

16-19.IV.2024 AUGUSTÓW

XVI SYMPOSIUM FAST ION CONDUCTORS



XVI Symposium Fast Ion Conductors is organised by the Faculty of Chemistry and the Faculty of Physics of the Warsaw University of Technology.

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The conference is being held thanks to funding from the Warsaw University of Technology 's Programme of Excellence - Research University (POB Energy) and funding from the Warsaw University of Technology Doctoral School.

Conference programme

Tuesday (16.04)

15:00	Symposium inauguration prof. Władysław Wieczorek
Session I prof. Franciszek Krok	
15:30	K1 Andrzej Nowak
16:00	K2 Maciej Marczewski
16:30	O1 Michał Świętosławski
16:45	O2 Krzysztof Gadomski
17:00	O3 Konrad Kwatek
17:15	O4 Wojciech Zajac
17:30	Coffee break
Session II prof. Marek Marcinek	
18:00	K3 Marcin Kryński
18:30	K4 Tomasz Pietrzak
19:00	O5 Piotr Ryś
19:15	O6 Yu Chen
19:30	Dinner

Wednesday (17.04)

Session III prof. Janina Molenda	
09:00	IL1 Michel Armand
09:45	K5 Leszek Niedzicki
10:15	K6 Marcin Molenda
10:45	O7 Marek Broszkiewicz
11:00	O8 Boyang Fu
11:15	Coffee break
Session IV prof. Anna Lisowska-Oleksiak	
11:45	K7 Bartosz Hamankiewicz
12:15	K8 Michał Struzik
12:45	O9 Klaudia Zielińska
13:00	O10 Maciej Moździerz
13:15	O11 Andrzej Kulka
13:30	Lunch
Session V prof. Radosław Przeniosło	
15:00	K9 Anna Lisowska-Oleksiak
15:30	O12 Francis Oseko
15:45	O13 Martyna Czudec
16:00	O14 Michał Gogacz
16:15	O15 Joanna Pośpiech
16:30	O16 Aleksandra Ossowska
16:45	Coffee break
17:15	Poster session
19:30	Dinner

Thursday (18.04)

Session VI prof. Maria Gazda	
09:00	IL2 Janina Molenda
09:45	K10 Janusz Płocharski
10:15	K11 Mariusz Walkowiak
10:45	O17 Jan Adamczyk
11:00	O18 Beata Bochentyn
11:15	Coffee break
Session VII prof. Tomasz Brylewski	
11:45	K12 Konrad Świerczek
12:15	K13 Aleksandra Mielewczyk-Gryń
12:45	O19 Arkadiusz Dawczak
13:00	O20 Eva Del Campo Ortiz
13:15	O21 Jakub Lach
13:30	Lunch
Session VIII prof. Władysław Wieczorek and prof. Mirosław Karpierz	
15:00	IL3 Isaac Abrahams
15:45	K14 Sebastian Molin
16:15	K15 Radosław Przeniosło
16:45	O22 Jagoda Budnik
17:00	O23 Marcin Małys
17:15	O24 Maciej Nowagiel
17:45	Dinner

Friday (19.04)

Session IX prof. Konrad Świerczek	
09:00	IL4 Maria Gazda
09:45	K16 Tomasz Brylewski
10:15	O25 Keyun Li
10:30	O26 Margarita Nowakowska
10:45	O27 Piotr Winiarz
11:00	Coffee break
Session X prof. Janusz Płocharski	
11:30	K17 Piotr Jasiński
12:00	O28 Kun Zheng
12:15	O29 Maciej Smoliński
12:30	O30 Aginmariya Kottarathil
12:45	End of symposium prof. Władysław Wieczorek
13:00	Lunch

List of presenting authors/alphabetically

Abrahams Isaac IL3
Adamczyk Jan O17
Armand Michel IL1
Bakierska Monika P1
Bielewski Jakub P2
Bochentyn Beata O18, P3, P4
Broszkiewicz Marek O7
Brylewski Tomasz K18
Budnik Jagoda O22
Chen Yu O6
Czerwiński Arkadiusz P5
Czudec Martyna O13
Dawczak Arkadiusz O19
Del Campo Ortiz Eva O20
Domaradzki Kamil P6
Dominów Michał P7, P8, P9
Dzięgielewska Aleksandra P10
Fabiański Michał P11
Fu Boyang O8
Gadomski Krzysztof O2, P12
Gazda Maria IL4
Gogacz Michał O14
Hamankiewicz Bartosz K7
Izdebska Natalia P13
Jasiński Piotr K17
Kottarathil Aginmariya O30
Kryński Marcin K3
Kulka Andrzej O11
Kwatek Konrad O3
Lach Jakub O21
Lemieszek Bartłomiej P14, P15
Leszczyńska-Radek Marzena P16
Li Keyun O25
Lisowska-Oleksiak Anna K9
Małys Marcin O23
Marczewski Maciej K2
Michalski Kamil P17
Mielewczyk-Gryń Aleksandra K13
Molenda Janina IL2
Molenda Marcin K6
Molin Sebastian K14
Moździerz Maciej O10
Mrówczyński Jakub P18
Niedzicki Leszek K5
Nowagiel Maciej O24, P19
Nowak Andrzej K1
Nowakowska Margarita O26
Oseko Francis O12
Ossowska Aleksandra O16
Ostrowska Katarzyna P20
Pachulska Klaudia P21
Pietrzak Tomasz K4
Płocharski Janusz K10
Płotek Justyna P22
Pośpiech Joanna O15
Przeniosło Radosław K15
Rogala Klaudia P23
Ryś Piotr O5
Słojewska Magdalena P24
Smoliński Maciej O29
Struzik Michał K8
Szpakiewicz-Szatan Aleksander P25
Świerczek Konrad K12
Świętosławski Michał O1
Walkowiak Mariusz K11
Wieczorek Władysław
Winiarski Paweł P26
Winiarz Piotr O27
Witkowska Agnieszka P27
Wtulich Mariusz P28, P29
Zajac Wojciech O4, P30
Zdankiewicz Jakub P31
Zheng Kun O28
Zielińska Klaudia O9

Invited lectures

RECENT PROGRESSES IN POLYMER ELECTROLYTES

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Polymer electrolytes are contenders for the future solid-state batteries due to their easy processability as compared to the ceramic ion conductors. The three main difficulties associated with polymer electrolytes are:

- A low room temperature conductivity even with the best materials;
- A low transference number of the cations (Li^+ , Na^+), ≈ 0.25
- A limited anodic stability of poly(ethers) beyond 3.9 V

Poly(ethylene oxide), —PEO—, is still the workhorse of solvating macromolecules due to its outstanding capacity to wrap around cations and dissolve salts. The polymer is however crystalline and the ordered complexes are not conductive. From this simple linear polymer, we searched for means to suppress crystallinity and found that easily synthesized comb polymers where medium-length (Mw 1000 – 2000) PEO segments are tethered to a robust carbon-carbon backbone [poly([ethylene-alt-maleic anhydride])] —PEMA— give rise to improved conductivities down to RT. Furthermore, the mechanical properties can be further augmented with the co-grafting of polystyrene segments with minimal impact on the electrochemical performances.

To address the problem of improving the transport number of the cation, several strategies have been employed: i) to attach the anions to a polymer (polysalt) forming an alloy with PEO or other solvating backbone. Recently, the grafting of delocalized anions to a cellulose backbone was found to give high T^+ alloys with excellent mechanical properties, thanks to the rigidity of the poly(anhydro glucose) units. Besides, the synthesis of the cellulose polysalt is remarkably simple. ii) in another development, anions are attached to nanoparticles (SiO_2 , Al_2O_3 ...) using silane coupling chemistry and the particles dispersed in PEO. Again, excellent mechanical properties of the composites are displayed, and batteries can operate with high utilization of the cathode material. iii) in a last strategy, new discrete salts are designed so as the mobility of the anion is diminished. Starting from well-known TFSI [$(\text{CF}_3\text{SO}_2)_2\text{N}$]⁻, we synthesized [$\text{RSO}_2\text{NSO}_2\text{CF}_3$]⁻, where R = CF_2H — (hydrogen bonds), $(\text{CH}_3)_2\text{N}$ — (dipolar interactions), $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{N}$ — (entanglement with the polymer chains), C_6H_5 — (“p”stacking). In all cases, there was a marked increase in T^+ and despite a lowered total conductivity, the $s\text{Li}^+$ was increased.

The competitors to polyethers (PEO) are poly(esters) like poly(propylene carbonate) (PPC). The latter macromolecule is stable to high voltages like those for operation of layered oxides (NMC) but decomposes in contact with lithium. PEO is stable to Li° . The quite obvious remedy to have a two-layer electrolyte with the sequence $\text{Li}^\circ|\text{PEO}|\text{PPC}|\text{NMC}$ does not work with conventional polymer electrolytes, as the far more solvating power of PEO results in the total transfer of all the salt available into its compartment. We found a solution by using, in both layers, a polysalt which prevents migration and allows cycling of the cell quite efficiently, with a 4.2 V emf

ELECTRONIC STRUCTURE ENGINEERING IN THE DEVELOPMENT OF HIGH VOLTAGE CATHODE MATERIALS FOR Na-ION BATTERIES

Janina Molenda¹

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Transition metal compounds with a general formula $A_xM_aX_b$ ($A = \text{Li, Na}$, $M = \text{transition metal}$, $X = \text{O, S}$) constitute a group of potential electrode materials for a new generation of alkaline batteries. This application is related to the fact that these compounds can reversibly intercalate high amounts of alkaline ions (1 or more moles per mole of M_aX_b) already at room temperature, without significant changes in their crystallographic structure. Nowadays, further development of rechargeable batteries is focused on the discovery of new, high-performance and low-cost electrode materials. Recently, Na-ion batteries have attracted much attention due to their many advantages, such as: high abundance of sodium in the Earth's crust, its low cost and suitable redox potential (only 0.3 V above that of lithium).

The author of this work basing on her own investigations of numerous group of cathode materials has demonstrated that the electronic structure of the electrode materials plays an important role in the electrochemical intercalation process. The paper reveals correlation between crystal and electronic structure, chemical disorder, transport and electrochemical properties of layered $\text{Na}_x\text{Ni}_{1/5}\text{Co}_{1/5}\text{Fe}_{1/5}\text{Mn}_{1/5}\text{Ti}_{1/5}\text{O}_2$ high entropy oxides and polyanions $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ cathode materials. The complex studies, including experimental as well as theoretical parts (electronic structure calculations performed using the Korringa-Kohn-Rostoker method with the coherent potential approximation KKR-CPA to account for chemical disorder), showed a strong correlation between structural, transport and electrochemical properties of these materials.

The detailed analysis presented in this work provides a strong proof that the high-entropy $\text{Na}_x\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Ti}_{0.2}\text{O}_2$ oxide with reduced content of cobalt and nickel and $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ might be applicable in sodium batteries technology, especially in terms of large-scale energy storage units.

STRUCTURE AND CONDUCTIVITY IN SOLID ELECTROLYTES: A HISTORICAL PERSPECTIVE ON A HIGHLY SUCCESSFUL RELATIONSHIP

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Ionically conducting solids can be used as electrolytes in a variety of electrochemical devices, ranging from fuel cells and batteries to gas sensors. Their conducting properties are intimately related to their structures and an understanding of the relationship can allow for optimisation of the material for particular applications. In parallel, relationships forged between scientists of different disciplines has led to the development of the field now known as solid state ionics. This talk focuses on the near 40 year relationship between a chemist (Isaac Abrahams) and a physicist (Franciszek Krok) that has developed into a highly successful collaboration that has sought to understand fundamental aspects of the interaction between structure and conductivity in solid electrolytes.

From their early work on the oxide ion conducting BIMEVOXes, to more recent work doped cerias (Fig. 1), this talk will take a retrospective look at how the complementary skills of structure determination and electrical characterization have allowed for a comprehensive understanding of conduction mechanisms and defect structure in relatively complex solids.

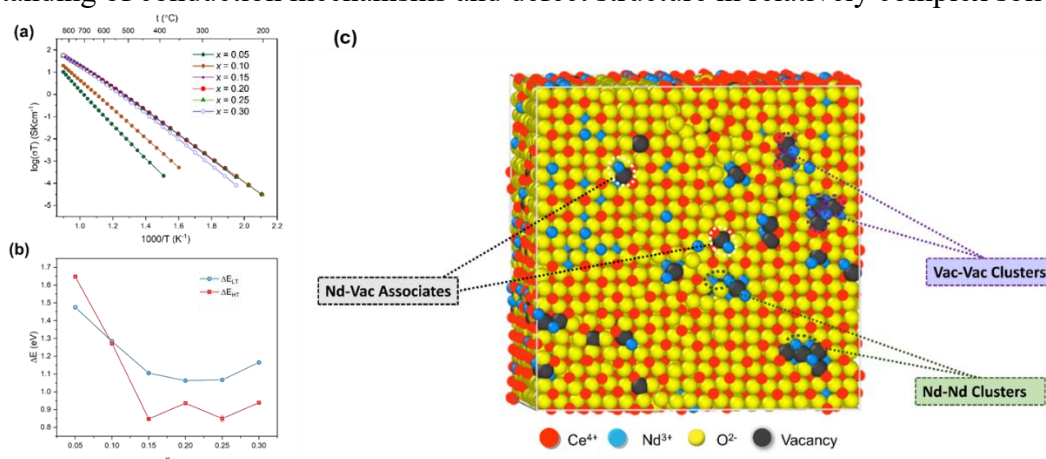


Fig. 1. Structure and conductivity in $Ce_{1-x}Nd_xO_{2-x/2}$ (a) Arrhenius plots of total conductivity; (b) compositional dependence of high and low temperature activation energy; (c) representative RMC configuration for $Ce_{0.8}Nd_{0.2}O_{1.9}$ at room temperature showing three types of local structure features as indicated [1].

References:

[1] J. Ming, M. Leszczyńska-Redek, M. Malys, W. Wrobel, J. Jamroz, M. Struzik, S. Hull, F. Krok and I. Abrahams, J. Mater. Chem, A, 2024, Advance Article DOI: 10.1039/d3ta07668g

MULTICOMPONENT OXIDES AS ION- AND MIXED CONDUCTORS

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Multicomponent oxides accommodate multiple metal cations in equimolar or nearly equimolar ratios occupying equivalent lattice sites, leading to a high degree of short-range disorder and complexity. Because of that, they may have unexpected properties. Exploring their electrochemical and electrical properties opens up new possibilities for diverse applications, ranging from energy storage and conversion to catalysis.

In this work, selected properties of four groups of either multicomponent or high-entropy or entropy-stabilised oxides are presented and discussed. Perovskites, ABO_3 , fergusonites, ABO_4 , pyrochlores, $A_2B_2O_7$ and zirconium and hafnium niobates and tantalates $A_6B_2O_{17}$ ($A=Zr, Hf$, $B=Nb, Ta$) are discussed. What these diverse groups of materials have in common is the presence of disorder, strain and lattice distortions though their origins are different. In this presentation, structural, vibrational, thermochemical and charge transport properties are shown. Special attention was focused on the properties related to ionic conduction.

Acknowledgment: The research was partially financially supported by the National Science Centre (NCN), Poland, within the project 2019/35/B/ST5/00888.

Keynotes

BEYOND LITHIUM-ION BATTERIES: TRANSITION METAL DICALCOGENIDES AS NEGATIVE ELECTRODE MATERIAL

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Lithium-ion batteries (LIBs) are the most common energy storage sources utilized worldwide [1]. However, the rarity in the earth's crust of lithium (0.0017 wt%) and the increasing cost of lithium compounds have raised concerns over the long-term and large-scale supply availability of LIBs. Therefore, great efforts have been devoted to exploring new rechargeable battery alternatives to LIBs, i.e., sodium-ion batteries (SIBs) [2] or potassium-ion batteries (PIBs) [3]. Regardless of whether we are dealing with LIBs, NIBs or KIBs, the choice of battery components i.e. cathode material, anode material, electrolyte and separator play a vital role in the electrochemical performance of battery.

Transition metal dichalcogenides (TMDs) have attracted significant attention in recent years due to their unique electronic, optical, and electrochemical properties, making them promising candidates for various applications, including energy storage devices. Among TMDs, molybdenum sulphide (MoS_2), tin sulphide (SnS_x , $x=1,2$) has attracted attention as a potential anode material in battery application, owing to their layered structure and remarkable performance in energy storage systems [4,5].

Synthesis and characterization of MoS_2 and SnS_x as electrode material for NIBs and/or PIBs will be discussed. Utilization of solid-state physics techniques coupled with electrochemical measurements will be shown demonstrating the importance of the synthesis route on the electrochemical performance of anode.

References:

- [1] IEA, Renewables 2021, Int. Energy Agency Publ. Int. (2021) 167.
- [2] C. Wang, C. Yang, Z. Zheng, *Adv. Sci.* 9 (2022) 2105213.
- [3] M. Mojtaba, Q. Abbas, M.R.C. Hunt, A. Galejeva, R. Raza, *Smart Mater.* 2 (2022) 135–147.
- [4] X. Wei, C.C. Lin, C. Wu, N. Qaiser, Y. Cai, A.Y. Lu, K. Qi, J.H. Fu, Y.H. Chiang, Z. Yang, L. Ding, O.S. Ali, W. Xu, W. Zhang, M. Ben Hassine, J. Kong, H.Y. Chen, V. Tung, *Nat. Commun.* 13 (2022) 6006-6017.
- [5] J. Liu, X. Yu, J. Bao, C.F. Sun, Y. Li, *J. Phys. Chem. Solids* 153 (2021) 833-838.

BEYOND LITHIUM ION BATTERIES - DEVELOPMENT OF ELECTROLYTES FOR Li-S AND BIVALENT BATTERIES SYSTEMS

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EU has set an ambitious target of reducing greenhouse gas emission by 50% till 2030 and becoming completely climate neutral in 2050 [1]. To enable this energy transfer we need to design short and mid-term storage capacities enabling us to store energy produced by renewable energy resources, which are often intermittent in their nature (wind, solar), causing big fluctuation in their power output. Batteries are one of the prime candidates for this task due to their high energy efficiency and the fact that they are compact and can be used on dispersed locations. Currently, Li-ion batteries are dominating the market and their future demand is projected to increase. However, with the huge increase in the market demand, availability and sustainability as well as future price of used materials are being actively questioned. At the moment EU lists several materials used in contemporary Li-ion cells as critical (Li, Co, Ni, graphite) [2]. Hence, a new generation of batteries based on abundant, cheap and environmentally benign materials is needed.

One idea is to replace the graphite electrode for lithium and metal oxide cathode with more capacious sulfur electrode (lithium-sulfur batteries – Li-S) or oxygene/air (lithium-air batteries – Li-O₂). This enable to obtain significantly higher theoretical capacity, up to 2500 Wh/kg and more than 3000 Wh/kg, respectively in case of Li-S and Li-O₂ batteries. Both technologies, although very promising, are facing with a huge amount of principal problems. Firstly, they need to be solved at the level of the basic research to be able to consider application of these high capacious technologies eg. in electric vehicles [3]. Another idea is to replace Li based systems with elements which are more abundant in Earth's crust like Na, Ca, Mg and Al [4,5].

This presentation will focus mainly on historical and recent development of electrolyte in Li-S and bivalent batteries systems. The particular emphasis will be placed on the work carried out in Conversion & Energy Storage group at WUT, where research on beyond LIB's systems is conducted since 2011.

References:

- [1] EU climate action and the European Green Deal
- [2] S. Bobba, S. Carrara, J. Huisman, F. Mathieux, C. Pavel, Critical Raw Materials for Strategic Technologies and Sectors in the EU - a Foresight Study, 2020.
- [3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon, Nature Materials, 2012, 11, 19
- [4] J.-M. Tarascon, Joule, 2020, 4, 1613
- [5] Y. Liang, H. Dong, D. Aurbach and Y. Yao, Nature Energy, 2020, 5, 646

**BRIDGING THE GAP BETWEEN THEORETICAL MODELLING AND
EXPERIMENTS – SOLID ION CONDUCTORS**

**M. Kryński¹, A. Dzięgielewska¹, K. Kwatek¹, M. Malys¹, J. Jamroz¹, W. Wróbel¹,
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At temperatures just above 1000 K, the pure bismuth oxide in its high temperature cubic δ -phase demonstrates remarkable oxide ion conductivity, reaching approximately 1 S cm⁻¹. However, a phase transition occurs below this threshold, resulting in a sudden decline in conductivity. Extensive scientific endeavors have been directed towards developing bismuth oxide-based compounds capable of maintaining the high conductivity observed in the δ -phase at lower temperatures. Strategies encompass doping techniques or the synthesis of materials where bismuth does not predominate among the cations. In this study, we illustrate how a comprehensive understanding of conduction mechanisms in novel solid electrolytes can be attained through a combination of experimental approaches and theoretical modeling, specifically employing molecular dynamics simulations.

We employ a variety of Density Functional Theory (DFT) methods, with a focus on utilizing versions of the general gradient approximation within molecular dynamics simulations, particularly at high temperatures of up to 1200 K. Depending on the particular aspect being studied, we adapt the traditional ab initio approach by integrating van der Waals interactions or Hubbard corrections as required. All simulations are executed using the Vienna Ab initio Simulation Package. Our calculations typically involve systems ranging from as large as three hundred atoms, particularly when modeling lighter elements, to as small as one hundred atoms for compounds predominantly comprised of heavy ions.

In the rhombohedral Bi_{1-x}PxO_{1.5} system, characterized by a layered structure we look at a tremendous level of dynamical heterogeneity, with centers of the diffusion processes migrating between the fluorite-like blocks and the van der Waals gap as the Bi/Pr ratio is changed. Within the perovskite sodium bismuth titanate structure, we elucidate the modulation of ionic conductivity attributed to the presence of composition-dependent polarons, which results in the formation of uncommon clusters of oxide ion vacancies. This phenomenon has been leveraged to account for a rapid decline in ionic conductivity observed experimentally with minor alterations in the Bi/Na ratio. In the case of two BIMEVOX Bi₂V_{0.9}Ge_{0.1}O_{5.45} and Bi₂V_{0.95}Sn_{0.05}O_{5.475} compositions a combination of first principle simulations and machine learning methods was used to distinguish between the polar (C2) and nonpolar (C2/m) structures of α -phase, both being considered based on the experimental data.

Acknowledgements: This work was supported by the National Science Centre (Narodowe Centrum Nauki), Poland under grant number UMO-2018/30/M/ST3/00743 UMO-2018/31/B/ST5/03161.

SIZE AND STRAIN-RELATED PHENOMENA IN HEAT AND PRESSURE-TREATED GLASSES AND RESULTED NANOCOMPOSITES

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It is well known that nanostructured materials for energy applications (cathodes, anodes, solid electrolytes) exhibit better performance than their coarse-grained polycrystalline counterparts. Most of these nanomaterials were obtained by solid-state reaction techniques. However, our group, has systematically explored the thermal crystallization of glasses as a simpler alternative way to synthesize nanostructured materials for energy storage. We have carried out a series of studies on thermal nanocrystallisation [1] of glassy analogues of cathode materials for sodium/lithium batteries [2, 3] or oxygen ion conductors [4]. Thanks to this alternative technique, it was possible to synthesize nanostructured cathodic materials exhibiting interesting morphology and unique physical properties. An application of a high pressure (abbr. HP, orders of gigapascals) during high-temperature treatment becomes a new player that may introduce further modifications of material properties, e.g. non-linear increase in the glass transition temperature in HP-treated materials [5].

On the one hand, nanocrystallisation may lead to a giant and irreversible increase in conductivity (even by a factor as high as 10^9) in improving the poor conductivity of the starting glasses without introducing carbon additives [1]. The microstructure of the samples consisted of 5–50 nm nanocrystallites. The conductivity increase has been attributed to the appearance of highly disordered shells around such small grains (cores), which facilitated the electron hopping, e.g. between aliovalent V^{4+}/V^{5+} or Fe^{2+}/Fe^{3+} centres. Additional HP treatment facilitated the formation of easy-conduction paths because of the reduction of the average distance between the hopping centres.

On the other hand, nanocrystallisation of Bi_2O_3 -like glass led to the stabilization of delta and beta-like phases, presumably due to confinement effects of the nanocrystallites embedded in a residual glassy matrix. Application of HP led to a better understanding of the role of SiO_2 and Al_2O_3 glass formers in this phenomenon [6].

Acknowledgments: This research was supported by the National Science Centre (NCN) through grant OPUS-23 no. 2022/45/B/ST5/04005 and Preludium BIS-2 no. 2020/39/O/ST5/00897.

References:

- [1] T.K. Pietrzak, M. Wasiucionek, J.E. Garbarczyk, *Nanomaterials* 11 (2021) 1321.
- [2] T.K. Pietrzak et al., *J. Power Sources* 194 (2009) 73-80.
- [3] M. Nowagiel et al., *Energies* 15(7) (2022) 2567.
- [4] T.K. Pietrzak et al., *Scientific Reports* 11 (2021) 19145.
- [5] A. Drozd-Rzoska et al., *J. Phys. Chem. Lett.* 13(31) (2022) 7269–7272.
- [6] A. Szpakiewicz-Szatan et al., *Materialia* 33 (2024) 101975.

DEVELOPMENT OF QUASI-SOLID LITHIUM-CONDUCTING POLYMER ELECTROLYTES WITH NOVEL SALTS AND PLASTICIZERS

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Lithium-ion batteries are well known for their high energy and power density which caused their popularity in electronics and electric vehicles of all types. However, their disadvantages are inadequate high-temperature stability, the potential for the leak after damage, and degradation over time - slow but still troublesome in the case of bigger battery packs. Solid polymer electrolytes can help with the leak issue, as well as they can mitigate the degradation over time. However, they come with their own issues, such as low conductivity limiting the power density and the requirement to use lithium salt that could withstand the high temperature of anolyte and catholyte processing. The use of plasticizer can improve the conductivity of the solid electrolytes. However, issues of high-temperature stability of the salt or ionic liquid plasticizer and the cell degradation over time should be addressed by the anion choice.

The currently available and long-used salts are LiPF_6 for liquid electrolytes and LiTFSI - mostly for solid polymer electrolytes and ionic liquids. Both have their downsides. Namely, LiPF_6 is unstable in the presence of any water trace or temperature higher than 70°C (in carbonate solutions), so it limits the stability of the whole cell. Also, it cannot be used in polymer processing taking place usually above 150°C . LiTFSI is known for its corrosivity of aluminum current collectors. Thus, new salts have their chance. LiTDI , developed at the Warsaw University of Technology, is one such salt, which has been in production since 2019. It has much higher thermal stability than LiPF_6 , similar lithium cation conductivity (in liquid electrolytes), and uses much less fluorine. TDI anion works well with various cations to form ionic liquids with good stability properties. LiPCP , developed recently at the Warsaw University of Technology, is a fluorine-free salt that exhibits great lithium cation conductivity (better than LiPF_6) and even higher thermal stability. PCP anion can also be used to form room-temperature ionic liquids.

The presentation will show how the use of LiTDI , LiPCP and ionic liquids based on new anions improved the effective conductivity of lithium-conducting electrolytes and the overall stability of cells. Thermal stability, electrochemical stability, conductivity, lithium cation transference numbers and galvanostatic cycling of the novel salts, ionic liquids and ready electrolytes will be presented.

CAN SUSTAINABILITY GO HAND IN HAND WITH PERFORMANCE OF Li-ION BATTERIES? – THE CASE OF CARBON ADDITIVES FREE ELECTRODES

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The latest market analyses and the forecast for worldwide battery energy storage systems reveal the demand can easily exceed 5TWh/year in 2030 with a target value of over \$400 billion. This is at least a 5-times increase from the year 2023. The very fast growth rate will be mainly driven by the emerging market of electric vehicles (EV) but the rising renewable energy sector should be stated as well. Especially the latest one is crucial for green transformation and decarbonization of the energy sector. Huge demand for Li-ion batteries production strongly affects the existing raw materials market, especially for key metals (Li, Co, Ni) and graphite, which results in price increase and instability, as well as supply shortages disturbing the value chain. The fast scaled-up technologies, especially those dedicated to green energy transformation, need to be sustainable obviously, and this could be a challenge as well. The sustainability of Li-ion batteries technology is required at any level of the value chain, from raw materials to recycling and production processes, and with respect to carbon footprint to achieve green transformation targets. Moreover, preferably the sustainability of batteries should be implemented without sacrificing their performance. Is it possible?

In the work, we demonstrate a concept – solution for carbon additives free electrodes (CA-free electrodes) based on Conductive Carbon Layers (CCL) nanocomposite technology [1]. For this purpose, a set of CCL/LFP nanocomposite materials was prepared from two commercial sources of LFP (Freyr, Pulead) diversified with basic powder properties (texture, morphology). The cathodes for test cells were prepared without using any carbon additive, i.e. carbon black (CB), only composed of CCL/LFP and PVDF binder. As reference standard C/LFP+CB electrodes were prepared. The results clearly indicate that the performance of CA-free electrodes and energy density was at least the same or better than for standard types of electrodes. Thus, the CA-free solution simplifies the electrode production, needs less energy for slurry homogenization and assures less carbon waste in the recycling process. This seems to be a sustainable alternative for State-of-the-Art cathodes with carbon additives and is not only limited to LFP cathode material.

References:

[1] M. Molenda, R. Dziembaj, A. Kochanowski, E. Bortel, M. Drozdek, Z. Piwowarska; „Process for the preparation of conductive carbon layers on powdered supports”; PAT.216549; US 8,846,135 B2; KR 9-5-2015-047561689; JP 5476383 B2; EP 2326745 A2

NEW 3D CURRENT COLLECTORS FOR LITHIUM-ION BATTERIES

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Lithium-ion batteries are among the most modern energy sources for consumer electronic devices. Each reversible lithium cell consists of components responsible for delivering charge and electrochemically inactive materials. The active components of a lithium-ion cell include electrode materials (such as graphite and lithiated cobalt oxide) and electrolyte. These compounds participate directly in the electrode reactions, generating the voltage and energy supplied by the battery. In addition to electrochemically active materials, lithium-ion cells contain several components that are not electrochemically active but perform important functions in the battery. Such components include the outer casing, internal and external leads, the separator, and the copper (for the negative electrode) and aluminium (for the positive electrode) current collectors. Current collectors are essential components connecting lithium-ion batteries to external circuits. They serve as a matrix that holds the active material in a mechanically stable form and are also involved in dissipating the charge generated by electrode processes. Thus, current collectors largely determine the capacity, performance, and long-term stability of lithium-ion batteries. Conventional current collectors, aluminium and copper foils, have been used since the first commercial lithium-ion battery. They account for about 15 percent by weight of the total cell, and because they are inactive components of the battery, there is a continuing need to reduce their mass share without losing functionality. Over the past two decades, in order to increase the energy density of lithium cells, the thickness of current collectors has decreased significantly. However, to further improve performance, alternative materials and structures are being explored, as well as specific collector treatments such as etching or carbon coating. These treatments aim to enhance the electrochemical stability and electrical conductivity of current collectors for the next generation of lithium-ion batteries with higher capacity and longer life. The presentation will review various types of current collector materials in terms of their electrochemical stability, electrical conductivity, mechanical properties, and durability. It will also include alternatives to traditional structures, such as 3D current collectors. Two types of three-dimensional current collectors will be presented: a 3D structure on a copper film collector and conductive porous carbon. The electrochemical properties of lithium-ion batteries utilizing these collectors will be demonstrated.

Acknowledgements: This presentation include the results of research funded by The National Centre for Research and Development (grant no. LIDER/28/0148/L-10/18/NCBR/2019) and European Union's Horizon 2020 Research and Innovation Program (grant agreement No. 875514).

TAILORING MIXED IONIC-ELECTRONIC CONDUCTIVITY IN TRANSITION METAL DOPED $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ SOLID ELECTROLYTES**K. Pachulska¹, A. Cuper², M. Michalski¹, M. Winkowska-Struzik³, M. Struzik^{1,2}**¹ Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw² Centre for Advanced Materials and Technologies CEZAMAT, Warsaw University of Technology, Poleczki 19, 02-866 Warsaw³ Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw
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Solid-state electrolytes based on lithium garnet frameworks, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), offer a promising avenue for enhancing the safety and performance of next-generation lithium-ion batteries. Despite the promise of higher energy and power density than liquid electrolyte-based cells, superiority of their solid-state counterparts has not yet been demonstrated in the working system. One of the explanations can be attributed to the mismatch of the design and composition of the currently used battery electrodes to work with the solid electrolyte. One possible scenario for improving the electrochemical performance of solid-state electrolyte cells could be the use of composite electrodes, one component of which would be LLZO-based material modified to conduct both lithium ions and electrons to serve as a medium between the solid electrolyte and the electrochemically active material.

In this study, we report on the simultaneous doping of transition metals on both La- and Zr-sites in LLZO to achieve a mixed ionic-electronic conductor with enhanced overall conductivity. We investigate the crystal structure using X-ray diffraction (XRD) and elucidate the local structural changes through Raman spectroscopy. The electric transport properties, crucial for battery performance, are thoroughly characterized via impedance spectroscopy and DC measurements.

Our results reveal a systematic enhancement in the electronic contribution to total conductivity. These findings not only advance the fundamental understanding of LLZO doping mechanisms but also offer practical insights into tailoring solid electrolytes for high-performance lithium-ion batteries.

STRATEGIES TOWARDS TITANIA PHOTOANODE ACTIVITY ENHANCEMENT

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It has been common knowledge for over half a century that the photoelectrochemical decomposition of water into oxygen and hydrogen can be carried out thanks to titanium dioxide used in the PEC cell as a photoanode [1]. The first problem that had to be taken into account when working with TiO₂ electrode was the frequency range of the light absorbed by this semiconductor, where for none of the pure forms of anatase and rutile the size of the energy gap E_g does not allow for the absorption of visible light. Without losing any absorption in the UV range of the electromagnetic wave, attempts can be made to introduce changes in the electronic structure of the semiconductor in order to reduce the bandgap width. Good results were achieved by doping TiO₂ with non-metals N, I, B capable of occupying interstitial positions in oxide structure. The effectiveness of the procedure applies to both the doping of TiO₂ particles with simple morphology and to specially prepared anodic nanostructures known as Titania nanotubes TNTs. The activity of nanotubes is influenced by hydrothermal modification and the type of electrolyte used in the hydrothermal process [2].

In another strategy, doped or pure TiO₂ electrode layers constituting the photoanode are subject to surface modification by creating systems capable of relay charge transfer at the phase boundary. The essence of this approach is the precision of the selection of the position of the conduction and valence bands of TiO₂ and electronic structure of the modifier used. An effective system illustrating this strategy may be the use of polymer layers of conductive p-type conductors with redox systems imbedded the use of organic p-type conductors also plays a role in the separation of photogenerated charges. In addition, experience gained from electrocatalysis translates into the use of surface modifiers in PEC cells. The reaction of water oxidation to O₂ is effectively catalyzed by cobalt compounds like Co[Co(CN)₆], CoO_x and CoO(OH) oxides [3]. Therefore, the use of oxygenated cobalt compounds is a good choice of cocatalyst for surface modification of TiO₂ nanotubes. Effective optimization of the amount of cocatalyst is achievable through the use of electrochemical techniques. This is chronoamperometry, forgotten as a technique that allows determining the type of nucleation and crystal growth without using microscopic methods. These two types of cobalt compounds have the characteristics of an OER reaction catalyst thanks to the ability to change the oxidation state of the Co(II/III/IV) center. Comparison of the activity of both OER reaction cocatalysts on the TiO₂ photoanode indicates a better effect of CoO(OH) as a result of proton assisted electron transport during RDS. Photoanode research is important for applications in the area of photoassisted water splitting, in environmental protection for the mineralization of organic pollutants. It was found that the use of CoO(OH) significantly increases the effectiveness of the anodic process compared to the use of cobalt oxides CoO_x. This is due to the availability of protons for electron transfer reactions at RDS.

References:

- [1] M. Graetzel *Nature* 414 (2001) 338.
- [2] Wtulich, M., Szkoda, M., Gajowiec, G., Jurak, K., Trykowski, G., Lisowska-Oleksiak, A. *Electrochimica Acta* 426 (2022) 140802.
- [3] Trzciniński, K., Szkoda, M., Mirosław, S., & Lisowska-Oleksiak, A. *Electrocatalysis*, 11, (2020). 180-187.

FORTY YEARS OF COMPOSITE POLYMER ELECTROLYTES – A SUBJECTIVE VIEW

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The presentation reflects a point of view of a person who witnessed the development of Composite Polymer Electrolytes (CPEs) from the very beginning. It is dedicated primarily to younger researchers who have just started or plan to start their research activity in this area. The author believes that such a concise review can be useful in the face of a huge amount of related information. There is about nine thousand documents in the SCOPUS database dedicated to polymer electrolytes and as many as 881 publications with the keywords “composite polymer electrolytes” having appeared during the last year (2023).

The concept of technological applications of complexes of polar polymers with inorganic salts is 45 years old [1]. Within these years it has become clear that Solid Polymer Electrolytes (SPEs) have unique properties predestinating them to use in modern batteries as well as in other devices. These materials, however, exhibit some serious deficiencies like too low total conductivity, too low contribution of cations in conduction as well as frequently insufficient electrochemical stability. Starting from a rather unexpected observation that addition of a fine inert powder into SPE significantly increases its conductivity [2] this procedure became one of important pathways of SPEs improvement. The name Composite Polymer Electrolytes (CPEs) was coined for materials prepared in this way.

The most frequently used matrix polymer in CPEs is poly(ethylene oxide) (PEO), however, other materials like poly(propylene oxide), polyacrylonitrile, poly(methyl methacrylate), poly(vinylidene fluoride), their blends and many others were studied. The salts delivering cations upon dissociation in polymer matrices comprise typically the so called weakly coordinating anions (WCAs) like ClO_4^- , Γ^- , PF_6^- or $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ for example. The additives can be inert but modifying properties of the matrix (Al_2O_3 , TiO_2 , SiO_2 , YSZ, *etc.*) or active ionic conductors contributing to the ion transport in CPE (NASICON, Li_3N , LATP *etc.*). The latter additives must form continuous networks within CPE foils.

There are a few critical features of a solid electrolyte designed to work in a solid state batteries. Probably the most important are ionic conductivity, cation transference number, electrochemical stability, electrolyte/electrode impedance and flexibility. These properties of some selected CPEs are commented in the presentation.

At present the ionic conductivity of the best CPEs is only slightly above 10^{-4} S/cm at RT. This feature as well as some other deficiencies impede wide applications of CPEs (and SPEs as well) in commercial technologies. Despite the apparent lack of a significant progress the ceaseless efforts continue. They are propelled by the vision of all solid state lithium batteries (ASSLBs) regarded as a Holy Grail of the energy-storage community.

References:

- [1] The technological relevance of PEO-based electrolytes: M.B. Armand, J.M. Chabagno, M. Duclot, in: P. Vashishta et al. (Eds.), *Fast Ion Transport in Solids*, Elsevier, New York, 1979, p. 131.
- [2] J. Płocharski, W. Wiczonek, PEO based composite solid electrolyte containing NASICON, *Solid State Ionics*, 28-30 (1988) 979–982.

LITHIUM-SULFUR BATTERY: MATERIALS STUDIES AND TECHNOLOGICAL CHALLENGES

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Low temperature lithium-sulfur (Li-S) batteries have recently emerged as one of the candidates for next-generation lithium-based storage system, especially for mobile applications. They potentially offer some important advantages over the existing Li-ion technologies, like significantly higher gravimetric energy densities and reliance on inexpensive and abundant cathode active material. After a short introduction about Łukasiewicz Research Network and its activities in the field of electrochemical energy storage, this presentation focuses on current state-of-the-art in so-called post-Li-ion” concepts in the area of lithium-based battery systems with particular attention to Li-S batteries. Main mechanisms of the cell operation will be briefly reviewed, as well as state-of-the-art materials concepts for composite sulfur cathodes and how they respond to the key performance issues faced by modern Li-S cells being under developments in labs. Scientific results recently obtained at Łukasiewicz-IMN will then be briefly reviewed. Among them, preliminary attempts to apply sub-stoichiometric titanium oxides as new promising idea for a component of the sulfur cathode will be presented. These materials, especially so-called Magneli phases, offer some appealing properties, such as high electronic conductivity and the presence of lattice defects, making them potentially attractive by hindering polysulfide (PS) dissolution and catalytically enhancing the PS reaction kinetics, while at the same time not impairing the cathode conductivity. The extent of these favorable effects is, however, yet to be confirmed in real life. In the second part of this presentation, a case study of the development works on prototype pouch-type Li-S cell and battery will be presented. Steps of the pouch fabrication using relatively simple, lab-scale equipment will be briefly reviewed and the results will be shown in terms of electric battery tests and trials in model vehicle. The presentation will end with conclusions as for future prospects of Li-S technology.

**COMPLEX PEROVSKITES WITH MIXED IONIC-ELECTRONIC
CONDUCTIVITY IN SELECTED ELECTROCHEMICAL APPLICATIONS****K. Świerczek**¹

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Due to their compositional flexibility, perovskite-type and related oxides often exhibit unique structural features, e.g. with formation of various superstructures and localization of the oxygen vacancies. Consequently, their physicochemical properties, including mixed ionic-electronic conduction (MIEC), as well as thermomechanical characteristics, are often complex and may be highly anisotropic. Nevertheless, those properties can be optimized, and the compounds can be tuned for using in various electrochemical applications. For example, different perovskites showing sufficient electrocatalytic activity are utilized as the oxygen electrode materials in Solid Oxide Cells (SOCs).

In this work several perovskite groups are described in more detail, including the A-site layered RE(Ba,Sr)Co_{2-y}Mn_yO_{5+δ} (RE: selected rare-earth cations; 0 ≤ y ≤ 2). It is documented that through a proper selection of the Mn content, the oxides can be optimized for application as the oxygen electrode materials for SOCs, or alternatively, as candidate oxygen storage materials [1,2]. If copper is used to replace Co instead of Mn, an interesting family of RE(Ba,Sr)Co_{2-y}Cu_yO_{5+δ} oxides is formed, which shows decreased thermal expansion, but still very high electrocatalytic activity toward the oxygen reduction reaction (ORR) [3]. Also, a subgroup of oxides with a formula of La_{1-x}(Ba,Sr)_xCuO_{3-δ} shows unique oxygen vacancy ordering phenomenon, but at the same time, exhibits sufficient catalytic activity toward ORR at high temperatures, with several oxides showing very promising performance when applied in SOCs [4]. In order to improve electrocatalytic characteristics at moderate temperatures, possibility of finding (partially) disordered at the anionic sublattice systems can be explored [5]. Finally, with the so-called high entropy approach, multicomponent perovskites, either at the A- and/or B-site are also of interest. In this case, however, no definitive description of how the high entropy really affects various physicochemical properties is yet provided [6].

References:

- [1] A. Olszewska, Z. Du, K. Świerczek, H. Zhao, B. Dabrowski, *J. Mater. Chem. A* 6(27) (2018) 13271-13285.
- [2] A. Olszewska, K. Świerczek, W. Skubida, Z. Du, H. Zhao, B. Dabrowski, *J. Phys. Chem. C* 123(1) (2019) 48-61.
- [3] K. Li, K. Świerczek, P. Winiarz, A. Brzoza-Kos, A. Stępień, Z. Du, Y. Zhang, K. Zheng, K. Cichy, A. Niemczyk, Y. Naumovich, *ACS Appl. Mater. Interfaces* 15(33) (2023) 39578-39593.
- [4] A. Niemczyk, Z. Du, A. Olszewska, M. Marzec, M. Gajewska, K. Świerczek, H. Zhao, B. Poudel, B. Dabrowski, *J. Mater. Chem. A* 7(48) (2019) 27403-27416.
- [5] K. Li, A. Niemczyk, K. Świerczek, A. Stępień, Y. Naumovich, J. Dąbrowa, M. Zajusz, K. Zheng, B. Dabrowski, *J. Power Sources* 532 (2022) 231371.
- [6] J. Dąbrowa, A. Olszewska, A. Falkenstein, C. Schwab, M. Szymczak, M. Zajusz, M. Moździerz, A. Mikuła, K. Zielińska, K. Berent, T. Czeppe, M. Martin, K. Świerczek, *J. Mater. Chem. A* 8(46) (2020) 24455-24468.

THERMAL ANALYSIS AND THERMODYNAMICS PERSPECTIVES ON MATERIALS FOR PROTONIC CERAMIC ELECTROCHEMICAL CELLS

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The thermal analysis of materials encompasses a range of techniques employed to assess the functionality of engineering materials. The analysis of water uptake phenomena of proton conducting oxides is a research topic that has been explored for the last two decades by different groups [1,2]. However, the new developments of materials for protonic ceramic electrochemical cells (PCECs) [3] have shown the need to develop, or adapt, methods for the determination of water uptake in not only proton conductors but also in MIEC (Mixed Ionic and Electronic Conductor) [4]. The latter can exhibit multiple different phenomena which are often hard to describe. Furthermore, an integral part concerning the thermodynamic characteristics of materials for PCECs relates to their stability. We believe that evaluating the stability of materials for PCECs should encompass both structural stability at elevated temperatures and an analysis from a thermodynamic perspective.

This presentation will showcase research dedicated to identifying crucial attributes within various protonic conductors and MIEC systems. The utilization of cutting-edge techniques will be elucidated, accompanied by the presentation of the collected data.

Acknowledgments: The research has been supported by the National Science Centre Poland (2016/22/Z/ST5/00691), the Spanish Ministry of Science and Innovation (PCIN-2017-125, RTI2018-102161, and IJCI-2017-34110), and the Research Council of Norway (grant no. 272797 “GoPHy MiCO”) through the M-ERA.NET Joint Call 2016. The calorimetry at Arizona State University received financial support from the U.S. Department of Energy, Office of Basic Energy Sciences, grant DE-SC0021987. The research was financially supported by the National Centre for Research and Development (IX Polish-Taiwanese project, no. DWM/POLTAJ9/3/2022).

References:

- [1]Y. Yamazaki et al. Chemistry of Materials. 20 (2008) 6352–6357.
- [2]T. Miruszewski et al. Materials. 13 (2020) 965.
- [3]C. Duan et al. Appl Phys Rev. 7 (2020).
- [4]S.L. Wachowski et al. Acta Mater. 199 (2020) 297–310.

INTERCONNECT PROTECTIVE COATINGS FOR NEXT-GENERATION SOLID OXIDE CELLS: NEW MATERIALS AND PROCESSING CHALLENGES

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Solid Oxide Cells and Stacks are gaining technical maturity and entering commercialization, especially for highly efficient high-temperature electrolysis. However, further research is needed to increase power density and address degradation issues. Corrosion of steel interconnects is a significant contributor to stack degradation and requires advancements in the near future.

Our group has extensive experience in high-temperature corrosion and protective coatings development, with over 15 years of national and international collaborations. We have investigated various alloys and developed and tested diverse coating materials. This presentation will provide an overview of historical and recent developments in ceramic protective coatings. It will address alloy selection, coating materials, deposition techniques, and other factors, emphasizing next-generation coatings for lower-temperature stack technology.

SUBTLE CRYSTAL SYMMETRY CHANGES IN $\text{Bi}_x\text{Pr}_{1-x}\text{O}_{1.5}$ OXIDE ION CONDUCTORS

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Lanthanide doped bismuth oxides with the rhombohedral Bi-Sr-O type structure exhibit one of the highest oxide ion conductivity, comparable to the fluorite $\delta\text{-Bi}_2\text{O}_3$ type compounds [1]. A characteristic property of bismuth-oxide rhombohedral type systems is order-disorder phase transition at ca. 700 °C, associated with a step change of total conductivity of 1 order of magnitude [2]. In our previous work, we concluded that this change of conductivity is related with redistribution of O atoms [3]. This anion redistribution is followed by subtle rearrangement of cations, which is not yet fully understood.

The crystal structure of $\text{Bi}_x\text{Pr}_{1-x}\text{O}_{1.5}$ oxide ion conductors with compositions $x=0.20$, $x=0.25$ and $x=0.325$ was studied by using synchrotron radiation X-ray powder diffraction (SXRPD). The measurements were focused on the phase transition from the low-temperature β_2 phase to the highly conducting disordered phase β_1 which is observed near 730°C[3]. In order to avoid large absorption of Bi and Pr ions the measurements were done with high energy x-rays corresponding to a wavelength $\lambda=0.3267\text{\AA}$. For each sample the SXRPD measurements were done in two cycles, i.e. 300°C→800°C→300°C→800°C→300°C.

The present studies confirm the earlier findings obtained by laboratory X-ray diffraction and neutron time-of-flight diffraction done with the instrument Polaris@ISIS [3]. Due to the combination of high flux and high angular resolution SXRPD patterns provide some additional information. The SXRPD patterns can be described by using the usual rhombohedral structure model with the space group $R\bar{3}m$. At all temperatures, i.e. both below and above the transition better fit quality is obtained with a modified symmetry model assuming monoclinic symmetry with the space group $C2/m$. The monoclinic space group $C2/m$ is obtained from $R\bar{3}m$ by removing the 3-fold rotations around the hexagonal [001] axis. The Rietveld refinements in monoclinic symmetry were done with a pseudo-hexagonal unit cell which is similar to unit cell of the hexagonal setting of $R\bar{3}m$. In this non-standard monoclinic unit cell the pseudohexagonal angles may deviate from the values of 90° and 120°, i.e. $\beta\approx 90^\circ$ and $\gamma\approx 120^\circ$. For all $\text{Bi}_x\text{Pr}_{1-x}\text{O}_{1.5}$ samples with $x=0.20$, $x=0.25$ and $x=0.325$ the value of γ is equal to 120° within experimental error ($\pm 0.01^\circ$) while the angle β is larger than 90°, i.e. about 90.04(1)° outside the phase transition region. At temperatures close to the phase transition the angle β show a narrow peak with a maximum of about 90.08(1)° in all heating and cooling cycles. The refined monoclinic structure model of $\text{Bi}_x\text{Pr}_{1-x}\text{O}_{1.5}$ is discussed in the context of possible stacking faults.

References:

[1] M. Drache, et. al, Chem. Rev. 107 (2007) 80–96.

[2] M. Drache, et. al, Journal of Solid State Chem. 149 (2000) 341–348.

[3] J. Jamroz, M. Malys, F. Krok, J. Maier, A. Kyriacou, S.J. Ahmed, I. Abrahams and W. Wróbel, *Solid State Ionics* **348** (2020) 115284.

COMPOSITE MATERIALS AS FUNCTIONAL PROTECTIVE-CONDUCTING COATINGS FOR STEEL INTERCONNECTS APPLIED IN SOLID OXIDE ELECTROLYZER CELLS

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The widespread adoption of the technology used to produce hydrogen by means of solid oxide electrolyzer cells (SOECs) from surplus electrical energy generated by wind and solar power sources, which are themselves affected by weather conditions, will only be possible if the price of such devices is not overly high and provided that they can offer several dozen thousand hours of failure-free operation. The lowest possible manufacturing cost and the highest achievable durability are therefore concerns that need to be taken into account as early as at the research stage.

These requirements have been addressed by designing a new type of composite material for protective-conducting coatings applied on metallic interconnects for solid oxide electrolyzer cells (SOECs); the developed material features a matrix consisting of the $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$ (CM) spinel, in which the lanthanum-containing $\text{LaNiFeO}_{3-\delta}$ (LNF) perovskite is dispersed. The material serves two main functions. It acts as a barrier that prevents the formation of volatile chromium compounds responsible for the so-called "electrode poisoning" effect, and in this respect it should be more effective than the currently applied Mn-Co-O spinel coatings. In addition, it serves as a reservoir of the reactive element in the layered system consisting of the steel substrate, the reaction zone, and the coating, which effectively improves not only the heat resistance but also the electrical conductivity of materials that form protective Cr_2O_3 scales, such as high-chromium ferritic steels used as interconnect materials. It should be emphasized that – unlike the coating materials currently applied with interconnects – the newly developed coating does not contain the scarce and environmentally unfriendly cobalt, which has been replaced with the much less expensive copper.

The presented study evaluated the effect of the performed LNF addition on the physicochemical properties of the tested CM/LNF composite material samples via a number of investigations, including electrical conductivity and Seebeck coefficient measurements as well as XRD, IR, XAS, and SEM observations. Adding LNF to the CM matrix yields a composite system that exhibits significantly improved electrical properties at temperatures below 800°C and increases stability in the presence Cr_2O_3 , confirming that CM/LNF can be applied as a material for functional protective-conducting coatings on SOEC metallic interconnects.

Acknowledgements: Funding of National Science Centre (NCN) project No. 2021/41/B/ST8/02187 is gratefully acknowledged (TB).

ENCHANCING THE H₂O-CO₂ COELECTROLYSIS PROCESS IN SOECs WITH DEPOSITED NANOPARTICLES OF THE TRANSITION METALS

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The ongoing technical development and global industrialization have resulted in a growing demand for fossil fuels. The reduction of the amount of the carbon dioxide and the development of the renewable energy sources are the challenges we are facing nowadays. One of the most promising methods to utilize CO₂ from fossil fuels, is the conversion of carbon dioxide into valuable chemicals. Affordable production of the hydrocarbons can be achieved using e.g., Fischer-Tropsch synthesis from H₂ and CO. Unfortunately, green hydrogen and carbon monoxide production is still problematic. Electrochemical reduction of CO₂ and H₂O is believed to be one of the most promising conversion strategies, that could possibly consume excess energy to efficiently produce value-added chemicals.

Higher operating temperature of the SOECs enhance the kinetics of the water electrolysis process. Furthermore, these are capable of simultaneous reduction of CO₂, if it is delivered to the inlet mixture along with water vapor. Although coelectrolysis of H₂O/CO₂ has been studied for a long time, a clear description of the process is still lacking due to its complex nature. In spite of the increase in catalytic activity, a proper catalysts should be used to the cells. An interesting group of catalysts are metal-based nanoparticles supported on the SOEC's electrode.

In this study, a series of novel SOECs has been fabricated by β CD-assisted fast impregnation method. The conventional Ni-YSZ bulk cermet electrodes were enriched with 3.6 wt.% of the nanoparticles of the Mn, Co, Fe, Cu, and Zn oxides which upon reduction formed mixed core-shell-like structures on the Ni grains. The obtained structure was deeply characterized using synchrotron radiation in Scanning Transmission X-ray Microscopy (STXM) to reveal the complexity of the structures. The chemical imaging studies were accompanied by the measurements using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) performed under the flow of reactant mixture at elevated temperature. The addition of the secondary metal alters the energy levels on the Ni surface and increases the tendency to form carbonates, what prolongs the retention time of CO₂. Finally, the cells with infiltrated electrodes were tested i.a. in the H₂O/CO₂ coelectrolysis regime at 700 °C. The addition of the guest catalytic metal increased the CO₂ conversion and selectivity towards CO production due to the existing surficial modifications of e.g. basic-acid sites. Long-term tests revealed low degradation levels of the modified cells. This simple approach for modification of the SOEC can lead to better understanding of the correlation between the properties of the fuel electrode material and the overall efficiency of the coelectrolysis process.

Acknowledgements: This work was supported by a project OPUS22 funded by National Science Centre Poland, based on decision UMO-2021/43/B/ST8/01831. We also acknowledge SOLARIS Centre for the access to the Beamline DEMETER. The XAS experiments were performed on beamline BM08 (LISA) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

Oral presentations

LIMITING THE AGING PROCESS OF SPINEL-BASED Li-ION CELLS BY CATHODE SULFUR DOPING

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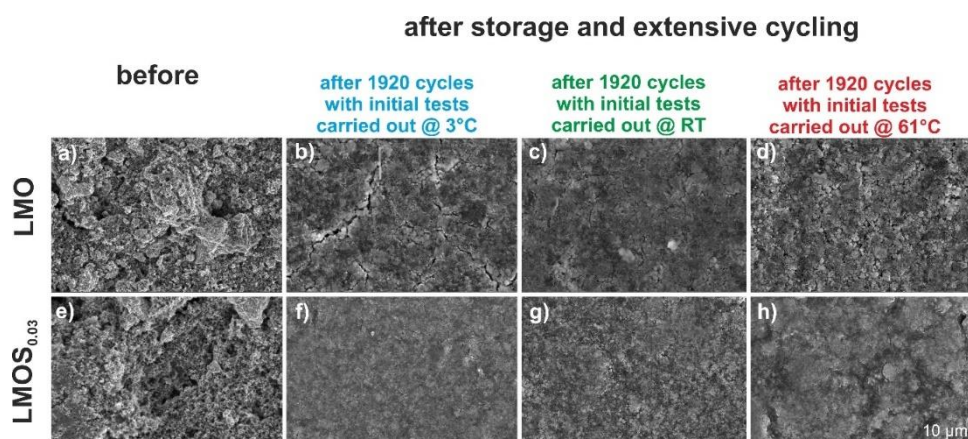
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The degradation of stoichiometric lithium-manganese spinel (LiMn_2O_4 , LMO) is a critical concern in the longevity and efficiency of eco-friendly, cheap lithium-ion batteries. The complex mechanisms of degradation, involving Jahn-Teller distortion of Mn^{3+} , as well as Mn^{2+} dissolution, are well-known to be accelerated by reactive species like HF.

This study explores sulfur substitution into the LMO's oxygen sublattice as a targeted approach to mitigate these aging factors.

The effect of sulfur doping is revealed to have multiple impacts. Firstly, S limits the passive dissolution of manganese in the electrolyte which occurs in the cell regardless of working regime. Secondly, the S-stretched spinel structure has less diffusion limitations and is less susceptible to mechanical strains, and arising from this electrode cracking and material loss under high current flows. Thirdly, the results suggest higher stability of the passivation layer formed on the LMOS surface. Finally, sulfur presence in the electrode influences PVDF binder stability, limiting the defluorination of the polymer at higher working potentials, which enhances the electrode's durability and restricts fluorine content in an electrolyte.



Although a full understanding of sulfur's role in the cell aging process remains intricate, the findings affirm that sulfur substitution significantly increases the structural stability of the material and overall cell performance, especially under severe working conditions. These insights into sulfur doping open new avenues for developing more robust and environmentally friendly LMO-based materials for large-scale battery systems, and this work offers valuable contributions to ongoing efforts in advancing energy storage technology.

**TOWARDS HIGHLY CONDUCTIVE NANOCRYSTALLISED
VANADATE-PHOSPHATE GLASSES**

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Nowadays, the increase in energy production from renewable power sources is an indisputable fact. One of their biggest disadvantages is the fact that such power sources are heavily dependent on weather conditions. This causes the need for assembly battery systems to stabilize the power grid during bad weather or night.

Vanadate-phosphates are a wide group of materials – candidates for cathodes in Li-ion batteries, and they have a long history of research & development, including crystalline VOPO4 [1], or Li3V2(PO4)3 [2]. At the same time, our group studied glassy analogues of different vanadate-phosphate glasses [3] and proved that their thermal nanocrystallisation may lead to a significant increase in their electronic conductivity. E.g., 90V2O5·10P2O5 glasses exhibit conductivity around $\sigma = 7 \cdot 10^{-5}$ S/cm but after nanocrystallization the electronic conductivity dramatically increased to $\sigma = 7 \cdot 10^{-2}$ S/cm at room temperature [4]. Moreover, the gravimetric capacity of these nanomaterials reached 225 mAh/g in first cycle (C/20 current), but it dropped to 140 mAh/g in the subsequent cycles.

The objective of this work was to synthesise glassy analogues of 95V2O5·5P2O5 and to optimise their conductivity even further. For this purpose, many different measurement methods were applied: XRD, SEM and EDX to confirm the glassy state, to investigate their microstructure and elemental compositions, DSC to check the thermal stability of the pristine glasses, and DC for electrical measurements. With these methods, changes in material during heat treatment can be observed, and correlations with changes in conductivity and other structural factors will be shown.

This work is also a starting point for high temperature – high pressure optimisation, which is expected to bring even better results in terms of electrical conductivity.

Acknowledgments: This research was supported by the National Science Centre (NCN) through grant OPUS-23 no. 2022/45/B/ST5/04005.

References:

- [1] Z. Chen, Q. Chen, L. Chen, R. Zhang, H. Zhou, N. A. Chernova, M. S. Whittingham, J. Electrochem. Soc. 160 (2013) A1777.
- [2] H. Huang, S.C. Yin, T. Kerr, N. Taylor, L.F. Nazar, Adv. Mater., 14: 1525-1528.
- [3] T.K. Pietrzak, J.E. Garbarczyk, I. Gorzkowska, M. Wasiucioneck, J.L. Nowiński, S. Gierlotka, P. Joźwiak, Journal of Power Sources 194 (2009).
- [4] T.K. Pietrzak, Ł. Pawliszak, P.P. Michalski, M. Wasiucioneck, J.E. Garbarczyk, Procedia Engineering 98 (2014) 28-35

**EFFECT OF THE LITHIUM SOURCE ON THE MICROSTRUCTURE,
ELECTRICAL PROPERTIES AND STRUCTURE OF THE LiTa₂PO₈ CERAMICS**

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Recently, lithium tantalum phosphate LiTa₂PO₈ (LTPO) has emerged as a promising candidate as a solid electrolyte, meeting strict requirements, such as high ionic conductivity, as well as robust thermal, mechanical, and chemical stability [1,2]. LTPO exhibits outstanding bulk ionic conductivity on the order of 1 mS/cm at room temperature. However, its total ionic conductivity is hindered by highly resistive grain boundaries. The overall electrical properties of LTPO ceramics are heavily influenced by processing parameters, such as sintering time and temperature [3]. Notably, LTPO requires high sintering temperatures exceeding 1000°C, which can lead to the evaporation of Li₂O and adversely affect its ionic conductivity.

To address Li⁺ loss at elevated temperatures, we have modified and optimized the synthesis procedure by introducing an excess of lithium ranging from 5 to 15 wt.% (with respect to the stoichiometric amount). The electrical and structural properties of the LiTa₂PO₈ ceramics including the selection of different lithium-containing substrates (Li₂CO₃, LiNO₃, LiOH.H₂O, Li₂O) and their excess, were studied applying several different and complementary methods, like X-ray diffractometry (XRD), ⁶Li and ³¹P nuclear magnetic resonance (MAS NMR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermomechanical analysis (TMA), impedance spectroscopy (IS), density (Archimedes) and Hebb-Wanger polarization methods.

The samples prepared without an excess of LiNO₃ or Li₂CO₃ sources exhibited the highest value of σ_{tot} , ca. 5×10^{-4} S/cm at 30°C. Notably, the grain conductivity remained constant at ca. 3 mS/cm, irrespective of the chosen lithium source and excess. The microstructural analysis uncovered correlations between variations in total ionic conductivity and changes in the nature and concentration of secondary phases. Additionally, it revealed the influence of the arrangement of grains affecting the grain boundaries and porosity regions.

Acknowledgments: The Polish group has received funding from the National Science Centre, grants MINIATURA 5, 2021/05/X/ST5/00530 and SONATA 18, 2022/47/D/ST5/00362, and IDUB MOBILITY PW as a part of “International scholarship exchange of doctoral students and academic staff”. The Spanish group has received funding from the MINECO MAT2016-78362-C4-2R and PID2019-106662RB-C42 projects.

References:

- [1] J. Kim et al., J. Mater. Chem. A 6 (2018) 22478–22482.
- [2] K. Kwatek et al., J. Eur. Ceram. Soc. 43 (2023) 5548–5556.
- [3] B. Huang et al., J. Mater. Sci. 56 (2021) 2425–2434.

INTERFACIAL ENGINEERING FOR IMPROVED SODIUM / SOLID ELECTRODE CONTACT IN SOLID STATE SODIUM BATTERIES

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Electrochemical energy storage requires development of low-cost, high-energy density battery technologies, beyond current Li-ion. Solid state sodium batteries offer many advantages such as elimination of scarce elements, increased energy density due to application of metal electrode as an anode with prevented dendrite growth through ceramic solid electrolyte barrier, and improved safety owing to elimination of highly reactive and flammable liquid electrolyte [1,2]. On the back side, however, are issues related to high polarization resistance of solid-solid interfaces at the electrolyte/electrode contacts.

This work reports investigations of symmetrical cells built with standard Na- β -alumina solid electrolyte sintered discs with metallic sodium anode using galvanostatic and AC impedance techniques. Various surface treatments of solid electrolyte were used in order to reduce interfacial resistance, cell polarization and prevent dendrite growth, as well as to improve tolerance to high current loads. X-ray Photoelectron and Raman spectroscopies were applied to reveal chemical composition of surface after heat treatment at various temperatures in controlled atmosphere and explain high interfacial resistance of the untreated electrolyte. Optical profilometry allowed to estimate surface roughness of the electrolyte after polishing with several grits and discuss the effect of surface roughness on electrode polarization under various current densities, as well as maximum achievable current density.

In search of further ways to improve the electrode-electrolyte between sodium metal and ceramic solid electrolyte contact, we communicate here the results obtained after increased temperature (up to 60°C) and applied external pressure (up to 19 MPa). Whereas the former increases the rate of all processes in the electrochemical cell decreasing resistance and polarization, the later is closely related to creep deformation of sodium metal electrode, which helps to fill in the voids formed when the sodium is stripped from the electrode during discharge and should affect performance chiefly at higher current densities.

Last part of the work is focused on the effect of alloying additives introduced to sodium metal electrode on wetting angle, polarization resistance and maximum current density. A positive correlation was observed between wetting angle, polarization resistance and maximum current density suggesting that this factor can be a good criterion of selection of new metal electrodes for solid state batteries.

References:

- [1] C. Zhao, L. Liu, X. Qi, Y. Lu, F. Wu, J. Zhao, Y. Yu, Y.-S. Hu, L. Che, *Adv. Energy Mater.* 8 (2018) 1703012 (1-20).
- [2] J. A. S. Oh, L. He, B. Chua, K. Zeng, L. Lu, *Energy Storage Materials* 34 (2021) 28-44.

**THE INTERPRETATION OF DIFFUSION AND DISPERSION ELEMENTS
PRESENT IN ELECTROCHEMICAL IMPEDENCE SPECTRA**

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The rapid growth in the areas of batteries and fuel cells lead to the need for deep analysis of their component materials. More often than not these materials are porous or multiphased, where traits such as composition, gradient of concentration of various material components, as well as electrochemical properties are vital in their characterization. Electrochemical/Dielectric Immitanceance Spectroscopy (E/DIS) offers the possibility of insight into their structure and estimation of the various qualities of said materials. This is invaluable for proper understanding of processes that can occur during the operation of batteries or fuel cells.

In the ‘electrochemical’ spectra of such materials, one can observed specific elements that are related to their inner structure in the lower frequency region. In earlier works by De Levi [1], a selection of diffusion elements have been purposed that can be used to characterize ionic transfer occurring inside of a medium, including a solid state or a porous one. However, the later introduction of the Gerischer element [2], and the development of its modifications [3] proved to be an invaluable asset in the field of electrode material science. As it lead to better understanding of the changes that occur during a battery operation such as changes in porosity, electrode active surface and other structural changes that might occur due to ageing processes. Furthermore, same principles can also be applied to the fuel cell operation.

On the other hand the relaxation elements present in high frequency ‘dielectric’ part of the spectra of many highly dispersive materials [4] including porous conductive glasses are very similar in nature to the Gerischer ones, as well as, their modified counterparts. It was observed that glasses with different composition exhibited different dispersion elements, related to their internal structure. Furthermore the changes in these elements’ values in the function of temperature could be related to the changes in the phase composition of the glass and their electrochemical properties such as ionic transfer capabilities.

Finally, it worth to conclude that whereas the high frequency ‘dielectric’ dispersion of various materials is often and usefully studied the counter-parting Impedance Spectroscopy of the lower frequencies, is most often overlook, but can prove to be an invaluable if not complementary tool in the fields of material science. The interpretation of these elements - modified and unmodified Gerischer, as well, of symmetrical and asymmetrical dispersion elements can help understand the processes occurring during the operation of fuel cells and/or batteries, such as defining ionic transfer and phase shifts.

References:

[1] R. De Levie, *Electrochim. Acta*, 8(1963) 751.

[2] H. Gerischer, *Z. Phys. Chem.* 198 (1951) 286.

[3] R. Kumar, R. Kant, *J. Phys. Chem. C* 113(45) (2009) 19558.

[4] W. Lai, S.M. Haile, *J. Am. Ceram. Soc.* 88 (2005) 2979.

**COMPARATIVE ANALYSIS OF SYNTHESIS ROUTES AND ALUMINUM
DOPING EFFECTS ON NMC TYPE CATHODE MATERIAL**

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This study presents a comprehensive analysis of the synthesis techniques and the impact of aluminum doping on Nickel Manganese Cobalt (NMC) 811 cathode materials. Our research focuses on comparing two distinct synthesis methods: hydroxide co-precipitation followed by solid-state calcination for polycrystalline (PC) cathodes and molten salt calcination for single-crystalline (SC) cathodes. Additionally, the study systematically integrates aluminum dopants at various stages of these processes. The objective is to explore the influence of doping via various approaches on the structural, morphological, and electrochemical properties of NMC cathodes. Through extensive characterizations using methods like X-ray diffraction (XRD), scanning electron microscopy (SEM), and galvanostatic cycling tests, our results highlight the promise of aluminum doping in enhancing the performance of polycrystalline NMC cathodes.

LITDI-ACETONITRILE ELECTROLYTE FOR LI-ION BATTERIES

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Lithium-ion batteries are one of the most important components in energy transformation as a prime candidate for energy storage and electric vehicle applications. The key component of lithium-ion batteries determining their properties in terms of safety, capacity retention and operating conditions limits is an electrolyte. Improving electrolyte properties can be achieved by replacement of the salt or solvent. In the presented research we are investigating electrolytes containing lithium 4,5-dicyano-2-trifluoromethylimidazolid (LiTDI), which is the most promising salt to replace LiPF_6 , in acetonitrile (AN). The acetonitrile is a good solvent, possessing high dielectric constant, low viscosity, and excellent electrochemical stability. The physicochemical properties of LiTDI-AN electrolytes were investigated, including conductivity, lithium transference number, thermal properties, and electrochemical stability. The maximum of conductivity was observed at $0.6 \text{ mol}\cdot\text{kg}^{-1}$ having a value of $18.6 \text{ mS}\cdot\text{cm}^{-1}$ at 20°C . The electrochemical stability is sufficient for operation with commonly used electrodes. A very low melting point of the electrolyte expands lower temperature limit of its application. Galvanostatic cycling was also performed using lithium titanate (LTO) and graphite as anodes with nickel-manganese-cobalt oxide (NMC) as a cathode. LiTDI-AN electrolytes provide excellent capacity retention and rate capability in LTO-NMC cells without the necessity of using any additives. Acetonitrile is incompatible with graphite anodes, which demands the application of a SEI-stabilising additive. Vinylene carbonate (VC), fluoroethylene carbonate (FEC), ethylene sulfite (ES) and ethylene sulfate (DTD) were tested. The best results were obtained using 10% VC while other additives were not effective.

HIGH-ENERGY LITHIUM-ION CELLS: ISSUES OF COMBINING STATE-OF-THE-ART ANODES AND CATHODES

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Today, lithium-ion batteries are among the most crucial energy storage devices, dominating both, portable electronic products and the electric vehicles (EV) sector. The burgeoning EV market is driving a surge in demand for greater cruising ranges, prompting the necessity for the development of high-energy-density cathodes and anodes. Concerning cathode materials, currently there are two noteworthy approaches. One involves further development of Ni-rich layered oxides [1], and alternatively, so called Li-rich oxides, having a specific structural properties, are also gaining significant attention [2]. Both categories of materials hold promise for a significant advancement in constructing high-capacity and high-power density cells, which can be attributed to their very high reversible discharge capacity ($> 200 \text{ mAh g}^{-1}$), high operating voltage ($\sim 3.7 \text{ V vs. Li/Li}^+$), and comparatively low costs. However, these oxides still suffer from severe issues, including surface sensitivity, structural problems, such as Li/Ni mixing effects, and inadequate thermal stability, limiting their practical application. Of the particular concern is presence of lithium residuals like LiOH/Li₂CO₃ in the active material, stemming from the synthesis process.

In this study, we systematically produced a range of Ni-rich materials with varying lithium excess using the commercial [Ni_{0.905}Co_{0.043}Al_{0.052}](OH)₂ precursor, and carefully selected them to create a high-nickel layered oxide cathode demonstrating outstanding performance. Additionally, an advanced lithium-rich layered oxide cathode Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ was synthesized using a co-precipitation method and small amount of Al element doping. Both cathodes were assembled alongside with the next class of anode materials, the high-performance high-entropy Sn_{0.8}(Co_{0.2}Mg_{0.2}Mn_{0.2}Ni_{0.2}Zn_{0.2})_{2.2}O₄. Various issues related to combining of those electrodes into a full cell were studied, including selection of N/P ratio, electrode prelithiation process, and electrolyte additives. The resultant, optimized full cells exhibited very good performance. For example, the NCA905@high-entropy anode full cell delivered an initial discharge capacity more than 206 mAh g⁻¹ at 0.5 C (cathode limited), and a very high energy density of 377 Wh kg⁻¹. A capacity retention of 77.9% was measured after 50 cycles, indicating promising electrochemical characteristics.

Acknowledgements: This research was supported by the AGH Excellence Initiative - Research University program (IDUB AGH, grant no. 501.696.7996, Action 4, ID 6354), and by the National Centre for Research and Development under grant agreement number: LIDER/36/0131/L-11/19/NCBR/2020.

References:

- [1] W. Li, E.M. Erickson, A. Manthiram, High-nickel layered oxide cathodes for lithium-based automotive batteries, *Nat. Energy*. 5 (2020) 26-34.
- [2] W. He, W. Guo, H. Wu, L. Lin, Q. Liu, X. Han, Q. Xie, P. Liu, H. Zheng, L. Wang, X. Yu, D. Peng, *Adv. Mater.* 38 (2023) 20686-20700.

ROLE OF 4d/5d DOPANTS IN MODIFICATION OF SrCoO_{3-δ} PEROVSKITE FOR USE AS OXYGEN ELECTRODE FOR SOFC

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Currently, one of the most promising directions for development of oxygen electrode materials for Solid Oxide Fuel Cells (SOFCs) is stabilization of SrCoO_{3-δ} (SCO) perovskite by chemical doping at the B-site. Typically, such modified oxides have a high catalytic activity toward the oxygen reduction reaction (ORR), and exhibit excellent mixed ionic and electronic conductivity (MIEC). The most effective way to stabilize the structure of SCO is to substitute cobalt with higher valence, 4d/5d ions. Those elements have a relatively small ionic radius, adjusting the Goldschmidt tolerance factor, and with +4 or +5 oxidation state are strongly affecting the oxygen content. The most established materials in the literature Nb- and/or Ta-doped SCO-based oxides [1]. Importantly, the reported electrochemical performance of such electrodes exceeds that of the current state-of-the-art materials, resulting in a possible, significant reduction in the operating temperature. This should not only improve the cell's longevity, but also portability, and may mitigate typical shortcomings associated with presence of alkaline ions.

In this work, possibility of obtaining phase-pure SCO-doped materials is studied for several compositions, including SrCo_{0.8}Ta_{0.2}O_{3-δ} (SCT20), SrCo_{0.8}Nb_{0.2}O_{3-δ} (SCN20), as well as SrCo_{0.8}Nb_{0.1}Ta_{0.1}O_{3-δ} (SCNT10), which were synthesized and tested toward their functional properties. Attempts were also made to obtain material with additional Mo/W elements, e.g. SrCo_{0.7}Ta_{0.1}Mo_{0.1}Mn_{0.1}O_{3-δ} (SCTMM10) with the aim to develop high-entropy oxides [2]. The conducted experiments involve structural measurements, studies of the transport properties, evaluation of thermal expansion behavior and chemical stability at high temperatures. It is found that the maximum conductivity of the doped samples remains sufficiently high, e.g. ~200 S cm⁻¹ at 350 °C for SCNT10. The main disadvantage of the materials is still too high thermal expansion, with the TEC coefficient reaching values as high as ~27·10⁻⁶ K⁻¹. However, some decrease can be obtained, for instance, ~21·10⁻⁶ K⁻¹ for the novel SCTMM10. Evaluation of the electrochemical performance is also carried out by the cathodic polarization resistance measurements, with a composite cathode approach used. Low values of 0.172, 0.118, and 0.082 Ω cm² are recorded respectively at 700, 750, and 800 °C, for the 60:40 wt.% SCNT10:GDC composite oxygen electrode. This corresponds to a decrease of almost 30 °C of the threshold temperature (0.15 Ω cm² at ca. 750 °C) in relation to the pure SCNT10. With the encouraging initial results, further experiments are needed to optimize the electrode composites.

Acknowledgements: This research was supported by Minister of Education and Science under project Perły Nauki PN/01/0127/2022.

References:

[1] M. Li, M. Zhao, F. Li, W. Zhou, V.K. Peterson, X. Xu, Z. Shao, I. Gentle, Z. Zhu, *Nat. Commun.* 2017, 8, 13990.

[2] J. Dąbrowa, A. Olszewska, A. Falkenstein, C. Schwab, M. Szymczak, M. Zajusz, M. Możdziej, A. Mikuła, K. Zielińska, K. Berent, T. Czeppe, M. Martin, K. Świerczek, *J. Mater. Chem. A* 2020, 8(46), 24455-24468.

IMPACT OF THE HIGH-ENTROPY APPROACH ON THE CYCLING STABILITY OF CONVERSION-ALLOYING ANODE MATERIALS FOR LI-ION CELLS

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To increase the energy/power density and safety of Li-ion batteries, the commercial graphite anode needs to be replaced with other chemistries. A particularly interesting direction to obtain high-energy-density anodes is to utilize the so-called conversion-alloying materials (CAMs) [1,2]. However, despite having numerous advantages, CAMs suffer from poor cycling stability. The only solution proposed in the literature so far is to employ advanced synthesis methods and additives, which are often expensive and difficult to scale.

We have utilized the high-entropy approach to a solid-state synthesized CAM, introducing a new method to achieve good cyclability for micrometer-sized powders. Specifically, a spinel-structured anode material, $\text{Sn}_{0.80}\text{Co}_{0.44}\text{Mg}_{0.44}\text{Mn}_{0.44}\text{Ni}_{0.44}\text{Zn}_{0.44}\text{O}_4$, was found to deliver 680 mAh g^{-1} at 50 mA g^{-1} , with excellent capacity retention of nearly 100% after 500 cycles at 200 mA g^{-1} , outperforming conventional CAMs. To understand the mechanism behind this, we thoroughly studied that HEO and found that the stability results from the altered Li-storage mechanism, with the reversible lithiation of an amorphous multicomponent matrix [1]. In the follow-up study, we decided to approach the problem differently, and tried to improve the stability of the solid-state synthesized low-entropy Zn_2SnO_4 anode, i.a. by the electrochemical prelithiation. The material was evaluated in half-cells and full Li-ion cells with a commercial layered cathode. Although the obtained capacity was higher than that for the previously studied HEO, the capacity retention was found to be inferior (41% retention at 500 mA g^{-1} , 200th to 2nd cycle) [2]. Based on what we have learned from those studies, we formulated a hypothesis that to significantly improve cycling stability it is not necessary to maximize the configurational entropy, as long as multiple cations are well-mixed in the initial CAM structure. To verify this, we synthesized a new multicomponent single-phase spinel, $\text{Zn}_{1.6}\text{Co}_{0.1}\text{Mg}_{0.1}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{SnO}_4$, chemically much closer to the low-entropy Zn_2SnO_4 , but with a mixture of Co/Mn/Mg/Ni substituting partially for Zn. The material exhibits improved long-term stability, being equally good to the mentioned HEO (91% capacity retention at 500 mA g^{-1} , 200th to 2nd cycle), while delivering a higher capacity at a lower potential. The results provide strong evidence that to design high-energy-density CAM anodes, it is desirable to use multicomponent complex oxides, and not necessarily near-equimolar high-entropy materials.

Acknowledgements: This research was supported by the National Science Centre, Poland, (NCN) on the basis of the decision number UMO-2019/35/O/ST5/01560 and by the AGH Excellence Initiative – Research University program (IDUB AGH, grant no. 501.696.7996, Action 4, ID 6354).

References:

- [1] M. Moździerz, K. Świerczek, J. Dąbrowa, M. Gajewska, A. Hanc, Z. Feng, J. Cieślak, M. Kądziołka-Gaweł, J. Płotek, M. Marzec, A. Kulka, *ACS Appl. Mater. Interfaces*. 14 (2022) 42057–42070.
- [2] M. Moździerz, Z. Feng, A. Brzoza-Kos, P. Czaja, B. Fu, K. Świerczek, *J. Mater. Chem. A*. 38 (2023) 20686–20700.

EVOLUTION OF TM AND OXYGEN REDOX REACTIONS IN Li- AND Mn-RICH NMC CATHODE MATERIALS DURING CYCLING**A. Kulka¹, K. Walczak¹, J. Plotek¹, A. Hanc¹, E. Hanc², A. Maximenko³, B. Fu¹, K. Świerczek¹, G – H. Lee⁴, W. Yang⁴, A. Ditter⁴, D. Shapiro⁴, R. Kostecki⁵.**¹AGH University of Science and Technology, Krakow, Poland, akulka@agh.edu.pl²Mineral and Energy Economy Research Institute, Polish Academy of Sciences, Poland³National Synchrotron Radiation Centre SOLARIS Jagiellonian University, Krakow, Poland⁴Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA⁵Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Further improvement of low-emission technologies is hindered by the intrinsic limitation of their key elements, Li-ion batteries, where the positive electrode is one of the major bottlenecks that restrains their electrochemical performance. A significant increase in the energy density of the cathode materials for lithium-ion batteries may be realized by accessing the reversible redox reactions involving lattice oxygens (anionic redox) within Li- and Mn-rich NMC cathode materials (LMR-NMC). However, the reactions associated with the occurrence of oxygen redox are believed to be the primary cause of the observed voltage fade in LMR-NMC impeding practical applications of those electrodes. Importantly, the voltage fade progresses gradually over the cycling, thus the evolution of the deterioration processes driven by extended cycling needs further investigation. In this report, we present detailed studies of the evolution of the structural and electronic properties of $\text{Li}_{1.1}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ electrode material during cycling. The synthesized material with optimized round-shaped morphology was subjected to electrochemical testing that included galvanostatic cycling, voltammetry tests, operando XRD and GITT measurements. To evaluate the evolution of oxygen redox reactions occurring within the electrode during cycling, ex situ resonant inelastic X-ray scattering measurements of the O K-edge (mRIXS) were conducted for charge samples after various number of cycles (1 – 300). Apart from the oxygen redox reaction, TM oxidation state spatial redistribution was proposed to influence the voltage modification during the extended cycling. Thus, to assess the evolution of the heterogeneities of the oxidation state of Mn within the primary particles of the electrodes, the selected samples in the discharge state were subjected to X-ray ptychography in the energy range corresponding to the Mn L3-edge. To further elaborate the evolution of the Co and Ni during the electrode processes, the operando XAS experiments (charge-discharge step) for the Co and Ni K-edges were performed for studied electrodes during the first two cycles and for electrode after cycling. The minor specific capacity fade over the cycling was recorded, starting from around 270 mAh/g for the first cycle, while substantial change in voltage profile was recorded after 300 cycles. The capacity fade observed within the $\text{Li}_{1.1}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ material during cycling is in good agreement with the decrease in the intensity of the unique anionic redox feature spot on mRIXS spectra at an emission energy of ~ 524 eV and an excitation energy of ~ 531 eV. The operando XAS studies showed complex redox reactions of Ni and Co ions changing their oxidation states both during initial charge and discharge. The operando XAS for the electrodes after cycling showed different behavior of the redox reaction involving Co and Ni, comparing to first cycles.

Acknowledgments: The work was financed by National Centre for Research and Development under grant agreement number: LIDER/36/0131/L-11/19/NCBR/2020

**HETEROGENEOUS EXSOLVED SILVER AND COBALT OXIDE
NANOPARTICLES ON $(\text{BaGd}_{0.8}\text{La}_{0.2})_{1-x}\text{Ag}_x\text{Co}_2\text{O}_{6-\delta}$**

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Slow surface reaction kinetics is a limiting factor in the electrochemical performance of air-electrodes and increases the concentration polarization which results in increased cathodic losses [1]. Electrochemical processes occur at the double-phase boundaries of triple-conducting oxides. Thus, it is essential to increase the number of reaction sites. To improve the rate of oxygen reduction reaction on the cathode's surface, several approaches such as infiltration and physical vapor deposition of noble metallic catalysts have historically been explored with less desirable outcomes. Infiltration and deposition techniques tend to produce agglomerated and unevenly distributed nanoparticles [2]. The results can also be non-reproducible. As such, this has created the need for 'intelligent' catalysts using a novel approach known as exsolution [1, 2]. Exsolution of nanoparticles refers to the spontaneous expulsion of catalytically active cations from either the A-site or B-site of the host perovskite. They co-segregate with oxygen vacancies, diffuse through the lattice and nucleate to form partially submerged metallic or oxide nanoparticles on the surface [2]. The exsolution method is deemed to be an efficient way to produce resilient and evenly distributed nanoparticles. Exsolution can be achieved in reducing conditions, lattice strain or via voltage induction [1, 2].

In this work, we present the results of exsolution achieved from both the A-site and B-site of silver doped $(\text{BaGd}_{0.8}\text{La}_{0.2})_{1-x}\text{Ag}_x\text{Co}_2\text{O}_{6-\delta}$ ($x=0.04, 0.10$ & 0.20) perovskite. Notably, the exsolution of nanoparticles is often achieved from either the A-site or B-site of the perovskite structure [2]. The concept of double exsolution is enabled by the ease in reduction of Ag cations to their metallic state. At the right temperatures in reducing conditions, this leads to exsolution of metallic Ag from the A-site, creating a non-stoichiometric compound. Due to the resultant A-site deficiency, subsequent exsolution of B-site transition metals follows which results in a heterogeneous mixture of catalytically active metal and oxide nanoparticles at the surface. Given that not all exsolved nanoparticles will produce electrochemically active sites, it is crucial to have a high density of nanoparticles. Moreover, silver nanoparticles exhibit good catalytic effects even at room temperature [3]. Cobalt oxide nanoparticles equally have high catalytic activity that could improve electrochemical activity on the cathode [4]. The aliovalent substitution of Ag^+ and Ba^{2+} in the A-site of the host perovskite not only increases hydration properties but also increases the formation of oxygen vacancies which are essential for exsolution [4]. The presence of multi-valent Co cations enable electronic conductivity. Hence, the host perovskite has desirable ionic-electronic properties [4]. The results to be presented include scanning electron microscopy micrographs, X-ray diffraction patterns, thermogravimetric data, hydration, iodometric titration, total conductivity in dry and wet air. In addition, the chemical diffusion and reaction coefficients from conductivity relaxation measurements in oxidizing and reducing atmospheres will also be presented.

References:

- [1] Ji, H. et al., Journal of the Korean Ceramic Society, 57 (5), 480-494 (2020)
- [2] Kwon, O. et al., Nature Communications, 8, 15967 (2017)
- [3] Jun, K. et al. Energy & Environmental Science, 15, 1097-1105 (2022)
- [4] Papac, M et. al., Nature Materials, 20(3), 301–313 (2020)

THERMOELECTRIC PROPERTIES OF MULTICOMPONENT OXIDES
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Multicomponent high-entropy oxides (HEOs) boast unique attributes including exceptional thermal stability, adjustable electronic properties, and a rich array of chemical compositions, rendering them highly promising for applications in thermoelectric devices. These oxides, characterized by their intricate and disordered crystal structures resulting from the presence of multiple cations, present exciting opportunities for tailoring thermoelectric performance. Various synthesis methods, such as solid-state reaction and the sol-gel approach, are employed to craft HEOs with precise compositions and microstructures. Subsequently, the Seebeck effect is measured across a wide range of temperatures to assess the thermoelectric performance of HEOs. Investigation into the influence of composition, crystal structure, and microstructure on the Seebeck coefficient represents a nascent area of research, shedding light on the underlying thermoelectric mechanisms in multicomponent HEOs [1,2]. Furthermore, diverse strategies, including compositional engineering and doping with multiple elements, are being explored to enhance the thermoelectric figure of merit (ZT) of multicomponent oxide materials [3].

The present work consisted in characterizing the thermoelectric and electrochemical properties of selected multicomponent oxides based on perovskite ABO_3 structure. Analyzed materials contain barium in the A-site and multiple elements - Fe,Zr,Hf,Sn,Ti,Ce,Co,In,Sm,Y and/or Yb - in the perovskite B-site. The structure and microstructure of these materials were analyzed by X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM). To determine the temperature dependence of total Seebeck coefficient, the 4-wire technique was performed at different water-vapor containing atmospheres. Electrical studies of total electrical conductivity were performed by 4W-DC and EIS techniques also as a function of pO_2 and pH_2O . An important aspect of the work was to discuss the transport properties of HEOs in the presence of protonic defects, which can significantly improve thermoelectric effects.

References:

- [1] A.Salian & S.Mandal, Entropy stabilized multicomponent oxides with diverse functionality – a review, *Critical Reviews in Solid State and Materials Sciences* 2022, 47:2, 142-193
- [2] M.Gazda et al., Novel Class of Proton Conducting Materials—High Entropy Oxides *ACS Materials Lett.* 2020, 2, 10, 1315–1321
- [3] Wei, J., Yang, L., Ma, Z. et al. Review of current high-ZT thermoelectric materials. *J Mater Sci* 55, 12642–12704 (2020)

THE MORPHOLOGY MODIFICATION OF PEROVSKITE ELECTRODES WITH *IN SITU* EXSOLUTION OF NANOPARTICLES FOR IMPROVING THE PERFORMANCE OF SOFCS

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In recent years, solid oxide fuel cells (SOFC) have become increasingly popular due to the crucial role they can play in energy systems based largely on renewable energy sources (RES). Year by year, power capacity installed in RES grows systematically around the world and this trend is expected to accelerate in the future [1]. Nevertheless, RES are characterized by intermittent electricity production, which requires energy storage systems, while present technologies are not fully fit for this purpose. SOFCs can be an important integrated part of modern energy systems, and during the oversupply of electricity, the surplus energy can be stored in the hydrogen produced by SOFCs in electrolysis mode. Moreover, the hydrogen can also be used to generate electricity by SOFCs to meet the high demand. Unfortunately, the high operating temperature of SOFCs (>800 °C) generates problems including fast material degradation and thermal compatibility, limiting the commercialization. The limiting factor hindering the reduction of operating temperature is the drastic decrease of the electrochemical performance of electrodes at the desired temperatures (≤ 700 °C). The development of electrodes with enhanced electrocatalytic activities at lower temperatures is crucial for advancing cost-effective and high-performance SOFCs. Recently, there is a growing interest in fabricating heterostructured electrodes, employing methods like mechanical milling, infiltration, *in situ* assembling, and *in situ* exsolution of nanoparticles. The undeniable benefit of heterostructured electrodes lies in their ability to exhibit high mixed ionic-electronic conductivities (MIEC) and improved catalytic activities [2-3].

In this work, A-site deficient $\text{Sr}_{2-x}\text{Fe}_{1.4}\text{Ti}_{0.2}\text{M}_{0.2}\text{Ni}_{0.1}\text{Co}_{0.1}\text{O}_{6-\delta}$ (M = Cr, Mn, Mo, W) perovskites were systematically investigated as new electrode materials for SOFCs. It has been found that the A-site deficiency and the phase transition from simple perovskite to Ruddlesden-Popper structure in reducing conditions significantly promote the *in situ* exsolution of nanoparticles, leading to the enhancement of electrochemical performance of cells. The morphology of electrodes was further optimized by fabricating nanofibers using the electrospinning technique, contributing to a significant improvement of performance at intermediate temperature range (≤ 700 °C).

Acknowledgements: The work is funded by the National Science Centre Poland (NCN) based on the decision number UMO-2021/43/D/ST5/00824. Kun Zheng acknowledge the financial support of research project supported by the program „Excellence Initiative – Research University” for the AGH University of Krakow.

References:

- [1] L. Li, J. Lin et al., *Energy and Built Environment* 3 (2022) 139-157.
- [2] K. Kousi, C. Tang, et al., *Small* 17 (2021) 2006479.
- [3] Z. Gao, L.V. Mogni et al., *Energy Environmental Science* 9 (2016) 1602.

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

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The barium lanthanum cobaltite with a perovskite structure can be classified as triple conducting oxide (TCO), which exhibits conductivity of three mobile charge carriers, namely oxygen ions, electrons/holes, and protonic defects. Because of the possibility of reaction of those three charge carriers in the bulk, it is considered as potential electrode material for proton ceramic electrochemical cells (PCEC). The total electronic conductivity and formation of proton defects have already been determined for that composition [1,2]. Furthermore, studies have demonstrated that B-site substitution with a more basic transition metal might increase the concentration of protonic defects [3]. Studies of the charge carriers' transport in barium lanthanum cobaltite are necessary to fully evaluate the possible application of that material in electrochemical devices.

This work was devoted to understanding the charge transport in barium lanthanum cobaltite substituted by iron ($\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ - BLCFx). The compound was synthesized using a solid-state reaction route and its structure and phase composition were characterized by X-ray diffraction. To provide information about the oxygen ionic conductivity, the modified Hebb-Wagner polarization method was performed. To investigate the oxygen transport in materials, the Electrical Conductivity Relaxation (ECR) method was performed in a wide range of temperatures. The chemical surface exchange coefficient (k) and the chemical diffusion coefficient of oxygen (D) were established and the activated energies for both processes were calculated. To investigate predominant mobile charge carriers, the temperature dependence of the total Seebeck coefficient was also analyzed. Measurements were carried out in galvanic cells (Pt/BLCFx/Pt) by the conventional 4-wire method at different $p\text{O}_2$ and $p\text{H}_2\text{O}$.

References:

- [1] I. Szpunar, S. Wachowski, T. Miruszewski, K. Dzierzgowski, K. Górnicka, T. Klimczuk, M. H. Sørby, M. Balaguer, J. M. Serra, R. Strandbakke, M. Gazda, A. Mielewczyk-Gryn *Electric and magnetic properties of Lanthanum Barium Cobaltite*. Journal of the American Ceramic Society, (2019)103, 3, 1809-1818
- [2] S.L. Wachowski, I. Szpunar, M. H. Sørby, A. Mielewczyk-Gryn, M. Balaguer, C. Ghica, M. Cosmin Istrate, M. Gazda, A. E. Gunnæs, J. M Serra, T. Norby, R. Strandbakke, *Structure and water uptake in $\text{BaLnCo}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb and Dy}$)*. Acta Mater. (2020) 199, 297–310
- [3] Zohourian, R.; Merkle, R.; Raimondi, G.; Maier, J. *Mixed-conducting perovskites as cathode materials for protonic ceramic fuel cells: understanding the trends in proton uptake*. Adv. Funct. Mater. (2018), 1801241, 1–10

NOVEL GENERATION OF ANODES BASED ON HALIDE PEROVSKITES FOR LI-ION BATTERIES

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The escalating global energy demands require development of clean energy sources and efficient energy storage systems. In this pursuit, a range of energy storage devices, including batteries, fuel cells, and supercapacitors, have been subject to extensive investigation. At this point, lithium-ion cells have been the dominant choice for portable power storage devices for over 30 years. Despite their many advantages, continuous research is being carried out to improve the performance of the cells. There is a need to search for new battery components including electrodes and electrolytes, assuring higher battery capacity, better safety, and enhanced electrochemical stability range. Critical research area involves understanding and controlling the phenomena at the anode-electrolyte interface where energy storage occurs, and the initiation of degradation takes place. The formation of solid electrolyte interphase (SEI) is a crucial property responsible for ensuring cycling stability and extended thermodynamic stability of organic electrolytes in Li-ion batteries.

Metal halide perovskites (MHPs) represent a revolutionary class of compounds that can be used in lithium-ion batteries. While metal halide perovskites are predominantly recognized for their applications in energy conversion, their unique structure allowing fast lithium-ion diffusion has prompted exploration in energy storage. The typical preparation of halide perovskites relies on solution-based methods, yet this approach encounters challenges in both compositional engineering and long-term storage. In this context, solid-state chemical reactions induced by mechanical forces have emerged as an effective and straightforward method for solvent free compositional engineering within a relatively short timeframe.

In this work we present the development of a new generation of electrodes using all-inorganic and hybrid inorganic-organic halide perovskites. Different MHPs have been used as the main active material for high-performance electrodes. Beyond serving as anodes, MHPs have also found application as an electrode additive. In this case, the use of another well-known active material as the head component of the anode and MHPs as an additive involved in the formation of the SEI layer is likely to improve the cyclability, capacity and lifetime of the cell. Our study includes electrochemical characterization and cycling performance analysis of electrodes based on carbonous materials and tailor-made halide perovskites.

Acknowledgments: This research was supported by the National Science Centre (NCN) through grant OPUS-21 no. 2021/41/B/ST5/04450 “Towards novel generation of anodes based on halide perovskites for Li-ion batteries”

MID-ENTROPY PEROVSKITE OXIDES FOR APPLICATION IN SOLID OXIDE FUEL CELLS

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Selected medium-entropy subsystems of Sr-free La(Co,Cu,Fe,Mn,Ni)O₃ perovskite are synthesized and investigated in the context of their possible application as cathodes in solid oxide fuel cell technology. Using the Pechini sol-gel method, the following materials are obtained: La(Co,Fe,Cu,Mn)O₃, La(Co,Fe,Mn,Ni)O₃, La(Co,Fe,Cu,Ni)O₃, La(Co,Fe,Ni)O₃, La(Co,Fe,Cu)O₃, La(Co,Fe,Mn)O₃. Special attention is paid to the influence of individual elements, such as copper, nickel, and manganese, on the properties of the obtained compositions. SEM+EDS measurements show typical single-phased perovskite *R-3c* and *Pnma* structures for Mn-free and Mn-containing materials, respectively, with only a small amount of Ruddlesden-Popper-type phase for La(Co,Fe,Cu)O₃ at temperatures greater than 1000°C. Relatively high amounts of oxygen vacancies at room-temperature combined with near lack of a temperature dependence of the oxygen non-stoichiometry, exemplify the beneficial behavior of the presented materials. The thermomechanical performance is evaluated using the dilatometry method and, apart from highly atypical results for La(Co,Fe,Mn,Ni)O₃, all thermal expansion coefficients are moderate, varying in the range of 15-17·10⁻⁶ 1/K. Most importantly, no sign of deleterious chemical expansion mechanism is visible. The results of the electrical measurements display profound influence of manganese on the character of conductivity, with the values ranging from 32.4 S/cm up to 643.8 S/cm. The observed good chemical stability toward GDC and LSGM electrolytes confirms the possibility of applying all of the studied materials as cathodes in SOFC technology. The electrochemical performance is investigated using electrochemical impedance spectroscopy for symmetrical cells with both GDC and LSGM electrolytes. Obtained values of cathodic polarization resistance, in Sr-free compositions, of 0.101 Ω·cm² at 750°C for La(Co,Fe,Cu)O₃ and 0.122 Ω·cm² at 700°C for La(Co,Fe,Cu,Ni)O₃ are superior to most state-of-the-art cathode materials including LSM, LSF and LSCF. In general, the Cu-based materials are markedly superior to Mn-containing ones in terms of the overall performance in SOFCs. These results allow us to state that medium-entropy approach is a promising alternative for improving SOFC-relevant properties.

Acknowledgments: This research was supported by the Polish National Science Center (NCN) under project No. UMO-2021/41/B/ST8/04365.

TAILORING EFFICIENT AND STABLE ANODE CANDIDATES FOR SOLID OXIDE FUEL CELLS – CHALLENGES IN OUR RESEARCH PROJECTS**B.Bochentyn¹, A.Ducka¹, P.Błaszczak¹, K.Kujawska¹, J.Karczewski¹, P.Jasiński²**¹ Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland² Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12 Poland
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The global demand for energy implies a constantly growing interest in Solid Oxide Fuel Cell (SOFC) as an environment-friendly device that can directly convert the chemical energy of various gaseous fuels into electrical energy and heat. Due to relatively high operation temperature (up to 800 °C) an internal reforming of alternative fuels, such as biogas, is possible directly on the SOFC anode, without the external reformer. However, in practice the commercially used SOFCs with Ni-YSZ anode suffer from carbon deposition and sulfur poisoning during the internal reforming process. Therefore some alternative solutions can be applied to improve the stability and the performance of SOFC fed with biogas.

One of the possibilities is to use the ceria-based catalytic layers deposited on the anode side. They present high mobility of oxygen ions, high oxygen storage capacity (OSC), attractive redox catalytic properties and chemical compatibility with water and carbon dioxide at high temperatures. 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.

Another method is to exsolve metallic nanoparticles from the perovskite lattice of an anode candidate material. These nanoparticles can act as catalytic centers for the process of electrochemical oxidation of a fuel as well as for the internal reforming reactions. The exsolution process occurs under reducing conditions and offers an even distribution of particles as well as very well attachment to the host material. When bimetallic or even ternary alloys are formed, the properties of the materials can be even further improved. As compared to the monometallic Ni nanoparticles, the Fe-Ni alloy nanoparticles exhibit higher activity, greatly improved durability over long-term testing and increased tolerance towards sulfur-based atmospheres [1]. Simultaneously, these bimetallic alloys demonstrate outstanding microstructural stability and high tolerance towards coking, similar to that presented by monometallic Ni nanoparticles [2].

The aim of this presentation is to show materials synthesized and characterized for SOFC anode application within various scientific projects of our team. Compounds from the ceria group as well strontium titanate-based ones will be presented. Both achievements and obstacles in understanding their anode activity will be discussed.

Acknowledgements: This work was supported by the National Science Center under grants No. 2017/26/D/ST8/00822 and 2021/42/E/ST5/00450 as well as by the Gdańsk University of Technology by the DEC-6/1/2022/IDUB/II.1a/Au grant under the AURUM IDUB program.

References:

- [1] S. Joo, O. Kwon, K. Kim, S. Kim, H. Kim, J. Shin, H.Y. Jeong, S. Sengodan, J.W. Han, G. Kim, Nat. Commun. 10 (2019) 1–9.
- [2] J.H. Kim, J.K. Kim, J. Liu, A. Curcio, J.S. Jang, I.D. Kim, F. Ciucci, W.C. Jung, ACS Nano. 15 (2021) 81–110.

STRUCTURAL, THERMAL AND ELECTRICAL PROPERTIES OF HIGH-ENTROPY RARE-EARTH ORTHO-NIOBATES**Arkadiusz Dawczak¹, Aleksandra Mielewczyk-Gryń¹, Maria Gazda¹**

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High-entropy oxides (HEOs) are one of the most interesting new groups of ceramic materials. Their complex properties, which can be easily modified by changes of elements in their composition, are interesting both from the basic research and application point of view. The idea behind entropy stabilization is that a single-phase crystal structure may be stabilized by raising the system's configurational entropy [1]. It is necessary to mix at least five different elements in one sublattice in order to obtain a high configuration entropy value. Since the discovery of proton conductivity in rare-earth ortho-niobates by Haugsrud and Norby [2] in 2006, the interest in this group of materials has begun to grow. One of the well-recognized materials is LaNbO₄, which can be stable in two polymorphs, low-temperature (monoclinic, Fergusonite-type structure), and high-temperature (tetragonal, Scheelite-type structure) [3]. In this work, we examine the structural, thermal and electrical properties of the high-entropy (La_{0.2}Nd_{0.2}Sm_{0.2}Gd_{0.2}Eu_{0.2})(V_{0.2}Nb_{0.2}Ta_{0.2}Sb_{0.2}Me₅)O₄, where (Me = Mo and W) series, based on the lanthanum ortho-niobate. The stoichiometries have been chosen to ensure both the entropic stabilization of the Scheelite phase and elevation of the electrical conductivity. The samples of the materials were synthesized via the solid-state synthesis method. We determined the structure and phase composition of materials by using X-ray powder diffraction at room temperature. Thermochemical properties studies were carried out with thermogravimetry and dilatometry. The measurements of the temperature dependence of electrical conductivity were carried out using electrochemical impedance spectroscopy under dry and wet air.

Acknowledgements: This research has been supported by National Science Centre Poland under OPUS scheme “High entropy oxides for energy conversion” (ref. no 2019/35/B/ST5/00888).

References:

- [1] Gazda, M. *et al.* Novel Class of Proton Conducting Materials - High Entropy Oxides. *ACS Mater Lett* **2**, 1315–1321 (2020).
- [2] Haugsrud, R. & Norby, T. Proton conduction in rare-earth ortho-niobates and ortho-tantalates. *Nat Mater* **5**, 193–196 (2006).
- [3] Jian, L. & Wayman, C. M. Monoclinic-to-Tetragonal Phase Transformation in a Ceramic Rare-Earth Orthoniobate, LaNbO₄. *Journal of the American Ceramic Society* **80**, 803–806 (1997).

**OPERANDO RAMAN MICROSCOPY STUDIES ON NEXT GENERATION
POSITIVE ELECTRODE AND ELECTROLYTE MATERIALS**

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Li-ion batteries (LIBs) are a major concern nowadays due to their wide-spread use in grid-scale energy storage. The ever-increasing demand for their better performance has encouraged researchers to deeply understand the impact of ageing mechanisms on various battery components [1,2]. Nickel rich metal oxides are currently garnering attention as electrode materials due to their applicability in electric vehicles. However, they suffer from capacity loss and thermal instability in highly deintercalated states [3].

Raman microscopy can be used to probe structural evolution and chemical composition of battery elements during cycling. Despite the advantages of this technique, it presents challenges related to limitations throughout Operando measurements [4]. The aim of this work was to monitor electrode and electrolyte materials using Raman spectroscopy under *in situ* commercially-relevant conditions. The relationship between the spectra features and battery properties was established with the support of Jupyter-based application PRISMA [5]. Additionally, intrinsic characteristics and dynamics were identified for several electrode materials over 3 cycles. Overall, the capability of Operando Raman microscopy to reveal physical and electrochemical phenomena of battery constituents was demonstrated.

Acknowledgements: As a part of the DESTINY PhD programme, this publication acknowledges funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Actions COFUND (Grant Agreement No- 945357).

References:

- [1] Eibar Flores. Development of operando diagnostics for Li-ion cathodes by Raman spectroscopy (2019) Doctoral thesis.
- [2] Matteo Bianchini et al. *Angew. Chem. Int. Ed.* (2019), 10434-10458, 58(31).
- [3] Edgar Bautista Quisbert et al. *Small* (2023) 19 (30) 2300616.
- [4] Christian M. Julien et al. *AIMS Mater Sci* (2018) 650–698, 5(4).
- [5] Flores E et al. *Chemistry-methods* (2022) 2(10).

ELECTRODE MATERIALS $\text{Sm}_{0.9}\text{Ba}_{0.9}\text{Mn}_{1.8-x}\text{Fe}_x\text{Ni}_{0.1}\text{Co}_{0.1}\text{O}_{6-\delta}$ WITH *IN SITU* EXSOLVED NANOCATALYSTS FOR SYMMETRICAL SOLID OXIDE CELLS

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Symmetrical Solid Oxide Cells (SOCs) are one of the most interesting energy conversion and storage devices. The incorporation of a symmetrical design involves employing identical compounds for both the anode and cathode site, reducing the number of cell components and simplifying the fabrication process. However, materials for electrodes in the symmetrical configuration must fulfill specific criteria, such as robust structural stability in both reducing and oxidizing conditions, along with high electrocatalytic activities for fuel oxidation and oxygen reduction. Using materials capable of *in situ* exsolution of nanoparticles within the electrodes of SOC is regarded as highly advantageous. *In situ* metallic nanoparticles enhance catalytic activities and stability, leading to improved overall performance [1-2].

In this work, the A-site nonstoichiometric $\text{Sm}_{0.9}\text{Ba}_{0.9}\text{Mn}_{1.8-x}\text{Fe}_x\text{Ni}_{0.1}\text{Co}_{0.1}\text{O}_{6-\delta}$ perovskites with double perovskite structure (*P4/nmm* space group) were successfully synthesized by the soft chemistry method. The measured thermal expansion coefficient (TEC) values are very close to TECs of mostly used electrolytes (including $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$), both in oxidizing and reducing atmospheres. The obtained compounds show excellent redox stability, favoring their application as potential electrode materials for symmetrical SOC. It has been found that the A-site nonstoichiometry ($\text{Sm}_{0.9}\text{Ba}_{0.9}$) favors the *in situ* exsolution of metallic nanocatalysts from the parent materials in reducing conditions. The presence of *in situ* exsolved nanoparticles (CoNi_x and CoNi_xFe_y) was confirmed on the surface of reduced compounds by the SEM and HR-TEM studies. Excellent electrochemical performance of the proposed perovskite electrodes was recorded in the reducing condition which indicates that the investigated oxides are particularly of interest for the application as anode material.

Acknowledgements: The work is funded by the National Science Centre Poland (NCN) based on the decision number UMO-2021/43/D/ST5/00824. Jakub Lach and Kun Zheng acknowledge the financial support of research project supported by the program „Excellence Initiative – Research University” for the AGH University of Krakow.

References:

[1] Y. Zhang, H. Zhao, M. Zhang, Z. Du, W. Guan, S.C. Singhal, K. Świerczek, *Chem. Mater.* 35 (2023) 499–510.

[2] K. Zheng, J. Lach, P. Czaja, M. Gogacz, P. Czach, A. Brzoza-Kos, P. Winiarz, J. Luo, *Journal of Power Sources* 587 (2023) 233707.

INFLUENCE OF IRON TRAPPING ON TRANSPORT IN $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2-x}\text{Fe}_x\text{O}_{3-\delta}$ TRIPLE-CONDUCTING OXIDES

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Triple-conducting oxides (TCOs) are a class of materials that, under specific conditions, exhibit the ability to conduct three different types of charge carriers: oxygen ions, electrons or holes, and protons. TCOs have gained considerable interest in the scientific community due to their potential applications in diverse electrochemical devices, such as protonic ceramic fuel cells (PCFCs).

The $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2-x}\text{Fe}_x\text{O}_{3-\delta}$ series is related to $\text{Ba}(\text{Ce},\text{Zr},\text{Y})\text{O}_{3-\delta}$ (BCZY), a mixed oxygen ionic-protonic conductor, often used as an electrolyte in PCFCs [1]. Substituting cerium, zirconium, or yttrium with mixed-valence cations like praseodymium, cobalt, or ruthenium can increase the electrical conductivity of this material [2–4]. However, higher electronic partial conductivity often results in deteriorated water uptake in TCOs. Investigating the diffusion kinetics of mobile species can provide an essential understanding of this intricate interplay of oxygen ions, protons, and electron holes in triple conducting materials, leading to a better design of the materials suited for the electrochemical devices of high efficiency.

This study explores the impact of iron content on the transport of charge carriers in the $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.05, 0.1$) series. Single-phase samples were synthesized via solid-state reaction sintering and characterized using the X-ray diffraction (XRD) technique. The proton defect concentrations were evaluated based on the thermogravimetric analysis (TGA). The total conductivity was determined via electrochemical impedance spectroscopy (EIS). Electrical conductivity measurements were conducted in dry and wet air to determine the total conductivity as a function of temperature, as well as under various oxygen partial pressures at 600 and 800 °C to estimate the transference numbers of electron holes and oxygen vacancies. Furthermore, the electrical conductivity relaxation (ECR) method was utilized to investigate the influence of iron on the surface exchange and diffusion of water and oxygen.

Acknowledgments: This research was supported by the National Science Centre Poland under grant number 2021/41/N/ST5/03437.

References:

- [1] Y. Okuyama, N. Ebihara, K. Okuyama, Y. Mizutani, ECS Meeting Abstracts MA2015-03 (2015) 364–364.
- [2] J. Melnik, J. Luo, K.T. Chuang, A.R. Sanger, The Open Fuels & Energy Science Journal 1 (2008) 7–10.
- [3] T. Shimura, H. Tanaka, H. Matsumoto, T. Yogo, Solid State Ion 176 (2005) 2945–2950.
- [4] H. Matsumoto, T. Shimura, T. Higuchi, H. Tanaka, K. Katahira, T. Otake, T. Kudo, K. Yashiro, A. Kaimai, T. Kawada, J. Mizusaki, J Electrochem Soc 152 (2005) A488.

**CONDUCTIVITY AND DIELECTRIC RELAXATION PHENOMENA IN
SELECTED OXIDE ION CONDUCTORS STUDIED BY IMPEDANCE
SPECTROSCOPY**

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An increase of the ac conductivity with increasing frequency, observed in ionic conductors, is accompanied by a finite decrease of the dielectric constant. In a range of materials, the dielectric function can be well described by the empirical functions of Cole–Cole or Havriliak–Negami, which in the limit of high frequencies give the power law frequency dependence of conductivity. The relaxation strength De , the dc conductivity s_0 and the relaxation frequency ω_C obey the Barton–Nakajima–Namikawa relation: $s_0 = P s_0 De \omega_C$, where P is a coefficient, whose value is characteristic for a given ionic conductor. The coefficient P relating the dc conductivity with the charge carrier relaxation, provides valuable information about the length scale and the time scale of nonrandom hopping, expressed respectively in units of jump length and units of average time between jumps of a hopping carrier [1]. This concept has been tested in the case of several selected oxygen ion conductors.

Impedance spectra of oxide ion conductors – several examples of CeO_2 or Bi_2O_3 based materials, like BIMEVOXex, sodium bismuth niobates NBT were analysed by the least squares fitting. Good quality of fit and accurate estimates of parameters were obtained when the equivalent circuit comprised contributions of all processes affecting the ac response. The frequency dependence of conductivity and complex dielectric relaxation were combined in one model of the ac response.

References:

J. R. Dygas, Solid State Ionics, 176 (2005), 2065–2078. DOI: 10.1016/j.ssi.2004.11.023

STABILIZATION OF DELTA-LIKE Bi₂O₃ PHASE AT ROOM TEMPERATURE BY THERMAL NANOCRYSTALLIZATION OF BISMUTH OXIDE GLASSES

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Bismuth oxide glasses have been observed as an interesting starting system for the stabilization of a few crystal structures of Bi₂O₃ [1]. In particular, δ -Bi₂O₃ is a candidate material for oxide ion conducting membranes in intermediate-temperature fuel cells. This phase is, however, stable only in the high-temperature range (>730°C). We observed the confinement of δ -like nanograins in an amorphous matrix down to room temperature. A convincing physical explanation of this phenomenon has not been given yet. There are a few working hypotheses: 1) stabilization due to the nanometric size of grains and the influence of the surrounding glassy matrix, 2) incorporation of glass-forming dopants into the crystal structure, 3) formation of non-stoichiometric Bi₂O_{4-x} by Bi⁵⁺ ions. In this research, we apply multiple experimental methods to verify the abovementioned hypotheses.

The studied materials are based on an oxide glassy system Bi₂O₃-Al₂O₃-SiO₂ [2]. The role of the dopants with regard to glass-forming ability has been checked by synthesizing material with a controlled amount of dopants in a platinum crucible. Local arrangement around Si and Al atoms has been investigated by MAS NMR studies. In combination with TEM and EDX measurements, it gave a consistent view of the location of the Si and Al dopants. From these experiments, one can conclude that these additives are unlikely to stabilize the δ -like phase directly because they were detected mainly outside crystalline grains of δ -Bi₂O₃, in the residual glassy matrix. On the contrary, they are believed to participate in forming glass and induce the confinement effect of pure δ -Bi₂O₃ nanocrystallites.

Acknowledgements: This research was funded by POB TechMat of WUT within the IDUB program, and by the National Science Centre (NCN), Poland, in frames of a grant Preludium BIS 2 no. 2020/39/O/ST5/00897. NMR experiments were funded by the European Union's Horizon 2020 program, grant agreement No 731019 (EUSMI).

References:

- [1] T.K. Pietrzak, J.E. Garbarczyk, M. Wasiucioneck, *Solid State Ionics* 323 (2018) 78-84.
- [2] T.K. Pietrzak et al., *Scientific Reports* 11 (2021) 19145.

STUDY OF NOVEL OXYGEN ELECTRODE MATERIALS WITH VARIED COPPER SUBSTITUTION AND HIGH ENTROPY STRUCTURE

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As an important energy technology, reversible Solid Oxide Cells (rSOCs) are known for their unique ability to efficiently convert chemical energy of hydrogen (and oxidizer) into electricity and heat, and to reversibly generate hydrogen (and oxygen), when supplied with surplus electricity, originating e.g. from renewables. However, due to the serious limitations in reaction kinetics of the oxygen reduction/evolution in the intermediate temperature range (500-800 °C), oxygen electrode has been the active research area. The aims directed toward developing and studying novel materials, which could maintain sufficient catalytic activity. At the same time, mitigation on cobalt reliance is also of importance. Lately, a new group of materials, high entropy perovskite-type oxides, emerged as a prospective solution to achieve the abovementioned goals [1].

In this work, an array of perovskite-type oxides based on the concept of high entropy is synthesized and studied. The chemical formula is $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ni}_{0.15}\text{Mn}_{0.15}\text{Fe}_{0.15}\text{Cu}_x\text{Co}_{0.55-x}\text{O}_{3-\delta}$ (LSNMFCC), with multiple 3d elements simultaneously occupying the B-site. The evaluation is primarily dedicated to evaluate impact of cobalt substitution with copper and enhancement of the micro-morphology brought by electrospinning. Interestingly, four compositions without any impurities are obtained within the substitution range of ($0.05 \leq x \leq 0.2$), either by sol-gel or electrospinning method. The samples demonstrate stable rhombohedral symmetry ($R\bar{3}c$) at a wide temperature range (25-900 °C). Smooth and continuous oxygen release behavior can be proven up to 800 °C. Electrical conductivity for all samples is above 400 S cm^{-1} , while Seebeck coefficient results suggest dominance of negative type of electronic charge carriers. Both, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (GDC) can be applied as electrolyte materials, since no interaction could be detected in compatibility tests with the LSNMFCC. In the electrochemical tests, the polarization resistance value of the $x = 0.2$ (LSNMFCC2035) electrode is found to be as low as $0.018 \Omega \text{ cm}^2$ at 850 °C, based on the GDC symmetrical cell. Further improvement ($0.014 \Omega \text{ cm}^2$) is obtained for the electrospun sample. Smaller cobalt content and high entropy structure make LSNMFCC2035 the very interesting candidate. Thus, a single full cell with LSNMFCC2035 as the oxygen electrode is prepared, demonstrating over 1.1 W cm^{-2} power density at 850 °C, as well as showing outstanding performance in the electrolyser mode.

Acknowledgements: This project was funded by the National Science Centre, Poland, on the basis of the decision number UMO-2020/37/B/ST8/02097.

References:

[1] J. Dąbrowa, A. Olszewska, A. Falkenstein, C. Schwab, M. Szymczak, M. Zajusz, M. Moździerz, A. Mikuła, K. Zielińska, K. Berent, T. Czeppe, M. Martin, K. Świerczek, *J. Mater. Chem. A* 8(46) (2020) 24455-24468.

HIGH-ENTROPY APPROACH AS A WAY TO IMPROVE THE PERFORMANCE OF SFM-BASED SYMMETRICAL SOFC ELECTRODES

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Based on the well-established $\text{SrFe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ [1], novel high- and medium-entropy transition metal-doped perovskites were synthesized for the first time and assessed as potential materials for Solid Oxide Fuel Cell (SOFC) electrodes, including their symmetrical variation. Four compositions: $\text{SrFe}_{0.8}\text{Mo}_{0.2}\text{O}_{3-\delta}$ (SFM), $\text{SrFe}_{0.6}\text{Mo}_{0.2}\text{Co}_{0.2}\text{O}_{3-\delta}$ (SFMC), $\text{SrFe}_{0.4}\text{Mo}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (SFMCMT), and $\text{SrFe}_{0.2}\text{Mo}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Ti}_{0.2}\text{O}_{3-\delta}$ (SFMCMT) were obtained by a solid-state synthesis method. For all samples, structural analysis was carried out along with the determination of the level of oxygen nonstoichiometry. The latter shows a very interesting behavior, which is especially visible in the composition of the high-entropy SFMCMT composition, which differs strongly from the prediction of the rule-of-mixtures. To evaluate the potential of these materials with respect to symmetrical-type operation (both cathode and anode), we studied their structural evolution under reducing conditions, which shows exsolution behavior in all the materials. Importantly, the analysis of the SFMCMT sample upon further reoxidation, indicated at least partially reversible exsolution of the catalytically active Co- and Fe-rich metallic precipitates. Such reversibility is a very useful feature in terms of application in symmetrical SOFCs, indicating that the single-phase structure can be restored after reversing the polarization direction of the operating cell. The functional properties of all materials, including electrical conductivity, thermomechanical properties, and chemical stability toward the most common solid electrolyte materials were studied. Each dopant has a prominent impact on the transport properties, in terms of the conductivity values, and the general character of its temperature dependence. The thermomechanical measurements suggest that the high-entropy approach leads to a significant decrease in the thermal expansion coefficient, with the TEC values for the SFMCMT equal to $13.1 \cdot 10^{-6} \text{ K}^{-1}$ and $15.1 \cdot 10^{-6} \text{ K}^{-1}$, below and above 500 °C, respectively. Such behavior is highly desirable from the point of view of compatibility with other elements of the fuel cell. Consequently, the SFMCMT was selected for further evaluation of the electrochemical performance, under both oxidizing and reducing conditions. The electrochemical impedance spectroscopy measurements prove that cathodic polarization resistance values for SFMCMT material are significantly lower than those for the conventional SFM material, obtained using the same procedure. The threshold value of $0.15 \text{ } \Omega \cdot \text{cm}^2$ was reached at 789 °C and 833 °C for SFMCMT and SFM, respectively. Overall, the high-entropy SFMCMT perovskite demonstrates a significant improvement in performance over the SFM composition, making it a highly promising alternative for application in conventional and symmetrical SOFCs.

Acknowledgements: This research was supported by the Polish National Science Center (NCN) under project No. UMO-2021/41/B/ST8/04365.

References:

- [1] Q. Liu, X. Dong, G. Xiao, F. Zhao, F. Chen, *Adv. Mater.*, 22 (2010) 5478–5482.

NEGATIVE THERMAL EXPANSION MATERIALS IN COMPOSITE ELECTROSPUN OXYGEN ELECTRODES FOR SOLID OXIDE FUEL CELLS

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The insufficient long-term stability of Solid Oxide Fuel Cells (SOFCs) is one of the major drawbacks limiting the commercial employment of these electrochemical devices. The thermo-mechanical issue due to the thermal expansion coefficient (TEC) mismatch between the electrode and electrolyte is the main reason for layer delamination, cracks, and unwanted strain. The application of negative thermal expansion materials (NTEs) may diminish this problem by adjusting the TEC between the layers. Negative TEC and high electronic conductivity were recently reported for $\text{Sm}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ ($\text{A} = \text{Zn}, \text{Cu}; x \leq 0.15$) perovskites [1,2]. The addition of such materials in oxygen electrodes for SOFCs allows to successfully tune the TEC, therefore, eliminating the possible degradation, which in effect greatly increases the electrochemical performance and the long-term stability.

Double perovskites $\text{REBa}_{0.5}\text{Sr}_{0.5}\text{CoCuO}_{5+\delta}$ (RE: Pr, Nd, Sm, Gd) are known for their high mixed ionic-electronic conductivities and electrocatalytic activities. In this work, $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{CoCuO}_{5+\delta}$ (SBSCCO) as the best candidate exhibiting attractive physicochemical and electrocatalytic properties were prepared by the sol-gel method and the electrospinning method, respectively. The total conductivity of SBSCCO is around $100 \text{ S}\cdot\text{cm}^{-1}$ between 300°C and 900°C . The measured polarization resistance (R_p) in SBSCCO|LSGM|SBSCCO symmetrical cell was $0.17 \Omega\cdot\text{cm}^2$ at 800°C , and the long-term stability tests showed that the relative increase of R_p is around 20% after 5 days at 700°C .

To enhance the performance of the SBSCCO electrode, selected NTEs: $\text{Sm}_{1-x}\text{Zn}_x\text{MnO}_{3-\delta}$ (SZMx) were synthesized through the solid state reaction and mixed with previously obtained SBSCCO to prepare composite oxygen electrodes. The dilatometry measurements confirmed the negative TEC for those materials, ranging from $-0.1 \times 10^{-6} \text{ K}^{-1}$ to $-11 \times 10^{-6} \text{ K}^{-1}$ in the $200\text{-}900^\circ\text{C}$ range. The preliminary results show that the R_p of the composite measured in the symmetrical cell in the $700\text{-}900^\circ\text{C}$ range, was significantly lower when compared with the unmodified electrode, e.g. 30% relative decrease at 800°C . The peak power density recorded in commercial anode-supported fuel cell: Ni-YSZ|YSZ|GDC10|SBSCCO:SZM15 at 800°C was $850 \text{ mW}\cdot\text{cm}^{-2}$, which is around 60% higher when compared to the same cell prepared with the SBSCCO electrode without NTE addition.

Acknowledgments: The work is supported by the program „Excellence Initiative – Research University”, for the AGH University of Krakow (IDUB AGH, action D21)

References:

- [1] K.Liu, F.Lu, X.Jia, H.He, J.Su, B.Cai, *J. Mater. Chem. A*, 2022,10, 24410-24421
- [2] X.Jia, F.Lu, K.Liu, M.Han, J.Su, H.He, B.Cai, *J. Phys.: Condens. Matter* 2022, 34 184001

IN SITU SELF-ASSEMBLING HETEROSTRUCTURED NANOFIBERS AS DURABLE HIGH-PERFORMANCE ELECTRODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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Solid Oxide Fuel Cells (SOFCs) are among the most promising green technologies to produce electricity and heat from traditional and renewable energy sources. When the consumption of electrical energy is low, excess electricity can also be stored in hydrogen produced in the electrolysis mode of SOFCs. However, excellent performance of SOFCs is documented rather at high temperatures (≥ 800 °C). The high operational temperature of SOFCs contributes to the high operational costs, the limitation of device materials choice, rendering SOFCs commercially unviable. To enhance economic competitiveness, it is urgent to lower the working temperature to a range of ≤ 700 °C while keeping a high-power yield. Therefore, the development of new electrodes with improved electrocatalytic properties at a low temperature range is indispensable. The design of heterostructured electrodes delivering a synergistic effect, substantially benefits the performance of SOFCs, including the fabrication of hybrid electrodes by the mechanically milling, self-assembling techniques and *in situ* exsolution of secondary phase [1-3].

In this study, various approaches to fabricate $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{CoCuO}_{5+\delta}\text{-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ dual-phases hybrid electrodes have been employed and explored, targeting to boost the performance of IT-SOFCs. Both mechanically milled composites and self-assembled heterostructured nanofibers were manufactured and investigated as high-performance electrodes, which extensively promote the electrochemical performance of electrodes at intermediate temperature range (≤ 700 °C). Self-assembled heterostructured nanofibrous electrodes present more than 40% lower electrode polarizations than composite electrodes obtained by the mechanically milling. The fabricated heterostructured electrode shows stable and excellent performance with electrode polarization $R_p \approx 0.05 \Omega \cdot \text{cm}^{-2}$ stable over 480 h at 800 °C, and excellent power outputs ($940 \text{ mW} \cdot \text{cm}^{-2}$ at 700 °C) were recorded.

Acknowledgements: The work is funded by the National Science Centre Poland (NCN) based on the decision number UMO-2021/43/D/ST5/00824. Kun Zheng acknowledges the financial support of research project supported by the program „Excellence Initiative – Research University” for the AGH University of Krakow.

References:

- [1] Z. Liu, Y. Bai, H. Sun, et al., *Nat. Commun.* 15 (2024) 472.
- [2] Kousi, K.; Tang, C.; Metcalfe, I.S.; Neagu, D., *Small* 17 (2021) 2006479.
- [3] K. Zheng, J. Lach, et al., *J. Power Sources* 587 (2023) 233707.

METALLIC ORGANIC FRAMEWORK (MOF) APPLICATIONS IN NOVEL LITHIUM-SULFUR BATTERIES

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Today lithium-ion batteries are the basis of portable energy source. Wildly used in electronic devices and electric vehicles lithium-ion type of batteries became a standard. Despite good electrochemical performance and their universality, fast development of the market for efficient power sources makes them unable to meet this challenge. As a promising competitor or even a successor of lithium-ion batteries often named are lithium-sulfur batteries. It's mostly because of their high specific capacity (1675 mAh g^{-1}) and relatively big deposit of sulfur on Earth. The main reason, why this type of batteries is not commercialized yet is the problem with the application and stability of the sulfur electrode. The expansion of the sulfur when charging, its insulation and dissolution in organic solvents from the electrolyte, resulting the creation of polysulfides chains, are the remaining problems to solve before lithium-sulfur batteries could be spread in the commerce devices. To solve these issues many additives and compounds have been examined. One of the idea is to use metal-organic frameworks (MOFs) as a sulfur host on the electrode. Because of the porosity of the structure of these materials they are able to "hold" sulfur inside them. Not only it improves the electronic conductivity but also can be a solution to reduce the electrode expansion and sulfur reactions with electrolyte. Here we present MOFs doped electrodes for lithium-sulfur batteries together with suitable for this type of cathodes electrolyte formulas.

Acknowledgements: All the research was made in cooperation of Warsaw University of Technology from Poland and NTNU and SINTEF from Norway in M-ERA.NET 2 MOGLiS project.

HUCKEL ANION BASED CONCENTRATED ELECTROLYTES FOR LITHIUM-SULFUR BATTERIES

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The electrolyte is a crucial component in lithium-sulfur (Li-S) batteries, governing essential aspects such as the problem of polysulfide (PS) dissolution and formation of the solid-electrolyte interphase (SEI) layer. Achieving long-term cycling stability of Li-S batteries necessitates to select anions exhibiting low mobility and weak interactions with PSs [1]. Electrolytes based on Li-salts with Hückel anions, widely employed in lithium-ion batteries, shows potential for enhanced performance in Li-S batteries owing to their reduced polysulfide solubility, as compared to for example the prevalent LiTFSI-based electrolytes [2].

We have here explored various Hückel anion based Li-salts, characterized by different alkyl chains attached: lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI), lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide (LiPDI), and lithium 4,5-dicyano-2-(heptafluoropropyl)imidazolide (LiHDI). All were dissolved in DOL:DME (1:1, v/v) to create Li-S battery electrolytes. The local structure as function of salt concentration was elucidated using Raman and FTIR spectroscopy, and correlated with ion transport properties and electrochemical performance. Additionally, we have calculated the PS solubility in the electrolytes using a combined DFT and statistical mechanics approach; the conductor-like screening model for real solvents (COSMO-RS).

Acknowledgements: As a part of the DESTINY PhD programme, this publication acknowledges funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Actions COFUND (Grant Agreement No- 945357).

References:

- [1] Han, Kee Sung, et al. "Effects of anion mobility on electrochemical behaviors of lithium-sulfur batteries." *Chemistry of Materials* 29.21 (2017): 9023-9029.
- [2] Armand, M., et al. "Development of Hückel type anions: from molecular modeling to industrial commercialization. A success story." *Journal of The Electrochemical Society* 167.7 (2020): 070562.

Poster session

FUNCTIONALIZATION OF PHYSICO- AND ELECTROCHEMICAL PROPERTIES OF SUSTAINABLE BIO-BASED CARBON ANODE MATERIALS

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Demand for naturally sourced and artificial graphite, which is widely used as anode material in lithium-ion batteries (being the second largest component, by weight), is projected to increase in the next years [1]. In this context, an important motivation to undertake further research in terms of carbonaceous anode materials is the desire to withdraw from the use of finite or synthetic (often toxic or expensive) carbon sources [2]. Thus, employing sustainable reserves is more reasonable about securing a supply chain, price stability and compliance with stringent environmental regulations. Our previous research demonstrated that the use of starch is particularly interesting. The idea of such a concept, apart from the fact that starch is a widely available, renewable and affordable raw material, that forms products of green technology with zero carbon footprint, has its justification in the wide diversity of this polymer [3]. Another important issue is that the properties of resulting carbons can be easily affected and controlled by the synthesis conditions or precursor composition, allowing for the design of materials with strictly defined properties, functionalized depending on the requirements of their application.

In this work, we report a comprehensive study on the synthesis as well as complementary physical and electrochemical characterization of nanostructured carbon materials (carbogels) derived from starch and modified in terms of process conditions and composition of precursor in the context of the use of carbogels in ion batteries (Li-ion and Na-ion).

To obtain carbons, proper compositions of polymeric carbohydrates were processed by the gelatinization route followed by the carbonization of organic precursors [3]. The chemical composition, structure and porosity of the produced modified carbons were determined using elemental analysis (EA), X-ray powder diffraction (XRD) and nitrogen adsorption-desorption method (N₂-sorption). The electrochemical characterization of Li-ion half-cells based on the fabricated carbon electrodes was conducted using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge tests (GCDT).

All the raw materials were successfully processed by gelatinization and carbonization processes that allowed the preparation of carbon materials. The obtained results regarding diverse carbons revealed that elemental composition, structure, degree of graphitization, surface development and electrochemical performance of obtained carbon anodes are strongly influenced by different conditions of synthesis and utilization of various additives in the precursor composition. Investigated samples exhibit increased characteristics including higher capacity and better rate capability compared to materials obtained only from starch.

References:

- [1] Graphite Industry: Future Scope and Predictions (2020-2025), https://www.reportlinker.com/p05826223/Graphite-Electrode-Market-Growth-Trends-and-Forecast.html?utm_source=GNW; (accessed 12th March 2024).
- [2] Z. Gao, Y. Zhang, N. Song, X. Li, *Materials Research Letters* 5 (2017) 69-88.
- [3] M. Bakierska, M. Lis, J. Pacek, M. Świętosławski, M. Gajewska, A. Tąta, E. Proniewicz, M. Molenda, *Carbon* 145 (2019) 426-432.

CAG/LTO COMPOSITE AS A SUSTAINABLE ELECTRODE MATERIAL FOR LITHIUM-ION BATTERIES

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Rapid advances in technology drive a need for more efficient, cheaper, and environmentally friendly lithium-ion batteries. As such, new electrode materials, that fulfil the demands of the market, need to be developed. One of the more promising developing types of materials are carbon-based composites. These composites, containing different allotropes of carbon, can show several improved electrochemical and physical properties, such as increased electric conductivity and capacity, improved rate capability, or higher long-term stability [1].

Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) is a promising anode material, thanks to its excellent rate capabilities and low volume expansion during cycling. Moreover, it does not contain any toxic elements. However, LTO is limited by its low electric conductivity, needing the addition of conductive carbon additives when used in an electrode, and low specific capacity [2]. Another electrode material, carbon aerogels (CAGs) based on potato starch have been previously proposed as an ecological anode material that could replace currently used carbon materials [3,4]. Herein we report the synthesis and characterization of carbon aerogel/lithium titanate (CAG/LTO) composite for use as a sustainable electrode material, with the CAG working as a conductive carbon matrix for the LTO.

CAG/LTO composites with different compositions have been prepared and studied alongside LTO containing carbon additives. Carbon content in the composites was measured by the elemental analysis (EA), and phase purity was investigated using X-ray powder diffraction (XRD). The morphology of the composite was investigated by transmission electron microscopy (TEM). The electrochemical performance was studied using galvanostatic charge-discharge tests (GCDT) and cyclic voltammetry measurements (CV). CAG/LTO composites were successfully synthesized, with no changes to the spinel's structure. Electrodes containing the composite were able to be cycled in an extended voltage range (0-3V). Thanks to this the CAG/LTO composites showed increased capacity due to the extra Li^+ ions inserted into the structure of LTO as well as the electrochemical engagement of the carbon aerogel matrix. As such, we propose the CAG/LTO composite as a sustainable alternative electrode material with enhanced properties for lithium-ion batteries.

References:

- [1] Mauger, A., Julien, C. *Ionics* 20 (2014) 751–787.
- [2] T. Yuan, Z. Tan, C. Ma, J. Yang, Z.-F. Ma, S. Zheng, *Adv. Energy Mater.* 7 (2017) 1601625.
- [3] M. Bakierska, M. Molenda, D. Majda, R. Dziembaj, Functional starch based carbon aerogels for Energy Applications, *Procedia Engineering*. 98 (2014) 14–19.
- [4] M. Bakierska, M. Lis, J. Pacek, M. Świętosławski, M. Gajewska, A. Tąta, E. Proniewicz, M. Molenda, Bio-derived carbon nanostructures for high-performance lithium-ion batteries, *Carbon*. 145 (2019) 426–432.

INCREASED STABILITY OF La-DOPED $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ IN REDUCING ATMOSPHERES: SYNCHROTRON STUDIES ON THE PHASE TRANSITION

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The increase in the environmental awareness has led to the significant worldwide trend of the development of alternative energy sources other than conventional use of fossil fuels. One of the alternatives is the use of Solid Oxide Fuel Cells (SOFCs). However, the usage of fuels other than hydrogen (e.g., biogas) is burdened with carbon deposition and sulfur poisoning when conventional Ni-YSZ cermet is used as an anode, leading to rapid decreases in cell efficiency. Among the materials studied as substitutes for Ni-YSZ, perovskites are among the most popular group. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFM) is one of the representatives of the double perovskites family extensively examined due to its high ionic and electronic conductivity, as well as the redox stability in both oxidizing and reductive atmospheres. However, it is possible that under highly reductive atmospheres, ferrites can transform into other phases, causing a severe distortion of the compound [1], therefore a deeper understanding of the phase transition should be considered in the case of SFM-based compounds.

The SFM-based materials doped with lanthanum and niobium, respectively, were synthesized by the Pechini method. The dopants were chosen to increase the conductivity of the materials and to hopefully stabilize the structure [2]. The reduction in the hydrogen atmosphere led to the formation of the Ruddlesden-Popper layered perovskite. However, as the transition occurred in all of the compounds considered, the amount of new phase was significantly limited for the La-doped compound. The HT-XRD proved that during the reoxidation, the structure firstly is distorted by the dissolution of iron exsolved during reduction. Then, the double perovskite structure is gradually restored to 700 °C. Due to ability of both Fe and Mo to be in different oxidation states, X-ray Absorption Spectroscopy measurements were performed on the samples in all three states: as-prepared, reduced and reoxidized to reveal the oxidation state of B-site elements. The analysis of the Fe K-edge allowed for the Fourier transform analysis of the EXAFS. For the reduced samples, the Fe-O bonds were elongated, as expected for the Ruddlesden-Popper structure. The stabilizing impact of La-doping was also confirmed in terms of Fe surroundings, as well as Mo d orbital splitting.

Acknowledgments: The research project was supported by the National Science Center under grant no. NCN 2022/45/N/ST5/02933. The authors acknowledge the SOLARIS Center for the access to the PIRX and ASTRA beamlines.

References:

- [1] H. Lv, L. Lin, X. Zhang, D. Gao, Y. Song, Y. Zhou, Q. Liu, G. Wang, X. Bao, *J. Mater. Chem. A* 7 (2019) 11967–11975.
- [2] X. Yang, J. Chen, D. Panthi, B. Niu, L. Lei, Z. Yuan, Y. Du, Y. Li, F. Chen, T. He, *J. Mater. Chem. A* 7 (2019) 733–743.

THE INFLUENCE OF OPERATING CONDITIONS AND THE PRESENCE OF ADDITIONAL ANODE CATALYTIC LAYER ON THE PERFORMANCE OF PLANAR SOFC

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A Solid Oxide Fuel Cell (SOFC) is a device that can directly convert the chemical energy of a fuel and an oxidant into electrical energy and heat. Among possible fuel one can find e.g. hydrogen, hydrocarbons, biogas or ethanol. The performance of operating fuel cells strongly depends on the water vapour content in a fuel as well as on the electrical loading of the system. The aim of this study is to present the influence of various conditions on the formation of electrical losses. Due to the comparison of two fuel cells: a reference one and the one with additional catalytic layer deposited on the anode some limitations in diffusion processes will be shown.

For this purpose the traditional 1-inch button Solid Oxide Fuel Cells (Ni-YSZ anode, YSZ electrolyte and LSM-YSZ cathode) were fabricated by the group of prof. Sea-Fue Wang from the Taipei University of Technology. Both a reference one without a catalytic layer and another one with a Rh/Ce-CuCa catalytic layer deposited on the anode side were examined in various fuel and oxidant compositions. The measurements were performed in a dedicated Open Flange SOFC measuring system purchased by the Fiaxell company.

Acknowledgements: This work was supported by the Gdańsk University of Technology by the DEC-6/1/2022/IDUB/II.1a/Au grant under the AURUM IDUB program.

3D PRINTED ELECTROLYTES FOR LITHIUM-ION BATTERIES

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Lithium-ion batteries are one of the most popular energy storage devices, with their production volume steadily increasing. Currently, most lithium-ion batteries are manufactured only in simple shapes such as cylinders and prisms. These shapes are achieved by creating electrodes and separators through a continuous, roll-to-roll process, which are then molded into the desired form. However, the ongoing miniaturization of electronic devices poses new challenges for batteries, particularly in producing cells with complex, customized shapes. Such advancements could significantly drive the development of various microelectronics, including wearable and even implantable microelectronics, or health monitoring sensors, where shape customization is crucial. Moreover, it is anticipated that the mutually penetrating three-dimensional architecture of the electrodes and electrolyte will enable significantly higher energy densities and cell performance compared to sandwich-type like batteries [1].

Our research focuses on the application of polymer materials in lithium-ion cells, which could be manufactured using additive manufacturing techniques, also known as 3D printing. One of the widely described polymers with potential applications as an electrolyte in lithium-ion batteries is polyacrylonitrile (PAN) [2]. Unfortunately, due to its high glass transition temperature ($T_g = 84 - 85^\circ\text{C}$), it is mostly used as a matrix in gel polymer electrolytes (GPE). The application of PAN in solid polymer electrolytes (SPE) is unlikely due to its low ionic conductivity at room temperature. Furthermore, 3D printing of PAN using Fused Filament Fabrication (FFF), one of the most popular additive manufacturing methods, is extremely difficult because the melting point of PAN (above 300°C) is higher than the temperature of its thermal decomposition. This leads to material degradation during extrusion in the 3D printer's heated nozzle. To address these issues, we used a branched copolymer with polar nitrile and oligoethylene groups obtained by free radical copolymerization of acrylonitrile (AN) and poly(ethylene glycol) methyl ether acrylate (PEGMEA). By adjusting the ratio of comonomers in the range of AN:PEGMEA from 1:1 to 10:1, we were able to lower the glass transition temperature and melting point of the polymer to enable 3D printing. We successfully printed three-dimensional electrolytes containing lithium trifluoromethanesulfonate salt. By using succinonitrile as a plasticizer, we achieved an ionic conductivity on the order of 10^{-5} S/cm and lithium cation transference number 0.5.

References:

- [1] Maurel, A., Grugeon, S., Armand, M., Fleutot, B., Courty, M., Prashantha, K., ... & Dupont, L. (2020). Overview on lithium-ion battery 3D-printing by means of material extrusion. *ECS Transactions*, 98(13), 3.
- [2] Long, L., Wang, S., Xiao, M., & Meng, Y. (2016). Polymer electrolytes for lithium polymer batteries. *Journal of Materials Chemistry A*, 4(26), 10038-10069

**NEW PERSPECTIVES ON $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4/\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ COMPOSITE
COATINGS
FOR FERRITIC STAINLESS STEEL INTERCONNECTS IN IT-SOFC
TECHNOLOGIES**

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The drive to reduce the operating temperature of SOFC and SOEC electrochemical devices below 800°C favors the use of Cr-based ferritic stainless steel as interconnect materials. However, the main problem with these materials is the increase in area-specific resistance (ASR) associated with the growth of a Cr_2O_3 scale on the surface during long-term exposure to high temperatures. To counteract this phenomenon, protective-conducting coatings are applied onto the interconnect surface. The coatings considered for this purpose are usually composed of spinel because of its high electrical conductivity, low Cr volatility and a thermal expansion coefficient (TEC) that is similar to that of ferritic steel [1].

In the presented study, a new $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4/\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ composite coating material in which the $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$ (CM) formed the matrix and the $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) perovskite was added as a dispersion phase was deposited on the Nirosta 4016/1.4016 low-chromium ferritic stainless steel. Ceramic coatings with selected compositions were deposited electrophoretically on metallic substrates and underwent long-term oxidation tests over 1500 h in air at 750°C. The samples after testing were examined by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). A 2-probe 4-point DC method was applied to measure the ASR.

Two selected composite samples obtained by adding 10 wt% LNF (CM10LNF) and 50 wt% LNF (CM50LNF) to the spinel matrix were successfully deposited on the ferritic stainless steel substrate via electrophoresis. The coatings obtained after a two-stage thermal treatment had a thickness of ca. 30 μm , and they were compact and characterized by very good adhesion to the substrate. The performed long-term thermal treatment of the Nirosta 4016/1.4016 steel with CM, CM10LNF and CM20LNF coatings and a steel sample without any modifications showed that the Nirosta/CM10LNF and Nirosta/CM20LNF systems were far more resistant to oxidation than other systems. Furthermore, the ASR values measured for these two steel/composite coating samples were far lower than that determined for the unmodified steel.

The study thus demonstrated the potential of the obtained CM10LNF protective-conducting composite for application as a coating material for SOFC/SOEC metallic interconnects.

Acknowledgement: Funding from the National Science Centre (NCN) project No. 2021/41/B/ST8/02187 is gratefully acknowledged (TB).

References:

[1] N. Shaigan, W. Qu, D.G. Ivey, W. Chen, J Power Sources 195 (2010) 1529-1542.

MACROSCOPIC MODELLING OF DIRECT INTERNAL REFORMING PLANAR SOFC – MODEL CONSTRUCTION APPROACH

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A Solid Oxide Fuel Cell (SOFC) is a device that converts the chemical energy of a fuel and an oxidant into electrical energy and heat. SOFC performance heavily depends on operating conditions and a used fuel. Many models [1][2] were shown before for macroscopic, phenomenological presentation of an operating fuel cell. Complexity of a model grows rapidly with number of reactions taken into account. Even if the approach for SOFC fueled with H₂ is quite well optimized, there is still a need for mathematical and experimental work to obtain a working simulation of Direct Internal Reforming SOFC (DIR-SOFC).

We present a report on constructing such a model. Problems, approaches and different parametrization methods are discussed. Multiple already-existing equations and assumptions for different models are presented. Implementation opportunities and possibility of empirical tests for a model are shown.

Acknowledgements: This work was supported by the Gdańsk University of Technology by the DEC-6/1/2022/IDUB/II.1a/Au grant under the AURUM IDUB program.

References:

- [1] J. Milewski, A. Szczesniak, and L. Szablowski, ‘A discussion on mathematical models of proton conducting Solid Oxide Fuel Cells’, *Int. J. Hydrog. Energy*, vol. 44, no. 21, pp. 10925–10932, Apr. 2019
- [2] M. M. Hussain, X. Li, and I. Dincer, ‘A general electrolyte-electrode-assembly model for the performance characteristics of planar anode-supported solid oxide fuel cells’, *J. Power Sources*, vol. 189, no. 2, pp. 916–928, Apr. 2009

NOVEL PLATINUM-DOPED STRONTIUM TITANATE MATERIALS FOR DRY METHANE REFORMING

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Methane reforming, specifically steam methane reforming, is a crucial industrial process used to produce hydrogen gas and carbon monoxide. It's one of the most common methods for large-scale hydrogen production. Both dry and wet method requires a catalyst, therefore there is a need for novel, more efficient catalysis materials. Ex-solution nanoparticles gathered interest in this and other fields of catalysis study [1][2].

With this problem in mind a synthesis of perovskites $(La_{0.3}Sr_{0.7})_{0.9}Ti_{1-x}Pt_xO_{3+\delta}$ was carried out for doping levels of $x = 0, 0.01, 0.02, \text{ and } 0.05$. A modified Pechini method was used to prepare the materials. Precursors combined with citric acid and ethylene glycol were mixed at 130°C . The resulting mixture of organic substances and powder was calcined at 1250°C for 12 hours. The obtained powders were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). TPR/TPO measurements were performed to optimize the process of reduction and formation of ex-solution nanoparticles Perovskites were synthesized to investigate their potential use as catalysts in methane reforming.

Acknowledgements: This work was supported by the Gdańsk University of Technology, IDUB program Technetium Talent Management Grants no. 21/1/2022/IDUB/III.4c/

References:

- [1] Sang Hun Kim, Hyeongwon Jeong, Bharat Sharma Jae-ha Myung, *In Situ Exsolution Catalyst: An Innovative Approach to Develop Highly Selective and Sensitive Gas Sensors*, ACS Appl. Mater. Interfaces 2022, 14, 16, 18275–18282
- [2] Lindenthal, L.; Buchinger, R.; Drexler, H.; Schrenk, F.; Ruh, T.; Rameshan, C. Exsolution Catalysts—Increasing Metal Efficiency. *Encyclopedia* 2021, 1, 249-260.

CATALYTIC PROPERTIES OF PECHINI-SYNTESIZED RUTENIUM-DOPED PEROVSKITES

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Dry methane reforming process is a reaction between carbon dioxide and methane. It has been proposed as a method of hydrogen obtaining, making use of two greenhouse gases. This process is highly catalyst-driven – thus the need to explore new materials. Ex-solution nanoparticles for usually used metals (Ni, Rh, Ru) attracted attention for this application [1][2].

$(La_{0.3}Sr_{0.7})_{0.9}Ti_{1-x}Ru_xO_{3+\delta}$ perovskite synthesis was carried out for doping levels of $x = 0, 0.01, 0.02, \text{ and } 0.05$ employing modified Pechini process. Precursors combined with citric acid and ethylene glycol were mixed at 130°C . The resulting mixture of organic substances and powder was calcined at 1250°C for 12 hours. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to investigate structural properties of these materials. TPR/TPO measurements were performed to optimize the process of reduction and formation of ex-solution nanoparticles. Catalytic activity studies in methane dry reforming process were conducted.

Acknowledgements: This work was supported by the Gdańsk University of Technology IDUB program Aurum Plus no. 2/1/2023/IDUB/II.1a/Au+

References:

- [1] Lindenthal, L.; Buchinger, R.; Drexler, H.; Schrenk, F.; Ruh, T.; Rameshan, C. Exsolution Catalysts—Increasing Metal Efficiency. *Encyclopedia* 2021, 1, 249-260.
- [2] Xiuli Wang, Michael Economides, CHAPTER 7 - Gas-To-Liquids (GTL), Advanced Natural Gas Engineering, Gulf Publishing Company.

ELECTRICAL PROPERTIES OF DOUBLE-DOPED BIMEVOXES
(ME=ME⁴⁺, ME⁶⁺)

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An important group of oxygen ion conductors are bismuth oxide-based compounds. An example is the compound Bi₄V₂O₁₁, which is formed by adding vanadium (V) oxide V₂O₅ to Bi₂O₃. It turns out that doping Bi₂O₃ allows high conductivity even at low temperatures. An interesting family of compounds are BIMEVOXes, which are formed by doping the parent compound Bi₄V₂O₁₁ with various metals replacing the vanadium atom [1]. The introduction of a dopant with a valence lower than vanadium introduces an additional vacancy in the anion sublattice, which can have a beneficial effect on increasing conductivity [2, 3, 4]. Double doping with a tetravalent and a hexavalent metal replacing the pentavalent vanadium does not introduce additional oxygen vacancies, and has a positive effect on the conductivity and stabilization of the highly conductive gamma phase.

A series of samples of doubly doped BIMEVOX (e.g. ME = Ti⁴⁺, W⁶⁺) were obtained by solid state reaction method. XRD measurements were performed at room temperature (RT) and various temperature (VT). As a result, unit cell parameters were obtained as a function of composition and temperature. Impedance spectroscopy measurements were also performed using Novocontrol over a wide range of compositions and temperatures.

Analysis of the X-ray diffraction results determined the limits of the occurrence of three phases depending on the amount of dopant. At a small amount of admixture ($x \leq 0.05$), a monoclinic α phase is present at room temperature. A larger amount of doping (up to $x = 0.10$) results in a stabilized orthorhombic β phase, and above $x = 0.10$ a tetragonal γ phase is observed. Several characteristic samples were examined by XRD as a function of temperature. The temperatures of the α - β and β - γ phase transitions were determined.

Impedance spectroscopy results confirmed the presence of several different phases depending on composition and temperature. It was shown that conductivity at low temperatures increases with increasing doping. The highest conductivity is for the BiWTiVOX.20 (Bi₂W_{x/2}Ti_{x/2}V_{1-x}O_{5.5}, $x = 0.20$) sample, where the γ phase is best stabilized. The figure shows an Arrhenius plot for several different doubly doped BIMEVOX. The sample with hexavalent W has a higher conductivity than the samples with Mo.

References:

- [1] F. Abraham, J. C. Boivin, G. Mairesse, G. Nowogrocki, *Solid State Ionics*, 40 (1990) 934 - 937
- [2] R. N. Vannier, G. Mairesse, F. Abraham, G. Nowogrocki, *Solid State Ionics* 70 (1994) 248 - 252
- [3] A. Dziegielewska, M. Malys, W. Wrobel, S. Hull, Y. Yue, F. Krok, I. Abrahams, *Solid State Ionics* 360 (2021) 115543
- [4] Y. Yue, A. Dziegielewska, S. Hull, F. Krok, R. M. Whiteley, H. Toms, M. Malys, M. Zhang, H. Yen, I. Abrahams, *Journal of Materials Chemistry A* 10 (2022) 3793 - 3807

A NEW CONCEPT OF TERNARY AQUEOUS ELECTROLYTES BASED ON LITHIUM 4,5-DICYANOIMIDAZOLATE HYDRATES.

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A new concept of aqueous electrolytes based on heterocyclic anions (hydrated anionic triplet electrolyte, HATE) has been presented. Structural studies showed that dimeric lithium 4,5-dicyanoimidazolate (LiTDI) dihydrate molecules, in the presence of acetonitrile, form an ionic system preserved in high concentrations and solid states. X-ray diffraction measurements show that electroneutral dihydrate units can coordinate additional lithium cations acting as charge carriers. The crystalline ionic phase was characterized using spectroscopic, thermal, and electrochemical methods and was used to prepare model electrolytes based on LiTDI hydrates. Linear sweep voltammetry and impedance spectroscopy measurements show, in this system, the depletion of water activity, high conductivity, and reversible cycling of full cells comprising examined electrolytes. We will prove that a concentrated triplet solution acts similarly to the anhydrous electrolyte; regardless of the concentration, it reaches high values of ionic conductivity (12-16 mS/cm at room temperature) and is electrochemically stable.

Acknowledgments: The research was funded by the POB Energy of the Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme, grant no. 1820/39/Z01/POB7/2021.

HIGHLY CONDUCTIVE GLASSY-CRYSTALLINE LiFePO₄ OLIVINE-LIKE NANOCOMPOSITES.

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One of the limiting factors of modern Li-ion batteries is the low electronic conductivity of their cathodes. There are many methods that try to handle it [1-2]. One of the most promising methods is the thermal (nano)crystallization of glasses. This method was applied before to, e.g., optimize the conductivity of LiFePO₄ with small additives of vanadium. Test cells based on those materials had very stable capacity at the level of 100 mAh/g (0.2C current) after 50 cycles [3]. The purpose of the work was to synthesise as glassy LiFePO₄ (i.e., without vanadium additives) as possible and to study their electrical and electrochemical properties of those pristine glasses and nanomaterials after proper thermal treatment.

The synthesis of samples was carried out using the twin rollers method. After synthesis, materials were characterized using: XRD (to verify the amorphousness of samples and study the process of (nano)crystallization), DTA (to determine temperatures of crystallization and glass transition), IS (to find the best thermal condition to maximize electrical conductivity) and electrochemical measurement (to determine capacity).

Several glassy-cystalline composites and a few of fully glassy materials were synthesised. Crystallisation temperature of those materials was around 500 °C. In the next step, electrical measurements of glassy materials were conducted. Conductivity of fully glassy sample increased from $\sigma = 6.5 \cdot 10^{-13}$ S/cm to $\sigma = 3.9 \cdot 10^{-9}$ S/cm after heat treatment to around 400 °C. Fully thermal optimisation of electrical conductivity was done for glassy-crystalline composites. In that case conductivity increased from $\sigma = 1.9 \cdot 10^{-11}$ S/cm to $\sigma = 8.7 \cdot 10^{-6}$ S/cm after heating to 265 °C. In the end, electrochemical measurements were done for the materials with the best conductivity. Unfortunately, test cells based on these materials had very low gravimetric capacity at the level of 8 mAh/g. Further investigation of low capacity will be presented.

References:

[1] B. Ramasubramanian, S. Sundarajan, V. Chellappan, M.V. Reddy, S. Ramakrishna, K. Zaghbi, Batteries 8 (2022) 133.

[2] A. Eftekhari, Journal of Power Sources 343 (2017) 395-411

[3] J.E. Frąckiewicz, T.K. Pietrzak, M. Boczar, D.A. Buchberger, M. Wasiucione, A. Czerwiński, J.E. Garbarczyk, Energies 14 (2021) 8042.

CORROSION INVESTIGATION OF CURRENT COLLECTOR IN SOLID STATE LITHIUM SULFUR BATTERIES

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Nowadays battery technology is searching for various alternatives of Li-Ion chemistry based systems. One of the promising types are lithium sulfur cells where cathode is reaching extremely high theoretical capacity. Considering challenges related with the process of the diffusion of polysulfides polymer electrolytes are attractive candidates in the targeted designs as being able to hinder this adverse phenomenon. The research scope presented herein covers the comparative study of the corrosion of the aluminum current collector in polymer electrolytes tested with two different types of lithium salts. The 'imide' one (lithium bis(trifluoromethanesulfonyl)imide LiTFSI) is well known and standardized in polymer electrolytes. Unfortunately it propagates corrosion of Al current collector. On the other side the 'imidazole' counterpart (lithium 2-trifluoromethyl-4,5-dicyanoimidazole LiTDI) might be the one preventing it as active organic corrosion inhibition by imidazole ring structure. Both salts are tested in PEO liquid analogue (PEG DME 500) at two different temperatures (RT and 70°C). Additionally, investigation of in situ synthesis of polysulfides occurring in the electrolyte allows to follow the influence of electrode reaction products on corrosion. Different electrochemical tests including two and three electrode configurations were supported by real Li-S batteries tests covering these two salts. Additionally the in situ Raman spectroscopy allow to follow the changes on Al electrode under potential change. The obtained results were found to comply with computational modelling studies performed.

It was also indicated that an electrochemical characterizations do not directly confirm corrosion of Al. The corrosion current is vanishing in the overall anodic current giving almost the same profile for all samples. However polysulfides present in the electrolyte may prevent corrosion by re-passivation of Al electrode especially at elevated temperature. Additionally LiTDI salt rise the corrosion potential much above Li-S operational potential, however the corrosion current is rising for LiTDI salt containing electrolytes. Two electrode configuration did not allow to draw clear conclusion about the value of the corrosion potential but electrodes studied exhibited significantly lower evidences of pitting corrosion for LiTDI containing electrolytes. Unfortunately, real cell tests indicates rather poor electrochemical performance for LiTDI salt based electrolyte despite corrosion elimination. It was as well demonstrated that confocal in situ Raman investigations allow to follow changes occurring on the electrode surface by means of space resolved spectroscopic inspection.

Moreover, in the course of immittance spectroscopy experiments performed one can observe that the systems follow one of two literature [1,2] immittance models of the corrosion processes. Thus, while the initial state of the electrodes is only slightly dependent on the composition of the respective electrolyte in terms of the capacitive parameters (Q,n) determined. On the other hand while the value of the corresponding resistivity remains intact upon the addition of sulfides to the LiTFSi containing solution the same operation performed for its LiTDi based counterpart leads to the significant fivefold decrease of the said value.

References:

- [1] Y. Li, P.G. Fedkiw, *Electrochimica Acta* 52 (2007) 2471.
- [2] V. F. Lvovich, *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena*, John Wiley & Sons, Ltd., Hoboken 2012, p 281-284.

DEVELOPMENT AND CHARACTERIZATION OF THE ELECTROCHEMICAL PROPERTIES OF PRO_x AS AN EFFICIENT OXYGEN ELECTRODE FOR INTERMEDIATE SOLID OXIDE CELLS

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Solid-oxide cells are a promising, potentially zero-emission energy source that could play a significant role in the future of global energy. The oxygen electrode is responsible for the reduction of oxygen in fuel cell mode. One of the main phenomena that needs to be solved is the high polarisation resistance of this electrode. A need for novel materials has emerged because of the push for high-performing SOCs at lower temperatures [1] One of the promising materials with potential use in SOCs is praseodymium oxide [2, 3]

The present work shows the result of the research on a high-performance oxygen electrode composed of praseodymium oxide for intermediate-temperature Solid Oxide Cells (SOCs). Praseodymium oxide is a complex compound with properties that need to be better understood. Simultaneously, it is among the most promising new-generation materials employed in SOCs.

The spin-coating method applied the oxygen electrode to CGO (Ce_{0.8}Gd_{0.2}O_{2-d}). The electrochemical properties were determined using electrochemical impedance spectroscopy. For this purpose, a series of symmetrical samples were prepared. The thickness of the oxygen electrode has been optimised. Annealing temperature's impact was investigated, and at 600 °C, a polarisation resistance of 24 mΩ cm⁻² was achieved. Detailed studies were conducted on various pO₂ values to identify the electrode processes. The experiments, supported by DRT analysis, demonstrated the electrode processes and their efficiency. Ageing experiments were conducted to demonstrate the electrode's stability during operation.

Acknowledgements: This research has been supported by National Science Centre (NCN) DAINA 2 project number UMO-2020/38/L/ST8/00513; “Porous metal supported micro-scale solid oxide fuel cells: fundamentals, fabrication and testing”.

References:

- [1] T.A.Z. de Souza, C.J.R. Coronado, J.L. Silveira, G.M. Pinto, J. Clean. Prod. 279 (2021) 123814 <https://doi.org/10.1016/J.JCLEPRO.2020.123814>.
- [2] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.M. Bassat, J.C. Grenier, Int. J. Hydrogen Energy 41 (2016) 15538–15544. <https://doi.org/10.1016/j.ijhydene.2016.04.024>.
- [3] L. Yefsah, J. Laurencin, M. Hubert, D.F. Sanchez, F. Charlot, K. Couturier, O. Celikbilek, E. Djurado, Solid State Ionics 399 (2023) 1–14. <https://doi.org/10.1016/j.ssi.2023.116316>.

**HIGH-PERFORMANCE OXYGEN ELECTRODES FOR INTERMEDIATE SOLID
OXIDE CELLS (SOC) PREPARED BY INFILTRATION OF $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-d}$
BACKBONE BY $(\text{La},\text{Sr})\text{COO}_3$**

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Solid oxide cells show potential as a potential zero-emission energy source. One of the most important issues that needs to be solved in SOC technology is obtaining high-performance cathodes with a low polarisation resistance value. Materials showing high oxygen reduction efficiency include LSC($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-d}$), LSCF($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d}$) and PrO_x . In addition, the use of composite materials is becoming more and more common. Among the various solutions used, the infiltration of cathode material into the porous backbone has so far yielded very promising results[1,2].

This work presents results for a porous backbone made of CGO ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-d}$) infiltrated with LSC, PrO_x , and the PrO_x -LSC composite material as effective cathodes for intermediate SOC. A spray-painted CGO backbone with a thickness of approximately 10 μm was deposited on dense CGO pellets. The infiltration process consisted of immersing the sample in 1 ml of the 1 M precursor solution and then, after removing excess liquid, heating it using a hot plate to 400°C. After the last cycle, the samples were annealed at 600°C (optimised temperature) for 2 hours. SEM-EDS measurements on fractures showed the presence of material in similar amounts both at the surface and near the electrolyte surface.

The symmetrical samples prepared were used to determine the performance of the proposed combination using electrochemical impedance spectroscopy. Measurements performed at range 600°C-300°C showed that, at the temperature of 600°C, the LSC-infiltrated CGO sample had a polarisation resistance of 42 $\text{m}\Omega\text{ cm}^{-2}$. For PrO_x infiltration, this value was 78 $\text{m}\Omega\text{ cm}^{-2}$, and for the composite, it was 107 $\text{m}\Omega\text{ cm}^{-2}$. The ageing measurements performed showed good stability. For the next stage of research, in the form of tests on cells, a version with a CGO backbone infiltrated with LSC was selected.

Cell measurements were made at a temperature of 600°C. The maximum power obtained for the proposed composition of materials, was higher than that of the reference sample that had an LSC cathode.

Acknowledgements: This research has been supported by National Science Centre (NCN) DAINA 2 project number UMO-2020/38/L/ST8/00513: “Porous metal supported micro-scale solid oxide fuel cells: fundamentals, fabrication and testing”.

References:

- [1] Y. Gao, M. Zhang, M. Fu, W. Hu, H. Tong, Z. Tao, Energy Rev. 2 (2023) 100038. <https://doi.org/10.1016/J.ENREV.2023.100038>.
- [2] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.M. Bassat, J.C. Grenier, Int. J. Hydrogen Energy 41 (2016) 15538–15544. <https://doi.org/10.1016/j.ijhydene.2016.04.024>.

REDUCTION BEHAVIOUR IN NEODYMIUM DOPED CERIA

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Doped cerium oxides are technologically relevant materials and used as electrolytes in intermediate temperature solid oxide fuel cells. An important issue for these materials is the reduction of ceria at low oxygen partial pressures, which leads to mixed ionic electronic conduction [1]. In this work, reduction behaviour in $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9-\delta}$ is examined under inert and strongly reducing conditions. Even under inert conditions, ca. 3.5% of the Ce is redox active at temperatures up to around 800 °C, which appears to be correlated with non-linear behaviour in the Arrhenius plot of conductivity and thermal expansion of the lattice.

Reduction experiments of the synthesised powder and sintered pellets were performed under flowing H_2 in a Carbolite EZS 1200 furnace, with an exchangeable quartz glass reactor tube. The samples were annealed at 700 °C for 5 hours with the heating and cooling rate of $10^\circ\text{C min}^{-1}$. After removal from the furnace, samples were vacuum sealed to prevent them from oxidising and were then rapidly transferred (ca. 1 h) to the XRD, impedance measurement and DTA-TGA setups. Subsequent to the reduction, all experiments were repeated in air to monitor the kinetics of the oxidation processes.

The X-ray diffraction study of reduced powder reveals the splitting of the main fluorite peaks indicating of existence of two phases, a cubic fluorite phase with a lattice parameter

$a = 5.454 \text{ \AA}$, which is slightly larger than that of the virgin sample prior to annealing; along with a fluorite-like phase related to triclinic $\text{Ce}_{11}\text{O}_{20}$ [2]. Rietveld analysis based on these two phases resulted in an excellent fit with approximate 1:1 w/w ratio of these two phases. During the heating in air, X-ray diffraction study shows that it is evident that at 100 °C the pattern simplifies to a single cubic fluorite phase, which is maintained throughout the rest of the thermal regime. DTA-TGA experiment confirmed the oxidising process (on heating the sharp exothermic peak is observed with a maximum at 89 °C). SEM images of a reduced pellet confirm no cracking of the surface, with grain boundaries less visible than prior to annealing. The impedance measurements results shows that the reduction process introduces significant electronic conductivity. Re-oxidation is relatively rapid in grains but is slower in the grain boundaries, the kinetics of which are dependent on the sample morphology.

References:

- [1] H.L. Tuller, A.S. Nowick, Doped Ceria as a Solid Oxide Electrolyte, *J Electrochem Soc* 122 (1975) 255–259.
 [2] E.A. Kuk, G. Heger, The Structures of $\text{C}+\text{Ce}_2\text{O}_3$, Ce_7O_{12} , and $\text{Ce}_{11}\text{O}_{20}$, *J Solid State Chem* 147 (1999) 485–500.

AQUEOUS SYNTHESIS OF SODIUM-IRON SULPHATES FOR NA-ION BATTERIES

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Developing large scale energy storage technologies is one of the main challenges of 21st century. Limited availability, vulnerability to political instability and high production costs limits the usage of lithium in large scale energy storage. To meet this challenge, usage of sodium instead of lithium was proposed. In our work we present synthesis of environmentally friendly, low cost and cobalt free cathode material based on polyanionic compounds based on sodium, iron, sulfur, and oxygen, which general formula can be presented as: $\text{Na}_{2+2y}\text{Fe}_{2-y}(\text{SO}_4)_3$. This material is based on low cost, commonly available resources and presents high redox potential (3.8 V vs. Na/Na⁺) and high energy density (>450 Wh/kg vs. Na/Na⁺), thus we expect it to be very promising in large scale energy storage technologies.[1]

The material was synthesized by dissolving substrates in deionized water in room atmosphere. Obtained mixture was then dried in vacuum and annealed at 350°C in reducing atmosphere (5 vol% H₂ in Ar). Structure was analyzed using X-Ray diffraction (XRD) and Raman spectroscopy. Chemical composition was studied using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Electrochemical performance of material was analyzed by assembling CR2032 cells with metallic sodium as counter electrode. Assembled cells were tested via cyclic charging and discharging under various current rates.

The synthesized materials present C₂/c structure. Observed bands refer mainly to carbon, which is presented in samples due to usage of organic antioxidants, which whereas providing reducing conditions also form carbon layer on material particles, which increases its conductivity. Antisymmetric stretching and bonding sulphate bands (around 465 cm⁻¹ and 635 cm⁻¹) are also present in Raman spectra. Materials charged to 4.2 V and discharged to 1.5 V present discharge capacity of 95 mAh/g at C/20. In long life tests material presents, charged to 4.2 V and discharged to 1.5 V, material presents capacity of 75 mAh/g at C/2. Material also presents coulombic efficiency of about 98% when charged/discharged at C/2 in the same voltage range as mentioned above.

The results confirm that sodium-iron sulphates can be very promising alternative for Li-ion batteries, especially due to their excellent long-term stability and low cost of resources used to obtain material.

This work was supported by The National Science Centre under project OPUS LAP nr 2021/43/ST8/01125.

References:

[1] A. Plewa, A. Kulka, E. Hanc, W. Zajac, J. Sun, L. Lu, J. Molenda, *J. Mater. Chem. A*, 2020, **8**, 2728

EFFECT OF DRY-MILLING COATING METHOD ON STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF LITHIUM IRON PHOSPHATE

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Lithium iron phosphate (LFP) is a cathode material for Li-ion batteries, which offers numerous advantages. These include good retention of gravimetric capacity in function of the subsequent charge-discharge cycles. Additionally, it consists of non-toxic elements which is beneficial for the environment. One of the challenges that this material presents is its incompatibility with one of the most well-known solid electrolytes: Li₇La₃Zr₂O₁₂ (LLZO). In comparison to liquid electrolytes, LLZO offers high thermal stability, low safety hazards and a wider electrochemical window. It also has fairly high ionic conductivity on the level of 10⁻³ S/cm at room temperature [1]. The incompatibility between LFP and LLZO is attributed to the high reaction energy (-1.75 eV/atom) between them [2]. The reaction of LFP and LLZO leads to the transformation of LLZO cubic structure to low conductivity tetragonal structure. However, it is implied in numerical papers [3] that there exists the possibility of coating application, which would result in a decrease of reaction energy between the cathode and electrolyte by forming a buffer layer.

There are a few methods of material coating, one of which is the dry-milling method, which is a simple and accessible process. In this work, we examine the impact of three coatings: LiNO₃, Li₂SO₄ and Li₃PO₄ on the electrochemical properties of LFP. The process is technically undemanding, but it has a lot of parameters that can be altered, like milling speed and time and amount of coatings. SEM images of pure and milled and coated LFP are shown on Fig. 1.

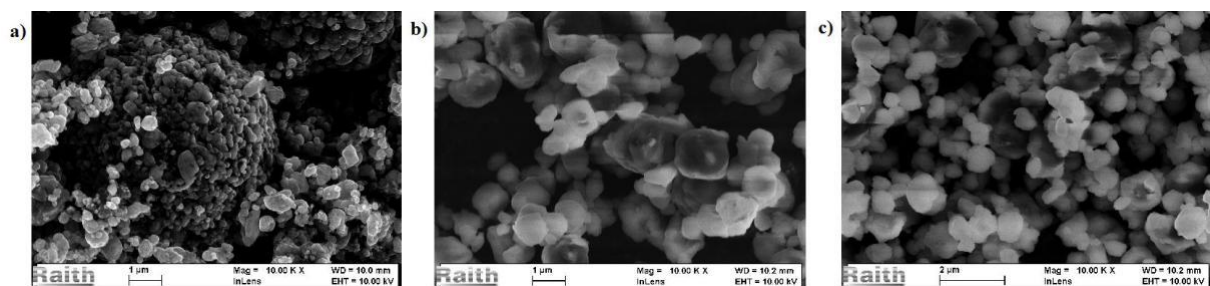


Figure 1. SEM images of a) pure LFP, b) pure LFP after the milling process and c) LFP milled with Li₂SO₄.

References:

- [1] M. M. Raju, F. Altayran, M. Johnson, D. Wang, and Q. Zhang, *Electrochem* 2(3) (2021) 390–414.
- [2] L. J. Miara, W. D. Richards, Y. Wang, G. Ceder, *Chem. Mater.* 27 (2015) 4040–4047.
- [3] A. M. Nolan, E. D. Wachsman, Y. Mo, *Energy Storage Mater.* 41 (2021) 571–580.

STABILIZATION OF DELTA-LIKE Bi_2O_3 PHASE AT ROOM TEMPERATURE IN NOVEL BINARY AND TERNARY OXIDE GLASS SYSTEMS CONTAINING Al_2O_3 , SiO_2 , GeO_2 , AND B_2O_3

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Bismuth oxide is an extremely interesting oxygen ion conductor. This compound exhibits rich polymorphism, and its high-temperature delta phase is characterized by record-breaking O^{2-} ion conductivity. It has been recently shown that the synthesis of bismuthate glass is possible, provided certain amounts of SiO_2 and Al_2O_3 impurities are introduced [1]. Nanocrystallization of such glasses leads to the stabilization of delta and beta phases at least down to room temperature, significantly below their stability range in bulk form [2].

In this research, we investigated the properties of bismuthate glasses synthesized with various glass-forming agents such as SiO_2 , GeO_2 , B_2O_3 , and Al_2O_3 . In particular, we investigated the glass-forming ability of four systems: Bi_2O_3 - SiO_2 , Bi_2O_3 - SiO_2 - B_2O_3 , Bi_2O_3 - Al_2O_3 - SiO_2 , and Bi_2O_3 - Al_2O_3 - GeO_2 . It was demonstrated that vitrification of all these systems is possible using a standard melt-quenching route.

Furthermore, the crystallization processes in the pristine glasses upon increasing temperature were investigated using thermal analysis and high-temperature XRD in-situ experiments. It was demonstrated that it is possible to stabilize crystallites isostructural with fluorite-type Bi_2O_3 . It appears that this phenomenon is not directly dependent on the valence or ionic radius of the additives. The foundations seem to be much more refined and may be related to the structure of the amorphous matrix.

References:

- [1] T.K. Pietrzak, J.E. Garbarczyk, M. Wasiucioneck, *Solid State Ionics* 323 (2018) 78-84.
- [2] T.K. Pietrzak et al., *Scientific Reports* 11 (2021) 19145.

PREPARATION OF ELECTRODES FOR ALKALINE WATER ELECTROLYZERS BY DIP- COATING OF CERAMIC PRECURSORS

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Due to the noticeable warming of the climate, researchers are seeking novel, low-carbon energy sources [1]. As a consequence, hydrogen generation technologies are becoming increasingly popular. The production of green hydrogen is possible, among other methods, through the utilization of water electrolyzers [2]. To maximize the efficiency of water electrolysis into oxygen and hydrogen, researchers are actively searching for new electrocatalysts to reduce the overpotential of this reaction [3],[4].

This research introduces a technique for preparing electrodes of alkaline electrolyzers. The process involves immersing nickel foam deeply in a precursor solution and depositing it onto the electrode surface using a heat curtain at the appropriate temperature. The objective of this study is to develop an effective and easily applicable method for commercial applications in the preparation of anodes for water electrolyzers. Although nickel foam is commonly used as an electrode material [5], its coating with materials like (La,Sr)CoO₃ opens up the possibility of significantly reducing the overpotential of the electrochemical water decomposition reaction. In this investigation, we devised a procedure for applying precursor layers, considering parameters such as temperature, the number of layers applied, and the composition of the precursor itself. The electrochemical properties of the prepared electrodes, in relation to the OER (Oxygen Evolution Reaction), were also assessed. Initial experiments indicated that the application of just one layer of material on nickel foam reduces the overpotential of the OER response by nearly 30 mV. To conduct a more comprehensive analysis, a structural examination of the test samples was also undertaken.

The method presented holds great promise for a substantial reduction in the OER overreaction rate and its potential use as a cost-effective and efficient approach in commercial applications, owing to its simplicity.

References:

- [1] M. Ligus. (2017), <https://doi.org/10.3390/en10101550>
- [2] S. Shiva Kumar,H. Lim. 2022, <https://doi.org/10.1016/j.egy.2022.10.127>
- [3] C.-T. Lu, Y.-W. Chiu, M.-J. Li, K.-L. Hsueh, J.-S. Hung. (2017), <https://doi.org/10.1155/2017/7494571>
- [4] F. Zeng, C. Mebrahtu, L. Liao, A. K. Beine,R. Palkovits. (2022), <https://doi.org/10.1016/j.jchem.2022.01.025>
- [5] D. E. Hall. (1985), <https://doi.org/10.1149/1.2113856>

DUAL DOPING FOR IMPROVED ELECTRONIC CONDUCTIVITY IN LITHIUM GARNET ELECTROLYTE $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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Currently, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) stands out as a promising solid electrolyte due to its high ionic conductivity up to 10^{-3} S/cm at room temperature and wide electrochemical stability window, offering a potential solution to some of the ongoing challenges in the development of solid-state lithium-ion batteries [1,2]. A desirable characteristic of a good electrolyte is as low electronic conductivity as possible. However, the evolution of next-generation composite electrodes challenges this norm by seeking both ionic and electronic conductivity. Dual doping LLZO's structure with transition metals (for example, niobium and praseodymium) facilitates electron conduction within the electrolyte structure. This intentional dual doping aims to facilitate ion-electron conduction in emerging composite electrodes, which consist only of an active material and a modified solid electrolyte [3].

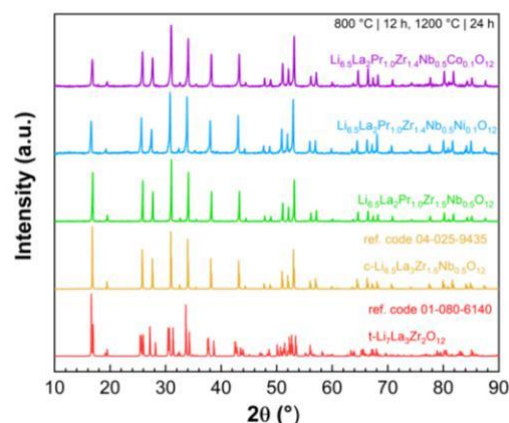
In this work we study the impact of cobalt (Co) and nickel (Ni) dopants on co-doped niobium (Nb) and praseodymium (Pr) LLZO. Figure 1 shows X-ray diffractograms of the investigated compositions: $\text{Li}_{6.5}\text{La}_2.0\text{Pr}_{1.0}\text{Zr}_{1.5-x}\text{Nb}_{0.5}\text{M}_x\text{O}_{12}$, where $\text{M}=\{\text{Co}, \text{Ni}\}$, and $x=\{0.0, 0.1\}$. Materials were prepared using a solid-state reaction method with calcination at 800°C for 12 hours, followed by sintering at 1200°C for 24 hours. Diffractograms indicate that this synthesis method yields single-phase materials with a well-formed regular structure.

Figure 1. XRD patterns for the LLZO electrolyte in the tetragonal and regular structure and the three samples $\text{Li}_{6.5}\text{La}_2.0\text{Pr}_{1.0}\text{Zr}_{1.5-x}\text{Nb}_{0.5}\text{M}_x\text{O}_{12}$ obtained, where $\text{M}=\{\text{Co}, \text{Ni}\}$ and $x=\{0.0, 0.1\}$

Acknowledgements: This work was conducted under support of National Science Centre, grant No. UMO-2019/33/B/ST5/02134.

References:

- [4] M. M. Raju, F. Altayran, M. Johnson, D. Wang, and Q. Zhang, *Electrochem* 2(3) (2021) 390–414.
- [5] A. Jonderian, E. McCalla, *Mater. Adv.* 2 (2021) 2846–2875.
- [6] A. J. Samson, K. Hofstetter, E. Wachsman, V. Thangadurai. *Journal of The Electrochemical Society* 165(10) (2018) A2303–A2311.



ANTIMONY-BASED ANODE MATERIAL MECHANISM ANALYSIS FOR NA-ION BATTERIES VIA OPERANDO AND EX-SITU METHODS

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Sodium-ion batteries are considered as an alternative system to Li-ion technology. One of the suggested anode materials is antimony due to its high theoretical capacity of $660 \text{ mAh}\cdot\text{g}^{-1}$ [1]. However, like all materials working via the alloying reaction, due to the huge volume changes (up to 293%), the pulverisation and microstructure degradation occur in the material during cycling, resulting in poor cyclability. The prospective strategy to overcome these obstacles is to reduce the size of the material or combine it with carbon or oxides.

In this work we present elucidation of the sodiation and desodiation mechanism of $\text{Sb/Sb}_4\text{O}_5\text{Cl}_2/\text{C}$, the composite material obtained by solvothermal reaction. In-depth analysis has been made via operando and ex-situ measurements: X-ray absorption spectroscopy at the L_3 -edge for Sb, scanning electron microscopy, Raman spectroscopy, and X-ray diffraction.

The pristine anode material is composed of rhombohedral antimony (R-3m space group), monoclinic phase of $\text{Sb}_4\text{O}_5\text{Cl}_2$ (P21/a space group) and nanometric amorphous carbon. Scanning electron microscopy revealed the presence of an extraordinary branch-like microstructure of antimony, which increases their volume together with sodiation and decreases in the opposite process. Comparison of the electrochemical results of the composite material together with pure Sb and pure $\text{Sb}_4\text{O}_5\text{Cl}_2$ has shown that both antimony-containing phases are electrochemically active. Through X-ray diffraction, Raman spectroscopy, and X-ray absorption spectroscopy measurements we define the sodiation mechanism in the composite material.

During the first sodiation reaction, conversion and alloying reactions occur forming the following phases: Na_3Sb , NaCl , and Na_2O . On the charge process, part of the material stays in the not completely desodiated state: NaSb phase. Interestingly, NaCl remains stable during the desodiation process and instead of $\text{Sb}_4\text{O}_5\text{Cl}_2$, a Sb_2O_3 phase is formed. The voltage curve of the second and further sodiation are similar with reversible sodiation to Na_3Sb and Na_2O . The composite material is characterised by good stability: after 100 cycles at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$ charge capacity is $508.5 \text{ mAh}\cdot\text{g}^{-1}$. The presented results contribute to the development of post-lithium-ion technology for energy storage.

Acknowledgements: This project is supported by the National Science Center Poland (NCN) based on decision number 2019/35/O/ST8/01799.

References:

- [1] J. He, Y. Wei, T. Zhai, and H. Li, *Mater. Chem. Front.* 2 (2018) 437–455

PVDF-HFP MEMBRANES WITH IONIC LIQUIDS AS A PLASTICIZER**K. Rogala¹, L. Niedzicki¹, M. Kasprzyk¹, A. Zalewska¹**

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In recent years, there has been a significant increase in interest in electric vehicles powered exclusively by lithium-ion batteries. However, widespread use of these batteries may pose a risk of electrolyte leakage, which could lead to ignition or explosion. Gel electrolytes have emerged as a potential solution to this problem, offering a combination of the benefits of both solid polymer electrolytes (SPE) and liquid electrolytes. Gel electrolytes have advantages such as high conductivity, high electrochemical stability and increased safety in the event of battery damage, as they are less susceptible to leakage. However, traditional gel electrolytes, membranes containing PVdF-HFP, have poor mechanical properties. To address this limitation, we have explored the use of ionic liquids as a plasticizing additive for membranes.

The research included the synthesis of membranes with different compositions of ionic liquids and PVdF-HFP, using acetone as a solvent. These membranes were analyzed using electrochemical, thermal and microscopic techniques. Differential scanning calorimetry (DSC) was used to test the thermal stability of the systems. The electrochemical stability of the membranes relative to the lithium anode was tested using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Additionally, conductivity measurements were carried out over a wide temperature range. All electrochemical tests were performed on a multi-channel potentiostat-galvanostat VMP3 by Biologic Science Instruments with the function of the frequency response analysis. The results show increased conductivity with no stability disadvantages, the details will be shown on poster.

INFLUENCE OF CHAIN LENGTH AND MATRIX BRANCHING ON THE PROPERTIES OF SHEAR THICKENING ELECTROLYTES FOR LITHIUM-ION BATTERIES

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Shear thickening fluids (STFs) are dense colloidal suspensions exhibiting an abrupt increase in viscosity with increasing shear rate. One of the main favorable features of STFs is that the process is reversible. They become solid-state under a sudden strike or impact. And when the strike or impact is removed, the STFs can turn back to their equilibrium properties. Due to their unique properties, they can be used as materials for sporting protective clothing and liquid body armor and other applications. The new concept is the use of electrolytes with the properties of shear thickening fluids, which could combine the advantages of liquid and solid electrolytes i.e., high conductivity of lithium ions and good mechanical properties [1,2,3]. Typical shear thickening systems consist of a continuous phase in the form of a polar solvent and a ceramic filler dispersed in it and possible additives. Aggregation of silica particles is an unfavorable phenomenon, and it is observed in typical electrolytes with low molecular weight carbonates. This leads to their sedimentation and deterioration of the rheological properties of the electrolyte. To prevent this, typical carbonate solvents can be replaced by polymers. This solution enables reduction of concentration gradient forms in the electrolyte volume. In addition, polymer components should allow elimination another serious problem, which is the high vapor pressure of organic solvents. This prevents an explosion and potential ignition of battery [4, 5].

We used as the matrix low molecular weight poly(ethylene glycols) (PEGs) due to their low melting point of the crystalline phase. Moreover, after adding the ceramic filler, they form shear thickening fluids. However, linear PEGs have relatively high melting point, so we replaced them with star-shaped oligomers. This allowed for lower the melting point of the compounds' crystalline phase. What's more, branched polymers typically exhibit lower viscosity compared to their linear counterparts, which can be beneficial for ionic conductivity. The star-shaped oligomers were synthesized via anionic polymerization by us. Potassium was reacted with the polyol to form a potassium alkoxide initiator. By using this type of reaction, we prepared well-defined product. The application of these star-shaped oligo(ethylene oxide) allowed us to obtain the shear thickening electrolyte, with a conductivity of approximately 10^{-4} S/cm at 40°C.

References:

- [1] Y.S. Lee, E.D. Wetzell, N.J. Wagner, *Journal of Materials Science* 38 (2003) 2825–2833.
- [2] J. Ding, T. Tian, Q. Meng, *et al. Sci Rep* 3 (2013) 2485.
- [3] Patent No.: PL 231979 B1.
- [4] B. H. Shen, B. L. Armstrong, M. Doucet, L. Heroux, J. F. Browning, M. Agamalian, W. E. Tenhaeff, G. M. Veith, *ACS Appl. Mater. Interfaces* 10 (2018) 9424–9434.
- [5] Patent No.: PL 243040 B1.

PHASE TRANSITIONS IN BISMUTH OXIDE BASED GLASS AT HIGH PRESSURES

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Bismuth Oxide is a promising superionic conductor for potential use in Solid Oxide Fuel Cells [1]. Our previous studies [2] on high pressure impact on electronic conduction of glassy materials has shown increase of electrical conductivity of 1-2 orders of magnitude with simultaneous reduction of activation energy.

In this study we performed preliminary research of high pressure thermal treatment on structural and thermal properties of Bi₂O₃-Al₂O₃-SiO₂ glass system in which Bi₂O₃ is a main glass former while Al₂O₃ and SiO₂ are glass forming additives. With use of unique on global scale technology glasses of such system were heated at increased pressure, which allowed for simultaneous DTA analysis and preparation of samples for XRD measurements. The pressure-thermal measurements were performed at 6 different semi-isobars that allowed us to observe glass transitions and subsequent crystallization peaks.

Cross-analyzing thermal data of XRD patterns allowed us to propose p-T plane of phase transitions what was published in [3]. Among detected phases were: supercooled liquid (above glass transition temperature), δ -Bi₂O₃ (desired superionic phase), β and γ phases of Bi₂O₃ (poor ionic conductors) and bismuth silicate Bi₂SiO₅ (ferroelectric phase). An explanation for formation of bismuth silicate has been proposed based on calculated densities of identified phases and material composition.

Acknowledgments: ASS, TKP, KS, MB, SJR and JEG were supported by the Polish National Science Centre through the grant no. 2022/45/B/ST5/04005.

References:

- [1] E.D. Wachsman, K.T. Lee, Lowering the temperature of solid oxide fuel cells, *Science* 334 (6058) (2011) 935–939, DOI: 10.1126/science.1204090
- [2] A. Szpakiewicz-Szatan, S. Starzonek, T.K. Pietrzak, J.E. Garbarczyk, S.J. Rzoska, M. Boćkowski, Novel high-pressure nanocomposites for cathode materials in sodium batteries, *Nanomaterials* 13 (2022) 164, DOI: 10.3390/nano13010164
- [3] A. Szpakiewicz-Szatan, T.K. Pietrzak, K. Sierakowski, M. Boćkowski, S.J. Rzoska, J.E. Garbarczyk, S. Starzonek, Nanocrystallization of Bi₂O₃ based system from the glassy state under high compression, *Materialia*, Vol. 33 (2024), DOI: 10.1016/j.mtla.2023.101975.

INFLUENCE OF DIFFERENT ATMOSPHERES ON THE OXIDATION OF FE-16CR FERRITIC STEEL MODIFIED WITH GADOLINIUM OXIDE, CERIUM OXIDE OR YTTRIUM-DOPED CERIUM OXIDE NANOPARTICLES

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Solid oxide cells (SOC) are one of the most useful means of storing or transforming energy. Single SOCs can be combined to form a stack using interconnects to yield an increased power output. The main issue with the use of ferritic steel based metallic interconnects is the increase in area-specific resistance (ASR). Most oxidation studies are conducted in air under isothermal conditions, but the atmosphere to which cells are exposed during real-life operation is a mixture containing hydrogen and water vapor.

For this study, an Fe-16Cr low-chromium ferritic stainless steel was used (brand name: Nirosta 4016/1.4016). To improve the resistance of this steel to high temperature oxidation, it was modified via dip coating or the electrolytic deposition of gadolinium oxide, cerium oxide and yttrium-doped cerium oxide ($\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_2$) nanoparticle layer. The oxidation experiments were carried out over 100 h in air, a mixture of air/ H_2O , and an $\text{H}_2/\text{H}_2\text{O}$ atmosphere at 1073 K. The structure, morphology and chemical composition of the oxidized samples were examined by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). The ASR of the layered steel/scale/coating systems was measured using a 2-probe 4-point DC method.

Oxidation studies showed that samples modified with gadolinium oxide, cerium oxide or yttrium-doped cerium oxide nanoparticles have better oxidation resistance than non-modified samples in all of the investigated atmospheres. This can be explained by the reactive element effect (REE), which reduces the thickness of the scale and improves its adhesion to the metal core.

Based on the obtained results, it was found that the Nirosta 4016/1.4016 ferritic steel modified with nanoparticles of gadolinium oxide, cerium oxide or yttrium-doped cerium oxide is suitable for the production of interconnects designed for SOC applications.

Acknowledgements: The corrosion investigations were supported by the program "Excellence Initiative – Research University" of the AGH University of Krakow, Grant ID 4138.

EXSOLUTION PROCESS IN CERIA DOPED WITH TRANSITION METALS – XAFS ANALYSIS

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Ceria-based compounds find a very wide range of applications in electrochemical devices such as solid oxide fuel cells, oxygen storage materials, oxygen sensors or catalysts of partial oxidation of hydrocarbons. The transport properties of CeO₂- δ compounds strongly depend on temperature, oxygen partial pressure, microstructure, and the presence of dopants and impurities. Such flexibility of properties makes them interesting candidates e.g. for catalytic materials working on the anode side of Solid Oxide Fuel Cells (SOFCs), significantly affecting the process of direct internal reforming of biogas and limiting the carbon deposition process on the fuel cell [1,2]. Ceria has also paid some attention due to the possibility of exsolving metallic nanoparticles to the surface of its grains. In this process occurring in reducing conditions, some cations from host compound are extruded in the form of nanoparticles on the oxide support. The exsolution method offers even distribution of particles as well as improved attachment to the host material [3]. Additionally, the exsolution process may be partially reversible, meaning the exsolved particles could be incorporated to the host lattice in the oxidative conditions [4]. Although the exsolution remains the hot topic and constant development in this field is observed, the research is mostly focused on the in situ growth of monometallic nanoparticles from perovskite-like structures. Only few experimental works on exsolution from fluorite structures can be found, and what is more, they have focused mostly on Ni-nanoparticles exsolution [5,6]. There is lack of systematic analysis of other types of transition metals exsolution depending on the process conditions.

In this study we focused on structural study of ceria-based compounds with general formula (Ce,Me)O₂- δ (where Me = Co, Cu, Fe, Mn, Ni) which were reduced in hydrogen atmosphere at various temperatures (900, 1000, 1100 °C) to force the exsolution process. For this purpose, we used hard X-ray and state-of-the-art technique such as X-ray Absorption Spectroscopy (XAS). A series of XAFS (X-ray Absorption Fine Structure) spectra at K-edges of Ce and transition metals were collected. Near-edge (XANES) and extended (EXAFS) range spectra analysis allowed to reconstruct the local structure of elements both in the as-prepared and reduced ceria, leading to a deeper understanding of the exsolution process in fluorite structures depending on the conditions of exsolution process, as well as a type of transition metal dopant. Moreover, the occurrence of cerium in the mixed valence state of Ce³⁺/Ce⁴⁺ was confirmed, what has a significant influence both on catalytic properties and on resistance to carbon deposition when this material is used as an anode for SOFC.

References:

- [1] B. Hołowko, P. Błaszczak, M. Chlipała, M. Gazda, S.-F. Wang, P. Jasiński, B. Bochentyn, *International J. Hydrogen Energy* 45 (2020) 12982-12996.
- [2] B. Bochentyn, M. Chlipała, M. Gazda, S.-F. Wang, P. Jasiński, *Solid State Ionics* 330 (2019) 47-53.
- [3] J.H. Kim, J.K. Kim, J. Liu, A. Curcio, J-S. Jang, Il-D. Kim, F. Ciucci, WCh. Jung, *ACS Nano* 15/1 (2021) 81-110.
- [4] Q.A. Islam, S. Paydar, N. Akbar, B. Zhu, Y. Wu, *J. Power Sources* 492 (2021) 229626.
- [5] A. Singhania, S.M. Gupta, *Nanotechnol.* 18/7 (2018) 4614-4620(7)

**EXPLORING THE ROLE OF CARBON NITRIDES
(MELEM, MELON, G-C₃N₄) IN ENHANCING PHOTOELECTROCATALYTIC
PROPERTIES OF TiO₂ NANOTUBES**

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Photoelectrocatalytic water splitting is one of the most promising artificial photosynthesis approaches to convert sunlight into sustainable hydrogen energy. A method of obtaining improved photocatalytic efficiency of photoanode toward water splitting is the use of titanium dioxide nanotubes (TiO₂-NTs) systems decorated with a cocatalyst. Unfortunately, most cocatalysts containing metal ions are not only hazardous but the amount of mineral resources of them, like Co minerals, is limited. Therefore carbon-based materials may be a competitor. The synthesis of such materials is complex and not cheap, but the yields are comparable. Here, we show how to easily obtain active material for Z-scheme photoanode formation namely carbon nitride (C_xN_y): melem, melon, and graphitic C₃N₄ on anodic titania nanotubes and how this construction enhances photoactivity towards oxygen evolution reaction (OER).

Titania nanotubes were obtained via anodization of Ti foil under specific conditions, followed by hydrothermal annealing in distilled water for 24 h at 100 °C [1]. The metal-free photococatalyst was prepared by thermal polycondensation of melamine powder in semi-closed conditions at two different temperatures: 400 °C and 525 °C for different times (3 hours, 12 hours) [2]. A heterojunction was attained by dip coating TiO₂-NTs in a Nafion /isopropanol/ distilled H₂O solution in a ratio of 1:5:14 containing 20 mg C_xN_y [3]. The obtained samples have been characterized using SEM, XRD, XPS, ATR-FTIR, and UV-Vis spectroscopy. All electrodes were tested using cyclic voltammetry, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) in the dark, and chronoamperometry (CA) under solar light illumination. Modified photoanodes show increased photocurrent generation compared to unmodified TiO₂ nanotubes. The band gap energy of a hybrid system has been decreased in comparison with pure TiO₂-NTs. The overpotential towards OER and flat band potential have been reduced. De-colorization of methylene blue (MB) shows significantly diminishing MB concentration over time.

Our experiment shows that the application of transition metal-free material for Z-photoanode formation is efficient towards photocurrent essential increase. The mechanism of hybrid photoanode activity will be discussed in the context of electronic band position.

Acknowledgements: Financial support from Gdańsk University of Technology by 17/2022/IDUB/III.4.1/Tc grant is gratefully acknowledged.

References:

- [1] Wtulich M., Szkoda M. Gajowiec G., Jurak K., Trykowski G., Lisowska-Oleksiak A., *Electrochimica Acta* 426 (2022) 140802.
- [2] Yan S. C., Li Z. S., Zou Z. G., *Langmuir* 25 (2009) 10397-10401.
- [3] Cheng F., Hainan W., Xiaoping D., *Chemical communications* 51 (2015): 7176-7179.

\ OPTIMIZING TiO₂ NANOTUBES PHOTOANODES ACTIVITY: INTERPLAY OF MECHANICAL AND ELECTROCHEMICAL PROPERTIES VIA HYDROTHERMAL ANNEALING

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The growing interest in the use of TiO₂ nanotubes (TiO₂-NTs) obtained by the anodization of titanium sheets outcomes from their application in photoelectrocatalytic processes involving water splitting [1]. The mechanical condition of the sheet metal used is crucial in the procedure of obtaining anodic TiO₂. All strains in the supporting material may affect the quality of the samples obtained and undergo specific mechanical interactions during crystal growth. The layer of nanotubes on a Ti substrate possesses mechanical properties that require control. The hydrothermal annealing (HA) method is a way to introduce beneficial changes in mechanical properties. Here, we focus on the correlation between mechanical properties introduced through HA and the photoelectrochemical activity of titania nanotubes.

The anodization of titanium foil in a 2-electrode cell, followed by calcination in the furnace (450 °C), was carried out to obtain crystalline TiO₂-NTs [2]. Further modification involved placing the material in a Teflon container, filled with distilled water, enclosed within a stainless steel reactor and subjecting it to the oven at different temperatures (75, 100, 125, 150, 175, 200 °C) for 24 hours to obtain HA TiO₂-NTs. XRD measurement confirmed the anatase crystal structure and also allowed us to calculate the microstrains and crystallite size of the tested samples, using Williamson-Hall analysis. It was observed that the linear fit of $B\cos\theta$ as a function of $\sin\theta$ is increasing, indicating that the stresses in the material were compressive. TiO₂-NTs without HA obtained the highest compressive stresses (150.95 ± 19.13 MPa). This phenomenon is explained by the uneven distribution of nanotubes that agglomerated into larger clusters. After HA 100 °C, the residual stresses decreased significantly, resulting in a more uniform distribution of nanotubes and nearly complete relaxation during the process. However, at higher temperatures, titania nanotubes get greater tensile stresses. The SEM images provide clear evidence of this calculation.

Furthermore, Raman, UV-Vis, and AFM spectroscopy were conducted to reveal the morphology and structure of TiO₂-NTs. Additionally, electrochemical and photoelectrochemical measurements were performed to investigate the correlation with mechanical properties. In summary, these results demonstrate that hydrothermal annealing enables the modification of an electrode material with enhanced photoactivity, improved adhesion, and reduced stresses compared to the starting material.

References:

- [1] Macak, J. M., Tsuchiya, H., Ghicov, A., Yasuda, K., Hahn, R., Bauer, S., Schmuki, P., *Current Opinion in Solid State and Materials Science* 11 (2007) 3-18.
- [2] Szkoda, M., Siuzdak, K., & Lisowska-Oleksiak, A. *Journal of Solid State Electrochemistry* 20 (2016) 563-569.
- [3] Wtulich, M., Szkoda, M., Gajowiec, G., Jurak, K., Trykowski, G., Lisowska-Oleksiak, A. *Electrochimica Acta* 426 (2022) 140802.

Na_{2.5}Fe_{1.75}(SO₄)₃ CATHODE MATERIAL FOR THE Na-ION BATTERIES**A. Milewska¹, W. Zając¹, M. Wolczko¹, J. Molenda¹**¹ Faculty of Energy and Fuels, AGH University of Krakow, al. A. Mickiewicza 30, 30-059 Krakow, Poland

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It is expected that Na-ion batteries may in the future provide an alternative to Li-ion batteries in large-scale power storage systems for storing energy from renewable energy sources and power plants. For this to happen, the development of low-cost technologies for producing electrode materials with high cell performance is needed. Na_{2.5}Fe_{1.75}(SO₄)₃ is a promising cathode material for sodium cells characterized by high Fe³⁺/Fe²⁺ redox potential equal 3.8 V vs. Na/Na⁺, monotonous charge/discharged curve between 3 and 4.5 V vs., high structural stability and large theoretical energy density. Also very important, this cathode material is based on earth-abundant and ecofriendly elements.

The poster contains the results of structural and electrochemical studies of the Na_{2.5}Fe_{1.75}(SO₄)₃ cathode material synthesized by reaction in solid state. Raman spectroscopy, FTIR spectroscopy and XRD studies confirmed the composition and structure of the synthesized material. Na_{2.5}Fe_{1.75}(SO₄)₃ forms alluaudite type structure with C_{2/c} symmetry [1]. Alluaudite type compounds can be written as AA'BM₂(XO₄)₃, where three different crystallographic positions: A, A' and B are occupied by sodium ions (Na1-B (4e), Na2-A (4b), Na3-A' (4e)) while M site is occupied by Fe (8f Wyckoff position) and X by S [2]. Activation energy of diffusion of Na⁺ ions varies for different structural positions of Na⁺ ions [3, 4]. Interestingly, an initial but irreversible Fe migration into the Na1 sites is also possible. Monotonic appearance of charging/discharging curves indicates for one-phase deintercalation/intercalation process of sodium ions in the operating voltage range. This is confirmed by in-situ XRD studies. Sharp peak in the differential galvanostatic dQ/dV profile at about 4 V measured upon the first charging process can be related to the migration of Fe³⁺ ions from the M sublattice to the Na1 crystal positions [4].

References:

- [1] J. Ming, P. Barpanda, S.I. Nishimura, M. Okubo, A. Yamada, *Electrochem. Commun.* 51 (2015) 19–22.
- [2] L.L. Wong, H.M. Chen, S. Adams, *Phys. Chem. Chem. Phys.* 17 (2015) 9186–9193.
- [3] A. Plewa, A. Kulka, D. Baster, J. Molenda, *Solid State Ionics*, 335 (2019) 15–22.
- [4] G. Oyama, O. Pecher, K. J. Griffith, Sh. Nishimura, R. Pigliapochi, C. P. Grey, A. Yamada, *Chem. Mater.* 28 (2016) 5321–5328.

INVESTIGATION OF THE IRON CONTAINING SrTiO_{3-x} POWDERS AS THE POTENTIAL CATALYSTS FOR NON-RECYCLABLE PLASTIC WASTES PYROLYSIS FOR HYDROGEN RECOVERY

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Pyrolysis is a promising method for energy recovery from plastics, because it doesn't require high chemical purity of wastes in contrast to mechanical recycling and is non-emissive. Nowadays pyrolysis of plastic wastes is mostly used for highly caloric pyrolysis oils production. One of the current trends is to maximize hydrogen and carbon yield to receive more sustainable fuel. Iron-based catalysts shows potential in this area. [1, 2]

In this work strontium titanate (STO) catalyst matrixes were synthesized using Pechini method, sintered at 1200°C for 12 h and enriched with iron in three different approaches: by milling with Fe_2O_3 provided by producer in ball mill, 2) by impregnating with iron nitrate and oxidized oxidizing to Fe_2O_3 , 3) exsolution of metallic iron nanoparticles from $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ matrix in reducing conditions. All materials were reduced in dry hydrogen atmosphere at 900°C for 10 h.

The phase composition of powders was determined using XRD method, whereas the microstructure was analyzed by SEM technique combined with EDS for chemical analysis. The specific surface area of samples was estimated using BET isotherm method. The XRD measurements confirmed a formation of preferred phases in all fabricated compounds. During reduction a formation of Fe metallic form was noticed, whereas the STO matrix remained in the primary form. The analysis of SEM images showed that achieved 0.5 - 1 μm STO grains agglomerated into structures even bigger than 10 μm . Reduction did not cause changes in the microstructure of samples. BET isotherm analysis showed absence of micro and mesoporosity. The greatest specific surface area equal to 10.7 m^2/g was achieved for Fe_2O_3 mixed with STO via ball milling. This specific compound presents the highest potential for plastic waste pyrolysis.

Acknowledgements: This work was supported by the 10th Polish-Taiwanese/Taiwanese-Polish Joint Research Project DWM/POLTAJ10/24/2023 "Solid Oxide Fuel Cell Using Non-Recyclable Plastic Waste as Fuel " granted by the National Centre for Research and Development of Poland and Ministry of Science and Technology of Taiwan.

References:

- [1] J. C. Acomb, C. Wu, P. T. Williams, Applied Catalysis B: Environmental 180 (2016) 497–510,
- [2] P.T. Williams, Waste and Biomass Valorization, 12 (2021) 1–28

