SSPC-20

LUND UNIVERSITY

Solid State Proton Conductors

27.9.-1.10.2021 Online Conference

Book of Abstracts

Organizers

Rotraut Merkle
Max Planck Institute for Solid State Research
Stuttgart, Germany

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Lund, Sweden

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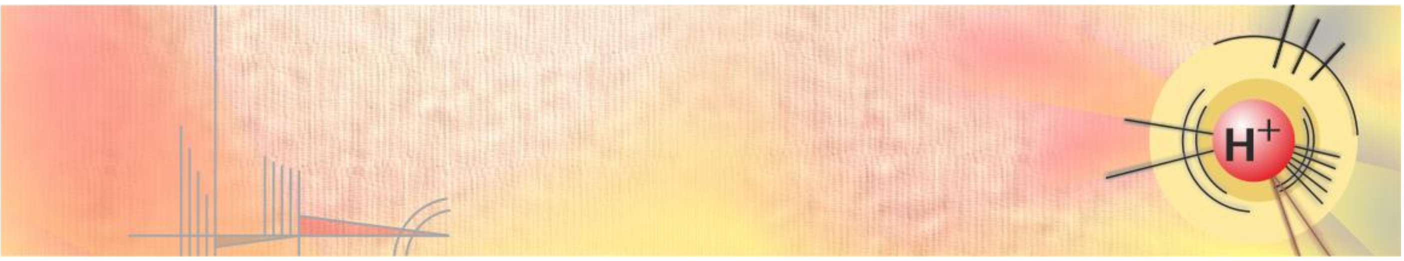

Dear SSPC-20 participants,

We are happy to welcome the Solid State Proton Conductor community for the SSPC-20 conference to continue the scientific exchange and discussion. Owing to the worldwide Covid-19 pandemic, SSPC-20 had to be cancelled in 2020 as many other conferences, and shifted to 2021. Since the Covid-19 situation is not finally overcome yet, as a specific exception we are operating SSPC-20 this year as an online conference.

The different time zones pose some challenge for the program. We allocated the keynote talks and some plenary discussion rounds in a central time slot 2-4 pm CEST, which allows for direct interaction with Asia and America. Further talks and the poster sessions are allocated in morning and afternoon session where still Europe and Asia, or Europe and America, overlap. All presentations are also available on-demand. As usual there will be a special issue in Solid State Ionics compiling papers from this conference.

We thank all contributors and participants for joining us in this exceptional format. Please generously use the various communication options - asking live questions after the talks, join the dedicated poster chatrooms, meet in public coffee break chatrooms, and contact participants in their individual rooms.

We received 117 abstracts from 18 countries, with a good mixture between experienced scientists and young colleagues entering the field. The conference has a strong focus on fundamental aspects of proton/hydroxide ion transport and defect chemistry. It spans the range to actual applications, and therefore also covers materials optimization, processing, and durability issues. Among polymers, anion exchange materials are a steadily growing field. In the group of inorganic materials, the understanding of protonic-electronic mixed conductors is strongly increasing. So there is a lot of achieved progress as well as still open and newly raised question to discuss.

We wish you a great SSPC-20 conference, and look forward to meeting you again in-person for SSPC-21 in 2023!

Rotraut Merkle and Patric Jannasch

September 2021

SSPC-20 online conference

Program Scheme

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo	Monday 27.9.21	Tuesday 28.9.21	Wednesday 29.9.21	Thursday 30.9.21	Friday 1.10.21	
		11	17	18		12-INV Miyatake	24-INV Joubert	Poster Session 2 *even numbers*	55-INV Yamazaki	11
		11:30				13-O Atanasov	25-O Kawamori		56-O Gazda	11:30
						14-O Nagao	26-O Winiarz		57-O Hyodo	
		12	18	19		15-INV Martinelli	27-INV Nazarenus	42-INV Henkensmeier	58-O Naumovska	12
								43-O Jankowska		
		12:30				16-INV N. Li	28-O Leonard	Poster Session 2 *odd numbers*	59-O Perrichon	12:30
		13	19	20		17-O F. Wang	29-INV Peng		60-O Makagon	13
						18-O H. Wei	30-O J.H. Kim		61-O Omata	
		13:30								13:30
					Introduction					
6	7	14	20	21	1-KN Tuckerman	19-KN Kreuer	31-KN Geneste	44-KN C. Bae	62-KN J.H. Lee	14
		14:30			2-KN O'Hayre	20-INV Di Noto	32-INV Matsumoto	Panel "General"	63-INV Haile	14:30
7	8	15	21	22		Panel "Polymer"	Panel "Inorganic"			15
								45-INV Di Vona	64-INV Takamura	
					3-INV Norby					
		15:30				21-KN Nibbering	33-KN Dekel	46-KN Amezawa		15:30
									Closing	
					Poster instruct.					
8	9	16	22	23						16
		16:30			4-INV Grimaud	Poster Session 1 *even numbers*	34-INV Madsen	47-INV Ricote		16:30
9	10	17	23		5-O Clemens		35-O Mossa	48-O Vollestad		17
					6-O Strandbakke		36-O Nederstedt	49-O Fontaine		
		17:30			7-O Raimondi	22-INV Benicewicz	37-O Q. Li	50-O Bretzler		17:30
						23-O Seselj				
10	11	18	24		8-INV Tsvetkov		38-O Safronova	51-INV Stange		18
						Poster Session 1 *odd numbers*				
		18:30			9-O Hoedl		39-O L. Wang	52-O Serra		18:30
					10-O Shin		40-O Dressler	53-O Kyriakou		
11	12	19			11-O Ivanova		41-O Laven	54-O Rorvik		19

Please check the online program for updates. Talks will be given live. To bridge the time zones, talk recordings (including questions+answers) and posters are accessible on demand for registered participants. All participants can be contacted in individual chat rooms.

Monday 27.9.2021 chairperson

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo		chairperson
					Introduction	R. Merkle, P. Jannasch
6	7	14	20	21	1-KN Tuckerman First-principles molecular dynamics investigations of proton and hydroxide transport in model PEM and AEM nanoconfined, low-hydration environments	
		14:30			3 -KN O'Hayre Scale-up and Progress in Protonic Ceramic Electrochemical Devices	
7	8	15	21	22	2-INV Norby Surface protonics of porous oxide ceramics	
		15:30				
					Poster session guidelines	
8	9	16	22	23		
						J. Serra
		16:30			4-INV Grimaud Mastering water/proton co-intercalation for designing better electrocatalysts	
					5-O Clemens Vacancy and anion ordering and its role for the stabilization of hydroxide-rich barium-based perovskite systems	
9	10	17	23		6-O Strandbakke Hydration and electrochemistry of A- and B-site substituted mixed conducting cobaltites	
		17:30			7-O Raimondi Trends in PCFC cathode materials: interplay of chemical, structural and electronic factors	
						R. Haugsrud
10	11	18	24		8-INV Tsvetkov Chemical expansion in proton-conducting materials	
					9-O Hoedl Proton uptake and defect interactions in mixed conducting BaxSr1-xFeO3-δ	
		18:30			10-O Shin Oxygen ion and proton transport in BaCo0.8-xFexZr0.1Y0.1O3-δ	
11	12	19			11-O Ivanova Y and Mn substituted BaZrO3 ceramics: material properties as a function of the substituents concentration	

1-KN First-principles molecular dynamics investigations of proton and hydroxide transport in model PEM and AEM nanoconfined, low-hydration environments

Tamar Zelovich,(1) Zhuoran Long,(2) Mark E. Tuckerman(1,2,3)

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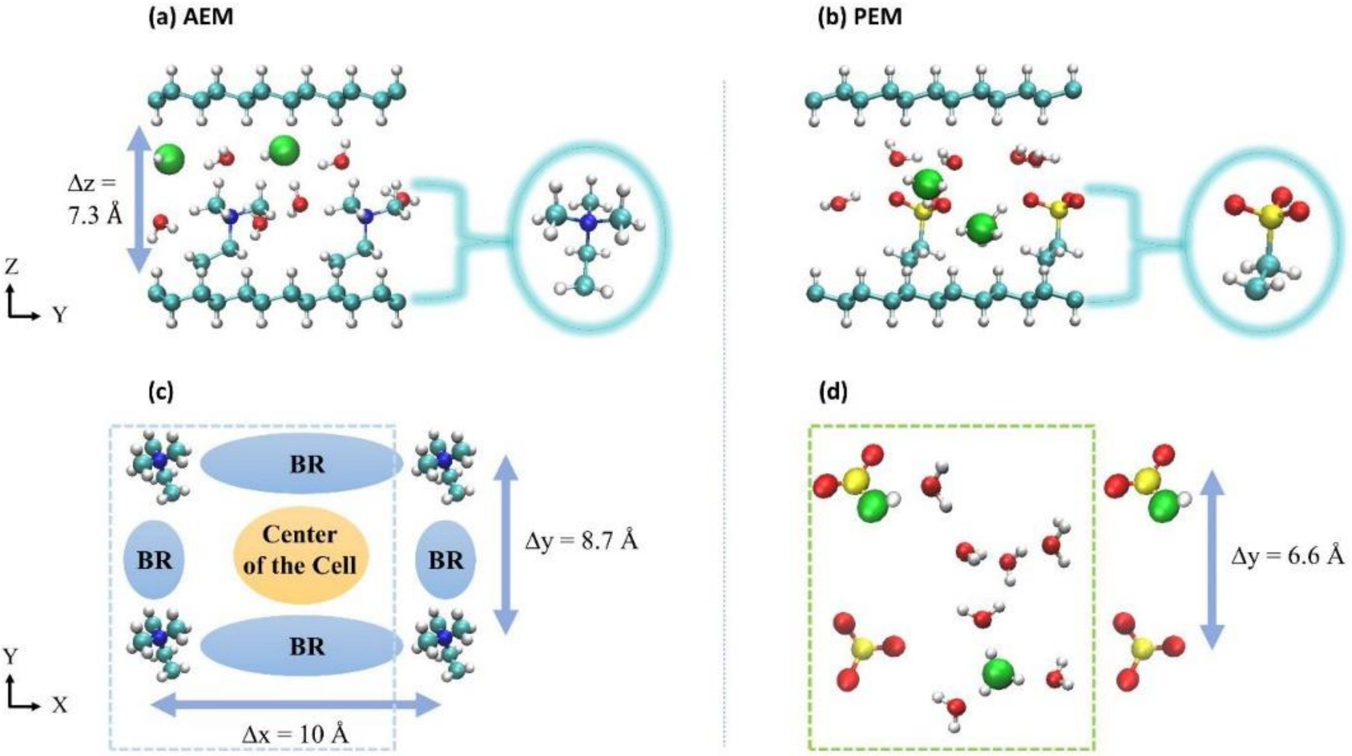
(2) Courant Institute of Mathematical Sciences, New York University, New York, USA
(3) NYU-ECNU Center for Computat. Chemistry at NYU Shanghai, Shanghai, People's Republic of China

Fuel cell-based anion-exchange membranes (AEMs) and proton exchange membranes (PEMs) have considerable potential as cost-effective, clean energy conversion devices. However, a fundamental atomistic understanding of the hydroxide and hydronium diffusion mechanisms in AEM and PEM environments is an ongoing challenge. In recent years, nano-confined structures have been exploited in the study of cost-effective and reliable polymer architectures for electrochemical devices. In this study, first-principles molecular dynamics simulations, in which interatomic forces are computed "on the fly" from electronic structure calculations, are employed to investigate the influence of the water distribution, temperature, and internal geometry on the diffusion rate of protons and hydroxide ions in nanoconfined geometries that serve as mimics of PEM and AEM environments. The simulations indicate that the water distribution is a determinative factor in the diffusion process. Moreover, it is found that hydroxide diffuison in AEMs is largely vehicular or a combination of vehicular and structural while proton diffusion in PEMs is largely structural. Pairs of cations in AEMs create bottlenecks for hydroxide diffusion while the anion groups in PEMs become active participants in proton diffusion. Finally, it is found that the temperature dependence of hydroxide diffusion in AEMs is non-monotonic, exhibiting a "kink" over a particular temperature range at which $\mathrm{d}D_{\mathrm{OH}^-}/\mathrm{d}T < 0$, a finding that is confirmed experimentally. Looking forward, we investigate the influence of the solvent chemistry on proton transport and propose new nanoconfined environments with the potential to enhance proton transport rates considerably using these liquids.



Monday 27.9.2021, noon session

2-KN Scale-up and Progress in Protonic Ceramic Electrochemical Devices

Ryan O'Hayre,(1) Neal Sullivan,(2) Rob Braun,(2) Bob Kee,(2) Long Le,(2) Carolina H. Hernandez,(2) Huayang Zhu,(2), Jake Huang,(1) Charlie Meisel,(1) Michael Pastula,(3) Tony Wood,(3) Eric Tang(3)

(1) Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, USA
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Because they can enable proton-mediated electrochemistry under both dry and wet environments at moderate temperatures, protonic ceramics provide unique opportunities to enhance or synergize a diverse range of complementary electrochemical and thermochemical processes. Because of this potential, significant efforts have been devoted to advancing numerous energy-related applications using these materials. Here, we will provide an overview of recent efforts at the Colorado School of Mines developing protonic ceramics for several applications, including hydrocarbon-tolerant fuel cells (PCFCs), protonic ceramic electrolyzers (PCECs) and protonic-ceramic electrosynthesis devices where electrolysis and thermochemistry are coupled to directly produce valuable fuels such as NH_3, CH_4, and C_2+ chemicals. In many applications, pressure is beneficial both for the thermodynamics of electrosynthesis as well as for the electrochemical cell performance, thus we will also present initial results in designing and operating PCECs at elevated pressures (up to ~20 bar). Finally, as protonic ceramics move closer to commercial application, we share our perspective in advancing protonic ceramic fuel cell (PCFC) technology from the small (<1 cm^2) laboratory button-cell scale to the large-area (81 cm^2) industrial manufacturing scale utilizing low-cost, volume-qualified processes with industrial partner Fuel Cell Energy (FCE). We will review progress and learnings achieved during this scale-up initiative, highlighting areas where key risks have been mitigated as well as areas of ongoing concern.

Monday 27.9.2021, noon session

3-INV

Surface protonics of porous oxide ceramics

Truls Norby
Department of Chemistry, University of Oslo, Oslo, Norway

Protonic conduction in adsorbed water on the internal surfaces of nanoporous ionic solids is receiving much interest due to its importance for insulation, catalysis and electro- and photocatalysis, and potential role in electrochemical energy conversion devices. However, the interaction with bulk transport and native charge carriers, the adsorption of different layers of water on different materials and crystal facets, and the different migration mechanisms of different protonic charge carriers make the matter very complex, preventing interpretation and parameterisation of experimental data. We present a unified nomenclature and physicochemical model of adsorption, dissociation, and proton conduction of chemisorbed water, followed by physisorption into solid-like and liquid-like layers and protonic conduction by Grotthuss and vehicle mechanisms in these. We furthermore offer simple models for the effects of grain size and porosity, discuss origins of dual time constants in impedance spectra, and the difficulty to make reversible electrodes. Results under publication and ongoing measurements on TiO_2, ZrO_2, and CeO_2 are used for illustration and examples of parameterisation.

Acknowledgement. This work is in part supported by The Research Council of Norway (projects 280868 SUPROX and 257653 MoZEES).

4-INV Mastering water/proton co-intercalation for designing better electrocatalysts

Alexis Grimaud

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(2) Réseau sur le Stockage Electrochimique de l’Energie (RS2E), CNRS Fr3459, Amiens, France

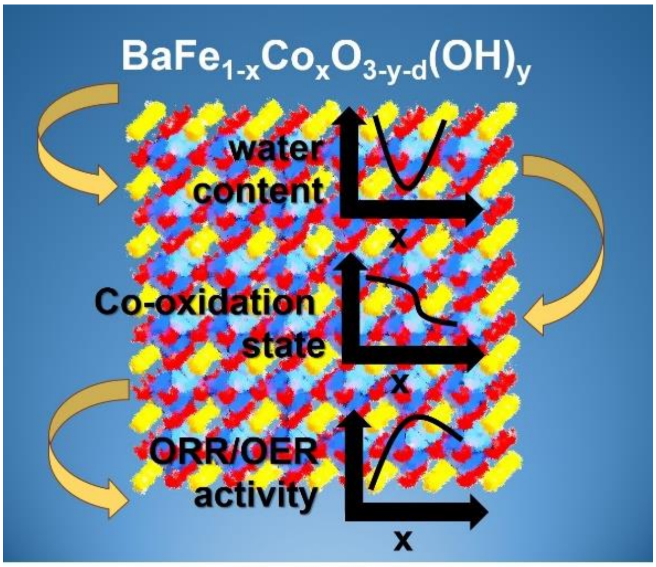
While the quest for new electro-active materials has led to the rapid development of energy storage and conversion devices such as Li-ion batteries, fuel cells, electrolyzers etc., their integration into a practical device relies on mastering the interface forming with the ionic conductor used as electrolyte. To understand the ions and electrons exchange occurring at such complex interface, methodologies must be developed. This is especially true for the solid/liquid interface which is found dynamic as a function of time, space, applied potential etc. Recently, searching for novel transition metal oxides as active oxygen evolution reaction (OER) electrocatalysts in both alkaline and acidic conditions, our group has uncover a new class of catalysts which activity and stability rely on the reversible exchange of hydrated cation/protons. Such finding, counter-intuitive at first for a reaction which should be confined to the solid/liquid interface and not involve the bulk of the catalysts, offer promising opportunities to develop novel catalysts with better performances. In this talk, emphasis will be paid on the driving force for such co-intercalation and diffusion processes in bulk of transition metal oxides. The strength of water-cations interaction, kinetics for desolvation at the solid/liquid interface and the role of the catalyst crystallographic structure on triggering this novel mechanism will be discussed. Drawing a parallel with the diffusion of protons in solids for high temperature applications, design principles will be given for the design of better OER catalysts.

5-O Vacancy and anion ordering and its role for the stabilization of hydroxide-rich barium-based perovskite systems

Oliver Clemens

Institute for Materials Science, University of Stuttgart, Germany

Barium-based perovskites have potential use in many applications, among them proton conductors (e. g., $BaZr_{1-x}Y_xO_3$) or electrode catalysts (e. g., $BaFe_{1-x}Co_xO_{3-y-d}(OH)_y$. In this contribution, the role of vacancy ordering for barium cobaltates and ferrates on the stabilization of hydroxide-rich perovskite phases and their electrochemical performance within alkaline fuel cells will be highlighted. Special emphasis will be given on how mixed valent oxidation states can be obtained for the different transition metals, together with structural relaxations occuring on heating under different atmospheres on hydrated and non-hydrated systems.



6-O

Hydration and electrochemistry of A- and B-site substituted mixed conducting cobaltites

R. Strandbakke,(1) S. Saeed,(1) S. Wachowski,(3) M. Balaguer,(4) A. Carrillo,(4) I. Szpunar,(3)
A. Mielewczyk-Gryń,(3) T. Miruszewski,(3) H. Andersen,(1) V. Øygarden,(2) E. Vøllestad,(2) T. Norby(1)

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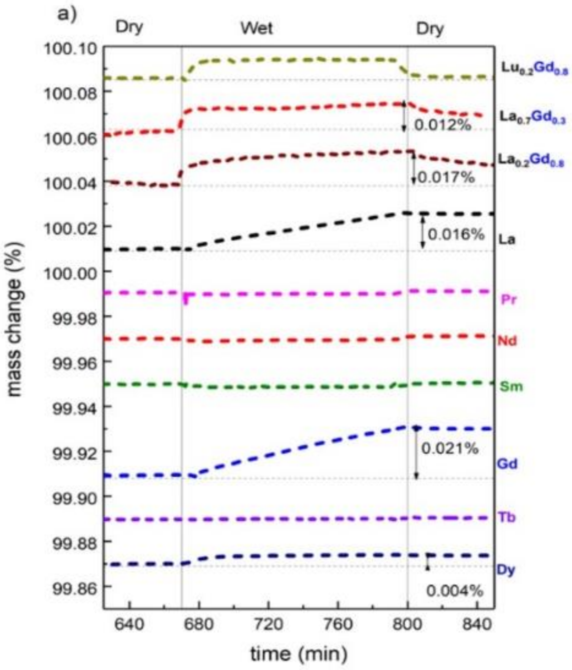
Mixed Proton and Electron conducting Ceramics (MPEC's) are central in the development of efficient electrodes for Proton Ceramic Electrochemical Cells. Mass transfer overpotential is limiting the electrode performance, and the interplay between catalytic activity and the inherent partial proton conductivity determines the electroactive surface. The electronic conductivity is important for low ohmic overpotential, but mobile electronic defects also affects proton stability. The stability of protons correlates with anion basicity, and electron structure and mobility is therefore essential with respect to both red-ox activity and partial proton conductivity. Perovskite A- and B-site substitutions are investigated for proton concentration and electrochemical performance in Ba- and La-based cobaltites. Thermogravimetric Analysis (TGA) has been used to investigate proton concentrations, and Electrochemical Impedance Spectroscopy (EIS) was used to investigate polarisation resistance of the positrode reactions for model electrodes and porous electrodes. In order to investigate the positrode in both anodic and cathodic operation, the EIS studies has been performed under positive and negative DC bias, and the results reveal that B-site substitutions affect water oxidation and oxygen reduction differently. Substituting Ti^{4+} for Co^{3+} in a $BaLa_{0.8}Gd_{0.2}Co_2O_{6-\delta}$ electrode promotes the anodic water oxidation reaction, while substituting Zn^{2+} for Co^{3+} impedes the anodic reaction.

Acknowledgements: The Research Council of Norway (Grant nº 272797 "GoPHy MiCO" and nº 299736 "FunKey Cat")



Selected $BaLnCo_2O_{6-\delta}$ – hydration at 300°C

Monday 27.9.2021, afternoon

7-O

Trends in PCFC cathode materials: interplay of chemical, structural and electronic factors

Giulia Raimondi,(1) Rotraut Merkle,(1) Maximilian Hoedl,(1) Francesco Giannici,(2) Alessandro Longo,(3) Joachim Maier(1)

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(3) European Synchrotron Radiation Facility, ID20, Grenoble, France

(Ba,Sr,La)(Fe,Co,Zn,Y)$O_{3-\delta}$ perovskites with mobile oxygen vacancies, holes, and protons can be used as cathode for protonic ceramic fuel cells. Their proton uptake via hydration (acid-base reaction) was determined by thermogravimetry for different cation composition.[1,2] A-site substitution with Sr,La lowers proton uptake by decreasing the material basicity and/or oxygen vacancy content. Partial substitution of Fe by redox-inactive and oversized Zn^{2+} or Y^{3+} increases the proton concentration. This can be attributed to local lattice distortions (buckled B-O-B bonds) decreasing the covalency of Fe-O bonds and thus enhancing the basicity of the oxygen ions. The local environments of cations and of O^{2-} anions are probed using EXAFS (Fe,Zn,Y K-edges) and XRS (O K-edge). The rather small Fe edge shift between reduced and oxidized samples and the pre-edge features at the O K-edge indicate that electron holes are largely delocalized over oxygen states.[3] The degree of the hole transfer from iron to oxygen depends sensitively on cation composition and distortions. B-site doping with first row transition metals leads to an anti-correlation of proton concentration and electronic conductivity (Cu being a positive outlier). Owing to the complex interplay of chemical, geometrical, and electronic structure, some properties are conflicting with each other, and their detailed understanding is necessary for further PCFC cathode material optimization.

[1] R.Zohourian et al. Adv.Funct.Mater. 28 (2018) 1801241
[2] R.Merkle et al. Ann.Rev. 51 (2021) 461
[3] G.Raimondi et al. Chem.Mater. 32 (2020) 8502

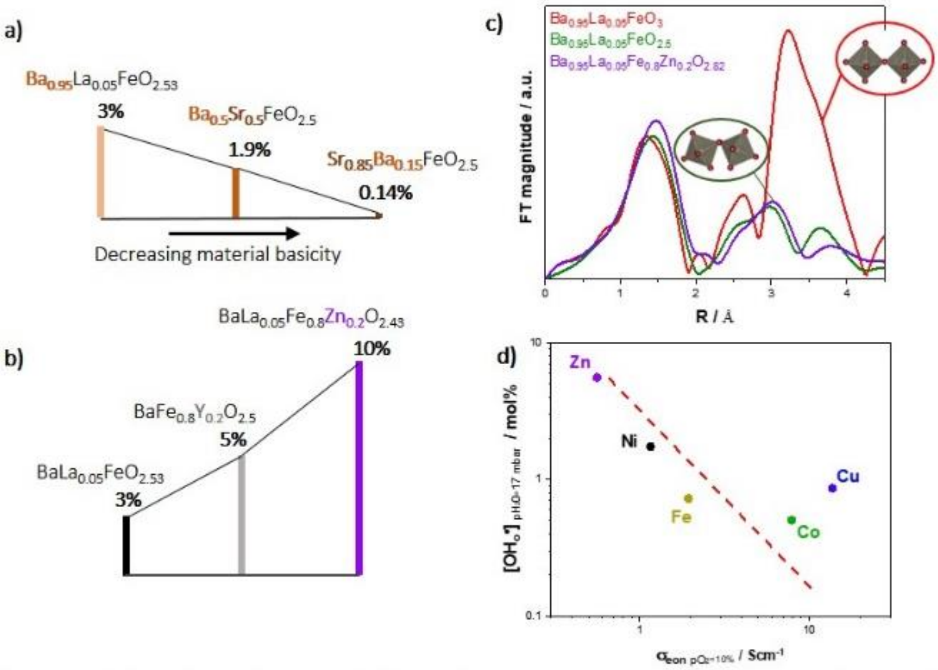


Figure 1. Effect of (a) A- and (b) B-site doping. Proton uptake measured at 250 ºC in 17 mbar pH_2O (c) Fourier Transform modulus (Fe K-edge) of B-site undoped oxidized, reduced and Zn-doped oxidized samples. (d) proton concentration vs σ_{eon} of $Ba_{0.95}La_{0.05}Fe_{0.8}(TM)_{0.2}O_{3-\delta}$ (TM=Co, Ni, Cu, Zn) measured at 400 ºC.

Monday 27.9.2021, afternoon

8-INV

Chemical expansion in proton-conducting materials

Dmitry Tsvetkov, Vladimir Sereda, Dmitry Malyshkin, Ivan Ivanov, Andrey Zuev

Ural Federal University, Ekaterinburg, Russia

In broad terms, chemical strain, or chemical expansion of solids can be defined as the change in their dimensions following any change in their composition. The latter may vary in situ with changing external parameters, such as temperature and composition of the gas atmosphere. For the oxides, chemical expansion started to be intensively investigated only after they had found their applications in such electrochemical devices as oxygen-permeating membranes and solid oxide fuel cells (SOFCs). They function at high temperatures and in varied pO_2 and pH_2O, so the nonstoichiometric oxides in these devices have an opportunity to exhibit chemical expansion due to the oxygen and water vapor exchange in operando. Undoubtedly, such an undesired chemical expansion may be detrimental to the mechanical integrity of an SOFC or a membrane, which underlines the necessity for its research. Much work has been done in this field for some fluorite oxides and perovskites, which are the state-of- the-art oxygen-conducting electrolyte and cathode materials for SOFC, respectively. We have recently proposed a simple model of chemical expansion upon hydration and/or oxidation of mixed conducting oxides. This is based on the defect chemical approach and allows quantitative estimation of the chemical expansion coefficient of an oxide provided that its defect thermodynamics is known. Results of extensive application of the proposed model to various technologically relevant oxide materials belonging to fluorite and perovskite families will be discussed during the presentation.

9-O

Proton uptake and defect interactions in mixed conducting $Ba_xSr_{1-x}FeO_{3-\delta}$

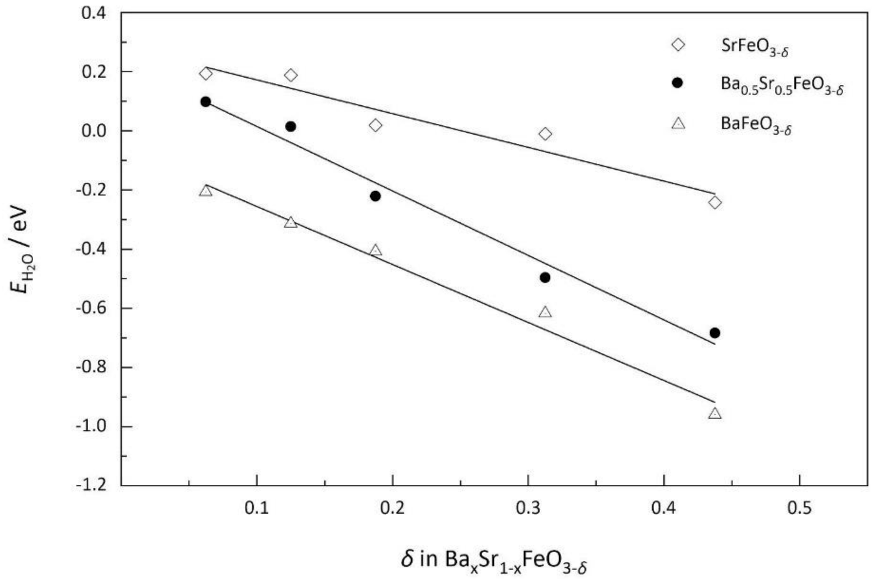
Maximilian F. Hoedl, Rotraut Merkle, Eugene Kotomin, Joachim Maier
Max Planck Institute for Solid State Research, Stuttgart, Germany

$Ba_xSr_{1-x}FeO_{3-\delta}$ perovskites are characterized by a mixed electronic-ionic conductivity, in which the ionic conductivity is realized by mobile oxygen vacancies and proton interstitials. The presence of three different charge carriers imparts exceptional properties to these materials with promising application in fuel and electrolyzer cells. However, experimental evidence [1] indicates that the charge carrier concentrations are highly correlated and affected by complex defect interactions.

Here we use density functional theory within a PBE+U approximation, to clarify the nature of these defect interactions. We analyze the electronic structure of $Ba_xSr_{1-x}FeO_{3-\delta}$ in terms of local atomic orbitals and calculate the energetics of oxygen vacancy formation and hydration in the oxygen non-stoichiometry range $0 < \delta < 0.5$.

The electronic structure of $Ba_xSr_{1-x}FeO_{3-\delta}$ is characterized by the so-called d^5L configuration (L = ligand hole), i.e., electron holes are largely transferred to the oxygen ions, rendering them the predominant red-ox active species. Oxygen vacancies are formed at the expense of these holes and consequently affect the properties – charge and ionic radius – of the oxygen ions in the crystal. The energetics of proton uptake strongly depends on these properties. The calculations show that the hydration energy becomes more negative, from e.g., ≈0 eV in $BaFeO_3$ to ≈-1 eV in $BaFeO_{2.5}$, hence, with increasingly negatively charged oxygen ions (Fig. 1).[2]

[1] R. Zohourian et al. Adv. Funct. Mater. 28, 1801241 (2018)
[2] M.F. Hoedl et al. J. Phys. Chem. C 124 11780 (2020)



Hydration enthalpy in $Ba_xSr_{1-x}FeO_{3-\delta}$ as function of oxygen stoichiometry

10-O

Oxygen ion and proton transport in $BaCo_{0.8-x}Fe_xZr_{0.1}Y_{0.1}O_{3-\delta}$

Yewon Shin,(1) Michael Sanders,(1) Steve Harvey,(2) Michael Walker,(1) Ryan O'Hayre(1)

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$BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY4411) has been appreciated as a promising protonic ceramic fuel cell (PCFC) cathode material due to its good electrochemical activity and its ability to support simultaneous triple-conduction of protons, oxygen, and electron holes. The low-activation energy for proton migration enables a decrease in the operating temperature while heavy transition metal doping ensures adequate electrical conductivity and electrochemical reactivity. Moreover, the multiple oxidation states of Co and Fe assist the electrocatalytic and redox ability of BCFZY4411. Despite the critical role of Co and Fe doping in BCFZY4411, the BCFZY compositions with various Co/Fe ratios have not been studied yet. For further support of the use of this material in applications, kinetic studies of the surface reaction and bulk transport are needed. In this work, we apply the isotope exchange technique to decouple and quantify oxygen ion transport in selected compositions of $BaCo_{0.8-x}Fe_xZr_{0.1}Y_{0.1}O_{3-\delta}$ and proton transport in BCFZY4411. 16O/18O and H_2O/D_2O line-scanning analyses were performed by ToF-SIMS to determine the tracer diffusion coefficients and surface exchange parameters. This work provides critical knowledge of the surface kinetics and bulk diffusion of oxygen ions and protons in BCFZY4411, thereby enable optimization and modeling of these materials for various applications. Also, we find that the surface kinetics and bulk diffusion of oxygen tracer strongly depend on Co/Fe ratio. It is our intent to suggest promising BCFZY compositions for further PCFC cathode development.

11-O

Y and Mn substituted $BaZrO_3$ ceramics: material properties as a function of the substituents concentration

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Norbert H. Menzler,(1) Olivier Guillon,(1,6)

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(2) Instituto de Tecnología Química, UPV - CSIC, Valencia, Spain
(3) Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
(4) JCNS-1, Forschungszentrum Jülich GmbH, Jülich, Germany
(5) Department of Microstructure and Residual Stress Analysis, HZB GmbH, Berlin, Germany
(6) JARA-Energy, Jülich, Germany

Innovations in material science are the key element for solving technological challenges. Various energy and environmental applications require designing materials with tailored compositions, microstructures and specific target-oriented performance. Y and Mn co-substituted $BaZrO_3$, e.g. $BaZr_{0.85}Y_{0.15}Mn_{0.05}O_{3-\delta}$ (BZYM5), has previously attracted attention as a membrane material for H_2 separation from gas mixture due to its mixed proton-electron conductivity leading to appreciable levels of H_2-flux at elevated temperatures and its good thermo-chemical stability under reducing environments. This material might serve additionally as a mixed-conducting electrode in proton conducting fuel and electrolysis cells (PCCs). In the present work, we developed ceramic materials within the $BaZr_{0.8}Y_{0.2-x}Mn_xO_{3-\delta}$ series, where x =0.02, 0.05, 0.10, and studied systematically their functional properties in dependence of the Y-to-Mn ratio, including thermal behaviour, hydration and electrical properties. In addition to that, near edge X-ray absorption fine structure spectra (NEXAFS) in the vicinity of O K-edge and Mn L2,3-edges was carried out for selected BZYM specimens to collect information on oxidation states and surrounding symmetry of Mn atoms in surface- and bulk-sensitive modes. Finally, we studied proton diffusion in hydrated BZYM samples using quasielastic neutron scattering (QENS). Two distinct dynamic processes were observed above 300 °C. We will present a model for atomic scale proton diffusion in these materials, and we will discuss how Mn doping influences the proton diffusion.

Tuesday 28.9.2021

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo	
					V. Di Noto
		11	17	18	12-INV Miyatake Polyphenylene ionomer membranes: effect of reinforcement
		11:30			13-O Atanasov Poly(pentafluorostyrene) functionalizations to polyelectrolyte
					14-O Nagao High Proton Conductivity in Organized Polymer Structure
		12	18	19	15-INV Martinelli Novel proton conductors based on protic ionic liquids
					K. Miyatake
		12:30			16-INV N. Li Anion Exchange Membrane with Bulky Organic Cations for Alkaline Fuel Cells and Electrolyzers
		13	19	20	17-O F. Wang Relations of OH- Conductivity and Water Uptake of Anion Exchange Ionomer
					18-O H. Wei Side-chain engineering strategy enabling poly(arylene alkylene)-based exchange membranes with phase-separated morphology and improved conductivity
		13:30			
					T. Norby
6	7	14	20	21	19-KN Kreuer Beyond Nafion and other PFSAs: Custom made proton conducting membranes and ionomers based on sulfonated poly-phenylene-sulfones s-PPS
		14:30			
					20-INV Di Noto The Electrical Response and Conductivity Mechanism in Hybrid Membranes for Electrochemical Applications
7	8	15	21	22	Panel "Polymer"
		15:30			21-KN Nibbering Probing elementary steps of proton transport pathways with ultrafast infrared and soft-X-ray spectroscopy
8	9	16	22	23	
		16:30			Poster Session 1
9	10	17	23		*even numbers*
					L. Madsen
		17:30			22-INV Benicewicz New Developments in Polybenzimidazole (PBI) Membranes for Electrochemical Devices
10	11	18	24		23-O Seselj Fabrication and Optimization Routes of Novel Polymer Electrolyte Membrane Electrolysis Cells
					Poster Session 1
		18:30			*odd numbers*
11	12	19			

12-KN

Polyphenylene ionomer membranes: effect of reinforcement

Kenji Miyatake(1,2)

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(2) Department of Applied Chemistry, Waseda University, Tokyo, Japan

We have developed a series of sulfonated polyphenylene (SPP) ionomer membranes for fuel cell applications. Due to the absence of heteroatom linkages, such as ether and sulfone groups, the membranes exhibited highly oxidative stability as well as proton conductivity. To improve the mechanical stability and durability in operating fuel cells, we designed reinforced membranes composed of the polyphenylene ionomer and a flexible porous polyethylene support layer. Using unique push coating method, dense, uniform, transparent, and thin reinforced membranes (SPP-QP-PE) were obtained. For the reinforced membranes, high ion exchange capacity (IEC) SPP-QP was adopted to achieve high proton conductivity and accordingly, high fuel cell performance even at low humidified conditions (at 80 °C and 30% relative humidity), which had not been attainable with the existing reinforced aromatic ionomer membranes. The flexible porous PE substrate improved the mechanical toughness of the membranes; the elongation at break increased by a factor of 7.1 for SPP-QP-PE compared with the parent SPP-QP membrane. The mechanical durability of the reinforced membrane was proved in wet/dry cycle test under practical fuel cell operating conditions according to the United States Department of Energy (USDOE) protocol. The reinforced SPP-QP-PE membranes exhibited balanced proton conductivity, mechanical strength, and gas impermeability, and therefore functioned well in fuel cells with high performance and durability.

13-O

Poly(pentafluorostyrene) functionalizations to polyelectrolyte

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Yu Seung Kim(3)

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(IEK-11), Erlangen, Germany

This talk will give an overview on preparation, properties and applications of polyelctrolytes based on functionalized poly(pentafluorostyrene) (PPFS). To convert this polymer to polyelectrolyte, functionalyzation with both acid (phosphonated and sulfonated) and base (mercaptotetrazole and guanidine) functional groups is going to be presented. Properties related to applications and cell performances in low and high temperature fuel cell (LT- & HT-PEMFC) and vanadium redox flow batteries (VRFB) will be shown.

The accent of the talk will be on the phosphonated poly(pentafluorostyrene) (PWN) [1–3]. This polymer showed high resistance to anhydride formation at temperatures up to 240°C. Because of the low phosphonation degree and the relatively low conductivity of the phosphonic acid in comparison with sulfonic acid, PWN is not suitable as an electrode separator for the fuel cell application. However, due to its stability at elevated temperature, PWN is applicable as a catalyst binder in HT-PEMFC. The best peak power density of 1.74 W cm^{-2} was obtained at 240°C for MEA having ion-pair PEM and PWN as a catalyst binder (Fig. 1). Durability tests last for more than 500 hrs with voltage decay rate of 0.35 µV h^{-1} at a constant current density of 0.6 A cm^{-2} at 160°C.

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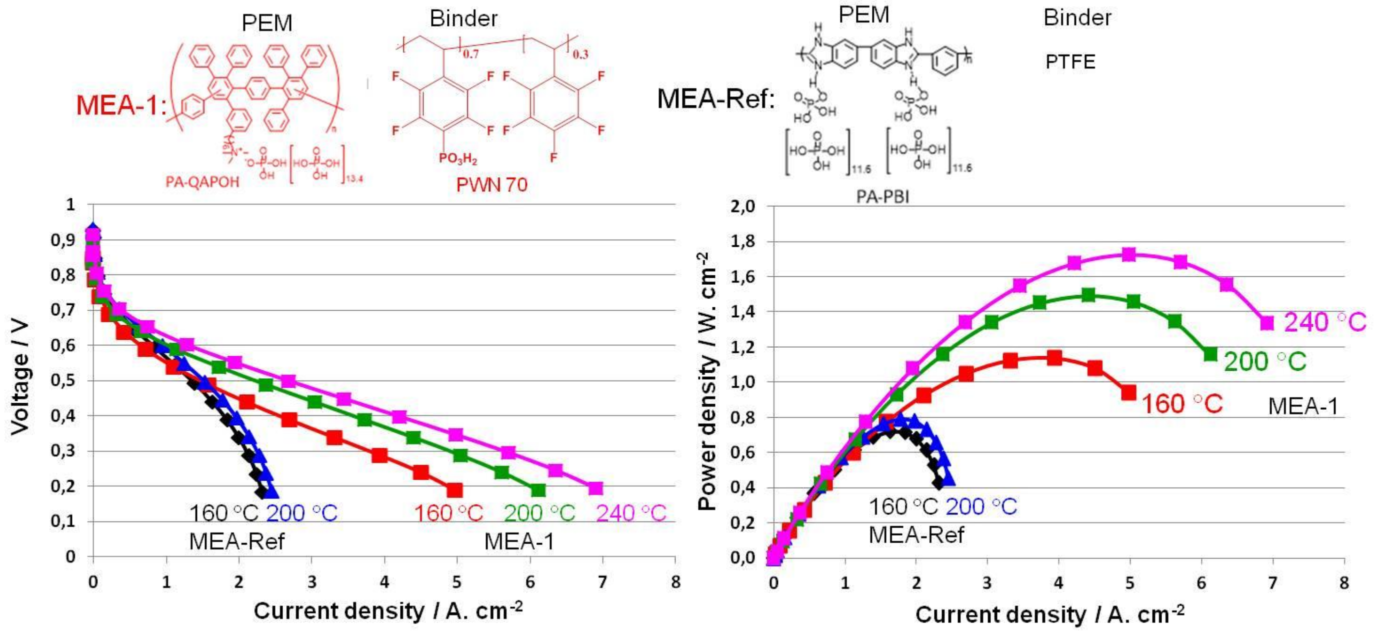

Figure 1. Polarization curves of MEA-1 with PWN as catalyst-binder and commercial MEA-Ref at 160-240°C

14-O

High Proton Conductivity in Organized Polymer Structure

Yuki Nagao,(1) Mitsuo Hara,(2) Shusaku Nagano(3)

(1) Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan
(2) Nagoya University, Fro-Cho, Chikusa, Nagoya, Japan
(3) Rikkyo University, Nishi-Ikebukuro, Toshima, Tokyo, Japan

Highly proton-conductive polymers have long attracted the attention of researchers for use in energy conversion, sensors, catalysts, and other applications. From the viewpoint of scientific history of creating highly proton-conductive polymers, one fundamental approach is based on the strategy of phase-segregated structures with strong acid groups. Wegner and co-workers reported on lyotropic liquid crystalline (LC) property using rigid main chains to have an organized structure.[1] The origin of the lyotropic LC property originates from the fact that the main chains are aligned in one direction because of the excluded volume effect of the main chain in the solvent. Based on their pioneering study, our group has demonstrated organized structure thin films with high proton conductivity using lyotropic LC property since 2014.[2,3] Organized structure is anticipated as more promising approaches than conventional less-molecular-ordered structure to elucidate mechanisms of high proton conduction. Alkyl sulfonated polyimides (ASPIs) are a promising candidate because they have not only high solubility because of the high polarity of the sulfonic acid groups at the side chains but also rigid and rod-shaped main chain. In this work, high proton conductivity and organized lamellar structure of ASPIs thin films would be discussed.

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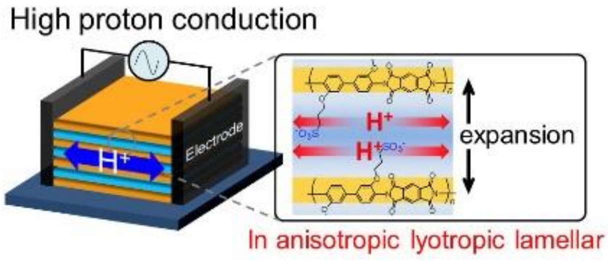
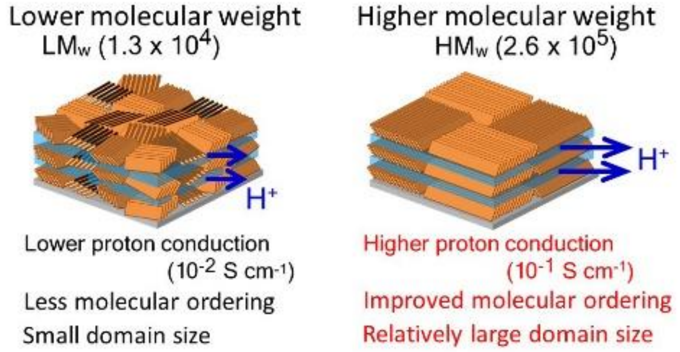
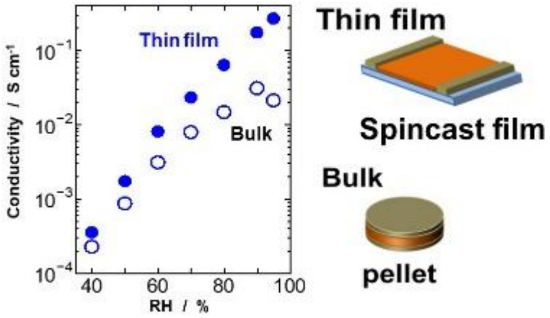
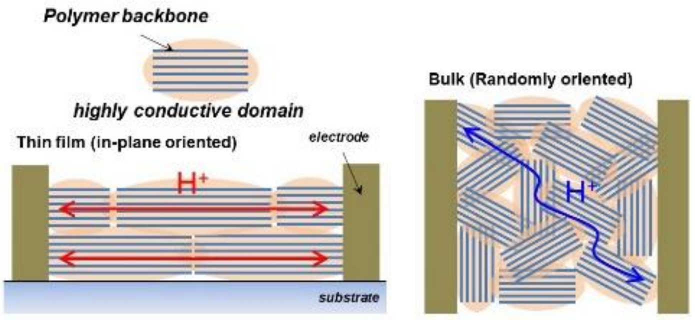








Tuesday 28.9.2021, morning

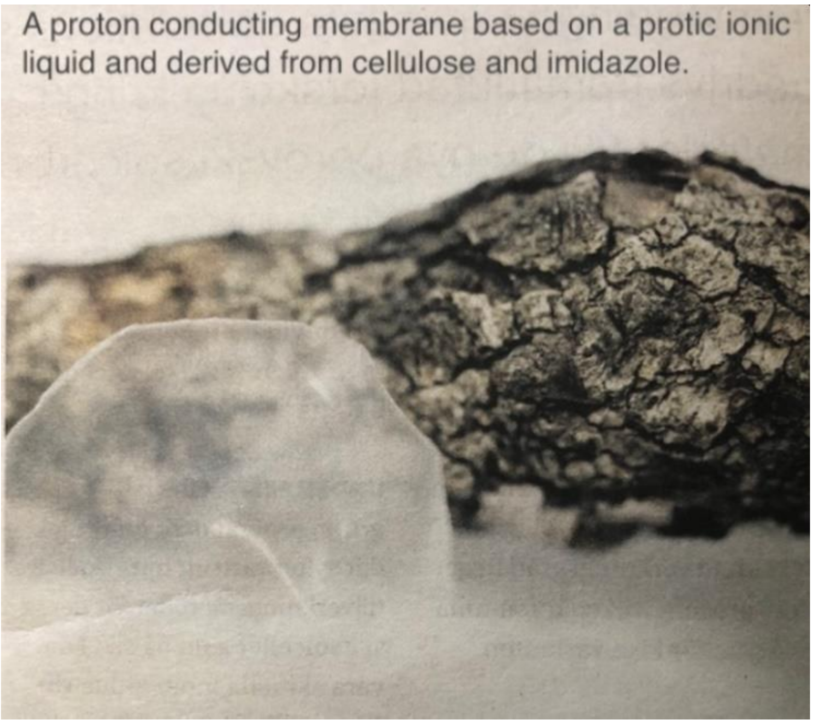
15-INV

Novel proton conductors based on protic ionic liquids

Anna Martinelli, Olesia Danyliv, Eduardo Mourina Morais

Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden

Protic ionic liquids are emerging materials with a set of interesting properties that appeal for use in diverse electrochemical devices; these include a low vapour pressure, a high ionic density coupled with relatively low viscosity and the availability of exchangeable protons, typically but not exclusively residing on the ionic liquid's cation. One technological device that is of our interest is the proton exchange membrane fuel cell operating at high temperatures (above 80 °C and up to 150 °C), that in turn requires fast proton motion through the material. The key scientific questions that relate to this aspect are investigating the chemical environments that promote longer range proton motion, understanding the interplay between thermochemical stability and mechanisms of proton transfer, as well as investigating the use of protic ionic liquids in real devices. In this respect, different solid state matrices are studied, such as Nafion or other materials based on nanoporous silica or even cellulose. A selection of results within this scientific context will be presented, based on vibrational, NMR and impedance spectroscopy.



A proton conducting membrane based on a protic ionic liquid and derived from cellulose and imidazole.

16-INV

Anion Exchange Membrane with Bulky Organic Cations for Alkaline Fuel Cells and Electrolyzers

Nanwen Li, Xiaojuan Zhang, Lei Liu, Xiaomeng Chu, Xin Wang

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, CAS, Taiyuan, China

The alkaline stability and device durability of anion exchange membranes (AEMs) have been considered as the biggest challenges for their practical application in alkaline fuel cells (AFCs). Thus, the improvement of the stability has got more and more attention recently in the academic and industrial area. The bulky organic cations having steric hinder groups which could protect the central cations from attacking by hydroxide has been developed as promising functional groups in AEMs. However, the research is still under infancy. Herein, 1) the steric hinder groups have been tuned and designed to protect the nitrogen center in the quaternary ammoniums. Although the alkaline stability has been improved significantly, the device performance in alkaline fuel cells is pretty poor. Mostly, no performance could be obtained when the membrane was been employed as electrolyte probably due to the hydrophobicity of bulky groups. Decrease the volume of bulky groups, and also change the position and conformation, introduction of hydrophilic groups have been developed in this reports to achieve fuel cell performance successfully. And also, the effect of polymer backbone alkaline stability on the functional groups has been investigated in detail. 2) Moreover, these bulky substitutes in the cations destroyed the entanglement of polymer chains, the film-forming ability of polymer was thus weaken significant. As a result, we can not get the tough and flexible membrane for the fuel cell application. Thus, the in-site crosslinking by thio-ene click chemistry have been employed.

17-O

Relations of OH^- Conductivity and Water Uptake of Anion Exchange Ionomer

Fangfang Wang, Dongjin Wang, Yuki Nagao,
School of Materials Science, Japan Advanced Institute of Science and Technology

Conventional power generating systems can cause environmental pollution. Hence, it is important to develop environment-friendly energy sources. Fuel cell is an ideal energy source. Anion exchange membrane fuel cells (AEMFCs) provide the possibility that eliminates the use of precious metal catalysts and offers higher oxygen reduction reaction kinetics in alkaline conditions. Ionomer plays a key role in the triple-phase interface of AEMFCs. Illustrating the OH- conduction and hydration properties of anion exchange ionomer is important. However, there is a lack of research on the anion exchange ionomer. This work demonstrated the OH- conduction and hydration properties of anion exchange ionomer for the first time.[1] Poly[(9,9-bis(6′-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-alt-(1,4-benzene)] (PFB+) was synthesized as a model ionomer. Fig. 1a indicated that OH^- conductivity is higher than Br- conductivity. The highest OH- conductivity of 273 nm-thick PFB+ thin film at 25 °C is 5.3×10^{-2} S cm^{-1}, which is comparable to the reported OH^- conductivity of PFB+ membrane.[2] To further understand the relations between OH^- conduction and hydration, the OH^- conductivity and water uptake of a thinner film were studied. Decreased OH^- conductivity and water uptake were observed in thinner film (Fig. 1b). The reduced OH^- conductivity was caused by the decreased water uptake in thinner PFB+ film.

References

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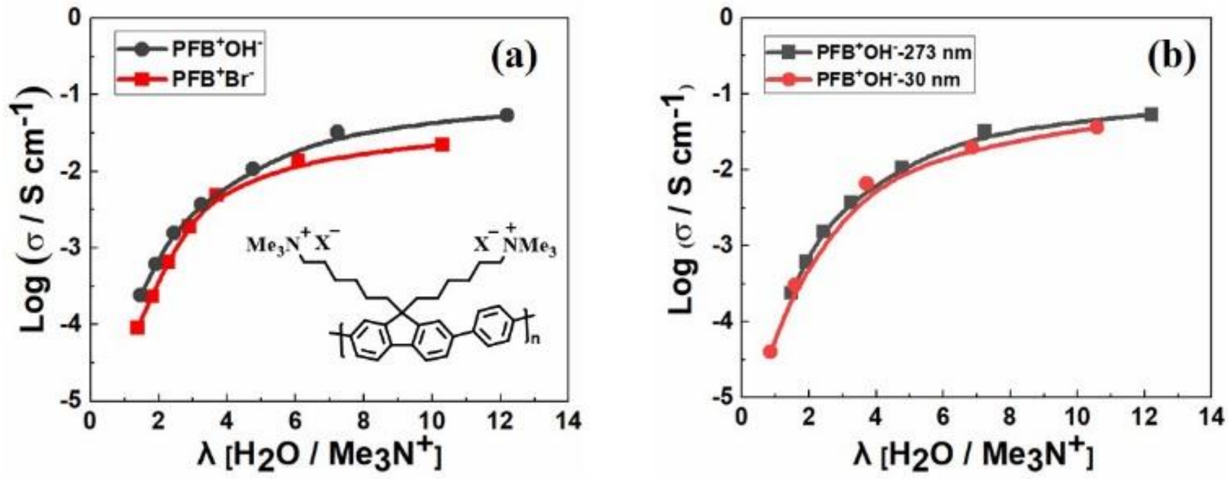

Fig. 1. (a) Anion conductivity of 273 nm-thick PFB^+ films as a function of number of water molecules at 25°C. (b) Number of water molecules dependence of OH^- conductivity for PFB^+ thin films in different thicknesses at 25°C. The inset figure in Fig. 1a is the chemical structure of PFB^+X^- (X=Br and OH).

18-O

Side-chain engineering strategy enabling poly(arylene alkylene)-based anion exchange membranes with phase-separated morphology and improved conductivity

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Recently, anion exchange membrane fuel cells (AEMFCs) have gained great interests in commercial and scientific communities, owing to the potential cost competitiveness. However, as a vital component for AEMFC, anion exchange membrane (AEM) often suffers from inferior conductivity and low ion-conducting efficiency, since the sluggish mobility of hydroxides.

Among the approaches to improve the conductivity of AEM, constructing of the well-defined ion conducting channels within the membrane was proved to be an effective strategy. In general, an efficient way to construct a phase-separated morphology is polymer blocking. However, limited by the polymerization mechanism, some promising ion-containing polymers, including poly(arylene alkylene)-based ionomers, used in AEM is not suitable to synthesize block polymers. Herein, we randomly tethered functional side chains, for example, multi-cations and fluorocarbon grafts, to the polymer backbone to improve the immiscibility between hydrophilic and hydrophobic segments, and further driving the formation of the phase-separated morphologies of the membranes. Moreover, by systemically tuning the flexibility of polymer backbone, the hydrophobicity of side chain as well as the charge number on the cationic side chain, we explored the fundamental relationships between the chemical architecture of the ionomer and the morphology of the resultant AEM as well as the conductivity. All in all, this side-chain engineering strategy is expecting to provide a scientific guidance for the design and fabrication of AEM with tailored performance.

19-KN Beyond Nafion and other PFSAs: Custom made proton conducting membranes and ionomers based on sulfonated poly-phenylene-sulfones s-PPS

K. D. Kreuer

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High ionic conductivity, reasonable (electro-) chemical stability and mechanical robustness still render PFSA membranes such as Nafion the first choice for many electrochemical applications such as PEM-fuel cells, PEM-electrolyzers and flow batteries. On the other hand, limited operation temperature, severe humidification requirements, high transport coefficients for dissolved gases, the strong coupling of solvent (e.g. water) and ion fluxes (electroosmotic drag) and poor selectivity of ionic transport are only few of the many downsides of PFSAs leaving significant space for the development of alternative membrane materials meeting the requirements of specific applications. This is particularly true for a recently developed materials platform based on very stable, highly conducting sulfonated poly-phenylene-sulfones (s-PPS). The intrinsic properties of this group of ionomers[1], the degrees of freedom of their molecular structure (sulfonation pattern, ion exchange capacity) and the possibility of blending, reinforcing and fracture toughening make this platform suitable for custom making membranes and ionomers for specific electrochemical applications.

After a brief summary of recent insights into the prevailing interactions governing PFSA's characteristic properties[2,3], these relations will be contrasted to those which are typical for s-PPS. Finally, s-PPS based membranes and ionomers with properties close to the specific requirements of PEM-fuel cells[4], PEM-electrolyzers[5] and VRFB (vanadium-redox-flow-batteries)[6] are presented.

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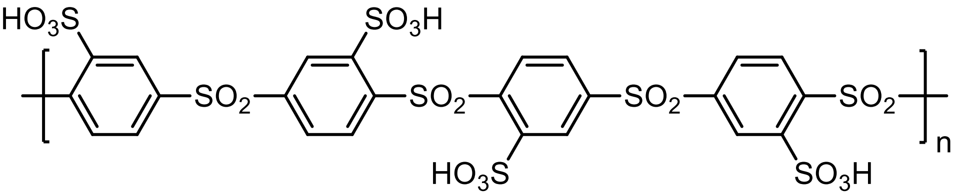

20-INV The Electrical Response and Conductivity Mechanism in Hybrid Membranes for Electrochemical Applications

Vito Di Noto,(1,2) Keti Vezzù, (1,2) Giovanni Crivellaro, (1) Enrico Negro, (1,3) Gioele Pagot(1,3)

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University of Padova, Italy
(2) Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali - INSTM, Padova, Italy
(3) Centro Studi di Economia e Tecnica dell'Energia Giorgio Levi Cases, Padova, Italy

Electrolyte membranes (EMs) are crucial components of advanced electrochemical energy conversion and storage devices such as ion-exchange membrane fuel cells (IEMFCs) and redox flow batteries (RFBs). The role of the EM in these systems is to: (i) keep separated the electroactive species involved in the redox reactions taking place at the electrodes and, at the same time, (ii) ensure a facile and selective migration of ions to prevent the polarization of the device and allow for the establishment of large current densities. The most widely adopted EMs for IEMFCs and RFBs are based on perfluorinated ionomers such as Nafion. The latter suffer from serious drawbacks, such as a drop in conductivity at high temperatures, poor mechanical properties and a large permeability. It is possible to address these drawbacks by a variety of approaches, that include the introduction of a filler in the EM. The resulting systems are known as hybrid inorganic-organic membranes (HIOMs). In HIOMs the introduction of the filler affects the physicochemical properties of the baseline EM, with a particular reference to the details of the phase segregation at the nano/mesoscale. Herein it is overviewed how the physicochemical properties of HIOMs affect the electrical response as determined by Broadband Electrical Spectroscopy (BES). As a result: (i) the interactions between the different phases and components within the HIOM are elucidated; and (ii) the conductivity mechanism is clarified. This allows to identify research approaches to obtain HIOMs for IEMFCs and RFBs beyond the state of the art.

Tuesday 28.9.2021, noon session

21-KN Probing elementary steps of proton transport pathways with ultrafast infrared and soft-X-ray spectroscopy

M. Ekimova,(1) F. Hoffmann,(2) G. Bekçioğlu-Neff,(2) C. Kleine,(1) J. Ludwig,(1) M. Ochmann,(3) T. E. G. Agrenius,(4) E. Kozari,(5) E.Pines,(5) N. Huse,(3) D. Sebastiani,(2) P. Wernet,(6) M. Odelius,(4) E. T. J. Nibbering(1)

(1) Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany
(2) Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Germany
(3) Institute for Nanostructure and Solid State Physics, CFEL, Hamburg, Germany
(4) Department of Physics, Stockholm University, Sweden
(5) Department of Chemistry, Ben Gurion University of the Negev, Beersheva, Israel
(6) Department of Physics and Astronomy, Uppsala University, Sweden

Much effort has been put in the elucidation of the structural dynamics of solvent-mediated proton exchange between acids and bases. Ab initio molecular dynamics (AIMD) simulations have provided key insight in the major roles of hydrogen bond dynamics and solvent shell rearrangements that accommodate the neutralization between acids and bases along particular proton transfer pathways. In the last two decades experimental studies have much benefitted from the development of ultrafast spectroscopic measurement methods probing local vibrational and electronic structure at the intrinsic time scales of the elementary steps of proton transfer. I will show our recent achievements in ultrafast infrared spectroscopy using bifunctional photoacids, where upon photoexcitation ultrafast proton transfer is monitored along a well-defined number of solvent molecules. Solvent-dependent free-energy-reactivity assessments and AIMD simulations reveal how one can distinguish between excess proton and proton vacancy pathways.

The impact of hydrogen bonding on the electronic structure of hydrated proton species can be probed with soft-X-ray spectroscopy. I will show how with oxygen K-edge spectra provide insight into the strong orbital interactions and field interactions of hydrated proton complexes in solution. Future extension into time-resolved soft-X-ray spectroscopy will enable to determination of transient electronic structure of acids and bases during the elementary proton transfer steps.

22-INV

New Developments in Polybenzimidazole (PBI) Membranes for Electrochemical Devices

Laura Murdock, Fei Huang, Brian C. Benicewicz

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, USA

Polybenzimidazole (PBI) polymers have been extensively studied for high temperature PEM fuel cells operating at 100-200˚C. As part of our ongoing work in developing and using the sol-gel PPA process, we have been exploring the effects of chemical structure on membrane properties, including issues related to membrane stability and durability. Membranes produced from this process showed the ability to maintain high levels of phosphoric acid (PA) and high proton conductivities while simultaneously exhibiting low levels of PA loss during operation in many simulated duty cycles. In many cases, the different operating conditions of the distinct devices advocate for a specifically designed polymer structure tailored for its environment.

Recently, we have developed a new process for making PBI membranes that results in much improved mechanical durability compared with the sol-gel membranes without compromising the proton conductivity or fuel cell performance. The improved mechanical durability results in membranes that operate at temperatures above 200 ˚C and are suitable for higher pressure operation that may be needed in emerging fuel cell applications such as air transportation. In this talk, we will review some of the emerging devices and describe a new process for producing PBI membranes with high proton conductivities, improved mechanical properties, and excellent performance in multiple devices.

23-O Fabrication and Optimization Routes of Novel Polymer Electrolyte Membrane Electrolysis Cells

N. Seselj,(1) E.D. Gomez Villa,(2) A. Maletzko,(2) A. Bornet,(3) C.M. Pedersen,(4) S. Pitscheider,(4)
C. Kallesøe,(4) M. Arenz,(3) C. Cremers,(2) H.A. Hjuler,(1) S. Primdahl(1)

(1) Blue World Technologies, Kvistgaard, Denmark
(2) Fraunhofer Institute for Chemical Technology ICT, Pfinztal, Germany
(3) Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Switzerland
(4) Teknologisk Institut, Taastrup, Denmark

Novel oxygen evolution reaction catalyst has been developed within the scope of Recycalyse project by University of Bern (UB) and Fraunhofer Institute for Chemical Technologies (Fh-ICT). The synthesis upscaling of the antimony-doped tin oxide-supported iridium-ruthenium oxide nanoparticle catalyst ($IrRuO_x$-ATO) was done by Danish Technological Institute (DTI). The catalyst was then used for manufacturing polymer electrolyte membrane electrolysis (PEMEC) cells at Blue World Technologies (Blue World). The cell optimization routes were accomplished with a feedback loop between Blue World and Fh-ICT, where the cells have been tested.

The initial cell fabrication effort focused on process standardization, where the 4 cm^2 single cells were made and tested for reproducibility. Afterwards, four parameters have been optimized: (1) cathodic and (2) anodic NafionTM ionomer loadings, (3) anode catalyst supports, and (4) anodic catalyst loading. Each cell configuration in the optimization rounds had a corresponding duplicate cell, for data reliability.

The results obtained show that cell fabrication is done in a reproducible manner. The optimal concentrations of NafionTM in cathodes and anodes are 20 and 10 wt. %, respectively. The commercially available support material exhibits higher electrocatalytic activity than the first in-house produced ATO supports. Anodic catalyst loading shows the best performance at around 1.0 mgIr/cm^2.

These conclusions will further be utilized for production of large-sized PEMEC cells that will be assembled and tested in a functioning 5 kW electrolyzer stack.

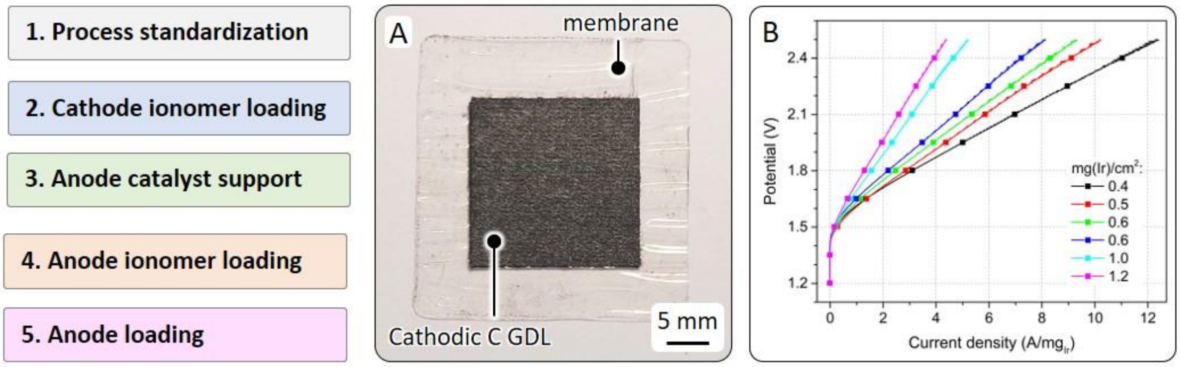

Figure 1. Optimization rounds sequence for making (A) PEMEC 4 cm^2 cells. (B) The IrO_2 mass activity performances of PEMEC MEAs.

P-1 Facet-engineered TiO_2 nanomaterials reveal the role of water-oxide interactions on surface protonic conduction X. Kang

P-2 Self-Diffusion of Cation, Hydrogen, and Oxygen Ions in Crystalline Hydroxide Family Y. Baikov

P-3 Investigation of water uptake in $Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O_3$ high entropy perovskite oxide W. Skubida

P-4 Heavily Sn-doped barium cerates $BaCe_{0.8–x}Sn_xYb_{0.2}O_{3–\delta}$: correlations between composition and ionic transport I.A. Zvonareva

P-5 Effects of sintering additives on the proton uptake of $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9}$ A.M. Dayaghi

P-6 ~~The influence of nickel on the chemical stability of nickel doped $BaCe_{0.9}Y_{0.1}O_{3-d}$ (BCY10) towards CO_2 and humidifcation V.C.D. Graca~~

P-7 Fabrication of multi-layered structures for proton conducting ceramic cells W.A. Meulenberg

P-8 ~~Fundamental study of proton and oxygen exchange of Proton Ceramic Electrochemical Cell's positrode by Gas phase Analysis V.Thoréton~~

P-9 High-Throughput Impedance Analysis of $Ba(Co,Fe,Zr,Y)O_{3-\delta}$ Electrocatalysts J. Huang

P-10 Energetics of formation and the stability of barium gadolinium lanthanum cobaltite positrode materials A.. Mielewczyk-Gryń

P-11 Investigation of Pr doping into the Ruddlesden Popper Materials $La_{n+1}Ni_nO_{3n+1}$ for potential use in Proton Conducting Electrolyser A. Siddiq

P-12 Temperature treatment optimization of $Pr_2Ni_{1–x}Cu_xO_{4+\delta}$ air electrodes for PCFC A. Tarutin

P-13 Impact of Y-substitution on structure-property relations of self-generated $Ba(Ce,Fe)O_{3-\delta}$–$Ba(Fe,Ce)O_{3-\delta}$ nanocomposites C. Berger

P-14 Hydration entropy for mixed conducting $BaFeO_3$ and $SrFeO_3$ P.E. Rosander

P-15 World class Innovative Novel Nanoscale optimized electrodes and electrolytes for Electrochemical Reactions: WINNER M.-L. Fontaine

P-16 Additive Manufacturing for Zero-emission Innovative Green Chemistry (AMAZING) M. Drazkowski

P-17 Towards Robust and Flexible Electrochemical Devices Using Proton Conducting Ceramics N. Sata

P-18 Infiltration of Metal Catalysts for NH_3 Synthesis in Protonic Ceramic Cells D. Schmider

P-19 Hybrid proton-conducting membranes based on metal-organic coordination frameworks V. Ponomareva

P-20 Non-trivial electric response of low-temperature proton conductors P. Ławniczak

P-21 Ultrafast soft X-ray and IR spectroscopy of proton transfer reactions in solution M. Winghart

P-22 Combination of negative, positive, and near-zero thermal expansion in bis(imidazolium) terephthalate with a helical hydrogen-bonded network A Łapiński

P-23 ~~Polymer composite electrolytes based on CsH_2PO_4 I. Bagryantseva~~

P-24 Sulfonated Poly-phenylene Sulfone Blend Membrane finding their Way into Proton Exchange Membrane Fuel Cells D. Yazili

P-25 Durable anion exchange membrane based on polyfluorenes functionalized with alicyclic quaternary ammonium cations A. Allushi

P-26 Zwitterionic Poly(terphenylene piperidinium) Membranes for Energy Applications A. Shirole

Tuesday 28.9.2021, afternoon poster I

P-1 Facet-engineered TiO_2 nanomaterials reveal the role of water-oxide interactions on surface protonic conduction

Xiaolan Kang,(1) Athanasios Chatzitakis,(1) Thomas Aarholt,(2) Xinwei Sun,(1) Chiara Negri,(1)
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Proton conduction in adsorbed water layers in porous nanocrystalline oxides is attracting attention for use in solid-state photoelectrochemical cells and low temperature fuel cells. In this work, we investigated the water adsorption and surface proton conduction at 25 – 400 °C in wet (H_2O and D_2O) atmospheres on nanocrystalline TiO_2 to a predominance of different crystal facets. In-situ Fourier transform infrared spectrometry shows that a portion of water molecules in the first chemisorbed layer adsorbs dissociatively on [100] and [001] surfaces, but molecularly on [101] surface. The ice-like water layer is more solid on the [100] and [001] surfaces, a fact that is attributed to relatively strong bonds to the surface terminating hydroxyls, whereas it is looser, liquid-like on the [101] surface due to the lack of rigid hydroxyl groups to bond to. These behaviors can be attributed to the different atomic arrangements and surface energies of the different crystal facets. Surface protonic conduction on [100] and [001] dominated samples exhibited high pre-exponentials, indicating a high concentration of sites for dissociative chemisorption water. The accompanied high activation energies reflects the limited proton mobility in the rigid layers of adsorbed water on those surfaces, resulting in high surface protonic conductivity at the highest and lowest temperatures. The surface protonic conduction on the [101] dominated sample shows a low concentration of dissociable adsorbed water and low activation enthalpies for protonic migration in the liquid-like adsorbed water.

P-2

Self-Diffusion of Cation, Hydrogen, and Oxygen Ions in Crystalline Hydroxide Family

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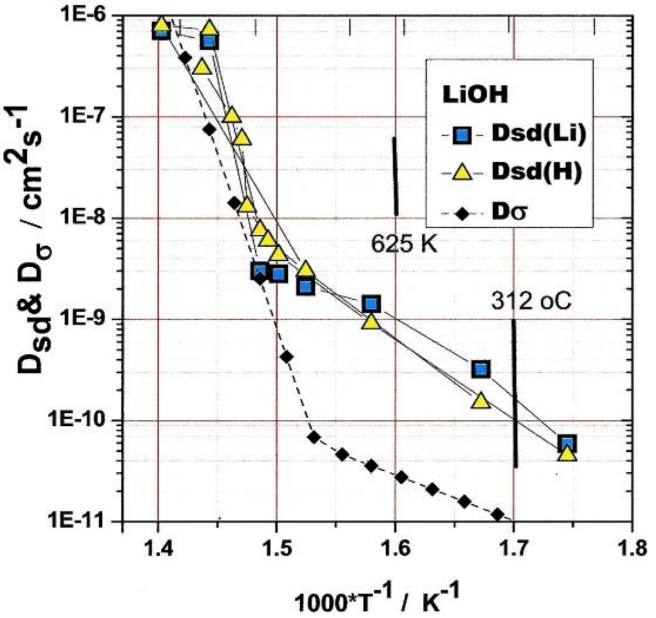
Alkaline hydroxides are to a broad class of metal hydroxides, which have formally two structural forming ions: alkaline and hydroxide. The features observed in the crystal lattice can be traced to the presence of the proton. Moreover, the electronic and internal atomic–ionic structures of the hydroxide ion defy treatment within the same approach, which in the simplest form can be conceived of as a competition among any states of O-H bonds. The self-diffusion coefficients of ions of the three chemical elements forming alkaline hydroxide have been determined by the heterogenic isotope exchange method in the temperature range 500–720 K. Crystal samples with different isotope compositions have been grown by the Bridgman method. The melting temperatures were according to accepted ones. More original methods have been developed for high-precision measurements of the isotope ratios of all three elements, i.e., lithium, hydrogen, and oxygen, and their changes after diffusion annealing with the use of the same sample. The self-diffusion coefficients of lithium and hydrogen ions differ but by a factor of no more than 3–5; however, their values exceed those for oxygen by several orders of magnitude. The self-diffusion coefficients of hydrogen and lithium increase sharply near phase transition to approximately 10^{-6} cm^2 s^{-1}. A mechanism of migration of protons in LiOH and the role played in this process by the oxygen ions with a lower mobility have been discussed.



D_{sd} - coefficient of diffusion, determined directly by isotopic exchange: H-hydrogen, Li-lithium

Dσ– coefficient of diffusion, evaluated by simple Nernst- Einstein relation from data on total conductivity from literatuture

P-3

Investigation of water uptake in Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O_3 high entropy perovskite oxide

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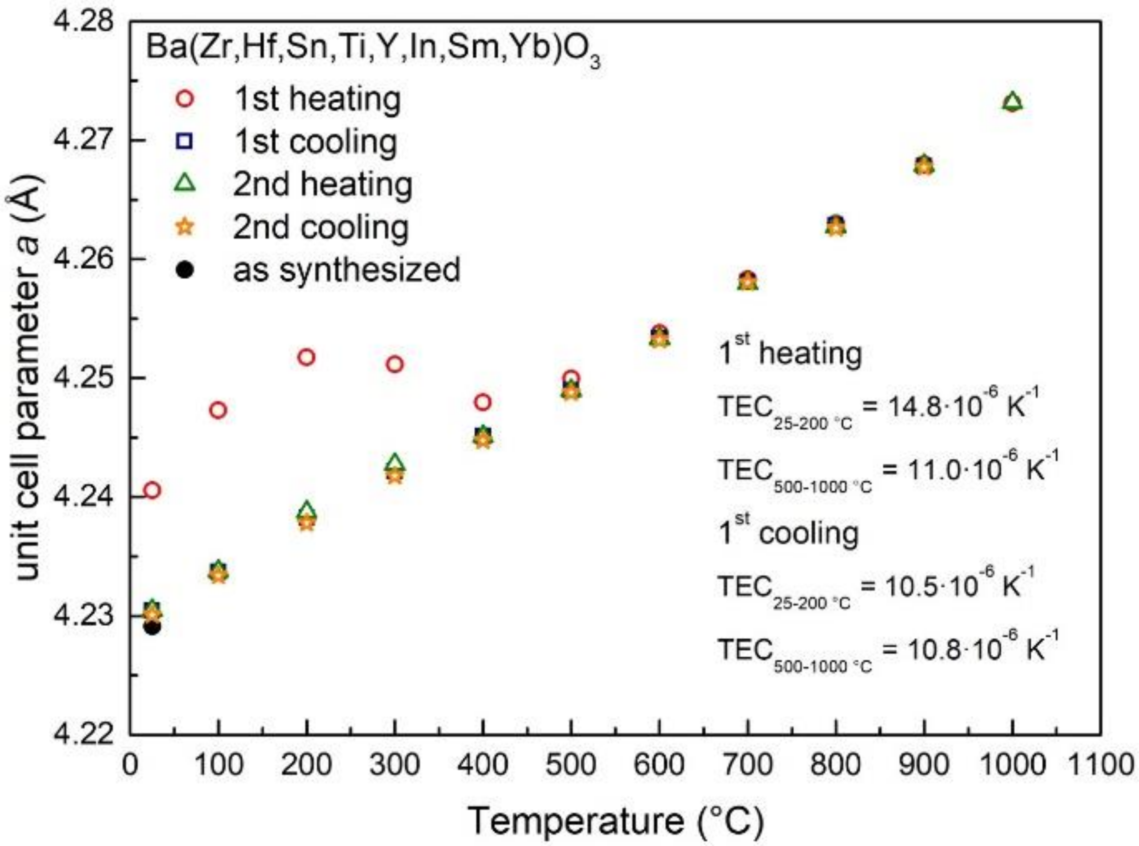
Incorporation of water into Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O_3 has shown an influence on the crystal structure at room temperature, structural transformation at high temperatures and ionic transport properties of the material. As documented by XRD measurements at room and elevated temperatures, water incorporation leads to the enlargement of the unit cell parameter. HT-XRD has shown temperature range of water release from the structure as well. This data aligns well with the results of TG measurements accompanied by mass spectroscopy analysis, which has shown that water release occurs at the same temperature range as structural changes. What is more, water incorporation was verified by isothermal TG measurements during the abrupt gas change from dry to wet conditions. Electrical properties of the sample were investigated by means of electrical impedance spectroscopy in dry, H_2O- and D_2O-containing air in 300-800 °C temperature range, which enabled to evaluate the proton and deuterium conductivities. At the same time, the relaxation kinetics of the electrical conductivity conducted in 300-600 °C temperature range showed a single-fold nature, which indicates a negligible component of the electronic hole conductivity in the hydrated material. Gathered data allowed to calculate the diffusion coefficient D and (in some temperatures) surface exchange coefficient k of water along with their activation energies.

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



Unit cell parameter dependence on temperature, as calculated from HT-XRD data, recorded in two cycles in synthetic air for previously hydrated Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O_3 sample.

Tuesday 28.9.2021, afternoon poster I

P-4 Heavily Sn-doped barium cerates $BaCe_{0.8–x}Sn_xYb_{0.2}O_{3–\delta}$: correlations between composition and ionic transport

Inna A. Zvonareva,(1,2) Liana R. Tarutina,(1,2) Gennady K. Vdovin,(1) Julia G. Lyagaeva,(1,2)
Albert R. Akhmadeev,(1) Dmitry A. Medvedev(1,2)

(1) Institute of High Temperature Electrochemistry, Yekaterinburg, Russia
(2) Ural Federal University, Yekaterinburg, Russia

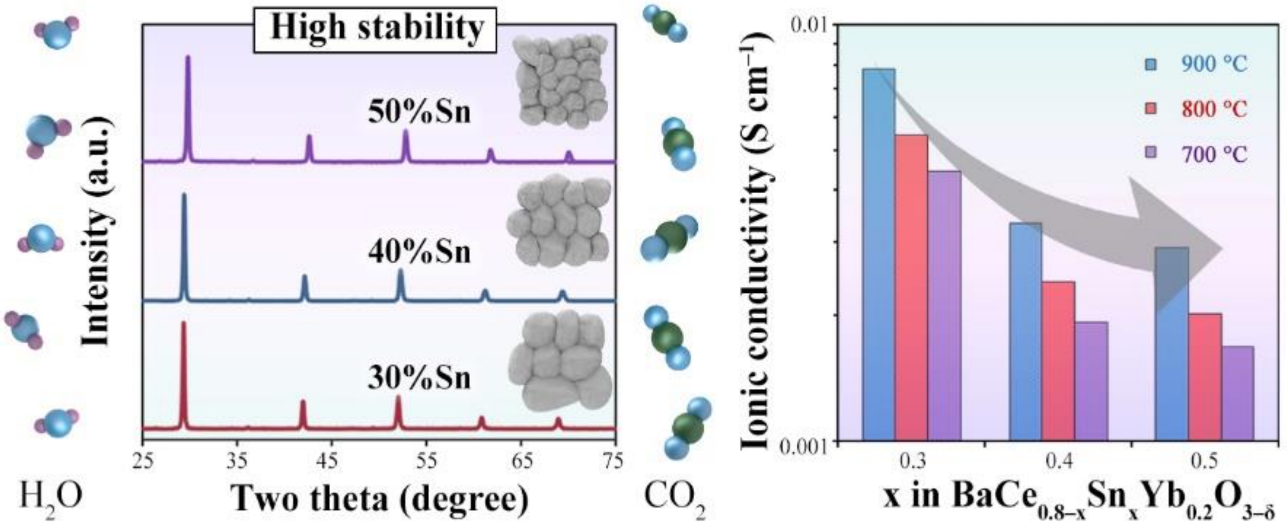
The design of new functional materials for solid oxide fuel cells demonstrating both efficiency and long-term stability is of great importance. In this view, Sn-substituted $BaCeO_3$ materials are proposed and thoroughly characterized as new proton-conducting electrolytes.

$BaCe_{0.8–x}Sn_xYb_{0.2}O_{3–\delta}$ (BCSY) compounds (x = 0.3–0.5) are formed by doping with tin to increase chemical stability and with ytterbium to provide protonic transport. The electrical properties were studied across wide ranges of temperatures (200–900 °C), oxygen partial pressures (10^{-18}–0.21 atm) and water vapour partial pressures (0.001–0.1 atm).

At high temperatures, BCSY are found to be mixed ionic-electronic conductors in oxidising conditions, while they become substantially ion-conducting ones under reducing atmospheres; at relatively low temperatures, ionic transport prevails over the whole pO_2 range. Under wet H_2, conductivity increases along with humidification due to a growth in proton defect concentration and, correspondingly, proton conductivity improvement.

In line with impedance measurements, the electrical properties of BCSY at high temperatures were determined by bulk transport and increased with air humidification. Across the low-temperature range, electrical conductivity is governed by grain boundaries, and decreased with the tin-doping due to a reduction in grain size.

Thus, total and partial conductivities decreased with the Sn content due to crystal features. Stability with respect to chemical interaction of the target phases with H_2O and CO_2 was improved compared with Sn-free cerates.



Tuesday 28.9.2021, afternoon poster I

P-5

Effects of sintering additives on the proton uptake of $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9}$

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(1) Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo, Norway
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(3) SINTEF, Oslo, Norway

Acceptor-doped $BaZr_{1-x}Ce_xO_{3-\delta}$ takes up protons by hydration of oxygen vacancies and exhibits high proton conductivity in its fully hydrated form. However, many factors reduce the effective acceptor dopant level, hence hydration and proton concentration are reduced. In the present work, we systematically investigate the effect of different sintering additives (0.5 to 2 wt% NiO, 1 wt% ZnO, and 1 wt% CuO) on the hydration thermodynamics and maximum proton uptake of $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9}$ by thermogravimetry (Fig. 1). We find that 1 wt% ZnO and CuO as well as 0.5% NiO have insignificant effects on the effective acceptor level, while using 1 and 2 wt% NiO has severely negative effects. Insights on secondary phase formation upon sintering, structural variations, grain size evolution, and conductivity measurements will be used to discuss these variations.

Acknowledgment: This study has received European Union's Horizon 2020 Research and Innovation funding under grant agreement No 838077

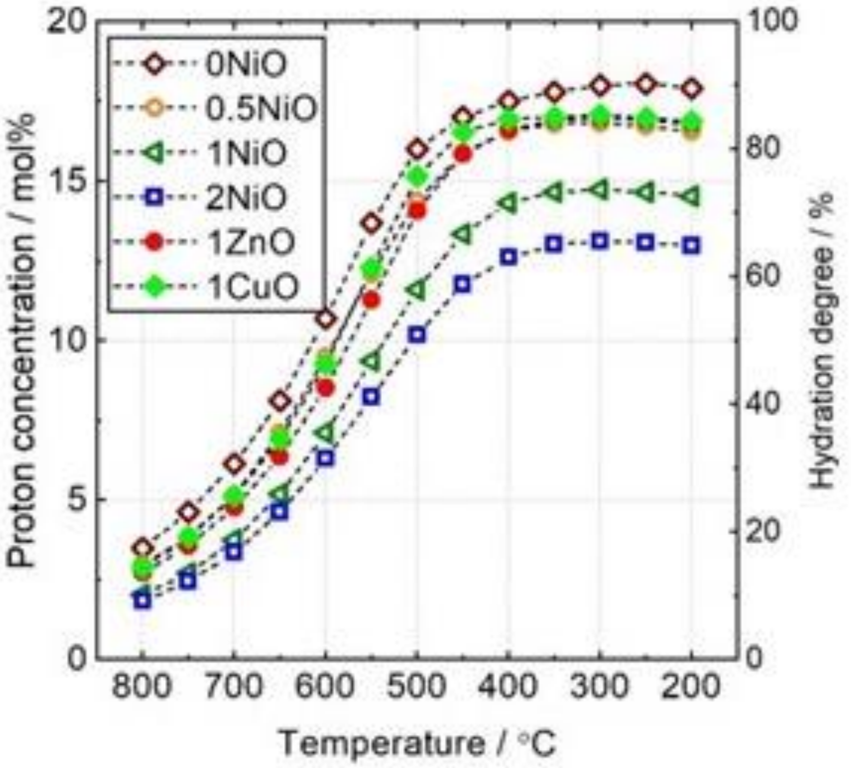

Fig. 1. Thermogravimtery of $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9}$ without (0NiO), and with 0.5 wt% NiO (0.5NiO), 1 wt% NiO (1NiO), 2 wt% NiO (2NiO), 1 wt% ZnO (1ZnO) and 1 wt% CuO (1CuO) sintering additive in humid (0.026 atm) air.

P-6 The influence of nickel on the chemical stability of nickel doped $BaCe_{0.9}Y_{0.1}O_{3-d}$ (BCY10) towards CO_2 and humidifcation

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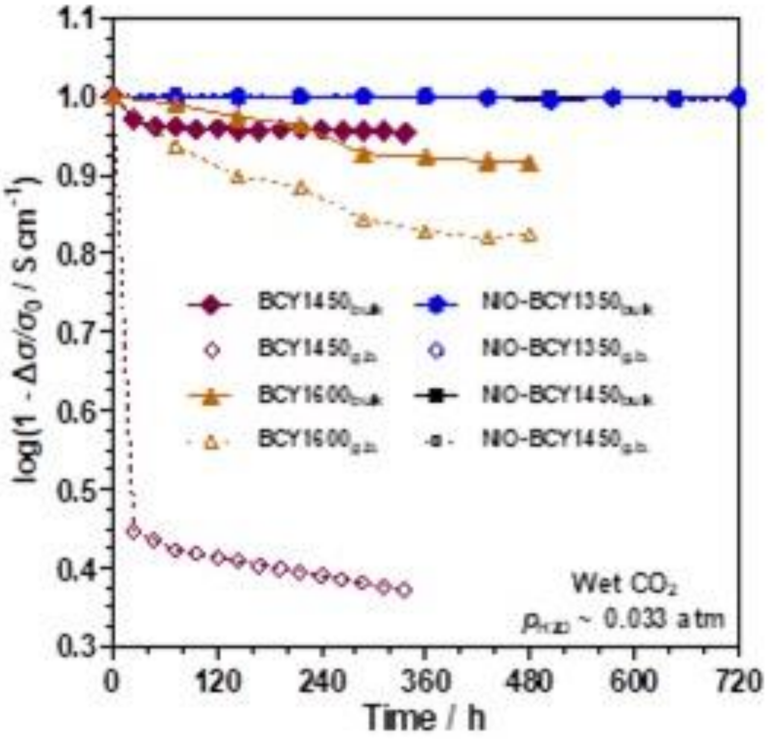
--- presentation cancelled ---

Yttrium-doped barium cerate (BCY) can provide high protonic conductivity at low temperatures generating interest for its use in protonic ceramic fuel cell devices. However, this composition has been, typically, discarded for real world applications, due to its very poor chemical stability in both humidified and CO_2 containing atmospheres. To try to overcome this limitation, we report an alternative based on the modification of the original BCY10 composition by the introduction of 1 vol% of NiO. Therefore, four different samples were used: the undoped samples, BCY10 sintered at 1450 °C and 1600 °C; and the NiO-modified samples, sintered at 1450 °C and 1350 °C. To evaluate the chemical stability, fresh samples were exposed to a humidified CO_2 atmosphere (pH_2O = 0.033 atm) at 400 °C for 30 days and electrochemical impedance spectroscopy was used to record impedance data each three hours. The results, Figure 1, reveal that the unmodified BCY10 samples suffer a substantial drop in total conductivity in this timeframe, while the NiO-modified samples remain stable through the tests.

This result is important as it reveals that the addition of small amount of NiO, not only offers its typical role of decreasing the sintering temperature but can also be successful for dramatically improving the stability of BCY10 against humidification and carbonation. The work offers a significant advance to the knowledge of this family of materials at low temperatures, potentially opening a way to use these previously discarded proton-conducting perovskite materials in real world applications.



Tuesday 28.9.2021, afternoon poster I

P-7 Fabrication of multi-layered structures for proton conducting ceramic cells

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Protonic ceramic fuel cells offer a high potential to produce electrical energy in a very efficient way. The performance of such a device is highly dependent on the electrolyte material and its thickness. Therefore, multilayer structures are used to reduce the electrolyte thickness down to 10-20 µm, supported by a much thicker porous anode. In this work sequential tape casting is used to fabricate half-cells consisting of a BZCY electrolyte and a BZCY/NiO support which also serves as anode layer. The starting powders are characterised as well as the thermal behaviour of the half-cells during heat treatment. Sintering experiments show that a temperature of $T \geq 1450$ °C is needed to achieve the desired microstructure. After that a scale-up approach to a size of the half-cells of about 25 cm^2 is shown. The influence of the processing temperature on the microstructure is shown by detailed XRD and SEM studies. The formation of a BaY_2NiO_5 transient liquid phase during the heat treatment of the cells is clearly demonstrated. Finally, the proton conductivity of the tape-cast cells shows competitive values of $\sigma = 0.003$ S/cm at 600 °C with the advantage of an industrially proven and up-scalable manufacturing technique. (This work was submitted for publication in the Journal of Materials Chemistry A on June 21st 2021)

P-8

Fundamental study of proton and oxygen exchange of Proton Ceramic Electrochemical Cell’s positrode by Gas phase Analysis

Vincent Thoréton, Reidar Haugsrud

Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, FERMiO, Oslo, Norway

--- presentation cancelled ---

Positrode materials for Proton Ceramic Electrochemical Cells (PCECs) require sufficiently high proton transport kinetics both in the bulk and at its interface with the gas phase. In that sense, fundamental understanding of the proton and oxygen transfer at the surface of Mixed Proton and Electron conducting Ceramics (MPECs) is desirable, to possibly improve the performance of the cell.

Isotopic Exchange Gas Phase Analysis techniques (Pulse Isotopic Exchange (PIE) or Gas Phase Equilibration (IE-GPE)) have been successfully applied for measuring the surface exchange kinetics of oxygen on Solid Oxide Electrochemical Cells (SOECs) and highlighting the limiting steps. Extending the methodology to the study of species containing protons and oxygen is a challenging but exciting task, allowing to understand the interaction of different species at the surface and their effect on the surface exchange kinetics. The surface exchange kinetics were determined on a PCFCs cathode material (BGLC) and an electrode/electrolyte (BGLC/BZCY) composite with varying the partial pressure of water and oxygen. The surface reaction mechanisms were assessed and interpreted in term of defect chemistry.

Acknowledgements

The authors acknowledge support of the FRINATEK project 262393 ‘‘Fundamentals of Surface Kinetics in High Temperature Electrochemistry’’ (FUSKE) of the Research Council of Norway.

P-9 High-Throughput Impedance Analysis of Ba(Co,Fe,Zr,Y)$O_{3-\delta}$ Electrocatalysts

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Protonic ceramic electrochemical cells (PCECs) are a promising class of devices with broad applications in energy conversion, energy storage, and chemical production. A key barrier to realizing the full advantages of PCECs is the lack of existing electrode materials with suitable conductivity and catalytic activity. However, development of novel electrode materials is impeded by the chemical complexity of protonic ceramic electrodes, the vast design space of candidate materials, and the multifaceted materials property requirements for favorable electrode performance.

Here, we present a combinatorial study of candidate PCEC electrode materials in the Ba(Co,Fe,Zr,Y)$O_{3-\delta}$ (BCFZY) system. Compositionally graded thin films were synthesized via pulsed laser deposition and subsequently characterized using high-throughput X-ray diffraction, X-ray fluorescence, and electrochemical impedance spectroscopy (EIS). Both the distribution of relaxation times (DRT) and equivalent circuit models are employed to construct a hierarchical Bayesian model which enables robust deconvolution of the EIS spectra, yielding resistances, time constants, and activation energies of discrete electrochemical processes. This rich dataset reveals how both individual processes and total polarization resistance change in magnitude with chemical composition, temperature, and atmosphere. It also provides clues about the chemical characteristics that govern performance, which can help guide further exploration and optimization of protonic ceramic electrocatalysts.

P-10

Energetics of formation and the stability of barium gadolinium lanthanum cobaltite positrode materials

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Barium gadolinium lanthanum cobaltites ($BaGd_{1-x}La_xCo_2O_{6-\delta}$) are a group of materials having a potential application as positrode for proton ceramic electrochemical cells (PCEC). They exhibit mixed proton-electron conductivity and have been evaluated in the past as a suitable material in view of their electrochemical performance. Therefore, the assessment of their stability under operating conditions seems crucial for future applications in hydrogen technologies. The information about the energetics of formation dependence on the sample's composition, as well as the stability under high and varying water vapor pressure has been gathered to do so. The compositions with different lanthanum to gadolinium ratios have been investigated.

Acknowledgements: Project FunKeyCat is supported by the National Science Centre, Poland under the M-ERA.NET 2, which has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement no 685451.

P-11 Investigation of Pr doping into the Ruddlesden Popper Materials $La_{n+1}Ni_nO_{3n+1}$ for potential use in Proton Conducting Electrolyser

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Ruddlesden-Popper phase's have the general formula $A_{n+1}B_nO_{3n+1}$, where A are large cations, such as alkaline or rare earths, and B are typically transition metals, and n is the number of perovskite layers that separate the rock salt layers in the structure [1]. Lanthanum and nickel are able to occupy the A and B site respectively, resulting in a series of Ruddlesden Popper-type lanthanum nickelates. These materials can be utilised as electrodes in solid oxide cells. For this application, they have been shown to have adequate electrical conductivity and thermal stability at high temperatures [2]. Praseodymium has also been shown to be able to occupy the A site with nickel on the B site [3]. As praseodymium is able to have variable oxidation states, it has been explored as a dopant into lanthanum nicklelates with a view to potentially improving the performance for use within proton conducting solid oxide electrolyser cells.

[1] Orera A, Slater PR. New Chemical Systems for Solid Oxide Fuel Cells. Chemistry of Materials. 2010;22(3):675-90.

[2] Amow G, Davidson IJ, Skinner SJ. A comparative study of the Ruddlesden-Popper series, $La_{n+1}Ni_nO_{3n+1}$ (n=1, 2 and 3), for solid-oxide fuel-cell cathode applications. Solid State Ionics. 2006;177(13):1205-10.

[3] Song J, Ning D, Boukamp B, Bassat J-M, Bouwmeester HJM. Structure, electrical conductivity and oxygen transport properties of Ruddlesden–Popper phases $Ln_{n+1}Ni_nO_{3n+1}$ (Ln = La, Pr and Nd; n = 1, 2 and 3). Journal of Materials Chemistry A. 2020;8(42):22206-21.

P-12

Temperature treatment optimization of $Pr_2Ni_{1-x}Cu_xO_{4+\delta}$ air electrodes for PCFC application

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In recent years, fundamental research has been devoted to the search for new Co-free complex oxide materials, since along with high electrochemical activity and low polarization resistance, the cobalt-based oxides have high thermal expansion coefficients and low chemical stability. As an alternative to traditional air electrodes, nickelate-based materials having a common formula $Ln_2NiO_{4+\delta}$ (Ln = La, Na and Pr) have gained considerable scientific interest. However, the thermal treated temperatures used for these materials remain rather high, which imposes restrictions on the technological processes and leads to higher production costs of electrochemical cells. Therefore, the aim of this work is to reduce the temperature of PCFC heat treatments with praseodymium nickelite-based electrodes by partially replacing nickel with copper.

Single-phase materials of the composition $Pr_2Ni_{1-x}Cu_xO_{4+\delta}$ (x = 0, 0.1, 0.2, 0.3) were synthesised using the citrate-nitrate synthesis method. For these materials their crystal structure, conductive and thermomechanical properties were studied and then electrochemical activity of the corresponding electrodes were evaluated varying composition and sintering temperature.

Copper doping was able to reduce the electrode sintering temperatures to 950°C for x = 0.2 and 880°C for x = 0.3. This was accompanied by a reduction in the average thermal expansion coefficients of the copper-doped derivatives and a decrease in their polarisation resistances.

P-13 Impact of Y-substitution on structure-property relations of self-generated $Ba(Ce,Fe)O_{3-\delta}$–$Ba(Fe,Ce)O_{3-\delta}$ nanocomposites

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(3) Institute of Electron Microscopy and Nanoanalysis (FELMI), Graz University of Technology & Graz Centre for Electron Microscopy (ZFE), Graz, Austria

Self-generated ceramic nanocomposites from the $BaCeO_{3-\delta}$–$BaFeO_{3-\delta}$ system [1] are mixed proton-, oxygen ion-, and electron-conductors for various applications such as protonic ceramic fuel and electrolyser cells, or hydrogen separation membranes. In the current work, partial substitution of Ce and Fe by Y in the $BaCeO_{3-\delta}$–$BaFeO_{3-\delta}$ system is investigated in order to gain a deeper understanding of the interrelation between chemical composition and proton uptake. Precursors with different Ce:Fe ratios were synthesised via a sol-gel process. After thermal treatment, an in-situ phase separation into a cubic (Pm-3m) Fe-rich and a trigonal (R-3c) Ce-rich perovskite phase took place. With increased annealing temperature, the proportion of the cubic phase increases (reaching 100 wt-% at 1400°C for $BaCe_{0.4}Fe_{0.4}Y_{0.2}O_{3-\delta}$) and the lattice parameters change systematically. Analytical scanning transmission electron microscopy is used to determine the distribution and the cation stoichiometry of both phases, and scanning electron microscopy is used to determine their local cation stoichiometry. The water uptake as measured by thermogravimetry depends on cation composition and Ce:Fe ratio and shows significant differences between the homogeneous $BaFe_xCeyY_{0.2}O_{3-\delta}$ perovskites and their two-phase composites. The results will be related to water incorporation trends including deviations from ideally dilute defect behaviour observed for $(Ba,Sr,La)FeO_{3-\delta}$ perovskites [2].

[1] S. Cheng et al., Angew. Chem. Int. Ed. 2016, 55, 10895.
[2] R. Zohourian et al., Adv. Funct. Mat. 2018, 28, 1801241.

P-14

Hydration entropy for mixed conducting $BaFeO_3$ and $SrFeO_3$

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(2) Max Planck Institute for Solid State Research, Stuttgart, Germany

Density functional theory (DFT) has become an important tool for functional materials. Finite temperature properties require sampling of very many different configurations and this becomes a challenge for DFT calculations.

Here we consider hydration of oxygen vacancies in mixed-conducting $(Ba,Sr)FeO_{3-d}$, a promising cathode material for protonic ceramic fuel cells. The computation of the temperature dependence of the hydration enthalpy and entropy requires evaluation of the vibrational properties. In fitting the force constants we displace all atoms in each single DFT calculation and then we make use of regression techniques to obtain the dynamical matrix [1]. This technique requires considerably fewer DFT calculations compared to the conventional direct approach where only one atom is displaced in each single DFT calculation.

Our study is based on the work of Hoedl et al. [2] who studied the energetics of dry and hydrated $(Ba,Sr)FeO_{3-d}$ at zero temperature. The PBE+U approximation is used in the calculations and in the appended figure a typical result for the phonon density of states is shown. The resulting hydration entropies at T=1000 K for $BaFeO_{3-d}$ and $SrFeO_{3-d}$ are -145 J/mol K and -132 J/mol K, respectively. This is in line with experimental values [3], which are about -160 J/mol K and -120 J/mol K, respectively, and more negative than the experimental value of -90 J/mol K for $Ba(Zr,Y)O_{3-d}$ electrolytes.

[1] Fransson et al. NPJ Comp. Mater. 6, 135 (2020)
[2] Hoedl et al. J. Phys. Chem. C 124, 11780 (2020)
[3] Zohourian et al. Adv. Funct. Mater. 28, 1801241 (2018)

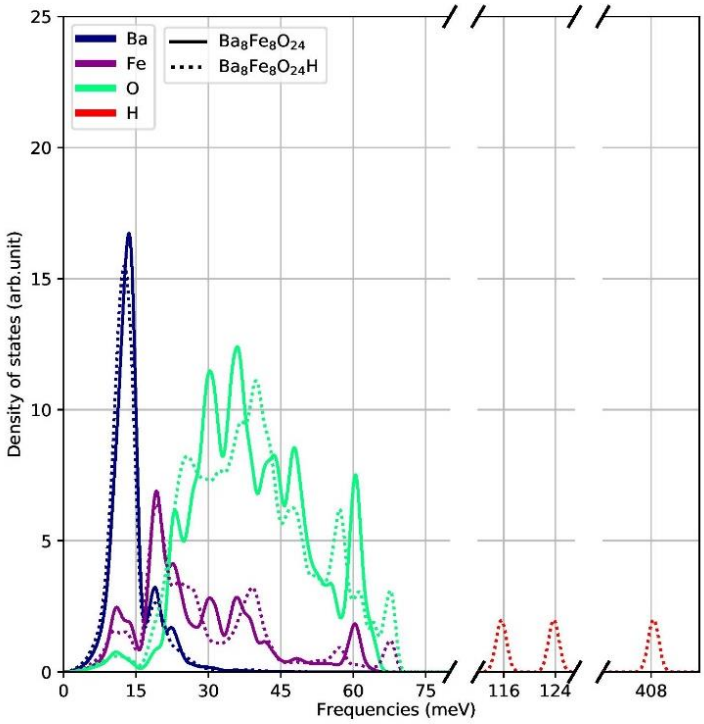


Figure 1: The phonon density of states for $Ba_8Fe_8O_{24}$ (with Jahn-Teller distortion) and $Ba_8Fe_8O_{24}H$. The red shift of the barium peak is due to the expansion of the cell when H is introduced, bond lengths are increased. For higher frequencies the peaks are blue shifted. This is related to the motion of the iron and oxygen in the chain O-Fe-O-Fe and is due to the compression of Fe-O bonds, leading to stiffer bonds. The peaks around 120 and 400 meV correspond to the wag and stretch modes of hydrogen, respectively.

Tuesday 28.9.2021, afternoon poster I

P-15 World class Innovative Novel Nanoscale optimized electrodes and electrolytes for Electrochemical Reactions: WINNER

Marie-Laure Fontaine, Einar Vøllestad, Christelle Denonville, Vegar Øygarden, Elena Stefan,
Yngve Larring

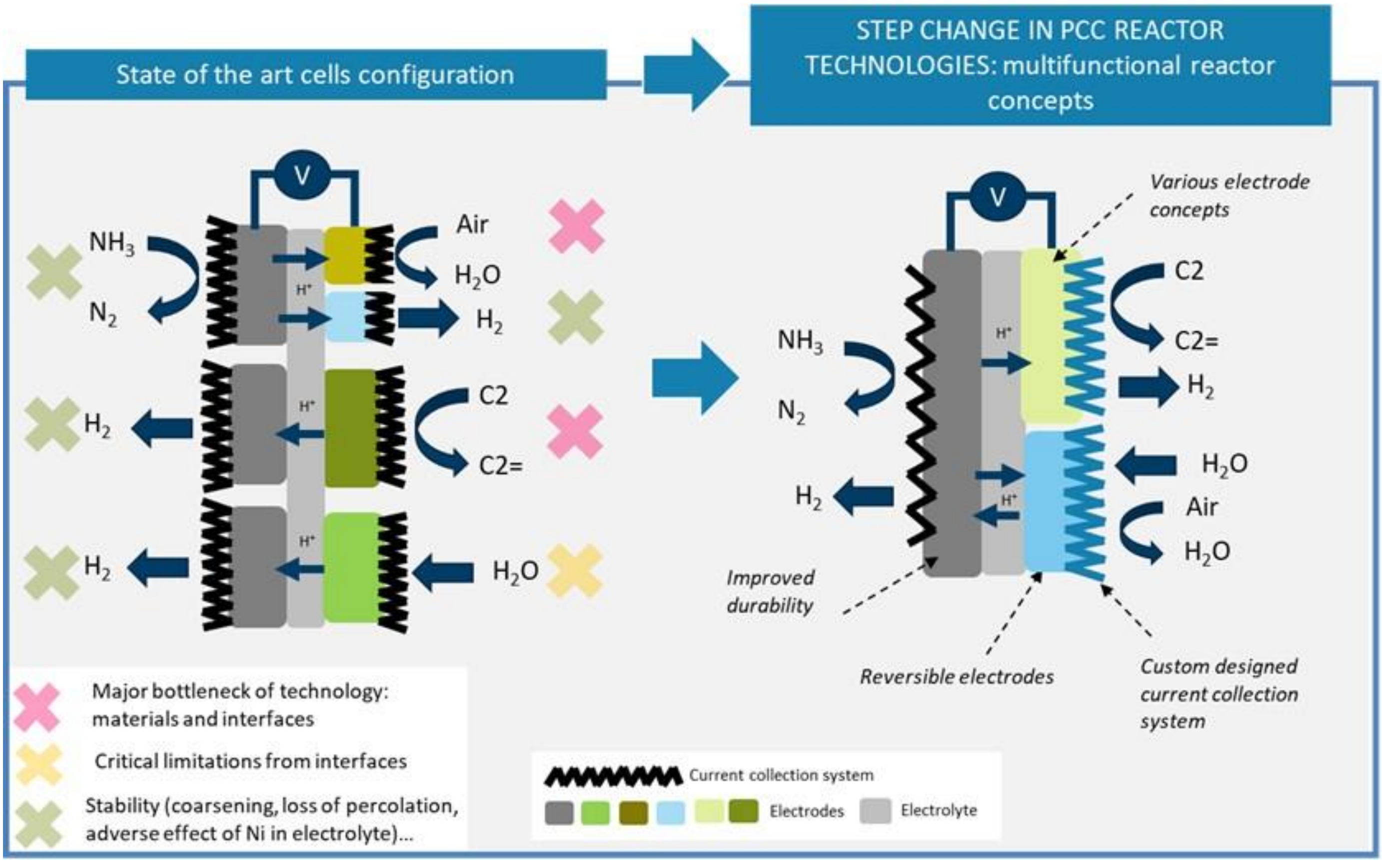
SINTEF Industry, Norway

This presentation gives an overview of the WINNER project, started in January 2021. The project aims to develop an efficient and durable technology platform based on electrochemical proton conducting ceramic (PCC) cells designed for unlocking a path towards commercially viable production, extraction, purification and compression of hydrogen at small to medium scale. This will be demonstrated in three applications: ammonia cracking, dehydrogenation of hydrocarbons, and reversible steam electrolysis.

WINNER will develop innovative cell architectures with multifunctional electrodes and a novel pressure-less current collection system steered by multi-scale multi-physics modelling and advanced in-situ and operando characterisation methods. The tubular PCC cells will be assembled in a flexible multi-tube module operating at industrially relevant conditions to establish correlations between performance and degradation mechanisms.

The project is coordinated by SINTEF with support from University of Oslo, Agencia Estatal Consejo Superior De Investigaciones Cientificas (CSIC-ITQ), Danmarks Tekniske Universitet (DTU), Aktiebolaget Sandvik Materials Technology, CoorsTek Membrane Sciences AS, ENGIE, Shell Global Solutions International B.V.

WINNER has received funding from the Fuel Cell and Hydrogen 2 Joint Undertaking under Grant Agreement No (101007165). This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation programme, Hydrogen Europe and Hydrogen Europe Research.



P-16

Additive Manufacturing for Zero-emission Innovative Green Chemistry (AMAZING)

M. Drazkowski,(1) A. Nijmeijer,(1) H.J.M. Bouwmeester,(1) W. Meulenberg(2)
(1) University Twente, Enschede, Netherlands
(2) Forschungszentrum Jülich, Jülich, Germany

Satisfying the ever-increasing global demand for energy and material goods while achieving the ambitious CO_2 emissions targets of the EU for 2030 on climate change requires the utilization of renewable resources in the fuels and chemical industries. The Amazing project directly addresses this by replacing large-scale high-temperature cracking processes with electrically driven thermo-catalytic activation of alkanes to produce chemical building blocks allowing significant reduction in the CO_2 emissions.

To achieve the goals of the Amazing project we will design and fabricate ceramic membranes and catalytic coatings for the dehydrogenation of alkanes to alkenes. The resulting membranes will be employed to perform transport and thermal stability studies to understand the interplay between the membrane topology structure and chemical composition with the (1) transport mechanisms and the (2) thermo-mechanical stability. The performance of the membranes will be evaluated for the conversion of light alkanes to olefins on a bimetallic catalyst supported on the ceramic membrane to create a ceramic membrane reactor. Finally, we will explore the fabrication of a new type of membrane that is capable of conducting only protons. These membranes will be tested for the separation of hydrogen. The results from these activities will lay down the foundations for the utilization of catalytic membrane reactors, proton membranes and 3D printing technology to create multi-material micro-/macro- structured membrane systems for the production of chemicals using renewable electricity.

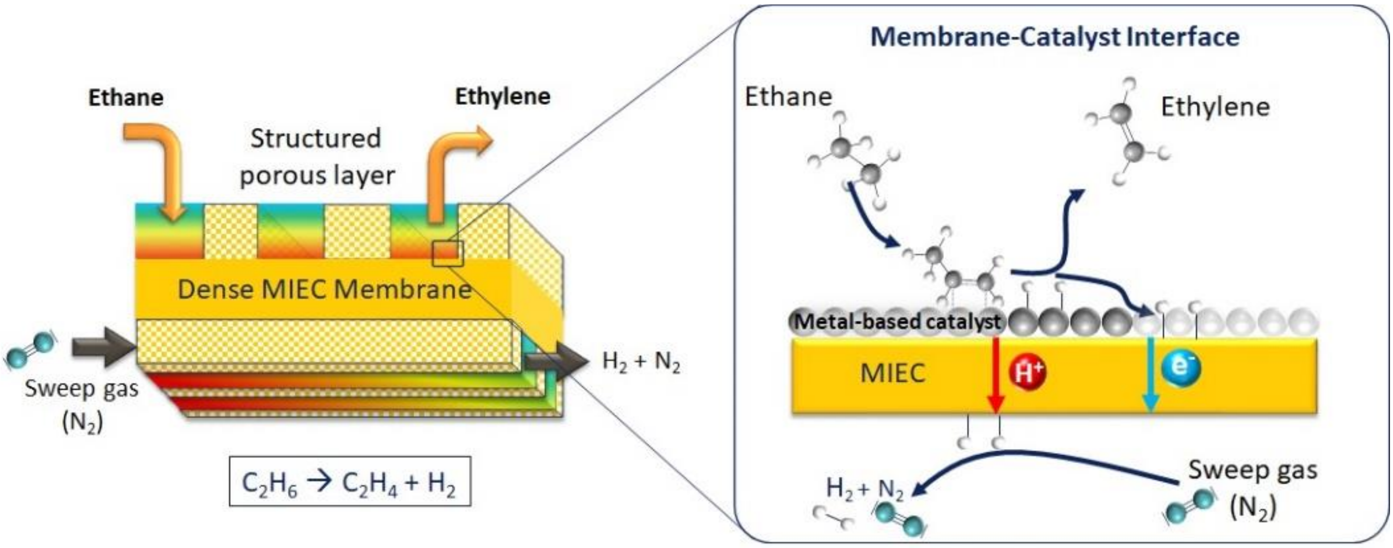


Fig. 1: Solid-solid interface of the catalyst-MIEC membrane surface during ethane dehydrogenation to ethylene

P-17

Towards Robust and Flexible Electrochemical Devices Using Proton Conducting Ceramics

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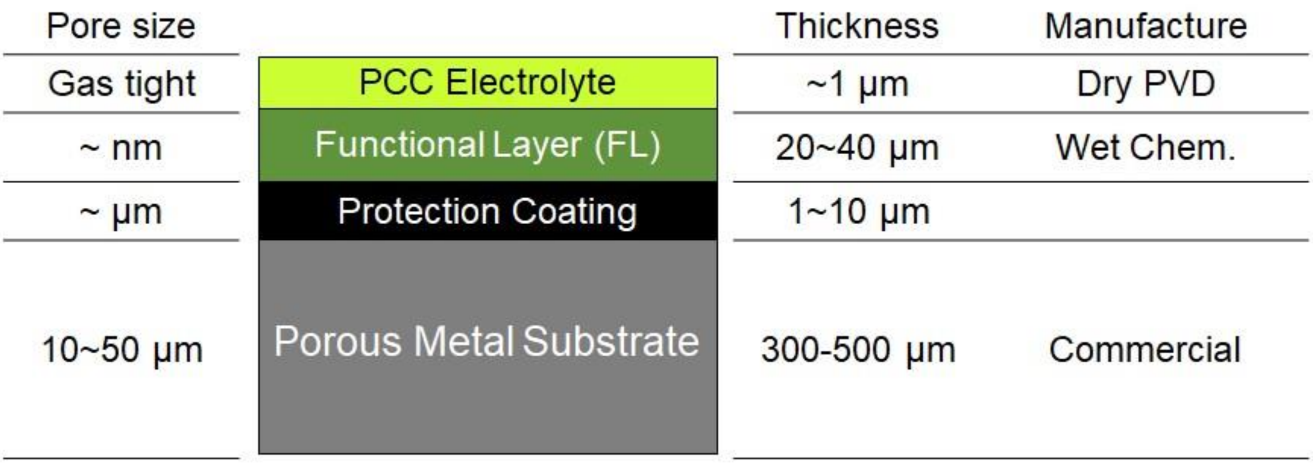
The high potential of Proton Conducting Ceramics (PCC) in fuel cell, steam electrolysis, and many other electrochemical applications has been demonstrated to achieve promising performances in the last decade. In the ceramic electrode supported cells, the refractory nature of state-of-the-art PCC electrolyte, e.g. trivalent cation doped $BaZrO_3$-$BaCeO_3$ perovskites, requires high sintering temperature that limits scalability and cost reduction for practical applications. Here we propose an alternative architecture based on planer porous Metal Supports (MS). MS architecture is advantageous over ceramic supported cells, in terms of high tolerance towards thermal/redox cycling that are key features for flexible and reliable operation in high temperature fuel cell and electrolysis applications, for example. The key challenge in the development of MS-PCC is to find a feasible process to fabricate gas-tight electrolyte on the porous metal support without degrading the metal. Our strategy is implementing multilayers combining wet chemical processes below 1000°C for the functional electrode and dry Physical Vapor Deposition (PVD) techniques below 800 °C for the gas-tight electrolyte coating. PCC in MS architecture provides potentially high performances, mechanical stability and flexibility for wide range of electrochemical applications. Our recent work in the development of MS-PCC half cells will be presented and prospects and challenges will be discussed.



Pore size		Thickness	Manufacture
Gas tight	PCC Electrolyte	~1 µm	Dry PVD
~ nm	Functional Layer (FL)	20~40 µm	Wet Chem.
~ µm	Protection Coating	1~10 µm	
10~50 µm	Porous Metal Substrate	300-500 µm	Commercial

P-18 Infiltration of Metal Catalysts for NH_3 Synthesis in Protonic Ceramic Cells

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The electrochemical synthesis of NH_3 represents a promising alternative to the conventional Haber-Bosch process, which currently relies on H_2 sourced from fossil fuels. It utilizes high pressures, resulting in high energy consumption. The interest on the prospect of solid state ammonia synthesis (SSAS) in proton conducting cells increased recently, because it features steam in place of H_2 as a reactant and the electrochemical activation of N_2 at the cathode through the use of a catalyst (like Ru or Fe, analogous to the thermocatalytic synthesis).

The implementation of the catalyst in the electrochemical cell is critical to the performance of the system. In order to augment the kinetics, high amounts of catalyst near the electrode-electrolyte interface are desired. Therefore, the microstructure of the electrode is of primary interest, as the void fraction of the layer must be large enough to enable a well-distributed deposition of catalyst particles. This may be achieved via the use of a pore-former, e.g. graphite powder, in the wet-route elaboration of the hydrogen electrode (Fig. 1). However, modifications must not compromise the structural integrity of the layer. Furthermore, the effect of various parameters (sintering conditions, thickness of the electrode layer, effect of additives to enhance wettability) on the final electrode structure are analyzed, as well as the influence of the infiltration protocol (evacuation time, number of infiltration steps, drying procedure). The findings along with preliminary electrochemical characterizations will be discussed.

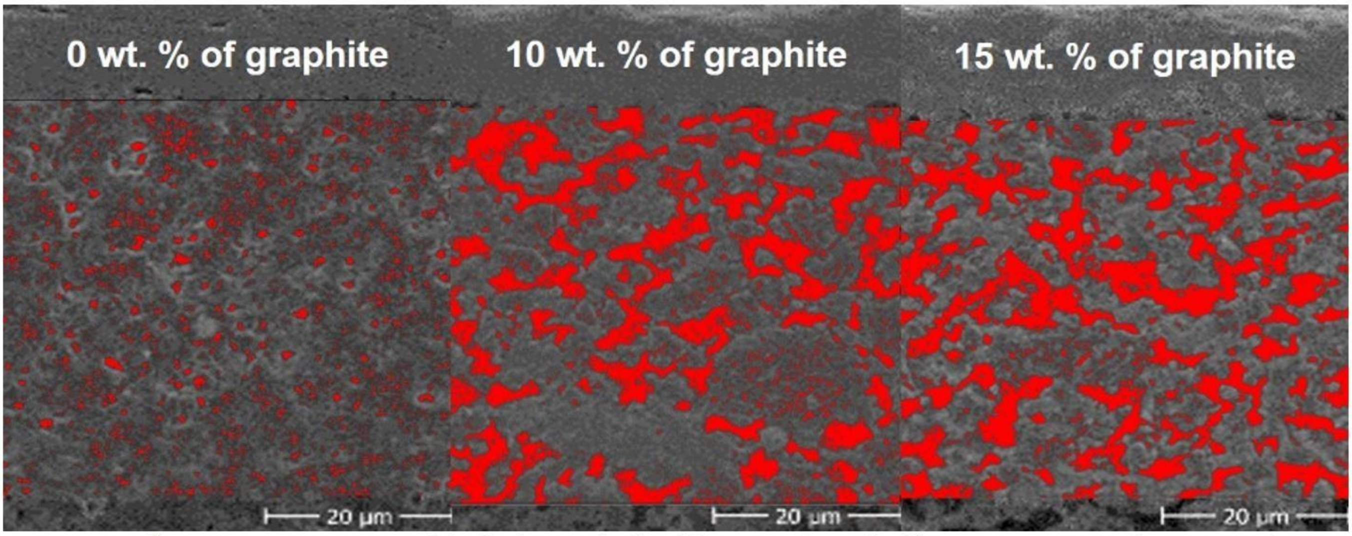

Figure 1: Cross-section views of fuel electrode backbones of a PCEC: microstructural impact of pore-former (graphite) mass fraction in the electrode slurry. Void fraction is shaded red.

Tuesday 28.9.2021, afternoon poster I

P-19 Hybrid proton-conducting membranes based on metal-organic coordination frameworks

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The development of hydrogen energy is associated with the creation of new functional materials, in particular effective proton-conducting electrolytes operating in medium temperatures. In the last decade, significant progress has been observed in the study of metal-organic coordination frameworks (MOFs). Micro and mesoporous structures with cavities for the inclusion of guest molecules, high specific surface area, combined with high porosity and crystallinity are of great interest. It creates wide possibilities for their functional design and obtain compounds embedded in the pores of MOFs with new properties combined ones of guest molecules and a mesoporous matrix. The introduction of strong acids and acid salts into the pores made it possible to create a new class of solid-state materials with high proton conductivity. The most thermally and chemically stable compounds were chosen as a matrix. CrMIL-101 and its analogue CrMIL-100 with a large pore volume, as well as UiO-66 were used as matrix. The chemical compatibility of compounds based on H_3PO_4 and CsH_2PO_4 and the invariability of the phase composition in the polymer were shown. For H_3PO_4@ MIL-100, the temperature dependence of conductivity obeys to the Grottguss mechanism. The conductivity is highly dependent on humidity and increases by orders of magnitude, approaching the conductivity of aqueous solutions. We show the correlation between the conductivity and sorption of water vapor on relative humidity at 10 to 100%. It permits to determine the concentration of H_3PO_4 at a fixed humidity. CsH_2PO_4@UiO-66 is characterized

Tuesday 28.9.2021, afternoon poster I

P-20

Non-trivial electric response of low-temperature proton conductors

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Impedance spectroscopy is a powerful tool to study and investigate the electric properties of ion-conducting materials [1]. However, as researchers focus on searching for new materials with high conducting values, some additional effects that can be observed are sometimes neglected as parasitic effects.

Here we present results of studies of low-temperature protonic conductors (mostly below 400K). Although studied materials are characterized by average conductivity (mostly maximum ~10^{-2} S/m) and it is hard to envision their potential applications in near future, they can still showcase some interesting and not so trivial electric behavior. We discuss the role of polar groups [2], additional embedded water [3], the influence of changes in structure that occur during thermal treatment [4,5] on electric properties, and its impact on impedance, conductivity, and dielectric spectra. We also discuss the effect of pressure on the hydrogen bond network and its effect on electric spectra and its consequence on the phase diagram in superprotonic compounds [6].

The research was partially financed from budget funds for science 2020–2023 as a research project under the PRELUDIUM-18 (National Science Centre, Poland, 2019/35/N/ST5/03324)

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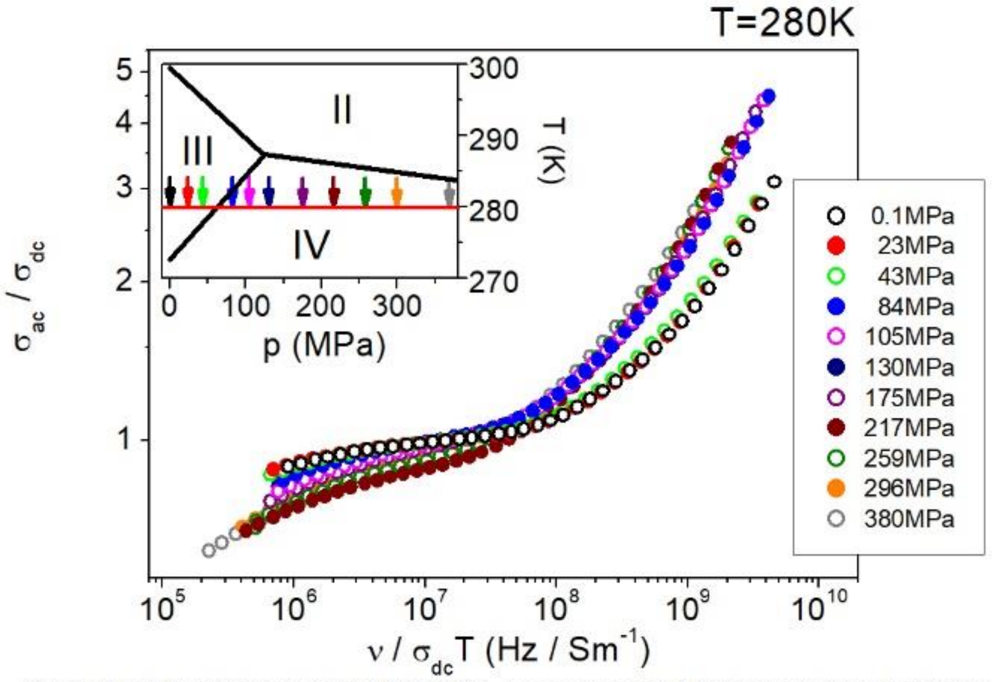

Scaled conductivity of $(NH_4)_3H(SeO_4)_2$ measured at different values of external pressure, at T = 280 K. In the inset the p–T diagram is shown with the arrows referring to the thermodynamic conditions under which the data were collected.

Tuesday 28.9.2021, afternoon poster I

P-21 Ultrafast soft X-ray and IR spectroscopy of proton transfer reactions in solution

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We investigate transient changes in the electronic structure of proton-donating and proton-accepting groups of molecules involved into proton transfer reactions in solution employing the local probe character of ultrafast soft X-ray spectroscopy. These measurements are complemented by transient IR spectroscopy of fingerprint modes of the molecules, to further benchmark the reaction dynamics.

By first considering the donor side, we address the question of the origin of photoacidity. While the concept of photoacidity is known as the Förster cycle, the underlying electronic structural mechanism leading to enhanced deprotonation upon photoexcitation is still under debate. We demonstrate that with time-resolved N K-edge absorption spectroscopy we selectively probe the changes in electronic structure at the amino ($–NH_3^+$) donor group of the 8-aminopyrenetrisulfonate (APTS) photoacid after UV excitation. Quantum chemical simulations of N K-edge absorption spectra point towards major changes in electron density at the $–NH_2$ site of APTS photobase as the main driving force for the photoacidic behaviour.

Recently, we have started investigating the microscopic mechanisms of proton transport by tracking protonated and unprotonated sites of imidazole molecules at the N K-edge after proton injection by a photoacid. Ultimately, we aim to gain insight into the electronic structure of hydrogen-bonded imidazole units associated with the solvation of excess protons and the elementary steps of proton transfer such as the proton-hopping mechanism famously described by von Grotthuss for water.

Tuesday 28.9.2021, afternoon poster I

P-22

Combination of negative, positive, and near-zero thermal expansion in bis(imidazolium) terephthalate with a helical hydrogen-bonded network

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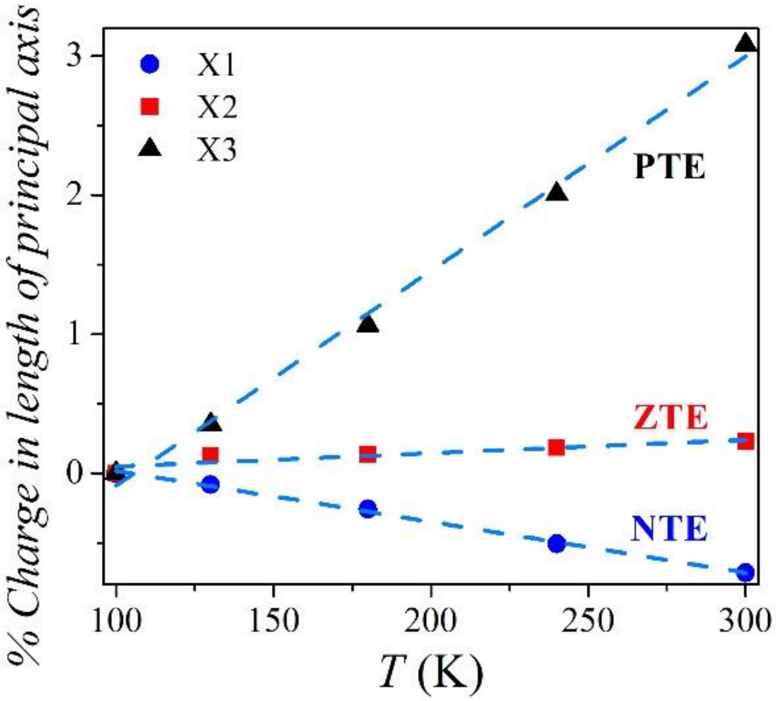
Many materials expand in all three directions when heated. However, some materials show the opposite trend in thermal behavior. This phenomenon is known as negative thermal expansion (NTE), caused by some structural peculiarities. NTE materials have attracted significant interest due to their potential applications as thermomechanical sensors or high-precision optical mirrors.

We report X-ray and FT-IR spectroscopic studies on bis(imidazolium) terephthalate. The coexistence of the negative, positive (PTE), and near-zero (ZTE) thermal expansion in a single crystal of this imidazolium salt with a helical hydrogen-bonded network has been observed for the first time. This study aims to explain the NTE phenomenon observed for bis(imidazolium) terephthalate. The unit cell parameters a, b, and c varies with temperature. Parameter b increases steadily with increasing temperature, while parameter c decreases. Parameter a undergoes very slight changes in the temperature range 150–300 K. The unusual thermal behavior of bis(imidazolium) terephthalate is most likely due to the scissor-like motion of the 2D flexible hydrogen-bonded network. The observed negative thermal expansion phenomenon was explained using the 'bond-rotation' effect. The folding trellis mechanism of NTE is proposed to explain the compound's thermal expansion mechanism.

The research was financed from budget funds for science in 2017–2020 as a research project under the "Diamentowy Grant" program (Ministry of Science and Higher Education, DI2016 015846).



P-23

Polymer composite electrolytes based on CsH_2PO_4

Irina Bagryantseva,(1,2) Valentina Ponomareva,(1) Daria Dormidonova(1)

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--- presentation cancelled ---

Acid salts of alkali metals with the general formula $M_xHy(AO_4)_p$ (A = S, Se, As, P) are promising proton conductors in the medium-temperature range. Synthesis of composite systems based on CsH_2PO_4 with polymer additives results in membranes combining the strength, flexibility, and hydrophobicity of a polymer component with the high ionic conductivity of an acid salt.

This work is devoted to the study of the morphological characteristics, transport, and mechanical properties of composite membranes based on CsH_2PO_4 and fluoropolymers (ultradispersed PTFE (Forum®), copolymer p(VDF/HFP) (SKF-26) and polyvinyl butyral (Butvar®B98). The selected polymer additives are stable in the investigated temperature range ($T \leq 250°C$). The optimal synthesis method of membranes with homogeneous distribution of components for each polymer was selected. The phase composition and proton conductivity of (1-x) CsH_2PO_4- x polymer electrolytes were investigated in the x range 0-0.3 wt.%. The crystalline structure of the salt and its thermal properties were not influenced by the polymer. When the mass fraction of the polymer is <15%, the proton conductivity slightly decreases, high polymer concentrations lead to the percolation of the "conductor-insulator" type with a further decrease in the conductivity. The mechanical properties of the CsH_2PO_4 and hybrid compounds were determined by the Vickers microhardness test. It was shown that increase in the volume fraction of the polymer results in the low HV values corresponding to the high robustness of the membranes to plastic deformation.

P-24

Sulfonated Poly-phenylene Sulfone Blend Membrane finding their Way into Proton Exchange Membrane Fuel Cells

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Sulfonated poly-phenylene ionomers have been considered one of the most promising candidates as building block for F-free membranes in PEM-fuel cells[1], because this class of polymers shows a significantly reduced gas crossover as well as relatively low production costs compared to the conventional fluorinated counterparts. The present work relies on the very high stability and proton conductivity of a sulfonated poly-phenylene-sulfone (s-PPS-220)[2,3]. Blending with a film forming strongly interacting poly-benzimidazole and additional fracture-toughening with a stretched nano-porous poly-ethylene support allows for the formation of thin membranes which are mechanically robust under wet and dry conditions. The availability of such membranes renders possible the formation of standard membrane electrode assemblies. These are tested for FC applications comparing performances in terms of activity and stability versus commercial Nafion® based MEAs. A mixed testing protocol has been developed by combining durability and performance tests under different temperature and humidity conditions. In addition, EIS combined with SEM cross-section analysis were carried out to investigate the influence of the membrane ageing on the anode and cathode performances. The newly developed PE reinforced sPPS-blend membrane shows similar I-V characteristics to the Nafion-based membrane, albeit with a greatly enhanced stability.

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P-25

Durable anion exchange membrane based on polyfluorenes functionalized with alicyclic quaternary ammonium cations

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Department of Chemistry, Lund University, Sweden

Anion exchange membranes (AEM)s are critical components of anion exchange membrane fuel cells (AEMFCs), which directly affect the performance and lifetime of the cell. Marino et al. have investigated the alkaline stability of different quaternary ammonium (QA) models compounds at elevated temperatures and reported that certain mono- and spirocyclic QA cations show superior alkaline stability.[1] Consequently, fluorene-based polymer backbones tethered with different mono-, bi- and spirocyclic QA side chains attached via alkyl spacers have shown high ion conductivity and long-term chemical stability.[2,3]

Here, we report on the synthesis of a new diphenylfluorene monomer functionalized with two dimethylpiperidinium (DMP) cations attached via methylene bridges. The monomer was copolymerized with dimethyldiphenylfluorene in superacid-mediated polyhydroxyalkylations to produce high-molecular weight poly(diphenylfluorene alkylene)s with well-controlled ionic contents (Figure 1). The impact of this synthetic approach on the water uptake, ion conductivity, and thermal and alkaline stability data of the resulting AEMs will be presented and compared with AEMs previously reported from our group.[4]

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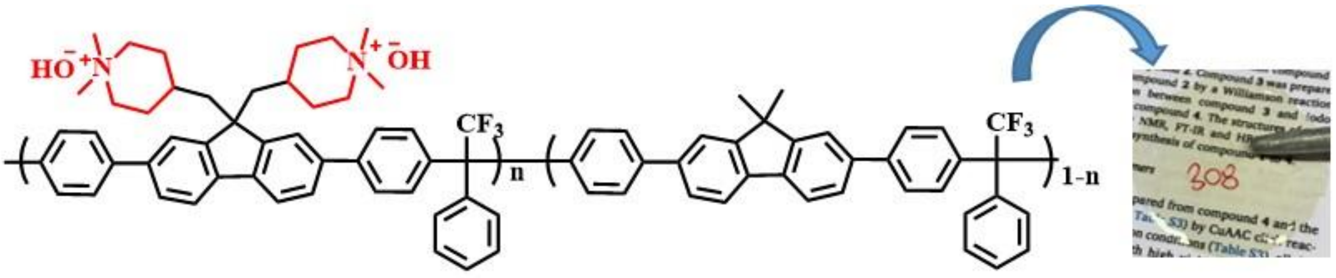

Figure 1. Representative molecular structure of poly(diphenylfluorene alkylene) functionalized with dual DMP cations.

Tuesday 28.9.2021, afternoon poster I

P-26

Zwitterionic Poly(terphenylene piperidinium) Membranes for Energy Applications

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Department of Chemistry, Lund University, Sweden

Both cationic and anionic membranes have been extensively studied in the pursuit of efficient, and cost-effective ion exchange membranes (IEMs).[1] To further improve the overall properties of IEMs, zwitterionic polymers bearing both cationic and anionic groups are now increasingly explored for certain applications.[2] In present work, ether-free poly(p-terphenyl-piperidinium) was selected for zwitterionic modifications owing to its straightforward synthesis and high chemical stability.[3] This contribution highlights the synthesis and polymerization of a zwitterionic piperidone monomer in combination with terphenyl and N-methylpiperidone using an established polymerization protocol.[3] The non-zwitterionic piperidone units of the polymer were subsequently quaternized via Menshutkin reactions to obtain the final polymer (Figure 1). Ex-situ characterization of membranes based on these polymers revealed ion exchange capacities of 1.8-2.2 mequivg^{-1}. The membranes reached excellent hydroxide conductivities, reaching up to 171 mS cm^{-1} at 80 °C, and showed reduced water uptake at lower temperatures, as well as good alkaline stability in 1 M NaOH solution at 80 °C.

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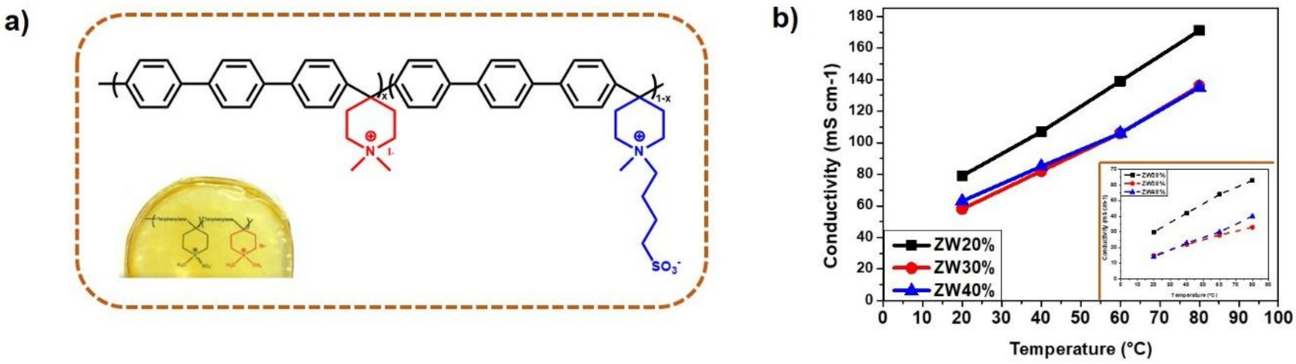

Fig. 1: Figure showing (a) the structure of a zwitterionic polymer and (b) graph showing the ionic conductivity of zwitterionic membranes in hydroxide form and chloride form (inset).

Wednesday 29.9.2021

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo	
					Y. Yamazaki
		11	17	18	24-INV Joubert Brief Overview of Current French Hydrogen Research Activities, Focus on electrolyte development for proton ceramic cells
		11:30			25-O Kawamori High-pressure synthesis of Ba-In-based perovskite-type oxide with proton-induced In deficiency
					26-O Winiarz Selected properties of thermally strained barium cerate – zirconate thin films
		12	18	19	27-INV Nazarenus Making Thin and Dense Ceramic Membranes at Room Temperature using Powder Aerosol Deposition
					K. Amezawa
		12:30			28-O Leonard Anode supported planar 5 cm × 5 cm SrZr0.5Ce0.4Y0.1O2.95 based solid oxide fuel cells processed via sequential tape-casting
		13	19	20	29-INV Peng Regulating the single-atom Pt coordination for an efficient and stable catalyst to reversible proton-conducting solid oxide cells
					30-O J.H. Kim Water as Hole-Predatory Instrumental to Create Metal Nanoparticles on Triple-Conducting Oxides
		13:30			
					K.-D. Kreuer
6	7	14	20	21	31-KN Geneste Proton transfer in barium zirconate and potassium tantalate: theoretical aspects
		14:30			32-INV Matsumoto Challenges and solutions for fuel/steam electrolysis cells using proton-conducting oxides
7	8	15	21	22	Panel "Inorganic"
		15:30			33-KN Dekel Alkaline Stability of Anion-Exchange Membranes
8	9	16	22	23	
					C. Bae
		16:30			34-INV Madsen Effects of nanoconfinement and local molecular environment on transport in polymer membranes
9	10	17	23		35-O Mossa From surfactants to Nafion through neural networks
					36-O Nederstedt Polyarylenes Bearing Perfluorophenylsulfonic and Perfluorophenylphosphonic Acid Groups as Proton Exchange Membranes
		17:30			37-O Q. Li Anion Conductivity in Cation Exchange Membranes
					D. Tsvetkov
10	11	18	24		38-O Safronova Sonochemical synthesis of high conductive and low permeable Nafion and hybrid Nafion-SiO2 from polymer solutions
		18:30			39-O L. Wang Novel Cs Deficient CsH2PO4 Superprotonic Phases
					40-O Dressler Proton Conductivity Simulations in Nanostructured CsH2PO4 with First-Principles Resolution
11	12	19			41-O Laven On the hydride-ion diffusion mechanism in perovskite oxyhydrides: insights from incoherent quasielastic neutron scattering

24-INV Brief Overview of Current French Hydrogen Research Activities, Focus on electrolyte development for proton ceramic cells

Olivier Joubert, Eric Quarez, Clément Nicollet, Annie Le Gal La Salle

Université de Nantes, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), Nantes, France

Twenty years ago, the French scientific community working in the field of hydrogen, started to federate under the leadership of the CNRS. It took the form of successive Research Grouping bringing together experts in solid oxide fuel cell, proton exchange polymer membrane fuel cells, hydrogen storage and systems mainly from CNRS but also from CEA. These GdRs promoted and structured an interdisciplinary field of research with excellent results.

Since January 1st 2020, the CNRS community has formed the Research network on Hydrogen energy (FRH2) based on the active nucleus of the former GDR laboratories (29 laboratories) with about 300 researchers and professors. The first part of the presentation will give a brief overview of this CNRS network including some highligts.

The second part will be dedicated to the development of materials used in proton ceramic cells and more precisely to the ceramic electrolyte: optimization of the microstructure of the material via accurate monitoring of the synthesis and temperature treatment steps. The objective is to reach a total conductivity level above 0.1 mS/cm for operating temperatures below 600°C in order to prevent premature aging of SO cells performance. This study is focused on BCZY solid solution showing properties which are compromise between the high proton conductivity of BCY and the stability of BZY. This material requires high sintering temperatures (≈1600°C) and new sintering are needed. This the study will focus on the influence of the cold sintering process (CSP) on the electrolyte conductivity.

25-O High-pressure synthesis of Ba-In-based perovskite-type oxide with proton-induced In deficiency

Hiroaki Kawamori, Akihiro Ishii, Itaru Oikawa, Hitoshi Takamura
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One of the concepts for realizing a highly proton-conductive perovskite-type oxide is to increase the proton concentration. $A^{2+}B^{3+}O_{2.5}$, which is well-known for its brownmillerite-type structure and great potential for a high proton concentration, is focused on in this study. High-pressure (HP) apparatus enabling hydrothermal condition at 1000ºC was utilized to obtain highly hydrated and densified samples. By using this technique, our group has recently succeeded in preparing fully hydrated $BaSc_{0.67}O(OH)_2$ with Sc deficiency (XRD pattern are shown in Fig 1a). This full hydration reaction caused by B-site (Sc) deficiency is a novel mechanism to increase the proton concentration without any dopants. Its electrical conductivity discontinuously increased at 350ºC and reached to 10^{-2} S/cm at around 450ºC (Fig1b). This conductivity enhancement caused by high proton concentration and B-site deficiency is expected to hold for other systems. Thus, B-site deficient hydrous perovskite-type oxides were prepared starting from $A_3B_2O_6$ (A: Sr and Ba, B: Al, Ga and In) and H2O. Among those oxides, only Ba-In-based oxide was successfully prepared as the B-site deficient perovskite-type structure by HP synthesis as well as the Ba-Sc oxide(Fig 1c). Proton-induced B-site deficiency is therefore considered as unique phenomena for oxides having the brownmillerite-type structure such as in Ba-Sc and Ba-In systems.

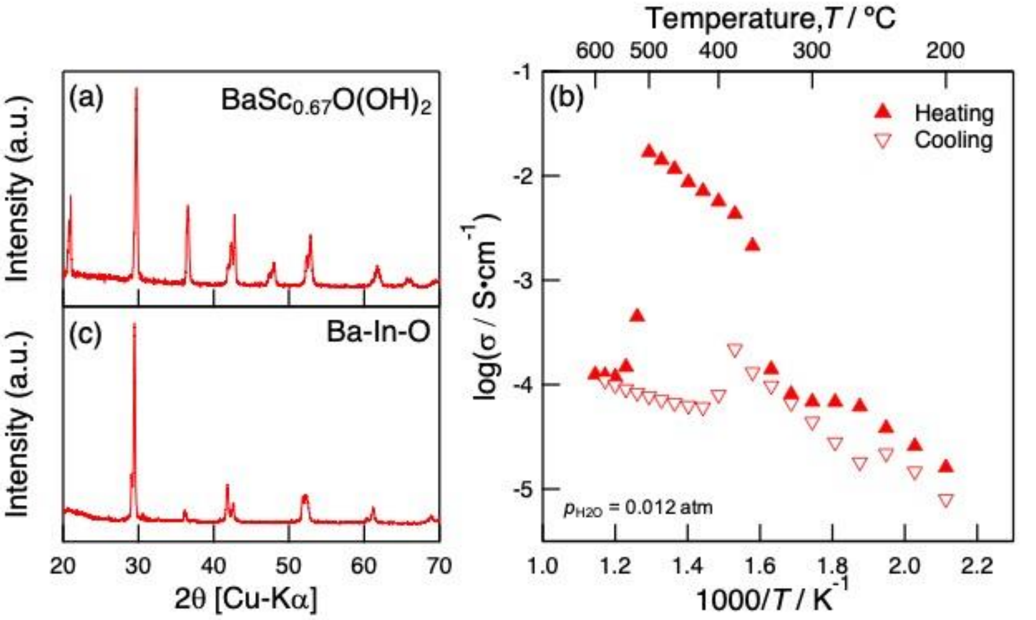

Figure 1 (a) XRD pattern of $BaSc_{0.67}O(OH)_2$. (b) Total electrical conductivity of $BaSc_{0.67}O(OH)_2$. (c) XRD pattern of Ba-In oxide after HP synthesis.

26-O Selected properties of thermally strained barium cerate – zirconate thin films

Piotr Winiarz,(1) Daniel Jaworski, (1) Mirosław Sawczak,(2) Monica Susana Campos Covarrubias,(3)
Mantas Sriubas,(3) Kristina Bockute, (3) Zivile Rutkuniene,(3) Giedrius Laukaitis,(3) Maria Gazda(1)

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Structural and electrical properties of barium cerate-zirconate thin films were examined and discussed. Strain in the materials was induced by the difference of thermal expansion coefficients (TECs) between the film and the substrate.

Thin films of $BaCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-\delta}$ (BCZY) and $BaZr_{0.6}Ce_{0.2}Y_{0.2}O_{3-\delta}$ (BZCY) were deposited using a PLD method. The materials used as substrates were commercial metal alloys and single crystal oxides.

The phase composition was checked using Phillips X'Pert Pro diffractometer, $\lambda = 1{,}54$Å. Additionally, SEM micrographs with EDX analysis were used to examine the cross-section of each material. Depending on the type of electrical measurement, two setups were used. For films deposited on metal alloys, Gamry 3000 potentiostat/galvanostat was used and measured through-plane with 1V excitation amplitude and in the temperature range 200°C – 400°C. For films deposited on oxides, Novocontrol Alpha-A frequency analyzer was used for in-plane measurement with amplitude 1V and temperature range 200° - 500°C. For both configurations, ProboStat (Norecs AS) was used as a measurement cell. Measurements were performed in the humidified N2 atmosphere and the frequency range of 1MHz – 0.01Hz.

All prepared samples were single-phase. Strained films exhibit lower activation energy in the 200°C – 350°C temperature range, probably because of the influence of oxygen–oxygen distances, which cause an increase in proton diffusivity and decrease the activation energy. Some of the metal-supported films degraded upon temperature and/or time.

27-INV Making Thin and Dense Ceramic Membranes at Room Temperature using Powder Aerosol Deposition

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Ceramic compounds based on the proton conducting perovskite material classes of $BaZrO_3$ and $BaCeO_3$ are potential candidates to improve solid oxide fuel cells (SOFC) by lowering their operation temperature and raising performance levels. However, a major drawback still limits the use of proton conducting solid electrolytes: very high sintering temperatures (up to 1800 °C) are necessary to produce the dense membranes. The challenge to fabricate dense yet thin membranes may be resolved by a novel ceramic spray coating technique called Powder Aerosol Deposition (abbreviated PAD or AD). This method enables to build ceramic films that meet the requirements of a very small porosity and high performance without the necessity of conventional sintering. Here, ceramic films are processed completely at room temperature by just spraying a dry, micrometer-sized powder. Directly after deposition, films already feature typical ceramic characteristics like a high hardness and a high wear resistance. These properties are the result of the dense, nanocrystalline film morphology that is obtained through the underlying deposition mechanism of PAD, described as Room Temperature Impact Consolidation (RTIC). Films with thicknesses up to 100 µm can be formed on almost all kinds of substrates, even with a porous structure. As-deposited PAD films typically exhibit a lowered electrical conductivity, but a moderate thermal annealing (way below sintering temperatures) enables to regain near-bulk-like values. In this contribution, we survey the PAD method and demonstrate its potential for SOFC membranes.

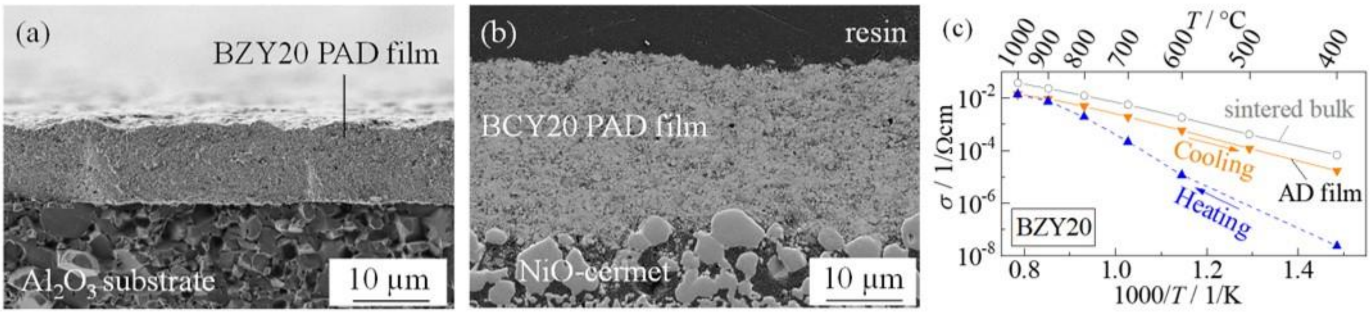

Fig. 1: SEM images of aerosol deposited solid electrolyte films of a) barium zirconate (BZY20) and b) barium cerate (BCY20); c) electric conductivity of a BZY20 AD film

28-O Anode supported planar 5 cm × 5 cm $SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{2.95}$ based solid oxide fuel cells processed via sequential tape-casting

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Tatsumi Ishiraha,(1) Hiroshige Matsumoto(1)

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Solid oxide fuel cells are the most efficient means to convert stored chemical energy to usable electrical energy directly. As a result, they constitute one of the most energy-efficient non-conventional power generating systems with almost zero pollution to the environment. Protonic electrolytes are particularly suitable for such devices because of their higher mobility of protons. On the lab scale, these devices have made significant progress in recent years. Ranging from newly developed, high-conductivity electrolytes and precisely adjusted cathode designs, providing a path for further performance improvement at moderate temperatures (~350°C), thus transforming the way we convert and store energy. Despite this progress, the challenge has been upscaling robust planar-type devices. In the present contribution, a cost-effective inverse tape casting route is employed to fabricate planar anode-supported fuel cells consisting of $NiO\text{-}SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ substrate, $SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ electrolyte, and $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ as the cathode. All the processing parameters were analyzed and adjusted to obtain flat single cells of dimension up to 5 cm × 5 cm × 0.5 mm with diminished warping. Besides electrochemical characterization, the morphology and microstructure of the half-cells were analyzed and compared with $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$ electrolyte-based cells using a combination of HAADF-STEM and EDS, post cell characterization. Our work features a facile approach for realizing low-cost fabrication of large-sized protonic cells, satisfying both high performance and durability.

29-INV

Regulating the single-atom Pt coordination for an efficient and stable catalyst to reversible proton-conducting solid oxide cells

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(2) CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory for Biomass Clean Energy and Department of Chemistry, University of Science and Technology of China
(3) National Synchrotron Radiation Laboratory, University of Science and Technology of China

Reversible proton-conducting solid oxide cells (R-PCCs) technologies have been proposed to surmount energy storage and conversion challenges. Obtaining more active sites on air electrode with a limited surface area is always a conundrum. Single-atom catalysts (SACs), enthusiastically admired, matching excellent platinum, is the most suitable new approach. However, SACs are prone to agglomeration and deactivation at high temperatures (above 650 °C). Here, we first proposed $Pr_4Ni_3O_{10+\delta}$ (PNO) as a support, with a simple and universal method to in situ synthesize catalysts of PNO supported single-atom Pt. Its structure unchanged after sintering at 700 °C for 800 hours. And an excellent catalyst with a maximum power density (FC mode) of 1040 $mWcm^{-2}$ and an electrolysis current (EC mode, 1.3 V) of 2020 $mAcm^{-2}$ at 700 °C is obtained by adjusting the ratio of the coordination of platinum, which improved more than twice compared PNO. This advanced R-PCCs can maximize the synergistic catalysis of platinum and the substrate, enhancing the technoeconomic value of the devices.

30-O

Water as Hole-Predatory Instrumental to Create Metal Nanoparticles on Triple-Conducting Oxides

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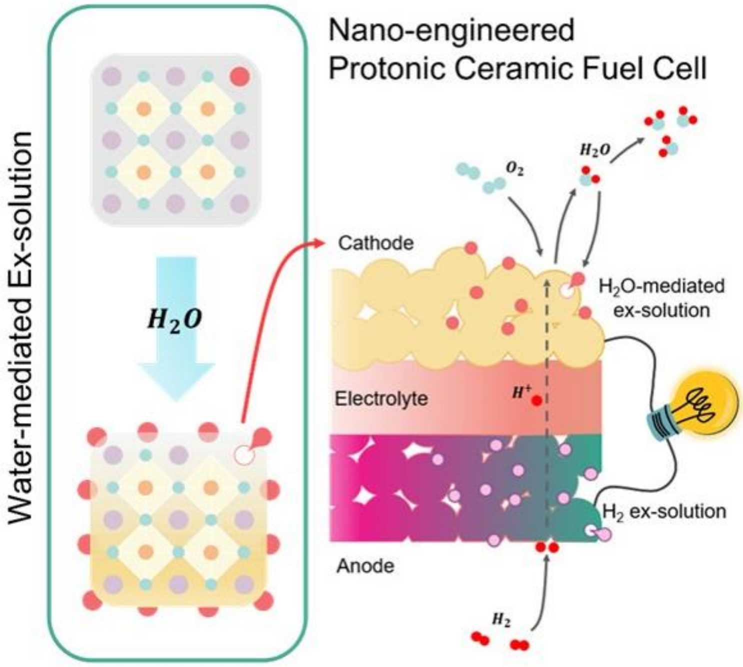
Single-phase materials with mixed ionic and electronic conductivity underpin multiple solid-state electrochemical devices as promising electrodes. In particular, triple-conducting oxides that carry protons, oxygen ions, and electron holes simultaneously have ushered in a breakthrough in improving the performance of ceramic fuel cells, but insufficient electrochemical activity on their surface remains a challenge with regard to the development of related technologies. Here, we present a novel methodology that spontaneously yields transition metal nano-catalysts well dispersed on triple-conducing oxide surfaces realized by simply supplying water vapor with a room-temperature bubbler. The central idea underlying this strategy is the hydrogenation reaction that occurs in protonic ceramics containing redox-active transition metals and the subsequent selective surface phase decomposition. As a case study, Ag-substituted $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ is chosen to exemplify the markedly enhanced electrode performance in a fuel cell. The water vapor generated during the operation induces the precipitation of Ag nanoparticles and significantly lowers the electrode resistance to a record level. These observations suggest a new design direction for oxide-supported catalysts with multiple charge carriers.



31-KN

Proton transfer in barium zirconate and potassium tantalate: theoretical aspects

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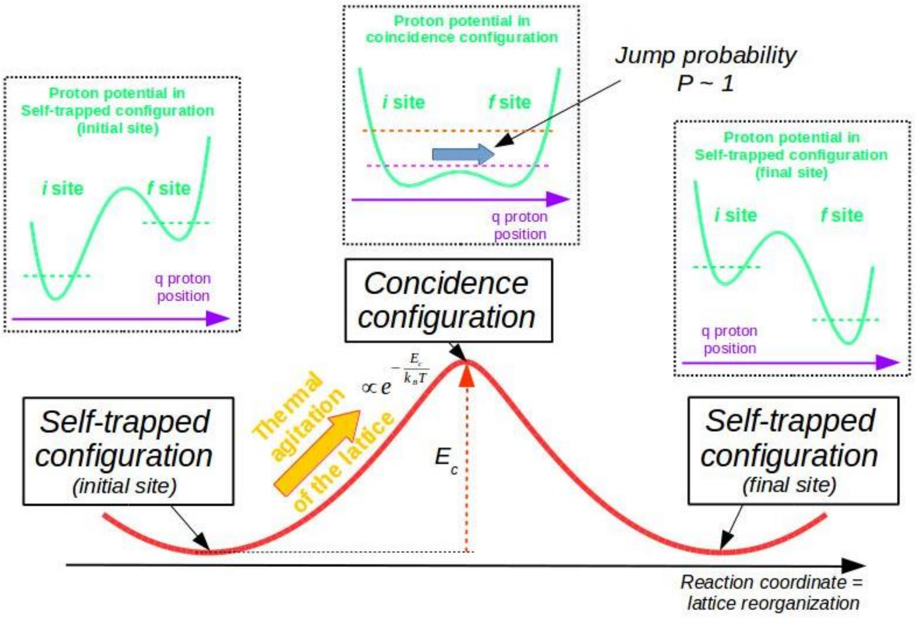
The diffusion of protons in hydrated perovkiste oxides proceeds via the succession of reorientations and transfers, two microscopic mechanisms strongly impacted by the quantum effects related to the light mass of the proton. A theory of proton transfer (PT) that accounts for all quantum (static and dynamic) effects is presented. Due to the large quantization of the OH stretching vibration, the proton may be considered as frozen in its ground state (for this vibration) up to high temperatures. PT, which is a thermally activated process, is assumed as taking place in specific lattice (coincidence) configurations, in which the energies of the protonic ground states in the two wells are equal [1,2]. At such coincidence events – that occur thanks to atomic thermal vibrations – the transfer itself happens with a certain probability, obtained as the solution of a quantum-mechanical curve-crossing problem, and described by the Landau-Zener formula. Two specific atomic vibrations play a fundamental role: a necessary one, the lattice reorganization, and a facilitating one. We apply this theory to two cubic perovskite oxides, $BaZrO_3$ and $KTaO_3$ [3], and highlight important differences between the two compounds: the PT regime is adiabatic in $BaZrO_3$ (absence of non-adiabatic tunneling regime down to ~ 150 K), while in $KTaO_3$, non-adiabatic tunneling contributions are larger.

[1] D. Borgis, J. T. Hynes, J. Phys. Chem. 100, 1118 (1996).
[2] A. Klamt, H. Teichler, Physica Status Solidi 134, 533 (1986).
[3] G. Geneste, Solid State Ionics 323, 172 (2018); Solid State Ionics 358, 115483 (2020).

Adiabatic proton transfer:



32-INV

Challenges and solutions for fuel/steam electrolysis cells using proton-conducting oxides

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This paper reports the challenges of proton-conducting solid oxide fuel and electrolysis cells and attempts to solve them. These devices have several advantages, such as reduced operating temperature and fuel concentration compared with conventional oxide ion conductors-based devices. The author's group has reported on intermediate-temperature steam electrolysis operated at a relatively low electrolysis voltage, as shown in the figure. However, given that proton conductivity is developed by hydration of oxide ion vacancies, several challenges such as electronic leakage due to electron-hole conduction, chemical expansion, and reduction of proton conductivity due to interdiffusion of transition metal originated from the electrode. This paper reports material development, cell processing, and attempts to contrive the electrode/electrolyte interface structure to solve some of these problems. For example, the diffusion of transition metals reduces the proton conductivity of the electrolyte. It is most severe when the cell consists of a very thin electrolyte on a Ni cermet substrate, in which case the diffusion of nickel increases the ohmic resistance several orders of magnitude. This problem can be avoided by a vapor deposition method such as sputtering or low-temperature firing using nanoparticles.

A new project to develop a fuel cell using protonic conductors “Development of Ultra-High Efficiency Protonic Ceramic Fuel Cell Devices” started last year funded by NEDO in Japan. This report also mentions the characteristics of the project and some preliminary results.

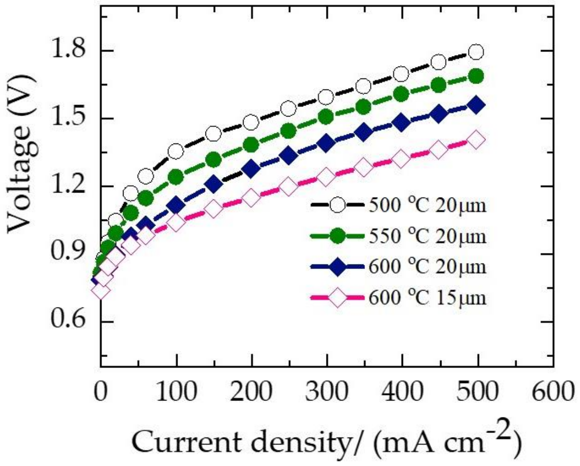

Figure 1. Typical steam electrolysis I-V performance using proton-conducting $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$ electrolyte based cell operated at 600, 550, and 500 °C. Kwati et al., Membranes 2020, 10(11), 339.

33-KN

Alkaline Stability of Anion-Exchange Membranes

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Fantastic progress has been recently achieved on Anion-Exchange Membranes (AEMs) for fuel cell and electrolyzer applications. Recent studies reported novel techniques for characterizing AEMs [1], showing ultra-high hydroxide conductivities of 200 or even 300 mS/cm [2]. In addition, new ionomeric materials and functional groups with increasing stability were introduced [3-5]. On the fuel cells front, AEMs able to operate under high-temperature AEM fuel cell (HT-AEMFC) operation mode were reported [6-7], simulated materials and conditions to achieve AEMFC lifetime of 15,000 hours were theoretically demonstrated for the first time [8-9]. However, AEM-based cell lifetime is still limited to ~2,000 hours of operation [10]. We still need to overcome several challenges to allow AEMs to reach suitable alkaline stability for durable electrochemical applications. To achieve that goal, we need a better understanding of the current challenges on the alkaline stability of AEMs. Dekel's group works on this critical challenge, aiming to impact the AEM research community significantly. The latest understanding and achievements of our group in the alkaline stability of AEMs will be presented.

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[10] Adv. Energy Mater., 2001986, 2020

34-INV

Effects of nanoconfinement and local molecular environment on transport in polymer membranes

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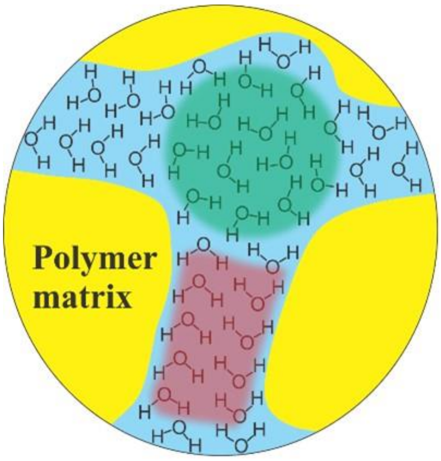
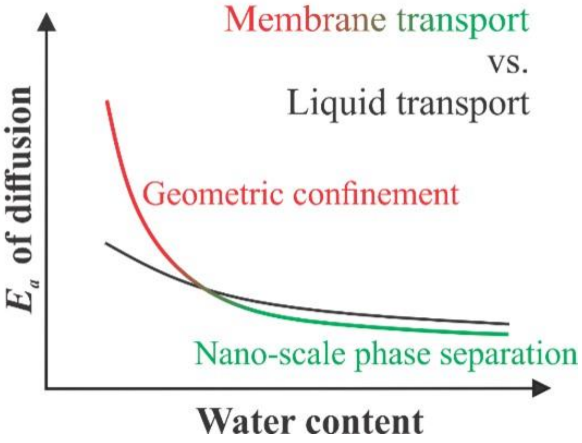
Investigating how nanometer-scale structure relates to diffusion in polymer membranes can both illuminate fundamental mechanisms for membrane transport and inform further membrane development. In this study, we employ NMR diffusometry and molecular dynamics (MD) simulations to determine diffusion coefficients and activation energies of diffusion (E_a) of mobile species in a perfluorosulfonic acid membrane and in analogous aqueous solutions. NMR shows that membrane transport exhibits much higher E_a at low hydration as compared to solutions. MD simulations of a model system consisting of carbon nanotubes with varying diameter reveal that E_a of diffusion clearly relates to both the geometric nanoconfinement of the hydrophilic pathways in the membrane as well as the local molecular environment that includes the degree of hydrophilic/hydrophobic phase separation. This work demonstrates that the combination of experimental and computational determinations of E_a can illuminate the study of molecular transport processes and how morphology couples with transport at the nanoscale.





35-O

From surfactants to Nafion through neural networks

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Attempts to develop a clear picture of the three-dimensional nano-morphology of Nafion ultimately rest on a wise choice of stylized arrangements of simple geometry domains, employed to make sense of neutrons and X-rays scattering data. While over the years a few competing alternatives have been proposed, no final general consensus has been reached. Recently, we have proposed a different point of view on the matter (10.1021/acs.jpcb.0c06172) by applying Machine Learning advances, convolutional neural networks (CNN), to three-dimensional (voxels) Molecular Dynamics simulation data. We have considered a simple coarse-grained model for both Nafion and hydrated ionic surfactants. These latter have been shown to display structure and transport properties at the nanoscale that are similar to those of the ionomer, but are also simpler to handle. We have employed the surfactants data to train a classifier to automatically detect the water quantity absorbed in the system, therefore associating to a given hydration level the corresponding most representative nanostructure of known symmetry. We have next applied the same network for inference on Nafion configurations, and have extracted a measure of the similarity of the two sets of data. I will show that this procedure amounts to describe the structure of the ionomer as a collection of patches corresponding to well characterized local morphologies of the related surfactants system.It also provides an intriguing agnostic data-driven view on the hydration dependence of Nafion morphology, without resorting to any a-priori model picture.

36-O Polyarylenes Bearing Perfluorophenylsulfonic and Perfluorophenylphosphonic Acid Groups as Proton Exchange Membranes

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In the present work we have prepared polyarylenes containing perfluorophenyl acid groups through superacid mediated polyhydroxyalkylation, followed by straightforward modifications to introduce sulfonic and phosphonic acid groups, respectively.[1, 2] The stiff polymer backbone provides good mechanical properties of the membrane and efficiently restricts the water uptake. Furthermore, the absence of any heteroatoms in the backbone improves the stability of the PEMs, and the molecular structure of the polymers induces efficient phase separation by ionic clustering. Membrane characterizations show that both the sulfonated[1] and the phosphonated[2] PEMs reach high proton conductivity, as well as excellent thermal and oxidative stability. Still, the sulfonated PEMs exhibit higher proton conductivity (116 mS cm^{-1} at 80 °C and 90% relative humidity, compared with 48 mS cm^{-1} for the phosphonated under the same conditions), while the phosphonated PEMs possess higher resistance against radical attack. The combination of properties such as good solubility and processability, high glass transition temperature, excellent radical resistance and thermal stability, moderate water uptake at high temperature, good mechanical properties and high proton conductivity under reduced humidity make these materials very attractive for the use in water electrolyzers and fuel cells.

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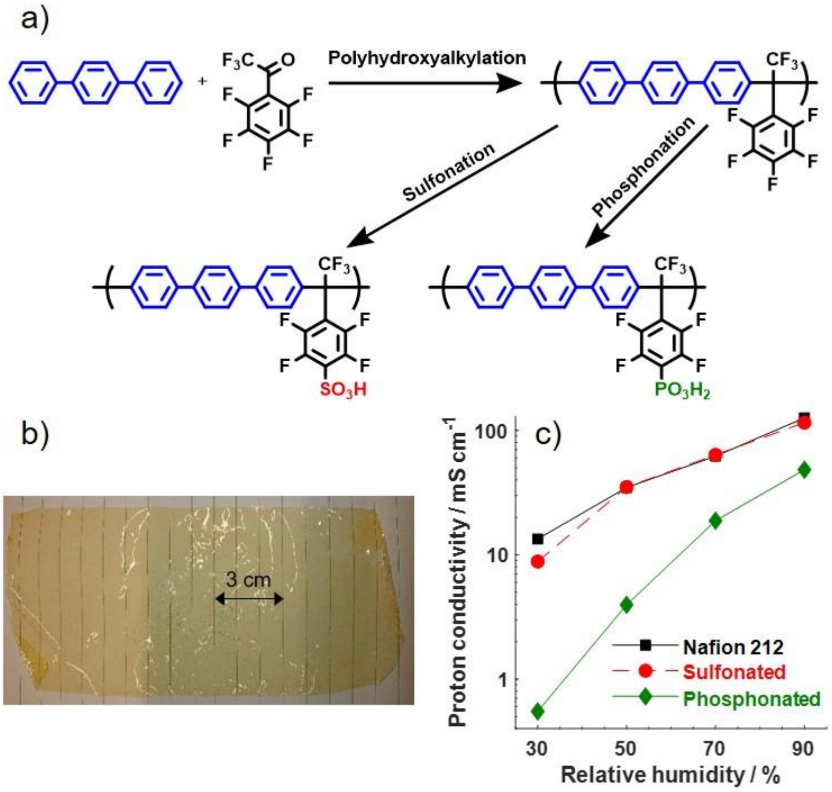

Figure 1. Synthetic pathway (**a**), membrane of sulfonated polymer with a thickness of 10 µm (**b**), proton conductivity at 80 °C under reduced humidity (**c**).

37-O

Anion Conductivity in Cation Exchange Membranes

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Cation exchange membranes are composed of immobilized anionic sites and allow for passages of movable cations while the conductivity of anions is limited due to the Donnan exclusion effect. The phenomenon of the anion conductivity through cation exchange membranes does exist and is of technical importance for, for example, the chlor-alkali process [1]. Cation exchange membranes are used for electrochemical reduction of CO_2 in alkaline media, where the conductivity of bicarbonate (HCO_3^-), likely carbonate (CO_3^{2-}) as well, causes the so-called CO_2 pumping, a critical issue for the technology [2]. The phenomenon is studied by assembling an electrolyser cell with a cation exchange membrane in either acidic (H^+) or salt (e.g. K^+) forms and purged with hydrogen. The total conductivity of the membrane is measured by electrochemical impedance spectroscopy, which in case of the salt (K+) form membranes includes contributions from cations (K^+) and bicarbonate anions (HCO_3^-). The steady I-V polarization curves are recorded corresponding to the hydrogen oxidation and evolution reactions. In the acidic (H^+) form, the ohmic resistances obtained from the impedance and hydrogen pumping I-V curves are identical showing the proton conductivity in both cases. For the salt (K^+) form membranes, comparison of the two measurements gives an up to 2.5 % contribution of the anion (HCO_3^-) conductivity through the cation exchange membrane.

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38-O

Sonochemical synthesis of high conductive and low permeable Nafion and hybrid Nafion-SiO_2 from polymer solutions

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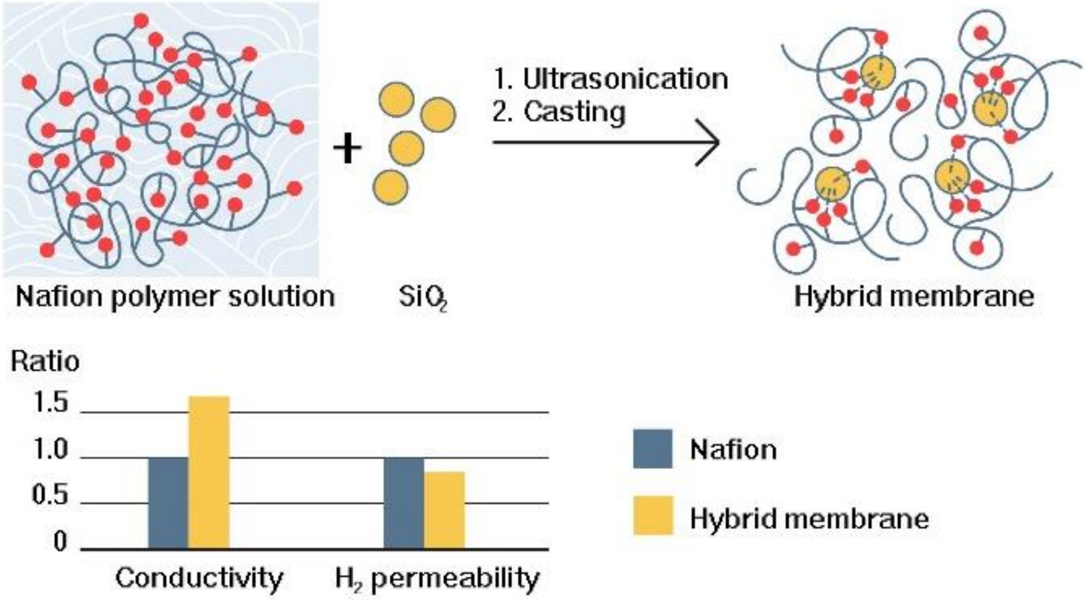
PFSA as Nafion® are widely used in diverse practical applications. This work reports the effect of ultrasonic (US) treatment of the PFSA solutions by itself and in the presence of SiO_2 nanoparticles on the characteristics of the cast Nafion and hybrid Nafion+SiO_2 membranes.

Upon ultrasonication, the length of macromolecules is reduced, and the number of sulfo groups decreases. Due to the sonication, proton conductivity of the membranes increases by 40-45%. When polymer solutions are ultrasonicated with SiO_2 nanoparticles, they are additionally crosslinked due to the interaction of SiO_2 with sulfo groups. Maximum conductivity at low RH (4.1 mS/cm at 30°C, 30% RH) is observed for the Nafion+1wt% SiO_2 membrane cast from polymer solutions upon the ultrasonication for 10 min and this value is 1.7 times higher than that of the pristine Nafion. Upon extended sonication, selectivity of the cation transfer (in NaCl solutions) through the membranes is reduced from 94 % for initial membrane to 85 %. Hydrogen permeability for membranes after long US treatment of polymer solution increases by 25%. Hydrogen permeability for hybrid Nafion+SiO_2 membranes appears to be lower than that of the pristine Nafion membranes by 15%.

The results highlight the importance of the proper selection of favorable conditions of the US treatment of the solutions of PFSA polymers for the preparation of membranes and for the development of catalytic layers. US-assisted dispersion of SiO_2 in the PFSA solutions allows preparation of hybrid membranes with improved transport characteristics.

This work was financially supported by the project of Russian Science Foundation No 21-73-10149, https://rscf.ru/project/21-73-10149.



39-O

Novel Cs Deficient CsH_2PO_4 Superprotonic Phases

Louis Wang,(1) Sawankumar Patel,(2) Sheel Sanghvi,(1) Yan-Yan Hu,(2) Sossina Haile(1)

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Investigations into Cs deficient CsH_2PO_4 samples, through mixtures of CsH_2PO_4 (CDP) and $CsH_5(PO_4)_2$, uncovered a rich phase space with several remarkable adaptations of the cubic superprotonic phase of CDP. A new superprotonic phase, $Cs_7(H_4PO_4)(H_2PO_4)_8$ or CPP, was discovered to form at 90 °C and, through single crystal diffraction, was revealed to bear extraordinary $H_4PO_4^+$ cations on select Cs sites of a structure that otherwise resembles cubic CDP [1]. Notably, CPP is stable without active humidification up to 151 °C at which it exhibits a proton conductivity of $9.3 * 10^{-4}$ S cm^{-1}. At 180 °C, CPP transforms into a solid-solution form of CDP, or α-CDP(ss), in which Cs deficiency is structurally accommodated by vacancies on the Cs site that result in an expansion of the unit cell. α-CDP(ss) displays eutectoid behavior over the composition range $0 \leq x \leq 2/9$ in $[Cs_{1-x}H_x]H_2PO_4$ with a eutectoid reaction temperature of 155 °C. Thus, Cs deficient CDP can exist entirely as the superprotonic cubic phase at temperatures well below the superprotonic transition of CDP (228 °C) and attain conductivities on the order of 10^{-2} S cm^{-1}. Therefore, introducing Cs deficiency in CDP can extend the low temperature operating range of CDP-based devices.

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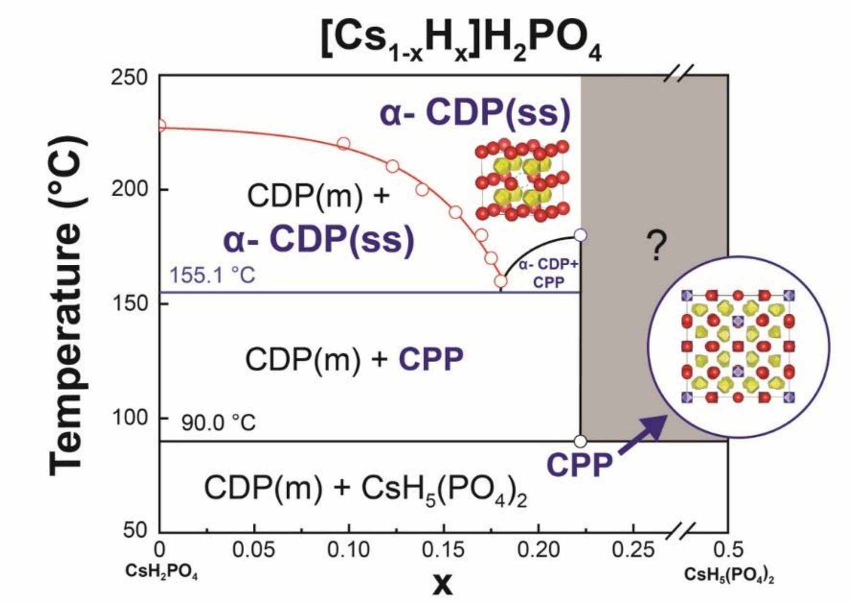

Phase diagram of Cs deficient CDP, $[Cs_{1-x}H_x]H_2PO_4$. A new superprotonic phase, $Cs_7(H_4PO_4)(H_2PO_4)_8$ or CPP, forms at 90 °C and its structure, shown in the inset, bears the remarkable $H_4PO_4^+$ cation. The cubic phase of CDP exhibits eutectoid phase behavior, accommodating Cs deficiency with vacancies on the cation site.

40-O

Proton Conductivity Simulations in Nanostructured CsH_2PO_4 with First-Principles Resolution

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The high temperature phases of the solid acids $CsHSeO_4$, $CsHSO_4$ and CsH_2PO_4 show extraordinary high proton conductivities, while the low temperature phases do not conduct protons at all. We explain both the phosphate/sulfate and temperature/phase-related variations of the proton conductivity on a molecular level via a recently developed coupled molecular dynamics/lattice Monte Carlo simulation approach (cMD/LMC). Our simulation method elucidates the relative importance of the two key components of the Grotthuss-type proton conduction mechanism, proton hopping and structural reorientation, as a function of the chemical/thermodynamical conditions.

The cMD/LMC approach uses the atomistic information from an ab initio molecular dynamics simulation to model microscopic proton transfer probabilities, while the actual long-range propagation of the protonation state is performed by the Monte Carlo part. The approach allows for an atom-level resolution of ion dynamics with quantum chemical accuracy but with final length- and time-scales of micrometers and milliseconds. We demonstrate the application potential of the scheme by computing the explicit dynamics of a non-equilibrium process in an 8 μm CsH_2PO_4 system during 5 ms.

41-O

On the hydride-ion diffusion mechanism in perovskite oxyhydrides: insights from incoherent quasielastic neutron scattering

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Michael Sannemo Targama,(2) Hua Guo,(2) Franz Demmel,(3) Masato Matsuura,(4) Maths Karlsson(1)

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(3) ISIS Facility, Rutherford Appleton Laboratory, Didcot, United Kingdom
(4) Neutron Science and Technology Center, CROSS, Tokai, Japan

Perovskite-type oxyhydrides are hydride-ion conducting materials of relevance for several types of solid state ionics applications. The hydride-ion conductivity of these materials, however, is often too low for practical use, and, on a fundamental level, the mechanism of hydride-ion diffusion remains unclear.

In this contribution, I will present and discuss our recent results from quasielastic neutron scattering (QENS) measurements on the hydride-ion diffusion mechanism in the perovskite-type oxyhydrides $BaTiO_{3-x}H_x$ and $SrVO_2H$. While $BaTiO_{3-x}H_x$ forms an average cubic perovskite structure, with a disordered anion sublattice (consisting of O^{2-} and H^-), in $SrVO_2H$ the anions are ordered in a layered, tetragonal arrangement.

For $SrVO_2H$, the results show that the hydride-ions exhibit correlated two-dimensional vacancy-assisted jump diffusion restricted to the hydride-ion sublattice of $SrVO_2H$, with an enhanced rate for backward jumps. For $BaTiO_{3-x}H_x$, a different scenario is encountered, as the hydride-ion diffusion is found to be virtually isotropic and with no such a correlated behavior as in $SrVO_2H$. Based on our findings, potential key-properties, such as structure, hydride-ion concentration, and anion vacancy concentration of the perovskite-type oxyhydrides that may allow for improving the hydride-ion conductivity, will be discussed.

Thursday 30.9.2021

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo	
		11	**17**	**18**	Poster Session 2 *even numbers*
		11:30			
					Q. Li
		12	**18**	**19**	42-INV Henkensmeier Polybenzimidazole and its use in HT PEMFC, flow batteries, alkaline and AEM water electrolyzers
					43-O Jankowska Proton conductive composites based on imidazole-functionalized cellulose micro and nanofibers
		12:30			Poster Session 2 *odd numbers*
		13	**19**	**20**	
		13:30			
					D. Dekel
6	**7**	**14**	**20**	**21**	44-KN C. Bae Molecular Engineering of Ion Conducting Polymer Electrolyte Membranes for Electrochemical Energy Conversion and Storage Technologies
		14:30			Panel "General"
7	**8**	**15**	**21**	**22**	45-INV Di Vona Intrinsically conductive double layer hydroxides as fillers for anion exchange membranes
		15:30			46-KN Amezawa How Do We Investigate Reaction Mechanism in Oxide Electrode on Proton-Conducting Electrolyte?
8	**9**	**16**	**22**	**23**	
					S. Haile
		16:30			47-INV Ricote Unveiling discrepancies in reported Faradaic efficiencies in protonic ceramic electrolysis cells
					48-O Vollestad Pressurized Steam Electrolysis using Proton Ceramics: Impact of Electrodes, Temperature and Pressure on Performance and Efficiency
9	**10**	**17**	**23**		49-O Fontaine Proton cermic electrolyser for pressurized hydrogen production: From tubular cells to module integration
		17:30			50-O Bretzler Cesium dihydrogen phosphate – An electrolyte for medium temperature water electrolysis and Power-to-X
					R. Strandbakke
10	**11**	**18**	**24**		51-INV Stange Processing route for Metal Supported Proton Conducting Ceramic Cells
					52-O Serra Designing a novel process for the direct conversion of CO2 to fuel in a co-ionic membrane reactor. Membrane components advances and challenges
		18:30			53-O Kyriakou Shifting the Equilibrium of Thermodynamically Limited Reactions with Protonic Ceramic Membrane Reactors
11	**12**	**19**			54-O Rorvik Development of electrodes and complete electrochemical cells based on surface protonics

42-INV

Polybenzimidazole and its use in HT PEMFC, flow batteries, alkaline and AEM water electrolyzers

Dirk Henkensmeier

KIST (Korea Institute of Science and Technology), Center for Hydrogen and Fuel Cell Research,
Seoul, Korea

Polybenzimidazole (PBI) is a versatile polymer. In contact with acids or bases, it becomes ion conductive. Therefore, it can be used at different pH conditions, opening a broad range of opportunities.[1] We will show the use of PBI in several applications:

High Temperature Polymer Electrolyte Fuel Cells (HT PEMFC):[2] A blend of PBI with a tetrazole-containing polymer showed a conductivity of 195mS/cm at 160°C (PBI: 147mS/cm) after doping in phosphoric acid. In the HT PEMFC, the membrane was tested successfully for over 2400h. 2000h of that were at 800mA/cm^2. The performance was not only high, but also very stable, with a voltage loss of just 27.7µV/h.

Vanadium Redox Flow Batteries (VRFB): PBI doped with sulfuric acid has a low conductivity of <5mS/cm, but effectively blocks vanadium ions.[3] By pre-swelling membranes in alkaline solutions, we increased the conductivity and selectivity.[4]

Alkaline Water Electrolysis:[5] By adjusting the membrane fabrication process, conductivities of around 300mS/cm are obtained. In the application, a performance of 1.9A/cm^2 at 1.8V was reached.

AEM Water Electrolysis:[6] Reinforcement of AEMs with porous supports is widely done, but the mismatch in the swelling properties can lead to voids at the materials' interface. We mitigate this risk by forming a covalent bond between the ion-conducting matrix and a PBI nanofiber mat support.

[1] J. Mater. Chem. A 8 (2020) 12855
[2] J. Membr. Sci. 614 (2020) 118494
[3] ACS Appl. Mater. Interf. 9 (2017) 36799
[4] Chem. Eng. J. 405 (2021) 126574
[5] KR10-2020-0171530
[6] EP21152812

43-O Proton conductive composites based on imidazole-functionalized cellulose micro and nanofibers

Iga Jankowska,(1) Paweł Ławniczak, (1) Jiri Brus,(2) Katarzyna Pogorzelec-Glaser,(1) Radosław Pankiewicz,(3) Andrzej Łapiński,(1) Jadwiga Tritt-Goc(1)

(1) Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland
(2) Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic
(3) Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poznań, Poland

The aim of present study was the synthesis and characterize properties of new composites based on cellulose micro and nanofibers (CMF, CNF) functionalized with imidazole molecules on the surface. The combination of a natural polymer such as cellulose fibers with heterocycles is the strategy, which allows to find new proton conducting polymeric materials, which can be used in the temperature range above 100 °C. These materials can be used in electrochemical devices, e.g., in fuel cells.

The synthesized polymeric composites containing imidazole molecules and pure, non-functionalized cellulose polymer matrix were comprehensively studied in terms of structural, thermal, and electrical properties (elemental analysis, X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, FTIR, NMR, impedance spectroscopy)

The obtained results have shown the differences between properties of polymer matrix – pure cellulose micro and nanofibers, and synthesized composites. The resulting composites reveals conductivity in the temperature range above the boiling point of water. The conductivity of composites under anhydrous conditions is related to the dynamics of imidazole molecules arranged in polymer matrix. Newly synthesized polymeric composites based on cellulose micro and nanofibers are inexpensive to obtain, non-hazardous, environmentally friendly and can be considered as a solid electrolyte for application in electrochemical devices.

This work was supported by the National Science Centre, Poland [grant number 2017/24/C/ST5/00156].

P-27 **The influence of A and B site elements on the phase stability and proton conductivity of high-entropy rare-earth ortho-niobates** Arkadiusz Dawczak

P-28 **Conduction Properties of Ti-doped $NaTaO_3$** Ximu Chen

P-29 **Effect of Dopant Concentration and Species on Proton Solubility and Diffusivity in Ceria** Takuya Yamaguchi

P-30 **Hydration and proton conductivity in vanadium-substituted variants of γ-$Ba_4Nb_2O_9$** Alex J. Brown

P-31 **Evaluation of both oxide-ion and proton transport number in $Sr_2Ti_{0.95}Al_{0.05}O_{4-d}$** Yutaro Yagi

P-32 **Effect of cerium in yttrium-doped barium zirconate: grain and grain boundary protonic conduction** Hye-Won Kim

P-33 **Reduced phase of cubic perovskite $BaZr_{0.5}In_{0.5}O_{2.75}$** Hajime Toriumi

P-34 **Structure and transport properties of $Ba(Zr,Hf,Sn,Ti,Ce,Y,Yb,Sm,In,Zn)O_3$ as a new high entropy perovskite oxide** Daniel Jaworski

P-35 **Proton conductivity in mixed cation phospahte with a layered strcuture** Yasuaki Matsuda

P-36 **Technique for evaluating isotope exchange reaction coefficients on proton-conducting phosphate glass surfaces by Raman spectroscopy** Tomohiro Ishiyama

P-37 **Synthesis, structure and proton conductivity of Mixed cation phosphate with the three-dimensional open framework** Yasuaki Matsuda

P-38 **Water uptake and electrical conductivity of $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (M = Pr, Tb, Fe) triple conducting oxides** Jagoda Budnik

P-39 **Hydration characteristics and electrochemical performance of the triple-conducting perovskite oxide $BaZr_{0.5}Fe_{0.5}O_{3-\delta}$** Shaochen Zhu

P-40 **Influence of magnetic properties and electronic configuration on proton conductivity of double perovskite cobaltites** Iga Szpunar

P-41 **Water uptake studies and conductivity of cobaltites and ferrites with perovskite structure** Sebastian Lech Wachowski

P-42 **Proton Pumping Modifies the Nature of Triple-Phase Boundaries at Cathode and Enables Fast Cathode Reaction of Fuel Cells at Low Temperatures** SeongWoo Jeong

P-43 **Exsolution in triple-conducting cathode materials for proton ceramic fuel cells (PCFCs)** Daria Gierszewska

P-44 **Development of protonic membrane reactors for the electrocatalytic conversion of CO_2 into chemical energy carriers** E. Stefan

P-45 **Stacking planar proton conducting ceramics – challenges and recent progress** X. Georgolamprou

P-46 **Switching between Proton Vacancy and Excess Proton Transfer Pathways** M.-A. Codescu

P-47 ~~**Physicochemical properties of solid composites formed by cellulose derivatives with imidazole investigated by two-dimensional correlation spectroscopy** Agata Piotrowska~~

P-48 **Temperature and pressure dependence of hydrogen bond network in new imidazolium salts of aromatic acids** Sylwia Zięba

P-49 **Dielectric and ionic conductivity properties in biopolymer chitin via loosely bonded water** Yuki Hirota

P-50 **Hydration and proton conductivity of dipeptide crystals (Gly-Ser)** Hitoki Semizo

P-51 **Fabrication and Characterization for Direct Ethanol Biofuel Cell using biopolymer "Chitin・Chitosan" as electrolytes** Yusuke Takahashi

P-52 **Fluorine-free membrane electrode assemblies for water electrolysis based on sulfonated polyphenylensulfone** Carolin Klose

P-53 **Poly(biphenyl piperidinium) anion exchange membranes with N-alicyclic quaternary ammonium cationic side chains** Dong Pan

P-27 The influence of A and B site elements on the phase stability and proton conductivity of high-entropy rare-earth ortho-niobates

Arkadiusz Dawczak, Wojciech Skubida, Aleksandra Mielewczyk-Gryń, Maria Gazda

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

Lanthanum orthoniobate is a well-known proton conductor. Depending on the temperature lanthanum niobate is stable in two polymorphs, low-temperature phase which is monoclinic and corresponds to Fergusonite-type structure, and high-temperature phase which is tetragonal and corresponds to Scheelite-type structure[1]. Lanthanum and niobium sublattices can accommodate different elements. It suggests that it is possible to form a high entropy material. In this work, we examine the structural properties and the conductivity of the series of the high entropy rare-earth orthoniobates. The choice of the constituent elements has been undertaken on the basis of their preferred valence state and ionic radius. The samples of the materials were synthesized through the solid-state synthesis method. We have determined the structure and phase composition by means of the powder X-ray diffraction method at room temperature. The measurements of temperature dependence of electrical conductivity were carried out using electrochemical impedance spectroscopy under dry and wet air.

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[1] M. Huse, T. Norby, R. Haugsrud, Int. J. Hydrogen Energy 37 (2012) 8004–8016.

Acknowledgements

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P-28

Conduction Properties of Ti-doped $NaTaO_3$

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In this research, 1-20 % Ti is doped into the Ta site of $NaTaO_3$ with the conventional solid-state reaction. The well-mixed raw materials are calcinated at 900 °C and then pressed into pellets for sintering at a temperature over 1000 °C. After calcination, the samples with Ti up to 10 % show the XRD pattern of orthorhombic $NaTaO_3$. For the samples with 15% and 20% Ti, peaks of $Na_2Ti_3O_7$ are observed. With ICP-AES, all samples sintered with sacrifice powder are found to have almost the same composition as nominal, while loss of 12% Na is determined in $NaTaO_3$:10 % Ti when sintering temperature is raised to 1300 °C and no sacrifice was used. The conductivity of $NaTaO_3$ samples measured by EIS is depicted in Fig.1. Through 300-700 °C the conductivity of $NaTaO_3$:10 % Ti is above undoped $NaTaO_3$. Under wet O_2 the $NaTaO_3$:10 % Ti sample shows higher conductivity than it under dry O_2, reaching 3×10^{-4} S/cm at 700 °C. When the atmosphere is alternated between wet and dry O_2, the conductivity changes reversibly as well, confirming the existence of proton conduction. When exposed to H_2, the conductivity of all samples increased in proportion to $p(O_2)^{-1/4}$ which suggests that Ta is reduced by H_2 in electronic conductivity. A rise of conductivity proportional to $p(O_2)^{1/4}$ is observed under O_2 by $NaTaO_3$:10% Ti at 700 °C and $NaTaO_3$:5% Ti at 600 °C and 7000 °C. Therefore, hole conduction can exist to an unignorable degree. The possibility of Na^+ conduction is excluded by direct current polarization, as the samples show similar conductivity under either direct or alternating current.

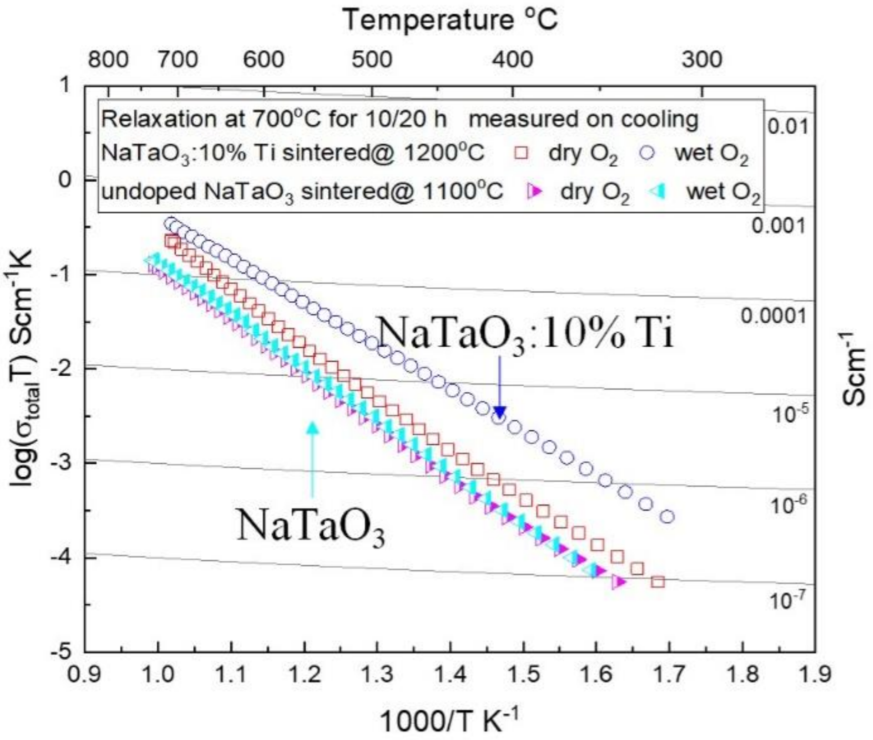

Fig.1 Electrical conductivity of $NaTaO_3$:10% Ti and undoped $NaTaO_3$.

P-29

Effect of Dopant Concentration and Species on Proton Solubility and Diffusivity in Ceria

Takuya Yamaguchi, Tomohiro Ishiyama, Haruo Kishimoto, Katherine Develos-Bagarinao, Katsuhiko Yamaji

National Institute of Advanced Industrial Science and Technology (AIST)

Accepter doped fluorite-type oxides are typical oxide ion conductors and it has been believed that protons hardly dissolve into them in contrast to perovskite-type oxides such as Y:BaZrO$_3$. The reason of this is still unclear, but its understanding will be beneficial to reveal the origin of high proton conductivity in perovskite-type oxides. In order to study proton dissolution behavior into zirconia and ceria, we recently developed a quantitative technique to determine deuteron solubility and diffusivity using SIMS with high sensitivity. Appling this technique to Zr$_{0.85}$Y$_{0.15}$O$_{1.93}$ and Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$, deuterons were found to be incorporated mainly into the grain boundaries. In this study, the effect of dopant concentration and species on deuteron solubility and diffusivity in ceria was examined. For the Gd doping, the solubility increased with Gd concentration and it was found that deuterons turned to be incorporated into bulk at ≥20 mol% doping in contrast to 10 mol% doping. For the dopant species, the solubility at 20 mol% doping, i.e., presumably solubility in bulk, increased with decreasing dopant ion radius. On the other hand, diffusivity exhibited opposite tendency with solubility. Based on IR spectra in νOH region, the solubility increments were attributed to increase in oxygen vacancies of which nearest-neighbor cations are two cerium ions and two dopant ions. Regarding to the decreasing diffusivity, one of the possible reasons is formation of strong O-H bond which cause increase in proton dissociation energy.

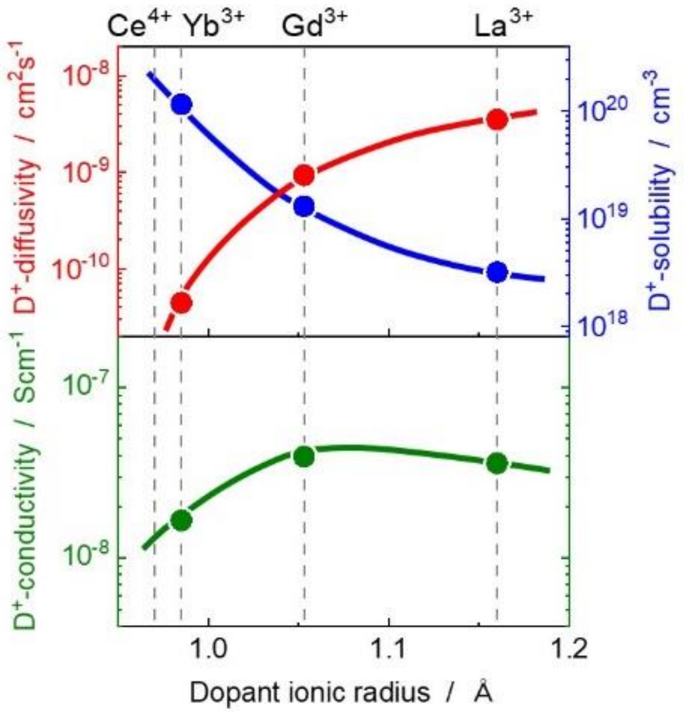

Fig. Deuteron solubilities and diffusivities in 20 mol% Yb$_2$O$_3$, Gd$_2$O$_3$, and La$_2$O$_3$-doped CeO$_2$ at 300°C in air with p_{D2O} = 0.017 atm.

P-30

Hydration and proton conductivity in vanadium-substituted variants of γ-$Ba_4Nb_2O_9$

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Ivana Radosavljevic Evans,(2) Chris D. Ling(1)

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(2) Department of Chemistry, Durham University, U.K.
(3) Institut Laue Langevin, Grenoble, France
(4) Australian Nuclear Science and Technology Organisation, Australia
(5) Australian Synchrotron, Clayton, Victoria, Australia

We have substantially expanded the chemical phase space of the hitherto unique γ- $Ba_4Nb_2O_9$ type structure by designing and synthesising stoichiometric ordered analogues γ-$Ba_4V_{1/3}Ta_{5/3}O_9$ and γ-$Ba_4V_{1/3}Nb_{5/3}O_9$ 9, and exploring the solid-solution series γ-$Ba_4V_xTa_{2-x}O_9$ and γ-$Ba_4V_xNb_{2-x}O_9$. Undoped $Ba_4Ta_2O_9$ forms a 6H-perovskite type phase, but with sufficient V doping the γ-type phase is thermodynamically preferred and possibly more stable than γ-$Ba_4Nb_2O_9$, forming at a 200 °C lower synthesis temperature. This is explained by the fact that Nb^{5+} ions in γ-$Ba_4Nb_2O_9$ simultaneously occupy 4-, 5- and 6-coordinate sites in the oxide sublattice, which is less stable than allowing smaller V^{5+} to occupy the former two and larger Ta^{5+} to occupy the latter. The x = 1/3 phase γ-$Ba_4V_{1/3}Ta_{5/3}O_9$ shows greatly improved ionic conduction compared to the x = 0 phase 6H-$Ba_4Ta_2O_9$. We characterised the structures of the new phases using a combination of X-ray and neutron powder diffraction. All compositions hydrate rapidly and extensively (up to 1/3 H_2O per formula unit) in ambient conditions, like the parent γ-$Ba_4Nb_2O_9$ phase. At lower temperatures, the ionic conduction is predominately protonic, while at higher temperatures conduction seems to be primarily due to oxide and electron-hole conduction.

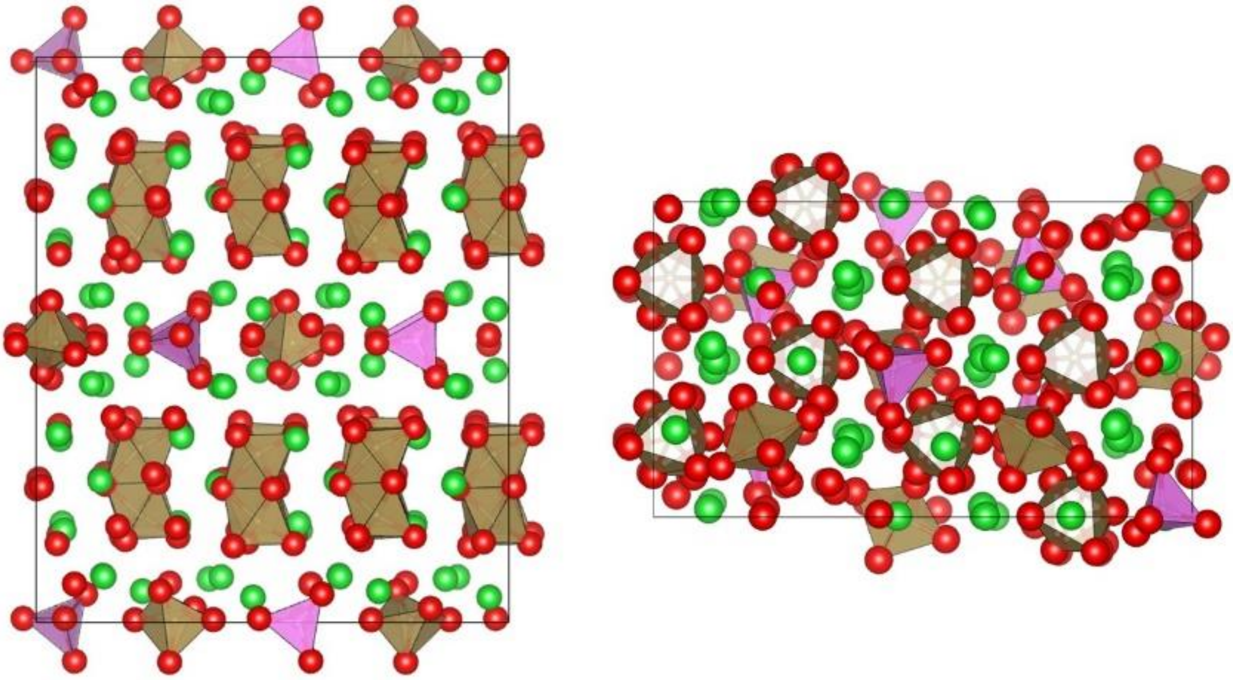

Figure 1 Dehydrated crystal structure of γ-$Ba_4V_{1/3}Ta_{5/3}O_9$ viewed from along *a* (left) and *b* (right). With Ba atoms light green, Ta polyhedra brown and V tetrahedra in pink.

Thursday 30.9.2021, morning poster II

P-31 Evaluation of both oxide-ion and proton transport number in $Sr_2Ti_{0.95}Al_{0.05}O_{4-d}$

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Sr-Ti based layered perovskites show protonic conductivity, which are candidate of electrolytes or electrodes for proton conductive solid oxide fuel cells (PCFCs). Our previous study found that the Al doped Sr-Ti based layered perovskite also showed an evidence of the protonic conductivity [1]. In addition, Sr-Ti based layered perovskites have possibilities of oxide ion conductivity. However, the details are still unclear. This study tries to evaluate both transport numbers of protons and oxide ions simultaneously by using the electromotive force (EMF) technique. At first of this study, we optimized the condition to investigate actual EMF by using yttria stabilized zirconia (YSZ), which is a typical oxide-ion conductor. The EMF results of YSZ revealed that the thermal EMFs were almost constant with decreasing pO_2, however the polarizations apparently depended on pO_2. By subtracting the thermal EMF and the polarization, this study obtained the actual EMF of YSZ as shown in Fig. 1. The optimized EMF method is available to evaluate transport number of $Sr_2Ti_{0.95}Al_{0.05}O_{4-d}$ (STA05). As a result, STA05 showed no oxide ion transport (Fig. 1). Thus, we conclude that STA05 is a proton and electron mixed conductor. On the conference, we will discuss the more detailed transport properties of STA05.

[1] Y. Yagi et al., Solid State Sci. (2020) 108, 106407.

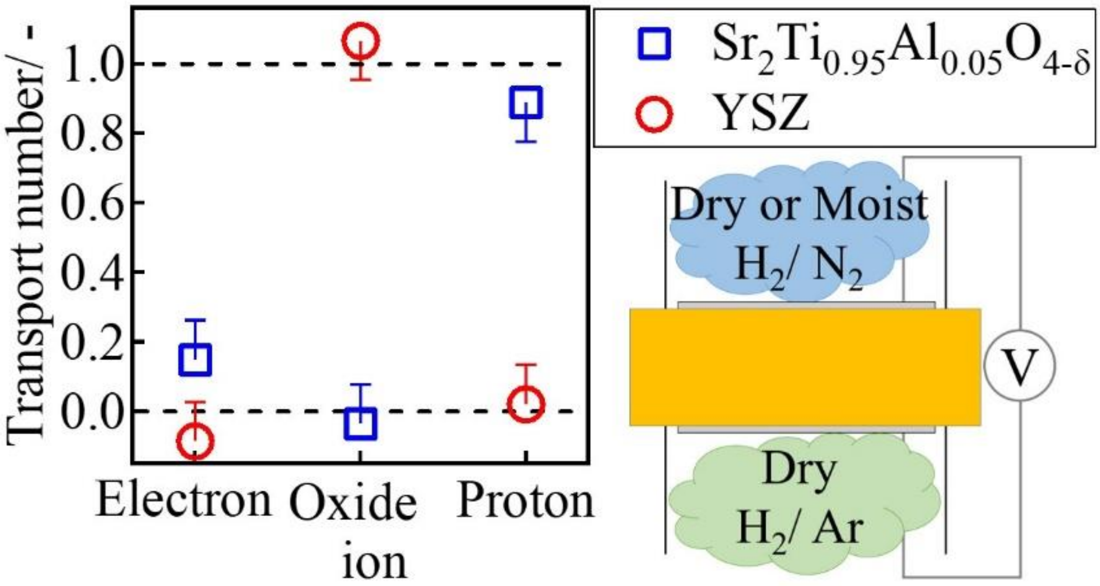

Fig. 1 Transport numbers evaluated at 600 °C in YSZ and $Sr_2Ti_{0.95}Al_{0.05}O_{4-\delta}$

P-32 Effect of cerium in yttrium-doped barium zirconate: grain and grain boundary protonic conduction

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The grain and grain boundary protonic transport of yttrium-doped barium zirconate has been investigated for various Ce-substituted concentrations, and the origins of blocking on the grain and grain boundary resistances are considered. $Ba(Zr_{1-x}Ce_x)_{0.85}Y_{0.15}O_{3-\delta}$ samples (BZCY, x = 0, 0.05, 0.1, and 0.2) have been prepared via conventional ceramic processing, and their grain and grain boundary resistances have been experimentally measured as a function of temperature under humid conditions using 2-probe AC impedance measurements. In the grain, a high-Ce-substituted sample with a large lattice volume is more conductive than a low-substituted specimen. The high-Ce-substituted sample also exhibits low resistance to the grain boundary. In the investigation of the origin of current blocking on the grain boundary, it is found that the space charge significantly affects grain boundary transport in the low-Ce-substituted sample. However, other mechanisms such as the charge-neutral effect (structural effect) of the grain boundary transport in the high-Ce-substituted samples are considered. In terms of the total conductivity (the summation of the grain and grain boundary components) of BZCY, it is found that the highest Ce-substituted barium zirconate (x = 0.2) exhibited the highest conductivity, demonstrating that it can potentially be utilized as a solid electrolyte in electrochemical devices such as solid oxide fuel cells.

P-33

Reduced phase of cubic perovskite $BaZr_{0.5}In_{0.5}O_{2.75}$

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Cubic perovskite type barium zirconate, $BaZr_{1-x}In_xO_{3-d}$ (0<x<0.7) [1], have been intensively studied for their excellent proton conductivity and tolerance to high pH2O atmosphere. Despite the fact that In(III) oxides are readily reduced at elevated temperature under reduced atmosphere, the thermochemical behavior of BaZr1-xInxO3-d under reduced conditions is still unclear. Herein, we demonstrated that $BaZr_{0.5}In_{0.5}O_{2.75}$ (BZI55) is converted to highly-oxygen-deficient perovskite phase with metallic conductivity by reduction in H2 gas at elevated temperature.

BZI55 was synthesized by solid state reaction method. Pale white BZI55 was changed to black-colored phase by heating at 800°C for 24h in dry H_2. Hereafter, the black phase after the H_2 reduction was denoted as H-BZI55.The XRD measurements confirmed that H-BZI55 still retained cubic perovskite structure and the change of lattice constants by the H_2 reduction was only -0.05%. TG measurements revealed that BZI55 lose the weight by 2.68% by H_2 reduction at 800°C, and thus the composition of H-BZI55 was estimated to $BaZr_{0.5}In_{0.5}O_{2.27}$ by assuming that mass loss was due to the loss of lattice oxygen and mass gain by hydrogen uptake was negligible. Electrical conductivity of H-BZI55 were measured by 4-probe DC method in dry H_2 atmosphere. H-BZI55 exhibits metallic conduction behavior with less-pronounced temperature dependence and the conductivity was significantly high in the range of from 10^{-1} to 10^{-2} S cm^{-1} at temperature above 300°C (Figure 1). The concentration and mobility of the hydrogen impurity were under investigation.

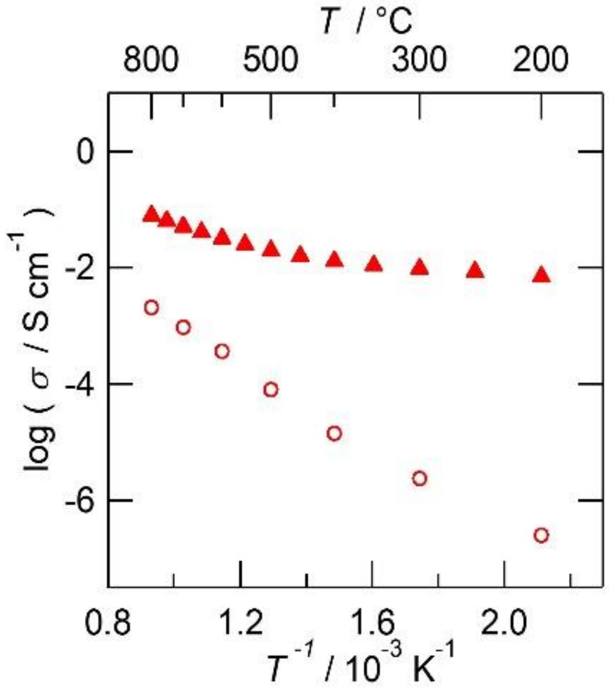

Figure 1. Electrical conductivities of H-BZI in dry H_2 (▲) and BZI in wet Ar (○).

Reference: [1] M. Karlsson et al., *Chem. Mater.* **20**, 3480–3486(2008)

P-34

Structure and transport properties of Ba(Zr,Hf,Sn,Ti,Ce,Y,Yb,Sm,In,Zn)O_3 as a new high entropy perovskite oxide

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Tadeusz Miruszewski, Maria Gazda

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In 2015, the findings published by Rost et al. [1] gave the chance for a new family of oxides to arise – high entropy oxides. A lot of them have been found exhibiting various crystal structures and still a lot of them are waiting to be discovered. With each stabilized oxide, there is plenty of room to examine their structural, microstructural, and transport properties.

In our previous work, we described four high entropy perovskite oxides containing 5 or 7 different elements in B-site [2]. Here, we present an oxide with 10 different elements in B-site exhibiting proton conductivity. Ba(Zr,Hf,Sn,Ti,Ce,Y,Yb,Sm,In,Zn)O_3 was synthesized using solid-state reaction route and characterized by X-ray diffraction, scanning electron microscopy, thermogravimetric analysis and electrochemical impedance spectroscopy.

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[2] M. Gazda, T. Miruszewski, D. Jaworski et al., Novel Class of Proton Conducting Materials – High Entropy Oxides, ACS Materials Lett. 2020, 2, 10, 1315–1321, doi: 10.1021/acsmaterialslett.0c00257

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P-35 Proton conductivity in mixed cation phospahte with a layered strcuture

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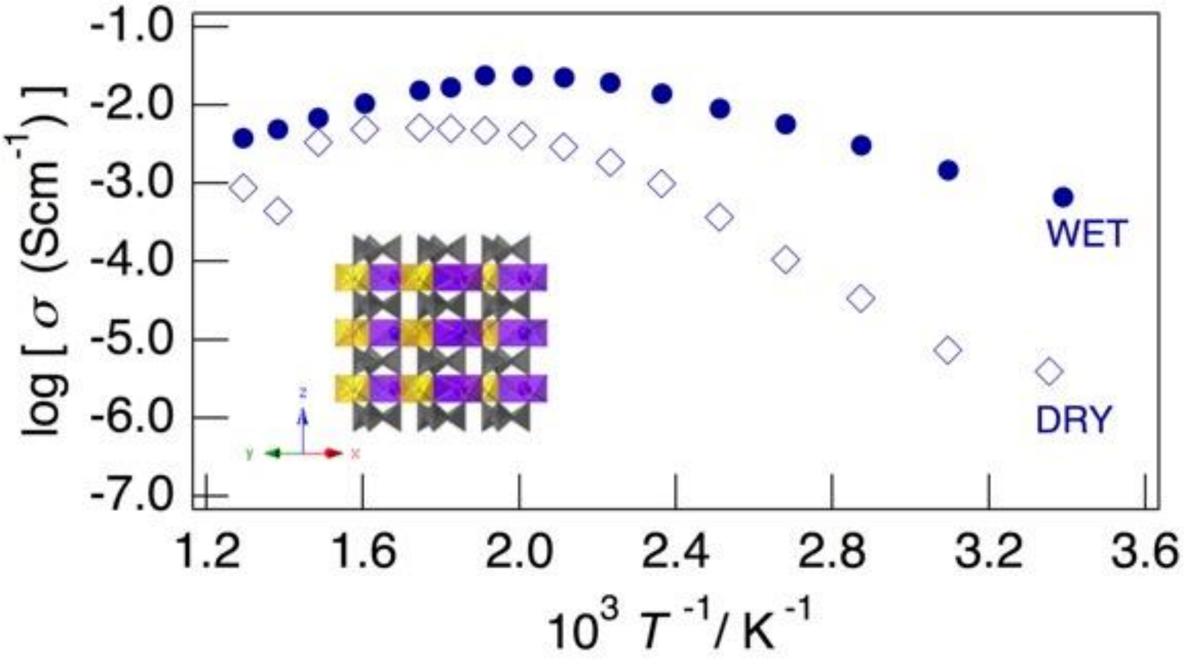
Proton solid electrolytes, which exhibit high proton conductivity at a wide range of low-intermediate temperatures (150–300°C), are key materials for the development of fuel cells for automobiles and cogeneration systems. In this study, a benitoite-type polyphosphate, $KMg_{1-x}H_{2x}(PO_3)_3\cdot yH_2O$, which has a non-combustible and layered structure, was investigated as a new proton conductor. The benitoite-type $KMg_{1-x}H_{2x}(PO_3)_3\cdot yH_2O$ was synthesised by a coprecipitation method. The solid solution formed in the range of x = 0 - 0.100 in $KMg_{1-x}H_{2x}(PO_3)_3\cdot yH_2O$. Multi-step weight loss due to dehydration was observed for TG/DTA measurement at 30°C and 150°C. We observed enhanced peaks of the vibration bands at around 1117 cm^{-1} and 1229 cm^{-1}, which were attributed to the symmetric and asymmetric PO_2 vibration modes, and at 743 cm^{-1} and 970 cm^{-1} due to the ns(P-O-P) and nas(P-O-P) modes as well as broad absorbance peaks at 2300 cm^{-1} and 2700 cm^{-1} corresponding to the vibration modes of ns(P-O-H) with increasing x for FTIR spectra, which suggest the introduction of protons to the crystal structure. Proton conductivity increased from x = 0 to 0.10 and then decreased at x = 0.125, where the impurity phase was observed. The sample with x = 0.10 in benitoite-type $KMg_{1-x}H_{2x}(PO_3)_3\cdot yH_2O$ exhibited high proton conductivity of 1.4×10^{-3} S cm^{-1} at 150°C and 6.5×10^{-3} S cm^{-1} at 250°C under a non-humidified N_2 gas flow.



P-36

Technique for evaluating isotope exchange reaction coefficients on proton-conducting phosphate glass surfaces by Raman spectroscopy

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Recently, our group has developed a proton-conductive phosphate glass electrolyte that exhibits high proton conductivity (σH+) in the intermediate temperature range of 300℃. The development of electrochemical devices requires not only the σH+ of the electrolyte but also the smooth mass transfer at the electrode-electrolyte interface. There is still limited knowledge about electrode materials and evaluation methods that are effective in promoting interfacial reactions in the intermediate temperature range. In addition to electrochemical methods, a quantitative method for evaluating material properties would provide a variety of new insights and accelerate the development of electrode interfaces. In this presentation, as a method to evaluate the hydrogen isotope exchange rate at the surface of proton-conducting phosphate glasses and at the interface between the electrode and electrolyte, we have developed a simple method to evaluate the surface exchange reaction coefficients and diffusion coefficients by measuring the concentration profiles of OH and OD in glass using Raman spectroscopy. The figure shows the deuterium concentration profile in the proton-conducting glass after isotope exchange treatment in D_2 atmosphere using Pd electrode. The surface exchange reaction coefficient k* and diffusion coefficient D* were estimated using the fitting equation shown in the figure. The value of D was comparable to the value calculated from the σH+. The k* values were estimated to be in the range of 1.0 ~ 2.0×10^{-6} cm/s, indicating that Pd was functioning as an anode.

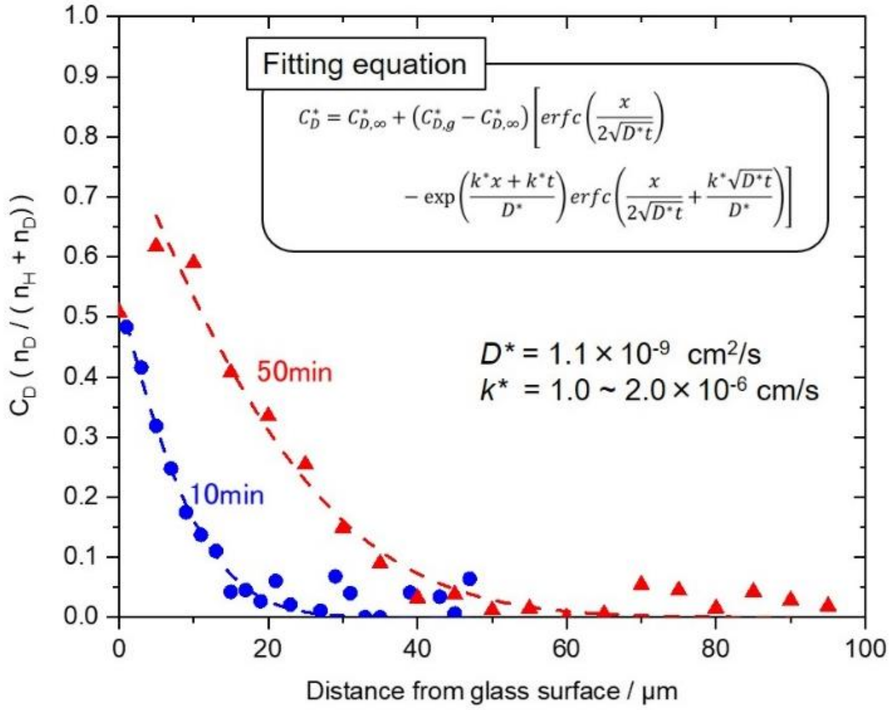

Fig. Deuterium concentration profiles in the proton-conducting glass after annealing at 200 °C for 10 and 50 min in D_2 atmosphere using Pd electrode.

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P-37

Synthesis, structure and proton conductivity of Mixed cation phosphate with the three-dimensional open framework

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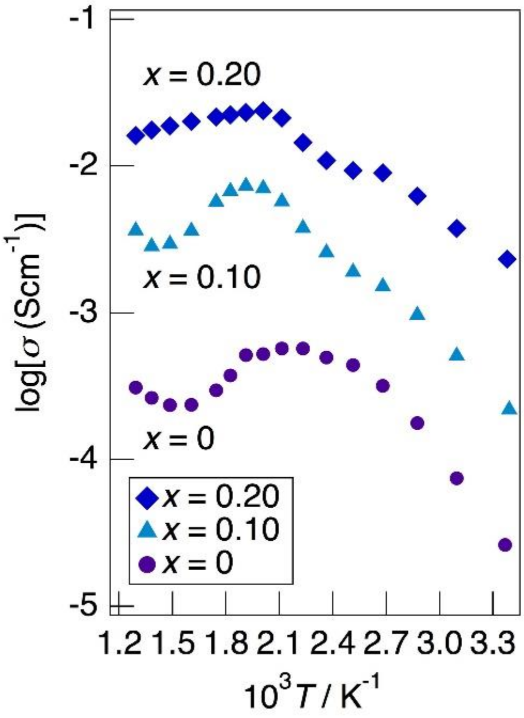
Proton solid electrolytes, which exhibit high proton conductivity and thermal stability at a wide range of intermediate temperatures, are desired to operate fuel cells at a temperature suitable for the application such as automobiles and cogeneration systems. A new proton conductor $NaMg_{1-x}Li_xH_x(PO_3)_3{\cdot}yH_2O$ was synthesized by a coprecipitation method. X-ray structure refinement reveals that the three-dimensional tunnel framework is formed by sharing of corner oxygens of PO_4 tetrahedral chains and face-shared $(NaO_6)(MgO_6)$ chains. In the three-dimensional tunnel, oxygen sites of water of crystallization were observed. In FTIR measurement, an increase in absorption peaks corresponding to the modes of O-H and P-O-H bonds for x in $NaMg_{1-x}Li_xH_x(PO_3)_3{\cdot}yH_2O$ were observed, which reflect the introduction of protons to the crystal structure. Although a multi-step weight loss due to desorption of water of crystallization was observed for TG curves, this material retained the framework up to 800°C. Fig. 1 shows the temperature dependence of the conductivity of $NaMg_{1-x}Li_xH_x(PO_3)_3{\cdot}yH_2O$ measured under a non-humidified N_2 gas flow. The proton conductivity shows a positive tendency for x. $NaMg_{0.8}Li_{0.2}H_{0.2}(PO_3)_3{\cdot}yH_2O$ exhibited the high proton conductivity over 10^{-2} Scm^{-1} in the temperature range of 150 - 500°C and the value reached to 2.4×10^{-2} Scm^{-1} at 225°C under the non-humidified atmosphere. In a humidified atmosphere (pH_2O = 4 kPa), $NaMg_{0.8}Li_{0.2}H_{0.2}(PO_3)_3{\cdot}yH_2O$ exhibited the conductivity over 10^{-3} Scm^{-1} from room temperature to 500°C and it reached to 2.6×10^{-2} Scm^{-1} at 225°C.



P-38

Water uptake and electrical conductivity of $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (M = Pr, Tb, Fe) triple conducting oxides

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Triple conducting oxides (TCO) are a family of materials exhibiting oxygen ion-, electron/hole-, and proton conductivity. Due to the interactions between the carriers, the description of the processes occurring in TCO materials is much more complex than in the case of only two mobile carriers present [1].

$BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ is a group of TCO materials related to the doped barium cerate-zirconate solid solution. Substitution of the transition metal in the B-position in the perovskite structure might enhance the electronic conductivity in comparison to the predominantly ionic conductor $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ [2]. The analysis of the influence of the substituent cation on the water uptake might provide information about the thermodynamics of proton transport in the materials. Total conductivity measured in dry and humidified air in $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (M = Pr, Tb, Fe) series is presented in Fig. 1.
In this work, $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (M = Pr, Tb, Fe) compounds were synthesized using solid state reaction method. The structural characterization was carried out using X-ray diffraction technique. Thermogravimetry allowed for water uptake process analysis. Electrical measurements in function of temperature and oxygen and water partial pressure enabled to determine the proton conductivity and thermodynamic parameters related to the proton transport.

[1] D. Poetzsch, R. Merkle, J. Maier, Adv. Funct. Mater. 25 (2015) 1542–1557.
[2] A. V. Kasyanova, L.R. Tarutina, A.O. Rudenko, J.G. Lyagaeva, D.A. Medvedev, Russ. Chem. Rev. 89 (2020) 667–692.

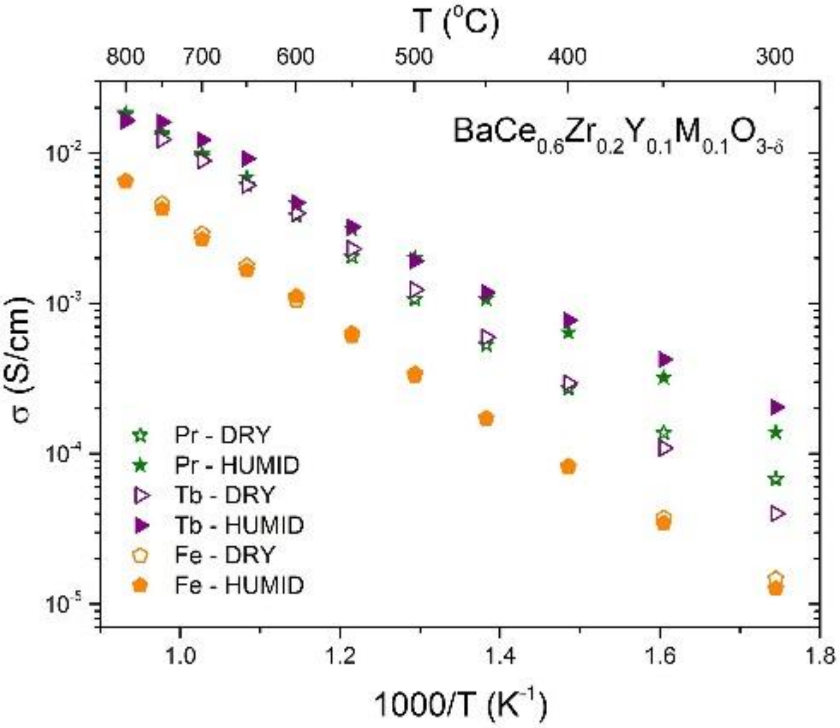

Fig. 1. Temperature dependence of total conductivity of $BaCe_{0.6}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (M = Pr, Tb, Fe) in dry and humidified air.

P-39

Hydration characteristics and electrochemical performance of the triple-conducting perovskite oxide $BaZr_{0.5}Fe_{0.5}O_{3-\delta}$

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The perovskite-type triple-conducting oxide (TCO) $BaZr_{0.5}Fe_{0.5}O_{3-\delta}$ (BZF55) has been identified as a potential air electrode for protonic ceramic fuel cells (PCFCs) and electrolysis cells (PCECs). Its hydration properties were studied by thermogravimetric analysis (TGA) in the temperature range 350 – 700 °C. The hydration equilibrium constant (K_{Hydra}) is found to dependent on pO_2, pH_2O and temperature. Increasing pO_2 and decreasing pH_2O and temperature lead to a higher values of K_{Hydra} and $[OH_O^{\cdot}]$. At pO_2 = 0.21 bar and pH_2O = 0.06 bar, the proton concentration $[OH_O^{\cdot}]$ decreases from 0.62 mol% at 350 °C to 0.27 mol% at 700 °C

The electrochemical performance of BZF55 was characterized by impedance spectroscopy at open circuit conditions using a $BaZr_{0.5}Fe_{0.5}O_{3-\delta}$ $|BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}|$ $BaZr_{0.5}Fe_{0.5}O_{3-\delta}$ symmetrical cell. The electrode area specific resistance (ASR) reaches a value as low as 0.28 Ω·cm2 at 600 °C in pO_2 = 0.21 bar and pH_2O = 0.03 bar atmosphere, which outperforms state-of-the-art triple-conductors like $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ and $PrBaCo_2O_{6-\delta}$. The obtained impedance spectra are de-convoluted by a 5-(RQ) equivalent circuit and inverted by a distribution function of relaxation times (DFRT) to the τ domain. The results indicate that there are 2 rate-limiting steps in the electrode reaction, characterized by time constants τ3 and τ4 (0.05 s and 0.7 s at 500 °C, respectively). The electrode process characterized by τ4 is found dominant at high temperature, while both processes τ3 and τ4 have about equal contributions to the impedance at low temperature.

P-40

Influence of magnetic properties and electronic configuration on proton conductivity of double perovskite cobaltites

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Double perovskite cobaltites, with a general formula $BaLnCo_2O_{6-\delta}$ (where Ln is lanthanide), is a widely studied group of materials, which gained attention due to their various electric and magnetic properties and potential applications. The complexity of this system results mostly from the nature of cobalt. It may exhibit different oxidation1 and spin states2. Thus, in this group both ferro and antiferromagnets can be found. What is more3, Double perovskite cobaltites are good mixed conductors4, and some even mixed proton and electron conductors. Despite the fact that this variety is beneficial from the aplicational point of view, it strongly impedes the understanding of fundamental phenomena. Many different factors should be taken into account during the analysis of this group of materials.

However, among the whole lanthanide range, only $BaLaCo_2O_{6-\delta}$ and $BaGdCo_2O_{6-\delta}$ exhibit significant water uptake5. This uniqueness cannot be explained on the basis of structural studies5. The key to understanding the phenomenon of hydration lies in magnetic properties and electronic structure.

In this work we present the in-depth studies on magnetic and electronic properties of $BaLnCo_2O_{6-\delta}$. For this purpose X-ray Absorption Spectroscopy, Electron Paramagnetic Resonance spectroscopy and magnetization studies were applied.

Acknowledgements: 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 n° 272797 “GoPHy MiCO”

Thursday 30.9.2021, morning poster II

P-41

Water uptake studies and conductivity of cobaltites and ferrites with perovskite structure

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Proton Ceramic Electrochemical Cells (PCECs) attracted substantial scientific attention over the last years. Development of electrochemical devices constructed from ceramics which operate at intermediate temperatures (300 – 700 °C) allows to avoid use of expensive noble metal catalysts as in Proton Exchange Membrane Cells combined with reduced corrosion and costs of operation due to lower temperatures of operation than in Solid Oxide Cells. Among many variations of PCECs steam electrolysers and fuel cells appeal as the most interesting. The element which limits the performance of these is small availability of materials suitable for positrodes (positrode – an electrode with higher electric potential). Positrode material must fulfil strict requirements such as high electronic conductivity, high protonic conductivity and Thermal Expansion Coefficient (TEC) matching the one of electrolyte.

Our studies show that barium lanthanide cobaltites with perovskite structure are good candidates for applications in PCECs since they have high electronic conductivity and uptake water, which indicates protonic conductivity. However, high TEC remains an issue. In this work we study barium lanthanum cobaltite and barium lanthanum ferrite solid solutions and evaluate their structure, thermochemical expansion, conductivity, and water uptake.

Acknowledgements: Project FunKeyCat is supported by the National Science Centre, Poland under the M-ERA.NET 2, which has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement no 685451.

P-42

Proton Pumping Modifies the Nature of Triple-Phase Boundaries at Cathode and Enables Fast Cathode Reaction of Fuel Cells at Low Temperatures

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An obstacle of protonic ceramic fuel cells (PCFCs) is large cathode polarization resistances at low temperatures, attributed to the limited effective reaction area within gas–electrolyte–cathode triple-phase boundaries (TPBs) due to the carrier mismatch between electrolyte and cathode. On the other hand, a hydrogen-permeable metal-supported fuel cell (HMFC), which consist of 1-micrometer-thick $BaCe_{0.8}Y_{0.2}O_3$ thin film on a solid Pd anode, have accomplished very low polarization resistance of only 0.21 ohm cm^2 at 400°C despite the similar cathode material with PCFCs [1], demonstrating that HMFC configuration can undergo fast cathode reaction even at 400°C. However, the mechanism remained veiled.

Here, we demonstrate that proton pumping, triggered by blocking of the oxide ion minor conduction at hydrogen-permeable metals/protonic ceramics heterojunctions [2], facilitates cathode reaction cycle at TPBs by accelerating interfacial proton diffusion to TPBs, which modify the nature of TPBs and change reaction pathway of cathode reaction (Fig. 1). Systematic study for the HMFCs with $BaZr_{0.5}Sc_{0.5}O_{3-d}$ (Sc50) and $BaZr_{0.8}Sc_{0.2}O_{3-d}$ (Sc20) electrolytes elucidate the correlation between proton pumping and the fast cathode reaction in HMFC. Further, HMFC with Sc50 electrolyte is capable of inducing enhanced proton pumping and thus achieved the cathode reaction resistance of 0.54 ohm cm^2 at 400°C under DC condition of −0.4 V vs. OCV with the conventional $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ cathode material.

[1] J. Power Sources 152 (2005) 200.
[2] ACS Appl. Energy Mater. 3 (2020) 1222.

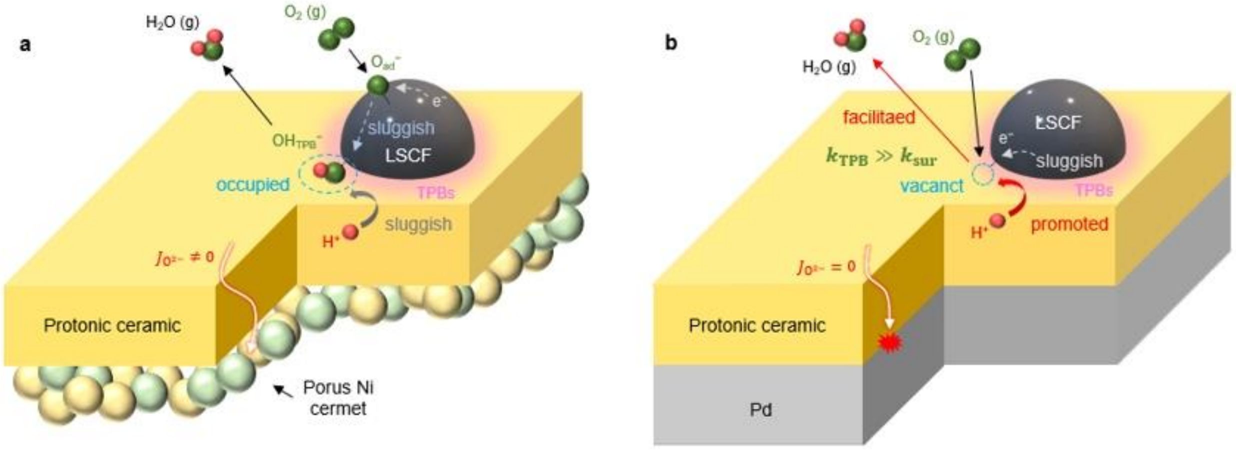

Fig. 1 (a) Cathode reaction mechanism in PCFCs. (b) Proposed mechanism of the fast cathode reaction in HMFC. Rate controlling steps, determined by previous studies and this work, are presented.↵

P-43

Exsolution in triple-conducting cathode materials for proton ceramic fuel cells (PCFCs)

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Perovskites designed for the cathode are mixed ionic-electronic conductors (MIEC), such as (Ba,La)(Fe,Co)$O_{3-\delta}$ group. They exhibit high chemical stability and electronic conductivity. Their great advantage is the ability of water uptake in a humidified atmosphere. The enhancement of cathode properties allows increasing PCFCs performance. One way of improvement is decoration of cathodes' surface with catalytically active nanoparticles (NPs). This can be achieved through exsolution. Oxide NPs exsolve on the perovskite surface under oxidizing atmosphere, due to structure destabilization [1]. The exsolution may be driven by oxygen partial pressure or stoichiometry changes. The latter may be changed by introducing the A-site deficiency or doping with Ln- or transition metals. Example of NPs on the (Ba,La)$CoO_{3-\delta}$ (BLC) surfaces are shown in Fig.1. Changes in temperature and atmosphere influenced the shape, dimension, distribution, and number of NPs. In this work, we report BLC-based cathode with exsolved NPs. The materials were characterized using X-ray diffraction and scanning electron microscopy. The thermal and electrical properties of selected materials were examined using thermogravimetric and DC-4W measurements.

Acknowledgements: Project FunKeyCat is supported by the National Science Centre, Poland under the M-ERA.NET 2, which has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no 685451.

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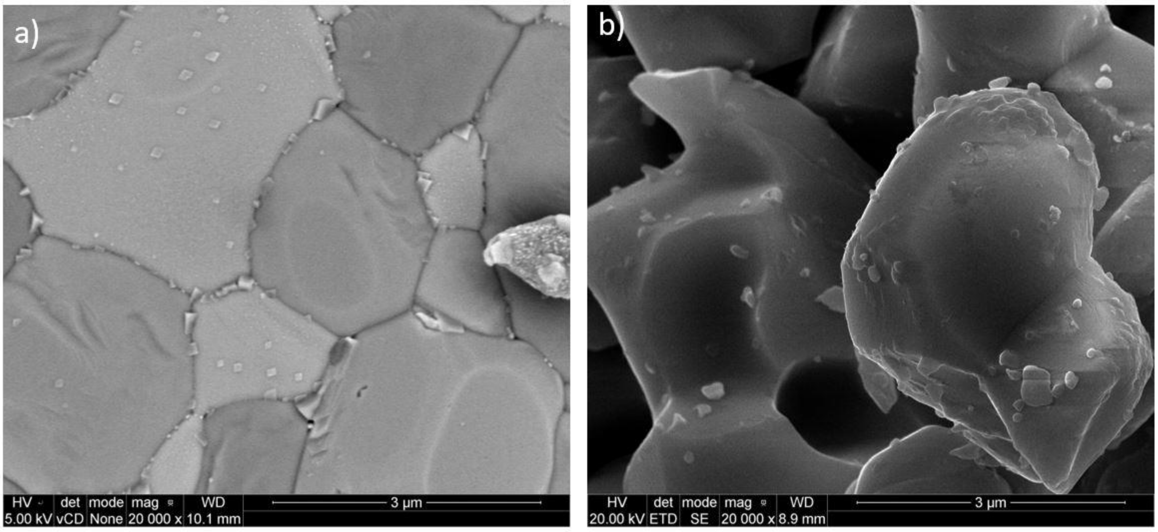

Fig.1. SEM images of nanoparticles exsolved on surface of BLC doped with a) 20% Lu on the A-site (pastille) and b) 50% Fe on the B-site of the perovskite (powder).

P-44 Development of protonic membrane reactors for the electrocatalytic conversion of CO_2 into chemical energy carriers

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The Horizon 2020 eCOCO2 project is developing an electrochemical membrane reactor for the conversion of CO_2 from industrial sources using renewable electricity and steam, to carbon-neutral synthetic liquid fuels for use as transport fuels. A first step of this work consists of defining suitable materials' formulation and processing routes for engineering a tubular cell integrating a proton conducting ceramic electrolyte with adequate conductivity in the temperature range 400-550°C. In this work, we develop thin dense electrolytes of BZCYYb based oxides (various dopant concentrations are screened) on Ni-BZCY tubular supports, as well as BZCYYb based oxides sintered as dense disks using the solid-state reactive sintering method for both architectures. We compare the conductivity of these architectures to discriminate the effects of the processing route and the use of Ni sintering aid. The results of this study are corroborated with hydration studies and conductivity measurements performed on these compositions as function of the amount sintering aid and the annealing profile. This systematic analysis is used to guide the design of the cell's architecture and its processing. The most promising compositions are produced as short tubular cells capped and sealed on alumina risers for dual atmosphere testing. Preliminary results on electrode screening in terms of adhesion and compatibility with the electrolyte layer will be presented. This study has received European Union's Horizon 2020 Research and Innovation funding under grant agreement N° 838077.

P-45 Stacking planar proton conducting ceramics – challenges and recent progress

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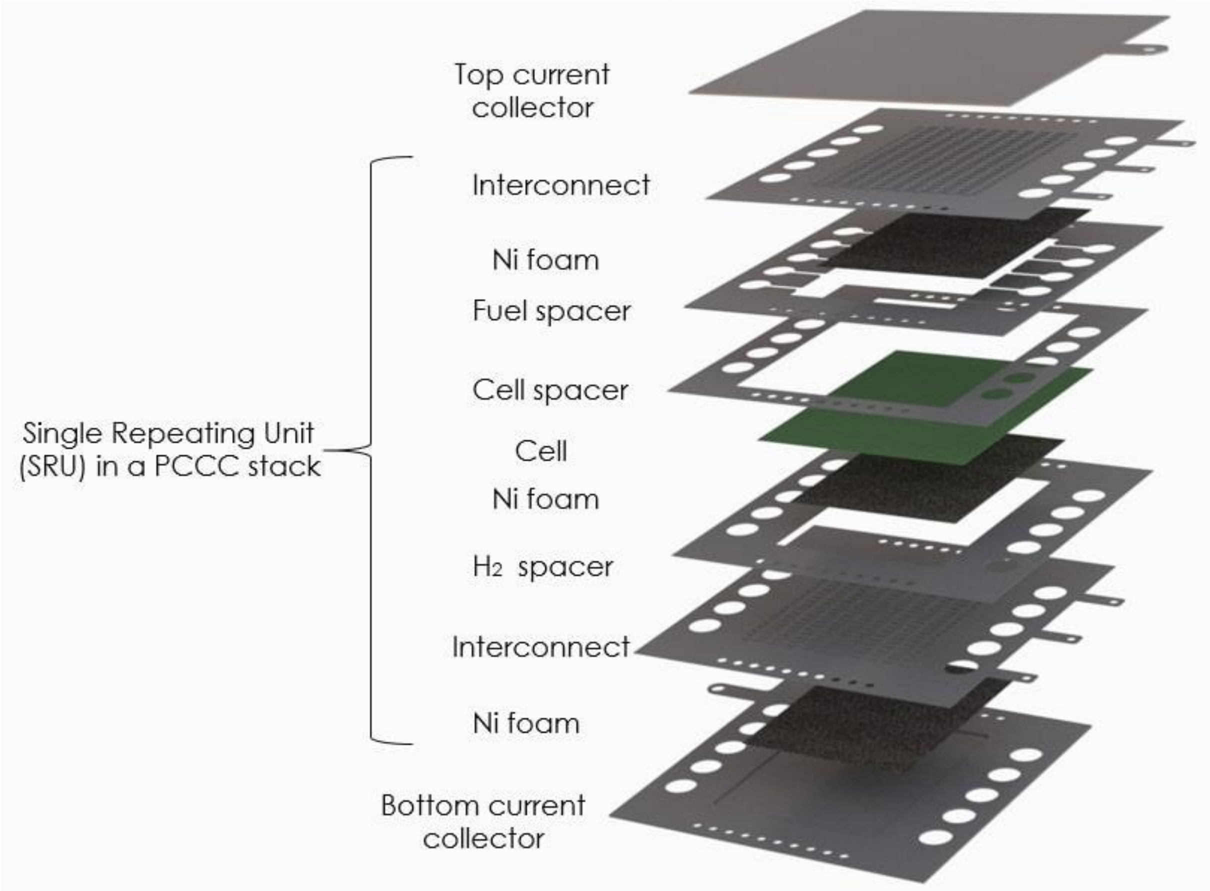
(2) Colorado School of Mines, Department of Mechanical Engineering, Golden, Colorado, USA

The overall goal of the work presented here is to develop a functional stack based on planar, symmetrical proton conducting ceramic cells (PCCCs) with focus on mobile applications. This PCCC stack will be able to produce high-purity hydrogen by steam reforming of any carbon-based fuel. The reformed hydrogen is electrochemically pumped through the proton - permeable electrolyte (BCZY27 ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$)) and pure hydrogen is retrieved on the other side of the membrane.

Developing such PCCC stacks comes with several challenges, which will be discussed in this contribution. Special focus will be given to cell development and stability, sealing of PCC cells and components, and design considerations in the stack layout to accommodate for the symmetrical cells.



P-46 Switching between Proton Vacancy and Excess Proton Transfer Pathways

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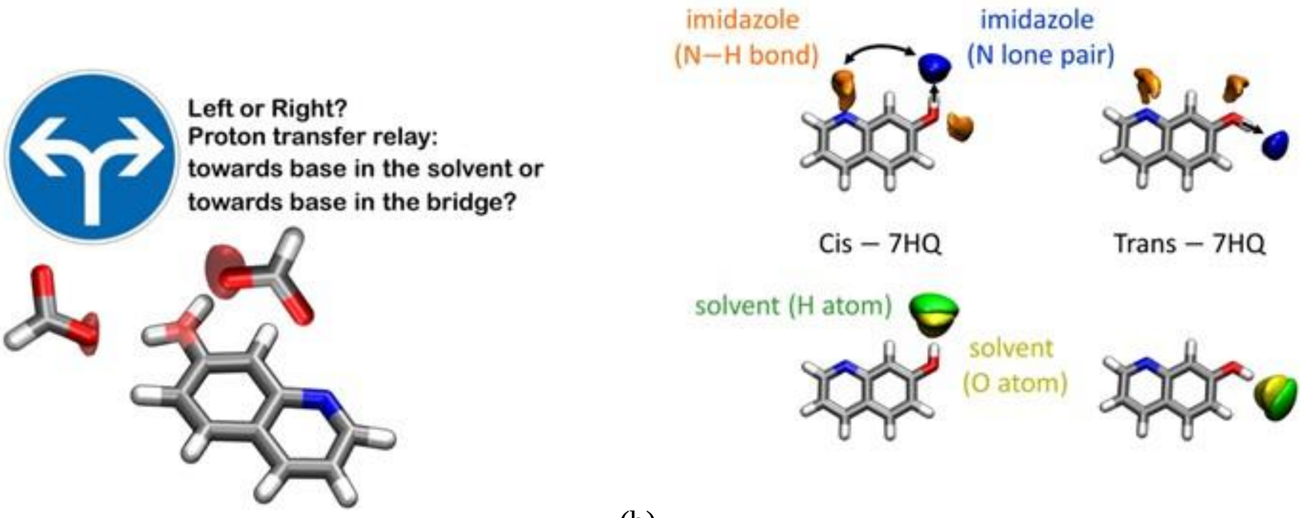
Bifunctional or amphoteric photoacids simultaneously present donor (acidic) and acceptor (basic) properties making them useful tools to analyze proton transport dynamics. Proton exchange is governed by the relative acidity or basicity strengths of the two reactive sites and can occur along two different pathways involving protolysis and hydrolysis mechanisms. We report here how the addition of a carboxylate base (formate anion) or a neutral compound like imidazole will alter the proton transport directionality of the bifunctional photoacid 7-hydroxyquinoline (7HQ), which has been previously understood to involve a von Grotthuss-like hydroxide/methoxide transport mechanism between the proton-accepting quinoline nitrogen atom toward the proton-donating –OH group in water or methanol. We monitor the reaction dynamics of the photo-excited 7HQ without and with sub-molar and molar concentrations of formate and imidazole in deuterated methanol (CD_3OD) solutions and follow the IR-active marker modes of the distinct charged species of 7HQ and of the formed conjugate acid species of the added bases, to determine the population kinetics of 7HQ reacting with formate and imidazole. To clarify the directionality of acid-base proton exchange in an amphoteric environment and learn about the molecular arrangements, we analyze our outcome by free-energy reactivity relationships and by calculating distribution functions of formate, imidazole and methanol solvent around the reactive sites of 7HQ from classical molecular dynamics simulations. We find that depending on the orientation of the –OH group (cis-7HQ or trans-7HQ) with respect to the quinoline aromatic ring system, the presence of formate or imidazole in the proton relay pathway can facilitate a fast and efficient, net von Grotthuss-like excess proton transport from the –OH group of 7HQ to the quinoline nitrogen atom. Our combined experimental and theoretical study provide key insight into the microscopic details of solvent-mediated proton transfer between acids and bases, directly relevant to the proton transport mechanisms in water-free fuel cells or any other confined systems with well-defined start and end points for proton transport.



(a) (b)

Figure 1 Spatial distribution functions (SDFs) of cis-7HQ and trans-7HQ illustrating the molecular arrangements of formate **(a)** and of imidazole/methanol solvent **(b)** with respect to the orientation of the –OH group and the quinoline nitrogen of 7HQ photoacid.

P-47

Physicochemical properties of solid composites formed by cellulose derivatives with imidazole investigated by two-dimensional correlation spectroscopy

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The idea of using a polymer electrolyte as an exchange membrane in electrochemical cells was first described for a fuel cell by Grubb in 1959 [1]. To this day, polymer proton conductors are of great interest to scientists. Such conductors based on biopolymers can potentially be used as a membrane because they are relatively cheap, widely available, and have good mechanical properties. Organic polymers are widely used as proton exchange membrane fuel cells (PEMFCs) for the space program and transport applications [2,3].

This work aims to present a group of new composites based on imidazole-functionalized cellulose. The analysis of the conductive, thermal (DSC, TGA, TOA), and spectroscopic (IR, Raman) properties of new proton-conducting composites will be presented. The two-dimensional correlation spectroscopy method will be used to analyze the above properties. This method enables the analysis of dynamic spectra in IR and Raman. As a result of the undertaken activities, it is possible to describe the dynamics of the hydrogen bond network and the thermal stability of the tested materials. Additionally, the research was supplemented with quantum chemistry calculations.

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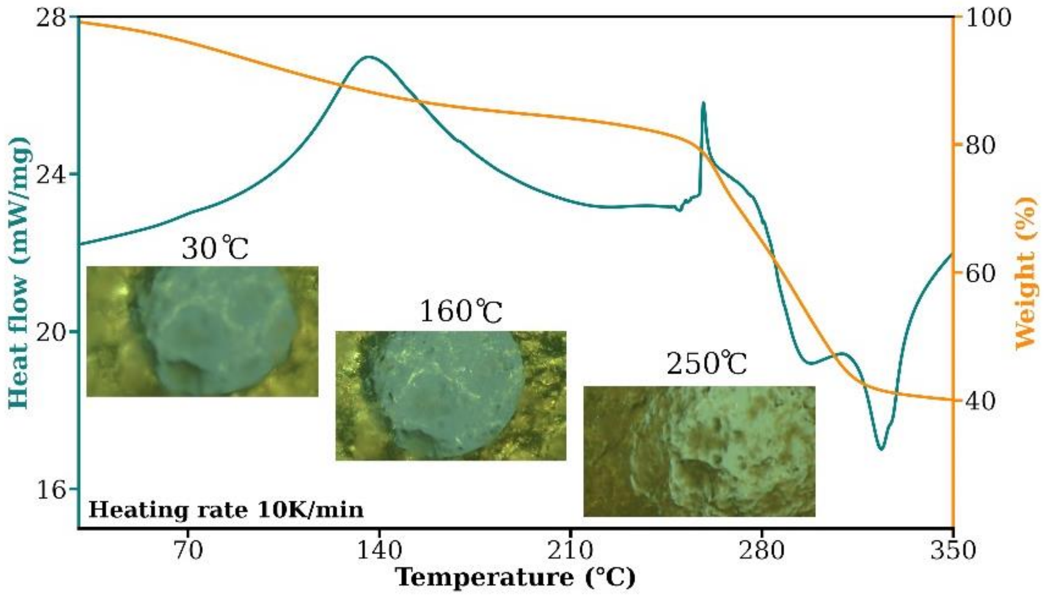
[3] Mauritz K. A., et al. Chem. Rev. 2004, 104, 4535−4586.



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P-48

Temperature and pressure dependence of hydrogen bond network in new imidazolium salts of aromatic acids

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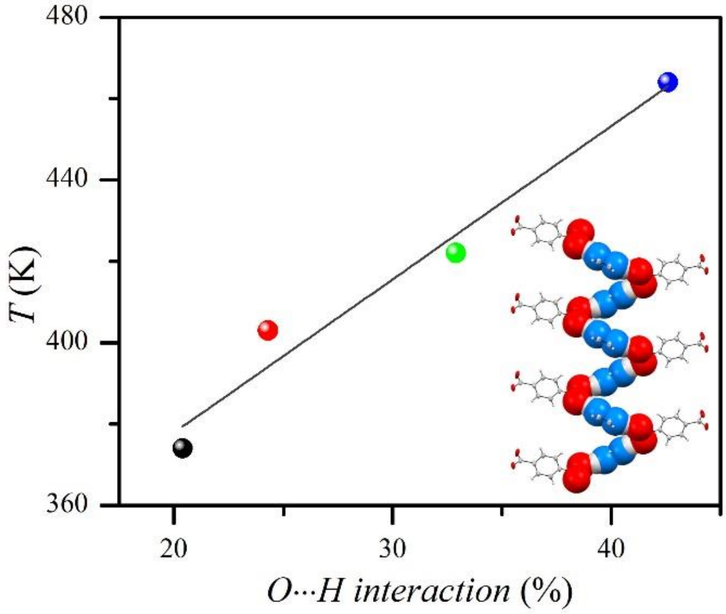
Understanding the mechanism of hydrogen bonding creation between molecules will allow the design of new materials with the desired properties. Imidazole is of great importance in material engineering because it can react with numerous acids. In addition, imidazole is a very promising building unit for conducting salts.

This study has been undertaken to investigate the correlation between the molecular structure and the physical properties of new proton conductors in temperature and pressure function. The imidazolium salts: imidazolium benzoate, imidazolium salicylate, imidazolium ortho-phthalate, and imidazolium terephthalate were investigated using experimental (X-ray, IR and Raman spectroscopy, DSC, impedance spectroscopy) and theoretical methods (DFT, QTAiM, Hirshfeld surface analysis).

These salts have a unique helical hydrogen-bonded system. In imidazolium terephthalate, we observed a combination of negative, positive, and near-zero thermal expansion. The unusual thermal behavior is due to the scissor-like motion of the 2D flexible hydrogen-bonded network. Furthermore, We showed a relationship between molecular structure and thermal stability. The appropriate distribution of carboxylic acid groups in the anion translates into the number of O···H interactions in the crystal (see figure). The higher the percentage of this type of interaction observed, the higher the melting point is present.

The research was financed from budget funds for science 2020–2023 as a research project under the PRELUDIUM-18 (National Science Centre, Poland, 2019/35/N/ST5/03324).



P-49

Dielectric and ionic conductivity properties in biopolymer chitin via loosely bonded water

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Setsunan University, Osaka, Japan

Bio-Materials with proton conductivity are essential for the application to the next-generation energy “fuel cells”. Recently, we demonstrated that the biofuel cell using biopolymer “chitin” drives electrical devices such as the LED light. In addition, we exhibited that proton conductivity in biopolymers is closely related to hydration water. As well-known, there are various types of hydrated water, such as tightly bound, loosely bound, and free waters. However, types of water related to proton conductivity have not been understood yet. In this work, we investigated proton conductivity in the loosely bonded water in chitin. Figure 1 shows the temperature dependence of the dielectric constant εr in hydrated chitin. εr begins to increase with the change of slope around 245 K and shows the small peaks around 260K and 273K. This result means that two types of water at least exist in the hydrated chitin. Considering that the melting point of bonded water is lower than that of free water, the peaks at 260K and 273K are caused by the melting of loosely bonded water and free water, respectively. In addition, from proton-conductivity measurement, the activation energy of proton conductivity in chitin is estimated to be 0.34 eV between 260K to 273 K. This value is close to the activation energy of proton migration at room temperature. These results suggest that proton conduction in chitin is realized via the loosely bonded water and that proton exchange between the loosely bonded waters and the chitin-side chain plays an important role in proton conduction in the hydrated chitin.

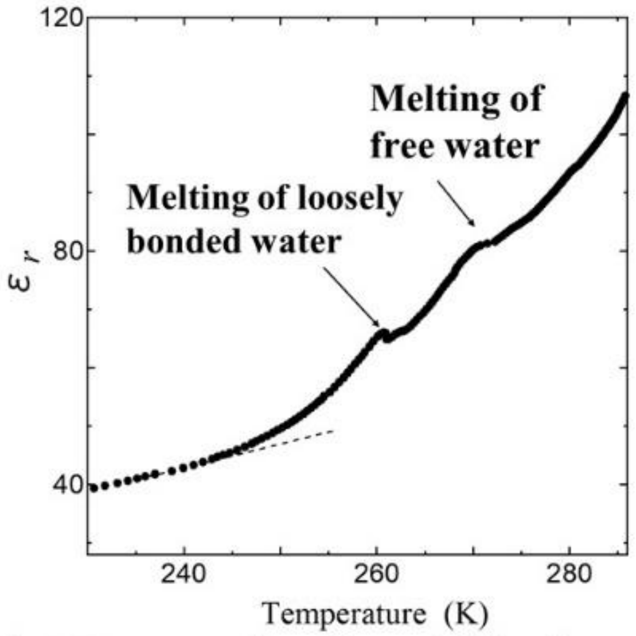

Fig.1 Temperature dependence of dielectric constant observed in hydrated chitin.

P-50

Hydration and proton conductivity of dipeptide crystals (Gly-Ser)

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As well known, the fabrication of a low-cost fuel cell without the environmental load in the manufacturing and waste processes is required. Biofuel cells using biomaterials are environmentally friendly and inexpensive. For example, collagen and chitin exhibit proton conductivity in the humidified condition and can be used as electrolytes of fuel cells. In previous studies, it is well known that functional groups bonded to the main chain of biological substances play an important role in the appearance of proton conduction. Glycine contributes flexibility to the structure of the main chain, and the hydroxyl groups in the side chains of serine are hydrophilic. Therefore, in this study, we have prepared the crystal of a dipeptide of glycine and serine (Gly-Ser crystal) and investigated their proton conductivity.

Gly-Ser crystals were grown by the slow evaporation method of the Gly-Ser solution. In order to measure proton conductivity, electrodes were deposited to Gly-Ser crystal, and AC impedance was measured by changing the relative humidity at a constant temperature.

Figure 1 shows the humidity dependence of the proton conductivity of Gly-Ser crystals. As shown in Fig. 1, proton conductivity in Gly-Ser crystals increases with increasing relative humidity. This result indicates that Gly-Ser crystals become proton conductors in the humidified condition. Further, this result suggests that the Gly-Ser crystal undergoes the hydration-induced phase transition accompanied by the hydration change of the side chain in the Gly-Ser crystal at around 90%RH.

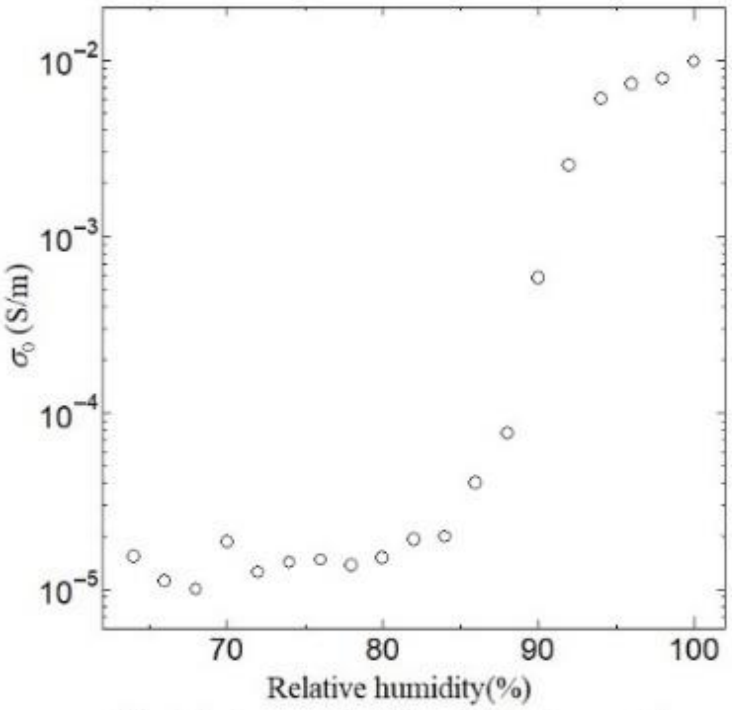

Fig. 1 Proton conductivity of Gly–Ser crystals

Thursday 30.9.2021, morning poster II

P-51 Fabrication and Characterization for Direct Ethanol Biofuel Cell using biopolymer "Chitin・Chitosan" as electrolytes

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As the energy in mobile devices, the direct alcohol fuel cells (DAFC) are investigated with much interest. However, in DAFC, there are significant problems such as the swelling of electrolytes under alcohol and the lowering of power density by fuel permeability of electrolytes. Therefore, in order to develop DAFC as mobile energy, the improvement of electrolytes is necessary. This study focuses on chitin and chitosan, which are biopolymers with low permeability to ethanol, and we have fabricated the direct-ethanol bio-fuel cells (bio-DEFC) using the chitin and chitosan electrolyte membranes and have measured the power generation characteristics. It was found that the ethanol permeability of chitosan is lower than that of chitin. Figure 1 shows the fuel concentration dependence of the power density in the fuel cell using the chitin or chitosan electrolyte. As shown in Fig. 1, the optimum ethanol concentration of these bio-DEFCs is 25%wt. In addition, the power density of fuel cells using the chitin electrolyte is about 2.5 times higher than that using the chitosan. Furthermore, to investigate the optimum condition of the chitin-chitosan complex electrolyte, we have fabricated the bio-DEFC using the chitin-chitosan complex electrolyte (Chitin(x)-Chitosan(1-x)). As a result, it was found that the power density of Chitin(x)-Chitosan(1-x) takes the peak at x=0.6. The analysis of proton conductivity of the chitin-chitosan complex membrane reveals that the peak at x=0.6 is derived from the proton conductivity of the chitin-chitosan complex membrane.

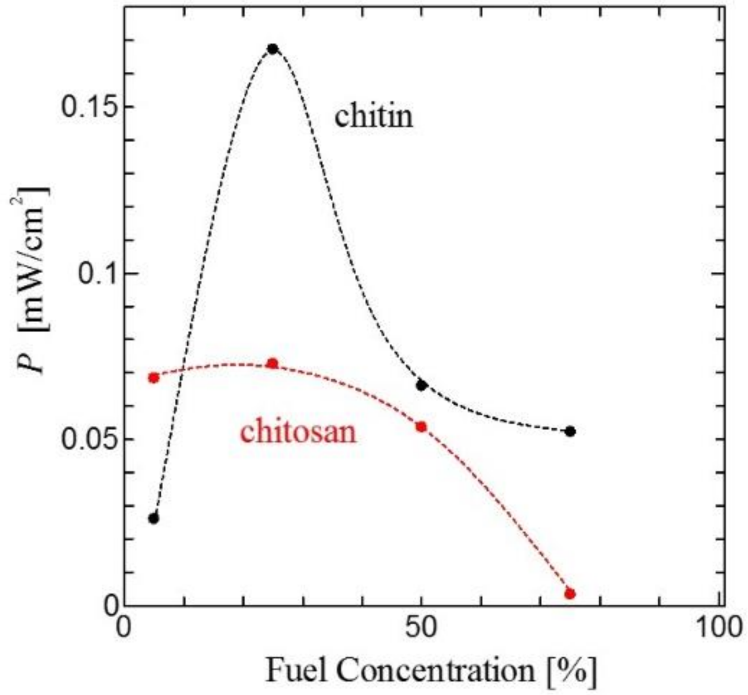

Figure 1. Relationship between power density and ethanol concentration.

P-52 Fluorine-free membrane electrode assemblies for water electrolysis based on sulfonated polyphenylensulfone

Carolin Klose,(1,2) Torben Saatkamp,(3) Andreas Münchinger,(3) Luca Bohn,(2) Giorgi Titvinidze,(4) Matthias Breitwieser,(1,2) Klaus-Dieter Kreuer,(3) Severin Vierrath(1,2)

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The most common polymers used in polymer electrolyte membrane water electrolysis are perfluorosulfonic acids (PFSAs) due to their high proton conductivity and mechanical and chemical stability. In the past years, hydrocarbon polymers have gained increasing attention since they promise lower gas permeation while maintaining high efficiency and potentially lower the material cost in comparison to PFSAs. In this work, we show polarization data and gas-crossover of water electrolyzer single cells with sulfonated poly(phenylene sulfone) (sPPS) as membrane and as electrode binder. The sPPS-cells reached 3.5 A cm^{-2} at 1.8 V outperforming state-of-the-art PFSA-cells (1.5 A cm^{-2} at 1.8 V) (Figure 1a), while their iR-free (corrected for the membrane-resistance) polarization is similar[1]. This indicates that the beneficial performance stems from a lower ohmic resistance and no major negative effects in the kinetic or mass transport were observed when using sPPS as ionomer binder or membrane. Despite the lower ohmic resistance the sPPS-cells show a two times lower gas crossover than the PFSA-PEMWEs in a oversaturated surrogate test (Figure 1b).

[1] Klose, Carolin, et al. All-Hydrocarbon MEA for PEM Water Electrolysis Combining Low Hydrogen Crossover and High Efficiency. Advanced Energy Materials 10.14 (2020): 1903995.

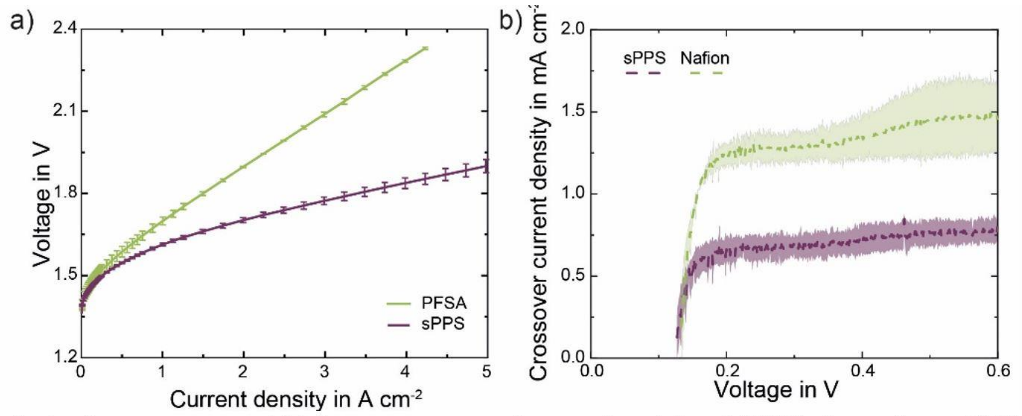

Figure 1 a) Polarization curves and b) linear sweep voltammetry data of CCMs based on sPPS (purple) and PFSA (green, Nafion N115) as PEM and ionomer binder material. Adapted from [1]

P-53

Poly(biphenyl piperidinium) anion exchange membranes with N-alicyclic quaternary ammonium cationic side chains

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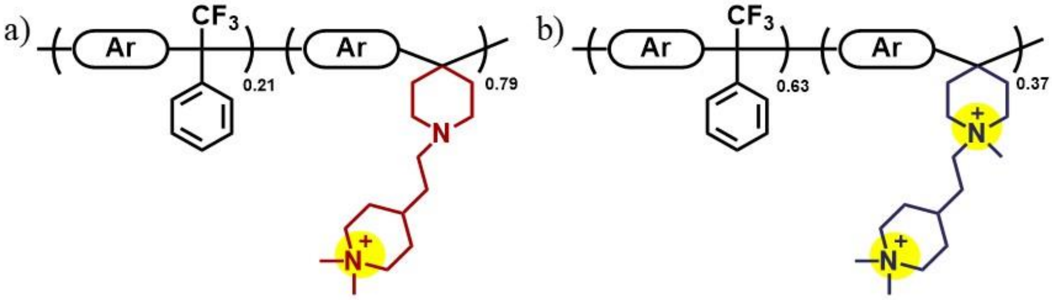
Poly(arylene piperidinium)s belong to a new class of cationic polymers which are suitable candidates for anion exchange membrane (AEM) applications. We have previously synthesized and studied poly(p-terphenyl piperidinium) AEMs1, and developed strategies to tune the structure and properties of poly(biphenyl piperidinium) AEMs by copolymerizations and crosslinking2. Here, we present new synthetic strategies involving cationic side chains to further improve the chemical stability and hydroxide conductivity of poly(arylene piperidinium)-based AEMs. Two series of poly(biphenyl piperidinium)s were prepared carrying alkali-stable mono- (Series 1) and di-cationic (Series 2) side chains, respectively. In Series 1, the cations were attached to the rigid polymer backbone via flexible alkyl spacers, resulting in AEMs with high alkaline stability. In Series 2, the di-cationic configuration provided AEMs with very high hydroxide conductivity, reaching almost 170 mS/cm at 80 °C at moderate water uptake and swelling, which indicated that the dual-cationic arrangement facilitates an efficient hydroxide transport. The results of the study offer valuable insights into the design and preparation of high-performing AEMs for fuel cells and water electrolyzers.

1. Olsson, J. S.; Pham, T. H.; Jannasch, P., Adv. Funct. Mater. 2018, 28(2), 1702758.
2. Olsson, J. S.; Pham, T. H.; Jannasch, P., J. Membrane Sci. 2019, 578, 183-195.



Scheme 1. Representative molecular structures of the side-chain modified poly(biphenyl piperidinium)s in a) Series 1 and b) Series 2. Ar = biphenyl.

44-KN

Molecular Engineering of Ion Conducting Polymer Electrolyte Membranes for Electrochemical Energy Conversion and Storage Technologies

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Proton exchange membrane (PEM) and anion exchange membrane (AEM) are a key component of electrochemical energy conversion and storage technologies such as fuel cells, electrolyzers, and flow batteries. AEM fuel cells have several advantages, such as fast kinetics and non-precious metal catalysts. New material developments by designing of new polymer backbones, side chain functional groups and new ion conducting groups have been extensively investigated over the past decade. Several research groups including us have reported that a long side chain between polymer backbone and ionic head group is helpful for enhancing micro-phase separation based on thermochemical stable backbone.

In this study, we will present the effects of ion-conducting polymer structures on the membrane morphology, properties and redox flow battery performance. To better understand polymer structure–membrane property relationships, aromatic PEMs with sulfonate side chains were prepared and their properties were evaluated. In addition to the fundamental study, how high performance AEMs can be produced in a kilogram scale by cost effective processes will be presented.

References

[1] S. Adhikari, M. K. Pagels, J. Y. Jeon, C. Bae* "Ionomers for Electrochemical Energy Conversion & Storage Technologies", Polymer, 2020, 211, 123080.

[2] S. Noh, J. Y. Jeon, S. Adhikari, Y. S. Kim, C. Bae* "Molecular Engineering of Hydroxide Ion Conducting Anion Exchange Polymers for Electrochemical Energy Conversion Technology" Acc. Chem. Res. 2019, 52, 2745–2755.

45-INV

Intrinsically conductive double layer hydroxides as fillers for anion exchange membranes

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The interaction of nanosized particles with a polymer matrix can induce a large variation of the original polymer characteristics. The extent of the modification depends on the amount of the interface interactions, the affinity between the two phases, the stability of the filler in the medium. Double layer hydroxides (LDH), contain mobile anions in the interlamellar space, assist the anion exchange membranes (AEM) conductivity due to the presence in the layered structure of linked oxygen or hydroxyl groups which allows a hydrogen bond network. They might also reduce the membrane swelling and excessive water uptake and mitigate the attack of AEM in alkaline conditions by composite effects.

In recent years we explored the synergistic effect between the two phases in hybrid organic-inorganic nanomaterials based on AEM and LDH [1-4]. The composition and morphology of LDH were varied (Mg/Al, Zn/Al, Mg/Al exfoliated,) and different loadings were used (from 7 to 30%). A modification of the LDH lamellar structure adding ionic liquids was achieved to prepare more conductive structures. Different anion exchange matrices were selected: polysulfone (PSU), poly(phenylene oxide) (PPO) with short (Fig. 1), and long side chain. The polymers were quaternized with small and flexible TMA and bulky and rigid DABCO.

[1] Pasquini L et al. ChemElectroChem, 2020, 13, 2917-2924
[2] Pizzoferrato R et al. ChemElectroChem 2018, 5, 2781-2788
[3] Pizzoferrato R et al. Solid State Ionics 2018, 314, 30-35
[4] Di Vona ML et al. Int. J. Hydrogen Energy 2017, 42, 3197-3205

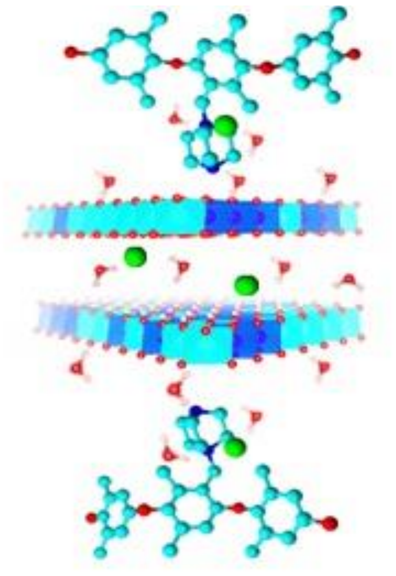

Fig 1. Schematic representation of PPO-DABCO containing LDH

46-KN

How Do We Investigate Reaction Mechanism in Oxide Electrode on Proton-Conducting Electrolyte?

Koji Amezawa
Tohoku University, Japan

Development of high-performance electrode is one of challenges for realization of proton-conducting ceramic fuel cells (PCFCs) and electolysis cells (PCECs). Electrode reactions in PCFCs and PCECs are electrochemical reduction/oxidation of gases. Since protons, electrons, and gas molcules exist in the electrolyte, electrode and gas phase, respectively, the electrode reaciton basically takes place at triple phase boundaries (TPBs). On the other hand, the reaction site can be expanded from TPBs to double phase boundaries (DPBs), when a mixed ionic-electronic conductor (MIEC) is used. In such an MIEC electrode, the dominant reaction sites are believed to be DPBs because of their large area. However, no clear experimental evidences have been provided to show how significantly TPB/DPB reactions contribute to the total reaction. Recently we proposed new and original model electrodes, as schematically shown in Fig. 1, to deeply investigate a gas reaction on a solid electrolyte. These so-called "patterned thin film electrodes" are kinds of thin film electrodes, but the electrode/electrolyte contact area was limitted by inserting a slitted insulating layer between electrode/electrolyte. In the electrode of Fig. 1(b), a part of the electrode film was removed from the electrode of Fig.1(a) to introduce TPBs. By applying these novel model electrodes, the contribution of TPB/DPB reactions can be separately evaluated. In this presentation, reaction mechanism in oxide electrodes for PCFCs and PCECs will be discussed based on results obtained by utilizing these model electrodes.

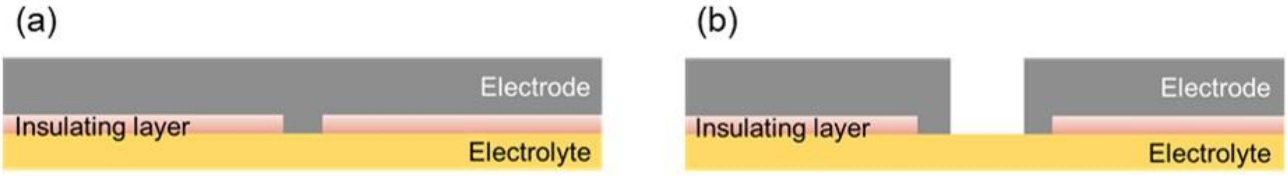

Figure 1. Schematic illustration of patterned thin film model electrodes (a) without and (b) with triple phase boundary.

47-INV

Unveiling discrepancies in reported Faradaic efficiencies in protonic ceramic electrolysis cells

Sandrine Ricote, Huayang Zhu, Robert J. Kee
Colorado School of Mines

Faradaic efficiency (FE) is an important performance metric for Protonic Ceramic Electrolysis Cells (PCECs). It is commonly accepted that FE increases with increasing steam partial pressure, decreasing oxygen partial pressure on the steam electrode, and decreasing operating temperature. These variations in operating conditions reduce the electronic contribution to the protonic-ceramic membrane conductivity. However, despite general agreement on the definition (hydrogen flux produced per unit of supplied electrical current), there are significant (even qualitative) discrepancies in the literature about how FE depends on current density. The present paper develops a physics-based Nernst-Planck model that is used to explore how FE depends on operating parameters (temperature, pressure, gas compositions, etc.). The model, which is based on a membrane-electrode assembly composed of Ni/$BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-d}$(BZCYYb)|BCZYYb|$BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-d}$ (BCFZY), is validated using recently published button-cell performance data [1]. In addition to operating conditions, the study also considers the influence of defect-incorporation and charge-transfer rates on the Faradaic efficiency.

[1] M. Liang, et al., Chem. Eng. J., doi.org/10.1016/j.cej.2020.127717

48-O

Pressurized Steam Electrolysis using Proton Ceramics: Impact of Electrodes, Temperature and Pressure on Performance and Efficiency

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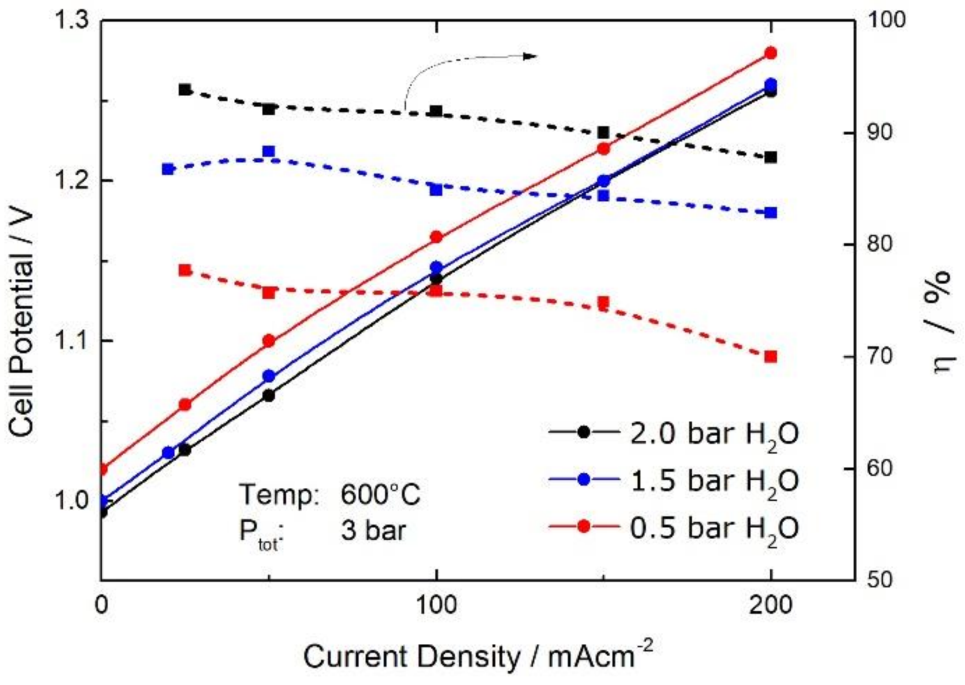
Proton Ceramic Electrolysis (PCEs) presents an intriguing advantage compared to other electrolysis technologies due to its potential for direct production of pressurized dry hydrogen, in addition to an intermediate operating temperature that allows for high electrical efficiency and thermal integration with industrial processes and renewable energy sources. Recent years have shown an impressive development in reported cell performances for PCEs, confirming the potential of the technology. However, there is still limited data on pressurized operation of PCEs, and the impact of increased pressure on the overall efficiency and performance of PCEs needs to be further elucidated.

Here, we will present new results on the development of pressurized tubular PCEs in the FCH-JU project GAMER, with special focus on the impact of pressurized operation on cell performance and how that affects individual components in terms of stability, performance and efficiency. Several tubular PCEs based on a BZCY81 electrolyte with an active area of 10-16 cm2 were tested using different positrode materials and architectures. We will present how these variations impact performance and stability in pressurized operation and provide a summarizing overview on the status of pressurized steam electrolysis using tubular PCEs.

GAMER has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement (number 779486). This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.



49-O

Proton cermic electrolyser for pressurized hydrogen production: From tubular cells to module integration

Marie-Laure Fontaine,(1) E. Vøllestad,(1) Michael Budd,(2) Jose M. Serra,(3) Truls Norby,(4)
Carlos Atli Córdova Geirdal,(5) Enrique del Pozo Polidoro,(6) Arian Nijmeijer,(7) Peter Veenstra(7)

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Incentives for developing high temperature electrolysers (HTEs) using proton conducting electrolytes stem from the fact that a proton ceramic electrolysis cell (PCE) pumps out and pressurises dry H_2 directly. Existing HTEs design utilises the high packing density of planar stacks, but the hot seal and vulnerability to single cell breakdown give high stack rejection rate and questionable durability. In the GAMER project, we develop a tubular Proton Ceramic Electrolyser (PCE) module technology for producing pure dry pressurized hydrogen. The cells are designed as innovative single engineering units (SEU) with each cell of 60-70 cm^2 active surface area encased in a steel shell for operation at 600°C. The tubular cells integrate BZCY based electrolyte, BZCY-Ni hydrogen electrode and BGLC-BZCY based composite steam electrode. Electrochemical performance of the produced SEUs are presented as function of temperature, potential and pressure at up to 10 bar showing high faradaic efficiency. The presentation also reports on the design of a 10 kW rated system for delivering pure hydrogen at minimum 30 bars outlet pressure, with the support of advanced modelling and simulation work. This system is under construction and we will present current status.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement (number 779486). This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.

50-O Cesium dihydrogen phosphate – An electrolyte for medium temperature water electrolysis and Power-to-X

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The efficient conversion of renewable, electrical energy available from wind and solar to chemical energy is one of the key challenges in the transition to a renewable energy economy. One method for this conversion, which has been the subject of growing interest over the last years, is the medium temperature electrolysis from 240 °C to 320 °C using cesium dihydrogen phosphate, CsH_2PO_4 (CDP) as a solid acid, proton-conducting electrolyte. CDP turns "super-proton-conducting", due to a phase transition at 230 °C.

Solid acid electrolysis has numerous, possible advantages compared to established electrolysis methods in either the low (< 120 °C) or high (> 600 °C) temperature range: (1) improved kinetics and thermodynamics, (2) facilitated mass transport in a solely gas phase system, (3) alternative and cheaper electrocatalysts are available, (4) known deactivation mechanisms of the electrocatalysts are circumvented, (4) no special high-temperature resistant materials are needed and (5) the temperature range lines up with that of chemical CO_2-reduction and will facilitate power to X.

We have developed a test environment for medium temperature electrolysis using CDP as electrolyte. By carefully controlling the high necessary water vapor pressure in the system, we are able to prevent dehydration, which is required to maintain a stable conductivity. In addition, we avoid the presence of a corrosive liquid phase in the electrolyte. This system enables us to investigate the advantages of this new type of electrolysis and develop improved methods for energy conversion and power-to-X.

51-INV

Processing route for Metal Supported Proton Conducting Ceramic Cells

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Metal-Supported (MS) Proton Conducting Ceramic Cell (PCC) architectures offer several advantages over state-of-the-art ceramic supported PCCs, such as high tolerance towards thermal/redox cycling and high mechanical stability which both are key features for flexible and reliable operation in high temperature fuel cell and electrolysis applications. The key challenge in the development of MS-PCC is to fabricate a gas-tight electrolyte and keep the functionality of the porous metal support. An alternative is to use thin film deposition techniques for fabrication of the electrolyte. The support layer should then have small pores and be smooth to obtain an even coverage of a gas tight thin film electrolyte. Additional challenges in fabrication come with large differences in the thermal expansion coefficients (TEC) between state-of-the-art proton-conducting electrolytes such as BZY and the porous MS, and air and fuel electrodes. To reduce issues with crack formation or spallation of the electrolyte layer, a Sr- and Ce-doped BZY (BSZCY151020) electrolyte has recently been developed to increase the TEC.

In this contribution, we present status of the development of MS-PCC cells using a combination of wet chemical processing and pulsed laser deposition (PLD) of a gas-tight, thin-film electrolyte (1 micron). A short overview of the literature status on MS-PCC will also be provided.

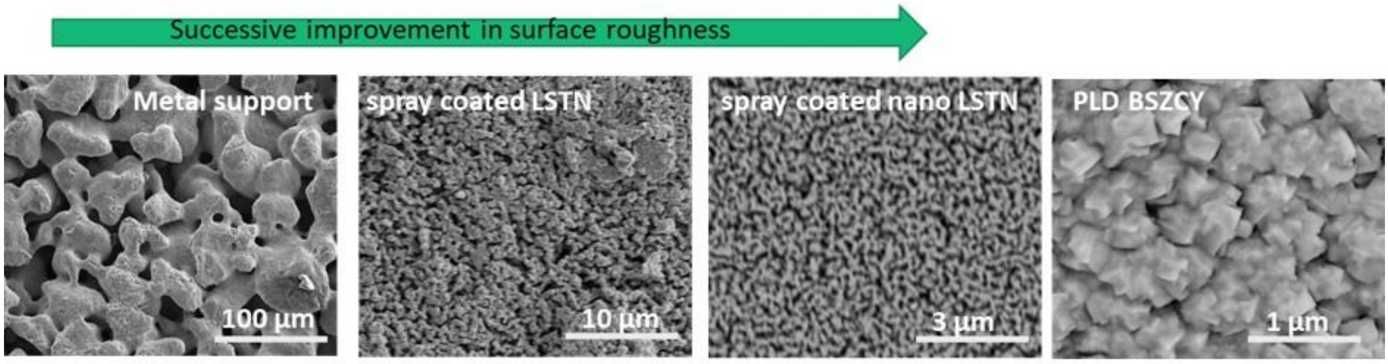

Figure: Illustration of the layered MS-PCC half-cell structure

52-O

Designing a novel process for the direct conversion of CO_2 to fuel in a co-ionic membrane reactor. Membrane components advances and challenges

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Hydrogenation of CO_2 to value-added products using green energy offers great potential to mitigate GHG emissions. Current alternatives rely on energy-intensive multi-step approaches limiting the energy efficiency of the overall process. The eCOCO2 approach (H2020 project) overcomes these issues by integrating a suitable CO_2 reduction in an electrochemical catalytic membrane reactor (e-CMR) that allows to couple: i) H_2O electrolysis and H_2 production using renewable electricity, and ii) CO_2 reduction to CO via RGWS followed by CO hydrogenation to valuable hydrocarbons. These two processes take place in a tubular reactor separated by a solid co-ionic membrane electrolyte enabling the simultaneous transport of H^+ and O^{2-} ions in opposite directions (Figure 1). O^{2-} ions are transported from the reaction chamber through the co-ionic electrolyte allowing the extraction of water generated in the reaction, thus shifting the thermodynamic equilibrium enabling to reach higher per-pass yield. In addition, coupling the endothermic water electrolysis with the exothermic hydrocarbons synthesis and Joule-effect heating will lead to unprecedented energy efficiency. Here, the novel concept behind the eCOCO2 approach will be presented. Recent advances regarding the development of BZCY-based electrolytes with adequate hydration, conductivity and stability under operating conditions (T=450 ºC, P=20 bar, CO_2 and H_2O rich atmospheres) will be discussed together with the characterization and optimisation of electrodes to reach the target performance within the electrochemical reactor.

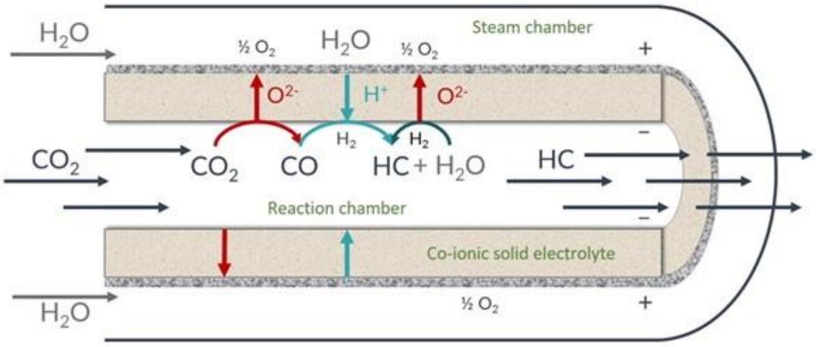

Figure 1. The concept behind eCOCO2.

This study has received European Union's Horizon 2020 Research and Innovation funding under grant agreement Nº 838077.

53-O

Shifting the Equilibrium of Thermodynamically Limited Reactions with Protonic Ceramic Membrane Reactors

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The discovery of high temperature protonic ceramic membranes by Iwahara and coworkers [1] enabled the development of electrochemical cells that can operate at temperatures between 400 and 700 °C. This temperature range is particularly interesting since several industrially relevant catalytic hydro- and dehydrogenation reactions take place, offering new routes for electrifying the chemical industry with renewable power. So far, protonic ceramic membrane reactors have been utilized with promising results in several catalytic systems, such as ammonia synthesis, water electrolysis, (hydro)carbon reforming and methane conversion to aromatics [2,3] In this contribution, we will present how the electrical power provided to the PCMRs shifts the equilibrium of such thermodynamically limited reactions towards higher conversions which are unattainable with conventional thermochemical reactors. Additionally, we exemplify how the decrease in operation temperature or pressure due to the supply of electrical work allows the combination of several complex industrial processes (e.g., Haber-Bosch process) in a single electrochemical device [4] thus, simplifying some traditionally complexed processes while increasing their efficiency.

References

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[3] S.H. Morejudo et al., Science, 353 (2016) 563-566.
[4] V. Kyriakou et al., Joule 4, (2020)

54-O

Development of electrodes and complete electrochemical cells based on surface protonics

Vegar Øygarden,(1) Einar Vøllestad,(1) Christelle Denonville,(1) Ørnulv Vistad(1) Asif Mahmood,(2)
Truls Norby,(2) Per Martin Rørvik(1)

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Surface protonics – the transport of protonic charge carriers along ionic surfaces – provides enhanced proton conductivity in porous oxide matrices at low temperature and high relative humidity. This has been shown to have significant importance for many catalytic and electrochemical applications such as the promotion of catalytic methane reforming and ammonia production. The formation of physisorbed water layers on the surface of the porous ceramics in humid atmosphere provides a medium for fast proton diffusion and conduction, similar to the water channels of a polymeric proton conductor. While surface protonic processes have been acknowledged and studied for over a decade, we have not seen any studies on electrodes for surface protonics and hardly any implementation of surface protonics in complete electrochemical cells.

In this contribution we will present and discuss ongoing work where we systematically study the electrode responses for surface protonic cells, and the distinct difference between the role of adsorbed water on oxide-based electrodes compared to metallic electrodes. Finally, we will report on our work on complete electrochemical cells based on surface protonics, using different cell architectures and material combinations to obtain a steady-state cell potential across a thin porous oxide electrolyte. The impact of electrolyte material, microstructure and complete architecture on the ohmic resistance as a function of relative humidity and temperature will be discussed using a Ni-YSZ(30 µm)-Au cell as an example.

Friday 1.10.2021

Colorado	Chicago	Stuttgart Lund	Beijing	Seoul Tokyo	
					J.-H. Lee
		11	**17**	**18**	55-INV Yamazaki Data-driven discovery of proton-conducting oxides
		11:30			56-O Gazda Proton-conducting high entropy oxides
					57-O Hyodo High Proton Conductivity and Chemical Stability in Heavily Scandium-Doped Barium Zirconate (HSBZ)
		12	**18**	**19**	58-O Naumovska The nature of proton diffusion in scandium doped barium zirconates investigated with neutron scattering techniques
					H. Matsumoto
		12:30			59-O Perrichon Unraveling the Ground-State Structure of BaZrO3 by Neutron Scattering Experiments and First-Principles Calculations
		13	**19**	**20**	60-O Makagon Non-classical electrostrictive phenomena in hydrated acceptor doped BaZrO3: proton trapping and dopant size effect
					61-O Omata Understanding the effect of oxide components on proton mobility in phosphate glasses; statistical analysis and experimental studies
		13:30			
					S. Ricote
6	**7**	**14**	**20**	**21**	62-KN J.H. Lee Sintering mechanism of thin and dense electrolyte layer for high performance protonic ceramic fuel cells
		14:30			
					63-INV Haile Reversible Electrochemical Cells for Interconversion between Fuel and Electricity
7	**8**	**15**	**21**	**22**	
					64-INV Takamura Diatomic Hydrogen Occupation in Perovskite-Type Oxyhydrides
		15:30			Closing
8	**9**	**16**	**22**	**23**	

55-INV

Data-driven discovery of proton-conducting oxides

Yoshihiro Yamazaki(1,2)

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Kyushu University, Japan
(2) INAMORI Frontier Research Center, Kyushu University, Japan

Materials discovery has been one of the biggest challenges in the fields of solid state ionics, materials science and chemistry because of the enormous number of chemical compositions to explore. Traditional materials discovery relies heavily on researchers' experience and intuition, which has resulted in a low success rate. Although density functional theory computations are becoming powerful, predicting the properties of heavily doped perovskites known to exhibit fast proton conduction is way beyond what current computational power can handle. In this talk, we demonstrate the accelerated discovery of proton-conducting oxide using data driven structure–property maps for the hydration of 8,613 hypothetical perovskite oxides in descriptor spaces characterized as being important by gradient boosting regressors. We constructed trustworthy hydration training datasets for 65 compounds, including literature data, by performing thermogravimetry measurements on 22 perovskites. Selecting hypothetical oxides with a hydration enthalpy of −100 ± 5 kJ/mol in the interpolative domains for three selected descriptor spaces nominates a host, which has not previously been recognized for either proton incorporation or proton conduction. Synthesizing the nominated oxide and subsequent thermogravimetric and electrochemical evaluations successfully demonstrated its proton incorporation and conduction. This approach shows a great promise for accelerating the discovery of materials for electrochemical applications.

56-O

Proton-conducting high entropy oxides

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

Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Gdansk, Poland

High entropy oxides (HEO) are oxides stabilized by configurational entropy, which originates from at least 5 elements occupying randomly one crystallographic site. The first known high entropy oxide is the rock-salt system of (Mg,Co,Ni,Cu,Zn)O, with an equimolar content of each cation, reported in 2015 by Rost et al. [1]. So far, not much has been learnt on the electrical properties of high-entropy oxides. The first studies on proton conduction in high-entropy perovskites have been published quite recently [2].

In this work, we present and discuss the electrical properties of high-entropy oxides based on proton-conducting oxides, that is, barium zirconates and lanthanum orthoniobates.

Single-phase oxides were prepared using solid-state reaction method. Electrical conductivity was studied by electrochemical impedance spectroscopy and/or by DC 4-terminal method in different atmospheres and temperatures. Electrical properties, in particular activation energy and preexponential factor of conductivity, are discussed in terms of their possible relation to the configurational entropy.

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57-O High Proton Conductivity and Chemical Stability in Heavily Scandium-Doped Barium Zirconate (HSBZ)

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(4) Kyushu University Platform of Inter-/Transdisciplinary Energy Research, (Q-PIT), Kyushu University, Fukuoka, Japan

We developed a proton-conducting electrolyte material that possesses both high proton conductivity and high chemical stability at intermediate temperatures. It is heavily 60 at% scandium-doped barium zirconate (HSBZ) that shows proton conductivity higher than 0.01 Scm^{-1} above 396 °C for 200 h. An accelerated stability test under a highly concentrated and humidified CO_2 stream using in situ X-ray diffraction shows that the perovskite phase is stable over 240 h at 400 °C under 0.98 atm of CO_2, equivalent to 67 years of exposure to the ambient atmosphere. These results suggest HSBZ is promising as an electrolyte for solid oxide fuel cells or electrochemical membrane reactor operated at the intermediate temperatures.

Reference

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58-O

The nature of proton diffusion in scandium doped barium zirconates investigated with neutron scattering techniques

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Maths Karlsson(1)

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(2) ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, United Kingdom
(3) Institut Laue-Langevin, Grenoble Cedex 9, France

Proton conducting perovskite type oxides are of interest due to their possible application in a number of technological devices such as environmentally friendly solid oxide fuel cells with an operational temperature in the intermediate temperature range, hydrogen sensors, and other electrochromic devices [1]. Among the most promising materials are scandium doped barium zirconates, $BaZr_{1-x}Sc_xO_{3-x/2}$, owning to their high chemical stability and proton conductivity at intermediate temperatures [2].

In this contribution, we will report on recent investigations of the nature of localized proton motions in $BaZr_{1-x}Sc_xO_{3-x/2}$, with x = 0.10 and 0.50, using quasielastic neutron scattering (QENS) techniques [3]. The results unravel significant differences in the localized motions of protons, manifested as proton transfers and -OH reorientational motions, respectively, between the two samples, with more pronounced and complex dynamics for the highly scandium doped material, x = 0.50. This suggests that tuning the scandium doping level is a promising route towards optimizing the proton conductivity.

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[3] E. Naumovska, J. Orstadius, R. Lavén, M. Karlsson et al., In manuscript.

59-O

Unraveling the Ground-State Structure of $BaZrO_3$ by Neutron Scattering Experiments and First-Principles Calculations

Adrien Perrichon,(1,3) Erik Jedvik Granhed,(2) Giovanni Romanelli,(3) Andrea Piovano,(4) Anders Lindman,(2)
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The all-inorganic perovskite barium zirconate, $BaZrO_3$, is widely used in the field of energy materials, with numerous proton-conducting oxide materials being obtained by, for instance, acceptor-doping of the Zr-sites [1]. However, fundamental questions remain surrounding the crystal structure of $BaZrO_3$, especially regarding its ground-state structure. While diffraction techniques indicate a cubic structure all the way down to T = 0 K [2], several first-principles phonon calculation studies based on density functional theory indicate an imaginary (unstable) phonon mode due to the appearance of an antiferrodistortive transition associated with rigid rotations of ZrO_6 octahedra. The first-principles calculations are highly sensitive to the choice of exchange-correlation functional and, using six well-established functional approximations, we show that a correct description about the ground-state structure of $BaZrO_3$ requires the use of hybrid functionals. The ground-state structure of $BaZrO_3$ is found to be cubic, which is corroborated by experimental results obtained from neutron powder diffraction, inelastic neutron scattering, and neutron Compton scattering experiments [3].

[1] K. D. Kreuer, Proton-Conducting Oxides, Annu. Rev. Mater. Res. 33 (2003), 333.
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[3] A. Perrichon et al., Unraveling the Ground-State Structure of $BaZrO_3$ by Neutron Scattering Experiments and First-Principles Calculations, Chem. Mater. 32 (2020), 2824.

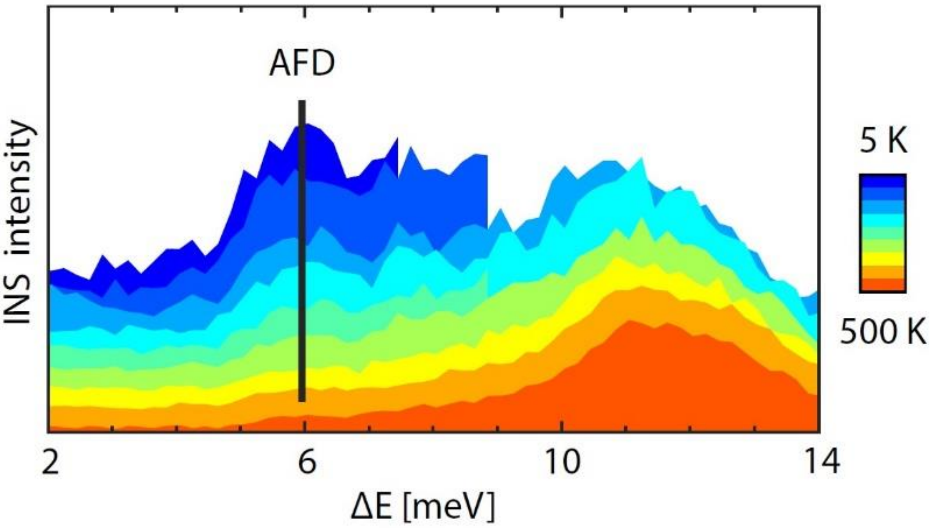

Figure 1 - Inelastic neutron scattering (INS) measurements of the antiferrodistortive (AFD) mode in $BaZrO_3$

Friday 1.10.2021, morning

60-O Non-classical electrostrictive phenomena in hydrated acceptor doped $BaZrO_3$: proton trapping and dopant size effect

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Igor Lubomirsky(1)

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(2) Max Planck Institute for Solid State Research, Stuttgart, Germany
(3) University of Riga, Institute of Solid State Physics, Riga, Latvia

We investigate the influence of dopants, oxygen vacancies, and protons on the macroscopic elastic and electromechanical properties of proton-conducting acceptor-doped $BaZrO_3$ ceramics. $BaZr_{(1-x)}X_xO_{(3-x/2+\delta)}H_{2\delta}$ ceramics with X=Ga,Sc,In,Y,Eu and $0.05<x<0.2$ were prepared by solid state reactive sintering and hydration. Ultrasonic pulsed echo time of flight measurements were used to infer the Young's and the shear moduli. Both moduli decrease by up to ~20% due to the presence of dopants and oxygen vacancies that cause local lattice distortions[1,2]. An unexpectedly large electrostriction coefficient (M33 ~10^{-15} m^2/V^2) was detected with a capacitive proximity sensor for all dopants indicating a new class of non-classical electrostrictors. The largest electromechanical response (M33 and electrostrictive strain saturation) and Young`s modulus was found for the dopant with the smallest size mismatch with the host (Sc). This suggests that lattice distortions, responsible for the change in Young`s modulus, are responsible for the non-classical electrostrictive response as well. M33 of the hydrated ceramics exhibits a Debye-type relaxation with the relaxation frequency exponentially increasing with the ionic radius, closely matching dielectric relaxation measured by impedance spectroscopy. This implies that protons are associated with the dopants, and the binding strength decreases from Ga to Y.

[1]M.F. Hoedl, E. Makagon, I. Lubomirsky, R. Merkle, E.A. Kotomin, J. Maier, Acta Mater. (2018) 160, 247
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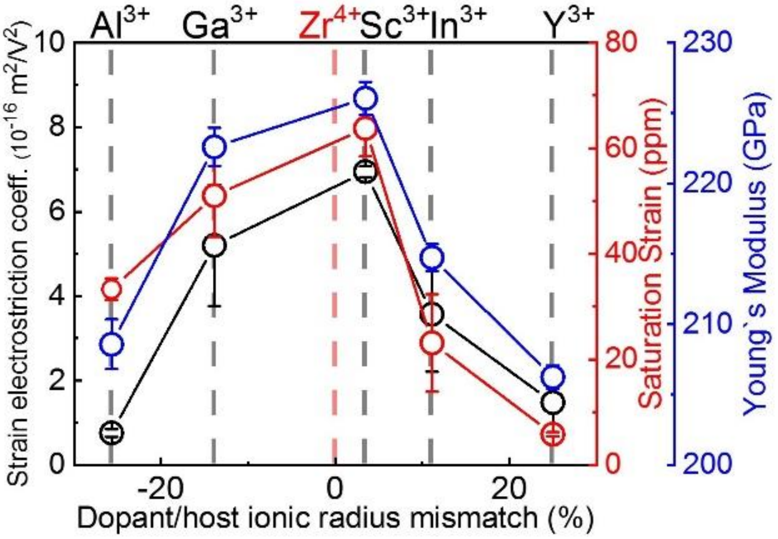

Strain electrostriction coefficient, saturation strain and Young`s modulus as a function of dopant/host ionic radius mismatch.
Similar ionic radius mismatch dependency shows that point defect induced lattice deformations are the source for both mechanical degradation and anomalous electromechanical response.

Friday 1.10.2021, morning

61-O Understanding the effect of oxide components on proton mobility in phosphate glasses; statistical analysis and experimental studies

Takahisa Omata,(1) Issei Suzuki,(1) Aman Sharma,(1) Takuya Kinoshita,(2) Tomohiro Ishiyama,(3)
Shinji Kohara,(4,5,6) Toshiharu Yamashita,(7) Hiroshi Kawazoe,(7) Tong Fang,(8) Yang Ren,(8)
Masaya Fujioka,(2) Madoka Ono,(2) Gaoyang Zhao,(8) Junji Nishii,(2)

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(7) Kawazoe Frontier Technologies Corporation, Yokohama, Japan
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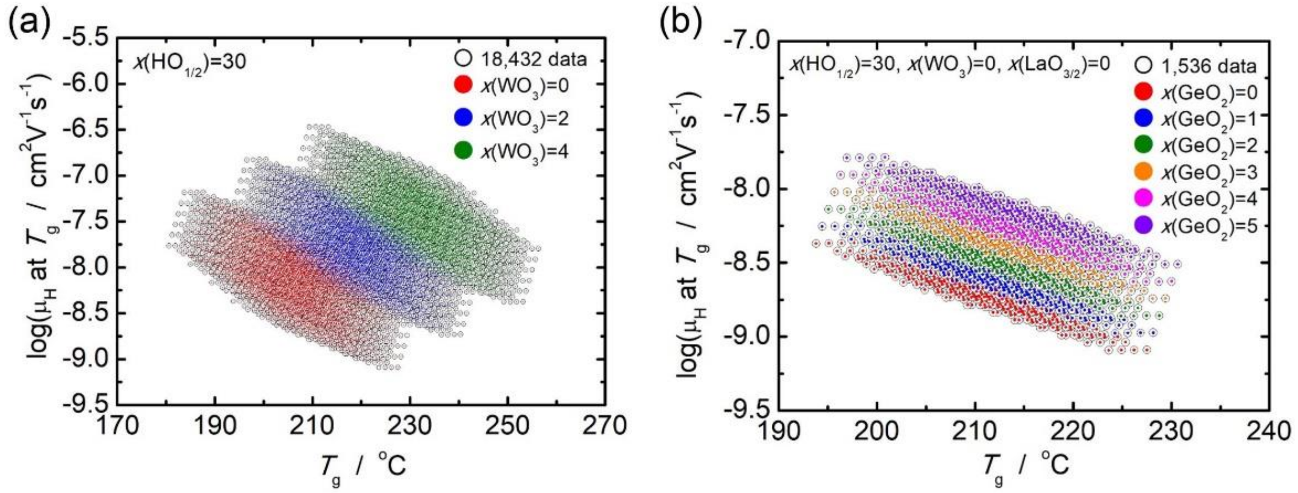
We have developed linear regression models, using a statistical analysis approach, to describe glass transition temperature (Tg) and proton mobility (μH) at of phosphate glasses according to the glass composition, i.e., the mol% of respective component oxides were employed as descriptors. According to the models, the additional $HO_{1/2}$, MgO, BaO, $LaO_{3/2}$, WO_3, $NbO_{5/2}$, $BO_{3/2}$ and GeO_2 as alternative to $PO_{5/2}$ were categorized into three groups according to the effects on μH at Tg and Tg. The group 1 oxides increase μH at Tg and decrease Tg, and $HO_{1/2}$, MgO, BaO and $LaO_{3/2}$ and $BO_{3/2}$ are involved in this group. The group 2 oxides increase both μH at Tg and Tg, and WO_3 and GeO_2 are involved in this group. The group 3 oxides increase Tg but do not vary μH at Tg. Only $NbO_{5/2}$ falls into the group 3 among the oxides examined in this study. From the viewpoint to improve thermal stability and proton conductivity, the group 2 oxides, GeO_2 and WO_3, are key components.

In addition to the statistical analysis, we have experimentally studied that the role of the GeO_2 on Tg and μH at Tg using $22HO_{1/2}-3NaO_{1/2}-(12-x)LaO_{3/2}-xGeO_2-63PO_{5/2}$ glasses. Increasing Tg and also μH at Tg were experimentally found out, when $LaO_{3/2}$ is substituted with GeO_2, and this behavior agrees well with the prediction from the linear regression models. Based on the glass structure and the nature of the P−O bond, both enhanced Tg and μH at Tg were strongly related with the formation of the heteroatomic P−O−Ge linkage.



Distribution of the relationship between predicted values of $\log(\mu_H$ at $T_g)$ and T_g depending on the WO_3 and GeO_2 concentration. (a) 18,432 predicted values for the glasses with 30mol% of $HO_{1/2}$ distinguished by the WO_3 concentration and (b) 1,536 predicted values for the glasses with 30mol% of $HO_{1/2}$, 0mol% of WO_3 and 0mol% of $LaO_{3/2}$ distinguished by the GeO_2 concentration.

Friday 1.10.2021, morning

62-KN

Sintering mechanism of thin and dense electrolyte layer for high performance protonic ceramic fuel cells

Jong-Ho Lee, Ho-Il Ji, Seunghyeok Im, Junseok Kim, Hyegsoon An, Byung-Kook Kim

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Proton conducting ceramic electrolyte possesses attractive features – higher ionic conductivity than oxygen ion conductor and lower activation dependency on the temperature – and enables SOFCs to operate at lower temperatures (400 – 600°C). However, crucial technical challenges on cell fabrication, especially establishing a chemically homogeneous and physically thin electrolyte layer, have been limiting its commercial implementation. These challenges mainly stem from the refractory nature of the proton-conducting electrolytes. It makes the densification behavior of the electrolyte in PCFCs difficult to control and in most cases, negatively impacts on its ionic conductivity. Here, we present the anode-assisted facile densification of a proton-conducting electrolyte on a (NiO)-(proton conducting electrolyte) composite anode support. It will be shown that an internal supply of sintering aid from the anode to the electrolyte, enabling the full densification of thin electrolyte (less than 10 µm thick) below 1350°C while retaining initial chemical composition. In addition, the probable mechanism of this behavior will be discussed.

63-INV

Reversible Electrochemical Cells for Interconversion between Fuel and Electricity

Sossina Haile

Northwestern University, Evanston, USA

Over the past decade, the availability of electricity from sustainable energy sources has risen dramatically while the cost has fallen steeply. These factors have driven a surge in activity in the development of energy storage technologies. While much of this effort has been directed towards photocatalytically generated solar fuels and grid-scale batteries, reversible hydrogen electrochemical cells offer untapped opportunities. In particular, electrochemical cells based on proton conducting ceramic oxides are attractive candidates for interconversion between hydrogen and electricity. The proton conducting nature of the electrolyte provides inherent advantages in the gas flow configuration over traditional solid oxide cells in which the electrolyte is an oxygen ion conductor. We describe here recent progress in reversible protonic ceramic cells achieved using a combination of three advances: a new electrolyte composition, a new air electrode, and processing methods to decrease the contact resistance between these two components. The resulting cells display exceptional performance in both fuel cell and electrolysis modes. In the latter case, conversion efficiency suffers a small penalty due to slight electronic leakage across the cell. The cells are extremely stable over hundreds of hours of operation and dozens of cycles between electricity generation and hydrogen production. As such, protonic ceramic electrochemical cells are likely to play a major role in a sustainable energy future.

64-INV

Diatomic Hydrogen Occupation in Perovskite-Type Oxyhydrides

Tai Misaki, Itaru Oikawa, Hitoshi Takamura

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Hydride ions (H^-) in solids have attracted much attention in a variety of research fields because of their unique properties such as ionic conduction, photochromism, ferroelectricity, and catalytic activity. To date, oxyhydrides having hydride ions and oxide ions, simultaneously, in their anion sublattice have been widely synthesized. In this research, diatomic hydrogen occupation (2H) in perovskite-type Ba-Ti oxyhydrides, which has been only proposed by means of first-principles calculations, is experimentally observed by a negative Knight shift in the 1H magic-angle spinning (MAS) NMR spectra combined with hydrogen concentration and X-ray photoelectron spectroscopic analysis. A negative Knight shift, an indicator of the interaction between conduction band electrons and a probe nucleus, is observed in the 1H MAS NMR signal of Ba-Ti oxyhydrides at room temperature. The presence of hydrogen species with different bonding characteristics indicates a flexible hydrogen configuration in Ba-Ti oxyhydrides, i.e. not only an ionic hydride ion with single occupation but also anionic diatomic hydrogen atoms. This also suggests the potential to modify the electronic structure and physical properties of perovskite-type oxyhydrides by manipulating their hydrogen configuration. The dynamics of hydride ions in the Ba-Ti oxyhydrides will be also discussed.

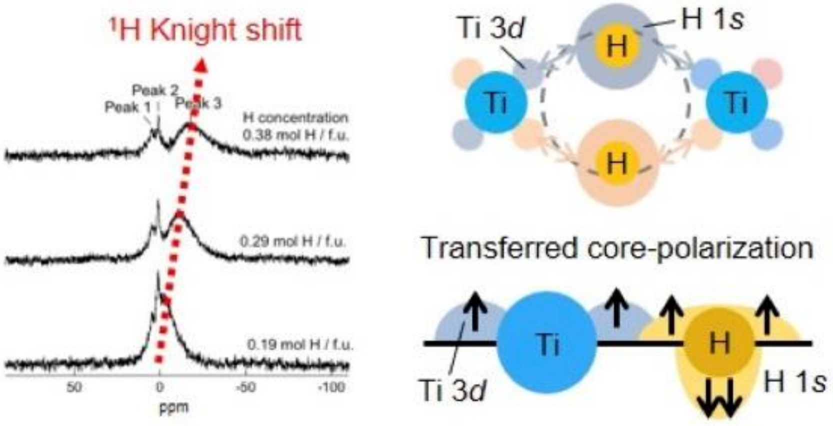

Fig. 1: ^{1}H MAS NMR spectra of Ba-Ti oxyhydride powder with hydrogen concentrations of 0.38, 0.29, and 0.19 mol H/f.u., and schematic view of the diatomic hydrogen configuration in Ba-Ti oxyhydride and the transferred core polarization interaction.

Friday 1.10.2021, noon session

Thank you vary much for your contributions, questions, and discussions!
We look forward to meeting you - and many new young faces -
again in "real life" for SSPC-21 in 2023!

Rotraut Merkle and Patric Jannasch

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Hoshino K 57-O
Hu YY 39-O
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Huang Y P-7
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