyn,^a P. Jasiński^c

^a *Advanced Materials Center, Faculty of Applied Physics and Math., Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland*

^b *Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei, 106 Taiwan*

^c *Advanced Materials Center, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland*
e-mail: patryk.blaszczak@pg.edu.pl

In recent years, the problem of air pollution increases the demand on the research focused on green energy provision. Even though it can be generated using renewable sources, the problem of storage of excess energy still exists. The conversion into chemical fuels is highly desired. Additionally, the circulation of CO₂ produced by power plants should be maintained to decrease the greenhouse gas emissions. Affordable production of hydrocarbons can be achieved using e.g., Fischer-Tropsch synthesis. Unfortunately, the ecological H₂ production for CO₂ hydrogenation is still a problem. Either it requires fossil fuels to produce hydrogen or the process is of extremely low efficiency.

The Solid Oxide Electrolysis Cell (SOEC) possesses two major advantages over other electrolysis techniques. First, the high operation temperatures favour the fast kinetics and thermodynamics of the water electrolysis. Second, the SOECs can simultaneously split CO₂, generating more reactive CO. The heat coming from SOEC set-up can be transferred into a hydrogenation reactor for the synthesis of e.g., methane, ethane, methanol, dimethyl ether, or ammonia [1]. The proper catalysts can allow to simplify the set-up configuration by combining the co-electrolysis process together with hydrogenation of CO_x species at the hydrogen electrode of SOEC.

In this study, we developed a novel method of SOEC modification by βCD-assisted wet impregnation of fuel electrode. The conventional SOEC Ni-YSZ cermet electrode was enriched with Co nanoparticles for performing the H₂O/CO₂ co-electrolysis followed by methanation of the mixture within a single chamber. The addition of native cyclodextrin into the precursor solution resulted in obtaining cobalt oxide nanoparticles of high dispersity and homogeneity throughout the whole electrode material. The nanoparticles and their interface were characterised by means of XRD, SEM, XPS, and H₂-TPR techniques. The impregnation route allowed to introduce 1.8, 3.5, and 5.2 wt.% of Co metal into Ni-YSZ after 1, 2, and 3 preparation cycles, respectively. The SOEC impregnated twice with the Co precursor solution increased CH₄ concentration in outlet stream from 0.6 for reference up to 1.5% at 640 °C after applying the potential equal to 1.3 V. The Co addition increased the CO₂ conversion and selectivity towards CH₄ generation at high temperatures, increasing the overall methane yield. The long-term tests revealed nearly no degradation of the cell under 1.3 V. The new approach of SOEC modification can lead to the development of combined systems of onsite H₂O/CO₂ electrolysis with fuel generation.

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Acknowledgements

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The electrochemical performance of the infiltrated SrTi_{0.3}Fe_{0.7}O_{3-δ} perovskite oxygen electrode for Solid Oxide Cells

Aleksander Mroziński,^a Sebastian Molin,^a Jakub Karczewski,^b Piotr Jasiński^a

^a *Laboratory of Functional Materials, Gdańsk University of Technology, Narutowicza Street, 80-233, Gdańsk, Poland*

^b *Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza Street, 80-233, Gdańsk, Poland*

e-mail: aleksander.mrozinski@pg.edu.pl

Solid Oxide Cells (SOCs) operating at ≥ 700 °C are the current state-of-the-art [1]. There are challenges to decrease the operating temperature of SOC to 600 °C or lower. The performance of SOC at intermediate temperatures is mostly limited by slow oxygen reduction reaction (ORR) rate [2]. Therefore, research on novel materials for oxygen electrodes with high ORR is required.

An interesting group of materials are mixed ionic and electronic conductors based on Co-free and abundant elements, e.g. the SrTi_{1-y}Fe_yO_{3-δ} (STFy) family. In our recent studies we have found that the polarization resistance (ASR) of Sr_xTi_{0.3}Fe_{0.7}O_{3-δ} (STF70, x = 0.90; 0.95; 1.00; 1.05) at 600 °C, are in the range 0.3 ÷ 0.5 Ω cm⁻². The results for STF70 are comparable with commercially used La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (1.05 Ω cm⁻² at 600 °C). Interestingly, high performance of STF70 is achieved even though its electrical conductivity is much lower than the conductivity of LSCF (~20 S cm⁻¹ and ~500 S cm⁻¹ respectively). Previous studies showed that the ORR limiting process for STF materials is dissociative adsorption and incorporation of oxygen [3,4], thus for further decrease of the ASR, these processes must be improved. Surface modification of STF backbone could improve its performance, e.g. by infiltration of STF70 porous material by nanoparticles with high catalytic activity and surface area.

In this work, the effect of infiltration of porous STF70 by catalytically active nanoparticles, on the electrochemical performance will be investigated.

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Cobaltites with perovskite structure as positrode materials for proton ceramic electrolyzers

Sebastian Wachowski,^a Iga Szpunar^a, Daria Gierszewska,^a Ragnar Strandbakke,^b Maria Balaguer,^c Maria Gazda,^a Jose M. Serra,^c Truls Norby,^b Aleksandra Mielewczyk-Gryń,^a

^a *Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland*

^b *Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway*

^c *Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Av. Naranjos s/n, E-46022 Valencia, Spain*

e-mail: sebastian.wachowski@pg.edu.pl

This study evaluates water uptake, and protonation of two groups of materials: $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{BaLnCo}_2\text{O}_{6-\delta}$. The former crystallizes in a simple cubic structure, while the latter in a layered, so-called double, perovskite structure. Both groups are mixed ionic-electronic conductors, with high oxide ion and electron partial conductivities [1]. Therefore, if mobile protonic defects dissolve in these materials upon exposure to humidified gases, it would make them candidate materials for positrodes in proton ceramic electrolyzers.

In this work we used X-ray and neutron diffraction methods to study crystal structure. Thermogravimetry was used to evaluate possible water uptake upon switching from dry to wet gas at various p_{O_2} conditions. Additionally, iodometric titration combined with thermogravimetry was used to evaluate oxygen content in the material. Finally, 4-wire DC conductivity measurements were performed as a function of temperature, p_{O_2} and $p_{\text{H}_2\text{O}}$ to evaluate partial conductivities of the materials.

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A Local View of the Disordered Structure of BIMEVOX Solid Electrolytes for Fuel Cell Applications

Yajun Yue,^a Isaac Abrahams,^a Stephen Hull,^b Francizsek Krok,^c Marcin Malys^c

^a School of Biological and Chemical Sciences, Queen Mary University of London, E1 4NS, U.K.

^b Science and Technology Facilities Council, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

^c Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw Poland.
e-mail: y.yue@qmul.ac.uk

The BIMEVOXes ($\text{Bi}_2\text{V}_{1-x}\text{M}_x\text{O}_{5.5-y-\delta}$) are well known for their fast oxide ion conductivity at intermediate temperatures ($\sim 600^\circ\text{C}$). A great deal of research effort has been invested into this interesting family of materials to characterize their highly disordered structure and clarify their relationship to electrical properties. However, detailed characterization of the short-range structure is difficult due to the problems in analyzing local atomic distributions in heavily disordered structures such as these.

In this work we have used reverse Monte Carlo (RMC) analysis of neutron total scattering data to characterize the local defect structure in the $\text{Bi}_2\text{V}_{1-x}\text{Ge}_x\text{O}_{5.5-x/2-\delta}$ (BIGEVOX) system. In the simulation, X-ray total scattering data was also applied to help constrain vanadium atom that is almost ‘invisible’ in neutron diffraction due to its nearly zero scattering length. Fig. 1a and b respectively shows the fitted neutron and X-ray total scattering data for $\text{Bi}_2\text{V}_{0.9}\text{Ge}_{0.1}\text{O}_{5.45}$. While the total pair correlation function $G(r)$ is shown in Fig. 1c. The final configuration is shown in Fig. 1d with selected individual pair correlations $g_{ij}(r)$ shown in Fig. 1e. The great advantage of using the total scattering approach is that not only can local coordination numbers (Fig. 1f) and atomic distributions be obtained, but also vacancy distributions, which are critical for the understanding of the oxide ion conduction mechanism.

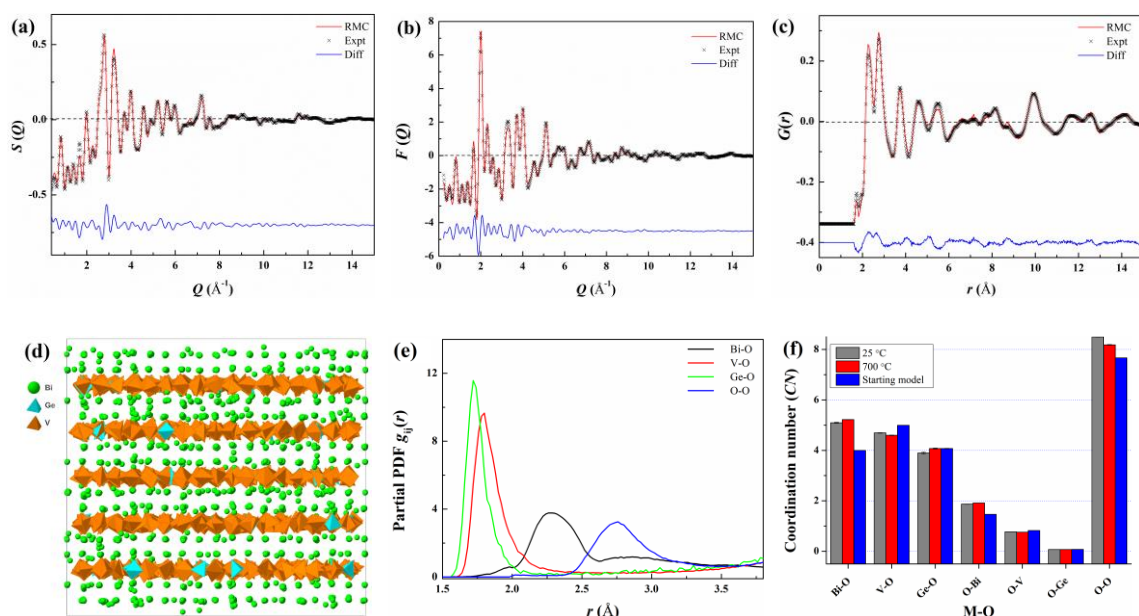


Fig. 1 Fitted (a) neutron $S(Q)$, (b) X-ray $F(Q)$, (c) total correlation function $G(r)$ and the (d) final atom configuration, (e) individual pair correlations and (f) short-range coordination numbers.

Multifunctional Materials in the ZrO₂ – Nd₂Zr₂O₇ System

A.V. Shlyakhtina,^a N.V. Lyskov,^b A.N. Shchegolikhin,^c J.C.C. Abrantes,^{d,e} E. Gomez^e

^aN.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia

^bInstitute of Problems of Chemical Physics RAS, Moscow region, Chernogolovka 142432, Russia

^cEmanuel Institute of Biochemical Physics RAS, Moscow, Russia,

^dproMetheus, Instituto Politécnico de Viana do Castelo, 4900-348 Viana do Castelo, Viana do Castelo, Portugal

^eCICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal

annashl@inbox.ru; annash@chph.ras.ru

Materials with the fluorite (ZrO₂ (8-11 mol% Ln₂O₃)) and pyrochlore (Ln₂Zr₂O₇) structure in the ZrO₂-Ln₂O₃ systems have a wide range of properties, including high oxygen-ion conductivity, low thermal conductivity, high radiation stability, luminescence. In the ZrO₂-Nd₂O₃ system, there are wide regions with substitution on Nd and Zr positions to the left and right of the nominally stoichiometric Nd₂Zr₂O₇. Earlier [1], X-ray diffraction and neutron diffraction methods showed the continuity of the fluorite – pyrochlore transition in the ZrO₂ – Nd₂Zr₂O₇ region.

In this study, to analyze the structure, we used not only long-range (XRD), but also short-range (Raman spectroscopy) method, according to [2], where the authors studied the Tm₂(Ti_{2-x}Tm_x)O_{7-x/2} (x = 0-0.67) region by XANES spectroscopy and found its local inhomogeneity.

We investigated 7 compositions with substitution to the neodymium position: (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0, 0.2, 0.4, 0.67, 0.96, 1.27). Samples were examined immediately after preparation and then after long-term storage in air to analyze their stability.

All fresh-prepared zirconates are single phase materials. The activation energies of the total conductivity and the bulk are very close, which indicate that the conductivity is controlled by the bulk behavior. Oxygen partial pressure measurements show a typical ionic conductor behavior, with a significantly increase of conductivity after doping with Zr. Long-term storage of the samples in air did not affect the oxygen-ion conductivity value. (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0.2-1.27) solid solutions demonstrated strong luminescence 2-2.5 times higher than that of Nd₂Zr₂O₇.

According to Raman spectroscopy data, the sample with the lowest degree of substitution (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x=1.27) demonstrated the spectrum identical to the spectrum of tetragonal single crystals of ZrO₂ co-doped with Y and Nd with a developed nanodomain structure [3]. Thus (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x=1.27) is the tetragonal phase in the short-range order. So the cubic high-temperature phase ZrO₂ stabilized at 12 ≤ Nd₂O₃ % < 15.

Raman spectra of (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0.2 - 0.96) solid solutions demonstrated the fluorite structural type in the short-range order. However, according to X-ray diffraction data and ND, solid solutions (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0.2 - 0.67) are pyrochlores in the long-range order and the corresponding superstructure reflections (111), (311), (331), (511) were presented in the XRD and ND [1].

Strong luminescence and high oxygen-ion conductivity of (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0.2-0.4) and (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 1.27) solid solutions can be associated with the presence of phases with the different degree of structural disorder (tetragonal phase, fluorite, pyrochlore) in local nanodomains in the ZrO₂ - Nd₂Zr₂O₇ region. Thus, the pyrochlore-fluorite transition (Nd_{2-x}Zr_x)Zr₂O_{7+x/2} (x = 0 - 1.27) is not continuous in the short order.

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Relaxation dispersion of ionic conductivity of the Mg-doped $\text{Na}_{0.5}\text{Bi}_{0.49}\text{TiO}_{3-\delta}$ ceramics studied by impedance spectroscopy

M. Malys^a, K. Kwatek^a, A. Dziegielewska^a, M. Krynski^a, W. Wrobel^a,
I. Abrahams^b, F. Krok^a

^a Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland

^c Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London, London, United Kingdom

e-mail: marcin.malys@pw.edu.pl

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is considered as a potential good candidate of electrolyte for solid-oxide fuel cells. Even small variations of Na and Bi content may lead to a significant change in electrical conductivity of these ceramic materials. So far, the highest oxide-ion conductivity has been observed for the $\text{Na}_{0.5}\text{Bi}_{0.49}\text{TiO}_{2.985}$ composition [1]. Our work is focused on further enhancement of oxide-ion conductivity by introduction of Mg to the B-site to replace part of Ti ions in the perovskite structure.

$\text{Na}_{0.5}\text{Bi}_{0.49}\text{Ti}_{0.99}\text{Mg}_{0.01}\text{O}_{2.975}$ powders were synthesized using standard solid state reaction. Dense ceramic samples were prepared and characterized by various methods to investigate the crystal structure and electrical properties as a function of temperature. For full characterization of electrical properties a.c. impedance spectroscopy and modified *EMF* [2] methods were used. The frequency dependence of conductivity and complex dielectric relaxation were combined in one model of the a.c. response. Cole-Cole and more general Havriliak and Negami relaxation functions were tested giving the opportunity to fit specific dielectric parameters as a function of temperature: relaxation strength $\Delta\varepsilon$, high frequency permittivity ε_∞ , onset ω_{onset} and relaxation ω_{relax} frequencies [3]. These fits also allowed investigation of the empirical relation of Barton-Nakajima-Namikawa.

Generally, Mg doping of parent material $\text{Na}_{0.5}\text{Bi}_{0.49}\text{TiO}_{2.985}$ enhances electrical conductivity. The ionic conductivity dominates and transference numbers reach values around 0.9. Fitting the parameters of the electrical model suggests that a subtle structural phase transition observed approximately at temperature 300°C in XRD measurements is reflected in a change of activation energy of conductivity as well as in a change of dielectric relaxation mechanism.

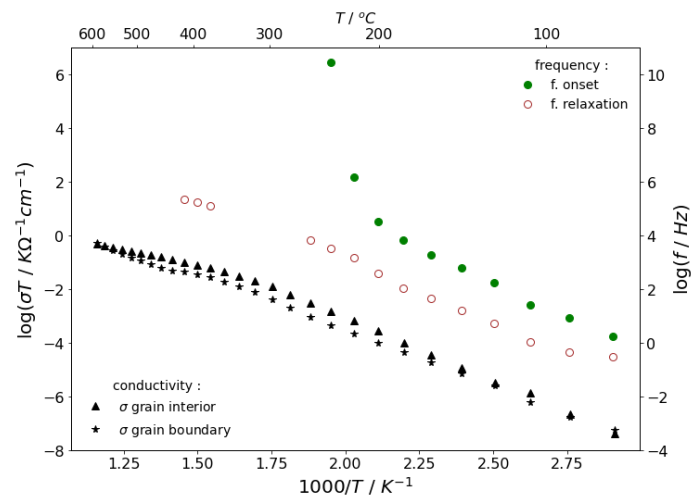


Fig. Temperature dependance of conductivity compared with temperature dependance of relaxation frequency and the onset frequency in $\text{Na}_{0.5}\text{Bi}_{0.49}\text{Ti}_{0.99}\text{Mg}_{0.01}\text{O}_{2.975}$

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Ionic conductivity mechanism in $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ system

J. Jamroz^a, W. Wrobel^a, M. Malys^a, I. Abrahams^b, F. Krok^a

^a Faculty of Physics, Warsaw University of Technology, Koszykowa75, 00-662 Warszawa, Poland

^b Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London

e-mail: jan.jamroz.dokt@pw.edu.pl

Due to the high oxide ion conductivity, bismuth oxide base compounds have been intensively studied [1]. In order to preserve highly conductive fluorite $\delta\text{-Bi}_2\text{O}_3$ type phase to room temperature, aliovalent metal doping is often necessary. In many rare earth doped bismuth oxide based systems, a rhombohedral type structure is observed. Praseodymium doped bismuth oxides, $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$, of rhombohedral structure exhibits oxide ion conductivity almost as good as that of the highly conducting $\delta\text{-Bi}_2\text{O}_3$ type phase and is more resilient during long-term annealing [2]. In the rhombohedral type system a step change of ionic conductivity is observed at ca. 700 °C and is believed to be associated with the ordering processes in the oxide ion sublattice and activation of additional conductivity pathway [3]. The aim of this work is to shed more light on the ionic conductivity mechanisms in the $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ system.

Compounds of general formula $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ $x = 0.200, 0.225, 0.250, 0.275, 0.300, 0.325$ were synthesized by a solid-state reaction method. Sintered samples show high densities, above 95% of theoretical values. XRD and neutron scattering data were collected over the temperature range 25 – 800 °C. Electrical properties were studied by the means of ac impedance spectroscopy combined with dielectric properties analysis. Conductivity data were modelled on the basis of the modified “cube-root” model using self-made fitting procedures in MATLAB software package.

Investigation of structural properties by powder X-ray and neutron diffraction confirmed rhombohedral structure throughout the studied temperature range for all of the compositions, with an order-disorder type phase transition ($\beta_2 \leftrightarrow \beta_1$) at ca. 700 °C. Rietveld analysis of diffraction patterns reveals a complex nature of a lattice parameters, varying with praseodymium content. A reversible step change in total conductivity, associated with the phase transition, is preceded by non-linear behaviour observed in the Arrhenius plot of total conductivity at lower temperatures, as presented in Fig. 1. A theoretical model based on a modification of the “cube-root” model successfully describes the conductivity data through the phase transition. Results of this fitting shows, that at the low temperature region conductivity is dominated by intra-planar conduction pathway. At the phase transition inter-planar pathway starts to dominate total ionic conductivity. Electrical properties of low temperature region conductivity were further investigated by the means of dielectric properties analysis. Combined approach sheds more light into the complex relation between structural and electrical properties at low and high temperature ranges in studied system.

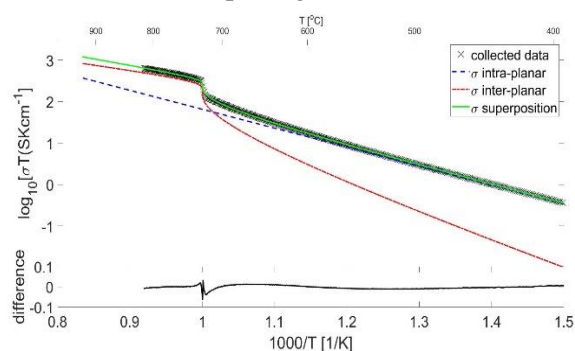


Figure 1 Arrhenius type plot of measured total conductivity for $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$, $x=0.250$, and model curves of intra- and inter-planar components [3].

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Building of the Glass Models by a self-assembly procedure with Non-constant Force Field Molecular Dynamics

Anton Raskovalov,^a Nailya Saetova^a

^a *Institute of High Temperature Electrochemistry of UB RAS, Akademicheskaya st., 20, 620137, Yekaterinburg,
Russian Federation
e-mail: other@el.ru*

Oxide glasses possess a wide range of interesting technological and physical properties, such as low porosity, ability to hot shaping, isotropy, wide range of homogeneity and etc. However, the absence of a regular structure makes glasses difficult to study by both experimental and numerical methods. The next problem with understanding of glass structure is the presence of several types of oxygen atoms. Usually, one highlights bridging and non-bridging oxygen atoms. They also can be double-bonded in some systems (phosphates, vananates and etc). Conventionally, in molecular dynamics (MD) simulations all oxygen atoms are considered as one type of particles with averaged properties. This leads to low portability of potential parameters (a force field) even for different compositions of the same system, due to changes in the ratio of bridging and non-bridging oxygen atoms. Sawaguchi [1] suggested to solve this problem in simulations of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses by varying of the oxygen potential parameters with composition. However, in this methodology all oxygen atoms are still the same for each simulation.

The reason why different types of oxygen are not set in the simulation is the random generation of the initial coordinates. With such a method we cannot know which oxygen atom should be bridging and which not. Thus, to simulate with classical MD, we must either set all oxygen particles equivalent, or use sophisticated generation algorithms that create a feasible glass structure with correct location of specified oxygen ions, as was done in [2]. Unfortunately, the used generator is very unstable, so here we proposed to use the methodology of non-constant force field MD [3] to build a glass model. The advantage of a non-constant force field is that particles can change their type runtime. So, we may start with a homogeneous melt containing free oxygen ions (O^{2-}) and set the rules by which these ions are captured by cations with the formation of covalent bonds. Thus, free oxygen transforms into non-bridged oxygen, and its capture leads, in turn, to the formation of bridged. Finally, we get a glass model which is a consequence of the “natural evolution” of the system.

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Electrical and structural properties of K₂O-Nb₂O₅-P₂O₅ glasses

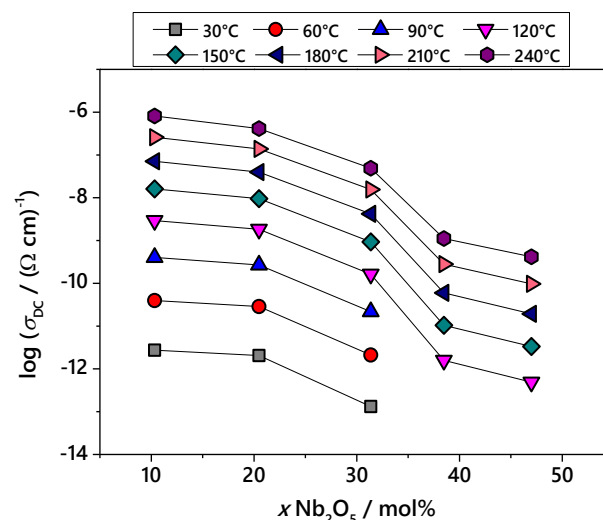
Marta Razum,^a Luka Pavić,^a Luciana Ghussn,^b Andrea Moguš-Milanković,^a Ana Šantić^a

^a Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

^b Department of Mechanics and Energy, Rio de Janeiro State University (UERJ), Resende, Brazil

e-mail: mrazum@irb.hr

Niobium phosphate glasses have functional properties which make them attractive for various fields of application, from optical and laser technology, nuclear waste immobilization to biomedicine. [1] Moreover, in combination with alkali oxides, niobium oxide can be incorporated in a phosphate network in a wide compositional range which makes these glasses interesting for electrical applications. In this study, glasses with composition $x\text{Nb}_2\text{O}_5-(100-x)[0.45\text{K}_2\text{O}-0.55\text{P}_2\text{O}_5]$, $x=10-50$ mol%, were prepared by microwave heating and their ionic conductivity and structure were investigated by impedance and Raman spectroscopies. Raman spectra reveal that the glass structure changes from predominantly orthophosphate ($x \leq 20$ mol%) to predominantly niobate ($x=50$ mol%) with increasing Nb₂O₅ content. In the glass network, niobium forms NbO₆ octahedra which, at higher Nb₂O₅ content, become mutually interconnected *via* Nb-O-Nb bonds. The changes of the electrical conductivity with composition suggest a strong influence of glass structure on the mobility of potassium ions. Glasses with predominantly orthophosphate structure and predominantly niobate glass network exhibit a slight decrease in DC conductivity with increasing Nb₂O₅ content, whereas intermediate glass compositions show a strong drop which could be attributed to the hampering effect of the mixed niobate-phosphate network on the diffusion of potassium ions. On the contrary, predominantly niobate glass network exhibits a rather facilitating influence which is evidenced not just by the trend of DC conductivity but also by the features of the frequency-dependent conductivity and typical hopping lengths of potassium ions.



DC conductivity at various temperatures as a function of Nb₂O₅ content in $x\text{Nb}_2\text{O}_5-(100-x)[0.45\text{K}_2\text{O}-0.55\text{P}_2\text{O}_5]$, $x=10-50$ mol%, glasses.

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Towards higher conductivity and better phase purity of alluaudite-type nanocrystallized glass-ceramics for sodium-ion batteries

Maciej Nowagiel, Mateusz J. Samsel, Tomasz K. Pietrzak

Faculty of Physics, Warsaw University of Technology, Koszykowa 75, PL-00-662 Warsaw, Poland
e-mail: maciej.nowagiel.stud@pw.edu.pl

Application of renewable power sources (e.g. wind and solar power plants) carries new challenges concerning energy storage. One of the remedies to stabilize their output is the utilization of battery storage stations. In this field, sodium-ion batteries (NIBs) are expected to be a sustainable and cheap alternative to lithium ones [1]. Alluaudites, first described by Fisher in 1955 [2], are among prospective cathode materials for NIBs, with the theoretical gravimetric capacity close to 170 mAh/g [3]. Poor electrical conductivity ($\sigma(275^\circ\text{C}) \approx 10^{-6}$ S/cm [4]) is one of the main obstacles to their implementation.

Alluaudite structure can be adopted by various compounds. In our research, we studied materials with nominal composition of $\text{Na}_2\text{Fe}_3(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_2\text{V}(\text{PO}_4)_3$ and $\text{Na}_2\text{FeMnV}(\text{PO}_4)_3$. Some of these compositions have been synthesized for the first time. Thermal treatment of glassy samples led to nanocrystallization of alluaudite phase [5]. Previous studies on amorphous analogues of cathode materials for Li-ion batteries show a significant increase of electrical conductivity as a result of their thermal nanocrystallization, due to the occurrence of the preferable conditions for polaron hopping mechanism of conduction [6]. We have shown that a similar procedure can be successfully applied to sodium compounds as well. We observed a significant (5 orders of magnitude) and irreversible increase of conductivity, which resulted in nanomaterials with $\sigma(25^\circ\text{C}) \approx 10^{-3}$ S/cm (Fig. 1). We also strived to elaborate optimal syntheses conditions to obtain alluaudite-like nanomaterials with maximum possible phase purity. The following parameters were taken into account: reagents used, presynthesis of the reagents, melting temperature, cooling rate, role of reducing atmosphere.

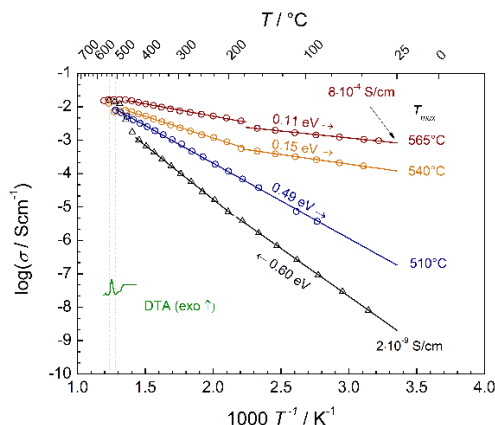


Fig. 1. Arrhenius plot for an as-prepared glassy $\text{Na}_2\text{Fe}_2\text{V}(\text{PO}_4)_3$ sample (triangles) and heated to different max. temperatures (circles) within 510–565°C range. DTA curve is given for comparison.

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Fast electronic conduction in tungsten phosphate glass-ceramics

Sanja Renka,^a Teodoro Klaser,^b Sanja Burazer,^a Petr Mošner,^c Peter Kalenda,^c Ana Šantić,^a
Andrea Moguš-Milanković^a

^a Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

^b Faculty of Science, University of Zagreb, Bijenička cesta 32, 10000 Zagreb, Croatia

^c Faculty of Chemical Technology, University of Pardubice, Studentska 573, 53210 Pardubice, Czech Republic
e-mail: srenka@irb.hr

In the last decades, various families of oxide glasses have been investigated as potential components in solid-state electrical devices. However, despite numerous advantages which glassy materials offer, the limiting factor for their application is usually low electrical conductivity. A versatile approach for improving electrical performance of glasses is thermally induced crystallization which modifies properties by tuning the nature and amount of crystalline phase(s) as well as (micro)structure. The goal of this study was to correlate electrical and structural changes which occur upon heat-treatment of $\text{WO}_3\text{-P}_2\text{O}_5$ glass at different conditions and to prepare highly electronically conductive glass-ceramics.

The parent $60\text{WO}_3\text{-}40\text{P}_2\text{O}_5$ (in mol%) glass was prepared by conventional melt-quenching technique and heat-treated at 700 °C, 800 °C and 935 °C for various times (from 1 to 24 hours). The electrical properties of prepared glass-ceramics were investigated by impedance spectroscopy in a wide frequency (0.01 Hz – 1 MHz) and temperature (-30 °C – 250 °C) range while structural properties were evaluated by X-ray powder diffraction (XRPD) and SEM-EDS analysis. Upon heat-treatment at 700 °C, the material retains fully amorphous structure, however with two types types of grains; the large ones with the composition of the parent glass and the small ones which act as precursors for crystallization of $\text{W}_2\text{O}_3(\text{PO}_4)_2$. At higher heat-treatment temperatures, the precursor grains evolve in large prismatic crystallites of $\text{W}_2\text{O}_3(\text{PO}_4)_2$ which become a dominant phase in all glass-ceramics. Along with $\text{W}_2\text{O}_3(\text{PO}_4)_2$ crystallites, the glass-ceramics prepared at 800 and 935 °C contain WO_3 nanocrystallites which increase in amount with heat-treatment temperature and time and reach 18.0 wt.% at 935 °C and 24 h. The electrical conductivity of prepared glass-ceramics is electronic in nature and shows a strong dependence on the evolution of crystalline phases (Figure 1.). The samples prepared at 700 °C exhibit lower electrical conductivity than the parent bulk glass due to the glass network rearrangement and breakage of the tungsten clusters that form easy pathways for polaronic conduction. However, a faster electronic transport can be seen in the samples prepared at higher temperatures owing to the formation $\text{W}_2\text{O}_3(\text{PO}_4)_2$ and WO_3 crystalline phases. Moreover, highly conductive glass-ceramics were obtained at 935 °C where the increase of semiconducting WO_3 nanocrystallites enhances the conduction of the glass-ceramics to the order of $\sim 10^{-4} (\Omega \text{ cm})^{-1}$ at 30 °C.

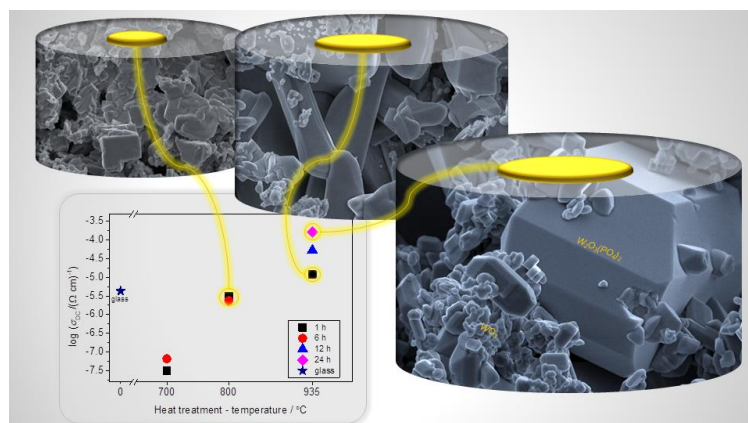


Figure 1. Electrical conductivity of parent $60\text{WO}_3\text{-}40\text{P}_2\text{O}_5$ glass and prepared glass-ceramics as a function of heat-treatment temperature and time and SEM micrographs of selected glass-ceramics.

Effect of Boron Oxide Addition on Electrical Properties of Iron Phosphate Glasses

Luka Pavić,^a Stjepko Fazinić,^a Mevlüt Karabulut,^b Andrea Mogoš-Milanković,^a Ana Šantić^a

^a *Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

^b *Department of Physics, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey*

e-mail: lpavic@irb.hr

Iron phosphate-based glasses (IPG) belong to a family of electronically conducting materials in which the conduction mechanism follows the small polaron hopping theory. Here, we report on the impact of the additional glass-forming oxide, namely B₂O₃, on the polaronic transport in binary IPG glasses. The electrical properties and their correlation to glass structure in the B₂O₃-Fe₂O₃-60P₂O₅ system are studied in detail utilizing Impedance spectroscopy in a wide frequency and temperature range [1].

The nature of electrical transport in these glasses is polaronic and shows a strong dependence on the polaron number density determined by the overall Fe₂O₃ content and the fraction of Fe²⁺ ions, while boron oxide is gradually added up to 17.7 mol% at the expense of both Fe₂O₃ and P₂O₅. The changes in DC conductivity are found not to be directly related to B₂O₃, however, a detailed investigation of the scaling properties of the conductivity spectra reveal that structural changes induced by its addition impact frequency-dependent conductivity. All individual glasses obey Summerfield and Sidebottom scaling procedures of conductivity spectra indicating that the time-temperature superposition (TTS) principle is valid and that the polaronic mechanism does not change with temperature. An attempt to construct a super-master curve revealed that the shape of the frequency-dependent conductivity is the same for glasses with up to 15.0 mol% B₂O₃, whereas it differs for the highest B₂O₃ content glass. This feature could be related to the presence of a high amount of borate units in the glass network. Moreover, the spatial extent of localized polaron motions increases with the decrease of polaron number density, but this increase shows a larger slope than for previously reported iron phosphate glasses due to the influence of B₂O₃ on glass structure and formation of polarons [2].

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Acknowledgements

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Abstracts

Poster Contributions

Properties of vanadium-doped lithium-manganese-borate glass and nanocomposites

Agata Jarocka^a, Przemysław P. Michalski^a, Jacek Ryl^b, Tomasz K. Pietrzak^a, Marek Wasiucionek^a, Jerzy E. Garbarczyk^a

^aFaculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

^bFaculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

agata.jarocka.dokt@pw.edu.pl

Rapid technology development in the field of portable devices needs adjusting those devices' batteries efficiency. One of the factors that has significant influence on cells' parameters is the electrical conductivity of their cathode material. Therefore, scientists search for ways to improve their conductivities. An interesting method to improve this property is thermal nanocrystallisation of glasses. Possible cathode material – LiMnBO₃ has found high interest in research due to its high theoretical gravimetric capacity of 222 mAh/g [1]. However, our research on this compound showed that final electrical conductivity after nanocrystallisation was still not sufficient enough. Basing on the studies [2] on vanadium-doped LiFePO₄, it was attempted to dope aforementioned LiMnBO₃ with vanadium.

Glassy LiMn_{0.925}V_{0.05}BO₃ was successfully synthesized using melt-quenching process. Then, the samples were nanocrystallised in different temperatures and characterized by: X-ray diffractometry, X-ray photoelectron spectroscopy, impedance spectroscopy and scanning electron microscopy [3].

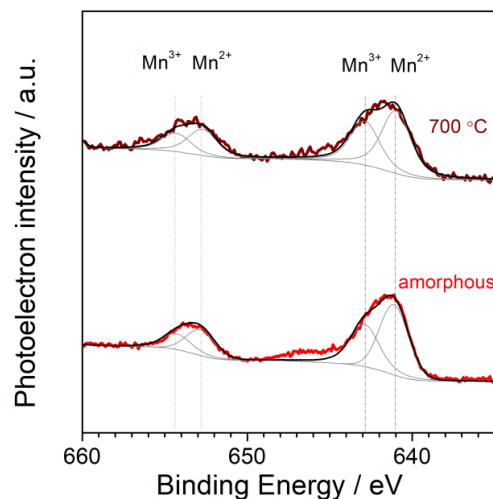


Fig. 1. High-resolution XPS spectra glassy sample and the sample crystallised at 700 °C.

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The mechanism of enhanced ionic conductivity in $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3-(0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3)$ composites

K. Kwatek^a, W. Ślubowska^a, C. Ruiz^b, I. Sobrados^b, J. Sanz^b, J.E. Garbarczyk^a,
J.L. Nowiński^a

^a *Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland*

^b *Instituto de Ciencia de Materiales de Madrid (ICMM CSIC), Madrid, Spain*

e-mail: konrad.kwatek@pw.edu.pl

The oxide-based Li^+ conductors are considered as potential solid electrolytes for lithium-ion batteries. Among the NASICON-type materials, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) seems to be a promising candidate for application. Although its bulk conductivity is of the order of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$, and seems to be sufficient for practical use, the total conductivity is considerably limited by the highly resistant grain boundaries. This shortcoming may be overcome by the formation of LATP-based ceramics with appropriate sintering aids. In this study, the $0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3$ (LBO) glass with a low melting point was chosen to improve the ionic conductivity of LATP. The properties of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_{3-y}(0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3)$ ($0 \leq y \leq 0.3$) system were studied employing: high-temperature X-ray diffractometry (HTXRD), $^6\text{Li}/^7\text{Li}$, ^{11}B , ^{27}Al and ^{31}P magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), thermogravimetry (TG), scanning electron microscopy (SEM), impedancespectroscopy (IS) and density methods.

In the case of the $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_{3-y}(0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3)$ ($0 \leq y \leq 0.3$) system, the experimental evidence clearly shows that the composite formation is an efficient way to synthesize material with high total ionic conductivity. In this study, we suggest that three main processes may be responsible for the enhancement of total ionic conductivity: (i) densification and better adhesion of neighboring grains, (ii) the decomposition of AlPO_4 , TiO_2 , and amorphous aluminophosphate phases at the grain boundaries and (iii) the formation of some lithium conducting phosphates in the presence of $0.75\text{Li}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3$ glass [1].

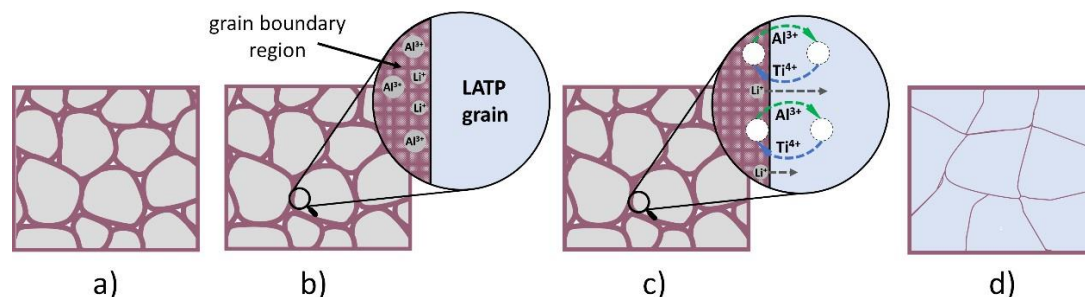


Fig. 1 Illustration of the sintering mechanism proposed for LATP-LBO composites: a) microstructure before sintering, b) release of Al^{3+} ions due to the decomposition of secondary phases at high temperatures, c) migration of Al^{3+} and Li^+ towards LATP grains and their incorporation into the crystalline lattice; diffusion of Ti^{4+} towards grain boundaries followed by the formation of new phases there, d) microstructure after sintering.

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Comprehensive study of lithium-borate glasses and nanomaterials

P.P. Michalski^a, A. Jarocka^a, J.Sz. Otrębski^a, O. Lafon^b, J. Trébosc^b, T.K. Pietrzak^a,
J.L. Nowiński^a, J.E. Garbarczyk^a

^a Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

^b University of Lille, CNRS, UMR 8181, UCCS-Unité de Catalyse et de Chimie du Solide, F-59000 Lille, France
e-mail: przemyslaw.michalski@pw.edu.pl

Introduction

Some time ago, interesting compounds with the composition LiMBO_3 ($M = \text{Fe, Mn}$) have emerged as potential cathode materials for Li-ion batteries [1]. The polycrystalline samples of those exhibited low electronic and ionic conductivity. Therefore, gravimetric capacity and cyclability were unsatisfactory.

The typical solution to these issues is obtaining materials in nanocrystalline form. Among others, thermal nanocrystallisation of glasses may be employed. It allows to obtain nanostructured materials by proper heat treatment of initially glassy samples. Here, we present our results of studies on selected physical properties of compounds obtained by thermal nanocrystallization of LiMBO_3 glasses.

Results

The ionic conductivities of initial glasses were as low as 10^{-12} – 10^{-15} S/cm. In nanocrystallised materials, the major part of conduction was due to electron hopping. The conductivity values exponentially decreased with increasing manganese content. The highest conductivity value obtained – 10^{-5} S/cm – was obtained for annealed LiFeBO_3 glass. The composite consisted of grains of LiFeBO_3 phase interconnected by highly conductive Fe_3O_4 paths. Electrochemical tests of this composite showed superior activity at low currents. The obtained capacity was 260 mAh/g which exceeds theoretical capacity of polycrystalline LiFeBO_3 (220 mAh/g) (Fig. 1).

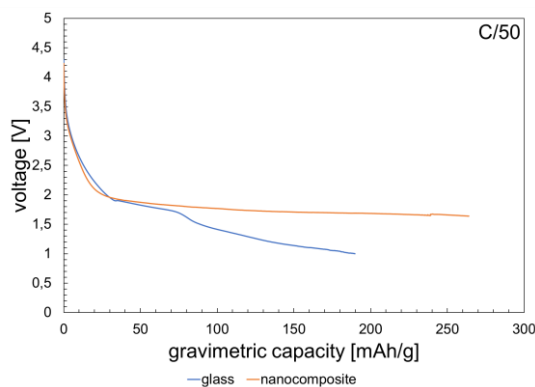


Fig. 1: Discharge curves for LiFeBO_3 glass/composite

In case of other, manganese-containing, samples interesting effects like phase-separation were observed. The local environment of lithium ions was studied by ^7Li NMR. It was shown that nanocrystallisation did not induce any significant changes in Li ions vicinity.

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Effect of high pressure on the electrical properties of olivine-like glasses

Aleksander Szpakiewicz-Szatan^{abc}, Emilia Pawlikowska^c, Tomasz K. Pietrzak^a, Jerzy E. Garbarczyk^a, Sylwester J. Rzoska^c, Michał Boćkowski^c, Justyna Zygmuntowicz^d

^a Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662, Warsaw, Poland

^b Doctoral School No. 1, Warsaw University of Technology, Plac Politechniki 1, 00-661 Warsaw, Poland

^c Institute of High Pressure Physics Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland

^d Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507

e-mail: aleksander.szpakiewicz-szatan.dokt@pw.edu.pl

Polycrystalline, lithium olivines of composition LiFePO_4 are currently one of the most common cathode material used in Li-ion batteries. Recently, because of shrinking lithium deposits and its increasing price, it is considered to replace lithium with sodium in olivines. Other drawback of olivines is their low electrical conductivity. Trying to solve this problem we proposed to use high pressure treatment of glassy analogues of olivines. In this study, NaFePO_4 olivine-like glasses were synthesized and their electrical properties were measured with broadband dielectric spectroscopy (BDS). Subsequently, the samples were pressed under high pressure (1 GPa) at temperature of 623 K. High pressure annealing was performed with use of gas pressure chamber. Fig. 1 presents the temperature dependencies of conductivity for glassy NaFePO_4 samples (measured at atmospheric pressure) before and after high pressure annealing. For comparison, the corresponding plots of lithium olivine-like samples [1] are shown. One can see that after pressure treatment conductivity increased 2 orders of magnitude and activation energy decreased. It is also worthy to note that conductivity of sodium olivine-like glass is higher than its lithium isomorph.

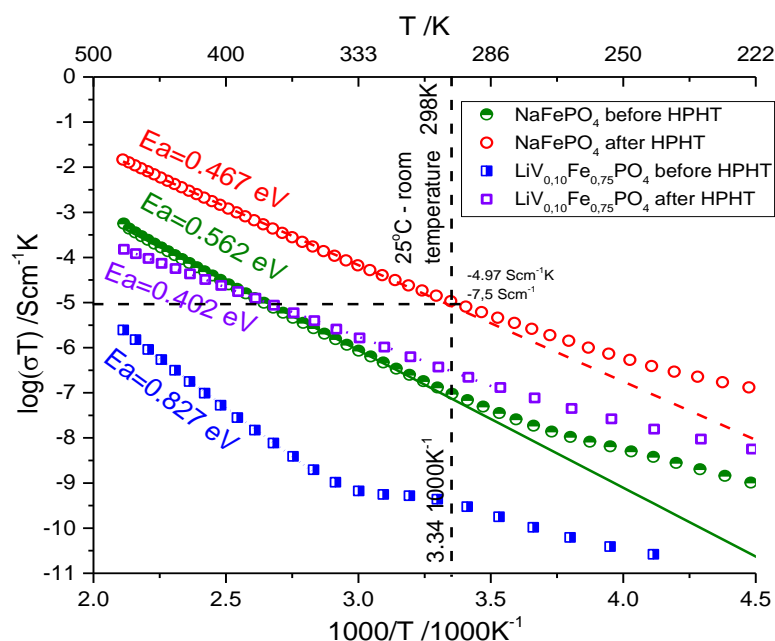


Fig.1 The effect of high pressure, high temperature (HPHT) on the conductivity of olivine-like glasses

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Acknowledgments

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Ionic conductivity of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ doped with lithium perchlorate

Artem S. Ulihin,^a Nikolai F. Uvarov,^{a,b,c} Vyacheslav R. Khusnutdinov,^a Tatyana A. Vasileva,^{a,b,c} Kamil S. Rabadanov,^d Malik M. Gafurov^d

^a Institute of Solid State Chemistry and Mechanochemistry SB RAS, 630090, Novosibirsk, Russia

^b Novosibirsk State University, 630090, Novosibirsk, Russia

^c Novosibirsk State Technical University, 630071, Novosibirsk, Russia

^d Federal Multiple-Access Centre "Analytical Spectroscopy" DSC RAS, 367025 Makhachkala, Russia

e-mail: ulikhin@solid.nsc.ru

Lithium-aluminum titanium phosphate of the chemical formula $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) is one of the most promising solid electrolytes for solid state lithium batteries. Important characteristics of this solid electrolyte are high thermal, mechanical and chemical stability, as well as, non-flammability and non-toxicity. The bulk ionic conductivity of LATP reaches 10^{-3} S/cm at room temperature [1]. However, despite the high values of the bulk conductivity, the grain boundary resistance greatly contributes to the total conductivity of LATP ceramics. As a result, the total conductivity is by several orders of magnitude lower than the bulk conductivity. In order to reduce the grain resistance, a compounds with high lithium-ion conductivity may be introduced into the intergrain volume of LATP ceramics. In such a composite the grain resistance may be significantly reduced and the total conductivity shall increase due to the formation of the ion-conducting layer on the grain boundaries in the ceramics. It has been shown [1] that the doping of LATP by ionic liquid [BMIM][BF₄] leads to the increase in the ionic conductivity of LATP by three orders of magnitude and to a significant decrease of the activation energy of conductivity compared to the undoped LATP. Similar effect was observed when LBO glass was introduced into the LATP ceramics [2]. The doped ceramics may be regarded as a composite solid electrolyte where heterogeneous additive is distributed along the grain boundaries of the second matrix. In our earlier studies it was demonstrated that lithium perchlorate has high ionic conductivity in oxide-based composites [3]. In the present work the effect of addition of lithium perchlorate to the LATP ceramics was studied.

Composite solid electrolytes LATP—LiClO₄ were synthesized using different techniques and characterized by XRD, DSC, Impedance and IR spectroscopy techniques. Conductivity was measured by HP-4284A Meter and Zive SP2 Electrochemical Workstation on pressed samples with silver electrodes in vacuum. The study of the ionic conductivity showed that the adding of LiClO₄ leads to the increasing of the total conductivity of LATP at room temperature by 3-4 orders of magnitude in comparison with the initial LATP.

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Temperature dependance of ionic transference numbers and stability of high entropy BIMEVOX (Me=Mg_{0.25}Cu_{0.25}Ni_{0.25}Zn_{0.25})

A. Dziegielewska,^a M. Malys,^a W. Wrobel,^a I. Abrahams,^b F. Krok,^a

^a Warsaw University of Technology, Faculty of Physics, 00-662 Warsaw, Poland

^b Department of Chemistry, Queen Mary University of London, Mile End Road London, E1 4NS, U.K.

e-mail: aleksandra.dziegielewska.dokt@pw.edu.pl

High entropy BIMEVOXes (HE-BIMEVOX) are defined as compounds based on the parent compound Bi₄V₂O₁₁ in which vanadium is partially replaced by several metals in an equimolar ratio. The stoichiometry of Bi₂Me_xV_{1-x}O_{5.5-3/2x} was maintained in relation to the specified value of parameter x (Me=Mg_{0.25}Cu_{0.25}Ni_{0.25}Zn_{0.25}) [1].

HE-BIMEVOX polycrystalline samples were prepared by standard solid state reaction. The electrical properties were investigated by a.c. impedance spectroscopy on dense samples with Pt electrodes. The impedance spectra were fully analysed to separate contributions of intragrain and intergrain conductivity in parallel with dielectric relaxation processes and those present at the electrode interface. The ionic transference numbers were determined by a modified *EMF* method [2] on dense ceramic membranes in the concentration cell: pure O₂ | Pt | pellet | Pt | air, in the temperature range 500 – 800 °C.

Generally, ionic conductivity values of HE-BIMEVOX are comparable to those obtained for single doped BIMEVOXes [3,4]. However interesting results suggest an increased stability of HE-BIMEVOXes during high temperature aging (450°C). In the studied temperature range (500-800°C), ionic conductivity strongly dominates the electronic contribution, as in classic BIMEVOXes, with a slight decrease (down to 5%) of ionic contribution at high temperatures. HE-BIMEVOXes exhibit some of the highest values of ionic transference numbers (Fig.1).

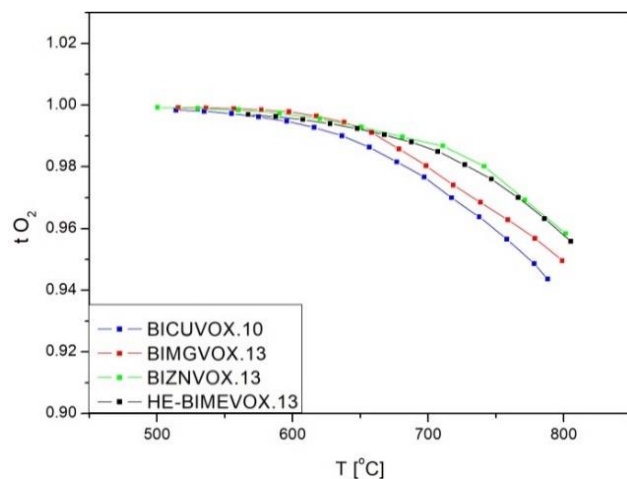


Fig.1 Transference numbers of HE-BIMEVOX and BIMEVOX with Cu, Mg and Zn with x=0.13

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Structural and electrical properties of nanocomposites in Bi₂O₃-Al₂O₃-SiO₂ system obtained with fast cooling technique

Paulina Kruk-Fura^a, Tomasz K. Pietrzak^a, Jerzy E. Garbarczyk^a

^a *Warsaw University of Technology Faculty of Physics, Koszykowa 75, 00-662 Warsaw, Poland*
e-mail: paulina.kruk-fura.dokt@pw.edu.pl

Polycrystalline Bi₂O₃ exhibits different properties, according to its crystalline phase. This fact makes it an exceptionally interesting material from the cognitive point of view and possible practical applications in electrochemical devices like e. g. fuel cells. Especially interesting remains the fluorite-like phase (δ) of Bi₂O₃, which exhibits the highest conductivity in high temperature range (1 S/cm at 750 °C) from among all known oxygen ion conductors. However, δ -phase is stable only in a narrow temperature range from 730 to 825 °C [1]. Record-breaking oxide ion conductivity of δ -Bi₂O₃ phase have motivated many researchers to stabilise fluorite-type structure down to lower temperature and to preserve high ionic conductivity. So far, successful strategies to achieve the stabilisation of the δ -phase have included obtaining solid solutions of various systems (e.g. with rare-earth elements [2]). In this paper different approach to reach the same goal is applied, based on our previous experience with studies on various materials, e.g. V₂O₅, when using fast cooling technique, e.g. twin-rollers, resulted in obtaining nanocomposites [3]. These kinds of structures quite often show very different structural properties than polycrystalline analogues, which led us to assumption that there might be possibility of stabilising fluorite-like phase (δ) by combining doping and fast cooling technique.

We chose two particularly interesting issues to examine. Firstly, how the amount of dopants of Al₂O₃ and SiO₂ influenced the process of stabilisation of δ -like phase in studied materials. Secondly, whether parameters of the synthesis affected thermal stability and electrical properties of as-received materials (and how – if these differences would be observed). We managed to obtain glass-crystalline nanocomposites of Bi₂O₃-Al₂O₃-SiO₂ system. Moreover, we showed that, under certain conditions, stabilisation of fluorite-like phase (δ) in as-received composites was possible. Synthesis and amounts of Al₂O₃ and SiO₂ dopants affected both structural and electrical properties of composites. X-ray diffraction measurements (XRD) showed that in some cases it was possible to synthesise Bi₂O₃-Al₂O₃-SiO₂ nanocomposites in the δ -like phase using twin-rollers technique. SEM results showed that obtained materials are homogenous, when distribution of grains in samples' volume is concerned. Regularity and small sizes of the grains (below 50 nm) are remarkable. Moreover, X-ray diffraction studies in function of temperature (HT-XRD) revealed that this phase remained stable up to ca. 550 °C, depending on amount of additives present and parameters of the synthesis.

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Transport properties of solid composite electrolytes

$(1-x)\text{NaNO}_2-x\text{Al}_2\text{O}_3$

Lina Andrea Rodriguez Rubiano,^{a,b} D.V. Alekseev,^{a,c} , Yu. G. Mateyshina^{a,b,c}

^a*Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Kutateladze 18, Novosibirsk, Russia*

^b*Novosibirsk State Technical University, Prospekt K. Marksa 20, 630071, Novosibirsk, Russia*

^c*Novosibirsk State University, Pirogova 2, 630090, Novosibirsk, Russia*

e-mail: liarodriguezru@outlook.com

Lithium-ion batteries (LIBs) have been widely used in portable devices and electric vehicles, due to their high energy densities and cycling stability. LIBs have certain fundamental advantages firstly, Li has the lowest reduction potential of any element, allowing Li based batteries to have the highest possible cell potential. Also, Li is the third lightest element and has one of the smallest ionic radius of any single charged ion. LIBs are composed of anode and cathode, a porous separator, and an electrolyte. Rising prices though, can be problematic for LIBs. The main disadvantages of LIBs are the shortage of Li in the earth; its high cost of extraction and production [1]. For this reason, increasingly batteries based on Na and K, are drawing attention due to the high abundance of these elements on Earth and therefore their potentially overall lower cost compared to LIBs. Therefore, the search for new electrolytes with high Na or K ion conductivity is an urgent task. Composite solid electrolytes of the ionic salt – oxide MeX-A type can be considered as a new class of ionic conductors with high ionic conductivity [2-3]. The combination of high conductivity with increased mechanical strength, wide possibilities of purposeful control of electrolyte properties by varying the type and concentration of the additive make the composites promising for practical use in real electrochemical systems. Various dispersed oxides (MgO, Al₂O₃, SiO₂, etc.) are used as an inert additive. The choice of an inert additive is carried out in such a way that it is chemically inert with respect to salt, thermally stable and has a high specific surface area. In this work, we investigated composite solid electrolytes with the composition $(1-x)\text{NaNO}_2-x\text{Al}_2\text{O}_3$ ($S_s=100$ and 200 m²/g), obtained by the ceramic method. The instrumental methods used to study this solid composite electrolytes were XRD, DSC and TG, scanning microscope, BET, impedance spectroscopy. Preliminary studies have shown that the ionic conductivity in composite solid electrolytes increases by 3-4 orders of magnitude in comparison with the initial salt.

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Acknowledgements

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Thermal, structure and transport properties study of composites (C₄H₉)₄NBF₄ - Al₂O₃

Artem S. Ulihin,^a Nikolay F. Uvarov,^{a, b, c} Konstantin B. Gerasimov,^a Kamil S. Rabadanov,^d Malik M. Gafurov^d

^a Institute of Solid State Chemistry and Mechanochemistry SB RAS, 630090, Novosibirsk, Russia

^b Novosibirsk State University, 630090, Novosibirsk, Russia

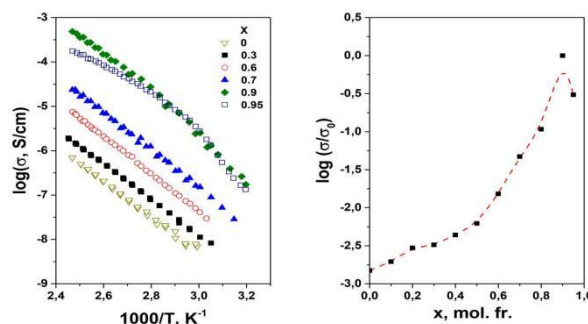
^c Novosibirsk State Technical University, 630071, Novosibirsk, Russia

^d Federal Multiple-Access Centre "Analytical Spectroscopy" DSC RAS, 367025 Makhachkala, Russia

e-mail: ulikhin@solid.nsc.ru

It is known [1] that tetrabutylammonium salt (C₄H₉)₄NBF₄ has an ionic conductivity 10⁻⁹-10⁻⁶ S/cm in the temperature range of 60-160°C. Composite systems based on this salt may be promising solid electrolytes with conductivity occurring via anions. However, to date there are no data in literature concerning composite solid electrolytes based on this salt. The goal of this work was to prepare composite solid electrolytes (C₄H₉)₄NBF₄ – Al₂O₃ with highly dispersed additives of alumina and investigate the influence of the heterogenous dopant on ionic transport and structure properties of the tetrabutylammonium salt.

Composites were prepared by mechanical mixing of the components followed by heating up to the melting temperature of the salt. The thermodynamic and structural properties of ionic salts in the obtained composites have been studied by DSC and X-ray techniques. Electrical properties were studied using impedance spectroscopy. The heterogenous doping of the ionic salt by high dispersed alumina resulted a change in the melting enthalpy of the salt accompanied by the decrease in the intensity of X-ray diffraction peaks attributed to the organic salt. It was shown that addition of γ-Al₂O₃ with the specific surface area of 200 m²/g leads to increase of the conductivity up to ~5·10⁻³ S/cm at 130°C.



The temperature dependence of conductivity of composites (1-x)(C₄H₉)₄NBF₄ – xAl₂O₃ and concentration dependence of conductivity relative change at 140°C.

According to IR spectroscopy data, the addition of the alumina leads to an increase in the mobility of ions in the anionic sublattice which determines ion transport.

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Influence of dopants on the crystallinity and grain size in barium zirconate cerate thin films formed by e-beam vapor deposition

Monica Susana Campos Covarrubias¹, Mantas Sriubas¹, Kristina Bockute¹, Piotr Winiarz²,
Maria Gazda², Giedrius Laukaitis¹.

¹*Kaunas University of Technology, Physics Department, Studentu str. 50, LT-51368, Kaunas, Lithuania*

²*Gdansk University of Technology, Faculty of Applied Physics and Mathematics, Narutowicza 11/12, 80-233
Gdansk, Poland*

monica.campos@ktu.lt

Proton conductive ceramics based on barium zirconate and barium cerate are highly studied due to their main applications to various electrochemical devices. However, barium zirconate is known to form small grain size and porous materials at low sintering temperatures leading to lower protonic conduction. Improvement of proton conduction in nanograined materials at low and intermediate temperatures between 50-300° C was demonstrated with a nanograined and highly crystalline yttrium doped barium zirconate due to the enhanced grain boundaries conduction [1].

The current research focuses on the investigation of proton conducting yttrium doped barium zirconate-cerate thin films formed by electron beam evaporation. This technique allows us to form dense yet nanograined and crystalline structures with a high protonic conduction. The comparison of BaZr_{0.8}Y_{0.2}O_{3-δ} and BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{3-δ} materials was also performed.

The structure of the deposited thin films was studied using an X-ray diffractometer (XRD) at a 2θ angle in a 20°–70° range using Cu Kα (λ = 0.154059 nm) radiation, a 0.01° step. The surface topography images and cross-section images were obtained using the scanning electron microscope (SEM). Elemental composition was controlled using an energy-dispersive X-ray spectroscope (EDS) and electrical properties were investigated by impedance spectroscopy.

It was found that deposition rates from 0.2nm/s to 2nm/s have influence in the microstructure, grain size, crystallinity, stoichiometry, and electrical properties of the formed thin films.

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Transport Properties of Proton-Conducting Electrolytes Based on Tin Substituted Barium Zirconate

A.V. Kasyanova,^{a,b} J.G. Lyagaeva,^{a,b} D.A. Medvedev^{a,b}

^a Institute of High Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences,
ul. Academicheskaya 20, 620137 Yekaterinburg, Russia

^b Ural Federal University, ul. Mira 19, 622002 Yekaterinburg, Russia
e-mail: kasyanova.1996@list.ru

High-temperature proton conductors based on acceptor-doped barium zirconate exhibit excellent chemical stability in atmospheres containing CO₂ or H₂O and, consequently, are promising for high-temperature applications. The conventional acceptor-doped zirconates show incomplete hydration ability. It was reported that the partial substituted of Zr⁴⁺-ions with Sn⁴⁺-ions resulted in full hydration [1]. However, experimental results in the referenced work were obtained for only one tin concentration; therefore, in this study we expended the concentration range of BaZr_{0.8-x}Sn_xSc_{0.2}O_{3-δ} materials and studied their transport properties in detail.

The BaZr_{0.8-x}Sn_xSc_{0.2}O_{3-δ} (x = 0, 0.1 and 0.2) powders were prepared by means of a citrate-nitrate synthesis method. Synthesis of the as-prepared powders was carried out in two stages, at 1050 °C (5 h) and 1150 °C (5 h); the ceramic samples were sintered at 1450 °C for 5 h. According to XRD data, all ceramic samples were single-phase and had a cubic perovskite structure with the *Pm3m* space group. According to SEM analysis, all sintered samples possessed high density reaching 90 % of the theoretical value. The average grain size decreases from 1 to 0.4 μm with a gradual increase of tin concentration. The total conductivity were measured by impedance spectroscopy (200–500 °C) and four-probe DC method (500–900 °C) in wet (pH₂O=0.03 atm) air and wet (pH₂O=0.03 atm) hydrogen atmospheres. It was revealed that high-temperature properties were governed by the ceramic morphology (particularly, average grain size), and low-temperature properties were determined by competing processes: a decrease in average grain size and an increase in the hydration ability. The composition with x=0.1 demonstrates the highest values in total, ionic, grain and grain boundary conductivities (Fig 1). Therefore, it was confirmed that a low Zr-to-Sn substitution degree is a promising approach for designing new proton-conducting electrolytes.

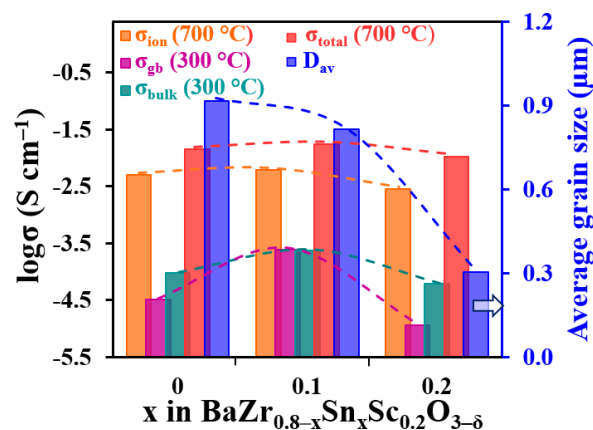


Fig. 1. Concentration dependences of morphological and electrical properties of BaZr_{0.8-x}Sn_xSc_{0.2}O_{3-δ}

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Synthesis and Cycle Life of Na_{2/3}MnO₂ Cathode for Sodium-Ion Batteries as Function of Electrode Binder

Gints Kucinskis, Beate Kruze, Inara Nesterova, Gunars Bajars

Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, LV-1063, Riga, Latvia
e-mail: gints.kucinskis@cfi.lu.lv

As growing price and demand for lithium motivates a search for alternatives to lithium-ion batteries, sodium-ion batteries emerge as a good candidate for stationary energy storage [1]. Although many of the materials used in Na-ion batteries are analogous to materials used in lithium-ion batteries, because of higher Na ion size and different chemical properties, further materials' optimization is needed.

In this study, we prepared Na_{2/3}MnO₂ cathode material for sodium-ion batteries and studied its electrochemical properties as a function of the electrode binder. We researched PVDF and alginate binder materials and found that solvent-based anhydrous slurries are most suitable for preparation of Na_{2/3}MnO₂ electrodes. This is due to water replacing sodium ions with protons, ultimately converting the P-2 layered crystal lattice of Na_{2/3}MnO₂ to a different phase [2]. We also find, however, that anhydrous alginate-based binder enables obtaining up to 5 % higher gravimetric capacity with comparably good cycle life (figure 1) compared to PVDF. Moreover, alginate binder prepared with anhydrous slurries also yields improved cycle life in electrolytes where no additional solid-electrolyte interphase stabilising additives are used.

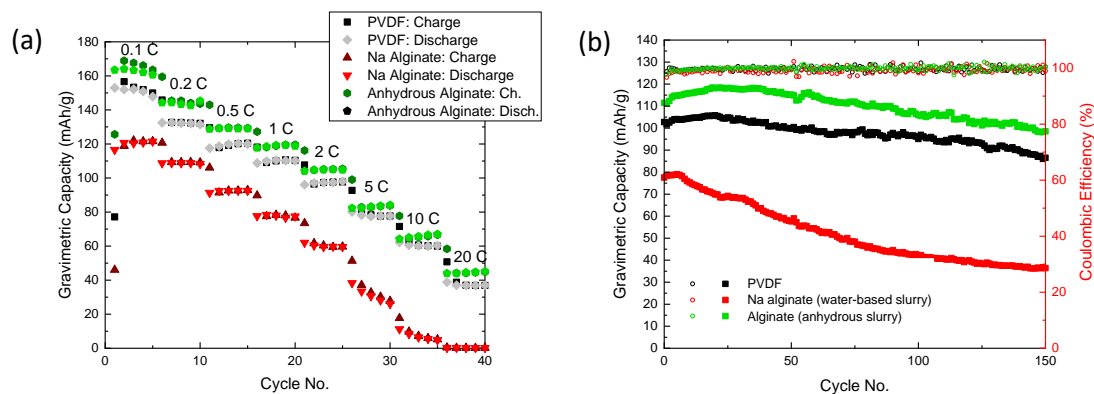


Figure 1. (a) Rate capability and (b) cycle life at 1 C of Na_{2/3}MnO₂ electrodes prepared with different binders

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Sn-doped barium cerates: structural, morphological and conductive properties.

L. R. Tarutina^{a,b,*}, I. A. Zvonareva^{a,b}, G. K. Vdovin^a,

J. G. Lyagaeva^{a,b}, D A. Medvedev^{a,b}

^a Institute of High Temperature Electrochemistry, 620137 Yekaterinburg, Russia

^b Ural Federal University, 620002 Yekaterinburg, Russia

*e-mails: lee.hakimova@gmail.com

There is great interest in promising environmentally safe devices capable of converting chemical energy into electrical one, namely solid oxide fuel cells (SOFCs). The application of chemically stable proton-conducting electrolytes in SOFCs allows achieving high power at lower temperatures and preventing materials interaction. A significant amount of research has been focused on the state-of-the-art proton-conducting perovskites based on BaCeO₃. While cerates display the highest proton conductivity at low temperatures, their instability in CO₂ and water-containing atmospheres remains a barrier to their real-world application. Thus, the design of novel proton-conducting materials that overcome the main limitations of cerates becomes an urgent challenge. For example, yttrium doped BaSnO₃ exhibits proton conductivity and chemical stability close to that of BaZrO₃. In this connection, tin (Sn) is additionally proposed as a suitable candidate for the partial substitution of cerium in BaCeO₃ owing to its lower melting point and ionic radius close to that of zirconium ($r_{Sn^{4+}} = 0.69\text{\AA}$ and $r_{Zr^{4+}} = 0.72\text{\AA}$), which can be expected to provide similar chemical stabilisation of cerates.

This work purpose is to obtain single-phase materials of the composition BaCe_{0.8-x}Sn_xYb_{0.2}O_{3-δ} (with x = 0.3, 0.4, and 0.5) and the further investigation of their structural and conductive properties. The BaCe_{0.8-x}Sn_xYb_{0.2}O_{3-δ} powders were prepared by solid-state synthesis method. According to the X-ray data, all samples are found to be single-phase with a cubic-type perovskite structure. The chemical stability of all Sn-containing samples was confirmed by XRD following treatment in water vapour and CO₂ for 10 hours. It was found that even 30 mol. % of tin in BaCeO₃ is sufficient to stabilise the structure. The measured relative density of the obtained samples was around 85% of the theoretical quantity. This indicates incomplete densification, which is probably associated with the more refractory nature of tin as compared with cerium. High-temperature electrical conductivity was measured using the four-probe DC method in wet hydrogen, nitrogen and air. It was found that Sn-doping leads to a decrease in total conductivity irrespective of the gas compositions used. Taking the type of gas atmosphere into account, the total conductivity for all three samples tends to decrease in a sequence of air → nitrogen → hydrogen and increase with hydrogen humidification. The latter comes from the increased concentration of protonic defects and correspondingly higher level of protonic conductivity. AC impedance spectra were collected while cooling from 600 °C to 300 °C in dry and wet air. To relate the semicircles with the corresponding electrochemical processes, an equivalent circuit scheme of R₀ – R₁Q₁ – R₂Q₂ – R₃Q₃ was applied. The fitting analysis of the spectra according to the proposed model allows the bulk, grain boundary and total conductivities to be determined. The electrical properties of BaCe_{0.8-x}Sn_xYb_{0.2}O_{3-δ} at high temperatures are determined by bulk transport and increase with air humidification, at low-temperature transport properties are governed by grain boundaries. Based on the results of this work it was concluded that these materials are shown to be suitable for application as proton-conducting electrolytes in SOFCs due to their good ionic conductivity and chemical stability.

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Electrical properties and protonic conductivity in yttrium-doped barium cerate-zirconate strained thin films

Piotr Winiarz,^a Daniel Jaworski,^a Mirosław Sawczak,^b Monica Susana Campos Covarrubias,^c Mantas Sriubas,^c Kristina Bockute,^c Zivile Rutkuniene,^c Giedrius Laukaitis,^c Maria Gazda^a

^a *Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland*

^b *Polish Academy of Sciences, The Szewalski Institute of Fluid-Flow Machinery, 80-231 Gdańsk, Poland*

^c *Physics Department, Kaunas University of Technology, Studentu str. 50, LT-51368, Kaunas, Lithuania*
e-mail: piotr.winiarz1@pg.edu.pl

Selected electrical properties of strained yttrium doped barium cerate-zirconate thin films were investigated and presented. Tensile or compressive strain in the films was induced through the difference in thermal expansion coefficients (TECs) of the support and the material. The obtained results were compared with their bulk counterparts.

Thin films of $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY) were deposited using a self-made PLD chamber described elsewhere [1] with 266nm Nd:YAG laser. The temperature and time of deposition were respectively 610°C, and 60 mins, under argon atmosphere with pressure 0.5 mbar. The pellets of sputtered materials were obtained via the co-precipitation route from nitrates. Resultant solutions were dried, mixed and calcined at 1450°C for 4h with 2°C/min heating and cooling rate. The materials used as substrates were: metal alloys (Invar, Inconel, Glass sealing alloy and Stainless steel – Goodfellow), single crystal oxides (Al_2O_3 , MgO and YSZ – CrysTec GmbH), and monocrystalline p-type silicon (100). The thickness of films was estimated using the DektakXT profilometer and was around 600nm. The phase composition was checked using Phillips X'Pert Pro diffractometer, $\lambda = 1,54\text{Å}$. The electrical experiments were performed using ProboStat (Norecs AS) and Novocontrol Alpha-A frequency analyzer. The measurements were carried out in dry and humidified N_2 atmosphere in the temperature range 200°C – 800°C with 20°C step, and frequency range of 0.01Hz – 1MHz.

All of the prepared samples (thin films and bulk BCZY) were single-phase. In the bulk samples, the total conductivity was higher in humidified nitrogen than in dry nitrogen. Moreover, the activation energies were lower in wet N_2 when compared with dry N_2 . In previously investigated metal-supported thin films, the possible decrease of activation energy may result from the compressive strain, what was described in our work [2]. The compressive strain induced through the influence of oxygen–oxygen distances, causes an increase in proton diffusivity and a decrease the activation energy.

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Conductivity of $(\text{Bi}_2\text{O}_3)_x(\text{Nd}_2\text{O}_3)_y(\text{WO}_3)_z$ compounds in dry and wet air

Elena Kharitonova,^a Ekaterina Orlova,^a Nikolay Gorshkov,^b Vladimir Goffman,^b Valentina Voronkova^a

^a M.V. Lomonosov Moscow State University, Leninskie gory, 119991, Moscow, Russia

^b Yuri Gagarin State Technical University of Saratov, 410054, Saratov, Russia

e-mail: harit@polly.phys.msu.ru

Bi_2O_3 , and its solid solutions attracts attention as oxygen conductors with extremely high conductivity (0.1-1 S/cm at 800 °C). Pure Bi_2O_3 has a complex polymorphism with four basic Bi_2O_3 phases: 1) α - Bi_2O_3 room temperature monoclinic phase; 2) β - Bi_2O_3 tetragonal phase; 3) γ - Bi_2O_3 cubic phase; 4) high-temperature δ - Bi_2O_3 cubic phase with fluorite structure. The main attention in literature is paid to the stabilization of the oxygen-conducting δ - Bi_2O_3 cubic phase by doping. The best results were achieved for codoping Bi_2O_3 with W(Mo) and rare earth [1-3]. In this work we investigated phase formation of Bi_2O_3 -based compounds in ternary Bi_2O_3 - Nd_2O_3 - WO_3 system and their conductivity in dry and wet atmosphere.

$(\text{Bi}_2\text{O}_3)_x(\text{Nd}_2\text{O}_3)_y(\text{WO}_3)_z$ ($x + y + z = 1$) polycrystalline samples have been obtained by solid-state synthesis at 800-1100 °C depending on Bi content. The samples were characterized by XRD, TG, DSC and impedance spectroscopy. Samples with monoclinic (α - Bi_2O_3), tetragonal (β - Bi_2O_3 and $\text{Bi}_{14}\text{WO}_{24}$ -type) and cubic (δ - Bi_2O_3) structure arises in narrow crystallization fields at high Bi content ($0.8 < x < 1$). At lower Bi concentration ($x < 0.8$) three large crystallization fields with monoclinic ($\text{Bi}_{3.24}\text{La}_2\text{W}_{0.76}\text{O}_{10.14}$ -type), additional fluorite cubic (δ' - Bi_2O_3) and rhombohedral ($\text{Bi}_4\text{Nd}_6\text{O}_{15}$ -type) structure have been found.

It is interesting that some above mentioned compounds exhibit hygroscopic properties. TG measurements with previously hydrated samples show significant water evaporation from all compounds except for the samples with cubic δ - Bi_2O_3 structure. In the samples with high Bi content and also for monoclinic $\text{Bi}_{3.24}\text{La}_2\text{W}_{0.76}\text{O}_{10.14}$ -type samples water evaporation was observed mainly from the pores of the ceramics. For δ' - Bi_2O_3 and $\text{Bi}_4\text{Nd}_6\text{O}_{15}$ -type samples the structurally bound water was found.

The conductivity of the $(\text{Bi}_2\text{O}_3)_x(\text{Nd}_2\text{O}_3)_y(\text{WO}_3)_z$ ceramics with δ - Bi_2O_3 , δ' - Bi_2O_3 and $\text{Bi}_{3.24}\text{La}_2\text{W}_{0.76}\text{O}_{10.14}$ -type structure has been measured in dry and wet air at 200-700 °C. In dry air all curves show Arrhenius behavior with activation energy 0.9 - 1.2 eV, which is typical for oxygen ion conductors. In wet air we have observed an increase in conductivity of δ' - Bi_2O_3 cubic samples, and lowering of their activation energy. Such behavior is typical for proton conductors. The conductivity of $\text{Bi}_{3.24}\text{La}_2\text{W}_{0.76}\text{O}_{10.14}$ -type compounds in wet air increases slightly. For δ - Bi_2O_3 samples we have found no difference when the humidity of the atmosphere changes, which is in good agreement with TG data.

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Connectivity and Resistivity Degradation of Ni-YSZ Cermets

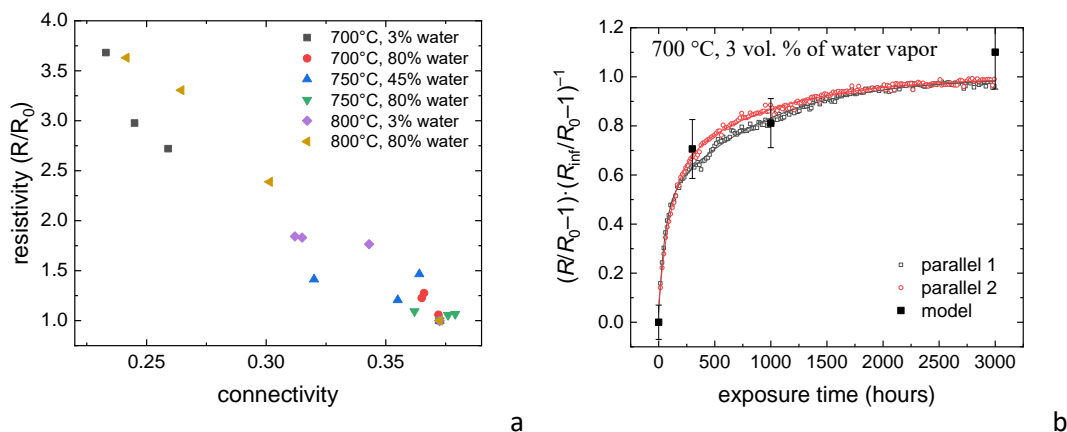
**A.V. Khrustov,^a M.V. Ananyev,^b D.I. Bronin,^a D.A. Osinkin,^{a,b} D.S. Pavlov,^a
N.M. Porotnikova^a**

^a Institute of High Temperature Electrochemistry, 20 Akademicheskaya, 620137, Yekaterinburg, Russia

^b Ural Federal University, 19 Mira, 620002, Yekaterinburg, Russia

e-mail: A_Khrustov@ihte.uran.ru

Long-term aging tests were carried out on Ni-YSZ cermets [1], performed for 3000 hours under a wide range of experimental conditions of 700, 750, and 800°C and humidified hydrogen with 3, 45, and 80 vol.% of water content. The microstructural analysis of the virgin samples and samples after aging tests was carried out using the unique approach to the SEM image processing for calculations of microstructural parameters (porosity, Ni and YSZ phase content, particle size distribution function). The development of the 3D models of the Ni phase anode based on the modeling approach of randomly filling a three-dimensional medium by spheres with a given diameter distribution [2] was performed. The finite element method was used for the calculation of the electrical conductivity of the 3D models. The effective resistance of the nickel phase of three-dimensional models calculated by the finite element method directly depends on the volume fraction of the connected nickel cluster (connectivity), which is determined by the exposure time under the conditions of the aging test. The particle coarsening and the nickel fraction decrease effect on the connectivity and lead to a rise in the effective resistance due to the formation of bottlenecks and complication of the electrical current pathways.



Effective relative resistivity estimated by FEM depending on connectivity of the Ni-YSZ cermet exposed to experimental degradation conditions (a); Comparison experimental and computed related resistivity of the Ni-YSZ cermet during the degradation experiment (b)

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The influence of preparation methods on conductivity and crystal structure of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0.1, 0.2$)

M. Leszczyńska,^a K. Kowalski,^a M. Małys,^a F. Krok,^a I. Abrahams^b

^a Faculty of Physics Warsaw University of Technology, Koszykowa 75, 00-662, Warsaw, Poland

^b Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

e-mail: marzena.redek@pw.edu.pl

Praseodymium doped cerium oxide, with compositions of general formula $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ show fast ion conduction depending on oxygen partial pressure ($p\text{O}_2$) and Pr content [1,2]. These properties are making them suitable as electrolyte but also, due to significant electronic conductivity, as an electrode. In this work we examined the influence of three selected techniques of preparation of ceramic materials on crystal structure and conductivity behaviour.

Samples of two compositions $x = 0.1$ and $x = 0.2$ were prepared by three methods: solid state reaction, co-precipitation and sol-gel based Pechini method. Crystal structure of all examined materials was characterised by X-ray powder diffraction at room temperature and as a function of temperature in air. Additionally, the neutron diffraction measurements (ISIS Facility, United Kingdom) for samples prepared by standard solid state reaction were performed. The expansion of lattice parameter with temperature for all samples due to thermal and chemical expansion is observed. For samples prepared by co-precipitation method the chemical expansion of unit cell due to oxygen loss ($\text{Pr}^{4+} \rightarrow \text{Pr}^{3+}$) is observed at lower temperature than for samples prepared by solid state reaction. The refinement of neutron diffraction data (for samples prepared by solid state reaction) reveal full occupancy of oxygen positions in this system which means that Pr has 4+ oxidation state at room temperature. Electrical properties as a function of temperature in air were obtained by a.c. impedance spectroscopy. All prepared samples of the same composition were measured in the same time using multi-sample holder to ensure the same conditions of environment (temperature and atmosphere). The highest total conductivity is obtained for samples prepared by Pechini method (fig. 1).

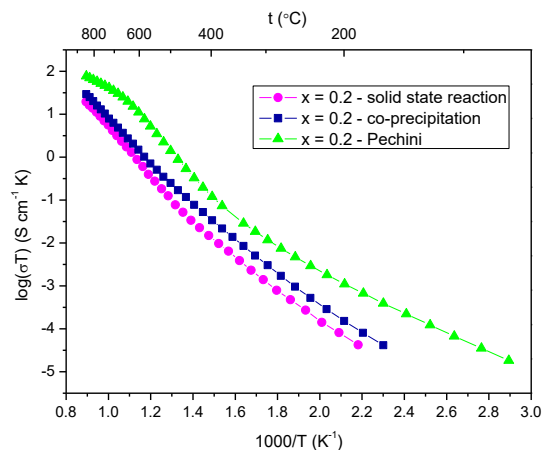


Fig. 1. The Arrhenius plots of total conductivity of $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ prepared using solid state reaction, co-precipitation and Pechini methods.

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Synthesis and properties of fluorine-substituted $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$

E. Pikalova,^{a,b} L. Ermakova,^c M. Vlasov,^a and D. Shepel^d

^a Institute of High Temperature Electrochemistry UB RAS, 20, Akademicheskaya st., 6200137, Yekaterinburg, Russia

^b Ural Federal University, 19, Mira st., 620002, Yekaterinburg, Russia

^c Institute of Solid State Chemistry UB RAS, 91, Pervomayskaya st., 620990, Yekaterinburg, Russia

^d Federal Research Center for Chemical Physics RAS, 4, Kosygina st., 119991, Moscow, Russia
e-mail: e.pikalova@list.ru

Recently it was revealed that a method of fluorine doping of perovskite-related oxides can be used for improving their oxygen-ion conductivity [1]. In this study, such approach was applied for the first time to modification of the fluorite structured CeO_2 -based solid state electrolyte. A synthesis method to obtain submicron materials of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-(3x)/2}\text{F}_{3x}$ series was developed. Structure and properties of as-prepared materials (calcined at 800 °C) and compact samples (sintered at 1300 – 1350 °C) were investigated using XRD, Raman spectroscopy, TOF-SIMS and impedance spectroscopy methods. Results of the XRD analysis showed that all of the materials possessed a fluorite structure with insignificant decreasing the unit cell parameter with the fluorine doping from 5.4292(5) ($3x=0.03$) down to 5.4258(5) ($3x=0.3$) due to the size factor. Presence of fluorine in the synthesized materials was confirmed by the TOF-SIMS analysis (Fig 1 a). Appearance of an additional component in the main Raman scattering peak (at $\sim 460\text{ cm}^{-1}$) related to a F_{2g} vibrational mode of anions in the fluorite structure (Fig. 1 b) indicates that fluorine is incorporated into the oxygen sublattice. The fluorine doping enhanced the total conductivity mainly due to decreasing the grain boundary resistance. The R_{gb} values for the compact samples with fluorine content of 0.03 and 0.3 (sintered at 1300 °C) measured at 600 °C in air were equal to 736 and 207 Ohm, respectively. It was demonstrated that increasing the sintering temperature had no effect on the conductivity value. The applied strategy to improve functional properties of CeO_2 -based oxygen-conducting electrolytes demonstrated its viability and can be further developed.

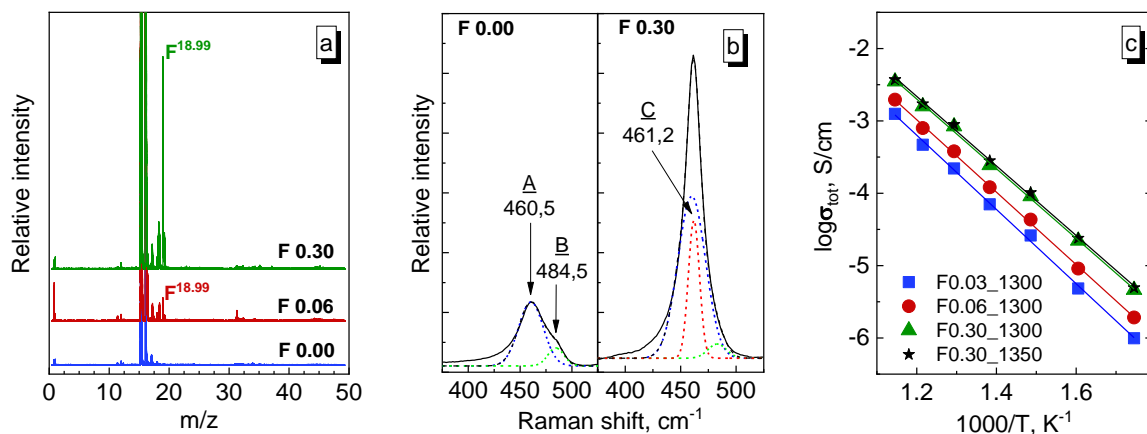


Figure 1: Mass-spectra (a), Raman spectra (b) and total conductivity (c) of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-(3x)/2}\text{F}_{3x}$

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Acknowledgements

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Structure, Electrical Conductivity and Magnetism of $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Sm}, \text{Er}, \text{Tm}, \text{Yb}$)

A.V. Shlyakhtina,^a S.N. Savvin,^b A.V. Kasyanova,^{c,d} D.A. Medvedev,^{c,d} I.V. Kolbanov,^a
K.N. Denisova,^e I.V. Shchetinin,^f A.N. Vasiliev^{e,g}

^a*N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia*

^b*Institut Laue-Langevin, 71 avenue des Martyrs, 38000, Grenoble, France*

^c*Institute of High Temperature Electrochemistry, Ural Branch, RAS*

^d*Ural Federal University, First President of Russia B.N. Yeltsin*

^e*Lomonosov Moscow State University, Moscow 119991, Russia*

^f*National University of Science and Technology "MISIS", Moscow 119049, Russia*

^g*National Research South Ural State University, Chelyabinsk 454080, Russia*

annashl@inbox.ru; annash@chph.ras.ru

Rare-earth lanthanide (Ln) tungstates and molybdates were found to have mixed ion–electronic conductivity with a potential ability of being used in solid oxide fuel cells and proton conducting membranes [1]. The least studied in terms of structure and properties are $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ and $\text{Ln}_{14}\text{W}_4\text{O}_{33}$ compounds. Tungstates $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Sm}, \text{Er}, \text{Tm}, \text{Yb}$) were synthesized using the mechanical activation method and subsequent short (3h) annealing of activated $5\text{Ln}_2\text{O}_3 + 2\text{WO}_3$ oxide mixtures at 1600 °C. Powder X-ray and neutron diffraction data collected at room temperature show that $\text{Sm}_{10}\text{W}_2\text{O}_{21}$ and $\text{Er}_{10}\text{W}_2\text{O}_{21}$ are isostructural and crystallize in the orthorhombic cell ($a \approx 16\text{Å}$, $b \approx c \approx 10.6\text{Å}$, SG $Pbcn$) that can be described as a $3 \times 2 \times 2$ anion-deficient fluorite superstructure. $\text{Sm}^{3+}/\text{Er}^{3+}$ and W^{6+} cations order in every other cationic layer stacked along the orthorhombic \mathbf{b} axis. One out of eight oxygen positions occupied in the parent cubic fluorite is vacant in $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ resulting in the average cation coordination number going down from eight to seven. The above orthorhombic fluorite superstructures could not be realized for heavier lanthanides. Annealing $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ with WO_3 under the above conditions produced a mixture of phases: rhombohedral $\text{Ln}_6\text{WO}_{12}$ isostructural with Pr_7O_{12} and previously unreported hexagonal phase.

The dependence of the total conductivity on the oxygen partial pressure for $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Tm}, \text{Yb}$) shows a two - step region of pure oxygen-ion conductivity, which agrees with the presence of two different phases established by powder diffraction for these composition. Ionic conductivity component of $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Tm}, \text{Yb}$) is $\approx 10^{-4}$ S/cm at 900° C. p -Type conductivity is absent in these samples at a high oxygen partial pressure, and n -type conductivity appears at low oxygen partial pressure and is associated with the reduction of tungsten. Tungsten is reduced in approximately the same way for $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Tm}, \text{Yb}$) at low oxygen partial pressures, while this process is more pronounced for $\text{Er}_{10}\text{W}_2\text{O}_{21}$.

The temperature dependences of magnetic susceptibility χ in $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ were studied in the temperature range of 2 – 390 K. The values of the Weiss temperatures for $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ ($\text{Ln} = \text{Er}, \text{Tm}, \text{Yb}$) are negative ranging between – 20 K and – 80 K, indicating the predominance of antiferromagnetic interactions between the rare – earth ions. No long-range magnetic ordering was detected in any of the samples down to 2K.

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New high-entropy BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}(Sm, In)_{0.2}O₃ proton conducting perovskites

Daniel Jaworski, Wojciech Skubida, Tadeusz Miruszewski, Maria Gazda

Gdańsk University of Technology, ul. Narutowicza 11/12, 80-233, Gdańsk, Poland
e-mail: daniel.jaworski@pg.edu.pl

The first studies on high entropy systems can be found in the work of F.K. Achard in the 1880s [1]. Over the last 20 years a rapid development in this field can be noticed, especially in the case of alloys [2]. The first report on high entropy oxides dates to 2015 and the substantial work of Rost et al. [3]. A large number of elements in one crystal structure may lead to unique properties that are still largely undefined.

Previously, we described the preparation and transport properties of several high-entropy perovskite oxides [4]. In this work we present the results concerning two single-phase high-entropy proton conducting perovskite-type oxides: BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}In_{0.2}O₃ and BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}Sm_{0.2}O₃. Materials were prepared by means of a high temperature solid-state route and examined with X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and electrochemical impedance spectroscopy. Both compounds exhibit significant proton conductivity (Fig. 1) with high estimated transference numbers (0.65 and 0.49, respectively) and isotope effect.

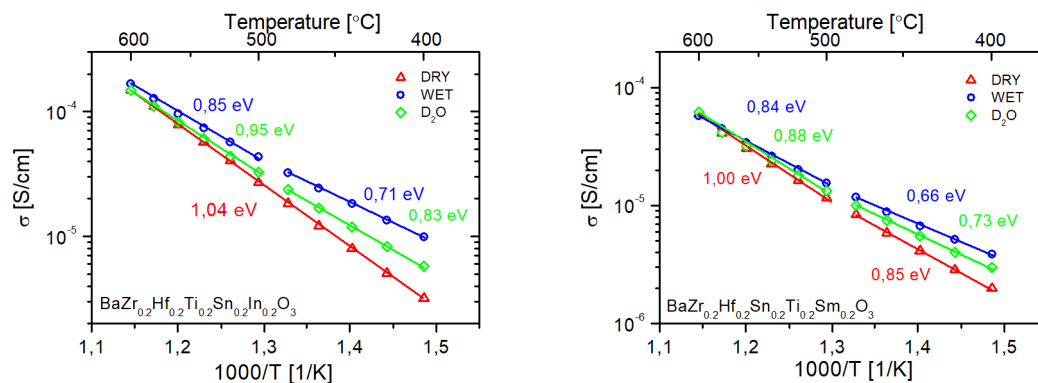


Figure 1. Conductivity of BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}In_{0.2}O₃ and BaZr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2}Sm_{0.2}O₃ in synthetic air

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Transition Metals High-Entropy Spinel Oxides Prepared by Spray Pyrolysis Technique: Microstructural and Electrical Investigations of Thin Films.

Bartosz Kamecki^{a,b}, Jakub Karczewski^a, Piotr Jasiński^b, Sebastian Molin^b

^a Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gabriela Naurutowicza 11/12, 80-233, Gdańsk, Poland

^b Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, Gabriela Naurutowicza 11/12, 80-233, Gdańsk, Poland

e-mail: bartosz.kamecki@pg.edu.pl

The idea of high-entropy stabilized materials was initiated in 1995 for metallic materials and in 2015 it was extended to oxide materials by Rost et al. [1]. The definition assumes the existence of multi-component materials with more than 5 elements in mostly equimolar ratios.

This research aims to fabricate and study a novel materials group broadly described as high-entropy oxides with a focus on thin-film crystallized in the spinel structure. The novelty of the research is a detailed study of entropy stabilized spinels based on transition metal elements (Cr, Mn, Fe, Co, Ni, Cu, Zn) prepared by an in-house developed spray pyrolysis technique in the form of nanocrystalline thin layers (~ 500 nm).

Fifteen different compositions of TM elements containing 5, 6, or 7 equimolar elements were deposited on amorphous SiO₂ or sapphire substrates. The prepared samples were evaluated in terms of microstructural and electrical transport properties in the temperature range of 400–700°C. For selected single-phase compositions a detailed characterization was performed as presented in Figure 1 containing TEM analysis of (Mn,Co,Fe,Ni,Cr)₃O₄ stoichiometry crystallized in Fd-3m space group.

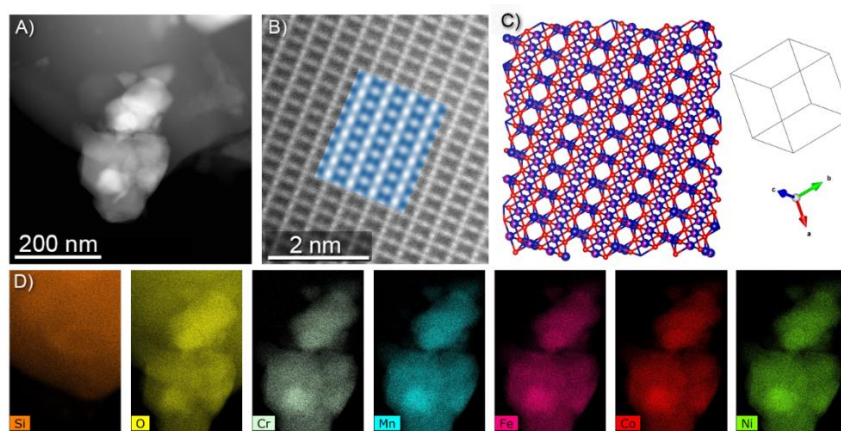


Figure 1. A) STEM image of HEO annealed at 700°C, B) HAADF-STEM image with simulated spinel structure in (112) direction C) Extended crystal structure simulation projected along (112) vector, D) STEM-EDS chemical composition maps of individual components.

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3D -printing of ceramic electrode materials

Małgorzata Nadolska^a, Joanna Pośpiech^a, Tomasz Sobczyk^a, Marek Chmielewski^a, Iga Szpunar^a, Sebastian Wachowski^a

^a*Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology, Gdansk, Poland*
e-mail: malgorzata.nadolska@pg.edu.pl

3D-printing technology has attracted much attention in the energy conversion and storage field and has emerged as a powerful tool for fabricating various goods. It not only enables for the rapid manufacturing of designed structures but also opens the possibility of creating complex architectures and stacks. To date, plenty of 3D-printing techniques and hence precursor materials have been reported. Most of them are devoted to the rechargeable ion batteries and carbon-based supercapacitors [1]. On the other hand, 3D printing of proton-conducting materials is scarce. Recently, Mu et al. presented novel laser 3D-printing method which allows to obtain protonic ceramics with the desired crystal structures, microstructures, and geometries [2]. The method consists of the preparation of printable paste from component raw materials (carbonate and single metal oxides) mixed with sintering aid, the deposition of a thin green film of the targeted protonic ceramics, and the reactive sintering by rapid CO₂ laser scanning. To the best of our knowledge, this is the first available reported method of 3D-printing of protonic ceramics and was successfully applied for the synthesis of dense electrolytes (e.g. BCZYYb, BZY20), porous electrodes (e.g. BCZYYb+NiO, BaCO_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ}), dense interconnect (La_{0.7}Sr_{0.3}CrO_{3-δ}/LSC), and dense mixed protonic and electronic-conduction composite (BaCe_{0.85}Fe_{0.15}O_{3-δ}– BaCe_{0.15}Fe_{0.85}O_{3-δ}/BCF) [3].

In this study, we developed 3D printing of protonic ceramics- Ba_{0.5}La_{0.5}Co_{1-x}Fe_xO_{3-δ} (0 ≤ x ≤ 1), which are promising materials for positrodes in protonic ceramic fuel cells [4]. Two printing technology- fused deposition modeling and extrusion-based 3D printing were selected for this project and embedded into one 3D printer. Moreover, the system was equipped with IR laser for post-processing. Ink (solid filament or gel) was prepared from ceramic powder and polylactic acid (PLA), which act as a matrix and is removed at the end. Various compositions and synthesis conditions were tested. In order to ensure printouts homogeneity, ceramic powder should be well dispersed in polymer matrix. Due to that we implemented various approaches such as ball-milling of ceramic and ultrasonification. A lot of work was also devoted to the laser post-processing optimization, by changing laser power, scan speed and number of scans. X-Ray diffraction, Fourier Transform Infra-Red spectroscopy and Scanning Electron Microscopy were used to determine the structure, composition and morphology of the samples before and after post-processing.

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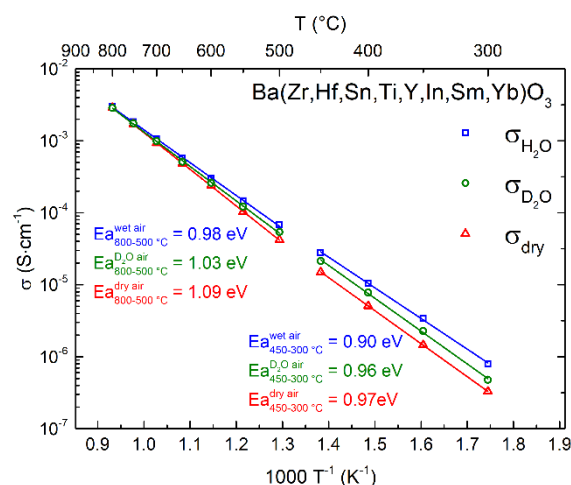
Electrical properties of high-entropy perovskite oxides

Wojciech Skubida, Daniel Jaworski, Maria Gazda

Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland
e-mail: wojciech.skubida@pg.edu.pl

Oxides containing cations introduced to the host structure as substitutions have always been studied, however, the research on high-entropy oxides (HEOs) in which entropy forces the cations in the random distribution, commenced in 2015 from the pioneering work of Rost et al. [1] who demonstrated that configurational disorder can, at a particular temperature, promote the formation of a homogeneous oxide. The idea of using high-entropy oxides as proton and mixed conductors is based on the possible influence of configurational entropy and related to that disorder on the possibilities of obtaining high concentration and mobility of proton defects.

In this work, we present the results of research on material from the group of high entropy perovskite oxides - $\text{Ba}(\text{Zr,Hf,Sn,Ti,Y,In,Sm,Yb})\text{O}_3$. The obtained data concern the crystalline structure of materials at room temperature and its evolution with the temperature increase in the range of 25-800 °C. For conductivity studies, dense sinters of the materials were obtained by addition of 1wt% of PVB and NiO in order to improve compressibility and sinterability of the materials. Samples were evaluated considering their electrical conductivity by electrochemical impedance spectroscopy. Such measurements were done in dry synthetic air, as well as in H_2O - and D_2O -containing atmospheres at elevated temperatures. The obtained results allowed to calculate the proton and deuterium conductivities reaching $2.61 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ and $1.21 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ respectively at 500 °C. Estimated values of proton and deuterium transference numbers were up to 0.38 and 0.22. Additionally water diffusion coefficient D and surface exchange reaction coefficients k were calculated as a function of temperature.



Temperature dependence, shown in Arrhenius-type coordinates, of the total electrical conductivity of $\text{Ba}(\text{Zr,Hf,Sn,Ti,Y,In,Sm,Yb})\text{O}_3$ in dry, H_2O - and D_2O -containing air, with calculated values of the activation energy in respective temperature ranges.

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Ternary composite electrode materials for electrochemical biosensors

N.F. Uvarov,^{a,b} A.S. Ulihin,^a A.I. Titkov,^a I.A. Malbakhova,^a T.A. Vasilyeva,^{a,c}

O.S. Protazanova,^c V.R. Khusnutdinov,^a D.K. Avdeeva,^d M.M. Yuzhakov^d

^aInstitute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, 630090, Russia

^bNovosibirsk State Technical University, Novosibirsk, 630071, Russia

^cNovosibirsk State University, Novosibirsk, 630090, Russia

^dNational Research Tomsk Polytechnic University, Tomsk, 634050, Russia,

e-mail: uvarov@solid.nsc.ru

Biosensor electrode materials are widely used in electrical measuring transducers of biomedical signals for electrocardiography, electroencephalography and other methods of clinical monitoring and medical diagnostics. Currently, silver chloride electrodes with a very low signal-to-noise ratio are widely used for these purposes. The disadvantage of silver chloride electrodes is relatively high impedance, which leads to additional noise, especially in the presence of other sources of electrical fluctuations.

In the present work, it is proposed to use nanocomposites in ternary systems Ag — AgI-based solid electrolyte — inert additive as materials for biosensors. Metallic silver is non-toxic, non-corrosive in contact with living tissue and has bactericidal properties. Silver ion-conducting solid electrolytes form electrodes of the second kind characterized by a stable value of the electrode potential, while silver iodide has much higher conductivity at room temperature, which significantly increase the quality of the measured biopotential. As a inert additive, we have taken aluminosilicate powder and ceramics, alumina and carbon materials.

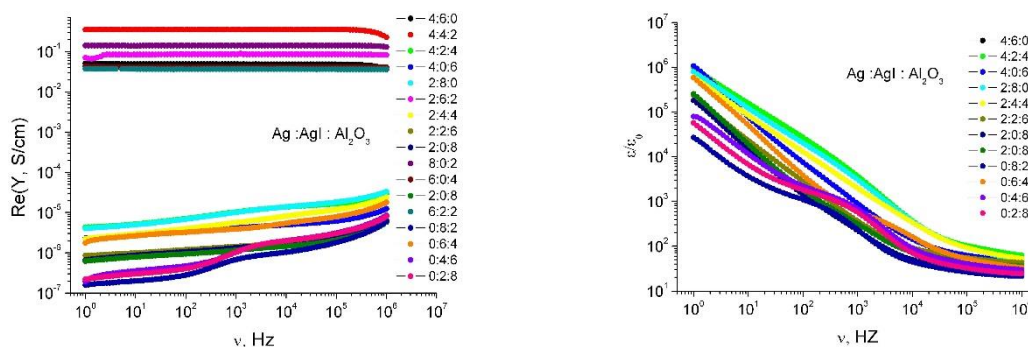


Fig.1. Frequency dependences of conductivity and dielectric permittivity of the Ag-AgI- Al_2O_3 composites with different concentration of the components.

Electric properties of the composites were investigated by impedance spectroscopy, typical results are presented in the Fig.1. The data were interpreted in frames of phenomenological mixing equations, Electrochemical response to voltage signal was investigated for ternary electrode systems Ag – silver salt – inert support of various type, where AgI and $\text{Ag}_{14}\text{I}_{12}\text{P}_4\text{O}_7$ were used as silver salts and carbon paper or porous ceramics were chosen as inert supports. It is experimentally shown that the Ag/AgI/ Al_2O_3 electrode has much lower polarization than a commercial Ag/AgCl cardiographic electrode. It may enable more accurate measurements of bio-potentials providing less pulse shape distortion caused by polarization of electrochemical biosensors. The obtained results are discussed in the report in more detail.

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The work is supported by the Russian Fund for Basic Research, grant 18-29-11054-mk

Structure, water uptake and electrical transport properties of $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.1}\text{M}_{0.1}\text{O}_3$ (M = Fe, Pr, Tb) triple conducting oxides

J. Budnik,^a T. Miruszewski,^a A. Mielewczyk-Gryń,^a M. Gazda^a

^aGdańsk University of Technology, Narutowicza 11/12, 80-233, Gdańsk, Poland
e-mail: jagoda.budnik@pg.edu.pl

Triple conducting oxides (TCOs) have gained much interest as electrode materials for protonic ceramic fuel cells (PCFCs) and protonic ceramic electrolysis cells (PCECs)[1]. TCO materials exhibit oxygen ion-, electron/hole-, and proton conductivity. These types of materials extend the electrochemical reaction sites to the entire surface of electrode. Understanding their charge transport properties in relation to the structure and microstructure is crucial to design and optimize them for electrochemical applications[2].

The acceptor-doped perovskite-type materials like BaCeO_3 , BaZrO_3 , as well as their solid solutions $\text{BaCe}_{1-x}\text{Zr}_x\text{O}_3$ are examples of mixed proton- and oxygen-ion conductors, which form proton defects in a humidified atmosphere. To design a triple conducting oxide, the protonic conductor can be modified, i.a. by introducing a transition metal (TM) to the structure, leading to an increase of its electron/hole partial conductivity[3].

In this work, the structural and charge transport properties of $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.1}\text{M}_{0.1}\text{O}_3$ (M = Fe, Pr, Tb) were investigated. Thanks to the presence of different transition metals in the B-site, enhanced electron/hole conductivity was expected. The structure and microstructure of the synthesized materials were studied by means of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The determination of water uptake was performed by Thermogravimetry (TG). The electrical transport properties and water diffusion analysis were determined by Electrochemical Impedance Spectroscopy (EIS) method in both wet and dry air. The influence of the TMs substituents on the water uptake as well as a charge transport mechanism was analyzed and discussed in relation to the electronic structure and defect chemistry.

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Interphase phenomena in $\text{La}_2\text{Mo}_2\text{O}_9$ – $\text{La}_2\text{Mo}_3\text{O}_{12}$ composite oxygen-ionic electrolytes

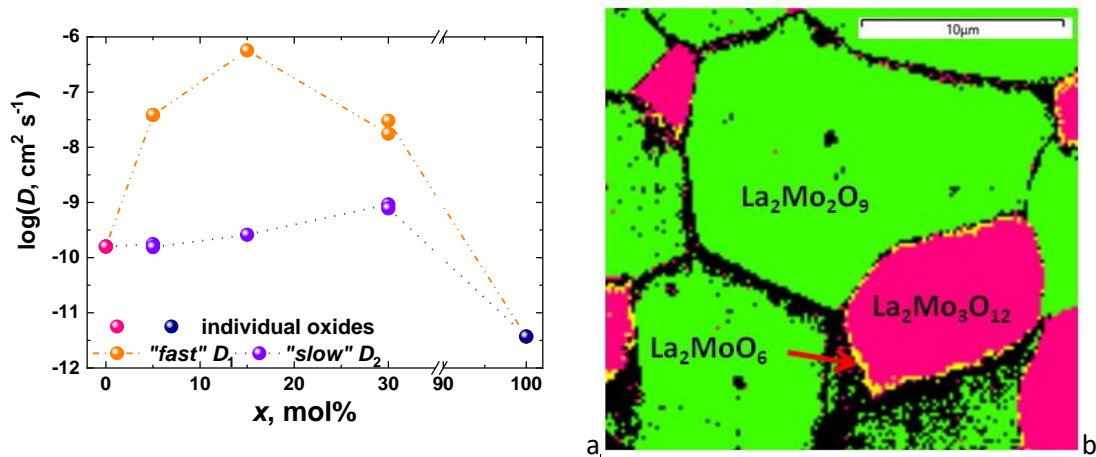
A. Khrustov,^a N. Porotnikova,^a M.V. Ananyev,^b A. Farlenkov,^b A. Khodimchuk,^a D. Pavlov^a

^a Institute of High Temperature Electrochemistry, 20 Akademicheskaya, 620137, Yekaterinburg, Russia

^b Ural Federal University, 19 Mira, 620002, Yekaterinburg, Russia

e-mail: A_Khrustov@ihte.uran.ru

The $\text{La}_2\text{Mo}_2\text{O}_9$ – $\text{La}_2\text{Mo}_3\text{O}_{12}$ composite materials represent a novel class of highly conductive materials demonstrating increased oxygen-ion conductivity. An extensive research of $(100-x)\text{La}_2\text{Mo}_2\text{O}_9 + x\text{La}_2\text{Mo}_3\text{O}_{12}$ composites over a wide range of concentrations ($x = 5, 10, 15, 20, 30$ and 100) was carried out. The increase in oxygen heterogeneous exchange rate and oxygen diffusion coefficients were observed for composites compared to individual oxides, which is associated with the segregation of different ions on the surface of grains and the formation of a $\text{La}_2\text{MoO}_{6-\delta}$ new phase at the contact boundary of $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{La}_2\text{Mo}_3\text{O}_{12}$ grains in composites. The presence of at least two pathways of oxygen diffusion in the composites was revealed: along the interphase layer (fast D_1) and in the bulk (slow D_2) at $T = 800\text{--}950\text{ }^\circ\text{C}$ and $p\text{O}_2 = 10^{-2}$ atm. 3D-modeling of the composite microstructure was performed based on data of analysis of SEM images to estimate the conductivity of the interphase layer between the $\text{La}_2\text{Mo}_2\text{O}_9$ grain and $\text{La}_2\text{Mo}_3\text{O}_{12}$ grain consisting of $\text{La}_2\text{MoO}_{6-\delta}$. The electrical conductivity values of the composite materials calculated from 3D-simulated microstructure and experimentally measured correlate and demonstrate a composite effect. Existence of $\text{La}_2\text{MoO}_{6-\delta}$ oxide at the boundary by itself cannot lead to a significant increase in conductivity of the composite, because its conductivity is comparable in magnitude with $\text{La}_2\text{Mo}_3\text{O}_{12}$ oxide. It is possible that in some surface and disordered state of the interphase layer has a high conductivity and provides the overall behavior of the system.



Concentration dependencies of oxygen diffusion coefficient at $T=850\text{ }^\circ\text{C}$ and $p\text{O}_2=10^{-2}$ atm $\text{La}_2\text{Mo}_2\text{O}_9$ – $\text{La}_2\text{Mo}_3\text{O}_{12}$ oxides (a); additional La_2MoO_6 phase between grains of composite (b)

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Partial protonic conductivity of $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_3$ studied by the modified DC Hebb-Wagner polarization method

Tadeusz Miruszewski^a, Kacper Dzierzgowski^a, Piotr Winiarz^a, Sebastian Wachowski^a,
Aleksandra Mielewczyk-Gryn^a and Maria Gazda^a

^a*Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland*
e-mail: tadeusz.miruszewski1@pg.edu.pl

It is challenging to measure the ionic conductivity of Triple Conducting Oxides (TCOs) with a high electron transfer number. Direct measurements of the partial conductivity of minority charge carriers were proposed by Hebb [1] and Wagner [2]. In the case of TCOs with three mobile charge carriers (oxygen ions, electrons/holes and protons), under non-steady state conditions, a chemical diffusion of oxygen ions and electrons occurs, whereas in steady state, only one type of carriers can be transferred through a TCO and all the others are totally blocked by a mixed blocking electrode [3]. $\text{Ba}(\text{Zr,Ce,Y})\text{O}_3$ proton conducting materials, at high $p\text{O}_2$ become a mixed conductor with a relatively high electron transfer number equal to 0.4 at 600 °C. In wet atmosphere, below 600 °C it becomes a pure protonic conductor [4]. The aim of this work was to determine the partial protonic conductivity (σ_{H}) of $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_3$ (BZCY721) by means of the modified DC Hebb-Wagner method with an electron and oxygen ion mixed blocking electrode (Ca-doped LaNbO_4). The σ_{H} was measured in a galvanostatic mode in the cell shown in Fig.1. In wet atmosphere at 600 °C we obtained 3.1×10^{-3} S/cm which is similar to the value reported in the literature [4]. The model and experimental technique was developed, described and analyzed.

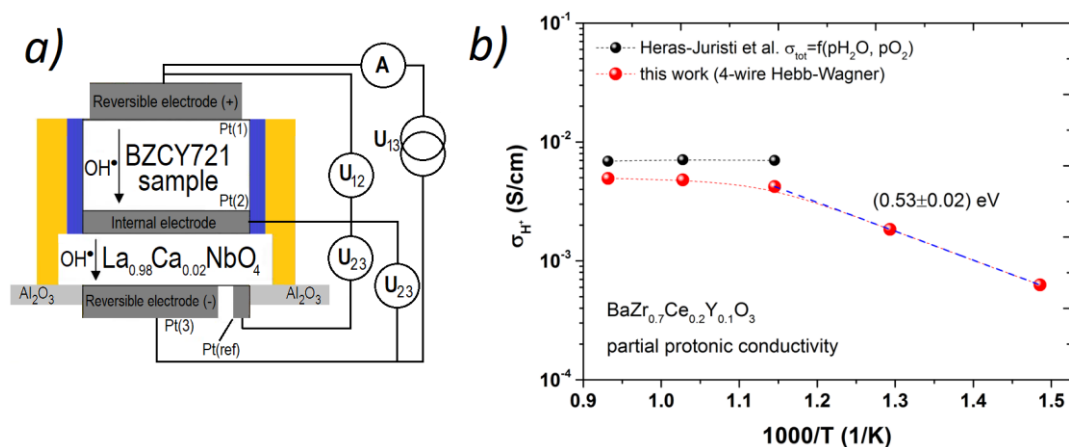


Fig.1. a) Experimental scheme; b) Partial protonic conductivity of BZCY721 measured in wet air.

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Properties of Al and Ce co-doped scandia stabilized zirconia

Darius Virbukas^a, Mantas Sriubas^a, Nursultan Kainbayev^{a,b}, Kristina Bockute^a, Giedrius Laukaitis^a

^a Physics Department, Kaunas University of Technology, Studentu str. 50, LT-51368 Kaunas, Lithuania;

^b Department of Thermal Physics and Technical Physics, Al-Farabi Kazakh National University, 71 Al-Farabi Ave., 050040 Almaty, Kazakhstan
e-mail: darius.virbukas@ktu.lt

Pure ZrO₂ does not exhibit high oxygen ion conductivity due to a low number of oxygen vacancies and its polymorphic nature. Both problems can be solved by adding aliovalent dopants, e.g., Sc, Y, Gd. However, not all aliovalent dopants are equally good. The ionic conductivity of electrolytes depends on dopant atomic radii, dopant concentration, electrostatic interactions between dopants and oxygen vacancies, and phase composition. Zirconia doped with 10 mol% of Sc (10ScSZ) exhibit the highest conductivity among all ZrO₂ based electrolytes [1]. However, the conductivity becomes equal or lower to the conductivity of YSZ at 500 °C. The oxygen ion conductivity and cubic phase stability can be increased by co-doping 10ScSZ with small amounts (0.5-2 mol%) of CeO₂, or Al₂O₃ [2]. The aim of the present research was to examine the properties of Al and Ce co-doped scandia stabilized zirconia (ScAlSZ and ScCeSZ). Therefore, ScAlSZ and ScCeSZ thin films (~1500 nm) were deposited using the electron beam method on different substrates at 450 °C and 600 °C deposition temperatures. The deposition rates were changed from 0.2 nm/s to 1.6 nm/s. The structural characterization and elemental composition estimation were done using XRD, SEM, and EDS techniques. The electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.1 ÷ 10⁶ Hz frequency range and in 400 °C ÷ 1000 °C temperature interval using the two-probe method (Fig. 1). It was found that the highest ionic conductivity ($\sigma_{bulk} = 4.52 \text{ Sm}^{-1}$ and activation energy $\Delta E_a = 1.08 \text{ eV}$ at 800 °C temperature) corresponds to the ScCeSZ thin film formed at 1.2 nm/s deposition rate.

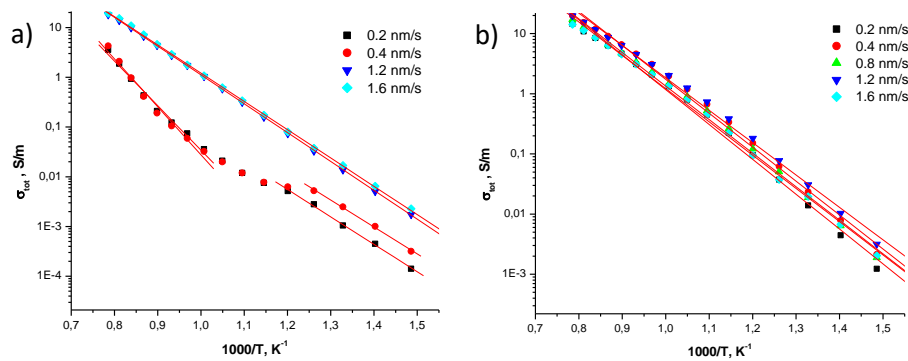


Fig. 1. Arrhenius plots of a) ScAlSZ and b) ScCeSZ thin films

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Structure and transport properties of donor-doped barium strontium cobaltites

Arkadiusz Dawczak,^a Tadeusz Miruszewski,^a Wojciech Skubida,^a Kacper Dzierzgowski,^a
Sebastian Wachowski,^a Aleksandra Mielewczyk-Gryń,^a Maria Gazda^a

^a*Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233, Gdansk, Poland.*

e-mail: arkadiusz.dawczak@pg.edu.pl

Triple-conducting oxides (TCOs) are single-phase materials that show the presence of three charge carriers like protons, oxide ions, and electrons or electron holes (H^+ , O^{2-} and e^- or h^+) [1]. Triple conducting positrodes in protonic ceramic fuel cells (PCFCs) can spatially expand the active electrochemical reaction zone (active oxygen reduction reaction (ORR) sites) from the interface between the cathode and the electrolyte to the entire surface of the positrode [2]. To develop electrochemically active TCOs, various elements are doped into pure proton-conducting oxides, for example, barium zirconates, cerates or their solid solutions, to enhance their concentration of mobile oxide ions and electrons or electron-holes [3]. In this work, we examine the conductivity, microstructure, and thermochemical properties of the series of the Nb-doped barium-strontium-cobaltites with the $Ba_{0.5}Sr_{0.5}Co_{1-x}Nb_xO_{3-d}$ formula (were $0.1 \leq x \leq 1$). Such stoichiometries have been chosen to stabilize the perovskite phase and enhance total conductivity. The samples of the materials were synthesized through the solid-state synthesis method in two steps. We have determined the structure and phase composition by the means of the powder X-ray diffraction method at room temperature. The surface and porosity of the synthesized samples were determined by scanning electron microscopy. The measurements of temperature dependence of electrical conductivity were carried out using the 4-wire DC method under dry and wet air. Thermochemical properties were carried out with thermogravimetry (for oxidation studies) and dilatometry (for coefficients of thermal expansion).

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Exsolution of oxide nanoparticles on Fe- or Lu-doped barium lanthanum cobaltite (BaLaCo₂O_{6-δ}) surface

D. Gierszewska,^a S. Wachowski,^a I. Szpunar,^a A. Mielewczyk-Gryń,^a M. Gazda^a

^a *Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233, Gdańsk, Poland*
e-mail: daria.gierszewska@pg.edu.pl

The perovskites with general formula BaLnCo₂O_{6-δ}, where Ln is a lanthanide such as Gd, La, Pr, have been recently widely studied as new cathode materials in proton ceramic fuel cells (PCFCs) and electrolysis cells (PCECs) systems[1]. BaLaCo₂O_{6-δ} attracted a lot of scientific interest and its structural, electrical and magnetic properties were widely characterized[2]. Cobaltites show high electrical conductivity in a wide range of temperatures[2]. The conductivity is related mainly to electronic- and oxygen ion charge carriers, however, in humid atmospheres, they uptake water and may also conduct protons. Therefore, being triple conducting oxides, they may be considered as promising positrode materials. However, this type of material suffers from slow surface oxygen exchange and large thermal expansion coefficient (TEC)[3]. To increase the oxygen kinetic exchange on the surface, a surface modification by exsolution of electrostatically active nanoparticles is one of the most promising methods. The process could be reversible what allows multiple regenerations of the electrode. Introducing disorder in perovskite structure such as nonstoichiometry or internal strain can be an additional driving force enhancing exsolution of nanoparticles. Both, the presence of iron substituting cobalt and the barium deficiency may promote the exsolution process. Another approach can be Lu doping on the A-site, which increases strain due to a large difference of ion radii between Lu³⁺ (0.98 Å) and La³⁺ (1.16 Å) and may lead to exsolution of one of the A- or B-site cations. In each case, the exsolution process can occur in oxidizing conditions, which is a novel approach.

In this study, we present the results on exsolution study in BaLnCo₂O_{6-δ} based perovskites. The structural and electrical properties of stoichiometric and 2%-Ba deficient BaLaCo_{2-x}Fe_xO_{6-δ} family of compounds (where 0 ≤ x ≤ 2) were investigated. Additionally, BaLa_{1-x}Lu_xCo₂O_{6-δ} (where x = 1%, 20%) were studied. The BaLa_{1-x}Lu_xCo₂O_{6-δ} materials were quenched from different annealing temperatures from range 400°C – 1200°C to maintain their structure at a particular temperature. The exsolution of the nanoparticles was performed under oxidizing, ambient and inert atmospheres. Different techniques were used to examine studied compounds. The powder X-ray diffraction method was used to determine the structure and phase composition of the samples and scanning electron microscopy enabled imaging of the materials surface and characteristic of nanoparticles exsolution. The electrical measurements were carried out using 4-wire DC method.

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Performance of Pr_{1.95}La_{0.05}CuO₄-Based Cathode in Micro-Tubular Solid Oxide Fuel Cells

Nikolay Lyskov,^{a,b} Marat Galin,^a Ilya Gvozdokov,^b Alexander Sivak,^b Vitaliy Sinitsyn^{a,b}

^a Institute of Problems of Chemical Physics RAS, Acad. Semenov av. 1, 142432, Chernogolovka, Russia

^b Inenergy LLC, 2nd Kotlyakovskiy lane, 18, 115201, Moscow Russia

e-mail: lyskov@icp.ac.ru

Currently the development of micro-tubular solid oxide fuel cells (μ -SOFCs) effectively operating in the intermediate-temperature (IT) range from 500 to 800°C is a very promising way to creating portable electrochemical power sources. To implement this complex scientific task, a comprehensive approach is required, the most important element of which is the selection of the cathode material. Perovskites based on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} (LSCF) have found wide practical application as the cathode material for IT-SOFCs. LSCF possesses high mixed electron-ionic conductivity, high values of the oxygen surface exchange and diffusion coefficients, and demonstrates acceptable thermo-mechanical compatibility with commonly used solid electrolytes based on yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC). However, these materials under SOFC operation conditions demonstrate a relatively low resource time in comparing with the most commonly used lanthanum-strontium manganite (LSM) cathode. In this regard, the development and research of new cathode materials for IT-SOFCs as well as μ -SOFCs is of undoubted practical interest.

It was previously shown that the Pr_{1.95}La_{0.05}CuO₄ – xCe_{0.9}Gd_{0.1}O_{1.95} (PLCO-xGDC) composite containing 40 wt. % of GDC can be considered as a promising cathode material for IT-SOFCs application [1] due to high electrochemical performance in oxygen reduction reaction comparable to one for the LSCF-GDC composite cathode. In this connection the presented work is aimed in:

- elaboration of modes of PLCO-40GDC paste deposition on an anode-supported micro-tubular half-cell with a thin YSZ solid electrolyte;
- determination of the optimal annealing conditions of the material to obtain the required thickness, adhesion and morphology of the cathode layer;
- carrying out of electrochemical studies of micro-tubular SOFCs with the PLCO-40GDC cathode.

Investigation of current–voltage characteristics of the micro-tubular SOFC with the PLCO-40GDC cathode was performed at 800°C under variation of the hydrogen content from 5 to 100 vol. % in the humidified fuel mixture supplied to the anode side. Air was used as an oxidant. It was established that the current–voltage characteristics are weakly dependent on the hydrogen content in the fuel mixture at the hydrogen concentration exceeded 50 vol. %, and the maximum power density of the tested fuel cell exceeded 600 mW/cm² at 800°C. The impedance studies of the cell under a 0.7 V potentiostatic bias demonstrated that the total polarization resistance of the electrode/electrolyte interface at these conditions is equal to 0.28 Ohm×cm², which is comparable to one for the fuel cell with the cathode based on LSCF-40GDC composite. It was found that there is no drop in the output power (within the experimental error) under the potentiostatic load for 60 h.

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Structure, transport features and electrochemistry of layered lanthanum nickelate substituted with rare earth elements

V. Tsvinkinberg,^{a,b} V. Sadykov,^{c,d} E. Sadovskaya,^c A. Kolchugin,^a E. Filonova,^b
N. Ereemeev,^c N. Pikalova,^{a,b} A. Vylkov,^a I. Baynov,^a **E. Pikalova^{a,b}**

^a*Institute of High Temperature Electrochemistry UB RAS, 20, Akademicheskaya str., 620137 Yekaterinburg, Russia*

^b*Ural Federal University, 19, Mira str., 620002 Yekaterinburg, Russia*

^c*Federal Research Center Boreskov Institute of Catalysis, Akad. Lavrentieva ave. 5, 630090 Novosibirsk, Russia*

^d*Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russia*

e-mail: e.pikalova@list.ru

Currently, the crystal structure and physicochemical properties of $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) are well studied, and this material is used in air electrodes of electrochemical devices and in membranes for oxygen and syngas production [1]. This study is aimed at studying the properties of LNO substituted with different rare earth elements with the sake to increase its oxygen over-stoichiometry and enhance oxygen transport thus improving electrochemical kinetic of the related electrodes. Materials of the $\text{La}_{1.6}\text{Ln}_{0.4}\text{NiO}_{4+\delta}$ series (where Ln = Gd (LGNO), Eu (LENO), Sm (LSNO), Nd (LNNO), Pr (LPNO)) were synthesized by a nitrate combustion technique and their structural features, oxygen over-stoichiometry, and oxygen transport properties were investigated by different methods such as X-ray diffraction, TGA, temperature programmed isotopic oxygen exchange with C^{18}O_2 (TPIE) in a flow reactor. Refinement of the XRD data showed that the unit cell volume in the $\text{La}_{1.6}\text{Ln}_{0.4}\text{NiO}_{4+\delta}$ series decreased from Pr ($V = 188, 4 \text{ \AA}^3$) to Gd ($V = 186, 8 \text{ \AA}^3$). According to the TGA data, the value of oxygen over-stoichiometry, δ , was determined to be equal to 0.15, while all substituted materials showed higher values: 0.16 for LE NO and LGNO, 0.17 for LSNO and LNNO, and the highest value equal to 0.18 was revealed for LPNO. The electrical properties of the materials were investigated using a four-probe method. The obtained temperature dependences of total conductivity, σ_{tot} , were bell-shaped similarly to that for LNO with a maximum at approximately 400 °C. At this point, LNNO and LE NO had the highest σ_{tot} values of 96 S/cm and 93 S/cm, respectively. For LNO and the rest of substituted samples, the obtained σ_{tot} values were in a range of 57 – 78 S/cm. Numerical analysis of the TPIE curves showed that, at the temperatures below 400 °C, the exchange in all samples is limited by the rate of interphase exchange at the gas-solid interface (R^*), while the process is limited by bulk diffusion at high temperatures. Since the TPIE curves for LPNO, LNNO, and LSNO almost coincide, they were all described by the same calculated curve with the same parameter values ($D^* = 1.8 \cdot 10^{-11} \text{ cm}^2/\text{s}$ and $R^* = 5.0 \cdot 10^1 \text{ s}^{-1}$ at 430 °C). The visual decrease in the rate of oxygen exchange with the addition of Pr, Nd, Sm, and Eu is associated exclusively with an increase in the length of the diffusion path caused by the difference in the specific surface area values. The best oxygen transport characteristics were acquired for LE NO sample ($D^* = 1.8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ and $R^* = 1.6 \cdot 10^2 \text{ s}^{-1}$ at 430 °C).

Electrochemical properties of the related $\text{La}_{1.6}\text{Ln}_{0.4}\text{NiO}_{4+\delta}$ electrodes were investigated in a contact with a $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ solid-state electrolyte. The influence of the temperature of the electrode formation and the effect of the collector layer on electrochemical activity were considered. The LPNO and LSNO-based electrodes demonstrated the best characteristics, possibly related to the enhanced oxygen kinetic. Substitution with Gd, contrarily, significantly deteriorated electrochemical properties of LNO.

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Influence of iron doping on functional properties of

$\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

Iga Szpunar¹, Aleksandra Mielewczyk-Gryń¹, Daria Gierszewska¹, Małgorzata Nadolska¹, Ragnar Strandbakke², Maria Balaguer³, Jose M. Serra³, Maria Gazda¹, Sebastian Wachowski¹

1. Institute of Nanotechnology and Materials Engineering, Gdańsk University of Technology, Gdańsk, Poland

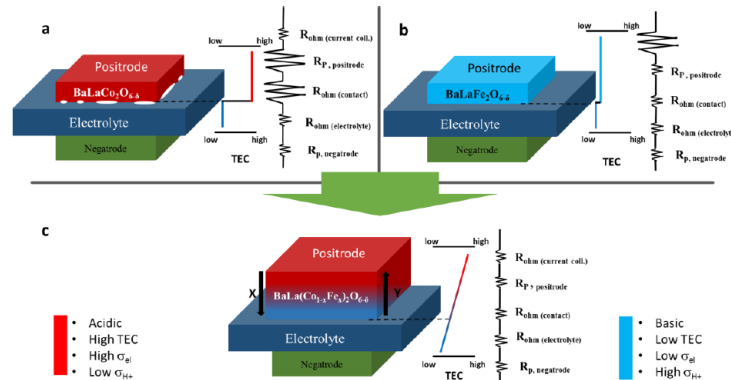
2. Department of Chemistry, University of Oslo, FERMIØ, Gaustadalléen 21, NO-0349 Oslo, Norway

3. Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Av. Naranjos s/n, E-46022 Valencia, Spain

e-mail: iga.lewandowska@pg.edu.pl

Lanthanum barium cobaltite with perovskite structure has been extensively studied due to its potential application in electrochemical devices¹. It exhibits high electrical conductivity and good catalytic properties. However its thermomechanical properties seem to be challenging. Thermal expansion coefficient of $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ (BLC) is significantly higher than $\text{BaZr}_{1-x}\text{Ce}_x\text{Y}_y\text{O}_{3-\delta}$ (BZCY)², which is a typical electrolyte material. Thus, application of BLC as an electrode on BZCY electrolyte may lead to mechanical wear, what limits its application potential. Doping on cobalt sublattice with iron is a promising solution for these challenges. As it is stated in the literature, Fe substitution not only lowers the TEC, but also can affect the concentration of proton defects in the structure of the material³. With lowered TEC and high proton conductivity $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ may be successfully applied as a positrode in protonic ceramic fuel cells (PCFC). What is more, the application of the electrode with gradient chemical composition, will allow to use the advantages of each material (Fig.1).

In this study we present the iron influence on functional properties of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. The series of materials with wide range of Fe content ($0 \leq x \leq 1$) were synthesized with solid state reaction. The structure was investigated by the means of powder X-ray diffraction. The thermogravimetry was used for hydration and oxidation studies. TEC was determined by the means of dilatometry, and electrical conductivity were investigated with 4-point DC method.



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