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RPPR Final Report

as of 20-May-2019

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INVESTIGATOR(S):

Name: Stephen J. Paddison Ph.D.

Email: spaddison@utk.edu

Phone Number: 8659743466

Principal: Y

Organization: **University of Tennessee at Knoxville**

Address: Office of Sponsored Programs, Knoxville, TN 379961529

Country: USA

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Final Report for Period Beginning 05-Aug-2018 and Ending 31-Jan-2019

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End Performance Period: 31-Jan-2019

Report Term: 0-Other

Submitted By: Stephen Paddison

Email: spaddison@utk.edu

Phone: (865) 974-3466

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STEM Degrees: 2

STEM Participants: 0

Major Goals: The SSPC conferences have, since their inception in 1980, generally been held every two years in Europe. Beginning in 2008, however, the venue has literally gone around the world: Kyoto, Japan ?08; Santa Barbara, U.S.A., ?10; and Seoul, Korea, ?14. The goal is now to bring the series back to North America (specifically the north east) and expose a broader community to this important area of science. By bringing together traditional protonics researchers and new recruits, we anticipate the creation of new collaborations that can address important areas in energy sciences, fundamentals of proton incorporation and transport, and protons in biological and geological systems. Beyond increasing participation among current researchers not traditionally active in this field, we aim, by providing partial support for travel and registration fees, to ensure a representative participant population. We will, in particular, encourage participation by students and junior researchers of diverse backgrounds in the program so as to expose them to a high level of research at an early age, and through these means, lay the groundwork for future professional development.

Accomplishments: The 19th International Conference on Solid State Protonic Conductors took place on Sept. 16-21, 2018 at the Stoweflake Conference in Stowe, Vermont. The meeting attracted 104 delegates from around the world and featured 1 plenary presentation, 4 historical keynote presentations, 6 keynote talks, 15 invited talks, and 22 contributed talks and 56 poster presentations.

In keeping with past SSPC conferences, SSPC-19 had a scientific program with the usual broad range of presentations on both theoretical and experimental investigations of soft and hard materials. Unique to this SSPC meeting however, was a particular focus on hydroxide ion (OH⁻) conducting materials. The quint essential features of hydrogen bonding and proton 'hopping' are shared in many alkaline systems exhibiting OH⁻ transport. Two unique sessions were also organized during the week. On the second evening of the conference, a special "Popcorn Session" occurred where 7 graduate students each gave a brief 8 minute presentation on their research work. The time was rigorously enforced and this encouraged the students to be supremely organized and selective in their material. On the Wednesday morning of the conference four historical perspective presentations (each 1 hour) were given by senior and distinguished members of the SSPC community. In many ways these were the highlight of the conference as they sought to trace the history of the entire field proton conductors, a posthumous tribute to individuals who made important contributions, and a case study of how progress in science is made through falsification.

A special issue in Solid State Ionics is underway that is devoted to contributions from the conference.

The majority of the funds were used to support registration waivers for graduate students. A few invited speakers also received partial financial support.

Training Opportunities: Nothing to Report

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as of 20-May-2019

Results Dissemination: As indicated earlier, a number of the presentations given at the conference will be published as a special issue in the journal: Solid State Ionics.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Stephen John Paddison

Person Months Worked: 15.00

Project Contribution:

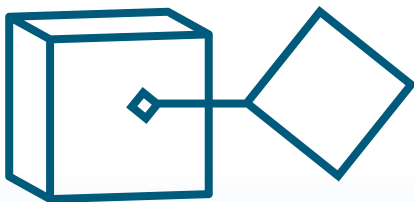
International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:



SSPC-19

**19th International Conference on
Solid State Protonic Conductors**

ABSTRACTS

September 16–21, 2018

**Stoweflake Conference Center
Stowe, Vermont**



The 19th International Conference on Solid State Protonic Conductors (SSPC-19)

Organizing Committee

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Letter of Welcome

Dear SSPC-19 Delegates:

On behalf of the Organizing Committee, it is my pleasure to welcome you to Solid State Protonic Conductors 19. In the long and distinguished history of this scientific conference series on the fundamentals and applications of proton conducting solids, this is only the second time for it to take place in America (SSPC-15, 9/2010, Santa Barbara). We are delighted to share the wonders and natural diversity of America as displayed in Stowe, Vermont. Although Stowe is well known as a premier alpine and Nordic skiing destination in the northeastern part of the country, we felt it would also offer an excellent venue for SSPC because of the presence of the AAA four diamond Stoweflake Conference Center and Resort. This conference center has hosted numerous Gordon Research Conferences (GRCs) and medical society meetings and provides a setting that is private, spacious, and very well suited to the needs of the SSPC community.

We are pleased to present in SSPC-19 a scientific program with the usual broad range of presentations on both theoretical and experimental investigations of soft and hard materials, but also a particular focus on hydroxide ion conducting materials. The quint essential features of hydrogen bonding and proton 'hopping' are shared in many alkaline systems exhibiting OH⁻ transport. Two additional unique sessions will also occur during the week: on Tuesday evening a select group of graduate students will each give brief 8 minute presentations on their research work; and then on Wednesday morning four historical perspectives from senior and distinguished members of our community will seek to remind us the value in not only being cognizant of prior research but also that progress sometimes comes through falsification.

We are very grateful for the financial support from the Army Research Office and both the Tickle College of Engineering and Department of Chemical & Biomolecular Engineering at the University of Tennessee, Knoxville.

Finally, we hope that it will be evident during this week that we have sought to respectfully preserve the unique and proven traditions of the SSPC meetings while adding a few unique and hopefully memorable sessions in a forum that promotes rigorous discussion and viewpoint diversity.

Stephen J. Paddison, Chairman of SSPC-19
Gibson Endowed Professor of Engineering
University of Tennessee, Knoxville, TN, U.S.A.



Sponsorship and Support

Tickle College of Engineering
(University of Tennessee, Knoxville)

Department of Chemical & Biomolecular Engineering
(University of Tennessee, Knoxville)

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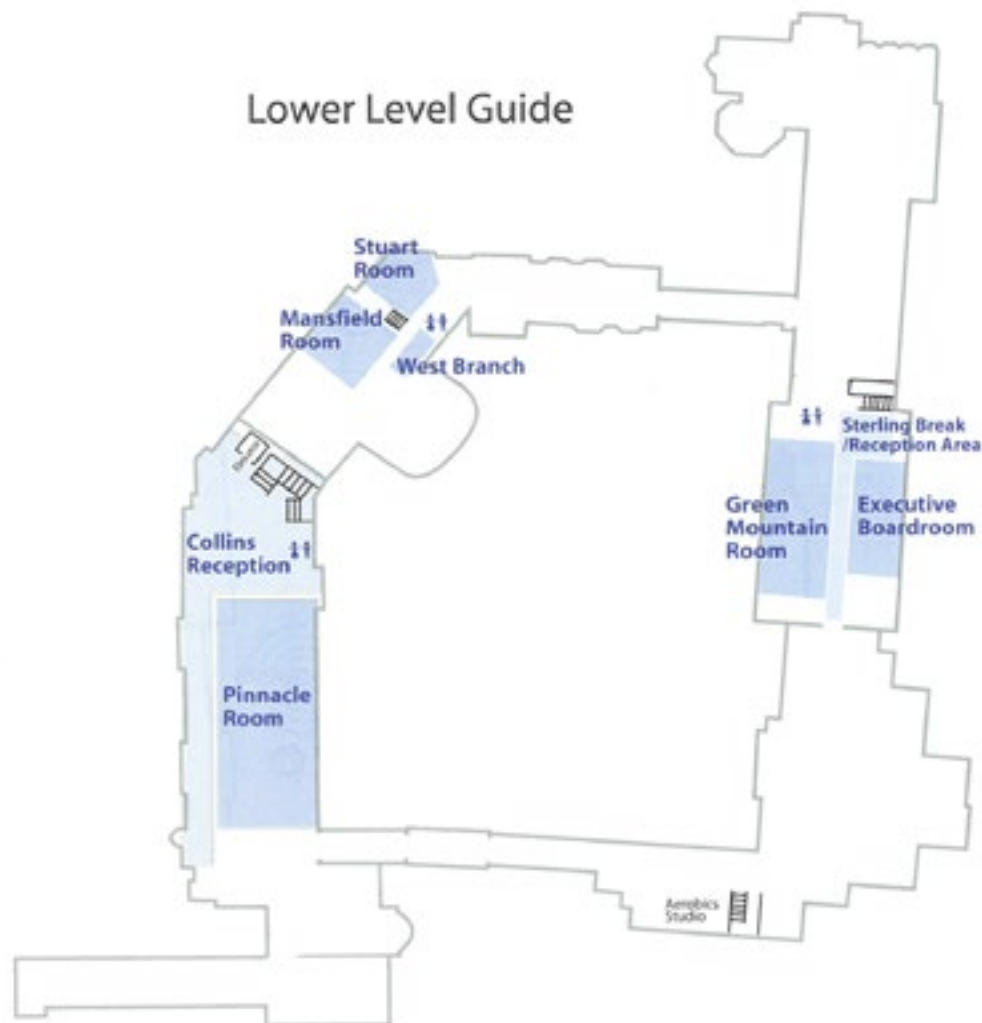
Outline of Program

Time	Sunday (Sept. 16)	Monday (Sept. 17)	Tuesday (Sept. 18)	Wednesday (Sept. 19)	Thursday (Sept. 20)	Friday (Sept. 21)
8:00		Registration (8:00-17:00)				
9:00		Session I (8:30-10:00)	Session V (8:30-10:00)	Session IX (8:30-10:00)	Session XI (8:30-10:00)	Session XV (8:30-10:00)
10:00		Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00		Session II (10:30-12:20)	Session VI (10:30-12:10)	Session X (10:30-12:00)	Session XII (10:30-12:20)	Session XVI (10:30-12:00)
12:00		Lunch (12:30-13:45)	Lunch (12:30-13:45)	Lunch (12:15-13:15)	Lunch (12:30-13:45)	Lunch (12:00-13:00)
13:00				Excursions (13:30-17:00)		
14:00		Session III (14:00-15:30)	Session VII (14:00-15:30)	Session XIII (14:00-15:30)		
15:00		Coffee Break	Coffee Break	Coffee Break		
16:00		Session IV (16:00-17:40)	Session VIII (16:00-17:40)	Session XIV (16:00-17:30)		
17:00						
18:00	Reception (18:00-19:30) Atrium	Dinner (18:00-19:15)	Dinner (18:00-19:15)	Reception (17:30-18:30) Atrium	Dinner (18:00-19:15)	
19:00						
20:00	Poster Session I (19:30-21:30)	Student Oral (19:30-21:00)	Banquet (18:45-21:00)	Poster Session II (19:30-21:30)		
21:00						

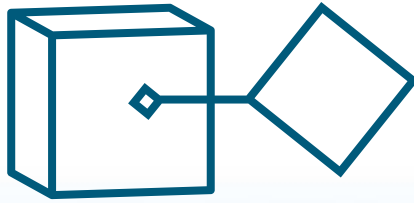
Location Information

Breakfast, Lunch, and Dinner:	Stowe
Oral Sessions	Pinnacle
Poster Sessions	Pinnacle
Banquet Dinner	Stowe

Lower Level Guide



1746 Mountain Road, P.O. Box 369, Stowe, VT 05672 USA
800-253-2232 • 802-253-7355
www.stoweflake.com • info@stoweflake.com



MONDAY

SEPTEMBER 17TH





Monday (17/9/18)

Presentation	Abstract Title	Presenter	Affiliation
Session I (Session Chair: S. J. Paddison)			
Plenary Lecture (8:30-9:20)	Electrodes for proton ceramic electrochemical cells	Truls Norby	University of Oslo
Oral 1 (9:20-9:40)	Chemical analysis of elemental excess and depletion at grain boundaries of Ba(Ce, Zr, Y)O ₃ proton conductors	Dan Zhou	Max Planck Institute for Solid State Research
Oral 2 (9:40-10:00)	Water uptake measurements of materials with low protonation level	Aleksandra Mielewczyk-Gryń	Gdańsk University of Technology
Coffee Break (10:00-10:30)			
Session II (Session Chair: R. O'Hayre)			
Keynote 1 (10:30-11:10)	The space-charge effect: Insights from first-principles modeling	Göran Wahnström	Chalmers University of Technology
Oral 3 (11:10-11:30)	Mixed-conducting PCFC cathode materials: Proton uptake and defect interaction	Rotraut Merkle	Max Planck Institute for Solid State Research
Invited 1 (11:30-12:00)	Breakthrough performance and scalability of protonic ceramic fuel cells	Jong-Ho Lee	Korea Institute of Science and Technology
Oral 4 (12:00-12:20)	Protonic ceramic electrochemical cells for fuels/chemicals production	Chuancheng Duan	Colorado School of Mines
Lunch (12:30-13:45)			
Session III (Session Chair: D. Jones)			
Keynote 2 (14:00-14:40)	Structure-transport relationship in PFSA, aromatic, and blend ionomers for PEMFC	Sandrine Lyonard	CEA-INAC
Oral 5 (14:40-15:00)	Parasitic transport of phosphoric acid in high temperature polymer electrolyte membranes	Qingfeng Li	Technical University of Denmark
Invited 2 (15:00-15:30)	PBI polymers for fuel cells and related devices	Brian C. Benicewicz	University of South Carolina
Coffee Break (15:30-16:00)			
Session IV (Session Chair: H. Matsumoto)			
Invited 3 (16:00-16:30)	Ga ³⁺ boundary hydride ion conduction in nanocrystalline metal nitrides	Yoshitaka Aoki	Hokkaido University
Invited 4 (16:30-17:00)	Membrane reactors based on proton-conducting ceramics	Sandrine Ricote	Colorado School of Mines
Oral 6 (17:00-17:20)	Conductivity of polymer-ceramic composite membranes at high <i>T</i> and <i>p</i> (H ₂ O) using a novel PEEK sample holder	A. Chatzidakis	University of Oslo
Oral 7 (17:20-17:40)	Particle size effects on the protonic conductivity of a zeolitic imidazolate framework	Filipe M. L. Figueiredo	University of Aveiro
Dinner (18:00-19:15)			
Poster Session I (19:30-21:30) Poster 1 – Poster 28			

Electrodeics for proton ceramic electrochemical cells

Truls Norby

Department of Chemistry, University of Oslo, SMN, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway.

Tel.: +47-22840654
truls.norby@kjemi.uio.no

Abstract

Recent years have seen promising progress and demonstrations of proton ceramic fuel cells, electrolyzers, and reactors with BaZrO₃-based electrolytes. While robust and cheap fabrication of such electrolytes with low overall resistance still pose challenges, other components deserve equally much attention, notably sealing, interconnects, current collection, and not least electrodes.

The study and development of solid-state electrodes is generally troubled by the inherent complexity, yet poor establishment of the theory and interpretation of the many types of charge and mass transfers at the many interfaces involved. For proton ceramics, we have the additional problem that three carriers – protons, oxide ions, and electrons – often contribute significantly in the electrolyte. Failure to recognise this may lead to erroneously parameterised electrode kinetics, and lost possibilities to improve kinetics and faradaic and process efficiencies.

Electrodes on the reducing (hydrogen) side of fuel cells and electrolyzers – hereafter denoted negatodes – usually have Ni as electron conducting and electrocatalytic component, while Cu is considered for coking (e.g. CH₄) atmospheres. Charge and mass transfer on such metals as well as Pt as model electrode appear to follow expected pathways and theories, while there are indications that a charged metal-electrolyte interface and the associated space charge region in the electrolyte adds a significant resistance due to depletion of protons.

On the positrode side, however, the process must necessarily be more complicated, involving adsorption/desorption of both oxygen and water vapour molecules, a variety of possible mobile intermediate species and pathways on surfaces and in bulk of the oxide electrodes, and experimental challenges. Little reliable parameterisation is therefore available. Minor mixed proton conduction in oxide electrode materials expand the active area for charge transfer, and is under investigation and debate.

The role of oxide ion conductivity in the positrode materials – giving rise to the term triple conducting oxides (TCOs) – is questionable for proton conducting electrolytes, but may enhance co-ionic (proton and oxide ion) operation.

All in all, the prospects of proton ceramic electrochemical cells rely on developments based on systematic studies and critical interpretation and parametrisation properly founded on electrode theory.

Work supported by funding from the Research Council of Norway (Grant n° 228355 “FOX CET”).

Chemical analysis of elemental excess and depletion at grain boundaries of Ba(Ce, Zr, Y)O₃ proton conductors

Dan Zhou, Wilfried Sigle, Yuanye Huang, Rotraut Merkle, Peter A. van Aken, and Joachim Maier

Max Planck Institute for Solid State Research, Germany
Heisenbergstrasse 1, Stuttgart 70569, Germany
Tel.: +497116893584
d.zhou@fkf.mpg.de

Abstract

We focus on the system of Ba(Ce,Zr,Y)O_{3-δ} electrolyte materials owing to its very high bulk proton conductivity. Major problems of this system are the strongly blocking grain boundaries (GBs).¹ In the present investigation, two sintering methods are applied: (i) solid-state reactive sintering (SSRS) employing NiO which leads to the transient formation of a liquid phase,² and (ii) spark-plasma sintering (SPS).

Here, we report on the elemental distribution and chemical variation in the vicinity of GBs by quantitative energy-dispersive X-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). In SSRS-sintered samples with GBs decorated by Ni, quantitative EDX at GBs showed excess of Ba, Ni, Y and deficiency of mainly Zr at the GBs. This confirms substitution of Zr by Y at the GB which partially compensates the positive GB core charge and decreases the blocking character. With increasing NiO doping, an increase of GB excess of Ba and Ni was detected along with O deficiency indicating partial replacement of ABO₃ by BaO in the GB core. This indicates that in the SSRS process NiO doping pulls Ba out of the bulk towards the boundary.

We used EELS to analyze the chemical change across GBs. In Figure 1, a pronounced reduction of the Ce valence state inside GBs is observed, as revealed from the shift of the Ce M-edge peak position to lower energy.³ More results and their correlation to factors influencing proton-conducting efficiency will be presented and discussed.

We would like to acknowledge the Bundesministerium für Bildung und Forschung (BMBF) for funding this project (No. 03SF0537C “ProtoMem”).

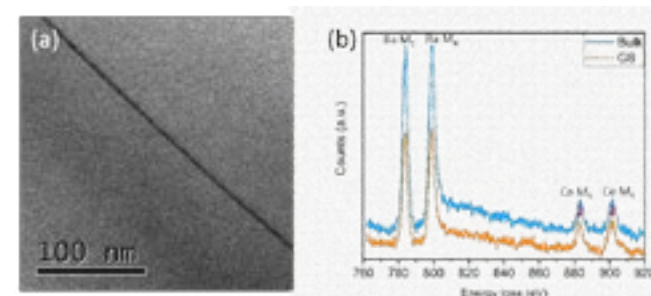


Figure 1. (a) HAADF image of a NiO doped Ba_{1.015}Ce_{0.2}Zr_{0.664}Y_{0.136}O_{3-δ} sample; (b) EELS spectra from the bulk and GBs of the sample shown in (a).

1. G. Gregori, R. Merkle, J. Maier, *Prog. Mater. Sci.* 89 (2017) 252.

2. J. Tong, D. Clark, M. Hoban, R. O'Hayre, *Solid State Ionics* 181 (2010) 496.

3. S. O. Kucheyev *et.al.*, *Phys. Rev. B* 76 (2007) 235420.



Water uptake measurements of materials with low protonation level

Aleksandra Mielewczyk-Gryn,¹ Sebastian Wachowski,¹ Kacper Dzierzgowski,¹ Piotr Winiarz,¹ Marta Przeźniak-Welenc,¹ Iga Lewandowska,¹ Mayra Dancini Gonçalves,² Tadeusz Miruszewski,² and Maria Gazda¹

1) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology
Narutowicza 11/12 80-233 Gdańsk, Poland

2) Peter A. Rock Thermochemistry Laboratory & NEAT University of California Davis One Shield Ave Davis, CA 95616, USA
Tel.: +45 58 348 66 19
alegryn@pg.edu.pl

Abstract

The thermogravimetry is one of the main sources of data concerning water uptake of various compounds. Starting from the hygroscopic materials which absorb water within the macroscopic structure in big extent (i.e. PMMA) and ending at materials with a really small degree of hydration like ceramic proton conductors. The issues with the proper methodology in the case of the latter group are occurring due to the limited resolution of used measuring systems. On the other hand, high temperature proton conductors are a group of materials with a broad spectrum of applications. Therefore, information about their water uptake in the conditions of operation seems crucial, especially for an understanding of the underlying phenomena of the occurring charge transport. The most recognized materials exhibiting proton conduction are barium cerate-zirconate system and lanthanum orthoniobates [1]. In the last decade, some studies on these two systems have been undertaken to show how complex the thermochemistry of them is. Starting from the energetics of the formation [2–4], through heat capacities [5], phase transitions thermodynamics [3,6], and what is the most important for the understanding of their electrical performance - hydration energetics [7,8]. However, some questions concerning the huge differences in water uptake of these two most known systems occurred and this work aims to address them. The measurements of the series of proton conducting oxides have been performed by the means of thermogravimetry and the outputs of experiments in different conditions have been analyzed.

This research is supported by the Ministry of Science and Higher Education Poland (grant no. 0513/IP2/2016/74).

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2. A. Mielewczyk-Gryn and A. Navrotsky, *Am. Mineral.* **100**, 1578 (2015).
3. A. Mielewczyk-Gryn, S. Wachowski, K. I. Lilova, X. Guo, M. Gazda, and A. Navrotsky, *Ceram. Int.* **41**, 2128 (2015).
4. M. D. Gonçalves, P. S. Maram, R. Muccillo, and A. Navrotsky, *J. Mater. Chem. A* **2**, 17840 (2014).
5. A. Mielewczyk-Gryn, S. Wachowski, J. Strychalska, K. Zagórski, T. Klimczuk, A. Navrotsky, and M. Gazda, *Ceram. Int.* **42**, 7054 (2016).
6. A. Mielewczyk-Gryn, K. Gdula-Kasica, B. Kusz, and M. Gazda, *Ceram. Int.* **39**, 4239 (2013).
7. Y. Yamazaki, F. Blanc, Y. Okuyama, L. Buannic, J. C. Lucio-Vega, C. P. Grey, and S. M. Haile, *Nat. Mater.* **12**, 647 (2013).
8. Y. Yamazaki, P. Babilo, and S. M. Haile, *Chem. Mater.* **20**, 6352 (2008).



The space-charge effect: Insights from first-principles modeling

Göran Wahnström

Department of Physics, Chalmers University of Technology

SE-412 96 Göteborg, Sweden
Tel: +46 76 1010523
goran.wahnstrom@chalmers.se

Abstract

Acceptor-doped BaZrO₃ (BZO) and BaCeO₃ (BCO) both exhibit considerable proton conductivity in humid atmospheres. They are two of the more promising candidates for electrolytes in proton ceramic fuel cells and a lot of attention has been given to mixtures of the two materials, such as BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-δ} [1]. In these polycrystalline materials, however, the grain boundaries (GBs) display high proton resistivity, severely limiting the overall proton transport. The low GB conductivity has been thought to be due to an intrinsic mechanism, the space-charge effect.

The key issue in space-charge formation is the likelihood of segregation of charged defects to the GB core. Using density functional theory (DFT) proton and oxygen vacancy segregation have been investigated for several different tilt GBs. Both these defect species are found to segregate to the GB core, with typical segregation energies between -1.5 and -0.5 eV. Below 900 K and at wet conditions space-charge potential barrier heights around 0.6 V are obtained, which is consistent with experimental results, and the protons are found to be the main source to the space-charge potential [2]. Furthermore, a clear correlation is found between the compressive strain at the different segregation sites and the segregation tendency [3]. This is reasonable since both the oxygen vacancy and the proton (hydroxide ion) are smaller than the oxygen ion.

Defect segregation of various acceptor dopants has also been investigated. At high temperatures, where the material is being fabricated, the dopants are mobile. Accurate determination of the segregation properties then requires temperature dependent free energy calculations. Dopants are found to segregate and reduce the space-charge potential with about 0.2 V [4], in line with experimental findings.

Experimentally it is found that the detrimental effect of GBs is less prominent in BCO compared with BZO, but it is not understood why. We find that the oxygen vacancy segregation energy is quite similar in both materials, while the tendency for proton segregation is larger in BZO compared with BCO. However, this is not directly related to the GBs, which display similar proton formation energies in both materials, but is due to different formation energies for protons in the bulk regions and it can be understood from a stronger hydrogen bond formation in bulk BCO compared with bulk BZO [3]. This implies that if the protons could be stabilized in the bulk region of BZO, without sacrificing its high mobility, the overall proton conductivity in BZO could be increased.

[1] C. Duan *et al.*, *Science* **349**, 1321 (2015).

[2] E. E. Helgee, A. Lindman, and G. Wahnström, *Fuel Cells* **13**, 19 (2013).

[3] A. Lindman, E. E. Helgee, and G. Wahnström, *Chemistry of Materials* **29**, 7931 (2017).

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Mixed-conducting PCFC cathode materials: Proton uptake and defect interaction

Reihaneh Zohourian, Rotraut Merkle, Giulia Raimondi, and Joachim Maier

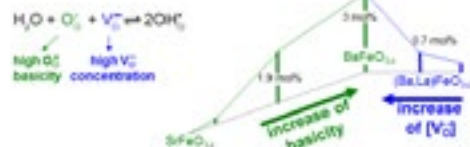
Max Planck Institute for Solid State Research

Heisenberg street 1, 70195, Stuttgart, Germany
Tel.: +49 (0) 711 689 1762
r.zohourian@fkf.mpg.de

Abstract

A cathode in a proton-conducting ceramic fuel cell (PCFC) should meet several criteria including high catalytic activity, electronic conductivity, sufficient proton conductivity, phase stability, *etc.* to achieve good performance. The proton conductivity allows the oxygen reduction reaction to extend from the triple phase boundary to the whole surface of the cathode.

The present work specifically studies the hydration thermodynamics of 18 compositions in the mixed-conducting perovskite family $(\text{Ba,Sr,Lu})(\text{Fe,Co,Zn,Y})\text{O}_{3-\delta}$ using thermogravimetry [1]. The degree of the hydration is significantly smaller for cathode perovskites compared to typical electrolytes (acceptor doped $\text{Ba}(\text{Zr,Ce})\text{O}_{3-\delta}$, which are fully hydrated below ≈ 400 °C) [1-3]. The cathode materials typically have a less negative hydration enthalpy and more positive hydration entropy. The highest proton uptake in this family was found for $(\text{Ba}_{0.95}\text{La}_{0.05})(\text{Fe}_{0.8}\text{Zn}_{0.2})\text{O}_{3-\delta}$ with 10% of protons per formula unit at 250 °C in 17 mbar water partial pressure, which decreases to 2.3% at 500 °C. Based on these results, the bulk path is expected to be active for Ba-rich cathode materials.



The figure shows the trends of proton uptake at 250 °C with variation of the cation composition. The increase with Ba substitution for Sr or La indicates that the proton uptake is closely related to the oxide ion basicity. Also a partial substitution of Zn in the B-site increases the proton uptake, while Co has the opposite effect due to increased covalency of the Co-O bond that decreases the oxide ion basicity. The defect concentrations measured as a function of temperature and partial pressures indicate the presence of detrimental hole-hole and hole-proton interactions [4]. Qualitatively, they can be explained by partial delocalization of holes from the transition metal to the adjacent oxide ions, which increases the effective volume influenced by one hole and in parallel decreases the oxide ion basicity. Quantitatively, one can describe this effect by a first order correction (linear decrease of oxidation and hydration enthalpies with the hole concentration).

This detailed defect chemical insight may serve as the basis for further PCFC cathode development, in particular since a number of desired properties (proton uptake, catalytic activity, electronic conductivity, *etc.*) have conflicting tendencies and an insightful optimization strategy is required.

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Breakthrough performance and scalability of protonic ceramic fuel cells

Jong-Ho Lee,¹ Hyegsoon An,^{1,2} Ho-Il Ji,¹ Dongwook Shin,² Hyounghul Kim,¹
Kyung Joong Yoon,¹ Ji-Won Son,¹ Byung-Kook Kim,¹ and Hae-Weon Lee¹

1) Korea Institute of Science and Technology, Republic of Korea
2) Hanyang University, Republic of Korea

Tel.: 82-2-9585532
Fax: 82-2-9585529
jongho@kist.re.kr

Abstract

The features of proton-conducting ceramic electrolytes—high ionic conductivity with a low activation energy of ion conduction (< 0.5 eV)—enable SOFCs to operate in the low-temperature regime (400 – 600 °C), allowing for utilization of the existing merits. Moreover, fuel dilution and detrimental anode oxidation (operating on hydrogen fuel) can be prevented, and a higher methane conversion and carbon coking resistance (on hydrocarbon fuels) can also be achieved. In spite of these advantages, distinct skepticism currently remains about the applicability of protonic ceramic fuel cells (PCFCs) owing to their lower-than-predicted performance and difficulty with scale-up in cell fabrication (an anode support size of at most 3 cm²). These challenges mainly stem from the refractory nature of proton-conducting ceramic electrolytes and the low chemical stability of these materials during the sintering process. Here, we show a breakthrough in the performance and scalability of PCFCs through facile anode-assisted densification of the protonic ceramic electrolyte on an anode support. An internal supply of the transient phase from the anode to the electrolyte as well as an excess shrinkage force driven by the anode uniformly promote the densification of the electrolyte at a much lower temperature than that required for the electrolyte alone while retaining the initial chemical composition, even for an electrolyte layer 5 μm thick in a large cell of 5 × 5 cm².



Protonic ceramic electrochemical cells for fuels/chemicals production

Chuancheng Duan, Robert Kee, Huayang Zhu, Neal Sullivan, Liangzhu Zhu, and Ryan O'Hayre

Colorado School of Mines, Golden, CO, USA

cduan@mines.edu

Abstract

In recent years, water electrolyzers based on polymer exchange membrane (PEM) and oxygen-ion conducting ceramics have been commercialized/deeply explored to address energy storage and conversion challenges associated with the rise in intermittent renewable electricity generation and to provide versatile pathways for renewable fuels production (1–4). Both technologies presently suffer challenges associated with cost, durability, low energy efficiency (especially for PEM-based devices) and the need to separate H₂O from the product fuel in electrolysis mode operation (especially for oxygen-ion conducting ceramic-based devices). This work seeks to develop a highly efficient energy storage technology based on protonic ceramics by addressing the following questions: 1) why is the Faradaic efficiency of protonic ceramic electrolysis cells (PCECs) lower than conventional solid oxide electrolysis cells (SOECs)? 2) how to improve the Faradaic efficiency of PCECs? Here, we present a electrochemical cell based on emerging protonic ceramic fuel cell (PCFC) technology. Our PCECs achieve high Faradaic efficiency (90 – 98%) and can operate endothermically (if an appropriate waste heat source is available) with > 97% overall electric-to-hydrogen energy conversion efficiency (based on the lower heating value of hydrogen, LHV_{H₂}) at a current density of 923 mAcm⁻² (corresponding to 6.34 mL H₂ cm⁻²s⁻¹). Even higher efficiencies are obtained for H₂O electrolysis with co-fed CO₂ to produce renewable hydrocarbon fuels (e.g. CH₄, C₂H₄, C₂H₆, C₃H₈, C₃H₆) and the operating conditions can be tuned to directly produce CH₄ with a CO₂ conversion rate of 81.7% and CH₄ selectivity of 99.1%.

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Structure-transport relationship in PFSA, aromatic, and blend ionomers for PEMFC

Sandrine Lyonnard,¹ Quentin Berrod,¹ Samuel Hanot,¹ Stefano Mossa,¹ Huu-dat N'Guyen,² Olessia Danyliv,² Luca Assumma,² and Cristina Iojoiu²

1) CEA-INAC, UMR 5819 (CEA-CNRS-UGA)

2) CNRS, LEPMI, F-38000

CEA-INAC-SyMMES, Bat C5, 17 avenue des Martyrs, 38000 Grenoble, France

Tel.: +33 04 38 78 92 86

sandrine.lyonnard@cea.fr

Abstract

The PEM is the key component of low temperature fuel cells, which are one of the most promising technologies for powering small portable devices and automobiles. It acts as a separator between the electrodes, electronic insulator and proton conductor. A microscopic understanding of the relation between the chemical structure of the polymer membrane, its morphology, and the proton transfer is essential to improve fuel cell performances. In recent years, we have explored the structure-transport relationship in benchmark PerfluoroSulfonic Acids (PFSA [1-4]), alternative aromatic copolymers [5-8] and blends [9]. In the presence of water, interconnected nanoscale ionic domains are formed upon swelling in the ionomers. The mean sizes of ionic channels, d_w , were determined by using Small Angle Neutron Scattering techniques in function of relevant parameters such as hydration, ionic exchange capacity, nature of ionic function, nature of polymer backbone. The transport properties were characterized using a combination of microscopic (e.g. quasi elastic neutron scattering), mesoscopic (PFG-NMR) and macroscopic (conductivity) measurements. The mobility of species is controlled by the balance between short range interactions, local topology (e.g. nanoscale confinement) and connectivity. By systematically exploring the relations between d_w and the transport numbers (diffusion coefficients, proton conductivity), we establish the general relation between swelling laws, nanostructure, proton concentration and dynamical behavior of water and protons in different types of ionomers.

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Parasitic transport of phosphoric acid in high temperature polymer electrolyte membranes

Qingfeng Li,¹ Hans Becker,¹ Uwe Reimer,² David Aili,¹ Tonny Søndergaard,¹
Lars N. Cleemann,¹ Werner Lehnert,^{2,3} and Jens Oluf Jensen¹

1) Section of Proton Conductors, Department of Energy Conversion and Storage, Technical University of Denmark, Building 375, 2800 Kgs Lyngby, Denmark

2) Forschungszentrum Jülich, IEK3: Electrochemical Process Engineering, 52425 Jülich, Germany

3) Modeling in Electrochemical Process Engineering, RWTH Aachen University, Germany

Tel.: +45 45252318
qli@dtu.dk

Abstract

The high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) is currently based on phosphoric acid doped polymer membranes, typically based on poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (*m*-PBI). Long-term durability of the fuel cell has been demonstrated for over 10,000 hours with an average degradation rate of 0.5 μ V/h under mild operating conditions. At higher current loads, however, the degradation primarily via the acid loss mechanism becomes significant, hinting towards the parasitic acid mobility which is inherently connected to the proton conductivity of phosphoric acid and its doped membranes.^[1,2] New insight is recently achieved showing significance of the vehicle mechanism and mobility of the ionic and molecular acid species.^[3,4]

For phosphoric acid doped *m*-PBI membranes an *in situ* determination of the acid transport upon passage of an electrical current is achieved by monitoring the ohmic resistance of membrane layers with imbedded microelectrodes.^[5] The current driven migration of acid anions from the cathode to the anode gives rise to a concentration gradient across the cell, a driving force for back diffusion of the acid. Both transport mechanisms are assessed, from which the anion transference number and diffusion coefficient of phosphoric acid are determined at varied current densities, temperatures, and atmospheric water activities.^[6] Compared to the bulk phosphoric acid, the presence of a dense polymer phase and its acid-base interaction results in little change of the anion transference number but a reduced diffusion coefficient by about 2 orders of magnitude.

In case of phosphoric acid doped perfluorosulfonic acid membranes, e.g. Aquivion®, the measurements show the migration of proton carrying cations from the anode to the cathode, direct evidence of the malfunction of the membranes in fuel cells.

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PBI polymers for fuel cells and related devices

Andrew Pingitore, Fei Huang, Lihui Wang, and Brian C. Benicewicz

Department of Chemistry and Biochemistry
University of South Carolina
541 Main St., Horizon I Bldg, Rm 232
Columbia, SC 29208

Tel.: 803-777-0778
Fax: 803-777-8100
benice@sc.edu

Abstract

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. The knowledge base created by a broad search of different PBI backbone chemistries and variations in molecular architecture (random and block copolymers, crosslinking, etc.) originally directed at high temperature fuel cells, is now being used to design PBI polymers for other electrochemical devices such as hydrogen pumps, electrolyzers, and flow batteries. In many cases, the different operating conditions of the distinct devices advocate for a specifically designed polymer structure tailored for its environment. In these devices, the general polybenzimidazole backbone structure provides outstanding chemical and thermal stability, high ionic conductivities when doped with acids, and resistance to oxidatively challenging environments. In this talk, we will review some of the emerging devices and the PBI membranes that are being developed for their needs.



Grain boundary hydride ion conduction in nanocrystalline metal nitrides

Yoshitaka Aoki,¹ Yuji Kunisada,¹ and Satoshi Hinokuma²

1) Faculty of Engineering, Hokkaido University

2) Faculty of Advanced Science and Technology, Kumamoto University

Faculty of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo, 060-8628 Japan

Tel.: +81-11-706-6752

Fax: +81-11-706-6575

y-aoki@hokudai.ac.jp

Abstract

The production of pure hydrogen for use in energy applications and related industries often relies on the permeation of hydrogen through palladium-based membranes. However, the scarcity of Pd reserves necessitates the development of affordable alternatives with high hydrogen permeability. Here we report room-temperature hydrogen permeability of titanium nitrides (widely used as tough and inert coating materials) enabled by mixed hydride ion-electron conductivity. Mixed proton-electron conductors (MPECs) are promising alternatives to dense separation membranes, featuring ambipolar diffusion of H^+ and e^- . Although perovskite-type $BaM_{1-x}M'_xO_{3-\delta}$ ($M = Ce, Zr$; $M' = Y, Yb$, etc.) proton-conducting ceramics have been extensively studied as potential MPECs, they require operation at elevated temperatures ($T > 600$ °C) due to high migration activation energies ($50 - 60$ kJ mol^{-1}) attributed to trapping by negatively charged aliovalent dopants or defect-induced structural distortions.

Recently, we have reported the pronounced hydride ion-electron conductivity of nanocrystalline metal nitride (MN_x ; $M = Ti, Hf$, etc), attributed to interfacially controlled diffusion aided by hydridic M-H terminal groups on the hydrogenated grain surface.^{1,2} MN_x membranes comprising tens' nm-sized, (100)-oriented nanocubes were demonstrated to exhibit room-temperature hydrogen permeability due to the mixed conductivity with the flux of hydrogen through 500 nm-thick membranes exceeding that observed for technologically-limit thickness 5 μm Pd membranes at ambient temperature. The hydrogen solubility of $MN_{1.0}$ was drastically improved by reducing crystallite size as the number of the coordination M sites is linearly proportional to the reciprocal of crystallite size. In addition, the grain-growth orientation of crystallites is important to improve the hydrogen permeability. Since the (111) face of NaCl-type TiN has a higher Ti concentration than the (100) face, (111)-oriented nanocrystalline films exhibit smaller diffusion energy and higher solubility than (100)-oriented ones due to the relatively short Ti-Ti jump distances. Accordingly, 200 nm (111)-oriented TiN_x membranes with sub-10 nm crystallites yield permeation fluxes of 4×10^{-6} mol $s^{-1} cm^{-1}$ under an applied hydrogen partial pressure of about 50 kPa at ambient temperature. This value was only one order of magnitude smaller than the fluxes of state-of-the-art $Pd_{0.75}Ag_{0.25}$ membranes at 450 °C.

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Membrane reactors based on proton-conducting ceramics

Sandrine Ricote,¹ Benjamin L. Kee,¹ David J. Curran,¹ Canan Karakaya,¹ Angelique Jarry,² Ethan Crumlin,³ and Robert J. Kee¹

1) Mechanical Engineering Department, Colorado School of Mines, Golden, CO 80401, USA

2) Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

3) Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Tel.: +1 303-384-2091

Fax: +1 303-273-3602

sricote@mines.edu

Abstract

Membrane reactors based on proton-conducting ceramics offer significant opportunities for process intensification by combining catalytic hydrocarbon chemistry with hydrogen separation [1]. The present paper is concerned with yttrium-doped solid solutions of barium zirconate/cerate (BZCY, $BaZr_{1-x}Ce_xY_yO_{3-\delta}$). These materials are mixed ionic-electronic conductors (MIEC) with mobile charge defects including protons, oxygen vacancies, and small polarons. Upon applying an electrical bias across the membrane, protons are driven through the membrane. Applications of such technology include methane dehydroaromatization [2], methane reforming [3] and coal steam gasification [4]. In addition to separation, the polarized BZCY membranes offer the possibility of electrochemical H_2 compression [5].

The tubular membrane reactors used in the present research use a thin BZCY membrane (approximately 20 μm) that is applied onto a porous BZCY/Ni ceramic-metal (cermet) support (approximately 1 mm). The feed gases (e.g., CH_4 and H_2O for reforming) are introduced via an interior tube. The reactive gases flow in the annular space between the interior feed tube and the Ni/BZCY tube support. The Ni in the cermet acts as a reforming catalyst. The redox behavior of the BZCY acts to enhance the coke resistance of the Ni catalyst.

This presentation first discusses the model-based design of an autothermal membrane reactor that combines fuel reforming, hydrogen separation, and electrochemical compression. The experimental results focus initially on measuring material properties and fabricating the composite tube structures. Results also characterize aspects of the coke tolerance using Ambient Pressure X-ray photoelectron spectroscopy at the Advanced Light Source. Finally, the presentation discusses reactor development and early results for electrochemical H_2 compression.

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Conductivity of polymer-ceramic composite membranes at high T and $p(\text{H}_2\text{O})$ using a novel PEEK sample holder

A. Chatzitakis,¹ S. C. Simonsen,¹ M. L. Fontaine,² M. S. Thomassen,² and T. Norby¹

1) Department of Chemistry, University of Oslo, SMN, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway

2) SINTEF Industry, Forskningsveien 1, NO-0373 Oslo, Norway

Tel.: +47-22840693

a.e.chatzitakis@smn.uio.no

Abstract

Operating proton exchange membrane (PEM) fuel cells at temperatures above 100°C have several advantages such as limited cathode electrode flooding, improved electrocatalyst lifetime, reduced catalyst loading, as well as increased efficiency and simplicity of the system due to better energy management [1]. However, the high temperature compromises mechanical integrity, hydration, and proton conductivity of PEMs such as Nafion®. One approach to remedy these problems is to introduce inorganic fillers, for example silica. This may reduce hydrogen crossover and stabilise the membrane mechanically during otherwise critical heating and dehydration, while mechanisms for increased water retention at temperatures above 100°C, as well as improved proton mobility are debatable.

In this work we report a new sample holder and atmosphere control system for high throughput measurements of PEM conductivity, applied to cast composite films of PEMs with various silica micro- and nanopowder fillers.

A 4-probe polyether ether ketone (PEEK) stage (Figure 1) with replaceable gold wire contacts, provisions for reversible hydration, and accurate temperature control has been developed for spring-loading and enclosure in a ProboStat™ sample holder with heated base unit. A tailor-made humidifying system (HumiStat, NORECS, Norway) is used to supply gas with controlled high steam contents.

DC conductivity is measured vs T and $p\text{H}_2\text{O}$ and interpreted in terms of hydration and protonic mobility, as well as stability. With well-controlled and reproducible conditions and measurements, the effects on conductivity of the silica fillers used in this study, so far are small.

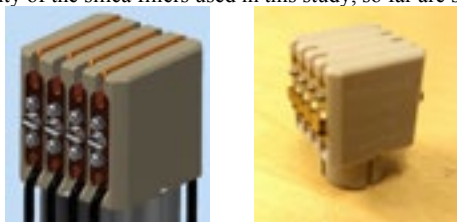


Figure 1. Left: Design sketch of sample stage with gold wire contacts and electrode connections mounted in a ProboStat™ support tube. Right: Photograph of the actual PEEK component with contact terminals.

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This work was performed within MoZEES, a Norwegian Centre for Environment-friendly Energy Research (FME), co-sponsored by the Research Council of Norway (project number 257653) and 40 partners from research, industry and public sector.

Particle size effects on the protonic conductivity of a zeolitic imidazolate framework

Daniel Muñoz-Gil, Paula C. Barbosa, and Filipe M. L. Figueiredo

CICECO – Aveiro Institute of Materials, Dep. of Materials & Ceramic Engineering, University of Aveiro

Campus de Santiago, 3810-193 Aveiro, Portugal

Tel.: +351 234 401 464

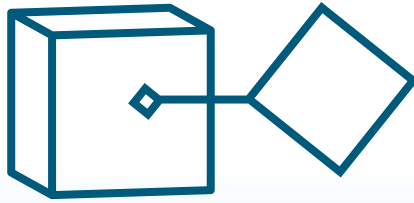
Fax: +351 234 401 470

lebre@ua.pt

Abstract

Zeolitic Imidazolate Frameworks (ZIF) are class of organic-inorganic hybrid materials with zeolitic topologies that may display very high microporosity. ZIF-8 is one of such materials, featuring a sodalite-type structure consisting of Zn (or Co) ions coordinated by imidazolate linkers forming micropores (*ca.* 11.6 Å equivalent spherical diameter) connected by narrow apertures (*ca.* 3.4 Å). The material has an exceptional thermal and hydrothermal stability that may be explored to design protonic conductors if one can overcome its hydrophobic character. In this work we explore size effects to enhance the conductivity of ZIF-8 by studying a set of samples with average particle size of 30 nm, 1 µm and 3 µm. The three samples display specific surface areas in excess of 1500 m².g⁻¹, as determined by nitrogen sorption isotherms, confirming their microporous structure. As expected due to the hydrophobic character of ZIF-8, the values obtained from dynamic water vapour type III sorption isotherms (for $P/P_0 < 0.5$) are much lower, decreasing slightly from 12.8 m².g⁻¹ for the nanopowder to 11.4 m².g⁻¹ and 8.1 m².g⁻¹ for the coarser 1 µm and 3 µm powders, respectively. In saturated conditions ($P/P_0 = 0.98$), the nanopowder adsorbs more than the double of the conventional microcrystalline powders is much higher for saturated conditions (55 cm³.g⁻¹ versus ~23 cm³.g⁻¹). The plot of the amount of adsorbed water as a function of the reciprocal particle size suggests that the water molecules adsorb predominately on the micropores of the coarser ZIF-8, whereas adsorption on the external particle surface becomes very significant for the nanostructured material. Following closely this trend in water uptake capacity, the protonic conductivity of the nanocrystalline ZIF 8 is about two orders of magnitude higher than that of the micron-sized powders, reaching ~ 0.5 mS/cm at 94 °C and 98 % relative humidity. This indeed suggests that size effects may be used to obtain major enhancements of the transport properties of ZIF-8, in this case probably due to differences on the composition and/or structure of the surface.

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TUESDAY

SEPTEMBER 18TH





Tuesday (18/9/18)

Presentation	Abstract Title	Presenter	Affiliation
Session V (Session Chair: R. Moore)			
Keynote 3 (8:30-9:10)	Solid state proton conductors comprising PBI-reinforced ionomers	Deborah Jones	CNRS –Université de Montpellier
Invited 5 (9:10-9:40)	Measuring transport on multiple scales in proton- and hydroxide-exchange membranes	Louis A. Madsen	Virginia Tech
Oral 8 (9:40-10:00)	Designing hydroxide-conducting polymer membranes	Michael A. Hickner	Pennsylvania State University
Coffee Break (10:00-10:30)			
Session VI (Session Chair: R. Merkle)			
Invited 6 (10:30-11:00)	Novel composite air cathodes for proton conducting fuel cells by exsolution	Mari-Ann Einarsrud	Norwegian University of Science and Technology
Oral 9 (11:00-11:20)	Novel mass transport model of proton conducting ceramics with multiple charge carriers	Keiji Yashiro	Tohoku University
Invited 7 (11:20-11:50)	Protonic ceramic electrochemical cells for power generation and renewable fuels production	Ryan O'Hayre	Colorado School of Mines
Oral 10 (11:50-12:10)	Lanthanum tungstate based membranes for H ₂ extraction and CO ₂ utilization: fabrication strategies	Mariya E. Ivanova	Forschungszentrum Jülich GmbH
Lunch (12:30-13:45)			
Session VII (Session Chair: M. Hickner)			
Keynote 4 (14:00-14:40)	Anion exchange membranes: correlation between physicochemical properties and anion conductivity by broadband electrical spectroscopy	Vito Di Noto	University of Padua
Oral 11 (14:40-15:00)	Discovering design principles for anion exchange membranes with high hydroxide conductivity: An ab initio molecular dynamics study	Mark E. Tuckerman	New York University
Invited 8 (15:00-15:30)	Effect of ultra-low hydration levels on anion conducting ionomers for fuel cell applications	Dario R. Dekel	Technion – Israel Institute of Technology
Coffee Break (15:30-16:00)			
Session VIII (Session Chair: K.-D. Kreuer)			
Invited 9 (16:00-16:30)	Blocky sulfonation of aromatic polymers as a means to enhance proton conduction pathways	Robert B. Moore	Virginia Tech
Invited 10 (16:30-17:00)	Anomalous diffusion in membranes for fuel cells	Stefano Mossa	Univ. Grenoble Alpes, CEA, CNRS
Oral 12 (17:00-17:20)	Chemical stability and transport properties of La _{0.5} WO _{11.25-δ} under H ₂ S atmospheres	Sonia Escolástico	Universitat Politècnica de València
Oral 13 (17:20-17:40)	Transition metal clusters as building blocks for multifunctional proton conducting materials	J. Cuny	Université de Toulouse
Dinner (18:00-19:15)			
Selected Student Oral: “Popcorn Protons” (19:30-21:00)			



Solid state proton conductors comprising PBI-reinforced ionomers

M. Zaton, N. Donzel, S. Cavaliere, J. Rozière, D. J. Jones

ICGM – Aggregates, Interfaces and Materials for Energy, CNRS – University of Montpellier, France

2, Place Eugène Bataillon, 34090 Montpellier, France

Tel.: +33 467 14 3330

Fax: +33 467 14 3304

Deborah.Jones@umontpellier.fr

Abstract

Proton exchange membrane fuel cells require disruptive solutions in materials in order to address the remaining challenges in increasing performance and durability while also reducing costs. These challenges include development of very thin polymer membranes with exceptional chemical and mechanical stability and very low electrical resistance. From the materials standpoint, some of these requirements are antagonistic and advanced solutions are required for a step-change in properties. Low equivalent weight (high ion exchange capacity) perfluorosulfonic acid ionomer membranes provide high proton conductivity, but have the disadvantage of high swelling in liquid water or at high relative humidity. Developing composite membranes of controlled heterogeneity and comprising an electrospun nanofibre polybenzimidazole web limits swelling very effectively, while also providing other benefits in terms of reducing gas crossover. This presentation will describe the development of PBI reinforced low EW short-side-chain PFSA membranes, their characterisation and proton conduction properties, and opportunities for this robust membrane design in PEMFC application.



Measuring transport on multiple scales in proton- and hydroxide-exchange membranes

Louis A. Madsen

Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech

Mail Code 0212, Blacksburg, VA 24061, USA.

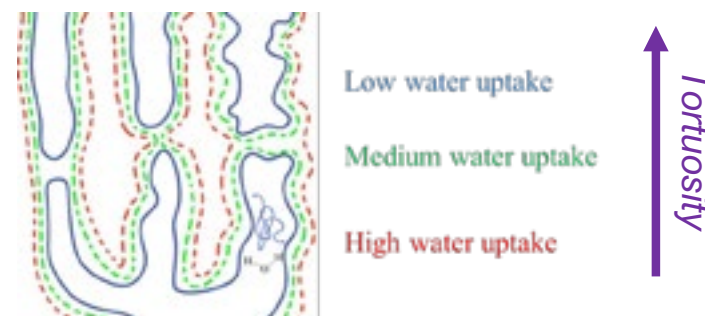
Tel.: 540-231-1270

Fax: 540-231-3255

lmadsen@vt.edu

Abstract

Self-organized polymeric systems conduct mobile species (ions, water, alcohols, etc.) according to a hierarchy of structural motifs that span sub-nm to > 10 microns in length scale. In order to understand molecular or ionic transport and couplings to other material properties, our group combines multiple types of NMR dynamics and transport measurements (spectroscopy, diffusometry, relaxation, imaging) with scattering, simulations, and microscopy as well as with theories of porous media, electrolytic transport, and oriented matter. In this presentation, I will discuss the quantification of *tortuosity* in a polymer membrane, meaning the restriction of pathways for diffusion. I will discuss the measurement of tortuosity *separately averaged over two distinct length scale ranges* – from nanometer to bulk and from micron to bulk. I will present NMR diffusometry measurements of these two quantities in representative systems of hydrophilic-hydrophobic random copolymer membranes, including proton-exchange membranes, hydroxide-exchange membranes, and all-neutral membranes. We follow these multi-scale tortuosity values as a function of water uptake (see figure). Using such knowledge, our group seeks to give more informed and precise feedback on the design of materials for use in, e.g., proton and hydroxide fuel cells, batteries, and water purification.





Designing hydroxide-conducting polymer membranes

Michael A. Hickner

Department of Materials Science and Engineering, The Pennsylvania State University

405 Steidle Building
University Park, PA 16802 USA

Tel.: +1-814-933-2204
Fax: +1-814-865-2917
mah49@psu.edu

Abstract

Hydroxide conducting polymers are one of the latest materials to be pursued for use in new electrochemical devices such as fuel cells, flow batteries, and advanced electrodialysis systems. Hydroxide, or generally, anion-conducting membranes, share a number of features with their proton-conducting membrane counterparts. Namely, the ionic content of the membrane must be balanced against the mechanical properties of the polymer backbone to facilitate water uptake for ion conduction. High ion content can facilitate high anion conductivity, but excessive swelling of the material with water renders an impractical membrane with low mechanical properties and conductivity can drop due to ionic dilution. Additionally, morphological development in terms of the microphase separation between hydrophilic and hydrophobic domains appears to enhance the conductivity of hydroxide-conducting membranes. Therefore, the identity, arrangement, and concentration of the ionic groups, the type of polymer backbone, and the water uptake of the material determine the initial structure-function relationships in these materials. This initial design space has given the community a head start in designing new materials given the wealth of information about sulfonated proton-conducting polymeric membranes. Currently, there are dozens of examples of anion exchange membranes reported in the literature, but the community is still converging on the details of materials that can be effectively deployed in electrochemical applications. The choice of backbone, the type of cationic group, and the best ways to interrogate these materials to make design choices towards next-generation materials are still being worked on in a number of groups across the globe. Aside from the similarities to water-absorbing sulfonated proton conducting membranes, the issue of stability is a key property in hydroxide-conducting materials that must be addressed. Many organic polymers are susceptible to attack by hydroxide. This important issue has prompted a wide search for stable organic cations and polymer backbones that are chemically stable to nucleophiles at temperatures up to 80 °C and beyond.

This talk will compare key features of proton and hydroxide conducting polymer membranes and point the way towards possible new designs for hydroxide conducting membranes. Key properties of these materials will be reviewed along with examples of important milestones in their development.



Novel composite air cathodes for proton conducting fuel cells by exsolution

Laura Rioja-Monllor,¹ Sandrine Ricote,² Carlos Bernuy-Lopez,¹ Ryan O'Hayre,² Marie-Laure Fontaine,³ Tor Grande,¹ and Mari-Ann Einarsrud¹

1) Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology
2) Colorado School of Mines, USA
3) SINTEF Materials and Chemistry, Norway

NTNU Norwegian University of Science and Technology, 7491 Trondheim, Norway
Tel.: +4748136521

mari-ann.einarsrud@ntnu.no

Abstract

Cathodes are one of the key components of protonic ceramic fuel cells (PCFCs) requiring further development for enhancing the performance of PCFCs. This encompasses optimization of material compositions and microstructures, as well as further understanding of the electrode processes. To address these issues we have developed a flexible synthesis route based on an exsolution of a single phase material for the preparation of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ - $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$ based composite cathodes. The single phase precursors were synthesized by a modified Pechini route. The synthesis was optimized by a systematic study of the fuel/oxidant ratio, pH of the solution, and the thermal treatment in order to obtain an amorphous solid-state precursor. The phase composition upon further thermal processing was defined by controlling the oxidation state of the transition metals under reducing atmosphere. The composites with nano-sized grains were subsequently formed by oxidative exsolution of the single phase precursor in air, resulting in a mixture of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ and $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$ -based phases. The composite powders were used to prepare electrodes with different microstructures by using two deposition methods, spray coating and screen printing, and by varying the firing temperature from 600 to 1100 °C. Further, we investigated the possibility of preparing the composite electrodes by directly coating and firing the single phase materials on dense electrolyte pellets to prepare symmetric cells. This method enables to combine several processing steps and to reduce the number of thermal treatments. In general, we observed a more homogeneous microstructure for the cathodes prepared by screen printing. The one step combined process encompassing exsolution of the single phase and firing of the symmetric cells yielded significant improvement of the cathode performance compared to the other routes. The best electrochemical performance was observed for $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ - $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ cathode with an area specific resistance of 4.02 $\text{Ohm}\cdot\text{cm}^2$ at 400 °C and 0.21 $\text{Ohm}\cdot\text{cm}^2$ at 600 °C in 3 % moist synthetic air. These results are among the best reported for cathodes of PCFCs as will be discussed. The described synthesis method shows great potential also for the preparation of other composite oxide materials by the novel processing of exsolution.

Financial support from The Research Council of Norway under the program Nano2021 to the project (Number 228355) "Functional oxides for clean energy technologies: fuel cells, gas separation membranes and electrolyzers" (FOX CET) conducted by SINTEF, UiO and NTNU, is gratefully acknowledged.



Novel mass transport model of proton conducting ceramics with multiple charge carriers

Keiji Yashiro, Arthur Bourdon, Kotaro Okuyama, and Tatsuya Kawada

Graduate School of Environmental Studies, Tohoku University

6-6-01 Aramakiyoba, Aoba-ku, Sendai 980-8579, Japan

Tel.: +81 22 795 6977

Fax: +81 22 795 4067

yashiro@ee.mech.tohoku.ac.jp

Abstract

A number of perovskite-type ceramic oxides exhibit a relatively high proton conductivity at high temperatures. Even though these materials are called proton conducting oxides, protons are not the only defects they contain. Along with protons themselves, holes and oxygen vacancies are conducted in quite significant quantities, and none of the three charge carriers may be neglected. Partial conductivities of protons, holes and oxygen vacancies are close enough that all of them need to be taken into account, which complexing analytical and numerical treatment. Due to mixed conduction and the presence of three charge carriers in non-negligible quantities, the understanding of proton-conducting perovskite oxides remains partial and their charge and mass transport properties are not known in details. Simulation appears as a natural way to acquire a more precise knowledge of these materials.

In this paper, we aimed at describing a novel way to simulate proton conducting perovskites, using an equivalent circuit which was based on transmission lines modeling charge and mass transport of all potential carriers- proton, oxygen vacancy, and hole. Here partial current density of each carrier is described as

$$J_{H_i^+} = -\frac{\sigma_{H_i^+}}{F} \nabla \eta_{H_i^+} \quad (1), \quad J_{O_V^{\bullet\bullet}} = -\frac{\sigma_{O_V^{\bullet\bullet}}}{2F} \nabla \eta_{O_V^{\bullet\bullet}} \quad (2), \quad J_{h^+} = -\frac{\sigma_{h^+}}{F} \nabla \eta_{h^+} \quad (3).$$

Defect equilibrium between protons and holes, and between oxide ions and holes, are written as

$$H_i^+ - h^+ = \frac{1}{2} H_2 \quad (4), \quad O_O^{\bullet\bullet} + 2h^+ = V_O^{\bullet\bullet} + \frac{1}{2} O_2 \quad (5),$$

Continuity equation for each carrier, i , is taken into account.

$$\frac{n_i F}{V_m} \frac{\partial c_i}{\partial t} = \nabla \cdot \left(\frac{\sigma_i}{n_i F} \nabla \eta_i \right) + J_{\text{exch},i} \quad (6)$$

The proposed transport model was tested and compared with literature for various configurations.



Protonic ceramic electrochemical cells for power generation and renewable fuels production

Ryan O'Hayre,¹ Chuancheng Duan,¹ Liangzhu Zhu,¹ Chris Cadigan,¹ Jake Huang,¹ Meagan Papac,¹ Andriy Zakutayev,² Huayang Zhu,³ Canan Karakya,³ Rob Braun,³ Sandrine Ricote,³ Bob Kee,³ and Neal Sullivan³

1) Metallurgical and Materials Engineering, Colorado School of Mines

2) National Renewable Energy Laboratory

3) Mechanical Engineering, Colorado School of Mines

1500 Illinois St. Golden, CO. 80401. USA

Tel.: 303-273-3952

rohayre@mines.edu

Abstract

Through years of steady technological advancement, proton-conducting ceramic materials are approaching a technology readiness level that rivals more well-established oxygen-ion conductors and polymer-electrolyte membranes. Doped barium cerate-zirconate electrolyte materials ($\text{BaCe}_{x-y}\text{Zr}_{1-x-y}\text{O}_{3-\delta}$) are the focus of these efforts. Devices based on these materials have demonstrated impressive performance at intermediate temperatures, often 200 – 300 °C below that of equivalent oxygen-ion conductors. Such lower-temperature operation can dramatically reduce device degradation rates, decrease the cost of stack and balance-of-plant materials, reduce thermal-cycling stresses, and enable a wider range of integration options. Our research efforts at the Colorado School of Mines are currently focused on developing protonic ceramics for a number of applications, including:

- Hydrocarbon-tolerant protonic ceramic fuel cells for electricity generation (PCFCs)
- Protonic ceramic electrolyzers for fuel synthesis (PCECs)
- Reversible protonic-ceramic electrochemical cells for energy storage (RePCECs).

In this presentation, we will discuss our recent progress in developing electrochemical energy conversion devices based on these materials, including remarkably high-performance H_2 and hydrocarbon-fueled PCFCs; exceptionally efficient (> 97% LHV efficiency) PCECs for H_2 production and for the co-conversion of steam and carbon dioxide to renewable methane; $\text{H}_2/\text{H}_2\text{O}$ -based RePCECs with > 75% round-trip efficiency (cell-level) for seasonal energy storage, and a reversible ammonia fuel cell for ammonia synthesis/power production.



Lanthanum tungstate based membranes for H₂ extraction and CO₂ utilization: fabrication strategies

Mariya E. Ivanova, Wendelin Deibert, Diana Marcano, and Georg Mauer

Institute of Energy and Climate Research IEK-1, Forschungszentrum Jülich GmbH
Leo-Brandt-Str., 52428 Jülich, Germany

Tel.: 00492461615194
Fax: 00492461612455
m.ivanova@fz-juelich.de

At the focus of energy conversion efficiency and decreasing greenhouse gas emissions from power generation and energy-intensive industries, membrane technology become pronouncedly important for H₂ extraction and CO₂ capture/utilization. In this context, the integration of proton conducting ceramic membranes (PCCMs) in H₂ extraction (fuel) or H₂/CO₂ consumption (raw materials for chemical production) would account for high environmental and economic impact. PCCMs may be therefore of interest for integrated gasification process, specifically in water gas shift reactors (T > 600°C) and catalytic membrane reactors (T < 600 °C). Materials largely at focus are Lanthanum tungstates (LaWO), which exhibit appreciable protonic conductivity at intermediate temperatures, non-blocking grain boundaries, n-type electronic conductivity (reducing atmosphere), good sinterability and stability in H₂S, CO/CO₂, steam.

The present talk focuses on the fabrication strategies for LaWO membranes for integration in membrane modules/reactors. Full ceramic (LaWO_{mem}/LaWO_{sub}, LaWO_{mem}/MgO_{sub}) and metal supported (LaWO_{mem}/Crofer_{sub}) asymmetric membrane systems were developed by means of sequential tape casting and PS-PVD. Cubic phase formation and gas tightness of the LaWO functional layer could be achieved both on porous ceramics and porous metallics. This study encompasses furthermore detailed insights on the fabrication parameters (e.g. plasma composition (ceramic-metallic assemblies); sintering behaviour (all ceramic assemblies)) and understanding their interplay to reach desired material/membrane functional properties. The talk will also address up-scaling aspect to shape components of industrially attractive size.



Anion exchange membranes: correlation between physicochemical properties and anion conductivity by broadband electrical spectroscopy

Vito Di Noto

Section of Chemistry for Technology, Department of Industrial Engineering, University of Padua

Via F. Marzolo 9, I-35131 Padova, Italy
Tel/Fax.: +39 049/827 5229
vito.dinoto@unipd.it

Abstract

In recent years, anion exchange membrane fuel cells (AEMFCs) have been extensively studied owing to significant advantages over their proton exchange membrane fuel cell (PEMFC) counterparts [1]. The possibility to adopt electrocatalysts that do not comprise of precious metals as well as diminished poisoning effects are among the most relevant reasons for which AEMFCs are believed to be advantageous. However, AEMFCs do suffer from some drawbacks, specifically concerned with the anion exchange membrane (AEM) which is responsible for the selective migration of OH⁻ anions from the cathode to the anode, and is one of the most critical components of the entire AEMFC. In particular, with respect to the proton exchange membranes used in PEMFCs, AEMs typically exhibit a lower ionic conductivity and an inferior chemical stability, the latter typically associated with the degradation of anion-exchange functionalities. For these reasons, it is very important to elucidate the details of the complex interplay between the nanostructure and the ion conductivity mechanism of the AEMs.

Over the last 30 years it has been demonstrated that conductivity in ion-conducting materials occurs via a number of different processes including: (a) the migration of ions between coordination sites [2-5]; and (b) the diffusion of conformational states of the host matrix (segmental motion). [2-5]. In ion-conducting membranes the long-range charge migration is often correlated with the dielectric relaxation modes of the polymeric chains; the latter are typically associated with the fluctuation of: a) the main backbone chain bearing permanent dipole moments; b) side chains; or c) functional groups involved in ion-dipole interactions. The key technique to investigate the interplay between structure and conductivity of ion-conducting materials is Broadband Electrical Spectroscopy (BES).

Here we present several case studies of AEMs paying particular attention to their thermal stability and the thermomechanical properties. BES is then adopted to study the electrical response of each material in terms of polarizations and relaxation phenomena. The results allow us to: (a) suggest a comprehensive model capable to rationalize the long-range charge transfer mechanism in AEMs; and (b) clarify how the chemical composition and nanostructure of the materials is influencing the coordination of mobile species.

The authors thank the StrategicProject “From materials for Membrane electrode Assemblies to electric Energy conversion and SToRAge devices” (MAESTRA) of the University of Padova for funding this activity.

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Discovering design principles for anion exchange membranes with high hydroxide conductivity: An *ab initio* molecular dynamics study

Tamar Zelovich,¹ Zhuoran Long,² and Mark E. Tuckerman³

1) Department of Chemistry, New York University, New York, NY 10003, USA

2) Courant Institute of Mathematical Science, New York University, New York, NY 10012, USA

3) NYU-ECNU Center for Computational Chemistry at NYU Shanghai, Shanghai 200062, China

mark.tuckerman@nyu.edu

Abstract

It is clear that in the identification and development of clean energy sources, a range of technologies will need to be leveraged. Electrochemical devices are an important part of this mix of technologies, and among these, fuel cells constitute some of the cleanest and most sustainable. However, several key hurdles to harnessing the potential of fuel cells (as well as various other electrochemical technologies) remain to be surmounted. We have mounted a Materials Genome Initiative project that aims to address these challenges by designing, synthesizing, and testing new materials for use in alkaline fuel cells and to discover a set of rules for best practices in the development of future materials for fuel cell applications. An interdisciplinary team of investigators has been assembled and is focusing on *anion exchange membrane (AEM) fuel cells*, which have advantages over other types of fuel cells in not requiring precious metals and being operable with a variety of fuels at low temperature [1]. The project employs a cohesive strategy involving mathematical and computer modeling of specific materials components, which, in turn, is guiding the synthesis of new materials, characterization and testing of these in actual fuel cells, and the determination of optimized key design principles that will govern future materials engineering for electrochemical applications. The strategy of the project employs density-functional theory based first-principles molecular dynamics calculations and dissipative-particle dynamics [2-5]. In this talk, I will present results from first-principle molecular dynamics component of the proposal, which includes simulations of bulk solutions and idealized confined geometries, both containing cations of interest in the AEM design. Connections to the dissipative-particle dynamics will be made, and comparative results of water structure and distribution, solvation structures and their lifetimes, and hydroxide diffusion constants as functions of temperature, water content, cation spacing, and confinement parameters will be presented. Suggestions of design principles that lead to AEMs with high hydroxide conductivity will be made.

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Effect of ultra-low hydration levels on anion conducting ionomers for fuel cell applications

Dario R. Dekel

The Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology

Technion City, Haifa 3200003, Israel

Tel.: (312)340-0584; +972(54)252-6370

dario@technion.ac.il

Abstract

Anion exchange membrane fuel cells (AEMFCs) can potentially revolutionize energy storage and generation; however, their commercial development is hampered by the chemical decomposition of the anion-conducting ionomeric materials during operation. The hydroxide anions, while transported from the cathode to the anode, attack the positively charged functional groups in the polymeric membrane, neutralizing it and suppressing its anion-conducting capability. In recent years, several new quaternary ammonium salts have been proposed to address this challenge, but while they perform well in ex-situ chemical studies, their performance is very limited in real fuel cells. While cation chemistry dictates the intrinsic chemical stability of the anion conducting ionomeric materials, it was recently shown that chemical degradation is significantly influenced by the hydration level at which the fuel cell operates. In this talk, we will discuss the relationship between ionomer degradation and AEMFC operating conditions. In addition, a novel numerical model capable of predicting AEMFC performance stability under this degradation environment will be presented. This model demonstrates for the first time, the strong impact of the operating current density and membrane characteristics on the cell performance stability and lifetime. Under certain conditions, the model predicts AEMFC lifetimes exceeding 8000 hours, which satisfies the DOE cell lifetime requirements for automotive applications.



Blocky sulfonation of aromatic polymers as a means to enhance proton conduction pathways

Lindsey J. Anderson, Kristen Felice, Samantha J. Talley, and Robert B. Moore

Department of Chemistry, Macromolecules Innovation Institute, Virginia Tech

800 West Campus Drive, Blacksburg, Virginia 24061
rbmoore3@vt.edu

Abstract

Sulfonated poly(ether ether ketone) (SPEEK) has long been regarded as a promising candidate for proton exchange membranes due to its low cost, excellent mechanical properties, and ease of production. Conventional methods of SPEEK preparation, however, afford little control over the functional group sequencing and produce membranes with large distributions in both the number and location of sulfonic acid functionalities. Recent findings from the ion-containing polymer membrane community have taught us the importance of controlled sequencing of ionic groups along polymer chains in the development of ordered polar domains for enhanced transport properties. When compared on an equal ion content basis, a blocked arrangement of ionic groups along polymer chains tends to produce more ordered nano-phase-separated domains while preserving the inherent properties of the unfunctionalized homopolymer over that of analogous random ionomers. Inspired by these demonstrated enhancements, we have begun to explore the impact of variable post-polymerization sulfonation reactions on the spatial distribution of functional groups in ionomers. Recently, we have discovered a non-functionalizing solvent for PEEK that allows for a homogeneous sulfonation reaction. Surprisingly, this new solvent also allows for the formation of a thermoreversible gel [1]. Following a method we previously developed to sulfonate syndiotactic polystyrene (sPS) in the gel state [2], we are now able to prepare a blocky form of sulfonated PEEK that has a high degree of sulfonation and preserves crystallizability. Additionally, the blocky SPEEK membranes exhibit enhanced solvent uptake and proton transport due to their well-ordered, phase-separated morphology. Thus, by functionalizing in the gel-state with simple post-polymerization techniques it is possible to obtain blocky architectures that provide membrane enhancements typically observed only in directly synthesized ion-containing block copolymers.

This material is based upon work supported by the National Science Foundation under Grant No. DMR-1507245.

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Anomalous diffusion in membranes for fuel cells

Stefano Mossa

Univ. Grenoble Alpes, CEA, CNRS, INAC-SyMMES

CEA Grenoble - INAC
17, Rue des Martyrs 38054 Grenoble Cedex 9, France

Tel.: +33 438 783577
stefano.mossa@cea.fr

Abstract

Dynamics of absorbed water determines proton transport in membranes employed in Polymer Electrolyte Membrane fuel cells. Among these soft charged materials, perfluoro-sulfonic-acid compounds like Nafion and Aquivion (differentiated by the length of the grafted side-chains) play a crucial role in technology but, due to their complexity, still constitute an extreme challenge. Simpler systems, like the PerFluoro-Octane-Sulfonic acid ionic surfactant, with a structure very similar to that of the Nafion side chain, also show alike properties. In the presence of water all these materials phase-separate assuming intricate multi-scale hydration-dependent morphologies, where mechanical strength is provided by the hydrophobic host matrix, and proton transport takes place in irregular ionic nanodomains. Conductivity in these structures ultimately depends on both the macroscopic total amount of water adsorbed in the network of interconnected channels, and the microscopic structure of the fluid molecules. This interplay is very difficult to grasp.

In this talk I will resume recent work [1-3] where these issues are addressed numerically by MD simulation, with reference to well established experimental activity with Neutrons. MD turns out to be extremely convenient, by providing synthetic materials templates useful even for mere visual inspection, or important information which could not be extracted in experiments. It can also help in proposing alternative arguments to better justify or extend the interpretation of the latter.

By jointly discussing experiments and simulations, I will provide two main take-home messages. First, by following the water molecules trajectories generated by MD we have made an observation impossible in experiments: the mean-squared distance covered by the confined molecules on a certain interval of time is not linear in the latter, as it is the case in the bulk. In contrast, it varies as a power-law with an exponent less than one, which decreases on decreasing hydration. This is the hall-mark of sub-diffusion, a feature not sufficiently highlighted in previous discussions. It implies that water diffusion coefficients measured on different time and length-scales are different, at variance with the Fick prescription. Second, the diffusion coefficients that we “read” in MD at well-chosen length scales reproduce the analogous values extracted from different experimental techniques, often on the basis of extremely complex fitting procedures. These assume the existence of different dynamical mechanisms active at increasingly extended length scales. I will show that, in fact, experiments seem to probe at a few quite spaced points the underlying anomalous dynamics of confined water, which is in contrast tracked continuously by MD.

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Chemical stability and transport properties of $\text{La}_{5.5}\text{WO}_{11.25-\delta}$ under H_2S atmospheres

Sonia Escolástico,^{1,2} María Balaguer,¹ S. Somacescu,³ Katja Haas-Santo,² Roland Dittmeyer,² and Jose M. Serra¹

- 1) Instituto de Tecnología Química (Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas), Av. Los naranjos s/n, E-46022, Valencia, Spain
- 2) Institute for Micro Process Engineering, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany
- 3) “Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, Spl. Independentei 202, 060021 Bucharest, Romania
Tel.: +34 96 387 7800
Fax: +34 96 387 9444
soesro@itq.upv.es, jmserra@itq.upv.es

Abstract

The integration of hydrogen permeable membranes in catalytic membrane reactors (CMR) allow to obtain an ultra-pure H_2 stream in addition to the improvement of the reaction yield in reactions such as methane dehydroaromatization or water gas shift [1]. Among the different H_2 permeable membranes, mixed protonic-electronic conductors (MPEC) are appropriate candidates for this kind of reactions due to their ability to operate at high temperature ($>500^\circ\text{C}$), high pressure, the high selectivity to H_2 and the good chemical stability at high temperature. In the reactions of interest, H_2 permeable membranes should work under reducing conditions and atmospheres containing CO_2 , CO , H_2O and H_2S [2]. Subsequently, membrane materials should possess an adequate chemical stability and an important H_2 permeation flux under harsh conditions [3,4].

The present work presents the study of the chemical stability, transport properties and H_2 permeation measurements under H_2S containing atmospheres of the $\text{La}_{5.5}\text{WO}_{11.25-\delta}$ (LWO). Chemical stability and changes in the crystalline structure under H_2S were evaluated by X-ray diffraction, Elemental Analysis, XPS, SEM and WDS analysis. The effect of the H_2S on the transport properties of the material was evaluated by electrochemical impedance spectroscopy and the H_2 permeation was measured in a double chamber reactor by gas chromatography.

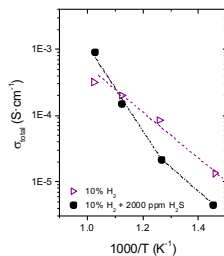


Figure 1: Total conductivity for LWO under wet 10% H_2 in N_2 and wet 10% H_2 and 2000 ppm H_2S balanced with N_2 atmospheres as a function of the reciprocal temperature.

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Transition metal clusters as building blocks for multifunctional proton conducting materials

G. Daigre,¹ J. Cuny,² P. Lemoine,¹ M. Amela-Cortes,¹ S. Paofai,¹ N. Audebrand,¹ A. le Gal La Salle,³ E. Quarez,³ O. Joubert,³ N. G. Naumov,⁴ and S. Cordier¹

- 1) Institut des Sciences Chimiques de Rennes (ISCR UMR 6226), University of Rennes 1 (UR1), General Leclerc, Rennes 35042, France
- 2) Laboratoire de Chimie et Physique Quantiques LCPQ/IRSAMC, Université de Toulouse (UPS) and CNRS, 118 Route de Narbonne, F-31062 Toulouse, France
- 3) Institut des Matériaux Jean Rouxel (IMN) - UMR 6502, 2 rue de la Houssinière BP32229 44322 Nantes cedex 3, France
- 4) Nikolaev Institute of Inorganic Chemistry, 3 Acad. Lavrentiev pr., 630090 Novosibirsk, Russia

Tel.: +33 (0)5 61 55 68 36

Fax: +33 (0)5 61 55 60 65

jerome.cuny@irsamc.ups-tlse.fr

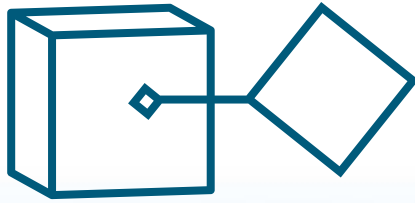
Abstract

Proton-conduction has been identified in a large variety of solid-state compounds: metal-organic frameworks, coordination polymers, polyoxometalates and covalent organic frameworks [1]. In the present contribution, I will present our recent study that demonstrates for the first time that efficient proton-conducting materials can also be synthesized from molybdenum metal clusters. Three compounds will be discussed: $(\text{H})_4[\text{Mo}_6\text{Br}_6\text{S}_2(\text{OH})_6] \cdot 12\text{H}_2\text{O}$ (1) and $(\text{H})_2[\text{Mo}_6\text{X}_8(\text{OH})_6] \cdot 12\text{H}_2\text{O}$ ($\text{X} = \text{Br}$ (2), Cl (3)). Both compounds are built on a 3D arrangement of $\text{Mo}_6\text{L}_8(\text{OH})_6^{12-/4-}$ cluster units link together by hydroxyl bridges and surrounded by crystallization water molecules (see Fig. 1a). The proton conduction was characterized experimentally at different temperatures and relative humidity and coupled to ab initio molecular dynamics simulations to provide an atomistic scale description of the proton conduction mechanism. We demonstrate that the hydroxyl bridges between the cluster units can promote proton transfer between adjacent oxygen atoms (see Fig. 1b and c) which leads to a Grotthuss-type mechanism through the hydrogen bond network.

Fig. 1: (a) View along the c (a) axis in (1) of the connection between a given $[\text{Mo}_6\text{Br}_6\text{S}_2(\text{OH})_6]^{4-}$ cluster unit and the surrounding six cluster units. (b) and (c) Figure 6: (a) Time evolution of the $\text{O}_1\text{-H}^*$, $\text{H}^*\text{-O}_2$ and $\text{O}_1\text{-O}_2$ distances along a 300 K AIMD simulation in (2).

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WEDNESDAY SEPTEMBER 19TH



Wednesday



Wednesday

(19/9/18)

Presentation	Abstract Title	Presenter	Affiliation
Session IX (Session Chair: T. Norby)			
KP 1 (8:30-9:15)	Proton conductors and proton conductivity, a tentative historical overview	Philippe Colombar	Sorbonne Université
KP 2 (9:15-10:00)	Relation between conductivity and structural relaxation times in highly conducting ambient temperature plastic crystal solid acids	C. Austen Angell	Arizona State University
Coffee Break (10:00-10:30)			
Session X (Session Chair: J. Rozière)			
KP 3 (10:30-11:15)	From layered phosphates and phosphonates to nanofillers for PEMFC membranes: a long research way with Giulio Alberti group	Mario Casciola	University of Perugia
KP 4 (11:15-12:00)	Trends in proton conduction research: A historical narrative	Klaus-Dieter Kreuer	Max-Planck-Institute for Solid-State-Research
Lunch (12:15-13:15)			
Excursions (13:30-17:00)			
Reception (Atrium) (17:30-18:30)			
Banquet (Stowe) (18:45-21:00)			

KP1

Proton conductors and proton conductivity, a tentative historical overview

Philippe Colomban

Sorbonne Université, CNRS, MONARIS UMR8233

Campus Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France

Tel.: 33 1 44272785

philippe.colomban@asorbonne-universite.fr

Abstract

Up to the first oil crisis in the 1970s attention was only restricted to the academic study of the proton specificity (its size is intermediate between those of electron and Li^+ cation) and proton transfer, although ‘good’ proton conductors had already been discovered and put into practice in some niche applications (e.g. the (poly(perfluorosulfonic) membrane used in Gemini orbiter program) or tested at the laboratory as prototypes (perovskite electrolyte in SOFC). Oil crisis led to a search for more genuine electrolyte and electrode materials, the superionic conductors, including fast proton conductors.^{1,2} Undeniably, this led to the discovery of new compounds.³ Funding rapidly decreased and the research activity declined. A renewal to the interest starts in 2000, in relation with Global Warming issues and search for decarbonated energy sources and storage. We will discuss here the history of proton conductors, with special emphasis on the first researches: i) proton conductors, including mixed conductors for electrodes, ii) methods of analysis and iii) understanding of proton transfer mechanism. To date, only the first discovered materials reached commercial production. The major developments conducted since 1980 concern technological issues.³⁻⁵

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KP2

Relation between conductivity and structural relaxation times in highly conducting ambient temperature plastic crystal solid acids

C. Austen Angell, T. Greg Tucker, Amanda Young-Gonzalez, Ranko Richert, Steven K. Davidowski, and Jeffery L. Yarger

School of Molecular Sciences, Arizona State University

Tempe, AZ 85287-1604, USA

austenangell@gmail.com

Abstract

Proton-conducting solids in which the conductivity is associated with the rotation of protonated anions, have been widely studied as candidate materials for fuel cells and ferroelectrics. The classic cases have been CsHSO_4 (1) and KH_2PO_4 (2) whose conductivities jump to very high values, of order 10^{-2} Scm^{-1} , above a phase transition occurring at temperatures somewhat above 100°C . It is generally supposed that above this temperature the anions undergo a greatly increased rate of reorientation on their crystal lattice sites, and that, in an incompletely understood manner, this lends the protons a much greater mobility. Such rotation-induced mobility for positively charged species in crystal lattices was much studied for the high temperature phase ($T > 575^\circ\text{C}$) of lithium sulfate, where a ‘‘paddle-wheel’’ mechanism was controversially advanced (3,4) as the relevant source of lithium ion mobility. A detailed ion dynamics study of that system by Impey et al. (5) did not yield unambiguous resolution of conductivity mechanism.

In this contribution we describe the preparation and characterization of a class of proton conductors that can have conductivities well above 10^{-2} Scm^{-1} at ambient temperature (6). Two examples are $\text{Si}(\text{SO}_3\text{H})_4$ and $(\text{CH}_3\text{O})_3\text{SiSO}_3\text{H}$. They exist as soft solid phases that can be worked into porous separators such as Celgard, and used with moderate success as fuel cell membranes. A comparison of conductivities with CsHSO_4 and pure phosphoric acid is shown in the Figure 1. In an effort to sort out the relation between structural relaxation times, reorientations, and conductivity, we have carried out frequency-dependent conductivity studies to obtain conductivity relaxation times which we compare with different structural relaxation times for anion components obtained from spin-lattice relaxation time measurements for the nuclei ^{13}C and ^1H , in the same sample sealed in the same NMR tube, by the technique described in ref. (7).

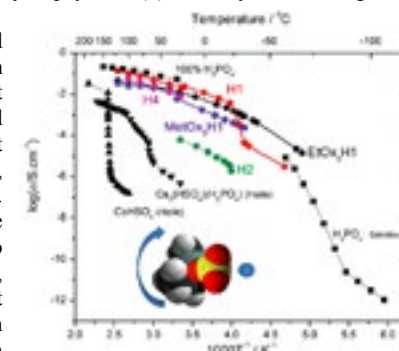


Figure 1. Comparison of dc conductivities of new proton conducting soft solids of this work with those of liquid H_3PO_4 and CsHSO_4 from the literature.

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From layered phosphates and phosphonates to nanofillers for PEMFC membranes: a long research way with Giulio Alberti group

Mario Casciola

Department of Chemistry, Biology and Biotechnology, University of Perugia

Via Elce di Sotto 8, 06123 – Perugia, Italy

Tel.: +39 075 585 5567

Fax: +39 075 585 5566

mario.casciola@unipg.it

Abstract

This lecture aims at giving a historical perspective on the work made at Perugia University in the field of proton conducting materials based on layered phosphates and phosphonates and at commemorating Professor Giulio Alberti, one of the most authoritative scientists who pioneered this research field. Layered zirconium phosphate (ZrP) is a well known ion exchange material characterized by high chemical inertia and good thermal stability. These properties stimulated research on its proton transport properties since mid 80s, but it was soon clear that the conductivity was too low for application in electrochemical devices working at high current densities. Attempts to enhance the ZrP conductivity led first to the development of intercalation compounds with aliphatic or aromatic amines. Due to the structural features of such compounds, proton transport must involve protonation of the guest molecule and its diffusion or rotation in the direction of an acceptor group. As a consequence, the conductivity of the anhydrous host material is strongly affected by the basic strength of the guest, being depleted by alkyl diamines and enhanced (up to two orders of magnitude) by aromatic amines. Unfortunately, the increase in conductivity is associated with a decrease in thermal stability. To avoid this issue, acidic functions, such as carboxylic or sulfonic groups, were covalently anchored to the phosphate through alkyl or aryl groups thus obtaining zirconium phosphonates with the same layered structure as the parent ZrP. The conductivity of sulfoaryl phosphonates is strongly affected by the hydration of the sulfonic groups and approaches the 0.1 S cm⁻¹ at 100°C and relative humidity close to 100%. It was therefore of interest to investigate these materials as fillers of aromatic and perfluorinated ionomers, and different synthetic approaches were developed to get nanometric filler particles dispersed within the ionomer matrix. Zirconium sulfophenyl phosphonates proved to be able to enhance proton conductivity and mechanical strength of the neat ionomer but showed poor hydrolytic stability, partly due to the high hydrophilic character of the sulfophenyl phosphonate. Attention was then focused on ZrP based hydrophobic nanofillers bearing alkyl or phenyl groups anchored to the ZrP layers. Although these materials are poor proton conductors, composite membranes loaded with 10-15 wt% zirconium alkylphosphates are more conductive than the neat ionomer, while the combined use of such hydrophobic fillers with hydrophilic zirconium phosphate leads to more effective mechanical reinforcement and better fuel cell performance than that achieved by single filler membranes with optimized filler loading. This seems to arise from a selective interaction of the two fillers with the hydrophilic and the hydrophobic components of the ionomer, and this aspect deserves further investigation.



Trends in proton conduction research: A historical narrative

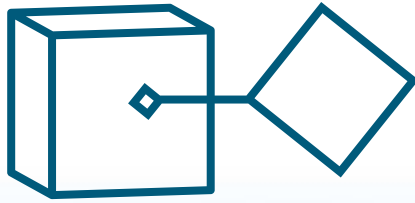
Klaus-Dieter Kreuer

Max-Planck-Institute for Solid-State-Research
Heisenbergstrasse 1, 70569 Stuttgart, Germany

kreuer@fkf.mpg.de

Abstract

Historically, approaching proton conduction phenomena always reflected concepts and methods which were popular at the given time. This presentation tells the story of some approaches within their historical context. For example in the early 30s, protons were first treated with the tools of quantum chemistry which became popular at that time, and today we may smirk about a publication in the counter-culture early 70s using the term “Non-conformist ion” for the proton in condensed matter. Substantial progress comprised not only *methods* such as NMR in high magnetic field gradients emerging in the early 80s and molecular dynamics simulations which became possible through the increasing computer power available in the 90s, but also *concepts* such as “complexity” which helped to describe non-linear proton dynamics in extended hydrogen bonded networks. Like in fashion, some approaches disappeared while others became part of today’s canon providing efficient guidelines for the development of proton conducting materials for applications defining specific sets of requirements. Yet, more than two centuries of continuous interest in proton conduction phenomena have not led to a general theory, model or at least a rational making the connection between the multitude of phenomena and basic chemical and physical principles.



THURSDAY SEPTEMBER 20TH



Thursday



Thursday (20/9/18)

Presentation	Abstract Title	Presenter	Affiliation
Session XI (Session Chair: S. Halle)			
Keynote 5 (8:30-9:10)	Perovskite non stoichiometry and proton conduction	John Irvine	University of St. Andrews
Invited 11 (9:10-9:40)	Hydration thermodynamics and lattice site basicity of proton conducting and mixed conducting oxides	Tor S. Bjørheim	University of Oslo
Oral 14 (9:40-10:00)	The microscopic model of ac conductivity in solid acids and the Jonscher law	Tomasz Maslowski	Rzeszów University of Technology
Coffee Break (10:00-10:30)			
Session XII (Session Chair: M. Casciola)			
Invited 12 (10:30-11:00)	Radiation-grafted hydroxide-conducting anion-exchange polymer electrolytes for alkali membrane fuel cells	John R. Varcoe	University of Surrey
Oral 15 (11:00-11:20)	Molecular engineering of hydroxide ion conducting polymer electrolyte membranes	Chulsung Bae	Rensselaer Polytechnic Institute
Invited 13 (11:20-11:50)	Multiscale water transport in model alkaline anion exchange membranes investigated by quasi-elastic neutron scattering	Jan-Patrick Melchior	Oak Ridge National Laboratory
Oral 16 (11:50-12:10)	Dual weight gain upon hydration of MIEC perovskites	Ragnar Strandbakke	University of Oslo
Lunch (12:30-13:45)			
Session XIII (Session Chair: L. Madsen)			
Keynote 6 (14:00-14:40)	Polymer electrolyte membranes + covalently bound photoacid dye molecules = photovoltaic action	Shane Ardo	University of California Irvine
Oral 17 (14:40-15:00)	Computational prediction of long distance hydride diffusion based on concerted hydride and oxide ion migration	Yoyo Hinuma	Chiba University
Invited 14 (15:00-15:30)	Humidity and carbon dioxide stable solid state proton conductors derived from perovskite-type structure	Venkataraman Thangadurai	University of Calgary
Coffee Break (15:30-16:00)			
Session XIV (Session Chair: Q. Li)			
Invited 15 (16:00-16:30)	Bottom-up electrochemical synthesis of ion exchange membranes for energy storage and conversion devices	Maria Luisa Di Vona	University of Rome Tor Vergata
Invited 16 (16:30-17:00)	Molecular design of hydroxide ion exchange membranes carrying alicyclic quaternary ammonium cations	Patric Jannasch	Lund University
Oral 18 (17:00-17:20)	Ab initio molecular dynamics study of proton transfer mechanisms in nano-confined structures for anion exchange membranes	Tamar Zelovich	New York University
Oral 19 (17:20-17:40)	Governing principles of surface protonics in porous oxides	Einar Vøllestad	SINTEF Industry
Dinner (18:00-19:15)			
Poster Session II (19:30-21:30) P29 – P56			



Perovskite non stoichiometry and proton conduction

John T. S. Irvine

School of Chemistry, University of St Andrews

St Andrews, Fife KY16 9ST, UK

Tel.: +44 1334 463817

jtsi@st-and.ac.uk

Abstract

Perovskite oxides such as barium cerate and barium zirconate are well known as proton conducting host lattices. Perovskite oxides are also known to exhibit formidable defect chemistry variations. Here we consider the influence of a range of defect chemistries upon the ion conducting, electronic, catalytic and electrochemical properties of proton conducting devices. The influence of A site and B site substitution and hence tolerance factor upon chemical stability will be revisited. The dependence of protonic and hole electron conductivities upon oxygen deficiency through aliovalent substitution will be considered. Similarly the role of oxygen vacancies in determining catalytic activity such as in water gas shift will be considered. Recent work on emergent nanoparticles will be presented and the influence of defects created by substitutions considered. The occurrence and influence of A-site deficiency and oxygen excess chemistries will also be considered.



Hydration thermodynamics and lattice site basicity of proton conducting and mixed conducting oxides

Tor S. Bjørheim,¹ Maximilian Hoedl,² Eugene Kotomin,² Rotraut Merkle,² and Joachim Maier²

1) Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway.

2) Max-Planck Institute for Solid State Research, Heisenbergstrasse 1, Stuttgart, Germany

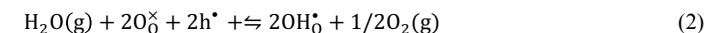
torsb@smn.uio.no

Abstract

The extent of hydration of acceptor doped proton conducting oxides, typically described by dissociative hydration



has been correlated to various materials properties such as cation electronegativity and is argued to reflect the oxides' basicity.^{1,2} The reaction is however amphoteric; lattice oxygen ions are protonated while oxygen vacancies are hydroxylated, suggesting that the extent of hydration rather is governed by the basicity of the lattice oxygen ions – and the acidity of the oxygen vacancies. Recently a number of mixed conducting perovskites with redox-active and typically more acidic elements on the perovskite's B-site have been shown to protonate according to



indicating that the hydration properties of *e.g.* novel cathode materials can be tailored by optimizing the oxide ion and vacancy basicity/acidity.

In this contribution we introduce the oxides' proton and hydroxide affinity (PA and HA) as a measure of the oxide ion basicity and vacancy acidity, respectively, and show how these parameters can be determined from first principles DFT calculations. The PA and HA, and thermodynamics of Eq. 1 are calculated for a selection of binary and perovskite structured oxides, and discussed in relation to the oxide's electronic, structural and bonding properties. The calculated affinities for the binary oxides generally follow the expected periodic trends, and are shown to correlated with the position of the O2p bonding states, rather than traditional correlation parameters such as the oxygen ion charge density. Lastly, the site acidity/basicity in model Co-based layered/double perovskites is evaluated and the relationships between the hydration/protonation properties and the atomic and electronic structure of such materials are discussed.

The research leading to these results has received funding from the Research Council of Norway (Grant n° 272797 “GoPhy MiCO”) through the M-ERA.NET Joint Call 2016.

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The microscopic model of ac conductivity in solid acids and the Jonscher law

Tomasz Masłowski

The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology

al. Powstańców Warszawy 6
35-959 Rzeszów, Poland

Tel.: +48 178651276
Fax: +48 178541114
tmaslowski@prz.edu.pl

Abstract

The question of the origin of the Jonscher power law [1] is aimed. For this purpose the one dimensional numerical model of solid acids consisting of rigid, rotating rods connected by hydrogen bonds is considered as a model of ac conductivity. The model assumes the Grotthuss mechanism for proton diffusion and its evolution in time is realized by means of the kinetic Monte Carlo method. The similar model was previously used to explain dc conductivity under varying pressure for solid acids [2] and the crystalline anhydrous proton conductor with heterocyclic compounds [3]. The model is able to reproduce the Debye behaviour of conductivity arcs in the complex impedance plane. The agreement of the results with the Jonscher power law is discussed and the Jonscher exponent is calculated. The exponent dependence on the hydrogen bond parameters as well as on pressure is analysed. The polarizability of the sample is also taken into account and its consequences for conductivity are presented.

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Radiation-grafted hydroxide-conducting anion-exchange polymer electrolytes for alkali membrane fuel cells

Lianqin Wang, Julia Ponce-González, Rachida Bance-Souahli, Daniel K. Whelligan, and John R. Varcoe

Department of Chemistry, The University of Surrey

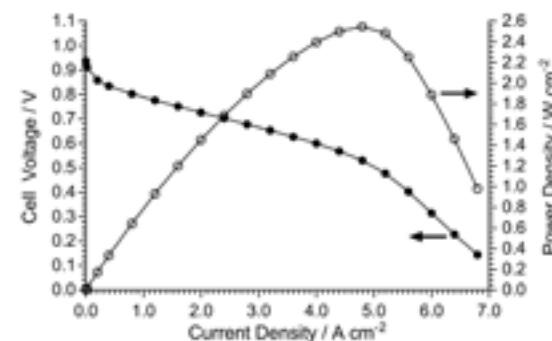
Guildford, United Kingdom
Tel.: +44 1483 686838

j.varcoe@surrey.ac.uk

Abstract

This presentation will discuss the current state-of-the-art in the development of highly conductive, high performance radiation-grafted anion-exchange polymer electrolytes for use in applications such as alkali membrane fuel cells. Anion-exchange membranes have been produced with hydroxide anion conductivities of 200 mS cm^{-1} and alkali degradation rates of < 7% over 500 h of testing (80°C in 100% relative humidity environments).

The figure shows the current state-of-the-art H_2/O_2 alkali membrane fuel cell performance at 80°C (PtRu/C anode and Pt/C cathode) when containing radiation-grafted anion-exchange polymer electrolyte components. Peak power densities of > 1 W cm^{-2} can also be achieved at $T > 60^\circ\text{C}$ with the use of non-Pt electrocatalysts (Pd-based anodes and non-PGM cathodes).



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Molecular engineering of hydroxide ion conducting polymer electrolyte membranes

Chulsung Bae

Department of Chemistry & Chemical Biology, Rensselaer Polytechnic Institute

110 8th Street, Troy, New York 12180
United States
Tel.: 1-518-276-3783
Fax: 1-518-276-4887
baec@rpi.edu

Abstract

Recently, anion exchange membrane (AEM) fuel cell has attracted attention as a clean energy technology device to convert chemical energy into electric energy. AEM fuel cells have several advantages, such as fast kinetics and non-precious metal catalysts. However, AEMs that have desired properties (e.g. high hydroxide conductivity, thermochemical stability at high pH for durable operation, and convenient synthetic process) are not commercially available yet. New material developments by designing of new polymer backbones, side chain functional groups and new anion conductive groups have been extensively investigated over the past decade. Several research groups have reported that a long side chain between polymer backbone and quaternary ammonium head group is helpful for enhancing micro-phase separation based on thermochemical stable backbone. In this study, I will present the effects of polymer structures on the membrane morphology, properties and fuel cell performance. To better understand polymer structure–membrane property relationships, aromatic polymers with different quaternary ammonium head groups, tether chain lengths, polymer backbone were prepared and their properties were evaluated. In addition to the fundamental study, how high performance AEMs can be produced in a kilo gram scale by cost effective processes will be presented.



Multiscale water transport in model alkaline anion exchange membranes investigated by quasi-elastic neutron scattering

Jan-Patrick Melchior and Niina H. Jalarvo

Neutron Scattering Division, Oak Ridge National Laboratory

Oak Ridge, TN, U.S.A. 37831

melchiorj@ornl.gov

Abstract

Alkaline Membrane Fuel Cells, employing Anion Exchange Membranes (AEM) as hydroxide conducting electrolyte, provide a potentially more cost-effective alternative to established Proton Exchange Membrane Fuel Cells. AEMs consist of a polymer phase with cationic sidegroups and a percolating aqueous domain through which ions are conducted. A recent study of long range water diffusion and conductivity showed that for well hydrated AEMs hydroxide conductivity tops that of all other ions [1]. Structural hydroxide diffusion enables efficient transfer of negative charge between neighboring water molecules in a series of localized events [2]. At lower water contents corresponding to fuel cell operational conditions, however, conductivity is drastically reduced. Structural diffusion brakes down and water diffusion is impeded in the increasingly narrow aqueous domain. The equivalent decrease of water diffusion in proton exchange membranes has been studied for a number of materials and depends on the membrane's chemistry and domain morphology. Additionally, a strong dependence of the water diffusion coefficient on the length and timescale it is being measured on was shown [3]. We show the first multiscale diffusion measurements for alkaline AEMs and discuss the evolution of the water diffusion coefficient from the local to the long-range length scale. Measurements were conducted through time-of-flight (TOF) and high-resolution backscattering (BS) quasi-elastic neutron scattering (QENS) and evaluated using the novel data treatment suite ICEMAN/Climax developed at ORNL.

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Dual weight gain upon hydration of MIEC perovskites

Ragnar Strandbakke,¹ Tor S. Bjørheim,¹ Aleksandra Mielewczyk-Gryn,² Sebastian Wachowski,² Iga Lewandowska,² Maria Gazda,² Maria Balaguer,³ Jose M. Serra,³ Magnus H. Sørby,⁴ and Truls Norby¹

- 1) Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway.
- 2) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza street s11/12, 80-233 Gdańsk, Poland
- 3) Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n.46022 Valencia, Spain
- 4) Department for Neutron Materials Characterization, Institute for Energy Technology, NO-2027 Kjeller, Norway

Tel.: +47-22840660
ragnarst@smn.uio.no

Abstract

Hydration of some La-containing Co-based perovskites and double perovskites is characterized by an initial fast mass gain followed by a much slower and larger weight increase. The latter process has equilibrium times of typically five days for a pre-calcined powder at 400 °C, accounting for around 80% of the total weight gain. Dehydration exhibits the same initial fast weight drop and a following slow weight loss. We hypothesize that the initial hydration changes the lattice so as to induce a slower secondary process. If the secondary process was a second hydration, dehydration would still be fast when water vapour was removed. This is however not the case, hence the secondary process must reflect another reaction. The exchange of oxygen is pronounced in these mixed conducting cobaltites, and we believe that hydration changes the degree of cation order, which in turn alters oxidation thermodynamics. In double perovskites with the general formula $A^I A^{II} B_2 O_{6-\delta}$, oxygen vacancies are formed to compensate for the size mismatch between Ba at A^I and a lanthanide (Ln) at A^{II} . The result is an increased Co radius, which accounts for most of the size compensation. At 300 °C, tetragonal $BaLaCo_2O_{6-\delta}$ (BLC) shows a δ of 0.1 [1], $Ba_{1-x}Gd_{0.8-y}La_{0.2+x+y}Co_2O_{6-\delta}$ with $x = y = 0$ (BGLC1082) shows a δ of 0.35 [2] and $BaGdCo_2O_{6-\delta}$ (BGC) shows a δ of 0.5 [3]. BGLC1082, exhibiting an intermediate oxidation of Co with respect to BLC and BGC, is shown to hydrate at high temperatures [4]. While hydration of BGC is limited, hydration of BGLC decreases with increasing x and increases with increasing y, before it returns to near zero at $x = 0$, $y = 0.8$ (BLC). Regarding the fast and slow mass exchange, we suggest that as hydration affects local structure and, in turn, preferred Co oxidation states, a reorganization of La with respect to Ba or Gd may be induced. As such, local domains of BLC (ordered or disordered) and BGC or local cation disorder may be formed, affecting overall oxidation thermodynamics. The result is that mass exchange in varying pH_2O and constant pO_2 may be misinterpreted as only hydration when it could rather be a mix of hydration and oxidation. DFT calculations are utilized to establish formation energies of protonic defects and oxygen vacancies at favourable hydration sites surrounding Gd/La, thermogravimetry is used to determine hydration – and/or oxidation – upon isothermal switches between wet and dry atmospheres, and activation energies for fast and slow processes are used as indicators of hydration and oxidation induced by cation diffusion.

The research leading to these results has received funding from the Research Council of Norway (Grant n° 272797 “GoPHy MiCO”) through the M-ERA.NET Joint Call 2016.

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Polymer electrolyte membranes + covalently bound photoacid dye molecules = photovoltaic action

William White,¹ Christopher D. Sanborn,¹ Margherita Taddei,¹ Simon Luo,¹ Eric Schwartz,² David M. Fabian,¹ Leanna Schulte,¹ Lawrence A. Renna,¹ and Shane Ardo^{1,2}

- 1) Department of Chemistry, University of California Irvine
- 2) Department of Chemical Engineering and Materials Science, University of California Irvine

University of California Irvine, Irvine, CA 92697-2025, USA

Tel.: 949-824-3796
ardo@uci.edu

Abstract

Many electrochemical technologies require ion-conducting polymer electrolytes. These polymers are passive in that electric bias across them drives ion migration in the thermodynamically favored direction.¹ Recently, my group engineered two important features into ion-selective polymer membranes to introduce the active function of photovoltaic action and demonstration of an ionic solar cell. These features were covalent bonding of photoacid dyes to the polymers such that absorption of visible light liberated protons, and polymers with charge-selective contacts to facilitate separation and collection of H^+ and OH^- .^{2,3} The most effective designs join a monopolar cation-selective polymer to a monopolar anion-selective polymer to form a bipolar membrane whose electrostatics and thermodynamics mimic those of a rectifying semiconductor pn-junction diode. Illumination from either side of a photoacid-modified bipolar membrane resulted in photoinduced deprotonation of photoacids followed by charge separation in a direction dictated by the built-in electrostatic asymmetry in the polymers.

Performance optimization is underway to increase the state-of-the-art voltage to beyond 120 mV and state-of-the-art current to beyond 100 $\mu A/cm^2$. The aim of these efforts is to gain a strong fundamental understanding of dye and material function using a variety of techniques. These include simulations of photoacid dye kinetics and drift-diffusion generation-recombination membrane physics using custom finite-element numerical models; pulsed-laser spectroscopies to elucidate light-driven mechanisms of ion transfer and transport; photoelectrochemical characterization to assess whether observations adhere to standard solar cell models; and optical, electron, and ion microscopies to elucidate materials morphology and function.

Collectively, these photo-responsive polymers represent a new class of functional materials that use light to trigger changes in local pH and/or electrostatic potential. These local changes can be used to affect macroscopic processes such as direct solar desalination of salt water, or triggering redox chemistry or chemical catalysis.

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Computational prediction of long distance hydride diffusion based on concerted hydride and oxide ion migration

Ryoji Kanno,^{1,2} Yuki Iwasaki,¹ Naoki Matsui,¹ Kota Suzuki,^{1,2} Yoyo Hinuma,^{3,4} Masao Yonemura,⁵ Genki Kobayashi,^{6,7} Masaaki Hirayama,^{1,2} and Isao Tanaka^{4,8}

- 1) Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
- 2) All-Solid-State Battery Unit, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
- 3) Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan
- 4) Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, 1-2-1, Sengen, Tsukuba 305-0047, Japan
- 5) Neutron Science Laboratory (KENS), Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
- 6) Department of Materials Molecular Science, Institute for Molecular Science, National Institute of Natural Sciences, 38 Nishigonaka, Myodaiji, Okazaki, Aichi, 444-8585, Japan
- 7) SOKENDAI (The Graduate University for Advanced Studies), 38 Nishigonaka, Myodaiji, Okazaki, Aichi, 444-8585, Japan
- 8) Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

Tel.: +81-45-924-5401
Fax: +81-45-924-5401
kanno@ecchem.titech.ac.jp

Abstract

The discovery of pure hydride conduction in La_2LiHO_3 [1] motivates pursuit of further improvement in hydride conductivity. We therefore investigated a family of analogous compounds with the same K_2NiF_4 -type structure, namely Ln_2LiHO_3 ($\text{Ln} = \text{La}, \text{Pr}, \text{or Nd}$, crystal structure in figure). A proposed anion conduction mechanism is migration of anions at an axial site of the perovskite units to another adjacent axial site [1-2]. However, there are two axial sites in La_2LiHO_3 , which are $2b$ and $2d$ sites that are occupied by H and O, respectively (see figure). Jumping of hydride ions directly from a $2b$ site to another $2b$ site is unrealistic because of the long distance between these sites.

We therefore propose a concerted migration scheme where migration of both hydride and oxide ions are necessary to attain long-distance diffusion of only hydride ions in this family of materials. Possible diffusion paths when vacancies are introduced in $2b$ and $2d$ sites will be discussed together with the predicted activation barrier based on first principles calculations and the nudged elastic band method.

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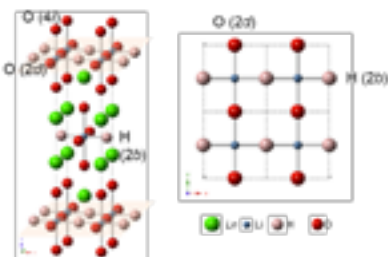


Figure. (left panel) Crystal structure of K_2NiF_4 -structure Ln_2LiHO_3 and (right panel) layer of axial anion sites and Li taken perpendicular to the c -axis.



Humidity and carbon dioxide stable solid state proton conductors derived from perovskite-type structure

Venkataraman Thangadurai

Department of Chemistry, University of Calgary
2500 University Drive NW, Calgary, T2N 1N4 Canada

Tel.: 1 403 210 8649
Fax: 1 403 289 9488
vthangad@ucalgary.ca

Abstract

Acceptor-doped perovskite-type ABO_3 ($\text{A} = \text{Sr}, \text{Ba}$; $\text{B} = \text{Zr}, \text{Ce}$) oxides have been studied as solid-state proton conductors (SSPCs) to replace Nafion membrane in proton exchange membrane fuel cells (PEMFCs) [1]. SSPCs exhibit several advantages over Nafion, including high proton conductivity under low humidity and high chemical stability at elevated temperatures, thus, allowing replacement of expensive Pt electrocatalysts with inexpensive metal oxides. The proton conduction mechanism in acceptor-doped perovskites occurs due to the presence of oxygen vacancies, which are formed by aliovalent substitution at B-sites [2,3]. Ba-based perovskites typically exhibit higher proton conductivities compared to Ca and or Sr analogues, but the chemical stability in CO_2 shows the opposite trend due to higher basicity [4]. The nature of A and B site cations play a critical role in determining the chemical stability of perovskites. Here, we report synthesis and characterization of novel chemically stable perovskite-type SSPCs for intermediate temperature solid oxide fuel cells [5].

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Bottom-up electrochemical synthesis of ion exchange membranes for energy storage and conversion devices

Maria Luisa Di Vona^{1,2} and Philippe Knauth^{2,3}

- 1) University of Rome Tor Vergata, Dep. Industrial Engineering, 00133 Roma, Italy
- 2) International Associated Laboratory (L.I.A.): Ionomer Materials for Energy (Aix-Marseille University, University of Rome Tor Vergata, CNRS) France/ Italy
- 3) Aix Marseille University, CNRS, Madirel (UMR 7246), Marseille, France

Tel.: +390672597184
divona@uniroma2.it

Abstract

Electrochemical deposition is a powerful and versatile technique for the preparation of thin and conformal solid ionomers directly on electrodes, particularly with complex shapes, such as nanostructured electrodes.

The main requirement for a high performance separator is the highest possible single ion conductivity by the electrochemically active ions. At the same time, a high chemical and mechanical stability is mandatory for solid electrolytes in order to guarantee a long life and safe operation.

These requirements drive our development work: we use aromatic polymers as base, given their excellent mechanical properties, which are decisive for a high durability of the separators. The single-ion conductivity is assured by grafting of the counter-ions on the polymer chain.

In this invited talk, we will address cation and anion-conducting separators.

For cation-conducting membranes, we use sulfonate groups grafted on the ionomer chain. These ionomers can be used for proton exchange membrane fuel cells and Li batteries.¹⁻²

Anion-conducting membranes contain quaternary ammonium as fixed groups.³ These ionomers can be applied for example in hydroxide exchange membrane fuel cells.

The talk will present the electrochemical synthesis procedures and the relevant structural, microstructural and electrical properties of the ionomers, including relevant data of applications.

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Molecular design of hydroxide ion exchange membranes carrying alicyclic quaternary ammonium cations

Thanh Huong Pham,¹ Joel S. Olsson,¹ and Patric Jannasch^{1,2}

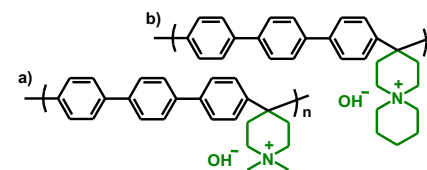
- 1) Department of Chemistry, Lund University P.O. Box 124, SE-22100 Lund, Sweden
- 2) Institute of Technology, University of Tartu, Nooruse 1, 50411 Tartu, Estonia

Tel.: +46 46 2229860
Fax: +46 46 222

patric.jannasch@chem.lu.se

Abstract

Intense research efforts are currently directed towards the synthesis and studies of durable anion exchange membranes (AEMs) with the aim to develop alkaline fuel cells and electrolyzers able to operate efficiently without platinum metal group catalysts [1]. The grand challenge is to identify and synthesize polymeric AEM materials with the necessary chemical and thermal stability. Studies of different small cationic model compounds have revealed that aliphatic mono- and spirocyclic quaternary ammonium (QA) cations have a very high alkaline stability, most probably because the constrained ring conformations increase the transition state energy of the degradation reactions [2]. We have previously reported on the functionalization of poly(phenylene oxide) with different cycloaliphatic QA cations attached via flexible alkyl spacers [3]. In a different approach, we have recently designed, synthesized and studied polyelectrolytes containing *N*-spirocyclic cations, including poly(*N,N*-dimethylpiperidinium)s [4] and *N*-spirocyclic quaternary ammonium ionenes ("spiro-ionenes") [5]. In addition, our group very recently reported on the preparation and properties of poly(arylene piperidinium)s as a new class of high-performance AEM directly accessible from commercially available and quite inexpensive starting materials (Scheme 1) [6]. In the current presentation we will discuss molecular design principles, synthetic procedures and important structure-property relationships of these new polymer electrolyte materials.



Scheme 1. Poly(arylene alkylene)s with pendant piperidinium (a) and *N*-spirocyclic quaternary ammonium cations (b).

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***Ab initio* molecular dynamics study of proton transfer mechanisms in nano-confined structures for anion exchange membranes**

Tamar Zelovich,¹ Zhuoran Long,¹ Michael Hickner,² Stephen J. Paddison,³ Chulsung Bae,⁴ and Mark E. Tuckerman^{1,5,6}

- 1) Department of Chemistry, New York University (NYU), New York, New York 10003, United States
- 2) Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, 16802, United States
- 3) Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States
- 4) Department of Chemistry and Chemical Biology, New York State Center for Polymer Synthesis, Rensselaer Polytechnic Institute, Troy, New York 12180, United States
- 5) Courant Institute of Mathematical Sciences, New York University (NYU), New York, New York 10003, United States
- 6) NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshan Rd. North, Shanghai 200062, China

tamizilo@gmail.com

Abstract

The development of reliable, cost-effective polymer architectures for use as anion-conducting membranes is an important challenge facing emerging electrochemical device technologies. A key ingredient to characterize the main design principles lies in the fundamental understanding of the hydroxide diffusion mechanisms. Recently, nano-confined structures have become a popular tool for exploring the functionalities of anion exchange membranes (AEMs). The water structure under nano-confinement is diverse, controlled by the shape and size of the confining volume and the nature of the boundaries. It is expected that the hydroxide diffusion mechanism would change dramatically from that in bulk solution and therefore the distinct character in different AEM cell constructions should be studied. To this end, we employ fully atomistic *ab initio* molecular dynamics calculations to obtain a molecular level understanding of the mechanisms of hydroxide solvation and transport in different chemical and geometrical environments. To mimic the complicated AEM environment, our theoretical model contains carbon nanotubes and graphane bilayer structures to which select cationic groups are attached. The cation groups are then surrounded by water and hydroxide ions up to experimentally-relevant ratios. Parameters to be varied include the number of water molecules solvating the system, the cation spacing, and the cell geometry.



Governing principles of surface protonics in porous oxides

Einar Vøllestad,¹ Sindre Ø. Stub,² Per Martin Rørvik,¹ and Truls Norby²

- 1) SINTEF Industry, Oslo, Norway
- 2) Department of Chemistry, University of Oslo, Norway

Tel.: +47 41107628
enar.vollestad@sintef.no

Abstract

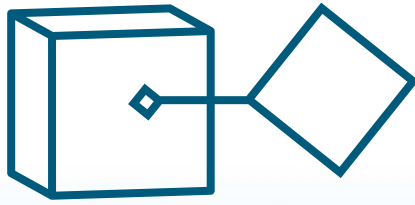
Surface protonics – the transport of protonic charge carriers along ionic surfaces – provides enhanced proton conductivity in porous oxide matrices at low temperatures and high relative humidity. This has been shown to have significant importance for many catalytic and electrochemical applications such as the promotion of catalytic methane reforming¹ and ammonia production.² The formation of physisorbed water layers on the surface of the porous ceramics in humid atmospheres provides a medium for fast proton diffusion and conduction, similar to the water channels of a polymeric proton conductor. This contribution aims to elucidate some of the fundamental governing principles and underlying thermodynamic parameters of surface protonics, using YSZ and doped TiO₂ as oxide matrices.

The nature of the proton diffusion is found to be highly dependent on both the acid-base behaviour of the oxide surface as well as the thickness of the water layer. As the relative humidity exceeds 60%, the water layer changes from an "ice-like" structure to a "water-like" structure, and the proton transport mechanism changes from structural diffusion (Grotthuss) to vehicular diffusion of hydrated protons. This coincides with a reduction in the activation energy as both the dissociation enthalpy and the enthalpy of mobility are reduced as the water layer thickness is increased.³ Similar effects are observed by altering the surface acidity of the oxide by aliovalent doping; donor dopants enhance the surface acidity and reduce the enthalpy of dissociation resulting in an increased surface proton conductivity.⁴

We also present evidence of two well-separated time constants for surface protonic conduction by impedance spectroscopy, which we assign to transport on grain surfaces and transport across grain boundaries intersecting the surface.⁵ The latter can be understood in terms of charge carrier depletion by the positive core charge of the grain boundary intersecting the surface and penetrating the adsorbed water layer.

These findings are finally summarized to give a general perspective of the prospects of surface protonics in applications, and how it can relate to – and have synergistic effects with – polymeric proton conducting systems.

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FRIDAY
SEPTEMBER 21ST



Friday



Friday (21/9/18)

Presentation	Abstract Title	Presenter	Affiliation
Session XV (Session Chair: J. Irvine)			
Keynote 7 (8:30-9:10)	Electrochemistry at the metal-electrolyte-gas interface of solid-acid proton conducting electrolytes	Sossina M. Haile	Northwestern University
Invited 17 (9:10-9:40)	Functional stability of carbon nanomaterials in solid acid fuel cell electrodes	Aron Varga	Leibniz Institute of Surface Engineering
Oral 20 (9:40-10:00)	Universality of low-temperature proton conduction in superprotonic conductors	Haruyuki Takahashi	Ibaraki University
Coffee Break (10:00-10:30)			
Session XVI (Session Chair: T. Bjorheim)			
Invited 18 (10:30-11:00)	Intermediate temperature steam electrolysis using BZCY and SZCY proton conducting perovskites	Hiroshige Matsumoto	Kyushu University
Oral 21 (11:00-11:20)	Oxygen ionic conductivity and chemical diffusivity in $\text{BaCe}_{0.6}\text{Y}_{0.2}\text{Zr}_{0.2}\text{O}_3$ investigated by the Hebb-Wagner polarization method	T. Miruszewski	Gdańsk University of Technology
Oral 22 (11:20-11:40)	Proton conducting ceramics for metal supported solid oxide cells	R. Wang	Lawrence Berkeley National Laboratory
Closing Remarks & Announcements			
Lunch (12:00-13:00)			



Electrochemistry at the metal-electrolyte-gas interface of solid-acid proton conducting electrolytes

Sossina M. Haile

Department of Materials Science and Engineering, Northwestern University

2220 Campus Drive, Cook Hall, Evanston, IL U.S.A. 60208-3109

Sossina.haile@northwestern.edu

Abstract

Fuel cells operating at intermediate temperatures are promising alternatives to combustion engines because of their fuel flexibility, high efficiency, and compatibility with inexpensive interconnect materials. Solid acid fuel cells (SAFCs), in particular, offer the advantage of operation at temperatures near 250 °C using an electrolyte, CsH₂PO₄, that is truly solid and supports fully anhydrous proton transport. Such a fuel cell is intolerant to high concentration of impurities, and can be easily operated on alcohol fuels. Here we review the status of our scientific understanding of electrochemical phenomena in SAFCs and their technological standing.



Functional stability of carbon nanomaterials in solid acid fuel cell electrodes

Felix P. Lohmann Richters, Olga Naumov, Maximilian Wagner, Daniel Krötschel,
Sergej Naumon, Bernd Abel, and Aron Varga

Leibniz Institute of Surface Engineering

Permoserstraße 15, 04318 Leipzig, Germany

Tel.: +49 341 235 3364

Fax: +49 341 2313

aron.varga@iom-leipzig.de

Abstract

Most high performance electrodes of solid acid fuel cells include carbon nanomaterials.¹ Graphite flakes, carbon black, and/or carbon nanotubes have been used as current collector, catalyst support or catalytically active material. This brings high catalyst utilization, low catalyst loadings and low electrode impedances to levels that are competitive with more established polymer electrolyte membrane fuel cells (PEMFCs).

However, a key challenge when utilizing carbon nanomaterials in fuel cell electrodes is long-term stability. The harsh thermal and chemical environment present in cathodes for example, leads to degradation reactions, material loss, ultimately causing loss of interconnectivity, catalyst detachment, etc.

With a combined computational-experimental approach, we investigate degradation reaction mechanisms of carbon nanomaterials at solid acid fuel cell cathode conditions. Doping and/or surface functionalization has been performed with plasma treatment, MeV electron or ion beam irradiation.² Electrochemical experiments together with surface analytics allow us to develop models for degradation reaction that are corroborated with results from DFT calculations.^{3,4} Effective strategies for stabilizing carbon nanostructures e.g. by depositing conductive oxide coatings are presented, bringing this technology further towards commercial viability.

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Universality of low-temperature proton conduction in superprotonic conductors

Haruyuki Takahashi,¹ Ryohei Nonaka,¹ Takahiko Murakami,¹ and Yukihiro Yoshida²

¹) Graduate School of Science and Engineering, Ibaraki University
Frontier Research Center for Applied Atomic Sciences, Ibaraki University

²) Nakanarusawa 4-12-1, Hitachi 316-8511, Japan
Shirakata 162-1, Tokai 319-1106, Japan

Tel.: +81-294-38-5236

Fax: +81-294-38-5236

haruyuki.takahashi.ssilab@vc.ibaraki.ac.jp

Abstract

In our previous study, it was proved that the proton conduction in the supercooled superprotonic phase of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ shows the non-Arrhenius temperature dependence in low temperature. The proton conductivity was described by the Vogel-Tammann-Fulcher (VTF) equation. The parameter T_0 in the VTF equation was estimated to be 190 K. The VTF-type temperature dependence is often seen in the viscosity for the glass-forming liquid. The T_0 is called the ideal glass transition temperature and known to be about 30 K lower than the glass transition temperature obtained by the thermal analysis or the thermal expansion. In the superprotonic phase of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, the stepwise thermal anomaly, the jump of thermal expansion and the change of dielectric susceptibility are observed at 220 K, that is 30 K higher than T_0 derived from the proton conductivity [1]. Hereafter the transition temperature obtained by the thermal analysis is abbreviated to T_g . These results suggest that the glass-transition-like phenomenon exists in the superprotonic conductors.

Low-temperature proton conduction in three types of proton conductors, several phosphate composites, a hydrate and the Nafion, has been investigated to verify the universality of glass-transition-like behavior in the superprotonic conductors. The proton conductivity for the phosphate composites shows the VTF-type temperature dependence. Obtained VTF parameter T_0 is around 160 K in all the composites. T_g was observed at around 190 K. In the ambient atmosphere, T_0 and T_g were observed at around 120 and 160 K, respectively. T_g correlates with T_0 in both cases. T_g for the same sample changes from 160 to 190 K depending on the humidity surrounding of the sample. It is obvious that the water uptake in the sample affects T_g . It was verified that a phosphate monohydrate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and the Nafion also show the VTF-type proton conduction. The superprotonic conduction of hydroxides has been investigated. The non-Arrhenius proton conduction for KOH in the low-temperature region has been reported [2]. The proton conductivity of KOH also gives T_0 . The glass-transition-like behavior for the proton conduction was observed in all of the superprotonic conductors examined. The hydrogen bond breaking and reformation is inevitable for the translational proton motion. Therefore the superprotonic conductors are considered to be a fragile supercooled liquid state in the hydrogen-bonded system. In conclusion, the proton conductivity and other physical properties in low temperature are important to understand the proton conduction mechanism of the low- and the intermediate-temperature superprotonic conductors.

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Intermediate temperature steam electrolysis using BZCY and SZCY proton conducting perovskites

Kwati Leonard,¹ Young-sung Lee,¹ Issei Okuzaki,² and Hiroshige Matsumoto¹

¹) International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University

²) Department of Hydrogen Energy Systems, Graduate School of Engineering, Kyushu University

744 Motooka, Nishi-ku, Fukuoka 819-0395 Japan

Tel.: +81-92-802-6705

Fax: +81-92-802-6706

matsumoto@i2cner.kyushu-u.ac.jp

Abstract

Steam electrolysis is characterized by high energy conversion efficiency compared to low temperature PEM and alkaline water electrolysis, and thus is useful for hydrogen production particularly from renewable energy. Proton conducting perovskites are studied to apply to steam electrolysis for intermediate-temperature operation. We have reported so far $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ (SZCY541) and $\text{BaZr}_{0.44}\text{Ce}_{0.36}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY(54)_{8/92}) to be suitable as the proton-conducting electrolytes for steam electrolysis, having both sufficient conductivity, e.g. $1.44 \times 10^{-2} \text{ S cm}^{-1}$ in wet 1 % H_2 at 600 °C in BZCY(54)_{8/92}, and acceptable stability in steam at operation temperatures. In this paper, our state-of-the-art steam electrolysis performance using these electrolyte materials is reported and challenges existing for their practical use is discussed.

Fig. 1 shows the i - V characteristics and H_2 evolution rates of a steam electrolysis experiment conducted with BZCY(54)_{8/92} with different thickness at 600 °C. A cell terminal voltage of 1.45 V at a current density of 500 mA cm^{-2} with Faradaic efficiency of ~ 0.82 was obtained (T : 12 μm). From these quantities, the electric power necessary for producing 1 Nm^3 of H_2 is calculated to be 4.2 kWh.

Electronic leakage seen in Fig. 1 (b), Ohmic resistance higher than that estimated from the original conductivity, and so on are the challenges and are discussed with experimental data.

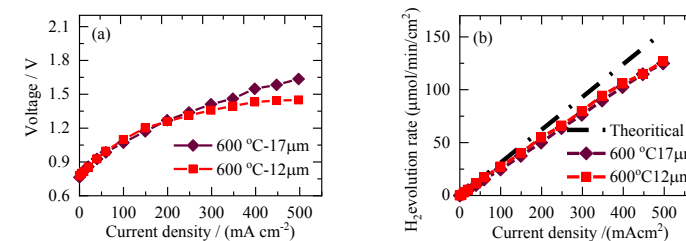


Fig. 1 (a) i - V characteristics and H_2 evolution rates of a steam electrolysis experiment (BZCY(54)_{8/92} with different thickness at 600 °C)(K. Leonard, et al., submitted to *J. Mat. Chem. A*)

This work was supported by the Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "energy carrier" (Funding agency: JST) and by World Premium International Research Center Initiative (WPI), MEXT Japan.



Oxygen ionic conductivity and chemical diffusivity in $\text{BaCe}_{0.6}\text{Y}_{0.2}\text{Zr}_{0.2}\text{O}_3$ investigated by the Hebb-Wagner polarization method

T. Miruszewski, K. Dzierzgowski, P. Winiarz, K. Zagórski, S. Wachowski,
A. Mielewczyk-Gryn, and M. Gazda

Center of Nanotechnology A, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology

Narutowicza street 11/12, 80-233 Gdańsk, Poland
Tel.: +48 58 348 66 12
tadeusz.miruszewski1@pg.edu.pl

Abstract

It is challenging to measure the ionic conductivity of Triple Conducting Oxides (TCOs) with a high electron transfer number. Direct measurements of the partial conductivity of minority charge carriers were proposed by M. H. Hebb [1] and C. Wagner [2]. Originally, this technique has been applied for measurements of a partial electronic conductivity in ionic conductors whereas its application to the opposite case like measurements of the partial ionic conductivity of materials with high electronic transfer number is still problematic [3]. In such a system with a three mobile charge carriers (oxygen ions, electrons and protons), under a non-steady state condition a chemical diffusion of oxygen ions and electrons takes place, whereas in a steady state, only one type of carriers (oxygen ions) can be transferred through a TCO and all the others (electrons and protons) are totally blocked by a mixed blocking electrode.

The aim of this work was to determine simultaneously the partial oxygen ionic conductivity (σ_o) and chemical diffusion coefficient (D_{chem}) of $\text{BaCe}_{0.6}\text{Y}_{0.2}\text{Zr}_{0.2}\text{O}_3$ (BCYZ) by the means of DC Hebb-Wagner method with an electron and proton mixed blocking electrode (YSZ). Acceptor-doped BaCeO_3 - BaZrO_3 solid solution is an interesting system due to its wide applicability in various electrochemical devices. $\text{Ba}(\text{Ce}, \text{Zr}, \text{Y})\text{O}_3$ material, at high $p\text{O}_2$ in dry conditions, becomes a mixed electronic and oxygen ion conductor with an electron transfer number $t_{\text{el}} \approx 0.5$ [4]. A small constant current was applied to the system and time dependence of voltage drops $U(t)$ across the dense BCYZ and YSZ samples were recorded both in a non-steady and steady-state condition between 600 and 800°C in dry and wet air ($p\text{O}_2 \approx 0.21$ atm.). Moreover, impedance spectroscopy method was also used in order to analyse the kinetics of oxygen transition through the interfaces in the proposed system. The theoretical model for the experimental setup was described and used for determination of an oxygen ions conductivity and chemical diffusion coefficient.

This work is supported by project no. 2016/23/B/ST5/02137 founded by National Science Centre, Poland.

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Proton conducting ceramics for metal supported solid oxide cells

Ruofan Wang, Conor Byrne, and Michael C. Tucker

Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
1 Cyclotron Rd, Berkeley, CA 94720, USA

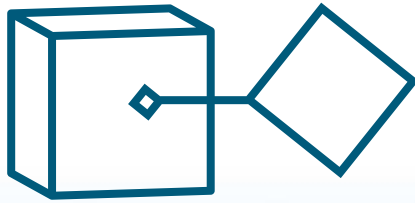
Tel.: +1 (510) 486-5635
ruofanwang@lbl.gov

Abstract

Proton-conducting solid oxide cells (H-SOCs) have attracted extensive attention over the past several years. Compared to conventional high temperature solid oxide cells (typically operated at 700 – 900 °C), H-SOCs can be operated at intermediate temperatures (400 – 600 °C) due to the high ionic conductivity of the proton-conducting ceramic electrolyte in this temperature range. Efforts have been widely made in the development of H-SOCs, but most of the developed cells were either electrode or electrolyte supported, which may limit the cell application to stationary operation. As a new generation design of solid oxide cells, metal-supported cell configuration has the potential to bring H-SOCs into mobile and intermittent applications, thanks to its high mechanical strength, good redox stability, and excellent thermal cycling resistance [1, 2]. However, little literature on developing metal-supported proton conducting solid oxide cells (MS-H-SOCs) is available, and focuses on pulsed laser deposition fabrication of the electrolyte layer [3, 4]. In this study, we investigate the alternative co-sintering route for fabricating MS-H-SOCs.

To incorporate proton-conductors into metal-supported cell configuration through co-sintering fabrication, a key factor is that the proton conductors must be compatible with reducing atmosphere sintering, as the porous metal substrate can not be fired in oxidizing atmosphere. In this work, candidate proton-conducting ceramics including perovskite-type oxides $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCY), $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ (SZCY), and $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ (BCN), pyrochlore-type oxides $\text{La}_{1.95}\text{Ca}_{0.05}\text{Zr}_2\text{O}_{7-\delta}$ (LCZ) and $\text{La}_2\text{Ce}_2\text{O}_7$ (LCO), and acceptor doped rare-earth ortho-niobates $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ (LCN) were synthesized via solid state reactive synthesis or sol-gel synthesis. These ceramics were sintered at 1450 °C in 2% H_2 -Ar environment, and their key characteristics such as phase formation (by X-ray diffraction), sintering property (by dilatometry), and proton conductivity were examined. Chemical compatibility of proton conductor with Fe-Cr alloy was also studied using scanning electron microscopy and energy-dispersive X-ray spectroscopy. This paper will discuss the viability of these ceramics as electrolyte materials for metal-supported proton-conducting solid oxide cells, and fabrication of cells via co-sintering.

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SESSION 1 POSTERS



Governing principles in hydration of mixed conducting oxides: Structure and hydration of $\text{BaLnCo}_2\text{O}_{6-\delta}$

Sebastian Wachowski,¹ Iga Lewandowska,¹ Magnus H. Sørby,² Maria Balaguer,³ Tor S. Bjørheim,⁴ Maria Gazda,¹ Jose Serra,³ Ragnar Strandbakke,⁴ Truls Norby,⁴ Aleksandra Mielewczyk-Gryń¹

- 1) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland
- 2) Department for Neutron Materials Characterization, Institute for Energy Technology, NO-2027 Kjeller, Norway
- 3) Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n.46022 Valencia, Spain
- 4) Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway.

Tel.: +48 58 348 66 12
sebastian.wachowski@pg.edu.pl

Abstract

Proton Ceramic Fuel Cells (PCFCs) and Electrolyzers (PCEs) are highly efficient electrochemical energy converters utilizing – or producing – both hydrogen and hydrogen-based fuels. The performance of PCFCs and PCEs is currently limited by the positive electrode (positrode) functionality, which relies on the functional properties of mixed protonic and electronic conducting ceramics. Cobaltites with ordered perovskite structures, with the general formula of $\text{BaLnCo}_2\text{O}_{6-\delta}$, are promising candidate materials for positrodes. Hydration of - and transport properties in – oxides, in general, depend on the defect structure, which in turn can be influenced by order-disorder transitions on both cation and anion sublattices. Therefore, identifying the structural properties underpin the understanding of mixed protonic-electronic conductivity. The layered perovskites can adapt different structures, depending on the ionic radius of the lanthanide and the oxygen content, starting from cubic perovskite (space group Pm-3m) to different types of layered perovskites, for instance tetragonal (P4/mmm) or orthorhombic (Pmmm) type, in some cases with superstructures. This study aims at identifying the principle governing the relation between structural properties of ordered perovskites and hydration of the material. The structure of $\text{BaLnCo}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb or Dy}$) has been studied by the means of synchrotron X-ray Powder Diffraction and Neutron Powder Diffraction in order to obtain a detailed description of possible protonic defect and oxygen vacancy sites in the cobalt, barium or the lanthanide layers. The structural data have been combined with Density Functional Theory simulations to identify preferential sites for oxygen vacancies formation. Oxygen deficiency of the compounds has been studied by the means of thermogravimetry, thermally programmed reduction and iodometric titration. Finally, for all of the compounds hydration has been measured via thermogravimetry. The combination of all of these techniques allows to identify the relation between the structural properties, preferred defect sites, and the hydration thermodynamics.

This work is a part of GoPHY MiCO project and authors would like to express their gratitude to M-era.Net consortium for support. The Polish contribution was supported by the European Commission and National Science Centre, Poland within M-era.Net initiative (project no 2016/22/Z/ST5/00691).



Hydration stability of mixed conducting layered oxides

Maria Balaguer,¹ Mateusz Tarach,¹ Ragnar Strandbakke,² Tor S. Bjørheim,² Aleksandra Mielewczyk-Gryn,³ Sebastian Wachowski,³ Iga Lewandowska,³ Magnus Helgerud Sorby,⁴ Maria Gazda,³ Truls Norby,² and Jose M. Serra¹

- 1) Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n.46022 Valencia, Spain
- 2) Department of Chemistry, University of Oslo, FERMIØ, Gaustadalléen 21, NO-0349 Oslo, Norway.
- 3) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza street s11/12, 80-233 Gdańsk, Poland
- 4) Department for Neutron Materials Characterization, Institute for Energy Technology, NO-2027 Kjeller, Norway

Tel.: +34-3877800
mabara@itq.upv.es

Abstract

Protonic ceramic fuel cells (PCFCs) enable direct electrochemical conversion of hydrogen to electricity with high energy efficiency and fuel utilisation. Their advantage regarding solid oxide fuel cells (SOFC) is that they produce water on air side electrode avoiding dilution of fuel. Moreover, reduction of working temperatures (400–600 °C) improves stack durability. However, the decrease in temperature also affects the catalytic activity of the electrodes, being especially limited in the case of the cathode. Cathode materials suitable for operation at reduced temperature must exhibit high catalytic activity for the oxygen reduction reaction (ORR), and high values of the surface exchange coefficient, while being known as mixed ionic-electronic conductors (MIECs).

Ordered double perovskite cobaltites with the general formula $\text{BaLnCo}_2\text{O}_{6-\delta}$, (where Ln is a lanthanide or a combination of lanthanides) are promising candidate materials for the air electrodes. By doping the perovskite structure, the local chemical properties may be tailored. The double perovskites can arrange in different symmetries (from cubic Pm-3m, to tetragonal P4/mmm or orthorhombic Pmmm) depending on the ionic radius of the lanthanide and the oxygen content. Thus, the incorporation of water in the lattice, present in the electrode may affect the structure stability or symmetry of the double perovskites.

For PCFCs, along with the microstructural stability during the thermal cycles or long-term operation, the stability of air electrodes in highly humid atmospheres is also required. A screening on the system $\text{A}^{1\text{A}}\text{Co}_2\text{O}_{6-\delta}$ is a complementary task in the GoPHY MiCO project, which aims to disclose the governing principles in hydration of mixed conducting oxides. The tests study the stability of these double perovskites in cathode working conditions. The double perovskites were submitted to several stability test at temperatures within 300 and 600 °C. Cathode operation water partial pressures (0.5 bar) and increasing total pressures were also studied. XRD measurements before and after exposing double perovskite powders to a series of high water partial pressures and high temperature indicate the ability to maintain the pristine structure and set the possible stability limits of the materials.

The research leading to these results has received funding from the National Research Agency (APCIN-2017-125 “GoPHY MiCO”) through the M-ERA.NET Joint Call 2016.



Applying a machine learning-based selection procedure to study defects in BaZrO_3 grain boundaries with DFT calculations

Tarjei Bondevik,¹ Ole Martin Løvvik,^{1,2} and Truls Norby¹

- 1) Centre for Materials Science and Nanotechnology, University of Oslo, Norway
- 2) SINTEF Materials Physics, Oslo, Norway

FERMIØ, Gaustadalléen 21, NO-0349 Oslo, Norway

Tel.: 0047 476 06 320
tarjei.bondevik@smn.uio.no

Abstract

Y-substituted BaZrO_3 (BZY) exhibits high grain interior proton conductivity, but grain boundaries have large resistances attributed to charge carrier depletion in space charge layers next to positively charged grain boundary cores. The positively charged grain boundary cores are believed to originate from the segregation of charged defects. In this work, we perform DFT computations to calculate defect segregation energies in several BZY grain boundaries.

Due to the large number of possible supercells for each grain boundary, it is not straightforward to select which supercell to perform computations on. The obvious choice of mapping out all possible supercells with DFT calculations is ruled out due to high computational cost. An alternative is to guess supercell structure based on intuition, but then low energy supercell structures may be missed. Instead, we apply a Machine Learning-based selection procedure called the Gaussian Process. In this procedure, we apply a statistical model that effectively maps out the most likely regions for low energy supercells. Hence, we are able to find the low energy grain boundary supercells at a low computational cost.

When the low energy supercells are identified, we introduce defects to the grain boundary supercells, and calculate the segregation energies of protons and oxygen vacancies. Both defects segregate towards the grain boundary core, leading to a potential barrier of 0.71 V for the $\Sigma 5$ grain boundary and 0.65 V for the $\Sigma 3$ grain boundary.

This work is part of the nationally coordinated project Functional OXides for Clean Energy Technologies (FOX CET, RCN, 102006684-1), with SINTEF, NTNU and UiO as active partners.

Defect cluster formation in BZY grain boundaries investigated with DFT calculations

Tarjei Bondevik, Tor Svendsen Bjørheim, and Truls Norby

Centre for Materials Science and Nanotechnology, University of Oslo, Norway

FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway

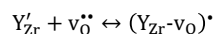
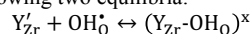
Tel.: 0047 476 06 320

tarjei.bondevik@smn.uio.no

Abstract

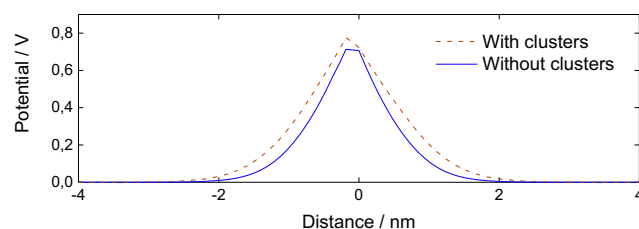
Y-substituted BaZrO₃ (BZY) exhibits high grain interior proton conductivity, but grain boundaries have large resistances attributed to charge carrier depletion in space charge layers next to positively charged grain boundary cores. The positively charged grain boundary cores are believed to originate from the segregation of charged defects.

In this work, we perform DFT computations to calculate defect segregation energies in several BZY grain boundaries. Specifically, we calculate the segregation energies of protons and oxygen vacancies in the grain boundary region. In addition, we study the effect of defect cluster formation with the yttrium dopant, by the following two equilibria:



The formation of both $(OH_O-Y_{Zr})^{\times}$ and $(v_O-Y_{Zr})^{\bullet}$ clusters is energetically favorable in the grain boundary region. This leads to a lower concentration of negatively charged yttrium dopants in the space charge region, while the positive core charge remains largely unaffected. Hence, a wider negative space charge region is needed to fully compensate the positively charged grain boundary core.

Two electrostatic potential profiles with and without cluster formation are shown below, across the (210)[001] grain boundary. The profiles reveal that, when considering cluster formation, the potential barrier across the grain boundary increases, reducing the proton conductivity.



This work is part of the nationally coordinated project Functional OXides for Clean Energy Technologies (FOX CET, RCN, 102006684-1), with SINTEF, NTNU and UiO as active partners.

Solid-state photoelectrochemical cell for wet air electrolysis and hydrogen production

K. Xu,¹ A. Chatzidakis,¹ E. Vøllestad,² Q. Ruan,³ J. Tang,³ and T. Norby¹

1) Department of Chemistry, University of Oslo, SMN, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway

2) SINTEF Industry, Forskningsveien 1, NO-0373 Oslo, Norway

3) Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K.

Tel.: +47-22840693

a.e.chatzidakis@smn.uio.no

Abstract

In this work, a solid-state photoelectrochemical (SSPEC) cell is developed with the use of proton conducting membranes as the electrolyte, hence replacing the traditionally used aqueous electrolyte [1]. The main aim is to design monolithic and easily deployable and transportable devices, and produce hydrogen in rural or areas where grid infrastructure and water sources are scarce or absent. The SSPEC button-like membrane is schematically given in Figure 1.

We have tested two different configurations; one with a Pt/C cathode as an electrocatalyst, and one where the cathode is replaced with an earth-abundant 2D photocathode, g-C₃N₄, forming a tandem photocatalysts configuration. Both configurations were run under purely gaseous conditions, where the anode was supplied with air of 80% relative humidity and the cathode with argon. The tandem configuration showed a three-fold enhancement in the obtained photovoltage (Figure 1) and a steady-state photocurrent density. The mechanism of operation is discussed in view of recent advances in surface proton conduction in absorbed water layers [2]. The presented SSPEC cell provides a new way towards systems of artificial photosynthesis, where the only requirements to make hydrogen are humidity and sunlight.

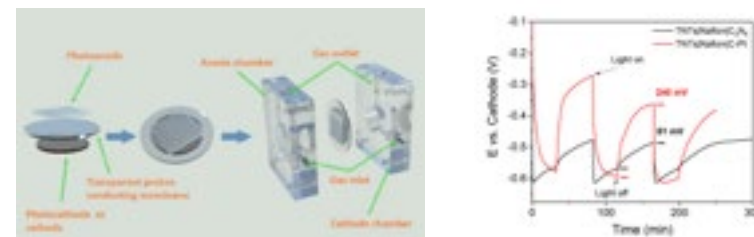


Figure 1: The construction of the button-like SSPEC membrane, as well as its mounting on the custom-made solid-state PEC device for operation under gaseous conditions [left]. Open circuit voltage (OCV) of the two SSPEC configurations under dark (2000 s) and light conditions (1000 s).

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Financial support from the Research Council of Norway (PH2BioCat project 239211 and CO2BioPEC project 250261) is acknowledged.

Design and development of next-generation protonic reactors

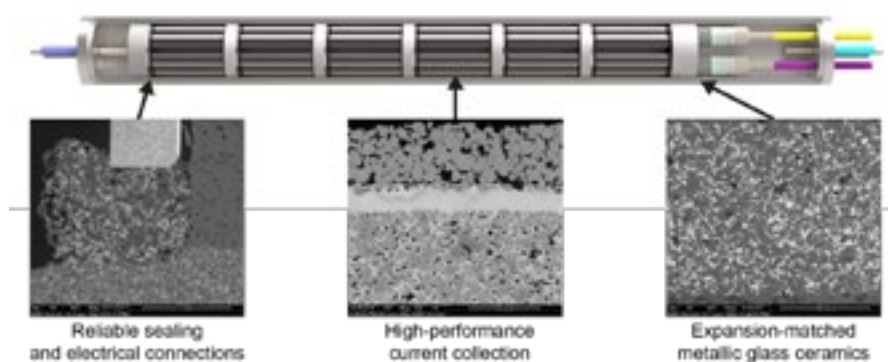
Daniel Clark,^{1,2} Harald Malerød-Fjeld,² Michael Budd,² David Catalán-Martínez,³ Dustin Beeaff,² Jose M. Serra,³ Truls Norby,¹ and Reidar Haugsrud¹

- 1) University of Oslo, Centre for Materials Science and Nanotechnology (SMN), Gaustadalleen 21, NO-0349 Oslo, Norway
- 2) Coorstek Membrane Sciences AS, Gaustadalleen 21, NO-0349 Oslo, Norway
- 3) Instituto de Tecnología Química (Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n, 46022 Valencia, Spain

Tel.: +4792262731
daniel.clark@smn.uio.no

Abstract

Today, more than 50 million tons of hydrogen are produced annually, predominantly through steam methane reforming (SMR) with subsequent water-gas shift (WGS) combined with pressure swing adsorption (PSA) for product separation. Protonic membrane reformers (PMRs) allow for a combination of SMR, WGS, and pressurization of a pure hydrogen product, enabling hydrogen production with a pure CO₂ waste stream. The results suggest that future declining electricity prices could make PMRs a competitive alternative for industrial-scale hydrogen plants integrating CO₂ capture. With the combined use of carbon-sequestering fuels, carbon-negative hydrogen production is possible when integrating CO₂ capture. This work demonstrated a PMR that produces high-purity hydrogen from steam methane reforming in a single-stage process. A BaZrO₃-based proton-conducting electrolyte deposited as a dense film on a porous Ni composite electrode with dual function as a reforming catalyst is used. At 800 °C in single-tube experiments, full methane conversion is achieved and hydrogen is simultaneously compressed electrochemically up to 50 bar. Segment-in-series reactors were constructed demonstrating over 1.2 L/min of produced hydrogen with > 98 % hydrogen recovery. In larger scale commercial protonic reactors, electrical performance of current collection and expansion-matched interconnects is crucial, and this work presents next generation designs implementing novel improvements in current collection, interconnect resistance/stability, and reactor design/fluid-dynamics.



Emergent transport and mechanical behavior in solvent-filled ionomers

Andrew Crothers,^{1,2} Timothy Quah,³ Ahmet Kusoglu,² Clayton Radke,¹ and Adam Weber²

- 1) University of California Berkeley, Department of Chemical and Biomolecular Engineering
- 2) Lawrence Berkeley National Laboratory, Energy Conversion Group
- 3) University of Utah, Department of Chemical Engineering

201 Gilman Hall, Berkeley, CA 94720-1462
Tel.: 510-486-5254
arcrothe@berkeley.edu

Abstract

Solvent-filled ionomer membranes are an important class of low-temperature proton-conductors that combine favorable solution-like ion transport properties with the mechanical stability of a solid. Typically, in these materials the solvent and membrane form a bicontinuous morphology with a solid phase that provides structural integrity and a solvent-filled hydrophilic phase that forms a network of domains, which facilitates solvent and ion transport. The mesoscale properties of the hydrophilic transport network (e.g. domain size, distribution, and connectivity) determine the effective macroscale transport properties of these membranes. Similarly, the topology of the hydrophobic network determines the mechanical properties. Consequently, our hypothesis is that emergent behaviour is an essential descriptor of these materials. We study this idea by simulating solvent and ion transport along with local stress distribution throughout the hydrophilic and hydrophobic phases.

In this work, a resistor and spring network coarse-grains the interconnected hydrophilic and hydrophobic domains to simulate transport and mechanical properties, respectively. A mean-field nanoscale model of the domains parametrizes the Onsager-Stefan-Maxwell resistances of the segments and the topology of the network is consistent with experiments; the mechanical and transport networks are the inverse of each other. The predicted modulus, diffusion and electroosmotic coefficients, and conductivity agree with measurements.

The model supports the hypothesis that macroscopic properties emerge from the collective behaviour of nanoscale components. For example, the distribution and connectivity of the hydrophilic phase dictates which pathways a species will take across the network. Figure 1 shows this in how the different modes of transport utilize different network pathways and have different effective tortuosities. These findings demonstrate the multiscale nature of solvent-filled ionomers.

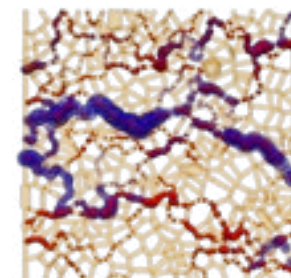


Figure 1. Visualization of modeled water (blue bulbs) and proton (red bulbs) transport through interconnected nanoscale hydrophilic domains (yellow tubes) in PFSA membranes. These simulations describe emergent transport properties in the multiscale membrane morphology.



On the stability of proton conductivity of Aquivion composite membranes loaded with neat or organically modified cerium oxide nanoparticles

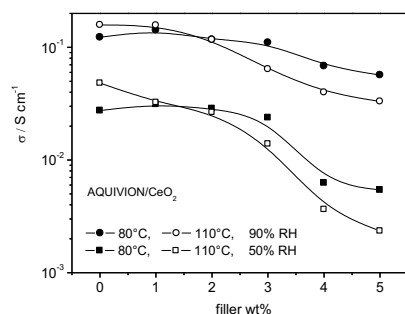
Roberto D'Amato,¹ Anna Donnadio,² and Mario Casciola¹

- 1) Department of Chemistry, Biology and Biothechnologies, University of Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy
2) Department of Pharmaceutical Sciences, University of Perugia, Via del Liceo 1, 06123, Perugia, Italy

roberto.damato@studenti.unipg.it

Abstract

The search for a clean way to produce energy is one of the greatest challenges we face today. Proton exchange membrane (PEM) fuel cells are one of the possible solutions of this problem because they combine high efficiency of energy conversion with zero pollution level. The PEM integrity is one of the most crucial factors affecting the fuel cell lifetime and the PEM degradation remains a critical issue in fuel cell systems. PEMs can suffer from both mechanical degradation, determined by the stress resulting from membrane hydration – dehydration, and chemical degradation due to the presence of radical species, generated by electrochemical or chemical processes during fuel cell operation. The use of radical scavenger species as membrane fillers is a suitable strategy to reduce chemical degradation and, hopefully, to improve the membrane mechanical strength. In the present work we investigated, under different conditions of temperature and relative humidity, the proton conductivity of composite membranes made of a short side chain perfluorosulfonic acid (Aquivion) filled with cerium dioxide based nanofillers. Besides neat CeO₂, the nanofillers include two organically modified oxides whose surface was coated with a fluoroalkylphosphonic acid (C₈F₁₇-C₂H₄-PO(OH)₂) and a fluorobenzylphosphonic acid (C₆F₅-CH₂-PO(OH)₂). The conductivity of the composite membranes was investigated as a function of relative humidity at 80 and 110 °C and, unlike pristine Aquivion, it was found to decay with increasing temperature. In all cases, the conductivity decay increases with filler loading and, for a given loading, is smaller for the membranes filled with organically modified CeO₂. On the other hand, the radical scavenger efficiency of the organically modified fillers is lower than that of neat CeO₂, as shown by the Fenton tests. It was found that the increase in temperature from 80 to 110 °C is associated with a decrease in the membrane IEC, which indicates partial solubilization of the filler particles. These results show that Aquivion membranes filled with CeO₂ based nanoparticles are intrinsically unstable, especially at 110 °C, which prevents their use in PEM fuel cells operating above 80 °C. Since the CeO₂ solubilization is caused by the strong acidic character of the sulfonic groups, a similar behaviour is also expected for other types of PFSA/ CeO₂ composite membranes.



Fabrication of multi layered structures for proton conducting ceramic fuel cells

Wendelin Deibert,¹ Mariya E. Ivanova,¹ Yuanye Huang,² Rotraut Merkle,² and Wilhelm A. Meulenbergh^{1,3}

- 1) Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), D-52425 Jülich, Germany
2) Max Planck Institute für Festkörperforschung, Heisenbergstr. 1, 70569, Stuttgart, Germany
3) University of Twente, Faculty of Science and Technology, Inorganic Membranes, P.O. Box 217, 7500 AE Enschede, The Netherlands

Tel.: +49 2461 618968

Fax: +49 2461 612455

w.deibert@fz-juelich.de

Abstract

Proton conducting ceramic fuel cells (PCFC) offer a large potential in the field of electrical power generation for stationary and mobile applications. Due to the direct conversion of chemical energy into electrical energy PCFC provide high efficiency. One main advantage compared to conventional SOFC is the lower operating temperature of typically 500 – 600 °C which reduces the costs for a PCFC system. The state of the art PCFC electrolyte material is Ba(Zr,Ce,Y)O_{3-d} (BZCY). BZCY has a high bulk conductivity and a high chemical stability especially under humid conditions which occur during the PCFC operation. Additionally, NiO is added as a sintering aid to overcome the poor sinterability of the BZCY. For planar PCFC-cells multi layered ceramic structures are needed. There are different concepts for the fabrication of these structures where the anode supported cell is chosen in this work. This means that the electrolyte layer should be very thin and must be supported by the anode layer. A well known and established fabrication method for ceramic multi layers is the tape casting process.

In this work we show the fabrication of PCFC half-cells consisting of a thin ($\approx 20 \mu\text{m}$) electrolyte layer from BZCY and a support layer consisting of a mixture of the same material and NiO (300 – 500 μm). By exposing the half-cell to reducing atmosphere, metallic Ni is formed in the support layer and serves as the anode for the PCFC. First we describe the synthesis of the BZCY powder and the manufacturing of the tape casting slurry. The powder properties have a crucial impact on the slurry characteristics and the sintering behavior of the layers and have to be controlled very carefully by particle size and BET (specific surface area) measurements. The sintering behavior of the single layers is characterized by an optical dilatometer where we can measure the shrinkage continuously during the heat treatment. With this method the temperature profile to achieve dense electrolyte layers can be adjusted very precisely. The results are supported by SEM-pictures of cross sections. Finally we show how to fabricate a multi layer structure by sequential tape casting and subsequent co-firing of the tapes. A large challenge for the co-firing of ceramic multi layers is usually the bending caused by the different sintering properties of the different layers. Here, the optical dilatometer also helps to develop a suitable sintering program to avoid bending. Additionally the conductivity of the tape-cast electrolyte layers is tested to proof the potential of the developed structures for application as PCFC.

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Polydopamine coated CeO₂: a novel filler to mitigate degradation of perfluorosulfonic acid ionomers

Anna Donnadio,¹ Roberto D'Amato,² and Mario Casciola²

- 1) Pharmaceutical Sciences Department and CEMIN, University of Perugia, Via del Liceo 1, 06123 Perugia, Italy
- 2) Chemistry, Biology and Biotechnologies Department, University of Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

anna.donnadio@unipg.it

Abstract

The chemical degradation of proton exchange membranes (PEM), arising from radical species produced during fuel cells operation, still represents one of the major factors limiting a widespread adoption of fuel cell technology. Incorporation of radical scavengers into the membrane is one of the most common approaches that have been proposed to improve the lifetime of PEM fuel cells. Cerium is a very effective radical scavenger that may be integrated into the membrane as cation Ce³⁺ or as CeO₂ nanoparticles. However, the presence of cerium ions, either incorporated by ion exchange or arising from partial oxide solubilization, leads to a reduction in proton conductivity and performance [1]. Therefore, an alternative approach to Ce³⁺ ion exchange or to addition of neat cerium oxide was investigated. In this work, we studied the impact on membrane properties of polydopamine coated CeO₂ (PDA@CeO₂) as membrane additive, where the surface PDA film is expected to prevent direct interaction between the ionomer sulfonic groups and the oxide surface. Dopamine self-polymerization allowed to form thin, surface-adherent polydopamine films onto CeO₂ nanoparticles that can promote a strong adhesion with the polymer matrix. PDA@CeO₂ nanoparticle aggregates with a diameter of about 150 nm and a uniform shell thickness of about 10 nm were obtained. Composite membranes were prepared by adding 3 and 5 wt% of the PDA@CeO₂ nanoparticles to Aquivion. Fluoride emission, proton conductivity and mechanical properties of the composite membranes were evaluated. The results show that the Aquivion/ PDA@CeO₂ membranes possess good anti-oxidation abilities, good interfacial properties, better mechanical properties than pristine Aquivion membranes and slightly lower chemical stability in comparison with the corresponding Aquivion/CeO₂ composite. Indeed these membranes, subjected to Fenton degradation tests to determine the fluoride emission rate (FER), show that the addition of 3 wt% and 5 wt% of PDA@CeO₂ nanoparticles lowers FER by 78% and 90% respectively, when compared with the neat Aquivion membrane. Moreover, in the relative humidity range 50 – 90%, the Aquivion/PDA@CeO₂ composite membranes are as conductive as neat Aquivion at 80 °C and slightly less conductive at 110 °C.

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Highly durable protonic ceramic fuel cells

Chuancheng Duan,¹ Robert J. Kee,¹ Huayang Zhu,¹ Canan Karakaya,¹ Yachao Chen,¹ Sandrine Ricote,¹ Angelique Jarry,² Ethan J. Crumlin,³ David Hook,⁴ Robert Braun,¹ Neal P. Sullivan,¹ and Ryan O'Hayre¹

- 1) Colorado School of Mines, Golden, CO, USA
- 2) University of Maryland, College Park, MD, USA
- 3) Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
- 4) CoorsTek, Golden, CO, USA

cduan@mines.edu

Abstract

Protonic ceramic fuel cells (PCFCs), like their higher-temperature solid-oxide fuel cell (SOFC) counterparts, offer the possibility to directly utilize both hydrogen and hydrocarbon fuels to produce electricity at > 50% efficiency, with combined heat-and-power efficiencies potentially exceeding 80% (1, 2). Additionally, PCFCs can offer compelling cost and durability advantages vs. SOFCs due to lower operating temperatures and the consequent relaxation in balance-of-plant constraints (2). Despite several encouraging studies suggesting good performance and excellent anti-coking resistance in hydrocarbon-fueled PCFCs (2–4), there have been no systematic studies of long-term durability. Here we present results from comprehensive, long-term testing that firmly establish the excellent coke- and sulfur-tolerance potential of PCFCs. These studies represent more than 19,000 hours of combined PCFC operation at temperatures between 500 – 600 °C using a total of 11 different fuels (hydrogen, methane, domestic natural gas (with and without H₂S), propane, n-butane, i-butane, iso-octane, methanol, ethanol, and ammonia). We demonstrate excellent performance and exceptional durability (< 1.5% degradation per 1000 hours in most cases) across all fuels without any modifications in the cell composition or architecture. Coking is not observed even after thousands of hours of continuous operation at steam-to-carbon (or oxygen-to-carbon) ratios in the vicinity of the thermodynamically predicted carbon deposition region. Finally, sulfur, a notorious poison for both low-temperature and high-temperature fuel cells, does not appear to affect PCFC performance when supplied at levels consistent with commercial fuels: we observe identical performance with sulfur-free domestic natural gas compared to domestic natural gas with 19.5 parts-per-million (ppm) H₂S. In this work, several unique thermodynamic and kinetic aspects of PCFC operation contribute to these exceptional results will be presented.

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Computational stress predictions of chemo-thermal expansions in a PCFC from sintering to operation

Alexis Dubois, Kasra Taghikhani, Sandrine Ricote, John R. Berger,
Robert J. Kee, and Robert J. Braun

Department of Mechanical Engineering, Colorado School of Mines

1610 Illinois Street, Golden, CO, USA

Tel.: 303-273-3650

Fax: 303-273-3602

a_dubois@outlook.com

Abstract

Protonic ceramic fuel cells (PCFCs) have shown potential competitive cost against current technology while operating at 500-600°C with high efficiencies [1]. Although these materials have been demonstrated at the laboratory scale and have the potential to deliver effective performance, the practical development is still in early stages. In addition to electrochemical performance, understanding and controlling mechanical robustness and reliability will be important in scaling to commercially viable technologies. The primary objective of the present study is to predict quantitatively the contribution of thermal stress during the high-temperature manufacturing process and the additional effect of chemical expansion during reduction of the nickel oxide and electrochemical operation of the cell.

The present computational study is based on a 2D Comsol model that includes a reformulation of the Nernst-Planck-Poisson (NPP) including chemo-thermo-mechanical expansion effects. The NPP formulation represents charge-defect transport within dense mixed ionic-electronic conducting (MIEC) materials [2]. The particular focus is on yttrium doped solid solution of barium cerate/zirconate (BCZY). Although the theoretical foundations and modelling approaches are reasonably well developed [3], establishing the physical and chemical parameters needed to predict chemo-thermal-mechanical coupling remains challenging. The present study uses X-ray-diffraction measurements [4] along 3D tomography to determine the needed material properties for the model.

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Structure and properties of doped lanthanum orthoniobates

Kacper Dzierzgowski,¹ Sebastian Wachowski,¹ Piotr Jasiński,² Maria Gazda,¹ and Aleksandra Mielewczyk-Gryn¹

1) Department of Solid State Physics, Faculty of Applied Physics and Mathematics,

2) Department of Biomedical Engineering, Faculty of Electronics, Telecommunications and Informatics,
Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

Tel.: +48 58 348 65 30

kacper.dzierzgowski@pg.edu.pl

Abstract

Rare earth orthoniobates are ceramic materials belonging to ABO_4 group. Since 1961 these materials have been widely studied due to their interesting ferroelectric and optical properties. In the last decade, their ionic conductivity was investigated. One of the main potential applications of these materials are solid oxide fuel cells. At room temperature RENbO_4 has a monoclinic structure while at high temperature (e.g. in LaNbO_4 above 500 °C) phase transition to tetragonal structure occurs [1, 2]. Figure 1 shows monoclinic and tetragonal unit cells of RENbO_4 .

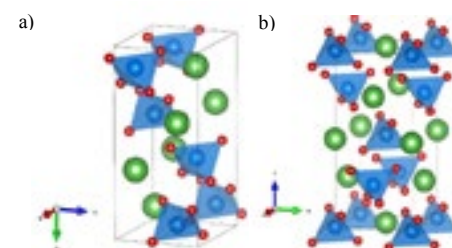


Fig. 1. Unit cell of RENbO_4 : (a) monoclinic, (b) tetragonal. Blue atoms: Nb, green: RE, red: O [3].

In this work properties of $\text{La}_{1-x-y}\text{Ca}_x\text{Tb}_y\text{NbO}_4$ and $\text{La}_{1-x-y}\text{Ca}_x\text{Pr}_y\text{NbO}_4$ are presented. The samples were prepared by solid state reaction method. Structural and electrical properties were characterized by X-ray diffraction method, scanning electron microscopy and electrochemical impedance spectroscopy. The influence of rare earth metal and calcium doping on the properties of the materials has been analysed and discussed.

This research is supported by the Ministry of Science and Higher Education Poland (grant no. 0513/IP2/2016/74).

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Silk fibroin membranes as protonic conductors

Tomás Almeida,¹ Paula C. Barbosa,² Ana B. Timmons,² and Filipe M. L. Figueiredo¹

- 1) CICECO – Aveiro Institute of Materials, Dep. of Chemistry, University of Aveiro
2) 2CICECO – Aveiro Institute of Materials, Dep. of Materials & Ceramic Engineering, University of Aveiro

Campus de Santiago, 3810-193 Aveiro Portugal

Tel.: +351 234 401 464
Fax: +351 234 401 470
lebre@ua.pt

Abstract

Fibroin is the crystalline protein underlying the outstanding mechanical properties of silk, showing strength and toughness comparable or better than some synthetic fibers, such as Kevlar. Silk fibroin is used mostly in biomedical applications, namely in tissue engineering, where it allies the excellent mechanical properties with biocompatibility. However, their ionic transport properties have not been studied so far, and this could pave the way for many other applications, namely in energy conversion technologies such as fuel cells, where materials research has been mostly focused in performance rather than in sustainability.

One reports in this work the preparation of silk fibroin membranes from a regenerated fibroin solution and their systematic study by a battery of tests, including X-ray diffraction, Fourier transform infrared spectroscopy, ion exchange capacity measurements, electron microscopy, thermal analysis, dynamic mechanical analysis, dynamic water vapour sorption analysis, and impedance spectroscopy under variable temperature and relative humidity (RH).

The fibroin was obtained from cocoons of the mulberry silk moth *Bombyx mori* containing 70-80% silk fibroin and 20-30 % of sericin, solubilized and casted in the form of thin membranes. The stability of SF in humid environments depends largely on the structure formed during drying, which must be carried out under controlled conditions of temperature and humidity. Highly crystalline membranes keep full structural integrity in contact with water and can absorb up to 30% of its mass at 25 °C and 98% relative humidity. Dynamic mechanical analysis reveals a material mechanically stable up to *ca.* 150 °C in air atmosphere. The ionic conductivity of pure silk fibroin membranes varies from 6×10^{-7} S.cm⁻¹ at room temperature and 20% RH to about 2×10^{-3} S.cm⁻¹ at 94 °C and 98% RH, with an activation energy in the range 20-40 kJ.mol⁻¹. As a biopolymer, silk fibroin offers potential for further functionalization or improvement allowing application outside of the biomedical field, namely in electrochemical energy conversion and storage.

FCT/MEC is acknowledged for the financial support to CICECO-Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013, POCI-01-0145-FEDER-007679) and to project UniRCell (Ref. SAICTPAC/0032/2015, POCI-01-0145-FEDER-016422), through national funds and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. FCT also supports the individual grant IF/01174/2013.



Electrochemical analysis of high-performance protonic ceramic fuel cells based on a bamboo-structured thin electrolyte

Ho-Il Ji,¹ Sung Min Choi,¹ Hyegsoon An,^{1,2} Hyoungchul Kim,¹
Kyung Joong Yoon,¹ Ji-Won Son,¹ Byung-Kook Kim,¹ Hae-Weon Lee,¹ and Jong-Ho Lee¹

- 1) Korea Institute of Science and Technology, Republic of Korea
2) Hanyang University, Republic of Korea

Tel.: 82-2-958-5521
Fax: 82-2-9585529
hiji@kist.re.kr

Abstract

High-performance and cost-effective fabrications should be simultaneously achieved for practical applications of fuel cells. Unfortunately, protonic ceramic fuel cells (PCFCs), which are considered next-generation solid oxide fuel cells operating at lower temperatures (≤ 600 °C), do not satisfy these requirements. While thin electrolyte and facile electrochemical reactions at electrode/electrolyte interfaces are crucial for cell performance, the thickness of the electrolyte, obtained via cost-effective ceramic processes, is still not satisfactory (currently capable of > 10 μm) and the electrode reaction(s) are yet to be clarified. Here we demonstrate the fabrication of a bamboo-structured thin electrolyte (~ 2.5 μm) of BaCe_{0.55}Zr_{0.3}Y_{0.15}O_{3-δ}, in which less perpendicular grain boundaries exist against the current direction, through a low-cost screen printing method. A high open-cell voltage of 1.10 V ensures that the thin electrolyte is sufficiently dense for gas-tightness, thereby achieving an extraordinary maximum power density of 350 mW/cm² at 500 °C. The electrode reactions are investigated using the distribution of relaxation time (DRT) method based on electrochemical impedance spectroscopy as a function of oxygen partial pressure and hydrogen partial pressure at 500 °C, suggesting that the reaction step, corresponding to the surface diffusion of an adsorbed oxygen to the triple phase boundaries at the cathode, is most probably the main contributor to the overall polarization resistances.

Electrochemical hydrogen pumping using high-temperature polybenzimidazole (PBI) membranes

Fei Huang, Andrew T. Pingitore, and Brian C. Benicewicz

Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA

541 Main Street, Horizon I Bldg, Columbia, SC, 29208
Tel.: 860-617-2355
huang85@mailbox.usc.edu

Abstract

Electrochemical hydrogen pumping was first developed and reported in the 1960s. The basic working principle of the electrochemical hydrogen pump process is that hydrogen molecules are oxidized to protons and electrons within the catalyst layer of the electrode on the anode side. The protons are driven through the ion exchange membrane while the electrons pass through the external circuit to the cathode side. The protons and electrons are recombined in the cathodic compartment to form hydrogen molecules. The overall chemical reactions are described in the following figure. The major difference between this cell and a fuel cell is that the hydrogen pump requires power to complete the chemical reactions instead of generating power. Both low-temperature and high-temperature devices have been investigated for hydrogen purification using this technique. However, the major disadvantages of the low-temperature (< 100 °C) devices based on the perfluorosulfonic acid family of membranes, e.g., Nafion®, are their low tolerance to selected impurities, e.g., carbon monoxide, and the demands of humidification. Therefore, the excellent thermal stability and chemical resistance of polybenzimidazoles (PBI) at high temperature (> 100 °C) when used in fuel cells lead to its great potential in hydrogen pumping applications. Operating at these high temperatures also offers increased Pt catalyst tolerance to fuel impurities and faster electrode kinetics. In this work, PBI membranes have been synthesized via a new sol-gel process which produces phosphoric acid-doped PBI membranes with higher levels of PA and ionic conductivity (> 0.13 S/cm at 180 °C). Various chemistries of PBI have been investigated to understand how the chemistry affects the electrochemical hydrogen pumping performance, including electrical efficiency, power consumption, durability of the MEAs, and the gas purities. The reformat stream containing H₂, N₂, and CO was used to establish the increased utility of hydrogen pumping when using a high-temperature PBI membrane. In addition, the mechanical properties (creep compliance) of these PBI membranes have been studied in order to evaluate their hydrogen pumping performance under the differential pressure conditions.

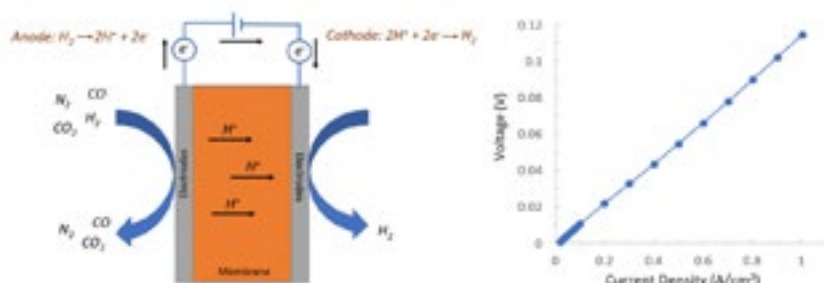


Figure. Schematic diagram of a hydrogen pump and polarization curve operating on pure H₂ at 160 °C.

Proton conducting SOFC/SOEC based on lanthanum scandate

Hikaru Takamata,¹ Fumitada Iguchi,¹ Tatsuya Oyama,² Hisashi Kato,² and Hiroo Yugami¹

1) Graduate School of Engineering, Tohoku University

2) Tohoku Electric Power Co., Inc., Nakayama 7-2-1, Aoba-ku, Sendai, 981-0952, Japan

Aoba 6-6-01, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

Tel.: +81-22-795-6922

Fax: +81-22-795-6923

f_iguchi@energy.mech.tohoku.ac.jp

Abstract

Proton conductors based on lanthanum scandate shows relatively high proton conductivity and chemical stability in intermediate temperature range. Among them, lanthanum scandates doped with strontium over 20 mol % shows higher proton conductivity than $5 \times 10^{-2} \text{ Scm}^{-1}$, and are considered to be potential candidates for an electrolyte of proton conducting solid oxide fuel cells (SOFCs). We already developed anode-supported type cells based on strontium doped lanthanum scandate (LSSC) using a pulsed laser deposition (PLD) method and tested [1]. Those cells consisted of a Ni based anode, a multilayered electrolyte of LSSC and yttrium doped barium zirconate (BZY), and a Pt cathode showed sufficiently low electrolyte resistivity, $R_{\text{electrolyte}} < 0.3 \text{ Wcm}^2$ at 600 °C although total resistivity of the cells were high caused by electrode resistivities. Hence, electrodes, which could adopt fabrication processes based on a PLD method, were required. In addition, protonic SOFCs are required to work as solid oxide electrolysis cells (SOEC) such as steam electrolyzers and chemical reactors at the same time. However, reversible power generation and electrolysis performances of protonic SOFCs based on lanthanum scandate are not reported, yet.

In this study, we attempted to investigate electrodes: materials and architecture using electrolyte supported type cells. Especially, the influence of the surface material of an electrolyte to electrode resistivities was focused because the surface layer was easily changed during a PLD process. Electrodes supported type cells with the surface of 15 mol % yttrium doped barium zirconate, 32.5 mol % strontium and 2 mol % cobalt co-doped lanthanum scandate and 15 mol % yttrium doped barium cerate were fabricated. Reversible electrical properties of those cells were evaluated.

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Hydration/Dehydration mass relaxation for proving decoupled mass transport in proton conducting BaCe_{0.9}Y_{0.1}O_{3-δ}

In-Ho Kim, Yeon Namgung, and Sun-Ju Song

School of Materials Science and Engineering, Chonnam National University

Yongbong-dong, Buk-gu, Gwang-Ju 61186, Republic of Korea
Tel.: +82-625301713
Fax: +82-625301699

www.dlsgh@gmail.com

Abstract

Among many well-known perovskite proton-conducting materials, acceptor-doped barium cerate and barium zirconate (BaCe_{1-x}M_xO_{3-δ}, BaZr_{1-x}M_xO_{3-δ}; M = Y, Yb) have been the most studied materials for application in practical solid-state devices, because they have high proton conductivities at intermediate temperatures (500 – 800 °C). The proton concentration and chemical diffusivity of water in these materials, as functions of thermodynamic parameters, have been investigated for their specimens exposed to sudden changes in water vapor content because of the functionality as solid electrolyte. However, in these proton conductors some recent reports, such as the electrical conductivity relaxation measurements showing a non-monotonic two-fold relaxation behavior and *in situ* optical absorption spectroscopy with impedance spectroscopy, have demonstrated that in the p-type oxidizing regime the proton transport depends on the two decoupled ambipolar diffusivities of proton and hole ($OH_O^{\bullet}$ - $h^{\bullet}$) and ($V_O^{\bullet}$ - $2h^{\bullet}$) pairs. Accordingly, the decoupled mass- and charge-transport theory, which was earlier based on the chemical diffusion of water, has been successfully revised by Yoo et al..

In this work, we tried to prove the non-stoichiometric water diffusion by conducting mass relaxation experiments during hydration/dehydration process by thermogravimetric analysis (TGA) for 10-mol Y-doped BaCeO₃ under various thermodynamic conditions. The mass relaxation experiments using TGA were uniquely performed to clearly confirm the reaction of decoupled diffusion of hydrogen and oxygen upon hydration and dehydration in a p-type conductor. The equilibrium constant also of the overall nonstoichiometric water uptake reaction as the ration of charge carrier concentrations based on the concentrations of decoupled hydrogen and oxygen could be calculated by the weigh change experiments.

The mass relaxation measurements are performed by TGA under various humidity conditions (Dry, $-3.0 \leq \log(p_{H_2O}/\text{atm}) \leq -1.6$) at a constant oxygen partial pressure ($\log(p_{O_2}/\text{atm}) = -1.00 \pm 0.01$). The decoupled ions participated in hydration/dehydration reactions were proven to be at different ratios from the result introduced by the $8R_m$ function. The enthalpy and entropy of non-stoichiometric hydration reaction, which considers each ratio of charge-carrier species, were -155.9 ± 10.0 kJ/mol and -123.1 ± 9.3 J/mol·K, respectively.

Proton transport characteristics in proton conducting phosphate glass under wide p_{O_2} range

Tomohiro Ishiyama,¹ Takuya Yamaguchi,¹ Haruo Kishimoto,¹ Katsuhiko Yamaji,¹ Satoshi Tsukuda,² Junji Nishii,³ Toshiharu Yamashita,⁴ Hiroshi Kawazoe,⁴ and Takahisa Omata²

- 1) National Institute for Industrial Science and Technology (AIST), Tsukuba, Japan
- 2) Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan
- 3) Research Institute for Electronic Science, Hokkaido University, Japan
- 4) Kawazoe Frontier Technologies Corporation, Yokohama, Japan

1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
Tel.: +81-29-861-2470
Fax: +81-29-861-4540
tomohiro.ishiyama@aist.go.jp

Abstract

We have reported fabrication of the proton conducting phosphate glasses by alkali-proton substitution (APS). The glass with the composition of 36H_{0.5/2}-4NbO_{5/2}-2BaO-4LaO_{3/2}-4GeO₂-1BO_{3/2}-49PO_{5/2} (36H-glass) exhibits high proton conductivity around 300 °C and its proton transport number evaluated in hydrogen concentration cell is unity [1,2]. Proton transport number is an important physical property when the proton conductor is used as an electrolyte in a fuel cell devices. It is important that the proton transport number is unity not only in the low p_{O_2} condition(fuel side) but also the high p_{O_2} condition(air side) for minimizing electrical leakage through the electrolyte in the fuel cell operation. In this study, the mean transport number of protons in the 36H-glass prepared by APS technique were evaluated by electromotive force (emf) of the water vapor concentration cell in air ($p_{O_2} = 0.21$ atm) atmosphere. The platinum porous electrodes were attached to both surfaces of the glass electrolyte and the emf was measured at 280 °C under flowing air with various water vapor pressure, p_{H_2O} . p_{H_2O} was fixed at 1.1×10^{-2} atm (dew point = 8 °C) at one surface of the electrolyte and varied between 2.8×10^{-2} atm (d. p. = 23 °C) to 3.4×10^{-4} atm (d.p. = -34 °C) at the opposite surface. The theoretical emf was calculated with the following equation.

$$V_{emf} = \frac{RT}{4F} \left[t_{ion} \ln \left(\frac{p_{O_2}^I}{p_{O_2}^{II}} \right) - 2t_{H^+} \ln \left(\frac{p_{H_2O}^I}{p_{H_2O}^{II}} \right) \right]$$

When p_{O_2} is identical at both surfaces, the former term can be ignored. The emf should be proportional to $\ln \left(\frac{p_{H_2O}^I}{p_{H_2O}^{II}} \right)$ as shown in Figure 1. The dashed line in the figure denotes emf under the assumption of $t_{H^+} = 1$. The observed emfs are given in the figure by red dots. The observed emfs matched well with theoretical estimations. From these results, it was shown that the proton transport number is unity even under the high p_{O_2} condition, and the proton transport number does not depend on p_{O_2} . The proton transport mechanism in the phosphate glass will be discussed comparing those of the other proton conducting materials.

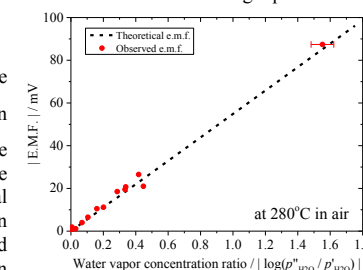


Fig. 1 Emfs for the water vapor concentration cell in air atmosphere

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Preparation of anion exchange membranes via Friedel-Crafts bromoalkylation on aromatic polymers

Jong Yeob Jeon, Angela D. Mohanty, Ding Tian, Sungmin Park, Chang Y. Ryu, and Chulsung Bae

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute

110 8th Street, Troy, New York 12180, United States

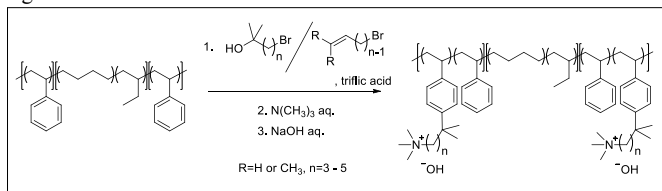
Tel.: 518-276-3783

Fax: 518-276-4887

baec@rpi.edu

Abstract

As a promising alternative to the high cost proton exchange membrane fuel cells, anion exchange membrane fuel cells (AEMFCs) have gained a lot of attention in recent years. Their high pH operating condition allows the use of non-precious metal catalysts and less expensive metal hardware.¹ Recently, a power density of 1.0 W cm⁻² has been achieved for AEMFC approaching close to that of PEMFC. Anion exchange membrane (AEM) is a key component for AEMFCs, and it requires high hydroxide conductivity, low water swelling and robust chemical and mechanical stabilities. Herein, we report a new synthetic route for AEMs using Friedel-Crafts bromoalkylation on aromatic polymers followed by quaternization. Elastic polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) is selected as backbone because it has good mechanical and alkaline stability. Moreover, its nanoscale phase separated morphology can help ion conducting channel formation and improve ion conductivity. There have been several reports of SEBS AEMs synthesized by chloromethylation. However, this conventional method generally results in low levels of functionalization or gelation. In this presentation, the acid catalyzed Friedel-Crafts bromoalkylation achieved a maximum of 95% degree of functionalization (DF), and it allowed to control the DF and cation tether length conveniently by changing the molar ratio and the structure of the bromoalkylated substrate. The new SEBS AEMs were investigated by measuring ion exchange capacity, water uptake, anion conductivity and alkaline stability. Among them, SEBS-C₃-TMA-0.8 (tether length, n = 3; 80% of PS functionalization) had the highest IEC (1.62 mequiv. g⁻¹) and OH⁻ conductivity of 93 mS cm⁻¹ at 80 °C in water. The SEBS AEMs showed good alkaline stability preserving the IEC and OH⁻ conductivity after alkaline stability test in 1 M NaOH at 80 °C for 500 h. This convenient polymer functionalization approach can serve as a versatile synthetic method to prepare stable aromatic AEMs with a wide range of chemical structures going forward.



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Synthesis, crystal structure, and ionic conductivity of hydride ion conducting oxyhydrides in Ln₂LiHO₃ system

Ryoji Kanno,^{1,2} Yuki Iwasaki,¹ Naoki Matsui,¹ Kota Suzuki,^{1,2} Yoyo Hinuma,^{3,4} Masao Yonemura,⁵ Genki Kobayashi,^{6,7} Masaaki Hirayama,^{1,2} and Isao Tanaka^{4,8}

- 1) Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
- 2) All-Solid-State Battery Unit, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
- 3) Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan
- 4) Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, 1-2-1, Sengen, Tsukuba 305-0047, Japan
- 5) Neutron Science Laboratory (KENS), Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
- 6) Department of Materials Molecular Science, Institute for Molecular Science, National Institute of Natural Sciences, 38 Nishigonaka, Myodaiji, Okazaki, Aichi, 444-8585, Japan
- 7) SOKENDAI (The Graduate University for Advanced Studies), 38 Nishigonaka, Myodaiji, Okazaki, Aichi, 444-8585, Japan
- 8) Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

Tel.: +81-45-924-5401

Fax: +81-45-924-5401

kanno@chem.titech.ac.jp

Abstract

The oxyhydride La₂LiHO₃ with the K₂NiF₄-type structure shows pure hydride conductivity in the anion sublattice¹. The hydride ion conduction mechanism in this system is still being debated. In this study, oxyhydrides Ln₂LiHO₃ (Ln=La, Pr, Nd, Sm) were synthesized under high pressure (2 GPa) to elucidate the phase formation limit of the K₂NiF₄-type structure as well as changes in electrochemical properties when the Ln element is varied.

A hydride ion conducting K₂NiF₄-type phase was obtained for Ln = La, Pr, and Nd, suggesting a threshold tolerance factor of approximately 0.83. In contrast, Sm₂LiHO₃ showed a totally different diffraction pattern; the main phase comprises of diffraction peaks assigned to Sm₂O₃. Structural analysis using neutron powder diffraction data revealed the crystal structure of the obtained materials as shown in Fig. 1. The choice of Ln element modifies the anion arrangement in axial sites of the perovskite unit and also strongly affects the hydride conductivity. Nd₂LiHO₃, which has space group *Immm* where ~0.7% H sites (2b) contain vacancies and ~5% of O sites (2d) are occupied by H instead, showed the highest conductivity at 280°C of 2.2×10⁻⁵ S cm⁻¹ with an activation energy of 62.3 kJ mol⁻¹.

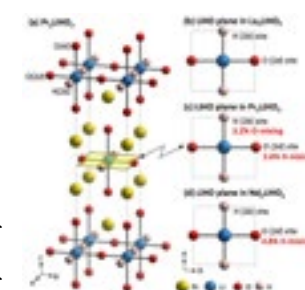


Figure 1. (a) Crystal structure of Pr₂LiHO₃ calculated by Rietveld-refinement of neutron powder diffraction data, and the LiHO plane at *z* = 0.5 of (b) La₂LiHO₃, (c) Pr₂LiHO₃, and (d) Nd₂LiHO₃. Each LiHO plane is a perovskite layer containing Li and axial anion sites. Dashed lines indicate the unit cell.

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Processing ceramic proton conductors by sequential tape casting for use in steam electrolysis

Kwati Leonard,^{1,2} Wendelin Deibert,² Mariya E. Ivanova,² Wilhelm A. Meulenberg,² Tatsumi Ishiraha,¹ and Hiroshige Matsumoto¹

1) International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University
744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

2) Team H₂ permeable membranes, Institute of Energy and Climate Research IEK-1
Forschungszentrum Jülich GmbH

Tel.: +81928026706

Fax: +81928026706

kwati@i2cner.kyushu-u.ac.jp

Abstract

Steam electrolysis using proton conducting electrolytes (PC-SOECs) are potentially the most efficient and cost-effective option for hydrogen production at intermediate temperatures (400–600 °C) from renewable sources. These class of electrolytes are particularly favored for their relatively high ionic conductivities within this regime. Although significant progress has been made with small scale laboratory type PC-SOECs devices, a significant challenge has been upscaling robust and affordable planar type devices for commercialisation. The fabrication of such multilayered devices *via* a tape casting process requires careful control of shrinkages of individual layers to prevent warping, cracking or even delaminating during sintering.

In this contribution, Y-doped BaZrO₃-BaCeO₃ (BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}) thin films were successfully prepared by sequential tape casting on a high shrinkage NiO-SZr_{0.5}Ce_{0.4}Y_{0.1}O_{2.95} cathode. Suitably high densification (1350 °C/5h) was achieved without the addition of sintering aids, which is unprecedented with this state-of-the-art composition. The low sintering behavior of the green tapes as well as the obtained final microstructure are direct results of careful control over casting parameters, such as slurry viscosities, thicknesses of individual layers, temperature and time scheme for firing. The shrinkage and microstructural evolution of the layers were investigated with an optical dilatometer. Current-voltage characteristics and hydrogen evolution rates measured in the temperature range 500–600 °C (Fig.1), demonstrate excellent performance and durability. A typical Ba_{0.5}La_{0.5}CoO_{3-δ}/BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}(20μm)/NiO-SZr_{0.5}Ce_{0.4}Y_{0.1}O_{2.95} cell at 600 °C with 80 % steam in the anode compartment reached reproducible terminal voltages of 1.5V @ 500 mAcm⁻², achieving ~86 % hydrogen production efficiency which is among the best PC-SOECs performance reported in literature. Further improvements in efficiency can be expected by a further reduction in film thickness and better optimization of the anode material.

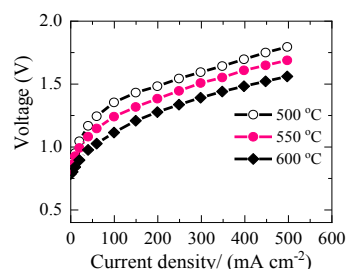


Fig. 1. steam electrolysis I-V curve performance with ~20 μm thick BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9} electrolyte

This work was supported by the Ministry of Economy, Trade and Industry (METI), and by the International Institute for Carbon Neutral Energy Research (WPI-I2CNER) sponsored by the World Premier International Research Center Initiative (WPI), MEXT, Japan.



Scaling behavior and morphology of hydrated Nafion

Hongjun Liu,¹ Sara Cavaliere,² Deborah J. Jones,² Jacques Rozière,² and Stephen J. Paddison¹

1) Department of Chemical and Biomolecular Engineering, University of Tennessee
1512 Middle Drive, Knoxville, TN, 37996-2200 U.S.A.

2) Institut Charles Gerhardt de Montpellier, Agrégats, Interfaces et Matériaux pour l'Energie, UMR 5253 CNRS
Université de Montpellier, 34095 Montpellier Cedex 5, France

Tel.: (865) 974-2026

Fax: (865) 974-7076

spaddison@utk.edu

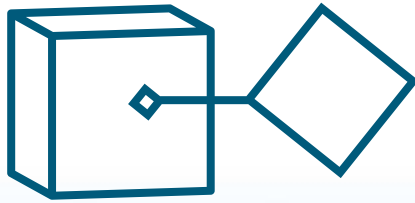
Abstract

The scaling behavior of the conformation and dynamics of mesoscopic models of a polymer melt, Nafion, and hydrated Nafion are investigated with dissipative particle dynamics (DPD) simulations. The scaling behavior of all studied systems generally follows the Rouse theory. For the polymer melt and dry Nafion, increase in chain stiffness slightly shrinks the polymer and leads to slower dynamics with longer polymer relaxation time. The addition of a stiff constraint to five different DPD parameterizations of hydrated Nafion expands the chain conformation, while the repulsion parameter effect on size is secondary. In contrast, softer repulsion predominately dictates faster dynamics of both the polymer and water, and stiffer chains also lead to improved water diffusion to a much lesser extent. Sufficiently long Nafion chains are required to realistically represent the relatively immobile Nafion framework and mobile proton conducting water domain. Direct quantitative cluster size analysis is advocated to characterize the water channel connectivity.

The evolution of the hydrated morphology of Nafion over a range of water contents was quantified through the cluster analysis method. Our findings are in contrast with those solely based on the radial distribution functions (RDFs) where cluster size and separation are approximated by certain characteristics of the RDF. The quantitative cluster analysis along with realistic microscopic images colored by unique IDs leads to a wealth of information on water domain size, shape, and connectivity, which is essential for a mechanistic understanding of proton transport. The percolation threshold of the water domains in hydrated Nafion was found to occur at a hydration level of 5 H₂O/SO₃H. Below the threshold, isolated individual water clusters cannot contribute to the ion transport. Water clusters grow from small aggregates into larger spheres, elongated rods, and branched and twisted cylinders as the hydration level increases. Beyond the threshold, the percolating water network is conspicuously dominant in the morphology. At the higher hydration levels, a larger percentage of the water beads contribute to the polar network and the size and number of nonparticipating clusters gradually diminish. Our work emphasizes the importance of a proper quantitative tool to understand the nature of ion-conducting domains.

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2. Hongjun Liu, Sara Cavaliere, Deborah J. Jones, Jacques Rozière, and Stephen J. Paddison. Scaling Behavior of Nafion with Different Model Parameterizations in Dissipative Particle Dynamics Simulations. *Macromolecular Theory and Simulations*, **2018**, 1800003.



SESSION 2 POSTERS



Highly conductive polybenzimidazole based membranes applied to all vanadium redox flow batteries

Lihui Wang,¹ Andrew Pingitore,¹ Wei Xie,² Zhiwei Yang,² Michael Perry,² and Brian Benicewicz¹

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

2) United Technologies Research Center, East Hartford, Connecticut, USA

541 Main Street, Horizon I Room 232, Columbia, SC 29208

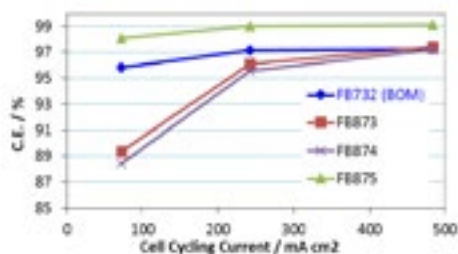
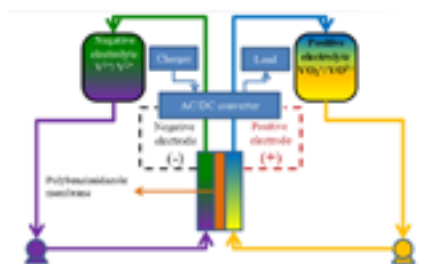
Tel.: 8037770778

Fax: 8037778100

bnice@sc.edu

Abstract

A series of polybenzimidazole (PBI) membranes were synthesized using sol-gel process and modified for all vanadium redox flow batteries (VRFB). These membranes demonstrated not only a high *in-situ* and *ex-situ* stability in concentrated sulfuric acid and in oxidative vanadium (V) solutions but also exhibited high conductivities and low performance degradation during in-cell testing comparing to the ‘conventionally imbibed’ meta-polybenzimidazole (m-PBI) membranes cast from N,N'-dimethylacetamide (DMAc) solutions. The PBI membrane doped with 2.6 M H₂SO₄ shows a proton conductivity of 390 mS/cm at room temperature and VO²⁺ permeability as 2.30E-08 cm²/s. Different strategies were anticipated to close the porous structure of PBI membranes and further decrease vanadium ion permeability while maintaining the high proton conductivity. A VRFB operated with the modified PBI membrane shows over 98% coulombic efficiency under a large range of applied cell cycling current densities from 100 to 450 mA/cm².



Fabrication and evaluation of electrode-supported type fuel cells with proton-conducting lanthanum tungstate

Hiroki Matsuo,¹ Gen Kojima,¹ Yoshio Matsuzaki,² and Junichiro Otomo¹

1) Department of Environment Systems, Graduate School of Frontier Sciences, The University of Tokyo, Japan
5-1-5 Kashiwanoha Kashiwa, Chiba 277-8563, Japan, +81-04-7136-4694

2) Tokyo Gas Co., Ltd. Fundamental Technology Dpt.
1-7-7 Suehiro, Tsurumi, Yokohama, Kanagawa 230-0045, Japan
otomo@k.u-tokyo.ac.jp

Abstract

Proton-conducting solid oxide fuel cells (p-SOFCs) can operate at intermediate temperature (around 600 °C), and water is produced at a cathode side in the cell. Because of these advantages, p-SOFC is one of the key devices which can be expected to exceed the performance of conventional SOFCs. Lanthanum tungstate ($\text{La}_{2-x}\text{W}_{4+x}\text{O}_{54+3x/2}\text{V}_{2-3x/2}$: LWO) is one of the promising electrolyte materials for p-SOFC owing to a high proton conductivity at intermediate temperature and high chemical stability under operating conditions of p-SOFCs. Besides, the amount of oxygen vacancy can be controlled by La/W ratio. In our previous studies [1,2], we synthesized LWO ceramics with various La/W ratio ($6.3 \leq \text{La}/\text{W} \leq 6.7$) and found that the proton conductivity can be enhanced by increasing La/W ratio as a result of the increase in oxygen vacancy concentration. In addition, oxygen partial pressure dependence of the conductivity showed that proton was dominant conduction carrier while hole-electron conduction was well suppressed at 500 – 800 °C.

Because of the high proton conductivity and the low hole-electron conductivity at the operation temperature, LWO is considered to have an ability to achieve a higher power generation efficiency than other conventional proton conducting electrolytes. In this presentation, we report performance of an anode-supported fuel cell using LWO as the electrolyte. The cell was fabricated with the LWO electrolyte and a Ni-10 % Gd-doped CeO_2 (GDC) cermet anode. To avoid chemical reactions between the electrolyte and the electrode, which causes degradation of cell performance, a GDC interlayer was employed. Figure 1 shows the cross sectional SEM and SEM-EDX images of the cell. Although high chemical reactivity between LWO and Ni-based anodes has been reported, we could not find any cation diffusion between them. The cell exhibited an open circuit voltage of 1.00 V in a power generation test at 600 °C, which agrees with that of a theoretical value calculated with theoretical equations [3,4]. This result presents suitability of LWO as an electrolyte for highly efficient p-SOFCs.

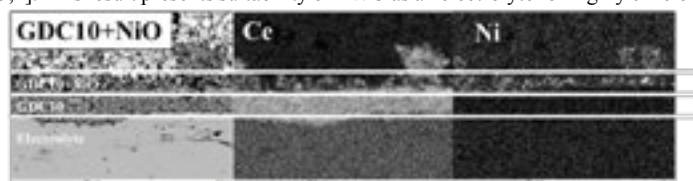


Fig. 1. SEM and SEM-EDX images at the interface between electrolyte and anode.

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Proton uptake and reduction of lanthanum tungstate $\text{La}_{2-x}\text{W}_{4+x}\text{O}_{54+\delta}\text{V}_{2-\delta}$ as a function of La/W ratio and doping

Rotraut Merkle,¹ Yuanye Huang,¹ Joachim Maier,¹ Wendelin Deibert,² Mariya Ivanova,² and Wilhelm A. Meulenberg²

1) Max Planck Institute für Festkörperforschung, Heisenbergstr. 1, 70569, Stuttgart, Germany

2) Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), 52425 Jülich, Germany

Tel.: +49 6891768
r.merkle@fkf.mpg.de

Abstract

Lanthanum tungstates $\text{La}_{2-x}\text{W}_{4+x}\text{O}_{54+\delta}\text{V}_{2-\delta}$ can dissociatively incorporate water into oxygen vacancies [1,2]. While their bulk proton conductivity remains lower than that of $\text{Ba}(\text{Zr},\text{Y})\text{O}_{3-z}$ perovskites applied as electrolyte in protonic ceramic fuel cells, they exhibit advantages for the use as hydrogen permeation membrane [3], e.g. (i) higher n-type electronic conductivity in reducing atmosphere, (ii) good chemical stability versus H_2S , (iii) good sinterability and nonblocking grain boundaries.

In order to improve the transport properties of $\text{La}_{2-x}\text{W}_{4+x}\text{O}_{54+\delta}\text{V}_{2-\delta}$, tungsten can partially be substituted by dopants such as Mo (to increase n-type conductivity) or Nb (to increase the oxygen vacancy concentration). The effect of doping with either Mo or Nb, as well as Mo+Nb co-doping and variation of La/W ratio, on proton uptake is investigated by thermogravimetry. Hydration enthalpies and entropies are extracted. While the proton uptake increases in parallel to the $\text{V}_{\text{O}^\bullet}$ concentration in dry state at low $[\text{V}_{\text{O}^\bullet}]$, deviations from this ideal behavior occur at high $[\text{V}_{\text{O}^\bullet}]$.

The formation of n-type electronic carriers is investigated by TG in reducing conditions. While Mo doping leads to a perceptible conduction electron concentration, Nb or V doping does not significantly increase the reducibility of the material.

Finally, the partial electronic, protonic and $\text{V}_{\text{O}^\bullet}$ conductivities were determined by conductivity measurements under different conditions ($p\text{O}_2$, $p\text{H}_2\text{O}$, T). In contrast to $\text{Ba}(\text{Zr},\text{Ce},\text{Y})\text{O}_3$ perovskites, the grain boundaries in $\text{La}_{2-x}\text{W}_{4+x}\text{O}_{54+\delta}\text{V}_{2-\delta}$ -based materials show negligible blocking.

Funding from BMBF (project Protmem, Förderkennz. 03SF0537C) is acknowledged.

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Structure, water uptake and conductivity studies of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ triple conducting oxides

T. Miruszewski, K. Dzierzowski, P. Winiarz, K. Zagórski, S. Wachowski,
A. Mielewczyk-Gryn, and M. Gazda

Center of Nanotechnology A, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology

Narutowicza street 11/12, 80-233 Gdańsk, Poland

Tel.: +48 58 348 66 12
tadeusz.miruszewski1@pg.edu.pl

Abstract

Triple conducting oxides (TCO) have gained much interest as cathode materials for devices with a proton-conducting electrolyte [1]. These type of materials are a new group of ceramic materials which total electrical conductivity is determined by the presence of three types of charge carriers *i.e.* holes/electrons, oxygen ions, and protons. Designing and understanding structural and charge transport properties of these materials is challenging [2-3]. There are two strategies for designing a triple conducting oxide. The first possibility is to modify an oxide having high electronic conductivity in such a way that its oxygen ion- and proton conductivities increase. The second one is a modification of a mixed proton- and oxygen ion conductor leading to an increase of its electron/hole conductivity [4-5].

The perovskite-type materials (ABO_3) are attracting intense interest for a variety of energy conversion applications. Proton conductivity in a humid atmosphere has been previously reported in many oxides belonging to this material family. For example, acceptor-doped SrTiO_3 and SrFeO_3 perovskites both exhibit hydration [6].

In this work, the structural and electrical transport properties for two groups of materials: $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0 - 1.0$) and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0 - 1.0$) were investigated. Enhanced proton conductivity in these materials was expected due to B-site acceptor doping by Fe and Co. The structural properties of analysed samples were characterized by X-Ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The determination of water uptake was performed by thermogravimetry. The electrical properties and water incorporation were analyzed by a conventional DC Four-wire method (4W) in both wet and dry air with a compensation of $p\text{O}_2$. The protonic conduction mechanism as a function of dopant concentration in $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ was discussed.

This work is supported by project no. 2016/23/B/ST5/02137 founded by National Science Centre, Poland.

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Enhancing conductivity through in situ Cu exsolution from $\text{Ba}_{0.95}\text{Ce}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.14}\text{Cu}_{0.06}\text{O}_{3-\delta}$

Mei Wang, Cristian Savaniu, and John T. S. Irvine

School of Chemistry, University of St Andrews
Fife, KY16 9ST, Scotland, UK

Tel.: +44-77-523-27173
mw222@st-andrews.ac.uk

Abstract

Conventionally, doped barium cerate possesses high proton conductivity in the intermediate temperature range (400 – 700 °C). However, for a given electrolyte, electrochemical performance is largely determined by the electrode process, which requires the electrode with not only high proton conductivity, but also good electronic conductivity and catalytic property. Recently, the in situ exsolution method was proposed to introduce nano-catalysts on perovskite surface by simply reducing the perovskite doped with the certain element on the B-site. After reduction, both electronic conductivity and catalytic property of electrode can be greatly improved. Here, barium cerate zirconate based proton conductor, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.14}\text{Cu}_{0.06}\text{O}_{3-\delta}$ (denoted as BCZYC), was prepared by solid state method. Then, nano-catalyst, Cu, was obtained by reducing the as-prepared BCZYC oxide in 5% H_2/Ar at temperatures in the range 500 – 900 °C for 12 h. Scanning electron microscopy images showed that different size range of particles were achieved not only on the native surface but also the inner surface due to the high mobility of copper. Moreover, the conductivity of the sample increased dramatically after exsolution, which was about 8.45 s/cm at 600 °C. Most interestingly, the material transferred from a semiconductor property to a metallic behaviour after reduction, *i.e.* conductivity increased on cooling. Therefore, the in situ exsolution of Cu from BCZYC provided a quite effective and promising method to improve the electrode properties.

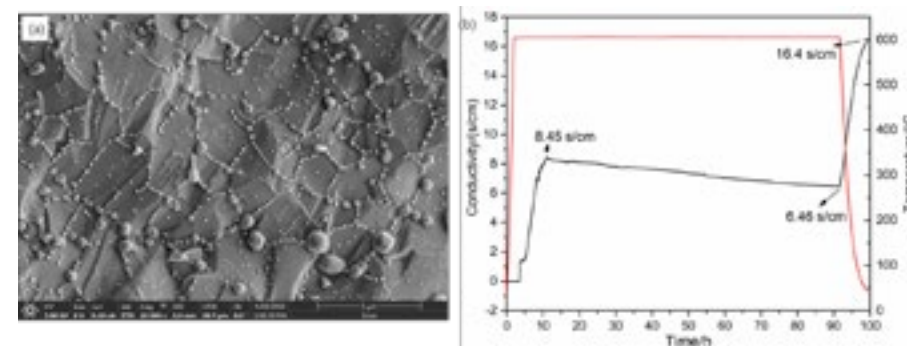


Figure 1. (a) SEM image of $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.14}\text{Cu}_{0.06}\text{O}_{3-\delta}$ after reduction in 5% H_2/Ar at 600 °C, (b) Conductivity test of $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.14}\text{Cu}_{0.06}\text{O}_{3-\delta}$ in 5% H_2/Ar at 600 °C.

Ionic conductivity of protonated layered titanate nano-powder compact in water

Munemitsu Nomura,¹ Yuki Terayama,¹ Hiroto Eguchi,² Miho Yamauchi,³ Yoshitsugu Sone,⁴ Omar Mendoza,⁴ Junko Matsuda,³ and Hiroshige Matsumoto³

1) Graduate school of Engineering, Kyushu University

2) Graduate School of Science, Kyushu University

3) International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University

4) Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (JAXA)

744 Motooka, Nishi-ku, Fukuoka 819-0395 Japan

Tel.: +81-92-802-6705

Fax: +81-92-802-6706

matsumoto@i2cner.kyushu-u.ac.jp

Abstract

Ion conduction in ceramic materials needs high temperature due to the necessity of thermal activation for the ionic defects to move through the crystal lattice. Analogous to the proton conduction in polyelectrolyte, the surface of hydrated metal oxide grains possibly works as proton conduction pathway with the aid of adsorbed water as conceptually shown in Fig. 1. We have reported so far high protonic conduction in Anatase nanoparticles surface-modified with sulphuric acid [1], but the sulphuric acid gradually detached on soaking with water, suggested by decreasing pH of the surrounding water. Recently, Wu et al., reported the synthesis of hydrated titania, $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$, via a solvothermal method [2]. This work has utilized this material to investigate possible proton conduction on the surface of hydrated metal nan oxide.

$\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ was prepared in the method reported in the literature [2], and spherical nano particles are obtained. XRD measurement revealed the layered structure which phase was stable up to 290 °C; further increase in the temperature resulted in dehydration to deform to Anatase. The obtained powder compacted in a rectangular bar shape showed high resistance in air but the resistance markedly decreased when soaked in water: a conductivity of $7.55 \times 10^{-3} \text{ s} \cdot \text{cm}^{-1}$ was obtained in water at 90 °C. pH was maintained almost neutral and the conductivity seems to take place not through water. We tried to use this material for water electrolysis and evolution of hydrogen and oxygen was confirmed [3]. From these results, it is conclusive that this material has a significant ionic conduction in water or at high liquid water activity.

This study has been financially supported my JST-CREST (JPMJCR1442).

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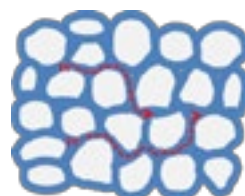


Fig. 1 A concept of surface proton conduction on metal oxide nanoparticles with adsorbed water.

Evaluation of proton incorporation in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ by isotope exchange

Kotaro Okuyama, and Keji Yashiro, and Tatsuya Kawada

Graduate school of Environmental Studies, Tohoku University

6-6-01 Aramaki Aoba, Aobaku, Sendai 980-8579, Japan

Tel.: +81-(0)22-795-6976

Fax: +81-(0)22-795-4067

koutarou.okuyama.p5@dc.tohoku.ac.jp

Abstract

Protonic ceramic fuel cells (PCFCs) exhibit better performance compared to traditional solid oxide fuel cells (SOFC) at an intermediate temperature (400 ~ 700 °C). This is due to high protonic conductivity at reduced temperatures, and offers advantages such as less cost of materials, lower thermal stress, and faster startup. Higher efficiency is also expected compared to SOFC since formation of water does not dilute fuels at the anode. However, PCFCs show high polarization resistances at the cathodes, and it is one of the biggest issues to be solved. To reduce the polarization resistance at cathodes, the use of protonic-electronic mixed conductive oxides has been considered. However, only limited information is available for the protonic conductivity of cathode candidate materials. In our preliminary experiments, we compared several popular cathode materials for SOFC such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$. Among them, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ showed the best performance as were reported also by other groups [1, 2]. However, the origin of the high performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ is not clear. In order to clarify the mechanism, proton incorporation in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ was tested by isotope exchange and Secondary Ion Mass Spectrometry (SIMS). Deuterium oxide (D_2O) was used as the isotope. A dense sample of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ was pre-annealed for 20 h at 873 K under 1% O_2 and 1.2% H_2O in order to equilibrate the defect concentration. The sample was quenched, transferred to the isotope exchange chamber, and then, rapidly heated again and annealed for 15 min. in D_2O -enriched oxygen which had the same oxygen partial pressure and water vapor partial pressure as pre-annealing atmosphere. The ratio of deuterium to proton (D/H) in the quenched sample was determined by SIMS, and compared with the natural abundance. Fig.1 shows the results of SIMS depth profiles for the samples with and without the isotope exchange treatment. The ratio D/H of the sample which was annealed in D_2O was about 30 times as much as the blank sample. Thus we concluded that proton is incorporated in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. We will present about the diffusion coefficient at the conference.

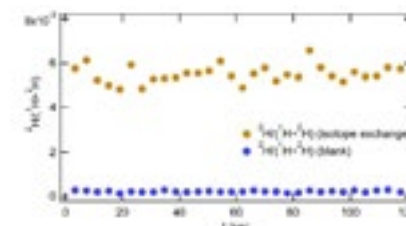


Fig.1 Hydrogen isotope exchange profile into the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$

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Heating-cooling procedure to avoid mechanical failure of proton conducting ceramics

Issei Okuzaki,¹ Young Sung Lee,² Kwati Leonard,² and Hiroshige Matsumoto²

- 1) Department of Hydrogen Energy Systems, Graduate School of Engineering, Kyushu University
- 2) International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University

744 Motooka, Nishi-ku, Fukuoka 819-0395 Japan

Tel.: +81-92-802-6705

Fax: +81-92-802-6706

matsumoto@i2cner.kyushu-u.ac.jp

Abstract

Hydration of oxide ion vacancy is a part of the mechanism of proton conduction to take place in aliovalent-cation-doped metal oxides but leads to chemical expansion at the critical temperature, typically 400 – 600 °C, where the degree of hydration changes. Thus, high proton concentration that may lead to high proton conductivity will be accompanied by large chemical expansion that causes mechanical failure of the ceramic specimens. In the case of $AB_{1-x}M_xO_{3-\delta}$ perovskite-type proton-conductors, the level of dopant M is mostly limited to 20 % to the total molar amount of M and B , because highly doped specimens frequently broke during preparation or conductivity measurement. In this study, we have investigated the relation between the dopant level and chemical expansion, and then a dry atmosphere or vacuum is partly introduced for the sintering and the heating-cooling during the conductivity measurement.

$Ba(Zr_5Ce_4)_{10/9-10x/9}Y_xO_{3-\delta}$ ($x = 0.2, 0.25$ and 0.3) was chosen to examine, based on our previous work [1] demonstrating high conductivity of $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{3-\delta}$. This composition corresponds to $x = 0.2$, and thus the present attempt has been to introduce further amount of Y doping. At $x = 0.2$, sintering at 1600 °C in a bar shape and the following conductivity measurement caused no break of the specimen. However, the specimens at $x = 0.25$ and 0.3 broke during sintering. High temperature XRD revealed that the chemical expansion increases with x , and the failure of the latter two specimens is attributable to too high chemical expansion due to high Y doping. Such failure of the specimen could be avoided by using a dry or vacuum atmosphere during the sintering and the measurement of the conductivity. As a result, it is found that the conductivity at $x = 0.25$ is higher than at $x = 0.2$ (Fig. 1).

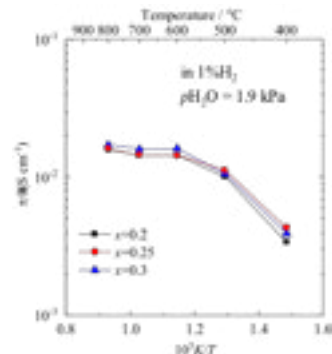


Fig. 1 Conductivity measured in wet 1% H_2 .

This work was supported by the Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "energy carrier" (Funding agency: JST) and by World Premium International Research Center Initiative (WPI), MEXT Japan.

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Potential of proton conducting phosphate glasses as fuel cell electrolytes

Takahisa Omata,¹ Masataka Tashiro,¹ Issei Suzuki,¹ Takuya Yamaguchi,¹
Tomohiro Ishiyama,² Junji Nishii,³ Toshiharu Yamashita,⁴ and Hiroshi Kawazoe⁴

- 1) Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan
- 2) National Institute for Industrial Science and Technology (AIST), Tsukuba, Japan
- 3) Research Institute for Electronic Science, Hokkaido University, Japan
- 4) Kawazoe Frontier Technologies Corporation, Yokohama, Japan

2-1-1 Katahira, Aobaku, Sendai 980-8577, Japan

Tel.: +81-22-217-5839

Fax: +81-22-217-5839

omata@tagen.tohoku.ac.jp

Abstract

Proton conducting phosphate glass is one of the promising materials as an electrolyte in ITFCs. We have recently focused on developing glasses that exhibits high proton conductivity and found that $36HO_{1/2}-4NbO_{5/2}-2BaO-4LaO_{3/2}-4GeO_2-1BO_{3/2}-49PO_{5/2}$ glass exhibits high proton conductivity of $1 \times 10^{-3} \text{ Scm}^{-1}$ at 280 °C remaining stable under fuel cell operating conditions. However, the conductivity is still not sufficient for the fuel cell electrolyte. In this study, we evaluated the highest proton conductivity of phosphate glasses based on the proton mobility of various phosphate glasses and discussed the potential of the glasses as fuel cell electrolytes.

Because the ionic conductivity of glasses are dependent on their viscosity, we summarized the proton mobility of various glasses at the glass transition temperature (T_g) (Fig. 1), where the viscosity of glasses are constant at $\sim 10^{12} \text{ Pas}$. Even though their composition (O/P = 2.8~3.6), T_g (160~620 °C), conductivity ($10^{-7} \sim 10^{-4} \text{ Scm}^{-1}$) and proton carrier concentration ($10^{-19} \sim 10^{-22} \text{ cm}^{-3}$) are broad-ranging, the mobilities at T_g are distributed only in a small range between 5×10^{-9} and $5 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating that the proton mobility at T_g is almost constant. When the proton concentration is $\sim 10^{22} \text{ cm}^{-3}$, T_g can be tuned as 170 °C at highest by controlling the composition, and the activation energy of the proton conduction is $\sim 0.75 \text{ eV}$; therefore the highest proton conductivity at 300 °C is calculated to be $7 \times 10^{-3} \text{ Scm}^{-1}$ assuming the proton mobility of $5 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The thickness of the glasses was easily reduced to $< 20 \text{ }\mu\text{m}$ without degradation of electrical properties by hot-pressing, suggesting that the thickness of the glass can be reduced to $< 10 \text{ }\mu\text{m}$, when the pressing conditions are optimized. When we obtain a glass ($\sigma_{H^+} = 7 \times 10^{-3} \text{ Scm}^{-1}$ at 300 °C) with a thickness of 10 μm , the area specific electrolyte resistance is $0.14 \text{ }\Omega\text{cm}^2$ indicating that the maximum output power (P_{max}) is not determined by the electrolyte resistance but the electrode polarization resistance. Assuming sum of the electrode polarization resistance at the anode and cathode of $1 \text{ }\Omega\text{cm}^2$, P_{max} is calculated to be 220 mWcm^2 . This indicates that the proton conducting phosphate glasses are practically applicable as an electrolyte in ITFCs, when the electrode materials exhibiting $< 1 \text{ }\Omega\text{cm}^2$ of total polarization resistance are developed.

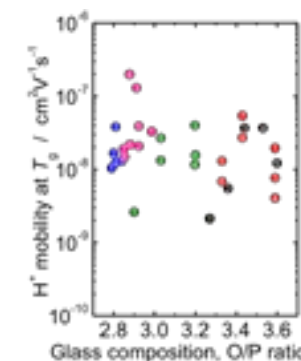


Figure 1. Proton mobility at T_g of various phosphate glasses.



Palladium as an electrocatalyst for solid acid fuel cells: Model thin-film studies

Haemin Paik,¹ Andrey V. Berenov,² Stephen J. Skinner,² and Sossina Haile^{1,3}

- 1) California Institute of Technology, Pasadena, CA, USA
- 2) Imperial College London, London, UK
- 3) Northwestern University, Evanston, IL, USA

1200 E California Blvd, Pasadena, CA 91125, USA

Tel.: (626) 840-3678
Fax: (847) 491-7820
hpaik@caltech.edu

Abstract

Solid acid fuel cells (SAFCs) with the proton-conductive electrolyte CsH_2PO_4 have drawn attention for delivering high power densities at a technologically attractive operating temperature, $\sim 250^\circ\text{C}$. While the performance characteristics of SAFCs have pushed the technology towards market adoption, Pt loadings remain higher than desirable. Furthermore, the electrochemical reaction mechanisms for hydrogen oxidation and oxygen reduction in these devices remain unknown. Palladium has shown impressive electrocatalyst activity for the oxygen reduction reaction in SAFCs, exceeding that of platinum, but stability is poor due to oxidation of Pd. Here, hydrogen oxidation kinetics on Pt, Pd and Pt-Pd bimetallic thin film electrodes on CsH_2PO_4 have been evaluated, with the aim of establishing whether Pd can have a beneficial role in SAFC anodes as well. Metal film electrodes with varying thicknesses were deposited by DC sputtering on both sides of CsH_2PO_4 electrolyte discs. These symmetric cells were used for studying hydrogen electro-oxidation across the gas | metal | CsH_2PO_4 structure. AC impedance spectroscopy (ACIS) performed under humidified H_2 at $\sim 248^\circ\text{C}$ showed Pd is substantially more active than Pt for hydrogen electro-reduction. X-ray photoelectron spectroscopy of the Pd film revealed that Pd reacts with CsH_2PO_4 and forms palladium phosphide at the metal-electrolyte interface. Remarkably, this reaction product does not appear to impede the electrochemical reaction. Bilayer films with Pd deposited over Pt showed much higher activity than Pt alone, as measured by ACIS. Ex-situ low energy ion scattering and scanning transmission electron microscopy showed that Pd diffuses into the Pt layer, despite the reported immiscibility of these elements. The presence of Pd throughout the film suggests it assists in reactions at both the metal-gas and metal-electrolyte interfaces, as well as increasing hydrogen diffusion rates through the films.



High-throughput study of conduction mechanisms in triple conducting oxides

Meagan Papac,^{1,2} Andriy Zakutayev,² Ryan O'Hayre,¹ and Elisabetta Arca²

- 1) Colorado School of Mines
- 2) National Renewable Energy Laboratory

1500 Illinois St.
Golden, CO 80401

Tel.: (208)320-8301
mcpapac@mines.edu

Abstract

Triple conducting oxides are a class of materials that conduct electrons and at least two ionic species. These transport properties are modulated by structural variables, such as unit cell volume and symmetry, as well as chemical variables, such as oxygen vacancy concentration and transition metal oxidation states.

The present work explores $\text{Ba}(\text{Co,Fe,Zr,Y})\text{O}_3$, a materials system based on a well-known proton conductor, BZY, doped with transition metals to introduce and enhance electronic and oxygen ionic conductivity. This is a material of interest for intermediate temperature ($400 - 600^\circ\text{C}$) proton conducting fuel cells because it addresses challenges, such as high polarization resistance and low oxygen reduction activity, that limit device performance in this temperature range.

In this study, combinatorial pulsed laser deposition of thin films is combined with high-throughput characterization methods to allow observation of composition-induced variation in properties across a broad range and to increase understanding of factors that drive the relevant trends. X-ray photoelectron spectroscopy provides insight into oxygen non-stoichiometry and transition metal oxidation states. The films' chemistries are correlated to transport properties as analyzed by high-throughput impedance spectroscopy and current-voltage curves in dry and wet (3% H_2O) air at temperatures up to 500°C . Trends in electrical properties with temperature and humidity illuminate mechanisms of hydration and electronic conductivity, indicating which types of conductivity can be enhanced concurrently and which are enhanced at the expense of others. These insights contribute to fundamental understanding of mixed species transport in complex oxides and tuning of transport properties within them.



Highly proton conducting MP_2O_7 – Nafion composite Membranes for intermediate temperature electrolyte applications

K. P. Ramaian, R. Mukundan, Y. S. Kim, M. Wilson, and C. R. Kreller

MPA-11, Los Alamos National Laboratory

Los Alamos, 87545, USA

Tel.: 5055707230
kramaian@lanl.gov

Abstract

Intermediate temperature operation between 150 to 400 °C allows improved kinetics and tolerance towards poisoning in many electrochemical applications such as fuel cells, batteries and electro-synthesis of fuels. For example, fuel cells operating with state of the art Pt electrocatalyst will have improved CO tolerance at intermediate temperatures in comparison to the ambient operating conditions. Phosphoric acid doped PBI membranes operate at the lower end of this temperature range up to 160 °C, though challenges with durability and phosphoric acid poisoning persist.¹ Above 160 °C, there is a shortage of reliable candidates available in the intermediate temperature range. In this regard, metal pyrophosphate based electrolytes (MPP technology) holds the promise of quick start-ups from ambient and extended operation at up to 250 °C. Recently, $\text{Sn}_2\text{P}_2\text{O}_7$ based materials with excess polyphosphate were reported to show remarkable proton conductivity up to 250 °C.²⁻⁴ Our work on $\text{Sn}_2\text{P}_2\text{O}_7$ revealed that the excess phosphate phase is crucial for proton conduction in contrary to the previous claims that indicated In doping as the key for proton conduction.⁵ However, the influence of doping in combination with excess phosphate base is not documented. In this presentation we present our work on preparing aliovalent doped $\text{Sn}_2\text{P}_2\text{O}_7$ and the role of dopants on the conductivity of the $\text{Sn}_2\text{P}_2\text{O}_7$. Further, the formation of MPP/ Nafion composite membranes and the influence of MPP phase on proton conductivity will be discussed.

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Viscoelastic reinforcement of a polyelectrolyte for fuel cell application via polymer blending

Torben Saatkamp,¹ Andreas Münchinger,¹ Giorgi Titvinidze,² and Klaus-Dieter Kreuer¹

- 1) Max-Planck-Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany
- 2) Agricultural University of Georgia, Georgia, 0131 Tbilisi, 240 David Aghmashenebeli Alley

Tel.: 0049 711 689-1705
Fax: 0049 711 689-1722
t.saatkamp@fkf.mpg.de

Abstract

Polymer blending is a complex field of research in which the goal is to combine desirable properties of different materials into one. The ease of implementation into a technical production process makes it – despite its intricacies – a sought after solution for material development.

Polymers used as separator membranes in PEMFCs generally are perfluorosulfonic acid-based ionomers (PFSA, e.g. Nafion). Their morphology and fluorinated (PTFE) backbone give rise to a unique set of properties both in terms of conductivity and of viscoelastic and chemical stability.

Alternative PEMFC materials that do not make use of a fluorinated backbone (i.e. hydrocarbons, HC) often are sulfonated polyarylenes. While high conductivities can be achieved in these materials, they lack the PTFE-typical softening at high temperature which in the fuel cell coincides with very low humidity, leading to brittleness and mechanical failure in many HCs.

Our approach to developing new PEMFC materials makes use of the striking properties of sulfonated poly(phenylene sulfone)s (sPSO₂s), a family of hydrocarbon polyelectrolytes. Their high chemical stability compared to PFSAs, superior proton conductivity compared to other sulf. pol(arylene)s – especially at low RH – and low electroosmotic water drag make them highly promising membrane materials.

Here, we present our concepts and first results of viscoelastic reinforcement via polymer blending of sPSO₂-360, which exhibits polyelectrolyte-typical brittleness in the dry state and exaggerated swelling in water. We make use of different interactions to form a compatibilized blend membrane and evaluate the suitability of different blend component properties to reduce brittleness in the blend membranes. We present our results on attaining viscoelastic reinforcement without sacrifice of the high conductivity of sPSO₂-360 in these blends.



Ab Initio molecular dynamics study of effect of acid-base modification on proton activity of oxide surface

Ryuhei Sato,¹ Yasushi Shibuta,¹ Fuyuki Shimojo,² and Shu Yamaguchi¹

1) Department of Materials Engineering, The University of Tokyo

2) Department of Physics, Kumamoto University

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

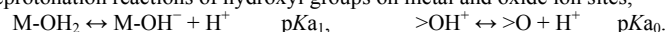
Tel.: +81-3-5841-7140

Fax: +81-3-5841-7140

sato@alto.material.t.u-tokyo.ac.jp

Abstract

Proton activity on oxide surface is paid much attention not only from the viewpoint of basic science but also the application to proton-conductive electrolytes. In previous *ab initio* molecular dynamic (AIMD) studies, it is found that proton conduction on oxide surface is originated from the proton migration between chemisorbed H₂O molecules (M-OH₂) and monodentate hydroxyl groups (M-OH⁺) on metal ion sites directly or via surrounding H₂O molecules like Grotthus mechanism [1]. In addition, thermodynamic discussion reveals that the hydration equilibrium on oxide surface is governed by the following deprotonation reactions of hydroxyl groups on metal and oxide ion sites,



Note that *pK*_as are acid dissociation constants of hydroxyl groups, which determines the proton migration property as follows.

$$\sigma_{\text{H}^+} \propto [\text{M-OH}_2][\text{M-OH}^+] = 10^{(pK_{a1}-pK_{a0})/2} / (10^{(pK_{a1}-pK_{a0})/2} + 1)^2$$

Therefore, proton conduction is strongly related to the acid-base chemistry on the oxide surface. For example, in the previous study, adsorption of acidic CO₂ molecules reduces the proton conductivity of YSZ nanoparticles. It is because CO₂ adsorption drastically decreases the basicity of >O sites, as suggested in AIMD simulation [2]. In this contribution, to further clarify the effect of the acid-base modification on the oxide surface, adsorption of other molecules like HCOOH and CH₃OH and subsequent hydration reaction on ZrO₂ surface are studied by AIMD simulation.

From the observation of adsorption of these molecules by AIMD simulation, it is found that these molecules first adsorb on the metal ion sites and subsequently release the proton to form >OH⁺. Because of the strong Brønsted acidity of HCOOH, all Zr-HCOOH release protons immediately, while half of the adsorbed Zr-OHCH₃ release protons under a hydrated condition. This result implies that *pK*_a of Zr-HCOOH is smaller than Zr-OH₂, while *pK*_a of Zr-OHCH₃ is comparable with that of Zr-OH₂. According to the frequency analysis and thermodynamic discussion of the stability of hydroxyl groups, *pK*_{a0} and *pK*_{a1} are kept at almost constant values with and without HCOOH and CH₃OH adsorption. Therefore, because of the weak hydrogen bond between Zr-OOCH⁻ and H₂O molecules, HCOOH adsorption is considered to reduce the proton conductivity. Besides, the CH₃OH adsorption also reduces the proton conductivity by the decrease in the number of hydrogen bonds on the surface compared to H₂O adsorbates, because of relatively inert characteristics of CH₃ groups to protonic species.

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Symmetric proton ceramic fuel cells

Wojciech Skubida,¹ and Konrad Świerczek^{1,2}

1) Faculty of Energy and Fuels, Department of Hydrogen Energy, al. A, AGH University of Science and Technology

2) AGH Centre of Energy, AGH University of Science and Technology

AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Hydrogen Energy, al. A, Mickiewicza 30, 30-059 Krakow, Poland

Tel.: +48 12 617 49 26

xi@agh.edu.pl

Abstract

In this work development of novel composite-type electrode materials for Proton Ceramic Fuel Cells (PCFC), which are based on Mo-containing cation-ordered perovskites with a high chemical stability in reducing and oxidizing conditions is presented. The main idea is based on a synergic interaction, which arises when composite electrodes are formed using one material with a high proton conductivity and the other one exhibiting a high mixed ionic-electronic (MIEC-type) transport. In the proposed approach, both electrodes (anode and cathode) are identical in terms of their chemical composition, which simplifies manufacturing process and limits unwanted chemical reactivity resulting in Symmetric Proton Ceramic Fuel Cells (SPCFC). Beneficial effects are expected if composite electrodes are used, in which the protonic component of the conductivity is realized by the same phase, as used in the solid electrolyte ((Ba,Sr)_{1-x}Ln_x(Zr,Ce,In,Sn)O_{3-δ}, Ln: selected lanthanides), while the electronic component is ensured by Sr₂Fe_{2-x}Mo_xO_{6-δ} phase, having apart from high electrical conductivity in reducing and oxidizing conditions, also good chemical stability and exhibiting oxygen ion transport. Laboratory-scale button-type Symmetric Proton Ceramic Fuel Cells were fabricated containing three different composite electrodes with electrolyte/electrode materials ratio of 2:1, 1:1, 1:2. Electrochemical studies of the cells (impedance spectroscopy measurements, current-voltage characteristics) were conducted using custom made sample holder, high temperature tube furnace, gas flow and temperature controllers. Impedance spectroscopy measurements and current-voltage characteristics were studied as a function of temperature and H₂ (in the anode) and air flow (on the cathode) rates. Additionally SEM studies of cross-section of composite electrodes were performed before and after measurements which allowed to determine the influence of the environment on the microstructure of the electrodes.

The project was funded by the National Science Centre, Poland on the basis of the decision number UMO-2016/21/N/ST8/00268.

Governing principles in hydration of mixed conducting oxides (“GoPhy MiCO”)

Ragnar Strandbakke,¹ Tor S. Bjørheim,¹ Aleksandra Mielewczyk-Gryn,² Sebastian Wachowski,² Iga Lewandowska,² Maria Balaguer,³ Magnus H. Sørby,⁴ Maria Gazda,² Jose M. Serra,³ and Truls Norby¹

- 1) Department of Chemistry, University of Oslo, FERMI, Gaustadalléen 21, NO-0349 Oslo, Norway.
- 2) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza street s11/12, 80-233 Gdańsk, Poland
- 3) Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n.46022 Valencia, Spain
- 4) Department for Neutron Materials Characterization, Institute for Energy Technology, NO-2027 Kjeller, Norway

Tel.: +47-22840660
ragnarst@smn.uio.no

Abstract

Double perovskite oxides can tolerate large compositional variations on the cation lattices, thus allowing fine tuning of the local chemical properties within individual layers. By systematically investigating substitution and doping strategies on both A and B sites, trends can be established both with respect to valence states, atomic radii and acidity/basicity, which in turn can be linked to the materials' ability to incorporate and transport protons. The relation between formation of vacancies in favourable positions in the oxygen sublattice and hydration of these vacancies are investigated by means of thermogravimetry (Figure 1a), electrical and electrochemical characterisation techniques, atomistic simulations, XRD and neutron powder diffraction. By favourable sites for hydration, we here mean oxygen vacancies with acidic character for the accommodation of a basic hydroxide ion, neighbored by oxide ions with a more basic character for accommodation of an acidic proton. In double perovskites, layers with varying acidic/basic character alternate throughout the structure, and oxygen non-stoichiometry and vacancy positioning can be manipulated by tuning average radii and valences on A- and B-site (Figure 1b). The project “Governing Principles in Hydration of Mixed Conducting Oxides” (GoPhy MiCO) investigates perovskite materials with the general formula $A_{1-x}A''_x A_{1-y}A''_y B_{2-z}B''_z O_{6-\delta}$. Fraction indicators x, y and z constitute substitution trends upon which structural ordering and formation and localization of oxygen vacancies favourable for hydration are expected to depend.

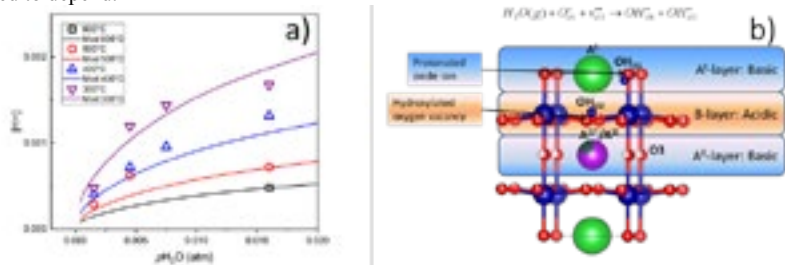


Figure 1: Experimental and modelled hydration of BGLC (a) and double perovskite structure with alternating basicity (b).

The research leading to these results has received funding from the Research Council of Norway (Grant n° 272797 “GoPhy MiCO”) through the M-ERA.NET Joint Call 2016.

K₂NiF₄-type oxyhydrides Ba_{2-x}Na_xScH_{1+x}O_{3-x} with fast hydride conduction

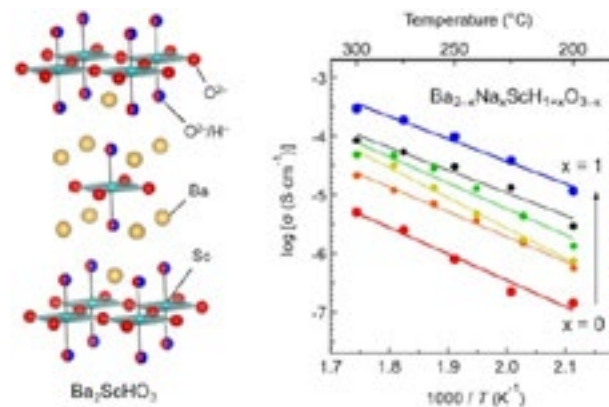
Fumitaka Takeiri,¹ Akihiro Watanabe,^{1,2} Haq Nawaz,¹ Masao Yonemura,³ Ryoji Kanno,² and Genki Kobayashi¹

- 1) Institute for Molecular Science, 38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585, Japan
- 2) Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502, Japan
- 3) High Energy Accelerator Research Organization (KEK), 203-1, Shirakata, Tokai, Ibaraki 319-1106, Japan

Tel.: +81-564-55-7244
Fax: +81-564-55-7245
fkobayashi@ims.ac.jp

Abstract

Hydrogen conduction as hydride (H⁻) has been recently confirmed in metal-hydrides [1] and oxyhydrides [2] which could give an alternative direction in energy storage and electrochemical devices. Here, we show a new series of H⁻ conducting oxyhydrides with K₂NiF₄-type structures, Ba_{2-x}Na_xScH_{1+x}O_{3-x} (0 ≤ x ≤ 1), which is synthesized by a high-pressure method [3]. Ba₂ScHO₃ (x = 0) with a selective H⁻ occupation at the rock salt layer exhibited a conductivity of 5.1 × 10⁻⁶ S cm⁻¹ at 300 °C, which is much higher than that of an ideal perovskite BaScO₂H. Moreover, the x > 0 compounds showed the higher conductivities compared to the pristine one; the maximum value of 3.0 × 10⁻⁴ S cm⁻¹ at 300 °C was observed in BaNaScH₂O₂ (x = 1).



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A first-principles study on proton trapping in yttrium-doped barium zirconate

Kazuaki Toyoura, Weijie Meng, and Tetsuya Uda

Department of Materials Science and Engineering, Kyoto University

Yoshida, Sakyo, Kyoto 606-8501, Japan
Tel.: +81-75-753-3551
Fax: +81-75-753-5284
toyoura.kazuaki.5r@kyoto-u.ac.jp

Abstract

Aliovalent doping is indispensable for incorporating protons into the crystal of barium zirconate (BaZrO_3) as charge carriers, while such dopants basically stabilize protons due to the electrostatic attractive interaction, leading to *proton trapping* responsible for reducing the proton conductivity [1]. In the present study, we have theoretically investigated the proton trapping effect using first-principles calculations, taking yttrium-doped BaZrO_3 (BZY) as a model system.

The proton diffusivity and conductivity of BZY were evaluated by taking a two-step approach. First, the potential barriers of the proton rotation and hopping were evaluated on the basis of the nudged elastic band (NEB) method in various local configurations of Y dopants on Zr sites. The NEB calculations were performed using first-principles calculations based on the projector augmented wave (PAW) method as implemented in the VASP code. The diffusion simulations were then performed on the basis of the kinetic Monte Carlo (KMC) method using the mean frequencies of all paths at the first step. In the KMC simulations, supercells of $10 \times 10 \times 10$ unit cells were used, where a part of Zr sites were randomly substituted by Y ions according to a given Y concentration.

Figure 1 shows the estimated proton diffusivity and conductivity at 600 K as a function of Y concentrations (fraction on the Zr sites, x). The diffusivity decreases monotonically with the Y concentration, while the conductivity has a maximum around $x = 0.25$. This indicates that the decrease of the proton diffusivity is dominant rather than the increase of the carrier concentration at high Y concentrations ($x > 0.25$). The estimated proton conductivity is in reasonable agreement with the reported bulk conductivity at 573 K measured by the impedance spectroscopy [2].

In consideration of the possibility of Y-Y association in the crystal [3], additional KMC simulations were performed in supercells with adjacent configurations of Y dopants. The broken lines in Fig. 1 are the estimated proton diffusivity and conductivity in the adjacent configurations, which are less than those in the random configurations of single Y dopants. This result suggests that the Y-Y association enhances the proton trapping effect in BZY. This work was supported by JSPS KAKENHI Grant Number (JP17H04948) and Research Grant from Nippon Sheet Glass Foundation for Materials Science and Engineering.

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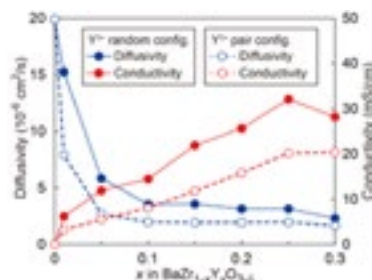


Fig. 1. Estimated proton diffusivity and conductivity at 600 K as a function of Y concentration.



Anion exchange membranes based on poly(ethylene-*block*-styrene-*block*-ethylene) triblock copolymer functionalized via Friedel-Crafts bromoalkylation

Carrie Trant,¹ Chulsung Bae,^{1,2} and Sangwoo Lee¹

- 1) Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute
2) Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute

110 8th Street, Troy, NY 12180, USA
Tel.: 518-276-8676
Fax: 518-276-4030

lees27@rpi.edu

Abstract

Anion exchange membranes (AEMs) containing semi-crystalline polyethylene hard-end triblock copolymers were synthesized and their ion-conducting properties and microphase morphologies were characterized. First, poly(ethylene-*b*-styrene-*b*-ethylene) (ESE) triblock copolymers were prepared from selective hydrogenation of anionically polymerized poly(butadiene-*b*-styrene-*b*-butadiene) triblock copolymer with symmetric volume fractions of polystyrene and polybutadiene. The quaternary ammonium group functionalization of the styrene middle block was quantitatively controlled by acid-catalyzed Friedel-Crafts bromoalkylation reaction followed by amination with trimethylamine. AEMs of three levels of ion exchange capacity (IEC) 0.64, 1.31, and 1.89 mequiv./g were prepared. While the two lower IEC membrane materials exhibited lamellar morphology and elastic stress-strain behavior, the highest IEC material exhibited a disordered morphology and plastic stress-strain behavior. The highest IEC AEM (ESE35-TMA-1.89) with 1.89 mequiv./g showed hydroxide ion conductivity of 55 mS/cm in water at 60 °C. All materials showed good alkaline stability, preserving over 90% of IEC and hydroxide ion conductivity of the initial values after alkaline stability tests in 1M sodium hydroxide solutions at 80 °C for 500 hours.

Synthesis of elastic anionic exchange block copolymers by thiol-ene click reaction of poly(styrene-*b*-butadiene-*b*-styrene)

Stefan Turan,¹ Sungmin Park,¹ Chang Ryu,¹ and Chulsung Bae^{1,2}

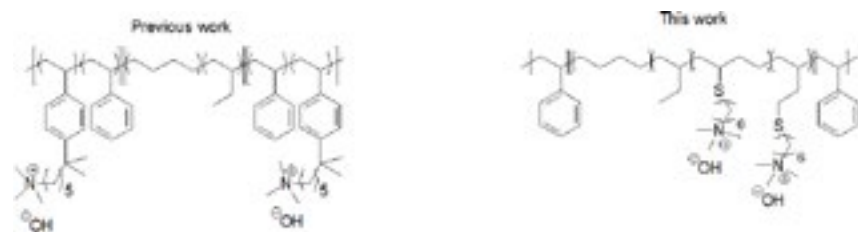
- 1) Department of Chemistry & Chemical Biology
2) Department of Chemical & Biological Engineering

Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180, United States

Tel.: 518-276-3783
baec@rpi.edu

Abstract

In anion exchange membrane (AEM) fuel cells, a major obstacle is the lack of a highly anion conductive and alkaline stable membrane. It has been reported that quaternary ammonium (QA) groups attached at the benzylic carbon of aromatic rings and aryl-ether bonds are vulnerable to hydroxide ion attack and degrade under alkaline conditions. Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) is a commercially available thermoplastic elastomer made of glassy polystyrene end block and rubbery polybutadiene middle block. We chose this polymer backbone as a base polymer for preparation of functionalized anionic block copolymers because of its excellent elastic properties derived from a combination of rubbery middle block and physically cross-linked polystyrene end block. Recently, our group has reported ionic group-functionalization of glassy polystyrene block of hydrogenated SBS with QA groups (see below). However, this functionalization disrupts the physical cross-links of polystyrene, thus negatively affects the mechanical properties of the membrane. In this work, we report functionalization of the rubbery mid-block of SBS with QA groups using thiol-ene click chemistry, which results in improved mechanical properties over the previous work. Thiol-ene click chemistry offers an efficient C-S bond formation between an alkene and thiol. Using thiol-ene click chemistry, a pendant hexyl alcohol group was attached to 10-50 mol% of the mid block of polybutadiene of SBS. Subsequent hydrogenation of the residual double bonds in the butadiene block followed by conversion of the pendant alcohol group to alkyl bromine was performed. This precursor polymer was cast from a solvent, then the alkyl bromide functionality was converted to trimethylalkyl ammonium by treatment with trimethylamine. Hydroxide conductivity, water uptake, ion exchange capacity, alkaline stability, and mechanical properties of these membranes were investigated.



Transport properties of yttrium-doped barium zirconate with Ni diffusion

Tetsuya Uda,¹ Donglin Han,¹ Takayuki Onishi,¹ Yohei Noda,^{1,2}
Naoyuki Hatada,¹ and Masatoshi Majima²

- 1) Department of Materials Science and Engineering, Kyoto University
Yoshida, Sakyo, Kyoto 606-8501, Japan

- 2) Sumitomo Electric Industries, Ltd., 1-1-1, Koyakita, Itami-shi, Hyogo 664-0016, Japan

uda.tetsuya.5e@kyoto-u.ac.jp

Abstract

Anode supported cell, fabricated by co-sintering process, is typical cell structure of BZY fuel cells. But a small percent Ni diffusion into electrolyte during co-sintering is always observed. We will introduce the experimental results on the influence of Ni diffusion on the transport properties of barium zirconate. Then the leakage current is estimated with results of overpotential measurements.

Figure 1 is the measured transport number of pure BZY20 and 2 wt% NiO-added BZY20 by electromotive force measurement [1]. The number was compensated by taking the effect from electrode polarization into consideration. Ni addition decreases the transport number dramatically even at low temperature such as 500 °C though the amount of added Ni is not so large. It is concluded that Ni decreases proton conductivity but does not affect hole conductivity so much. Figure 2 is the results of electrode overpotential measurements by the current interrupting method at 600 °C. After 2000 hour operation as fuel cell, the sum of electrode resistances was 0.49 Ωcm². Another experiments suggest that anode resistance is around 0.15 Ωcm² [2]. With these information, the oxygen potential profile in the Ni-diffused BZY20 electrolyte and the leakage current are estimated.

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) in Japan (Project code P14004).

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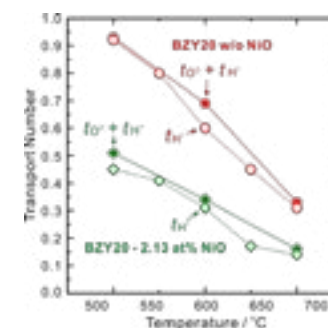


Fig. 1. Transport numbers of ionic conduction in pure BZY20 and 2 wt% NiO-added BZY20 by the EMF method. [1].

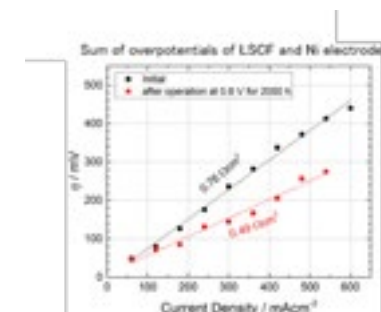


Fig. 2. Sum of overpotentials of LSCF cathode and 60 wt% NiO-0.98BZY20 anode under fuel cell mode before and after the durability test under constant voltage of 0.8 V for 2000 h [2].

Scaling up of tubular proton ceramic electrolyzers

Marie-Laure Fontaine,¹ Einar Vøllestad,¹ Wen Xing,¹ Zuoan Li,¹ Christelle Denonville,¹
Ragnar Strandbakke,² Dustin R. Beeff,³ Truls Norby,² and Jose M. Serra⁴

¹ SINTEF Industry, Forskningsveien 1, NO-0373 Oslo, Norway

² Department of Chemistry, University of Oslo, , Norway

³ CoorsTek Membrane Sciences As, Norway

⁴ Instituto Tecnológica Química, Spain

einar.vollestad@sintef.no

Abstract

Incentives for developing high temperature electrolyzers (HTEs) using proton conducting electrolytes stem from the fact that a proton ceramic electrolysis cell (PCE) pumps out and pressurises dry H₂ 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. We investigate instead tubular cells, mounted in a novel module with cold seals that allows monitoring and replacement of individual tubes. All cells consist of a porous Ni-BZCY cathode for the H₂ side (self-standing or supported on a porous BZCY tube), a dense BZCY-based electrolyte, a porous anode for the H₂O+O₂ side, and a current collector system. The tubular cells are developed along three main lines with increasing risks/rewards. The 1st line is based on solid state reactive co-sintering of BZCY based electrolyte coated on a slip-cast or extruded NiO based composite tube. Various cell architectures of 25 cm tube length were produced with varying Ce contents. In the 2nd line, the BZCY tubes are cut and stacked in series to build voltage and reduce overall current to improve current collection along the tube. The 3rd line takes a closed porous BZCY based extruded tube, on which segments of cathode, electrolyte, and interconnect are sequentially applied and sintered. Various H₂O/O₂ electrodes consisting of BZCY with e.g. the double perovskite Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6-δ} (BGLC) or LSM have been investigated in in electrolysis mode at up to 4 bars in the temperature range 400-700 °C. Results of this work and further scaling up development will be presented highlighting progress in materials development, cells manufacturing and performance.



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The influence of spark plasma sintering parameters on a BZCY72 proton conductor

Jan Wallis,¹ Wiktor Bodnar,¹ Andreas Richter,³ Guttorm Syvertsen-Wiig,³ Eberhard Burkel,²
Sandrine Ricote,⁴ and Angela Kruth¹

1) Leibniz Institute for Plasma Science and Technology, Felix-Hausdorff-Straße 2, 17489 Greifswald, Germany

2) University of Rostock, Albert-Einstein-Straße 23-24, 18059 Rostock, Germany

3) CerPoTech, Kvenildmyra 6, 7093 Tiller, Norway

4) Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, USA

Tel.: +49(0) 3834 554 3822

Fax: +49(0) 3834 554 301

jan.wallis@inp-greifswald.de

Abstract

Solid electrolytes for fuel cell applications require high protonic conductivity and chemical stability to increase their operating time and efficiency. For solid solutions from barium cerate and barium zirconate, there have been many attempts to find the right balance between those two end members and optimize their properties.¹ The resulting BZCY72, however, is difficult to fabricate due to the high temperatures of around 1600 °C that are required for densification, resulting in dissolution of barium. Spark plasma sintering (SPS) had been applied for sintering of BZCY72 in the past but only with limited success with regard to the grain boundary conductivity.^{1,2} Also, SPS mechanisms are still not well understood and the full potential of the SPS technique has not been explored yet.

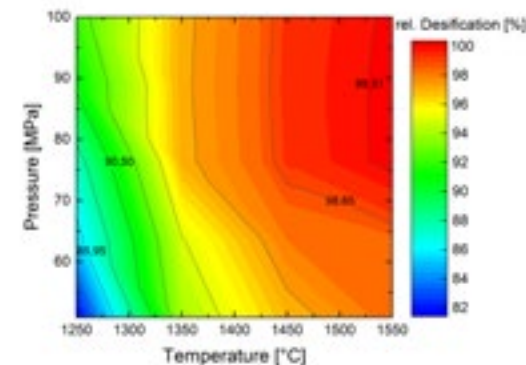


Figure 1: Densification of a BZCY72 proton conductor as a function of sintering temperature and pressure.

BZCY72 proton conductors were prepared by SPS process varying different parameters such as temperature (1150 – 1750 °C), pressure (40 – 100 MPa), heating rate (25 – 150 K/min) and holding time (5 – 40 min) in order to study correlation between process parameters and resulting materials properties. The densification of the sample was monitored *in situ* during the sintering process giving clues on possible sintering mechanisms. The resulting pellets were investigated with regard to their crystal structure, morphology, grain size distribution and conductivity. The results of this study will be presented in the poster presentation.

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DPD simulations of anion exchange membrane: The effect of the alkyl spacer of the functional group

Xubo Luo and Stephen J. Paddison

Chemical and Biomolecular Engineering, University of Tennessee

1512 Middle Drive, Knoxville, TN, 37996-2200 U.S.A.

Tel.: (865) 974-2026

Fax: (865) 974-7076

spaddison@utk.edu

Abstract

The polymeric membrane electrolyte serves as a key component in anion exchange membrane (AEM) fuel cells. To enhance both the membrane stability and ion (OH^-) conductivity, phase segregate copolymers have been chosen to function as the electrolyte in AEM fuel cells. The phase separation builds up the ion exchange channels, and hence the morphology of the material is important.

Among the candidates, polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene (SEBS), functionalized by the quaternary ammonium (QA) and its variants with alkyl spacer, has been reported as a promising material for AEM.¹ To investigate the morphology, Dissipative Particle Dynamics (DPD) simulation was adopted. The parameters of the DPD force field were obtained from *ab initio* calculations. This work simulated the effect of the alkyl spacer in the functional group. The spacer was grafted between the SEBS and QA as the linker, to the open end of the QA group as the tail and both the two positions as the coexisting linker and tail. The results were compared with our previous work of SEBS-QA with no spacer.² Cluster analysis was also performed to calculate water cluster sizes and percolation at different hydration levels.

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Proton and hydroxyl ion transport in porous ceramics

Tomoyuki Yamasaki and Shu Yamaguchi

Department of Materials Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Tel.: +81-3-5841-7140

Fax: +81-3-5841-7140

yamasaki@alto.material.t.u-tokyo.ac.jp

Abstract

Porous oxide materials are expected to be utilized as proton conductive electrolyte from RT to intermediate temperatures ($\sim 300^\circ\text{C}$) for PCFC. Although substantial number of challenge has been made to improve their proton conductivity so far, there still remains controversy about the mechanism of proton conduction, especially for the origin of the proton carrier. Recently, Stub et al. have measured the emf of Ag |porous-YSZ|Ag cell under small water vapor gradients and a constant oxygen pressure. They suggest that the charge carrier on porous YSZ is dependent on the thickness of accumulated water layers and the charge carrier is H_3O^+ in higher relative humidity ($\text{RH} > 0.6$) and single proton in lower RH [1]. In case of OH^- conductivity on strong basic oxide surface, detailed mechanism has never been established under high humidity condition, in which the charge carrier migrates along water layers accumulated on oxide surfaces. Here, inspired by their work, we analyze the emf measurements for compacted YSZ nanoparticles and layered double hydroxide (LDH), a proton conductor and a hydroxyl-ion conductor, respectively to clarify the charge carrier and its migration mechanism in accumulated water layer on these materials in detail.

Contrary to the previous work, our emf measurements suggest that the major charge carrier is hydroxyl ion for both YSZ and LDH. Estimated hydration number of hydroxyl ion is larger than 3, which well agrees with hydrated structure of hydroxyl ions estimated from DFT calculation [2]. Also, the H-D isotope effect is clearly observed in AC impedance measurements in the range of RH as far as hydroxyl ions conduct. Therefore, it is considered that the rate-limiting step of the hydroxyl ion transport is proton transfer from H_2O molecule to hydroxyl ion, as suggested in previous report.^[2] From the time variation of emf of the water concentration cell for LDH in intermediate RH region, a double relaxation process has been clearly observed, indicating the presence of two different ionic carriers with opposite polarity. Further details about the carrier species will be discussed at the presentation.

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Electrochemical properties of anode supported PCFC with Yb-doped BaZrO₃ electrolyte

Kosuke Yamauchi, Kaori Takeuchi, Yuichi Mikami, Takehito Goto, and Tomohiro Kuroha

Technology Innovation Division, Panasonic Corporation,
3-1-1 Yagumo-naka-machi, Moriguchi City, Osaka 570-8501, Japan

Tel.: +81-70-4016-3470

Fax: +81-6-6906-4595

yamauchi.kosuke001@jp.panasonic.com

Abstract

In recent years, PCFC (protonic ceramic fuel cell) has been widely studied and become more attractive for an intermediate temperature SOFC. Acceptor doped BaZrO₃ is well-known for the relatively high proton conductivity and the high stability against CO₂, compared with other proton conductors [1].

In this work, an anode supported planar cell using BaZr_{0.8}Yb_{0.2}O_{3-δ} as the electrolyte was fabricated, and then electrochemically investigated. NiO-BaZr_{0.8}Yb_{0.2}O_{3-δ} anode substrate and BaZr_{0.8}Yb_{0.2}O_{3-δ} electrolyte were tape-casted and co-fired. Then, LSC cathode was screen-printed on the electrolyte surface. Electrochemical measurements were performed at 600 °C under the condition with wet H₂-N₂ and wet O₂-N₂ flows for the anode and cathode sides, respectively. AC impedance was measured under the open circuit condition in the range from 500 kHz to 0.01 Hz.

Figure 1 shows impedance spectra for anode-supported PCFC under the open circuit condition at 600 °C. As shown in figure 1, new arcs at low frequencies around 1 Hz seems to exist in Nyquist plot under low P_{H₂} conditions (P_{H₂} = 0.10 and 0.24 atm), which suggests that the diffusion resistance in the anode were large at a low hydrogen concentration. In addition, the open circuit voltage of the cell under P_{H₂} = 0.10 atm condition was much lower than the theoretical one calculated by Nernst equation (Table 1). In the case of PCFC, an electron hole conduction causes the internal leakage current through the electrolyte, and thus might decrease the hydrogen concentration by the fuel consumption and increase the anode diffusion resistance.

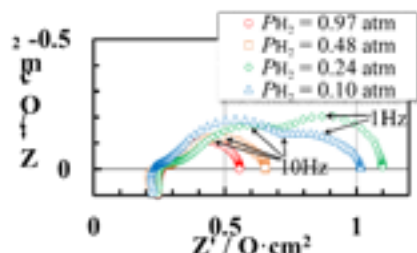


Figure 1 AC impedance spectra for anode-supported PCFC under the open circuit condition. Operating temperature: 600 °C, anode gas: x% H₂-3% H₂O-(97-x)% N₂ (x = 97, 48, 24, 10), cathode gas: 20% O₂-3% H₂O-77% N₂.

Table 1 Open circuit voltage of PCFC in this work

anode P _{H₂} [atm]	BZYb cell OCV* [V]	Theoretical OCV** [V]
0.97	0.986	1.136
0.48	0.951	1.123
0.24	0.890	1.110
0.10	0.052	1.093

* cathode gas condition: P_{O₂} = 0.20 atm

**calculated by Nernst equation

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Effects of Ni on sintering behavior and electrochemical properties of Ba(Zr,Ce,Y)O_{3-δ}

Yuanze Huang, Rotraut Merkle, and Joachim Maier

Max Planck Institute für Festkörperforschung, Heisenbergstr. 1, 70569, Stuttgart, Germany

Tel.: +49 15202618275

y.huang@fkf.mpg.de

Abstract

At temperatures of 400 to 700 °C, Y-doped BaZrO₃ with moderate (≤ 20%) Ce content (BZCY) possesses both high bulk conductivity and excellent chemical stability against H₂O and CO₂ [1,2]. However, its utilization as PCFC electrolyte has been long hindered due to poor sinterability and low grain boundary conductivity (proton depletion in the space charge zones). Solid State Reactive Sintering (SSRS) with NiO as sintering aid improves the sinterability of BZCY significantly [3,4]. Phase formation, densification and grain growth are achieved in the same step with a transient Ba,Ni,Y-oxide liquid phase. However, too high Ni contents are detrimental for bulk proton uptake and potentially lead to high volume changes and Ni formation under reducing conditions. Therefore, a compromise between grain growth and proton uptake needs to be found.

We investigate Ba_{1.015}Zr_{0.664}Ce_{0.20}Y_{0.136}O_{3-δ} + x wt% NiO with 0.125 ≤ x ≤ 1.0 (1 wt% NiO ≈ 4at% Ni). Ceramics can be fully densified at 1500 to 1550 °C. Despite the high density ≥ 95% grain sizes remain small (≤ 1 μm) when x ≤ 0.25 irrespective of high sintering temperature and long sintering time. For x ≥ 0.375 the grains grow up to ≈ 5 μm parallel to densification. Samples with substitutional Ni on the B site are prepared for comparison. The Ni addition can affect the defect chemistry in several ways, e.g. by entering the structure on the B site, or extracting Ba from the perovskite structure. While the SSRS procedure works also for Sc-doped BaZrO₃, it fails for undoped BaZrO₃.

Thermogravimetry measurements show a significant detrimental effect of Ni on proton uptake which indicates that Ni rather leads to Ba-deficiency in BZCY than entering the perovskite structure. Such an A-site deficiency is detrimental as it lowers the effective acceptor dopant concentration. Impedance Spectroscopy shows a decreased bulk conductivity with increasing NiO content, consistent with the decreased proton uptake. The grain boundary conductivity exhibits some scatter among samples, which is under further investigation by SEM, TEM-EDX, EELS. It increases with increasing NiO content which results from increased grain size as well as slightly higher specific grain boundary conductivity.

This study demonstrates the complexity of the transient liquid phase formation and its interplay with bulk defect concentrations. Overall, 0.375 to 0.5 wt% NiO can be recommended as compromise between good sinterability, improved grain boundary conductivity and acceptable bulk proton uptake.

Funding from BMBF (project Protmem, Förderkennz. 03SF0537C) is acknowledged.

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Electrochemical properties of cathodes for PCFC with Yb-doped BaZrO₃ electrolyte

Yuichi Mikami, Kaori Takeuchi, Takehito Goto, Kosuke Yamauchi, and Tomohiro Kuroha

Technology Innovation Division, Panasonic Corporation,
3-1-1 Yagumo-naka-machi, Moriguchi City, Osaka 570-8501, Japan

Tel.: +81-70-4016-3470

Fax: +81-6-6906-4595

mikami.yuichi001@jp.panasonic.com

Abstract

In recent years, protonic ceramic fuel cell (PCFC) has been expected as a high efficiency and low cost power generation system. As the electrolyte material for PCFC using reforming gas, it is required high conductivity and chemical stability against CO₂. Acceptor doped BaZrO₃ (BaZr_{1-x}M_xO_{3-δ}) is potential material because it has high ionic conductivity and chemical stability against CO₂.

Ni is generally used as PCFC anode. It was reported that Yttrium doped BaZrO₃ reacts with NiO at high temperature and form BaY₂NiO₅ as secondary phase [1], which phase is instable under wet CO₂ condition. Our recent study showed that BaZr_{0.8}Yb_{0.2}O_{3-δ} (BZYb) has lower reactivity with NiO than BaZr_{0.8}Y_{0.2}O_{3-δ} [2]. By using BZYb, it is expected to improve PCFC durability.

In this study, the electrochemical properties of cathodes for PCFC with BZYb electrolyte were focused. The properties of some well-known cathode materials, (La_{0.6}Sr_{0.4})CoO_{3-δ} (LSC), (La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_{3-δ} (LSCF), (La_{0.6}Sr_{0.4})FeO_{3-δ} (LSF), La(Ni_{0.6}Fe_{0.4})O_{3-δ} (LNF) are examined. First, polarization resistances of cathodes above written are compared by AC impedance measurement using cathode symmetric cells. Table 1 shows the polarization resistances of cathodes measured at 600°C, and it was found that LSC showed the lowest polarization resistance.

Then, electrochemical performances were measured for an anode supported planar cell using LSC as cathode and BZYb as electrolyte. During measurements, 3% H₂O-20 %O₂-77% N₂ and 3% H₂O-97%H₂ are flowed to the cathode and anode side, respectively. Figure 1 shows *I-V* and *I-P* curves of the cell, and the maximum power densities were 703 mW/cm², 498 mW/cm² and 262 mW/cm² at 700, 600, and 500 °C, respectively. It was found that PCFC with BZYb electrolyte and LSC cathode exhibits high electrochemical performances.

Table 1 Polarization resistances of cathodes measured at 600 °C in 3% H₂O-air using symmetric cells

Cathode	Polarization resistance [Ωcm ²]
LSC	0.18
LSCF	1.17
LSF	1.37
LNF	2.50

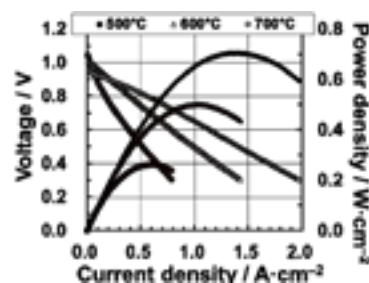


Figure 1 *I-V* and *I-P* curves of planar cell with LSC cathode and BZYb electrolyte. Anode gas: 3% H₂O-H₂, cathode gas: 20% O₂-3% H₂O-77% N₂.

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Optimization of the co-precipitation synthesis of BaCe_{0.6}Zr_{0.2}Y_{0.2}O₃ nanopowders

Krzysztof Zagórski, T. Miruszewski, S. Wachowski, A. Mielewczyk-Gryń, Katarzyna Wiciak, and Maria Gazda

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,

Center of Nanotechnology A
Narutowicza street 11/12, 80-233 Gdańsk, Poland
Tel.: +48 58 348 66 12

krzysztof.zagorski@pg.edu.pl

Abstract

Solid solutions of barium cerate and barium zirconate are considered to be the most widely used and state of the art ceramic proton conductors, thanks to their high protonic conductivity at intermediate temperatures provided by barium cerate and chemical stability granted by barium zirconate [1]. However, barium zirconates (and to a lesser extent, also BaCeO₃-BaZrO₃ solid solutions) as refractory materials suffer from poor sinterability [2]. Electrolytes are required to be as close to ideally dense as possible, therefore many works focus on densifying the BaCeO₃-BaZrO₃ ceramics. One of the approaches is utilizing powders with nano-sized grains [3].

Co-precipitation is a wet-chemical method commonly used to synthesize nanopowders. It is a straightforward technique that produces well-defined and less-agglomerated powders, when compared to solid-state methods. However, the phase purity and exact morphology of the resultant nanopowders depend on a range of different parameters [4].

In this work, the influence of synthesis protocol, reaction temperature, pH, choice of precipitant and precipitant concentration as well as calcination temperature on the morphology, purity and properties of BaCe_{0.6}Zr_{0.2}Y_{0.2}O₃ nanopowders is investigated.

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DPD simulations of anion exchange membrane functionalized with different cationic groups and associated anions

Zhenghao Zhu, Xubo Luo, and Stephen J. Paddison

Chemical and Biomolecular Engineering, University of Tennessee

1512 Middle Drive, Knoxville, TN, 37996-2200 U.S.A.

Tel.: (865) 974-2026

Fax: (865) 974-7076

spaddison@utk.edu

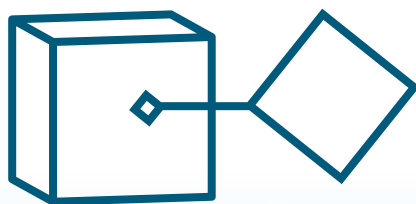
Abstract

Anion exchange membranes (AEMs) have drawn an increased interest over the past few decades. AEMs based on the triblock copolymer and polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene (SEBS) can be functionalized with different cationic groups. The coexisting anion, due to different routes of synthesis, can also be varied. The hydrated morphology of SEBS functionalized with various cationic groups plays a significant role in understanding the mechanism of anion transport and in preparing highly conductive and stable membranes. The morphology was controlled by the water content, as the SEBS copolymer consists of two parts: hydrophilic functionalized polystyrene blocks and hydrophobic ethylene/butylene blocks. Thus, it is necessary to study the effects of functional groups, anions, and water content on the morphology.

In this study, mesoscale dissipative particle dynamics (DPD) simulations were adopted and the SEBS polymer chain was modeled as a collection of connected compressible coarse-grained beads. The pair-wise interaction parameters of these beads were determined through DFT calculations.¹ We simulated the SEBS functionalized with various cationic groups (trimethylammonium $[(\text{CH}_3)_3\text{NH}]^+$; dimethylimidazolium $[\text{DMIm}]^+$; and trimethylphosphonium $[(\text{CH}_3)_3\text{PH}]^+$) under various degrees of hydration (4 – 20 H_2O /cationic head group). The effect of counterions (i.e., OH^- , Cl^- , and Br^-) was also investigated. The quantitative cluster analysis method² was utilized to extract the information on water cluster size, shape, and connectivity at different hydration levels, besides the radial distribution function. The results show that isolated water clusters do not contribute the anion transport until the water clusters build up the percolating networks as the hydration level increases beyond the threshold when the networks start to draw more water beads with small clusters disappearing gradually.

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