STOICHIOMETRY EFFECTS IN BULK AND AT INTERFACES: SOLID STATE IONICS AND BEYOND

Joachim Maier, Max Planck Institute for Solid State Research, Stuttgart, Germany s.weiglein@fkf.mpg.de

Key Words: Ion Transport, Storage, Batteries, Photovoltaics, Superconductivity

After an introduction on stoichiometric effects in bulk and at boundaries three selected examples are treated that show the relevance not only for Solid State Ionics but also beyond this field. *Example 1* gives a full picture of the storage in an electrode material including bulk and boundaries. In this way a unification of electrochemical electrode storage and supercapacitive storage is achieved. Several materials examples are discussed [1-3]. *Example 2* refers to photovoltaics. Organic-inorganic hybrid materials show a variety of anomalies at Iow frequencies and long times that can be explained by mixed conductivity. The nature of the mobile defects in MAPbI₃ and their dependence on stoichiometry is discussed. Furthermore, it is shown that the ionic conductivity can be increased by light by two orders of magnitude. This surprising phenomenon paves the way for future light-triggered or light-sensitive Solid State Ionics devices ("opto-ionics") [4-5]. *Example 3* shows the relevance of interfacial effects for superconductivity. By MBE replacing La-O layers atomistically sharply by Sr-O layers a two-dimensional doping is realized resulting in space-charge superconductivity. In this context the strength and weaknesses of zero, one- and two-dimensional doping are considered [6].

[1] C.-C. Chen, J. Maier, Nature Energy, 2018, 3, 102-108.

[2] C.-C. Chen., L. Fu, J. Maier, Nature, 2016, 536, 159-164.

[3] C. Zhu, R. E. Usiskin, Y. Yu, J. Maier, Science, 2017, 358, eaao2808.

[4] A. Senocrate, I. Moudrakovski, G. Y. Kim, T.-Y. Yang, G. Gregori, M. Grätzel, J. Maier, Angewandte Chemie International Edition, 2017, 56, 7755-7759.

[5] G. Y. Kim, A. Senocrate, T.-Y. Yang, G. Gregori, M. Grätzel, J. Maier, Nature Materials, 2018, 17, 445-449.
[6] F. Baiutti, G. Logvenov, G. Gregori, G. Cristiani, Y. Wang, W. Sigle, P. A. van Aken, J. Maier, Nature Communications, 2015, 6, 8586.

PHOTOCONDUCTIVITY ANALYZED IN THE FREQUENCY DOMAIN – AN INTRODUCTIORY CASE STUDY OF STRONTIUM TITANATE

Dino Klotz, Kyushu University and Massachusetts Institute of Technology dino.klotz@i2cner.kyushu-u.ac.jp Thomas Defferriere, Massachusetts Institute of Technology Jennifer L. M. Rupp, Massachusetts Institute of Technology Harry L. Tuller, Massachusetts Institute of Technology

Key Words: strontium titanate, photoconductivity, impedance spectroscopy.

Strontium titanate (STO, SrTiO₃) has been used for many applications in solid state electrochemistry and is considered a standard and model material. Its characteristics, and those of its derivatives such as STF (SrTi_{0.65}Fe_{0.35}O_{3-x}), have been characterized by many groups on various aspects, such as electronic/ionic conductivity, oxygen exchange kinetics and the impact of doping. Recently, the interaction of light with STO/STF has been of increased interest. A persistent photoconductivity has been observed [1] and enhanced oxygen exchange kinetics have been detected, opening up new fields of application, such as a light-driven fuel cell [2]. The reasons behind these effects remain subject to discussion or even speculation as the relation to the relatively large bandgap and the photoresponse at long wavelengths remains unclear. What makes the analysis of these effects difficult is the interplay of many electrochemical and photoelectrochemical processes that contribute to the photoresponse including the electronic and ionic conductivity, the number and nature of charge spectroscopy (EIS), one can distinguish diverse processes on the basis of their time constants and how they evolve as a function of operating conditions, such as temperature, atmosphere (leading to stoichiometry changes) and illumination. However, the impact of light can only be characterized implicitly as a change in other processes that also prevail in the dark.

Intensity modulated photocurrent/-voltage spectroscopy (IMPS/IMVS) have been shown to reveal valuable information about charge carrier dynamics for photoelectrodes and photovoltaic cells [3]. To the best of our knowledge, these techniques have never been applied to devices or materials that are not photoactive, or in other words, that do not show a photovoltage, such as a symmetrical model cells based on STO or STF. However, with the small signal light perturbation that is the key element of IMPS and IMVS, we can trigger the light effect directly and analyze the system response by its current and voltage signals.

In this contribution, we will begin with a brief introduction into IMPS and IMVS and show how these techniques can be applied to model electrodes consisting of STO and STF. The results are compared to EIS under different illumination and we will show how to extract the relevant information about the photoresponse. By evaluating the activation energies of the different electrochemical and photoelectrochemical processes, we can attribute those to physical effects and clarify some of the previously unknown processes that lead to anomalies observed in STO/STF under illumination.

The capacity of IMPS and IMVS have been underestimated so far and in this contribution, we will conclude with an outlook for their potential to other fields of application, such as ionic motion in perovskite solar cells that are thought to be responsible for their accelerated degradation under illumination. This work was supported by JSPS Core-to-Core Program, A. Advanced Research Networks: "Solid Oxide Interfaces for Faster Ion Transport".

References

- [1] M. C. Tarun et al., Phys. Rev. Lett. 111, 187403, 2013.
- [2] G. C. Bunauer, Adv. Funct. Mater. 26, 120, 2016.
- [3] D. Klotz et al., Phys. Chem. Chem. Phys. 18, 23438, 2016.

THE ELECTROCHEMICAL INTERFACE AND STOCHASTIC FUNCTIONS: A DATA-DRIVEN APPROACH TO MODELING NON-IDEAL BEHAVIOR IN CONCENTRATED SYSTEMS

David Mebane, West Virginia University david.mebane@mail.wvu.edu

Key Words: Defect chemistry, Thermodynamic properties, Theoretical approaches, Mixed conductors, Electrolytes

Researchers in the ionics field make frequent use of the mass-action principle – or the assumption of ideal thermodynamic behavior – in its physical models. These models are relatively easy to work with, leading to many useful and convenient formulae. However, they are strictly correct only in the limit of infinite dilution, and over-reliance on mass-action models in concentrated systems can lead to models that are grossly incorrect when compared with experimental reality. Recent microscopic experimental results gathered at surfaces and interfaces of ionic and mixed ionic-electronic conductors provide a striking example: classical models utilizing mass-action assumptions routinely underpredict the thickness of defect accumulation zones by an order of magnitude. Although atomistic models can be employed for concentrated systems, their utility is limited to very small simulation domains: continuum models must be used to predict the behavior of devices.

A key issue in any continuum-level thermodynamic treatment is the intractability of the microscopic defect interaction problem: beyond the ideal case, very few closed form solutions for the free energy in terms of concentrations are available. This presentation will introduce a data-driven methodology for determining these functions using either experimental or theoretical datasets. The method utilizes Gaussian process stochastic functions to represent the unknown functional relationships between defect concentrations and free energy, and calibrates these functions to data using Bayesian methods for calibration and model selection.

A continuum model for the structure of electrochemical interfaces in concentrated systems is the 'Poisson-Cahn' theory, which incorporates defect interactions and, crucially, gradient effects in a model that has proven successful in the replication of both macroscopic and microscopic experimental results. The data-driven approach to model building will be demonstrated in the context of Poisson-Cahn variational approaches applied to microscopic experimental datasets for grain boundaries in calcium-doped ceria.

EFFECT OF GRAIN BOUNDARIES ON ION MIGRATION IN STABILIZED d-Bi₂O₃ THIN-FILM ELECTROLYTES

Seung Jin Jeong, Dept. of MSE, KAIST jsjin1992@kaist.ac.kr Byung-Hyun Yun, Dept. of ESE, DGIST Incheol Jung, Dept. of ESE, DGIST Kang Taek Lee, Dept. of ESE, DGIST WooChul Jung, Dept. of MSE, KAIST

Key Words: stabilized bismuth oxide, pulsed laser deposition, solid electrolyte, grain boundary, thin film

Solid electrolytes with high oxygen-ion conductivity are of significant interest for many applications. Over the past several decades, numerous studies have been conducted on the effect of grain boundaries on the process of increasing the ionic conductivity of solid electrolytes. Given that nanocrystalline thin- or thick-films have been investigated in relation to lowering the operating temperature of solid electrolytes to less than 650 °C, more rigorous and quantitative assessments are necessary to determine how the ion transport characteristics are affected by the numerous interfaces formed in nano-grains devices.

In this context, we selected highly conductive stabilized δ -Bi₂O₃ as a target material and investigated the effect of grain boundary on ionic transport properties. More specifically, we focused on the oxygen ion conductivity and the phase stability that are closely associated with migration of anions and cations, respectively. The nanopolycrystalline thin films of yttria-stabilized Bi₂O₃ (YSB) and erbia-stabilized Bi₂O₃ (ESB) were prepared by the pulsed laser deposition (PLD), and the oxygen ion conductivity was analyzed by AC impedance spectroscopy (ACIS) as a function of temperature and oxygen partial pressure. First, both epitaxial and polycrystalline YSB films show nearly identical levels of oxygen ion conductivity at elevated temperature (350~500 °C) despite the fact that the poly-film possesses an extremely high density of the grain boundaries. Second, the epitaxial ESB thin film maintained cubic δ -phase for a long time (> 100 h) at 600 °C without any conductivity deterioration, whereas the poly film exhibited abrupt phase transition and reduced conductivity similar to bulk ESB. These observations provide precise, quantitative understanding of grain boundary effects through well-defined control experiments and a new direction for utilizing a stabilized δ -Bi₂O₃ as high-performance electrolytes for hightemperature electrochemical applications.



Figure 1 – (a) Arrhenius plot of the electrical conductivity of epitaxial and poly-crystalline YSB films and the (b) time-dependent conductivity behavior in epitaxial and poly-crystalline ESB films, respectively.

ENGINEERING ELECTROCHEMICAL NANOSCALE OXIDES

Harry L. Tuller, Massachusetts Institute of Technology, I²CNER, Kyushu University tuller@mit.edu

Key Words: Nonstoichiometry, in-situ characterization, defect equilibria, fuel cells, memory devices.

Oxides are playing an increasingly critical role as functional components in the fields of energy conversion/storage, microelectronics, sensors/actuators and catalysis. In turn, their electrical (ionic & electronic), optical and catalytic properties depend sensitively on their defect structure and oxygen nonstoichiometry, typically frozen in during processing, and rarely well defined. This is particularly true for thin films and nanoparticles/wires, where conventional methods, appropriate to bulk materials, do not apply. In this presentation, we review in-situ optical, electrochemical and dilatometric methods, developed or refined in our laboratory, to monitor, analyze and control nonstoichiometry, defect equilibria, transport and optical properties of oxide thin films and nano-sized particles. Examples include materials of interest as electrodes in fuel cells, and as components of sensors, catalysts and memory devices.

TRANSPORT PROPERTIES OF MIXED IONIC AND ELECTRONIC CONDUCTORS – FROM BULK TO NANOSTRUCTURE

Kathrin Michel, Center for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany kathrin.michel@phys.chemie.uni-giessen.de Juergen Janek, Center for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany Christian Reitz, Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany Torsten Brezesinski, Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany Matthias T. Elm, Center for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

Key Words: ceria, polaron, MIEC, mesoporous, surface

Ceria-based materials exhibit mixed ionic and electronic conductivity due to the redox-activity of the cation (Ce^{4+}/Ce^{3+}) and the oxygen ion mobility in the fluorite-type lattice, which intrinsically tends to form a high concentration of Anti-Frenkel defects. Both electrons and jons migrate by an activated hopping mechanism with activation barriers of 0.4 eV for the hopping process of small polarons, 0.8 eV and up to 1.6 eV for the migration and the extrinsic formation and migration of oxygen vacancies, respectively. This leads to a $p(O_2)$ -sensitive electrical conductivity, which can be dominated by each process depending on temperature and oxygen activity. Moreover, the material is quite tolerant regarding the substitution of cations. By choosing the type and range of substitution, electrical properties can be adjusted in different ways. Therefore, ceria and its substituted analogues qualify for various applications as solid electrolytes in oxygen membranes, electrode material in solid oxide fuel cells (SOFCs) and in combination with the high oxygen storage capacity for support material in heterogeneous catalysis. The defect chemistry of ceria is already extensively investigated in literature. Thus the material is an ideal model system to study interface effects, in particular the concentration and type of electronic and ionic defects as well as their transport properties in the vicinity of interfaces, complementing the established defect chemical models for bulk material. Within this work we compare the solid solution of ceria and praseodymia (Ce_{1-x}Pr_xO_{2- δ}) with the solid solution of ceria and zirconia (Ce_{1-x}Zr_xO_{2- δ}). It is already known, that due to the redox-activity of Pr-ions the combination with praseodymia can lead to an additional transport of polarons, increasing the electronic contribution to electrical conductivity. In contrast, the combination with isovalent zirconia results in an increase of the so-called reducibility of ceria due to the size mismatch of the cations. To gain a deeper understanding of the role of these substitutions on electrochemical transport processes at interfaces, highly ordered mesoporous thin films of Ce1-xPrxO2-5 (CPO) and Ce1-xZrxO2-5 (CZO) have been investigated. The mesoporous samples have been synthesized by a sol-gel process using evaporation induced self-assembly, resulting in a regular pore structure surrounded by a closed packed, interconnected 3D architecture of nanocrystallites. The structural properties were analyzed by SEM, WAXD, XRD, XPS and Raman spectroscopy, confirming the successful synthesis of a mesoporous material of high structural guality, where the surface dominates over the bulk behaviour. The electrical properties were investigated as a function of temperature and oxygen partial pressure using electrochemical impedance spectroscopy. The comparison of the results with previous results of single crystalline samples elucidates the effect of the continuous pore structure on electrical transport properties. The CZO thin films show an unusual $p(O_2)$ -dependence at high oxygen partial pressures, which cannot be explained by standard defect chemical models. Furthermore, both mesoporous samples reveal a conductivity plateau under strongly reducing conditions, which is discussed in terms of hopping statistics and defect-defect interaction.

TAILORING NON-STOICHIOMETRY AND MIXED IONIC-ELECTRONIC CONDUCTIVITY IN NANOSTRUCTURED Pr-SUBSTITUTED CERIA

George F. Harrington, Kyushu University, MIT harrington.frederick.george.302@m.kyushu-u.ac.jp Dmitri Kalaev, MIT Bilge Yildiz, MIT Kazunari Sasaki, Kyushu University Nicola H. Perry, I²CNER, Kyushu University Kyushu University, MIT, Illinois at Urbana–Champaign Harry L. Tuller, MIT, I²CNER, Kyushu University

Key Words: Pr-doped ceria, mixed ionic-electronic conductor, interfaces, grain boundaries, nano-structure.

High concentrations of mobile oxygen vacancies are crucial for devices such as SOFCs, SOECs, gas permeation membranes, and sensors, while for other applications such as ferroelectrics and piezoelectrics, oxygen vacancies are detrimental. Hence there is great interest in tailoring the oxygen vacancy concentration and mobility for given materials. Changes in oxygen non-stoichiometry also result in dilation of the crystal lattice, known as chemical expansion, and therefore there is a coupling between the electrical, chemical, and mechanical properties known as *electro-chemo-mechanical coupling*. Confined systems, such as thin films, are being investigated as a way to tailor the non-stoichiometry and transport properties of materials, shifting the paradigm away from searching for new materials or compositions.

Pr substituted CeO₂ (PCO) is an excellent model mixed ionic-electronic conductor (MIEC) for fundamental studies. In high pO₂ conditions, vacancy formation is accompanied by the reduction of Pr^{4+} to Pr^{3+} and the material displays MIEC behavior via oxygen vacancy migration and small polaron electron hopping between the valence-active cations. PCO has been extensively studied, and the defect chemistry, chemical expansion, and transport properties are well described in the bulk material.[1,2] Also, measuring the optical absorption has been demonstrated as a powerful tool for monitoring non-stoichiometry in PCO.[3] This makes it an excellent choice



Figure 2 – STEM images of PCO/SrTiO₃ multilayers. Conductivity as a function of pO2 and layer thickness

for studying the interplay of strain, space-charge, and electrochemo-mechanical coupling effects at homogeneous and heterogeneous interfaces, including their impact on transport properties.

In this contribution, we demonstrate how non-stoichiometry and transport properties can be modified in PCO for three nanostructured systems: (1) nano-granular polycrystalline films, (2) multilayers of PCO and SrTiO₃, (3) vertically aligned nano-composites (VANs). Each system was fabricated by pulsed laser deposition and comprehensively analyzed by using high-resolution X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy combined with electron energy loss spectroscopy.

In this work we measure both the optical absorption and conductivity *in-situ* as a function of pO_2 and temperature to deconvolute and extract the concentration of charge carriers and their mobility in the nanostructured materials. This contribution not only provides crucial insights into the way grain boundaries and interfaces affect electro-chemo-mechanical coupling, but also demonstrates a variety of routes in which mixed ionic-electronic conductivity can be tailored for a range of different device architectures.

References:

- [1] Bishop, et al., Phys. Chem. Chem. Phys. 13 (2011) 10165
- [2] Bishop, et al., J. Eur. Ceram. Soc. 31 (2011) 2351
- [3] Kim, et al., Chem. Mater. 26 (2014) 1374

DEPARTURE FROM SOLID SOLUTION BEHAVIOUR IN DOUBLE PEROVSKITES

David N. Mueller, Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Germany dav.mueller@fz-juelich.de

Daniel S. Bick, Institute for Materials in Electrical Engineering (IWE2), RWTH Aachen University, Germany Tomáš Duchoň, Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Juelich, Germany Jan Hempeelmann, Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Germany
Felix Gunkel, Institute for Materials in Electrical Engineering (IWE2), RWTH Aachen University, Germany Daniel Toebbens, KMC2, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany Jakub Drnec, 4ID31, European Synchrotron Radiation Facility, FR-38043 Grenoble, France
Rainer Waser, Institute for Materials in Electrical Engineering (IWE2), RWTH Aachen University, Germany Ilia Valov, Institute for Materials in Electrical Engineering (IWE2), RWTH Aachen University, Germany Claus M. Schneider, Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Germany

Key Words: Double Perovskites, MIEC, X-Ray Absorption Spectroscopy

Mixed ionic electronic conducting oxides (MIEC) serve a plethora of electrochemical applications such as cathodes for solid oxide electrochemical cells and oxygen evolution reaction catalysts for water splitting. These applications rely to a large extent on the MIEC's ability for electron and/or ion transfer across the solid/gas or solid/liquid interface. The efficacy of these reactions being governed by the surface defect chemistry and electronic structure, rational design of the (surface) chemistry presents itself as an auspicious path to tune these properties towards optimal device performance.

The perovskite structures' (ABO₃) unmatched capability to accommodate virtually the whole periodic table of elements in the cation sublattice suggests the ability to tune the electronic and ionic defect structure towards





favorable electrochemical activity by careful engineering of the cation composition. Many favorable choices of chemistry, however, may lead to a departure from the ideal cubic perovskite structure, be it in the form of a complete decomposition or more subtly by ordering phenomena in either sublattice, impacting defect and electronic structure profoundly and thus presenting a limit to guided design. One boilerplate example is the double perovskite Pr_xBa_{1-x}CoO_{3-d} (PBCO) where A-site as well as vacancy ordering may take place. In this work, we investigate the whole compositional space of PBCO with X-Ray absorption spectroscopy, Resonant and High Energy Grazing Incident X-Ray diffraction to assay the phase relations and their impact on electronic and defect structure and with that the electrocatalytic activity.

We find a departure from solid solution behavior that, in addition to the anticipated transition from the hexagonal to a cubic polytype, manifests itself in the formation of superstructures along the substitution series pointing to subtle ionic rearrangements. At

higher Pr contents we found A-site ordering to form the double perovskite structure $AA'B_2O_{6-d}$, which shows a profound impact on the electronic structure close to the Fermi level of the CoO_6 building block which is generally found to be responsible for electrochemical activity. Surprisingly, aliovalent A-site substitution, as well as the hexagonal to cubic transition, only has a minuscule effect on the electronic structure and the electrocatalytic efficiency, contrary to the A-site ordering showing a considerable one attributed to the rearrangement of the electronic states induced by ordering effects. Additionally, in oriented thin films of the ordered polymorph we found a hugely anisotropic electronic structure at the CoO_6 manifold by means of X-Ray linear dichroism spectroscopy pointing to a further avenue to engineer the density of states at the Fermi level and with that electrocatalytic performance.

A HIGH-TEMPERATURE MÖSSBAUER STUDY INTO IONIC AND ELECTRONIC DISORDER IN BSCF5582

Klaus-Dieter Becker, Technische Universität Braunschweig, Germany k-d.becker@tu-braunschweig.de Piotr Gaczynski, Technische Universität Braunschweig Ralf Kriegel, Fraunhofer Institute IKTS, Germany

Key Words: Mössbauer spectroscopy, defect chemistry, oxides.

Perovskite-type compounds of the (Ba1-xSrx)(Co1-yFey)O3-5 family have been intensely investigated in respect to their mixed ionic-electronic conductivity and their oxygen disorder which is characterized by extremely high δvalues. The latter properties have made (Ba0.5Sr0.5)(Co0.8⁵⁷Fe0.08Fe0.12)O3-5 (BSCF5582) one of the most promising ceramic materials for oxygen separation membranes. We report on ⁵⁷Fe Mössbauer in situ studies of BSCF5582 conducted between room temperature and 1000 °C in atmospheres of variable oxygen activity in order to obtain insight into local coordination and valence of iron at working conditions and into the distribution of oxygen vacancies on their different sites. The magnetically-split room-temperature Mössbauer spectra of BSCF5582 reveal the presence of two inequivalent iron species and show significant changes with oxygen content [1]. Evaluation of signal intensities confirms results from theoretical computations on vacancy formation in BSCF which indicate that formation energies of the various types of oxygen vacancies differ by the order of 0.1 eV only [2,3]. The spectral analysis also shows that the distribution of oxygen vacancies on the different sites of the perovskite structure of BSCF is far from random [1]. In the paramagnetic high-temperature phase (T ≥ 320 °C), the guadrupole-split signals demonstrate that local symmetry is lower than cubic. At 700, 850, and 1000°C, the spectra have been collected as a function of oxygen activity, a_{02} (5 $\cdot 10^{-5} \le a_{02} \le 1$). Isomer shifts (IS) as well as quadrupole splittings (QS) were found almost independent of ao2. This unexpected finding is discussed in respect to simultaneous, stoichiometry-related changes in valence and local coordination of the iron probes. The isothermal decrease of signal intensity observed with increasing oxygen deficit is attributed to changes in the vibrational properties of the highly oxygen-deficient material.

1. P. Gaczynski, A. Harpf, J. Boer, R. Kircheisen, R. Kriegel, K.-D. Becker, ⁵⁷Fe Mössbauer study into oxygen vacancy disorder of $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$, Solid State Ionics 316C (2018) 59-65.

2. E.A. Kotomin, Y.A. Mastrikov, M.M. Kuklja, R. Merkle, A. Roytburd, J. Maier, First principles calculation of oxygen vacancy formation and migration in mixed conducting $(Ba_{0.5}Sr_{0.5})(Co_{1-y}Fe_y)O_{3-\delta}$ perovskites, Solid State Ionics 188 (2011) 1-5.

3.Y.A. Mastrikov, M.M. Kuklja, E.A. Kotomin, J. Maier, First-principles modelling of complex perovskite $(Ba_{0.5}Sr_{0.5})$ (Co_{1-y}Fe_y)O_{3- δ} for oxide fuel cell and gas separation membrane applications, Energy Environ. Sci. 3 (2010) 1544-1550.

PREPARATION OF Ba_{1-x}Ln_xFeO_{3-δ} and BaFe_{1-x}Ln_xO_{3-δ} (Ln: TRIVALENT ION) WITH CUBIC PEROVSKITE STRUCTURE AND RANDOM DISTRIBUTION OF OXIDE ION VACANCY

Takuya Hashimoto, College of Humanities and Sciences, Nihon University takuya@chs.nihon-u.ac.jp Yunosuke Matsumoto, College of Humanities and Sciences, Nihon University Shogo Shimizu, College of Humanities and Sciences, Nihon University Masaki Kitadume, College of Humanities and Sciences, Nihon University Tsubasa Sato, College of Humanities and Sciences, Nihon University Takashi Okiba, College of Humanities and Sciences, Nihon University

Key Words: Ba_{1-x}Ln_xFeO_{3-δ}, BaFe_{1-x}Ln_xO_{3-δ}, perovskite structure, mixed conductor, oxide ion vacancy

Oxides with perovskite structure and random arrangement of oxide ion, such as $Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-\delta}$, attract much interest as oxygen permeation material. For wide spread of oxygen permeation devices, development of new material without Co is highly desired because of high cost of Co. Recently, we reported that arrangement of oxide ion vacancy in monoclinic $BaFeO_{2.5-\delta}$ changes from ordered to random by partial La^{3+} substitution for Ba^{2+} site, resulting in cubic perovskite structure and improvement of electrical conductivity [1, 2]. Fujishiro reported preparation of $BaFe_{1-x}In_xO_{3-\delta}$ with cubic perovskite structure and enhancement of electrical conductivity with In substitution [3]. It is expected that material with higher property may be developed by substitution of other trivalent ion, such as lanthanoid or Y, for Ba- or Fe- site in $BaFeO_{2.5-\delta}$. In this work, preparation of various $Ba_{1-x}Ln_xG_{3-\delta}$ (*Ln*: trivalent ion) was examined and factors determining substitution site and crystal structure were investigated.

The samples of Ba_{1-x}*Ln*_xFeO_{3-δ} and BaFe_{1-x}*Ln*_xO_{3-δ} were prepared with Pechini method. Each solution of Ba²⁺, Ln^{3+} and Fe³⁺ was mixed with nominal cation composition. After addition of citric acid and ethylene glycol, the solution was heated at about 450 °C, resulting in precursor. The precursor was calcined at 700 °C for 24 h in air, followed by 1300 °C for 10 h in air twice. The crystal structure and lattice constants of the specimens were investigated with X-ray diffraction. The chemical state of Fe and oxygen content of the specimens were evaluated with iodometric titration.

Single phase of Ba_{1-x}La_xFeO_{3- δ} and Ba_{1-x}Nd_xFeO_{3- $\delta} with cubic perovskite structure was obtained for <math>0.1 \le x \le 0.6$ and $0.1 \le x \le 0.5$, respectively. Cubic perovskite Ba_{1-x}Ln_xFeO_{3- δ} was also obtained for *Ln*=Sm, Eu and Gd despite that BaFe₂O₄ was observed as second phase and that compositional range where the cubic perovskite phase was obtained decreased with decreasing ionic radius of *Ln*. It was revealed that the cubic perovskite phase was obtained where tolerance factor was more than 0.98. For *Ln* with smaller ionic radius such as Y, Ho, Yb, Ba₁₋ *xLn*_xFeO_{3- δ} with cubic perovskite structure was never prepared.</sub>

For *Ln*=Nd, Sm, Gd, Ho, Yb and Y, single phase of BaFe_{1-x}*Ln*_xO_{3- $\delta}$ with cubic perovskite structure was successfully prepared although compositional range of *x* was narrow such as $0.075 \le x \le 0.1 \sim 0.2$. The *x* range where single cubic perovskite phase was obtained spread with decreasing ionic radius. The generation of BaFe₂O₄ in Ba_{1-x}*Ln*_xFeO_{3- $\delta}$ with *Ln*=Sm, Eu and Gd was attributed to compositional deviation due to partial Fesite substitution of Sm, Eu and Gd.}}

Figure 1 shows difference of ionic radius of 12-coordinated Ln³⁺ and Ba²⁺. Difference of ionic radius of 6-

coordinated Ln^{3+} and Fe^{3.3+} are also shown in Fig. 1. The smaller difference of ionic radius of La^{3+} and Ba^{2+} than that of La^{3+} and $Fe^{3.3+}$ is suggested to be an origin of substitution of La for Ba site instead of Fe-site. For Ho, Y and Yb, no substitution for Ba-site but Fe-site is ascribed to smaller difference of ionic radius of Ln^{3+} and Fe^{3.3+}. For Nd, Sm and Gd, the difference between Ln^{3+} and Ba²⁺ and Ln^{3+} and Fe^{3.3+} was similar, resulting in capability of substitution for both Ba- and Fe- site.

[1] T. Sato et al., Solid State Ion., 290 (2016)
71. [2] T. Okiba et al., Solid State Ion., 320
(2018) 76. [3] F. Fujishiro, Mater. Chem. Phys., 153 (2015) 5.



Figure 4 – Difference of ionic radius of 12-coordinated Ln^{3+} and Ba^{2+} and 6-coordinated Ln^{3+} and $Fe^{3.3+}$.

ENHANCED OXYGEN EXCHANGE OF PEROVSKITE OXIDE SURFACES THROUGH STRAIN-DRIVEN CHEMICAL STABILIZATION

WooChul Jung, Dept. of MSE, KAIST wcjung@kaist.ac.kr

Key Words: Perovskite oxide, Surface Sr segregation, Lattice strain, Thin films

Surface cation segregation and phase separation, of strontium in particular, have been suggested to be the key reason behind the chemical instability of perovskite oxide surfaces and the corresponding performance degradation of solid oxide electrochemical cell electrodes. However, there is no well-established solution for effectively suppressing Sr-related surface instabilities. Here, we control the degree of Sr-excess at the surface of SrTi_{0.5}Fe_{0.5}O₃₋₅ thin films, a model mixed conducting perovskite O₂-electrode, through lattice strain, which significantly improves the electrode surface reactivity. Combined theoretical and experimental analyses reveal that Sr cations are intrinsically under a compressive state in the SrTi_{0.5}Fe_{0.5}O₃₋₅ lattice and that the Sr–O bonds are weakened by the local pressure around the Sr cation, which is the key origin of surface Sr enrichment. Based on these findings, we successfully demonstrate that when a large-sized isovalent dopant is added, Sr-excess can be remarkably alleviated, improving the chemical stability of the resulting perovskite O₂-electrodes



Figure 5 – Comparison of the relative surface Sr enrichment and the surface oxygen exchange coefficient of epitaxial SrTi_{0.5}Fe_{0.5}O_{3-δ} thin films with the degree of induced in-plane strain

SURFACE MODIFICATION THROUGH OXIDE ALD TO IMPROVE OXYGEN EXCHANGE RATE ON PEROVSKITE SURFACE

Jongsu Seo, Dept. of MSE, KAIST jjong156@kaist.ac.kr Bonjae Koo, Dept. of MSE, KAIST YeonJu Kim, Corporate R&D, LG Chem Sanghoon Ji, Dept. of Land, Water and Environment, KICT Jeong Hwan Kim, Dep. of Nano-process, KIMM WooChul Jung, Dept. of MSE, KAIST

Key Words: Sr segregation, Atomic layer deposition, Electrical conductivity relaxation, Oxygen exchange coefficient

Segregation and phase separation on perovskite oxide (ABO₃) surface have been considered as a key detrimental factor to the performance of energy conversion devices such as solid oxide/electrolysis cells. Recently, the overcoat of less reducible cations has been suggested as a way to suppress the surface Sr segregation on Sr-containing perovskite oxides. However, the detailed requirements of the coating layer to sufficiently stabilize the perovskite surface hasn't been systematically investigated yet. In this wok, we fabricate La_{0.6}Sr_{0.4}CoO₃ (LSC) thin-film model electrode *via* pulse layer deposition and observe how the degree of Sr segregation varies with the type and thickness of the overcoat layer. Al₂O₃ and HfO₂ with different thickness are coated on LSC *via* ALD, and the oxygen exchange rate of both bare and ALD-coated samples is measured *via* electrical conductivity relaxation. It is found that both Al₂O₃ and HfO₂ layers suppress the Sr segregation only within a narrow thickness range, i.e., 1-2 nm for Al₂O₃ and 0.2 – 0.4 nm for HfO₂, respectively. These observations are discussed with solubility and diffusivity of Al and Hf in the host oxide lattice, providing a critical guideline of a new surface modification method to stabilize the perovskite surface at high temperatures.



Figure 6 – The surface oxygen exchange coefficient (k_{chem}) of LSC film with and without HfO₂ coating

CHEMICAL STRAIN IN PEROVSKITE-LIKE MATERIALS

Andrey Zuev, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia andrey.zuev@urfu.ru

Vladimir Sereda, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Ivan Ivanov, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Dmitry Malyshkin, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Dmitry Tsvetkov, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia

Key Words: perovskite, double perovskite, chemical strain, defect structure, preferable coordination.

Pseudo-cubic perovskites based upon substituted oxides RBO₃₋₅ as well as double perovskites RBaB₂O₆₋₅ and Sr₂BMoO₆, where R=rare-earth element and B=*3d*-transition metal, with A-site and B-site, respectively, cation ordering are very promising materials for a variety of different devices for moderate high temperature applications. The unique feature of the oxides is their ability to undergo both thermal strain and that induced by the defects of oxygen nonstoichiometry in the oxide crystal lattice. The latter is called as chemical or defect-induced strain, which is extremely sensitive to the defect structure of the oxide material. This property was shown recently to be isotropic for pseudo-cubic perovskites unlike that of double perovskites. The crystal lattice of a double perovskite expands along *a*-axis and simultaneously contracts along *c*-axis with the decreasing lattice oxygen content. The model of the oxide lattice chemical strain based on a change of mean ionic radius due to reduction of most reducible cation has been recently developed by us. In this work we introduced the new feature in the model such as change of preferable coordination of cations caused by change of oxygen content in the oxide.

The modified model was shown to enable correct prediction of chemical expansion upon increasing oxygen nonstoichiometry along **a**-axis for both pseudo-cubic and double perovskite oxides and simultaneous lattice contraction along *c*-axis in double perovskites. Thus most important finding is that simultaneous lattice contraction along *c*-axis in double perovskites is caused by aforementioned change of preferable coordination.

THE FERMI ENERGY IN OXIDES: ASSESSING AND UNDERSTANDING THE LIMITS USING XPS

Andreas Klein, TU Darmstadt, Germany aklein@surface.tu-darmstadt.de
N. Bein, TU Darmstadt, Germany
C. Castro Chavarria, TU Darmstadt, Germany
R. Giesecke, TU Darmstadt, Germany
Y. Hermanns, TU Darmstadt, Germany
B. Huang, TU Darmstadt, Germany
S. Kashiwaya, TU Darmstadt, Germany
C. Lohaus, TU Darmstadt, Germany
K. Schuldt, TU Darmstadt, Germany
H. Wardenga, TU Darmstadt, Germany
W. Jaegermann, TU Darmstadt, Germany

Key Words: Fermi energy, photoemission

The Fermi energy in semiconductors can often be freely controlled across the whole energy gap by doping. This is not the case in oxides, where different mechanisms exist, which can limit the range of the Fermi energy. These limits can be caused by i) dopants having deep rather than shallow charge transition levels, ii) self-compensation where the Fermi energy dependence of the defect formation energy leads to spontaneous formation of compensating defects, iii) the change of the oxidation state of either the cations or the oxygen. The latter is particularly relevant for compounds with transition metal or rare earth cations and has been recently demonstrated to explain the low water splitting efficiency of hematite [1].

This presentation will demonstrate that the limits of the Fermi energy can be assessed using X-ray photoelectron spectroscopy (XPS). The variation of the Fermi energy can thereby be achieved either by deposition of thin films on different substrates, by deposition of differently doped films, by different surface treatments including oxygen and vacuum annealing, oxygen plasma treatments and water adsorption, or by formation of interfaces with low and high work function metal oxides. Among the different treatments, oxygen plasma treatment and water adsorption are most effective in moving the Fermi energy down and up, respectively.

The presentation will give an overview on the experimental approach and its limitations and demonstrate the observation of the different limitation mechanisms. Extensive data sets for various oxides, including differently doped SrTiO₃, BaTiO₃, Pb(Zr,Ti)O₃, (La,Sr)FeO₃, (La,Sr)MnO₃, BiFeO₃, LaAlO₃, BiVO₄, CeO₂, Fe₂O₃, Co₃O₄, Bi₂O₃, ZnO, In₂O₃, SnO₂, NiO, Cu₂O, MgO, Al₂O₃ and SiO₂ are available. The effects will be illustrated using selected materials and the alignment of the Fermi energy limits will be discussed.



Figure 1 – Upper and lower limits of the Fermi energy in different oxides as observed

^{1.} C Lohaus et al., Nature Commun. 9, 4309 (2018).

NON-INNOCENT ROLE OF FLUORINE AS AN ELECTRON DONOR IN OXIDES

Tomáš Duchoň, Peter-Grünberg-Institut 6, Forschungszentrum Jülich GmbH, Germany t.duchon@fz-juelich.de Matthew J. Wolf, Department of Physics, University of Bath, United Kingdom Miroslav Kettner, Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberng, Germany Claus M. Schneider, Peter-Grünberg-Institut 6, Forschungszentrum Jülich GmbH, Germany

Key Words: cerium oxide, fluorine, covalency, photoemission spectroscopy

Engineering of reducible oxides is generally focused on the cation sites. As such, anion doping remains an underutilized tool despite its unique potential in altering the defect chemistry and steering redox processes. In this contribution, we explore the possibilities offered by substitution on the anion site on the case of a



Figure 1 – Calculated projected densities of states of the top two layers of fluorine-doped ceria(111) slabs. Ce⁴⁺ and Ce³⁺ are represented by large light and dark grey spheres, respectively. The fluorine dopants are distributed as follows: a) in the sub-surface layer, b) in the surface layer, and c) in the surface layer and adsorbed on top. The PDOS are separated vertically. Each line of PDOS is corresponding to the contribution from atoms with which it is aligned in the structural model to the left of each plot. The darker the color, the higher the PDOS.

prototypical reducible oxide, namely cerium oxide, doped with fluorine. The choice of fluorine is motivated by the general stability of fluorine in oxide lattices and the fact that it can be readily incorporated in these up to very high concentration with minimal structural distortion [1]. Utilizing photoemission spectroscopy in combination with density functional theory [2], we show that the general notion of fluorine acting as a straightforward ionic donor fails to capture the intricacies of electronic interactions at play. Specifically, we provide evidence for covalent hybridization in the nominally ionic fluorine-cerium interaction that allows for altering the anion derived electron density in cerium oxide beyond the oxygen 2p band (see Figure 1), contrary to the simplified picture of solely introducing a deeperlaying fluorine 2p band [3]. The emergent electronic configuration can be further coupled to standard valence band engineering methods, such as strain manipulation, to provide an unprecedented playaround for designing the oxide properties. Our results also demonstrate the practicality of interatomic resonant photoemission spectroscopy as a gauge of non-trivial electronic effects of ligand origin, allowing to efficiently probe the above-mentioned effects. We note that fluorine doping represents a complement to oxygen vacancy engineering and highlight the fact that, unlike oxygen vacancies, the electronic effects generated by fluorine can persist in an oxidizing environment. The latter represents an important contribution the electronic modification of mixedanion oxides can provide to a breadth of fields, ranging from superoxide stabilization to resistive switching.

[1] Kettner M. et al., Journal of Physical Chemistry C 120, 26782–26792 (2016).

[2] Duchoň T. et al., Physical Review B 95, 165124 (2017).

[3] Duchoň T. et al., Physical Chemistry Chemical Physics, submitted.

EVOLUTIONALLY SEARCH WITH DENSITY FUNCTIONAL CALCULATIONS FOR A NEW CLASS OF ONE-DIMENSIONAL *ELECTRIDE*

Tomofumi Tada, Materials Research Center for Element Strategy, Tokyo Institute of Technology Junjie Wang, Materials Research Center for Element Strategy, Tokyo Institute of Technology Hideo Hosono, Materials Research Center for Element Strategy, Tokyo Institute of Technology

Key Words: Electride, Evolutionally search, Density functional calculation

An *electride*, a unique material in which electrons serve as anions, has begun to attract attention for its high performances in electronic and catalytic applications. However, the chemically active property of electrides make the synthesis very difficult, and thus finding stable electrides is a big challenge. Based on a dimensional analysis on the stability of electrides [1], we focused on phosphide-based compounds, and we adopted a state-of-the-art theoretical evolutionally search combined with density functional calculations for a new class of electrides; Strontium phosphide in which anionic electrons are ordered in a one-dimensional network (Fig.1) was found [2]. The presence of the one-dimensional electride was proved by the successful synthesis and X-ray diffraction pattern of the compound. However, an interesting discrepancy appears in its electronic property:

metal from density functional theory, but insulator from experiment [2]. We analyzed the discrepancy in terms of the inherent instability of one-dimensional metal especially in halffilled systems, and found a gap-opening by introducing electron correlations, which implies the possibility of the one-dimensional electride as a Mott-insulator. Recently, ytterbium antimonide which takes the same crystal structure of the strontium phosphide is found as a Mott-insulating electride [3]. Although a standard density functional calculation is not preferred for correlated systems, the "structure prediction" by evolutionally search combined with density functional probably work well also for such a system because of the energy scale differences between structural changes and electron correlations.

References

[1] T. Tada, J. Wang, and H. Hosono, J. Comput. Chem. Jpn., 16, 135-138 (2017).

[2] J. Wang, K. Hanzawa, H. Hiramatsu, J. Kim, N. Umezawa, K. Iwanaka, T. Tada, and H. Hosono, J. Am. Chem. Soc. 139, 15668-15680 (2017).

[3] Y. Lu, J. Wang, J. Li, J. Wu, S. Kanno, T. Tada, and H. Hosono, Phys. Rev. B 98, 125128-1/12 (2018).



Figure 1 Crystal structure of Sr5P3.

DIFFERENT DEFECTS FORMATION MODES UNDER SEVIER REDUCING CONDITION IN PRIMITIVE CUBIC PEROVSKITES, BaZr_{1-x}Y_xO_{3-x/2} and BaSn_{1-x}Y_xO_{3-x/2}

Katsuro Hayashi,* Hiroshi Watanabe, Hirofumi Akamatsu, George Hasegawa Kyushu University, Japan, *k.hayhashi@cstf.kyushu-u.ac.jp

Key Words: hydride (H⁻) ion; *F*⁺ center, photochemical reaction; protonic conduction; lone-pair electrons.

Reduction processes using metal hydride agents modify the chemical and structural properties of metal oxide crystals with different manners, depending on the host crystals and the process conditions [1]. In BaTiO₃, a reduction using CaH₂ leads to partial and random substitution of H⁻ for the O²⁻ site, which is compensated by a formal valence change of Ti⁴⁺ to Ti³⁺, imparting an electronic conduction [2] (*Fig.* 1*a*). In contrast, a low temperature reduction of SrFeO₃ preferentially eliminates O²⁻ at axial sites in the FeO₆ octahedra without the H⁻-incorporation to convert to SrFeO₂ with a unique planner four-coordinated Fe²⁺ [3] (*Fig.* 1*b*). An intermediate result has been obtained in a layered perovskite, LaSrCoO₄, in which H⁻ ions are selectively incorporated in specific O²⁻ sites to form *trans*-configuration of H⁻ ions [4]. Herein, we focus on the metal hydride-reduction of BaZr_{1-x}Y_xO_{3-x/2} (BZY) and BaSn_{1-x}Y_xO_{3-x/2} (BSY) and relevant defect chemistry. Both system have the primitive cubic perovskite structure and are popular fast protonic conductor. The latter is related to our expectation that the H⁻ ions are incorporated with a similar manner with the OH⁻ formation via O₀^X + V₀^{••} + CaH₂ \rightarrow 2H₀[•] + CaO. BZY and BSY powders were annealed in vacuum-sealed glass tubes containing metal hydride agents at 350–550 °C.

The H⁻ ion incorporation in the processed zirconate samples was confirmed by in ¹H-NMR and TG-DTA. A purple coloration appeared under UV-light illumination in lightly-reduced samples. Its origin was identified to be F^{+} center (V_{0}^{+}) by EPR. The coloration is coupled with an enhancement in electrical conductivity. These results are similar and complemental to the photochemical reaction ($H^- + O^{2-} \rightarrow 2F^+$ (e⁻) + OH⁻) observed in H⁻-doped mayenite [5-7] and apatite [7,8]. An electronic conductivity emerges with the coloration in mayenite, while no conductivity enhancement is available in apatite, owing to the presence or absence of facile electron hopping path between F⁺ site and neighboring oxygen vacancy sites. The BZY should be classified into the later, but the proton conduction is not forbidden, because its conduction path is connected along the occupied O²⁻ ions. The photochemically-enhanced conductivity in BZY is, therefore, assigned to the protonic conduction (Fig. 1c). As for the stannate series, the sample color changed from white to yellow, red, and brown with keeping the cubic perovskite structure as the reduction proceeds, while no additional color change was found after the UVillumination. Partial reduction of Sn⁴⁺ to Sn²⁺ was observed by XPS. Chemical composition of a reduced sample with x = 0.3 was determined to be BaSn^{IV}_{0.50}Sn^{II}_{0.20}Y_{0.30}O_{2.61}H_{0.08} by Rietveld analysis of neutron diffraction data, implying that H⁻ ion on the order of 10²¹ cm⁻³ is incorporated in this sample. Moreover, high concentration of Sn²⁺ with a few tens of percent is formed. ¹¹⁹Sn Mössbauer spectra was analyzed by a DFT calculation of crystal models with oxygen vacancies, and revealed that 5s² lone pair electronic states of Sn²⁺ is formed in the band gap above the valence band, and its electronic transition to the conduction band is responsible for the coloration. This defect is stabilized by oxygen vacancy pair with cis-configuration around the Sn²⁺ (Fig. 1d).



[1] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield et al., Nat. Commun. 9, 772 (2018).

[2] Y. Kobayashi, O. J. Hernandez, T. Sakaguchi, K. Hayashi,

H. Kageyama, et al., Nat. Mater. 11, 507 (2012).

[3] Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H.

Kageyama et al., Nature 450, 1062 (2007).

[4] M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer,

M. J. Rosseinsky et al., Science 295, 1882 (2002).

[5] K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, H. Hosono, Nature 419, 462 (2002).

[6] K. Hayashi, M. Hirano, H. Hosono, Bull. Chem. Soc. Jpn. 80, 872 (2007).

[7] K. Hayashi, P. V. Sushko, Y. Hashimoto, A. L. Shluger, H. Hosono, Nat. Commun. 5, 3515 (2014).

[8] K. Hayashi, H. Hosono, Phys. Chem. Chem. Phys. 18, 8186 (2016).

Figure. 1 Defect formation by metal hydride reduction in primitive cubic perovskites.

MODULATING METAL-OXYGEN BONDING IN LITHIATED METAL OXIDES WITH POINT DEFECTS

William C. Chueh, Department of Materials Science & Engineering, Stanford University wchueh@stanford.edu

The strength of the metal-oxygen (M-O) bond in oxides principally determines the band structure and the stability of oxygen relative to O₂ gas. Accordingly, such bonding is central to energy storage (for determining the redox potential) and electrocatalysis (for determining adsorbate bonding strength at the electrochemical interface). Traditionally, the M-O bond strength is tuned by changing the metal. We have recently discovered another important knob in LixMO₂: metal vacancies and antisite defects. In these materials, which are ubiquitous as positive electrodes in lithium-ion batteries, metal vacancies can form by moving a metal into the Li van der Waals gap. X-ray and neutron scattering measurements confirmed that introducing metal vacancies can substantially contract neighboring M-O bond length, transforming single bonds to double bonds (i.e., terminal metal oxo ligand). In select local configurations, even the peroxo species (O-O)²⁻ can form. These variations of oxygen bonding leads to dramatic variation in the energetics of the bonding and antibonding states as well as the stability of oxygen relative O₂ gas. In this talk, I will discuss the connection between local defect configurations and the M-O and O-O bonding in LixMO₂, where M spans 3*d*, 4*d* and 5*d* transition metals.

OXIDE ION TRANSPORT AND PHASE STABILITY IN THE EXCESS OXYGEN SCHEELITE PHASES

Stephen J. Skinner, Department of Materials, Imperial College London, UK s.skinner@imperial.ac.uk

Key Words: Scheelite, Oxide ion conductor, Electrolyte, Fuel cell

Oxide ion conductors for use in electrochemical devices such as solid oxide fuel cells and electrolysers are typically viewed as requiring three-dimensional isotropic structures that will promote ion transport. The majority of materials considered as electrolytes in devices are based on either the fluorite or perovskite structure types. An essential feature of the materials is that they will accommodate a range of oxygen lattice defects, typically through cation substitution, that introduces vacancies to maintain charge neutrality, and it is the presence and mobility of these defects that produce fast oxide ion conductors. An alternative that has only recently been explored is the potential for oxygen interstitial species to provide fast ion transport pathways. Initially studies focussed on anisotropic materials such as the layered perovskites as potential electrode materials, but more recently our studies have focussed on new electrolyte families.

Here we report our studies on the solid solution series $LaNb_{1-x}W_xO_{4+d}$ (x = 0 – 0.2) which adopts the distorted scheelite type structure. Introducing the W cation induces the ordering of the cation species, and charge



Figure 7 - Oxygen diffusion profile of La(Nb, W)O_{4+d} elecrolyte. Inset shows pathways through the structure

compensation through additional oxygen species. This leads to a series of complex modulated crystal structures, evidenced through electron and neutron diffraction studies. From the preparation of ceramic samples it has been possible to demonstrate that these superstructured phases are indeed fast oxide ion conductors, Fig 1, and that there are three-dimensional pathways through the structure. Additionally, these electrolytes have been demonstrated to functional effectively in electrolysis mode and thus offer considerable potential for future development.

STRUCTURE-CONDUCTIVITY RELATION IN OXYGEN ION CONDUCTORS: DOPED CERIA AND LA-MELILITES

Steffen Grieshammer, Helmholtz-Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich Germany; Institute of Physical Chemistry, RWTH Aachen University, Germany s.grieshammer@fz-juelich.de

Key Words: Oxygen ion conductors, ab-initio, strain, Monte Carlo

Oxygen ion conductors are fundamental materials for various electrochemical applications such as solid oxide fuel cells. On the microscopic level, the transport of individual ions is determined by the migration barriers and the interactions between defects, which depend on the structure of the material and the response to local disorder. Density functional theory (DFT) calculations allow the study of both structures and defect energies. In this paper, the relation between structural details and defect energies is investigated on the basis of two examples: The effect of strain on vacancy migration and interaction in biaxially strained, doped ceria and the structural distortions during interstitialcy migration in melilite structured La_{1+x}Sr_{1-x}Ga₃O_{7+x/2}.

The migration barriers and interactions in ceria with small (Lu³⁺), medium sized (Gd³⁺) or large (La³⁺) dopant ions are calculated for different strain states. Results show that the migration energies are affected by both the strain and the ionic radius of the cations along the migration path, which can be combined in a critical radius model. The interactions between vacancies and dopants are primarily determined by the dopant radius with an additional contribution due to the applied strain that cannot be explained by simple electrostatic interactions. In the melilites the site energies and migration barriers of oxygen interstitials depend on the occupation of surrounding cation sites by La³⁺ and Sr²⁺ ions. Calculations show an increasing stability of the interstitials with increasing number of La³⁺ ions. The transport of interstitial ions by an interstitialcy mechanism in the a/b-plane is facilitated by the flexible framework of corner-shared GaO₄ units and the relaxation of the GaO₄ tetrahedrons allow migration barriers of 0.15 eV and below.

The DFT derived energies are applied in Kinetic Monte Carlo simulations to obtain the ionic conductivity, thus relating the microscopic processes with the macroscopic transport properties.



Figure 8 – Relation between critical radius of the ideal lattice and the migration energy obtained for different dopants and strain states in ceria.

LOCAL DISTORTION BY DOPANTS AND PERCOLATION CONDUCTIVITY IN OXIDES

Shu Yamaguchi, The University of Tokyo/NIAD-EQ Yamaguti-s@niad.ac.jp Masashi Hara, The University of Tokyo Shogo Miyoshi, The University of Tokyo/NIMS

Key Words: chemical doping, local distortion, percolation conductivity, Raman spectroscopy

The chemical doping is a typical method to modulate the physical and chemical properties of oxides and other ionic solids and is often applied to emerge ionic conductivity by introducing ionic defects such as oxygen vacancy with suppressed electronic defects. However, those chemical dopants, which can also be categorized as an ionic defect, attract mobile species and work as a trap center for mobile ionic and electronic defects. This study is motivated to understand the origin of such interaction by DFT calculation and Raman scattering spectroscopy. The percolation conductivity, which appears as a result of such strong interaction between dopants and mobile carriers, is further discussed with emphasis on the crucial role of local distortion and its dynamic contributions.

The present study consists of two parts: The DFT simulation and Raman spectroscopy measurements on tetravalent ion-doped CeO2 to estimate the local distortion around the dopant ions. In the second part, we discuss percolation conductivities of proton and holes in proton-conducting perovskite oxides based on electrochemical measurements and the DFT simulation.

Pure CeO2 with cubic fluorite structure, known as a host material for excellent oxide ion conducting electrolyte with relatively high partial electronic conductivity in reducing conditions, shows a sharp and single triply-degenerated F2g peak in Raman spectroscopy owing to the crystal symmetry. Upon chemical doping of acceptor dopants, CeO2 starts to show multiple broad peaks slightly higher wave number to the F2g main peak, usually attributed to oxygen vacancy-induced local vibrational modes. There is, however, controversy left on the assignment of these defect induced peaks because observed broad dopant induced peaks never agree with the finitely split peaks estimated by DFT calculation.

In the present study, we employed CASTEP code using GGA-PBE functional for DFT simulation and made careful calculations: At first, the stable local structure of doped and undoped CeO2 was estimated by a structural relaxation concerning local distortion and energy, and Raman spectra were simulated by calculating scattering cross section. The present results on the DFT calculation suggest that the origin of dopant-induced peaks is due to a broken local symmetry by the presence of foreign atoms of dopants, but the intensity is determined by the extent of local distortion and extended relaxation length by the difference of ionic size of dopant and the matrix Ce4+ ions (1). Large distorted shells are isolated each other at lower concentration regime while overlapping begins at a relatively low concentration around 1-2% in case of cubic fluorite CeO2 phase owing to an extended relaxation length of local distortion. When all dopant ions are isolated, overall properties are governed by the matrix properties. In contrast, the stress shell accommodating dopant ion begin contributing to the macroscopic physical and chemical properties above a critical concentration. The overlapping shell contributes to the broadening of the Raman F2g and dopant related peaks (2). The stress shell mentioned above serves as an attracting or repulsive center for mobile ionic and electronic defects. We find good examples, such as oxide ion conductivity in acceptor-doped CeO2() and holes and proton conductivities in acceptor-doped perovskite oxides (3, 4). In the latter system, a transition from isolated traps to the percolation conductivity has been clearly observed, and discussion on local distortion is developed on the basis of both experimental and theoretical results (5).

REFERENCES

- () M. Hara and S. Yamaguchi; To be published.
- () J. Koettgen, et al.; Phys. Chem. Chem. Phys. 20, 14291–14321 (2018).
- () D.-Y. Kim, S. Miyoshi, and S. Yamaguchi; To be published.
- () S. Miyoshi, A. Ebara, and S. Yamaguchi; To be published.

() H. Takahashi, et al.; Chemistry of Materials, 2017, 29 (4), pp 1518–1526.

COMPUTATIONAL AND EXPERIMENTAL STUDIES OF DIFFUSION IN MONOCLINIC HFO2

Michael P. Mueller, Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany mueller@pc.rwth-aachen.de

Katrin Pingen, Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany Alexander Bonkowski, Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany Alexander Hardtdegen, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, 52428 Juelich, Germany Stephan Aussen, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, 52428 Juelich, Germany Andreas Kindsmueller, Institute of Materials in Electrical Engineering and Information Technology II, RWTH Aachen University, Germany

Susanne Hoffmann-Eifert, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Germany Roger A. De Souza, Institute of Physical Chemistry, RWTH Aachen University, Germany

Key Words: diffusion, oxides, SIMS, molecular dynamics, ion transport

Research on hafnia and zirconia has received a boost in the last two decades, mainly because of their electrical properties. As materials with high dielectric permittivity and a wide band-gap, they can replace SiO₂ in Si-based semiconductor devices as the gate dielectric, and they can be employed as the insulator in metal—insulator—metal structures, showing memristive behavior.^[1,2] Anion, and possibly cation, transport is of fundamental importance for the annealing of such devices and the proposed mechanism of resistive switching (filament switching in the case of HfO₂).^[2,3] In this study, we investigated both cation and anion diffusion in HfO₂ using diffusion experiments, with subsequent determination of the diffusion profiles by Secondary Ion Mass Spectrometry (SIMS). For the diffusion of oxygen in dense ceramics of monoclinic HfO₂, (¹⁸O/¹⁶O) isotope exchange anneals were performed in the temperature range $573 \le T/K \le 973$ at an oxygen partial pressure of $pO_2 = 200$ mbar.^[4] All measured isotope profiles exhibited two features: the first feature, closer to the surface, was attributed to slow oxygen diffusion in an impurity silicate phase; the second feature, deeper in the sample, was attributed to oxygen diffusion in a homogeneous bulk phase. The activation enthalpy of oxygen tracer diffusion in bulk HfO₂ was found to be $\Delta H_{D^*} \approx 0.5$ eV.

In contrast to oxygen diffusion, diffusion of cations in HfO₂ and other oxide-ion conductors is experimentally much more challenging. It is slow, requiring, therefore, high temperatures and long diffusion times. In the case of HfO₂, there is also the problem of Si impurities (see above), which are hard to get rid of in ceramic samples. To alleviate these problems somewhat, we directly investigated the diffusion of Zr in thin films of nanocrystalline, monoclinic HfO₂, prepared by Atomic Layer Deposition (ALD) and coupled with a sputtered top layer of ZrO₂ as a diffusion source. Diffusion experiments were performed in the temperature range $1173 \le T / K \le 1323$ in air. All measured diffusion profiles exhibited bulk diffusion and fast grain-boundary diffusion. Using numerical simulations, we were able to describe the profiles and extract diffusion in both cases were, surprisingly, the same at $\Delta H_{Db/Dgb} \approx 2.1 \text{ eV}$. They are also much lower than activation energies predicted by static atomistic simulations.^[5]

In order to aid the interpretation of the experimental data, we conducted atomistic simulations of cation diffusion in HfO₂. Specifically we performed Molecular Dynamics (MD) simulations using the empirical pair potentials derived by Catlow and Lewis.^[6,7] These potentials are suitable for describing defect behaviour in HfO₂.^[8,9] The activation enthalpy of Hf diffusion in bulk HfO₂ we obtained from the MD simulations agrees exceedingly well with the experimental results: $\Delta H_{D^*} \approx 2 \text{ eV}$. The reasons for this behaviour are discussed.

- [1]: V. A. Gritsenko et al., Phys. Rep 613, 1 (2016).
- [2]: R. Waser et al., Adv. Mater. 21, 2632 (2009).
- [3]: S. Uhlenbruck et al., Solid State Ionics 180, 418 (2009).
- [4]: M. P. Mueller, R. A. De Souza, Appl. Phys. Lett. 112, 051908 (2018).
- [5]: S. Beschnitt et al., J. Phys. Chem. C 119, 27307 (2015).
- [6]: C. R. A. Catlow, Proc. R. Soc. Lond. A. 353(1675), 533 (1977).
- [7]: G. Lewis, C. R. A. Catlow, J. Phys. C: Solid State Phys. 18(6), 1149 (1985).
- [8]: M. Schie et al., J. Chem. Phys. 146, 094508 (2017).
- [9]: M. Schie et al., Phys. Rev. Mat. 2, 035002 (2018)

NON-STOICHIOMETRY AND ION TRANSPORT IN HALIDE PEROVSKITES: EQUILIBRIUM SITUATION AND LIGHT EFFECTS

Alessandro Senocrate, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland a.senocrate@fkf.mpg.de

Gee Yeong Kim, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany Tae-Youl Yang, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany Giuliano Gregori, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany Michael Grätzel, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany Joachim Maier, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

Key Words: halide perovskites, ion transport, CH₃NH₃Pbl₃, photo-enhanced ion conduction.

In recent years, hybrid halide perovskites have been attracting great attention due to their exceptional photoelectrochemical properties.[1-2] When used as light-harvesters in solar cells, device efficiencies exceeding 22% can be realized. We showed that a deeper understanding of (i) functionality, (ii) stability, as well as (iii) the possibility to improve the performance require a thorough insight into non-stoichiometry and ion transport.[3-5] In this contribution, we study the nature of the ionic conductivity in methylammonium lead iodide (MAPbI₃), the archetypal halide perovskite, by means of a great number of electrochemical and nuclear magnetic techniques.[4] To aid the experimental investigation, we include detailed defect chemical modelling describing the effects of iodine partial pressure (Fig. 1a), doping and interaction with oxygen.[5] We also discuss results that show the significance of ion redistribution phenomena for relevant interfaces. By extending this study to the situation under illumination, we observe a striking enhancement of ionic conductivity by more than 2 orders of magnitude in MAPbI₃, alongside the expected increase in electronic conductivity.[6] We provide a mechanistic explanation of this astonishing phenomenon and discuss its relevance for future light-triggered ionic devices ("opto-ionics", see Fig. 1b).



Figure 1- (a) Kröger-Vink diagram depicting defect concentrations in MAPbI₃ as a function of iodine partial pressure. (b) Potential opto-ionic device in which I_2 permeation through MAPbI₃ is triggered by illumination.

References

- [1] C. Stoumpos, C. Malliakas and M. Kanatzidis, Inorg. Chem. 2013, 52, 9019.
- [2] D. Shi, V. Adinolfi, R. Comin et al., Science 2015, 347, 519.
- [3] T.-Y. Yang, G. Gregori, N. Pellet et al., Angew. Chemie 2015, 54, 7905.
- [4] A. Senocrate, I. Moudrakovski, G. Y. Kim et al., Angew. Chemie 2017, 56, 7755.
- [5] A. Senocrate, T.-Y. Yang, G. Y. Kim et al., Solid State Ion. 2018, 321, 69.
- [6] G. Y. Kim, A. Senocrate, T. –Y. Yang et al., Nature Mater. 2018, 17, 445.

IODIDE-ION TRANSPORT IN METHYLAMMONIUM LEAD IODIDE PEROVSKITE: SOME SURPRISING ASPECTS

Roger A. De Souza, Institute of Physical Chemistry, RWTH Aachen University desouza@pc.rwth-aachen.de Denis Barboni, Institute of Physical Chemistry, RWTH Aachen University Dennis Kemp, Institute of Physical Chemistry, RWTH Aachen University

Key Words: MAPbl₃; perovskite; iodine vacancies; thermodynamics; kinetics.

Methylammonium lead iodide, CH₃NH₃Pbl₃ (= MAPbl₃), is a hybrid organic–inorganic perovskite that exhibits excellent photovoltaic properties. In comparison with traditional photovoltaic materials, such as Si or CIGS, MAPbl₃ is evidently characterised by one or more highly mobile constituent ions. In photovoltaic devices based on MAPbl₃, ion mobility is deemed to be responsible for current–voltage hysteresis, a huge low-frequency dielectric response, and long-term instability. Despite enormous interest in ion transport, debate surrounds almost every aspect. This is evident in the excessive scatter in activation enthalpies reported in the literature for ion conduction in MAPbl₃ (see Fig. 1).



Figure 9 – Activation enthalpies reported in the literature for ion transport in MAPbl₃. Experimental data are shown as green lines, plotted against the temperature range over which the data was acquired. Computational data, referring to migration barriers obtained in static atomistic calculations, are plotted at zero K (red triangles, MA-vacancy migration; blue circles, iodinevacancy migration). The vertical dotted lines indicate the phase-transition temperatures: orthorhombic-tetragonal and tetragonal-cubic

In a recent study [1], we demonstrated that a single model with one set of parameters could quantitatively explain diverse experimental data related to ion conduction in MAPbI₃. The model combines knowledge of the jump rate of iodine vacancies with the results of defect chemical modelling. A quantitative expression for the vacancy jump rate was obtained by studying iodine tracer diffusion as a function of temperature and iodine-vacancy concentration by means of classical molecular-dynamics (MD) simulations. The defect-chemical model yields acceptor concentrations in experimental samples of 10¹⁵ cm⁻³ and lower, and the enthalpy and entropy of anti-Frenkel disorder. We also demonstrated that the generation of additional iodine vacancies can explain quantitatively the increase in the ionic conductivity under illumination.

In this contribution, I will present our model [1] in detail. I will also draw attention to several surprising aspects regarding ion transport in MAPbI₃ [2,3]. These are (i) the activation enthalpy of iodine-vacancy migration is very low at $\Delta H_{mig,v} = 80$ meV; (ii) the diffusivity of iodine vacancies would appear to be surprisingly high as a result; (iii) the dominance of anti-Frenkel disorder in the close-packed (perovskite) structure; (iv) the diffusivity of iodine interstitials needs to be lower than that of vacancies; (v) the transport behaviour of point defects in electric fields. Finally I will also make comparisons with the behaviour of the point defects in the oxide perovskite SrTiO₃.

- [1] D. Barboni and R. A. De Souza, Energy Environ. Sci. 11 (2018) 3266.
- [2] R. A. De Souza and D. Barboni, submitted.
- [3] D. Kemp, D. Barboni and R. A. De Souza, in preparation.

INORGANIC/ORGANIC HYBRID SUPERLATTICE FILMS TOWARD NEXT-GENERATION FLEXIBLE/WEARABLE THERMOELECTRIC DEVICES

Kunihito Koumoto, Nagoya Industrial Science Research Institute koumoto@apchem.nagoya-u.ac.jp Ruoming Tian, Toyota Physical and Chemical Research Institute Chunlei Wan, Tsinghua University Yifeng Wang, Nanjing Tech University

Key Words: thermoelectric, hybrid, superlattice, exfoliation, self-assembly

Liquid exfoliation has proven to be a scalable and versatile technique to produce large-scale twodimensional (2D) nanosheets among graphene, boron nitrides, layered perovskites and transition metal dichalcogenides. This also provides new insights into the assembly of multilayer heterostructures for novel functionalities. Here we present a solution-processed method to fabricate 2D inorganic/organic superlattice film for thermal energy harvesting, which can be either freestanding or be deposited onto substrates. The organic layer provides charge carriers to the inorganic layer, suppresses the overall thermal conductivity, and allows the material to be flexible. We have fabricated a thermoelectric module, which can generate a high power density of 2.5 W/m² at a temperature gradient of 70K, hitting new record among the organicbased flexible thermoelectric devices. Flexibility of our newly developed superlattice materials combined with organic TE materials would enable us to design various types of TE modules that cannot be realized by using conventional hard and stiff inorganic materials. Our newly designed TE modules will be demonstrated to be useful for energy harvesting in the future IoT society.



Figure 1 - LESA Process

References

- [1] R. Tian, C. Wan, N. Hayashi, T. Aoai, K. Koumoto, MRS Bull., 43, 193-198 (2018).
- [2] C. Wan, R. Tian, K. Koumoto et al., Nature Commun., 8, 1024 (2017).
- [3] R. Tian, C. Wan, K. Koumoto et al., J. Mater. Chem. A, 5, 564-570 (2017).
- [4] C. Wan, R. Tian, K. Koumoto et al., Nano Energy, 30, 840-845 (2016).
- [5] C. Wan, R. Yang, K. Koumoto et al., Nano Lett. 15, 6302-6308 (2015).
- [6] C. Wan, R. Yang, K. Koumoto et al., Nature Mater. 14, 622-627 (2015).
- [7] K. Koumoto et al., "Materials Aspect of Thermoelectricity", CRC Press, 2016.

EXPERIMENTAL THERMOCHEMICAL VERIFICATION OF TRENDS IN THERMODYNAMIC STABILITY OF HYBRID PEROVSKITE-TYPE ORGANIC-INORGANIC HALIDS

Dmitry Tsvetkov, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Dmitry.Tsvetkov@urfu.ru

Maxim Mazurin, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Ivan Ivanov, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Dmitry Malyshkin, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Anton Sednev, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Vladimir Sereda, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia Andrey Zuev, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia

Key Words: thermodynamics of formation, calorimetry, hybrid perovskite-type organic-inorganic halids.

Hybrid perovskite-type methylammonium lead halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials. Since the time of the first demonstration photovoltaic devices based on the hybrid perovskites $CH_3NH_3PbX_3$ (X = CI, Br, I) have showed huge progress in increase of conversion efficiency reaching currently 20.1%. However, despite very promising achievements fundamental chemistry and physics of hybrid organic-inorganic (HOIP) perovskites is far from being completely understood. In particular it is true for thermodynamic properties of HOIP perovskite-type halides ABX₃ and A₂BX₄ (A=CH₃NH₃, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Moreover, reported results of DFT calculations aiming at estimating the stability of these materials often give controversial results. In addition, some of the HOIP perovskites (for example, $CH_3NH_3PbX_3$ (X = CI, Br, I)) are known to be entropystabilized phases. Therefore experimental verification of the stability trends in HOIP perovskite-type halide systems is strongly required. This is especially important for assessment of the stability of these materials under particular working conditions. Therefore, the main aim of this work was to study the thermodynamics of formation of HOIP perovskite-type halides ABX₃ and A₂BX₄ (A=CH₃NH₃, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Their standard formation enthalpy at 298 K was measured by solution calorimetry. Heat capacity was measured in the temperature range 2-298 K using PPMS system. Standard entropy was obtained by integration of the Cp/T vs T curve. Standard Gibbs free energy of ABX₃ and A₂BX₄ (A=CH₃NH₃, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I) was evaluated using measured formation enthalpy and entropy. Trends in variation of the thermodynamic functions with chemical composition and crystal structure of HOIP perovskite-type halides were analyzed and compared with available results of DFT calculations.

This work was supported by the Russian Science Foundation (grant No. 18-73-10059).

MIXED-CONDUCTING CATHODE MATERIALS FOR PROTONIC CERAMIC FUEL CELLS: PROTON UPTAKE AND DEFECT INTERACTIONS

Rotraut Merkle, Max Planck Institute for Solid State Research, Stuttgart, Germany r.merkle@fkf.mpg.de Reihaneh Zohourian, Max Planck Institute for Solid State Research Giulia Raimondi, Max Planck Institute for Solid State Research Joachim Maier, Max Planck Institute for Solid State Research

Key Words: protonic ceramic fuel cell, hydration reaction, defect chemistry, defect interaction.

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 (so-called "bulk path").

The present work studies the hydration thermodynamics of $(Ba,Sr,La)(Fe,Co,Zn,Y)O_{3-\delta}$ mixed-conducting perovskites using thermogravimetry.[1] The degree of the hydration is significantly smaller for cathode perovskites compared to typical electrolytes (acceptor doped $Ba(Zr,Ce)O_{3-\delta}$) which are fully hydrated below \approx 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 $(Ba_{0.95}La_{0.05})(Fe_{0.8}Zn_{0.2})O_{3-\delta}$ with 10% of protons per formula unit at 250 °C in 17 mbar water partial pressure. The proton mobility of $(Ba,Sr)(Fe,Zn)O_{3-\delta}$ was found to be comparable to that $Ba(Zr,Y)O_{3-\delta}$ in electrolytes.[2] Based on these results, the bulk path is expected to be active for Ba-rich cathode materials.



The figure shows the proton uptake at 250 °C for various cation compositions. The increase with Ba content indicates that the proton uptake is closely related to the oxide ion basicity. A partial substitution of Zn on 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. These experimental results will be compared to DFT calculations. 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.

[1] R. Zohourian, R. Merkle, G. Raimondi, J. Maier, Adv. Funct. Mater. 2018, 28, 1801241.

[2] D. Poetzsch, R. Merkle, J. Maier, Phys. Chem. Chem. Phys. 2014, 16, 16446.

[3] R. Zohourian, R. Merkle, J. Maier, Solid State Ionics 2017, 299, 64.

[4] R. Zohourian, R. Merkle, J. Maier, ECS Transact. 2017, 77(10), 133.

DEFECT THERMODYNIMCS AND LATTICE SITE BASICITY OF PROTON AND MIXED CONDUCTING OXIDES

Tor S. Bjørheim, Department of Chemistry, University of Oslo, FERMiO, Norway. Maximilian Hoedl, Max-Planck Institute for Solid State Research, Germany Eugene Kotomin, Max-Planck Institute for Solid State Research, Germany Rotraut Merkle, Max-Planck Institute for Solid State Research, Germany Joachim Maier, Max-Planck Institute for Solid State Research, Germany

Key Words: Protons, hydration, DFT, electronic structure

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

 $H_2O(g) + O_0^{\times} + v_0^{\bullet\bullet} \rightleftharpoons 2OH_0^{\bullet}$ ⁽¹⁾

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

 $H_20(g) + 20_0^{\times} + 2h^{\bullet} + \Rightarrow 20H_0^{\bullet} + 1/20_2(g)$ (2) 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 of the binary oxides generally follow the expected periodic trends and are shown to correlated with the position of the O2p bonding states, reflecting the relationship between the oxide's electronic structure and basicity. We furthermore assess a series of perovskite structured oxides and discuss correlations between their defect thermodynamics/ion affinities and electronic structure, basicity and A-O and B-O bond characteristics

The research leading to these results has received funding from the Research Council of Norway (Grant nº 272797 "GoPHy MiCO") through the M-ERA.NET Joint Call 2016.

- [1] T. Norby, M. Widerøe, R. Glöckner and Y. Larring, Dalton Transactions, 19, (2004)
- [2] K.D. Kreuer, Annu. Rev. Mater. Res. 33 (2003) 333–59

DEFECT CHEMISTRY OF MIXED CONDUCTING DOUBLE PEROVSKITES

Ragnar Strandbakke, Dep. of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, Norway. ragnarst@smn.uio.no

Tor S. Bjørheim, Dep. of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, Norway.

Magnus H Sørby, Inst. for Energy Technology, Department of Physics, Norway

Aleksandra Mielewczyk-Gryń, Faculty of Applied Physics and Mathematics, Solid State Physics Department, Gdańsk University of Technology, Poland

Sebastian Wachowski, Faculty of Applied Physics and Mathematics, Solid State Physics Department, Gdańsk University of Technology, Poland

María Balaguer, Instituto de Tecnología Química (Universidad Politécnica de Valencia – Consejo Superior de Investigaciones Científicas), `1wZXC (SPAIN)

Truls Norby, Dep of Chemistry, University of Oslo, FERMiO, Norway.

Key Words: Defect Chemistry, Proton Conductors, Mixed Conductors, Electrodes

Barium Gadolinium Lanthanum Cobaltites with the general formula Ba1-xGd0.8-yLa0.2+x+yCo2O6-5 (BGLC) are reported as Mixed Proton and Electron Conducting materials (MPECs), and have been utilized as positrode (positive electrode) materials for Proton Ceramic Electrochemical Cells (PCECs) [1]. A defect chemical model, treating various charge carrying defects in BGLC was published in 2017 [2] and in this work we expand the model to also comprise formation of protons in BGLC. Protons can be incorporated by two different reactions, in a ratio depending on measurement conditions and the oxidation state of the material. Low temperatures and high pO_2 leaves BGLC oxidized, and with increasing electron hole concentration, the hydrogenation reaction is promoted with respect to hydration. Hydrogenation is confirmed by use of isothermal Dry-H₂O-D₂O switches in thermogravimetric measurements, revealing a larger concentration of protons than expected from hydration only (Figure 1, left). The reduction of BGLC by hydrogenation is slowly counteracted by oxygen uptake combined with an expected cation reordering, bringing the material back to its initial oxidation state after equilibration in wet conditions. By combining oxidation and hydration thermodynamics, hydrogenation entropy and enthalpy can be obtained, making it possible to model proton concentrations from hydration and hydrogenation separately by use of advanced defect chemistry (Figure 1, right). Hydration is proposed to be facilitated by a minor concentration of oxygen vacancies in the O-Co-O layers, where acidic vacancies may accommodate basic hydroxyl groups. These vacancies are neighboured by more basic oxide ions in the O-Ba-O and O-Ln-O layers which in turn may accommodate protons.



Figure 10 Left: Weight gain in BGLC (x = 0, y = 0.5) in dry air, 2 % H₂O and 2% D₂O at 300°C. Right: Total oxygen non-stoichiometry (δ), oxygen vacancies available for hydration, protons from hydrogenation, protons from hydration, total, modelled proton concentration, and measured hydration by TG in air versus temperature.

1. Strandbakke, R., et al., Gd- and Pr-based double perovskite cobaltites as oxygen electrodes for proton ceramic fuel cells and electrolyser cells. Solid State Ionics, 2015. 278: p. 120-132.

2. Vollestad, E., et al., Relating defect chemistry and electronic transport in the double perovskite Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O₆₋₅ (BGLC). Journal of Materials Chemistry A, 2017. 5(30): p. 15743-15751. Financial and scientific contributions from the Research Council of Norway (Grant n^o 272797 "GoPHy MiCO") through the M-ERA.NET Joint Call 2016.

MANGANESE OXIDE BASE ELECTROCATALYSTS FOR PROTON-CONDUCTING CERAMIC CELLS

Yoshitaka Aoki, Faculty of Engineering, Hokkaido University y-aoki@eng.hokudai.ac.jp Ning Wang, Graduate school of Chemical Sciences and Engineering, Hokkaido University Hajime Toriumi, Graduate school of Chemical Sciences and Engineering, Hokkaido University Chunyu Zhu, Faculty of Engineering, Hokkaido University Hiroki Habazaki, Faculty of Engineering, Hokkaido University

Key Words: ORR, OER, PCFC, SOEC; Cathode and anode materials

There has been a strong interest in clean and renewable energy sources due to finite fossil fuel sources, increasing oil prices and environmental concerns. Hydrogen is regarded as the leading candidate fuel, because it releases only H₂O during combustion and it is compatible to use in high efficiency fuel system. Steam reforming of hydrocarbon gas is currently the main way to produce hydrogen but still relies on fossil fuel consumption. On the contrary, water electrolysis using electric power generated by renewable energy is attracted as sustainable hydrogen production method. Especially, steam electrolysis using solid electrolyte cells is promising for efficient hydrogen production because high-temperature heat partly offers the energy for water electrolysis cell (SOEC) using proton-conducting ceramics to achieve highly efficient conversion from electrical power into chemical fuel gas directly. However, sufficient performance has not be achieved yet in the current system because large overpotential is needed for oxygen evolution reaction at anode owing to the relatively slow kinetics and the limited active zone in the anode/electrolyte interfaces due to the mismatch of ionic carries, Accordingly, it is a great challenge to develop high performance oxygen electrode with efficient electrocatalytic ability for 4 electron transfer oxygen evolution reaction.

Recently, it is reported that high valence state metal oxide reveal superior electrocatalytic activity for water oxidation s because the energy levels between the occupied metal orbital and the O 2p orbital are very close, causing a strong hybridization and facilitating o-o bond formation. Herein, we examined electrocatalytic performance of high valence state Mn(V) oxide Ba₃(MnO₄)₂ as an anode for SOEC This oxide has been reported to be very stable at elevated temperatures in oxidative conditions. Proton-conducting BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-δ} (BZCY) was used as proton conducting electrolyte. Bulk electrolyte cell were constructed with a BZCY disc which were prepared by solid state reactive sintering (SSRS) method. The electrolyte precursor powder was prepared by mixing proper amount of BaCO₃, CeO₂, ZrO₂, and Y₂O₃ according to the desired stoichiometry with the addition of 1.0wt.% NiO as a sintering aid. This mixture was ball-milled for 48 h and uniaxially pressed under 20 MPa for 1 min and then cold-isostatic-pressed under 100 MPa for 1 min. Finally, green pellets were calcined at 1500°C for 10 h so as to obtain dense electrolyte disc (2 mmd, 9 mm ϕ)Pt paste was applied at one side of the surface as a cathode. LSCF or LSCF/Ba₃(MnO₄)₂ mixed ink were screen-printed at the other side of the surface as anode materials. Samples are evaluated by XRD and XAS. The electrochemical impedance spectroscopy and I-V measurements were carried out to evaluate the SOEC properties.

Two kinds of anode materials were examined in this research, namely, the cell-1: Pt | BZCY | LSCF and cell-2: Ba₃(MnO₄)₂/LSCF mixed anode cell. The cell-2 showed superior steam electrolytic performance compared to cell-1. The current density of steam electrolysis of cell-2 was 145 mA cm⁻² meanwhile cell-1 was 145 mA cm⁻² in bias voltage of 1.5 V at 600°C. Impedance spectroscopy was conducted to evaluate the anodic polarization resistance. LSCF anode gives 6 Ω cm², however, the Ba₃(MnO₄)₂/LSCF composite anode gives 3 Ω cm². Furthermore, the spectral features were completely different between both. The spectrum of LSCF anode had three semi-circles: high frequency arc (10x-10y Hz), middle frequency arc (10zz-10zy Hz) and low frequency arc (10zz-10zy Hz). On the other hand, Ba₃(MnO₄)₂/LSCF involves only two semi-circles: high frequency arc (10zz-10zy Hz). These results indicate Ba₃(MnO₄)₂ changes the reaction pathway of water oxidation electrode/solid electrolyte interface. The oxygen evolution rate was measured by gas chromatography when electrolysis was performed at a constant current density of 100 mA, 200 mA, and 300 mA. The flax of oxygen from anode side is corresponded to that of calculated from the current density, indicating that the faradaic efficiency was almost 100%. XRD pattern of the sample after electrolysis showed that there were no secondary phases, indicating stability of Ba₃(MnO₄)₂ is promising for OER electrocatalysts for SOEC.

HYDRATION IN FLUORITE-RELATED RARE-EARTH CERATES

Truls Norby, Department of Chemistry, University of Oslo truls.norby@kjemi.uio.no Liv-Elisif Kalland, Department of Chemistry, University of Oslo Andreas Løken, Department of Chemistry, University of Oslo Tor Bjørheim, Department of Chemistry, University of Oslo Reidar Haugsrud, Department of Chemistry, University of Oslo

Key Words: La₂Ce₂O₇, Nd₂Ce₂O₇, fluorite, hydration, protons.

Hydration enthalpy and water uptake in La_{2-x}Nd_xCe₂O₇ series (x = 0.0, 0.5, 1.0 and 2.0) have been measured using combined thermogravimetry (TG) and differential scanning calorimetry (DSC), TG-DSC. The DSC data unambiguously yield standard molar hydration enthalpies of around -74 kJ/mol independent of water uptake.

The TG results however needs interpretation according to a model, and it is clear that they cannot be fitted to a classical model of hydration of all disordered oxygen vacancies. Instead, the hydration appears to be limited to a small fraction of the free vacancies. Hydration further decreases as the Nd content (x) and long range order increases and regions of disorder decrease.

We propose a new model explaining why hydration occurs only in a small fraction of the nominally free vacancies: The higher basicity of La/Nd compared to Ce enables hydration, and high coordination with La/Nd around OH is needed to stabilize the proton/hydroxide in order to obtain exothermic hydration. The statistical variation of coordination around oxygen sites in a disordered fluorite oxide creates a limited number of such oxide ions sites which results in limited hydration.

It is expected that this new purely statistical approach to interactions in special cases of heavily defective compounds may apply to rationalize unexpected defect behavior also in other systems.

PERCOLATION EFFECTS DURING IONIC MOTION

Manfred Martin, Institute of Physical Chemistry, RWTH Aachen University, Germany martin@rwth-aachen.de

Key Words: Oxygen ion conductor, conductivity maximum, proton conductor, percolation.

Interest in materials exhibiting oxygen ion and/or proton conduction has increased during the last years owing to their great importance for energy and environmental applications.

Ceria-based oxides are regarded as key oxide materials because rare earth-doped ceria shows a high oxygen ion conductivity even at intermediate temperatures. Using density-functional theory (DFT), we have investigated defect interaction and oxygen migration energies as well. By means of Kinetic Monte Carlo (KMC) simulations we then investigated the oxygen ion conductivity. We show that all interactions between the defects, namely vacancy-dopant attraction, dopant-dopant repulsion and vacancy-vacancy repulsion as well contribute to the so-called conductivity maximum of the ionic conductivity [1].

BaZrO₃-based oxides are proto-type proton conductors. Using density-functional theory (DFT), we have investigated defect interaction and proton migration energies in Y-doped BaZrO₃. The macroscopic proton conductivity was then investigated by means of KMC simulations. We discuss the resulting proton conductivities concerning special percolation pathways for protons [2].

Finally, we compare our theoretical results with experimental ones and discuss similarities and differences for oxygen ion and proton conductors.

1. J. Koettgen, S. Grieshammer, P. Hein, B. Grope, M. Nakayama, M. Martin, Phys. Chem. Chem. Phys., 2018, 20, 14291-14321

2. F. Draber, C. Ader, M. Martin, submitted

MOLECULAR DYNAMICS AND KINETIC MONTE CARLO HYBRID APPROACH FOR EFFICIENT DYNAMICS AND PROTON CONDUCTION IN PHOSPHORIC ACID

Albert M. Iskandarov, Materials Research Center for Element Strategy, Tokyo Institute of Technology iskandarov@mces.titech.ac.jp Tomofumi Tada, Materials Research Center for Element Strategy, Tokyo Institute of Technology

Key Words: phosphoric acid, proton conduction, molecular dynamics, kinetic Monte Carlo.

Proton conducting media are important materials to facilitate further the progress of efficient energy conversion systems, such as proton-exchange membrane (PEM) fuel cells. Nafion, a sulfonic acid based proton conductor, is one of the most promising and commonly used H⁺-conductors due to its high chemical stability and high proton conductivity. However, because of the hydration requirement, the operating temperature of the Nafion membranes is limited to the range from 0 to 100 °C. The operating temperature above this range is one of the ways to enhance the proton conductivity and cell performance. Therefore, H⁺-conductors with working temperature above 100 °C are urgently required to substitute water in the Nafion membranes. Phosphoric acid (boiling temperature is 213 °C) is one of the candidates that can serve that purpose, because it conducts protons even when it is anhydrous [1].

To systematically design the phosphoric acid based H⁺-conductors, one has, firstly, to accurately describe the proton conductivity in phosphoric acid. Molecular dynamics (MD) based on density functional theory (DFT) calculations is the most reliable method that can describe the proton dynamics based on the accurate DFT estimation of the energy barriers for the H⁺-hopping. However, this DFT-MD approach is very time consuming. The kinetic Monte Carlo (kMC) is one of the methods that can provide accelerated dynamics of the system, if the energy barriers for the H⁺-hopping are estimated beforehand, for example, using the DFT method. However, the drawback of the kMC approach is ability to treat only solid phases [2], not liquid. Another possible method, to have accelerated system dynamics, is the classical MD. But, with the conventional MD models it is difficult to accurately describe potential profiles for the H⁺-migration between molecules and ions. Therefore, to overcome the limitations of the MD and kMC methods, we combine classical MD and kMC methods to develop a hybrid MD-kMC model that can describe the proton conductivity in phosphoric acid. Parameters of the interatomic interaction were adopted from Yan *et al.* [3]. The energy barriers for the H⁺-hopping were initially estimated by DFT calculations and then were slightly adjusted to get better agreement with experimental values of the self-diffusion coefficients of ¹H (D_H) and ³¹P (D_P) at 100 °C [4].



Figure 11 – D_H (filled) and D_P (open) derived from the simulation (circle) and experiment (square)

[1] R. He et al., J. Membr. Sci. 226 (2003) 169
[2] T. Tada et al., ECS Trans. 57(1) (2013) 2437
[3] L. Yan et al., J. Phys. Chem. B 111 (2007) 6357
[4] Th. Dippel et al., Solid State Ionics 61 (1993) 41

The accuracy of the developed model can be judged from Figure 1, where the self-diffusion coefficients D_H and D_P are estimated in the range of 0 - 100 °C. The absolute values of the self-diffusion coefficients are overestimated in comparison with experiment [4]. However, the value of $D_H/D_P = 2.52$ at 100 °C is close to the experimental value of 3.18, which proves significant contribution from the H+-hopping to the total diffusion of protons. In this paper we present details of the developed model, show how the model parameters affect the selfdiffusion coefficients, and illustrate that this model can be easily extended for more sophisticated systems containing phosphoric acid.

INVESTIGATION OF CATHODIC REACTION IN SOFCs AND PCFCs BY USING PATTERNED THIN FILM MODEL ELECTRODES

Koji Amezawa, Tohoku University koji.amezawa.b3@tohoku.ac.jp Keita Mizuno, Tohoku University, Japan Katsuya Nishidate, Tohoku University, Japan Yoshinobu Fujimaki, Tohoku University, Japan Yuki Shinomiya, Tohoku University, Japan Yuta Kimura, Tohoku University, Japan Takashi Nakamura, Tohoku University, Japan Keiji Yashiro, hoku University, Japan Fumitada Iguchi, hoku University, Japan Hiroo Yugami, hoku University, Japan Tatsuya Kawada, Tohoku University, Japan Kiyofumi Nitta, JASRI, Japan Oki Sekizawa, JASRI, Japan Yasuko Terada, JASRI, Japan

Key Words: SOFC, PCFC, Cathode, Model electrode, X-ray absorption spectroscopy

In recent years, fuel cells operating at relatively high temperatures, such as solid oxide fuel cells (SOFCs) using an oxide ion conducting electrolyte and proton ceramics fuel cells (PCFCs) using an proton conducting electrolyte, attract attentions as high-efficient energy-conversion devices. For further enhancements of the performance and the durability of SCFCs and PCFCs, it is essential to understand the electrode reactions. In particular, the knowledge on the dominant reaction path in the electrodes would help us to optimize the material and the microstructure of the electrode.

As cathodes for SOFCs and PCFCs, perovskite or perovskite-related oxides containing 3d transition metals are typically used. However, the cathodic reactions on these oxide electrodes are not fully understood. In this work, cathodic reactions on such oxide cathodes were investigated by using patterned thin film model electrodes.

In the case of a practical porous electrode, its complicated microstructures often make the precise investigation on the electrode reactions very difficult. In this work, for the detailed evaluation of the electrode reaction in SOFCs and PCFCs, we proposed to use patterned thin film electrodes as model electrodes. The schematic illustrations of the proposed model electrodes are presented in Fig.1. The patterned thin film electrodes are kinds of a columnar electrode simplifying the microstructures of a porous electrode. We fabricated patterned thin film electrodes with or without TPBs, as shown in Fig. 1(A) and (B), respectively, by helps of lithography and pulsed laser deposition techniques. By applying these model electrodes, we can expect to examine the electrode reaction while ignoring the influence of the microstructures. In the presentation, the cathodic reactions in SOFCs and PCFCs will be discussed based on the results of electrochemical and spectroscopic measurements with the proposed model electrodes.



Fig. 1. Schematic illustration of the patterned thin film electrodes: (A) without and (B) with triple phase boundary.

COMPREHENSIVE UNDERSTANDING OF CATHODIC AND ANODIC POLARIZATION EFFECTS ON STABILITY OF NANOSCALE OXYGEN ELECTRODE FOR REVERSIBLE SOLID OXIDE CELLS

Jong-Ho Lee, Korea Institute of Science and Technology, Korea, Republic of, jongho@kist.re.kr

Ho-II Ji, Korea Institute of Science and Technology, Korea, Republic of, Sung Min Choi, Korea Institute of Science and Technology, Korea, Republic of, Junsung Ahn, Korea Institute of Science and Technology, Korea, Republic of, Hyoungchul Kim, Korea Institute of Science and Technology, Korea, Republic of, Kyung Joong Yoon, Korea Institute of Science and Technology, Korea, Republic of, Ji-Won Son, Korea Institute of Science and Technology, Korea, Republic of, Byung-Kook Kim, Korea Institute of Science and Technology, Korea, Republic of, Hae-Weon Lee, Korea Institute of Science and Technology, Korea, Republic of,

Key Words: Solid oxide cell, Oxygen electrode, Degradation, Polarization, LSCF

Whereas solid oxide cells (SOCs), which perform dual functions of power generation (fuel-cell mode) and energy storage (electrolysis mode) with high efficiency at high temperatures, are considered a potent candidate for future energy management systems, it is yet far from their practical use due to the fact that the stable longterm operations have not been achieved. Particularly, degradations of oxygen-electrode in the both electrolysis and fuel-cell operations are considered as the most imminent issues that should be overcome. Unfortunately, even the origins and mechanisms of degradation in the oxygen-electrode have not been clearly established due to the difficulties in precise assessments of microstructural/compositional changes of porous electrode, which is a typical form in actual solid oxide cells, and due to the diversities in operating conditions, electrode structure and material, fabrication history, and so on. We simultaneously investigated the degradation phenomena in electrolysis and fuel-cell operations for 540h using identical two half cells composed of a geometrically welldefined, nanoscale La0.6Sr0.4Co0.2Fe0.8O3-5 (LSCF) dense film with a thickness of ~ 70 nm on Ce0.9Gd0.1O2-5 electrolyte. Owing to the benefit of well-defined geometry of LSCF thin film, the microstructural/compositional changes in LSCF films were successfully analyzed in nanoscale, and the correlation between the components of electrochemical impedance and the major origins resulting in degradations was clarified. Furthermore, we suggest the most probable degradation mechanisms, and importantly, it is newly suggested that kinetic demixing/decomposition of LSCF, which is not readily observable in the typical porous-structured electrode, are highly probable to affect the both fuel-cell and electrolysis long-term degradations.

OXYGEN DIFFUSION OF NON-STOICHIOMETRIC (La, Sr)MnO_{3-d}/CERIA NANO-COMPOSITE SOFC CATHODE

Seiichi Suda, Shizuoka University, Japan suda@shizuoka.ac.jp Haruka Sakuma, Shizuoka University, Japan Masashi Hase, NIMS, Japan

Key Words: SOFC, Cathode, LSM/Ceria, Nano-composite, and Inter-diffusion.

Solid oxide fuel cell (SOFC) is one of the highly efficient energy generation system, and it requires higher power density per unit volume to expand SOFC stationary market as well as vehicle. Co-sintering of stacks or cells including electrodes, electrolyte and separators is most promising approach to improve the power density significantly. Generally, cathode materials have low heat resistant temperatures, and they were easily decomposed or degraded by sintering at a high temperature which is suitable for densification of SOFC electrolytes. Cathode material of (La_{1-x}Sr_x)_{1-y}MnO₃ (LSM) shows relatively highly heat resistance and preferable low-reactivity with fluorite electrolytes during sintering at high temperatures. The addition of LSM also much increased degradation temperature. However, it shows lower cathodic properties than lanthanum strontium cobaltife and lanthanum strontium cobalt ferrite because of poor oxygen ionic conduction. We thus investigate LSM/ceria nanocomposite cathode materials to improve oxygen ionic conduction.

The nanocomposite precursor powder containing LSM and lanthanum doped ceria (LDC) was synthesized by glycine method. Two stoichiometric compositions, which are stoichiometric composition (y=0) and non-stoichiometric (y=0.05), were prepared as LSM, and LDCs that were dissolved with lanthanum at various ratios were used to investigate inter-diffusion of lanthanum between LSM and LDC. The composite ratio of LSM and CeO₂ was fixed at 9: 1 (molar ratio). Figure 1 shows SEM image of LSM/LDC nanocomposite sintered at 1200°C for 5 h in air. Sintering at 1200°C for 5h resulted in dense composite, and fine LDC particles were homogeneously dispersed with LSM. Lanthanum ratios of LDC and LSM in the composite were identified using XRD peak shift of LDC and magnetic properties of LSM, respectively. Electrical conductivity and oxygen diffusion coefficient were estimated with these dense composites. Oxygen diffusion coefficient were obtained by electrical conductivity relaxation method.

Non-stoichiometric composition of LSM increased oxygen diffusion coefficient as compared to stoichiometric LSM. LSM showed low oxygen diffusion coefficient, but nanocomposite with LDC much improved the coefficient even though LDC composite ratio is 10%. The coefficient of composite between non-stoichiometric LSM and LDC was similar to that containing stoichiometric LSM. Electrical conductivity of the composite showed

significant difference between non-stoichiometric and stoichiometric LSM composition of the LSM/LDC composite. Inter-diffusion of lanthanum between LSM and LDC would much affected the conductivity. The LSM/LDC composite with stoichiometric LSM showed much lower conductivity than LSM since lanthanum was easily diffused into LDC, and LSM composition of the composite was much deviated from that of adequate LSM. However, the conductivity non-stoichiometric LSM derived composite was hardly reduced as compared to non-stoichiometric LSM. Non-stochiometric LSM would restrain inter-diffusion of lanthanum from LSM into LDC. Therefore, Non-stoichiometric LSM would have an advantage for using LSM/LDC nanocomposite as SOFC cathode.



Figure 1. SEM image of LSM/LDC nanocomposite cathode obtained by sintering precursor powder synthesized by glycine method at 1200°C for 5 h in air.

La1-xSrxMnO3 $\pm \delta$ AS A NONSTOICHIOMETRIC MODEL SYSTEM FOR THE CATALYSIS OF OXYGEN EVOLUTION REACTION

Raika Oppermann, Justus Liebig University Giessen raika.w.oppermann@phys.chemie.uni-giessen.de Clarissa Glaser, Justus Liebig University Giessen Bjoern Luerßen, Justus Liebig University Giessen Jürgen Janek, Justus Liebig University Giessen

Key Words: oxygen-nonstoichiometry, electrocatalysis, water splitting, manganese perovskites

The main issue of electrochemical water splitting is the search for suitable catalyst materials for the kinetically hindered oxygen evolution reaction (OER) at the anode. The state-of-art precious metal catalysts suffer from their high price and insufficient long term stability in the common electrolytes. Binary or multinary transition metal oxides in alkaline medium are an cost-efficient alternative, since they can achieve both lower overvoltages as well as better long-term stability than precious metal oxides. One of the best-studied materials for SOFC applications is the perovskite system La1-xSrxMnO3 $\pm \delta$ (LSMO). Due to its general nonstoichiometry and the large variety of possible defect species it is a perfect model system for studying the influence of defect chemistry on the catalytic activity in OER. We have systematically investigated LSMO as a nonstoichiometric model catalyst system for OER in alkaline media. Nanocrystalline powders over the whole composition range have been prepared by a sol-gel based auto combustion method. XPS and XRD analysis verified the presence of pure phase materials with a continuous change of manganese oxidation state from Mn³⁺ to Mn⁴⁺. Measurements in an electrochemical RDE setup showed a clear trend in catalytic activity in OER with the highest values at medium La/Sr compositions. An equivalent trend could also be observed in the electrical conductivity of the powders, leading to the assumption of a higher polaron hopping probability at medium La/Sr compositions. Additional annealing of pristine powder samples in oxidizing and reducing atmospheres caused a further change in manganese oxidation state and ongoing electrochemical measurements should reveal whether the defined adjustment of the nonstoichiometry will lead to an improvement of catalytic activity compared to the untreated catalysts.

EQUIVALENT CIRCUIT ANALYSIS OF A THREE-CARRIER ELECTROLYTE/ELECTRODE SYSTEM

Tatsuya Kawada, Graduate School of Environmental Studies, Tohoku University kawada@ee.mech.tohoku.ac.jp

Keiji Yashiro, Graduate School of Environmental Studies, Tohoku University

Yuta Kimura, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Kotaro Okuyama, Graduate School of Environmental Studies, Tohoku University

Arthur Bourdon, Graduate School of Environmental Studies, Tohoku University

Koji Amezawa, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Key Words: Proton conductor, multi carrier, equivalent circuit, transient response, impedance

Perovskite type proton conductors are known to show non-monotonous transient responses due to nonignorable contributions of holes and oxide ions as minor carriers. Efforts have been made to simulate the behavior of the three-carrier systems by numerical calculations¹⁻⁴. In most cases, however, the calculation assumes reversible electrodes, and the results are not directly applicable for analyses of experimental results such as impedance spectra. The purpose of this study is to develop an equivalent circuit model of a three-carrier conductor as a simple but theoretically feasible tool to be used for practical analyses. In the modeling, charge carriers were assumed to be Hi⁺, Vo⁺⁺, and h⁺, for which the gradients of respective electrochemical potentials were taken as the driving forces in the following continuity equations,

$$C_{\rm H}\left(\frac{1}{F}\frac{\partial\eta_{\rm H_{i}^{\star}}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{\rm h}^{\star}}{\partial t}\right)+C_{\rm W}\left(\frac{1}{F}\frac{\partial\eta_{\rm H_{i}^{\star}}}{\partial t}-\frac{1}{2F}\frac{\partial\eta_{\rm V_{0}^{\star}}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{\rm H_{i}^{\star}}}{F}\nabla\eta_{\rm H_{i}^{\star}}\right)+J_{\rm exch,H_{i}^{\star}}$$

$$C_{\rm W}\left(\frac{1}{2F}\frac{\partial\eta_{\rm V_{0}^{\star}}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{\rm H_{i}^{\star}}}{\partial t}\right)+C_{\rm O}\left(\frac{1}{2F}\frac{\partial\eta_{\rm O_{0}^{\star}}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{\rm h}^{\star}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{\rm V_{0}^{\star}}}{2F}\nabla\eta_{\rm V_{0}^{\star}}\right)+J_{\rm exch,V_{0}^{\star}}$$

$$C_{\rm O}\left(\frac{1}{F}\frac{\partial\eta_{\rm h}^{\star}}{\partial t}-\frac{1}{2F}\frac{\partial\eta_{\rm O_{0}^{\star}}}{\partial t}\right)+C_{\rm H}\left(\frac{1}{F}\frac{\partial\eta_{\rm h}^{\star}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{\rm H_{i}^{\star}}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{\rm h}^{\star}}{F}\nabla\eta_{\rm h}^{\star}\right)+J_{\rm exch,h^{\star}}$$

where $C_{\rm H}$, $C_{\rm W}$ and $C_{\rm O}$ are the chemical capacitances. A source term, $J_{\text{exch.l}}$ takes non-zero value at a gas-solid interface. The above equations are equivalent to an electrical circuit shown in Fig.1, which has three conduction lines connected by chemical capacitances. The potentials on the conduction lines represent the electrochemical potentials of corresponding carriers, and the difference between two of them is chemical potential of oxygen, hydrogen, or water. The circuit is terminated with dc voltage sources which represent the chemical potentials in the gas phase. The electrode reaction resistances are inserted in series to the termination voltage assuming that the polarization loss is due to the chemical potential shift from the equilibrium. Numerical calculation of the circuit was made with a general-purpose circuit simulator LT-spice. Figure 2 shows calculated EMF over Sr(Ce,Yb)O₃ with reversible electrodes upon sudden increase of water vapor pressure on one side. The transport parameters were taken from the report by Yoo and Martin¹), in which they predicted the time dependence of EMF. The experimental results by the same group²⁾ was successfully reproduced with a certain electrode resistance. Figure 3 shows the simulated three-terminal impedance responses of a cathode on the same material when it is placed under fuel cell condition. Reference electrode potential was taken from the potential on the proton conduction line in the middle of the circuit. Variation of the cathode resistance was found to cause unexpected change of the impedance spectra on the Nyquist plot. References

(1) H.-I. Yoo and M. Martin, Phys. Chem. Chem. Phys. 12, 14699 (2010)

(2) E. Kim, et al., Solid State Ionics 235, 22 (2013)

(3) D. Poetzsch et al., Adv. Funct. Mater., 25, 1542 (2015)

(4) H. Zhu and R. J. Kee, Int. J. Hydrogen Energy, 41, 2931 (2016)



Figure 12 Main part of equivalent circuit of three-carrier conductor.



Figure 2 Transient EMF over Sr(Ce, Yb)O₃ at 700°C, $p(O_2)=10^{-4.5}$ bar, upon step change of $p(H_2O)$ from $10^{-4.5}$ bar to $10^{-2.3}$ bar.



Figure 3 Simulated impedance response of a cathode with various resistance on Sr(Ce, Yb)O₃ placed under a fuel cell condition.

A HIGHLY ACTIVE AND REDOX STABLE NOVEL CERAMIC ANODE WITH IN-SITU EXSOLUTION OF NANOCATALYSTS

Kang Taek Lee, DGIST(Daegu Gyeongbuk Institute of Science and Technology), KOREA ktlee@dgist.ac.kr Kyeong Joon Kim, DGIST(Daegu Gyeongbuk Institute of Science and Technology), KOREA

Manasa K. Rath, DGIST(Daegu Gyeongbuk Institute of Science and Technology), KOREA Hunho H. Kwak, DGIST(Daegu Gyeongbuk Institute of Science and Technology), KOREA Hyung Jun Kim, University of Seoul, KOREA

Jeong Woo Han, POSTECH(Pohang University of Science and Technology), KOREA Seung-Tae Hong, DGIST(Daegu Gyeongbuk Institute of Science and Technology), KOREA

Key Words: Solid oxide fuel cell, Ceramic anode, Layered perovskite, Redox stability, Exsolution,

Layered perovskite novel ceramic anode (referred to as SGNM) phases were evaluated for use in solid oxide fuel cells (SOFCs). Hydrogen temperature programmed reduction (H₂-TPR) analysis of the SGNM materials revealed that significant exsolution of Ni nanoparticles occurred. Consistently, the SGNM on the LSGM electrolyte showed low electrode polarization resistance in H₂ at 800 °C. Moreover, after 10 redox cycles at 750 °C, the electrode area specific resistance of the SGNM anode in H₂ slightly increased during cycle, indicating excellent redox stability in both reducing and oxidizing atmospheres. An LSGM-electrolyte supported SOFC employing an SGNM-based anode yielded a high power density of ~1 W cm⁻² at 800 °C, which is the best performance among the any SOFCs with Ruddlesden-Popper based ceramic anodes to date. After performance measurement, we observed that metallic Ni nanoparticles (~ 25 nm) were grown in situ and homogeneously distributed on the SGNM anode surface. These exsolved nanocatalysts are believed to significantly enhance the hydrogen oxidation activity of the SGNM material. These results demonstrate that the novel SGNM material is promising as a high catalytically active and redox-stable anode for SOFCs.



Figure 13 – SEM image and Schematic diagram of HOR mechanism for SGNM with Ni-nanocatalyst.

DEFECT STRUCTURE AND TRANSPORT PROPERTIES OF CERIA-ZIRCONIA-BASED OXIDES

Hitoshi Takamura, Tohoku University takamura@material.tohoku.ac.jp Akihiro Fujimaki, Tohoku University Yoko Sugawara, Tohoku University Itaru Oikawa, Tohoku University

Key Words: Oxygen nonstoichiometry, NMR, fluorite-type oxides, spinel-type oxides, surface exchange

CeO₂-ZrO₂ based oxides (CZ) showing excellent oxygen storage capacity (OSC) are widely used in three-way catalysts. To further improve their storage capacity and kinetics at low temperatures, defect structural analysis appears to play an important role. In this study, ⁸⁹Y NMR spectroscopy is performed to probe the preference sites of oxygen vacancies in CZ under not only oxidizing but also reducing atmospheres. Figure 1 shows the ⁸⁹Y NMR spectra taken for (Ce_{1-x}Zr_x)_{0.8}Y_{0.2}O_{2-d} annealed under (a) air and (b) Ar-5%H₂ atmospheres. 7- and 8- coordinated environments are clearly observed for both cases. Based on their integrated intensities as a function of Zr content (Fig. 1 (c)), the oxygen vacancies appear to favor Zr rather than Y and Ce; the same trend has been reported for various fluorite-type oxides [1, 2]. This suggests that doping of smaller cations is effective to enhance their OSC. Furthermore, OSC and kinetics of CoFe₂O₄-added CZ at around 400°C are evaluated. The spinel-type oxides such as CoFe₂O₄-added CZ were prepared by the Pechini and solid-state reaction methods. 5 vol% CoFe₂O₄-added Ce_{0.5}Zr_{0.5}O_{2-d} shows higher OSC and faster kinetics at 400°C than Ce_{0.5}Zr_{0.5}O_{2-d} itself. The microstructure including the distribution of CoFe₂O₄ and fabrication techniques. Their morphology was found to strongly depend on the volume fraction of CoFe₂O₄ and fabrication techniques. Their surface exchange kinetics is also discussed based on pulse isotope exchange results for powder samples.



Figure 1 ⁸⁹Y NMR spectra of (Ce_{1-x}Zr_x)_{0.8}Y_{0.2}O_{2-d} annealed under (a) air and (b) Ar-5%H₂ atmospheres, and (c) integrated intensities of 7- and 8-coordinated Y environments.

References

[1] H. Maekawa, K. Kawata, Y.P. Xiong, N. Sakai, H. Yokokawa, Solid State Ionics, 180 (2009), 314-319.

[2] K. Kawata, H. Maekawa, T. Nemoto, T. Yamamura, Solid State Ionics, 177 (2006), 1687-1690.

[3] H. Takamura, K. Okumura, Y. Koshino, A. Kamegawa, M. Okada, J. Electroceramics, 13 (2004) 613-618.

[4] Y Lin, S Fang, D Su, K.S. Brinkman, F Chen, Nature communications, 6 (2015), 6824.

DEMYSTIFICATION OF MIZUSAKI'S α-FACTOR FOR THE POSITIVELY-DEVIATED DEFECT BEHAVIOR OF HYPERSTOICHIOMETRIC OXIDES

H.-I. Yoo, Daegu-Gyeongbuk Institute of Science and Technology, Daegu, Korea hiyoo@snu.ac.kr J. Mizusaki, Tohoku University, Sendai, Japan

Key Words: Nonideal defect structure, Positive deviation, Hyperstoichiometric oxides, Excess enthalpy, Hole degeneracy effect.

Many hyperstoichiometric (p-type) ternary or higher oxides of present technological interests, e.g., $La_{1-x}Sr_xCrO_{3-\delta}$ exhibit a positive deviation from the ideal defect structure. Mizusaki et al. [1] could beautifully explain the positively-deviated defect structure by introducing an empirical factor α such as

ΔH^{×s}=αδ □.

Here, ΔH^{xs} stands for the excess enthalpy of oxidation reaction involving oxygen vacancies and holes or

$$1/2 O_2 + V_0 = O_0 + 2h$$
.

The authors[1] interpreted this α -factor as representing the interactions among lattice ions and defects, but its true physico-chemical face has since remained a mystery notwithstanding so frequent invoking to the defect chemistry stage.

It has recently turned out that this factor corresponds to the first order approximation of the hole-degeneracy effect. We will demystify this α -factor in this line.

[1] J. Mizusaki, S, Yamauchi, K. Fueki, and A. Ishikawa, "Nonstoichiometry of the perovskite-type oxide La₁₋xSr_xCrO_{3-δ}," Solid State Ionics 12 (1984) 119.

NON-STOICHIOMETRY IN MONOCLINIC ZIRCONIA AND AMORPHOUS ZIRCONIA

Simon C. Middleburgh, Bangor University, U.K. s.middleburgh@bangor.ac.uk Michael J.D. Rushton, Bangor University, U.K. Lee Evitts, Bangor University, U.K. Iuliia Ipatova, Bangor University, U.K. William E. Lee, Bangor University, U.K. and Imperial College London, U.K.

Key Words: Zirconia, oxidation, amorphous, grain boundary.

A combination of materials modelling techniques and targeted experimental investigations have identified the manner in which non-stoichiometry is accommodated within both crystalline and amorphous ZrO_2 . Not only is excess oxygen possible in both crystalline and amorphous ZrO_2 , but it is found that there is a high propensity for significant deviations – especially in the amorphous system – forming ZrO_{2+x} . This has clear implications to the behavior and degradation of ZrO_2 as a thermal barrier coating in aerospace and energy components, but also as the boundary oxide protecting zirconium alloys in aggressive environments, including within a water cooled nuclear power reactor.

The behavior was highlighted through a combination of both Raman spectroscopy and associated atomic scale predictions coupled with thermodynamic analysis of the system. As excess oxygen cannot readily oxidize Zr4+ ions beyond this charge state, the additional oxygen is accommodated instead as a peroxide ion $-O_2^{2-}$. This peroxide specie has a distinct covalent bond not expected in the stoichiometric ionic ZrO₂ system that is readily observable using Raman spectroscopy.

Now that excess oxygen accommodation in ZrO₂ has been highlighted, an understanding of how various dopant or alloying elements can impact its behavior can be targeted to improve component reliability. The presence of amorphous phases at grain boundaries is also discussed in terms of potential super-highways for oxygen transport through the oxide system.

SYNTHESIS AND CRYSTAL STRUCTURE OF NOVEL NONSTOICHIOMETRIC SUBOXIDE SOLID SOLUTIONS, Ti₁₂₋₅Ga_xBi_{3-x}O₁₀

Hisanori Yamane, IMRAM Tohoku University hisanori.yamane.a1@tohoku.ac.jp Shinsaku Amano, IMRAM Tohoku University

Key Words: titanium gallide bismuthide oxide, single crystal, Bi flux, single crystal X-ray diffraction.

Single crystals of new Ti_{12- δ}Ga_xBi_{3-x}O₁₀ compounds (x = 1.42-1.74. $\delta = 0.77-0.62$) were prepared at 900 °C with a Bi flux. Crystal structure analysis by X-ray diffraction (XRD) revealed that the solid solutions are isostructural with Ti₁₂₋₅Sn₃O₁₀ (cubic, space group *Fm-3m*).¹⁾ The δ and x values were determined by refinement of the occupancies for the Ti2 and Ti4 sites, and Ga site, respectively (Table 1). The cell parameter a decreases from 13.5616(3) Å to 13.5402(5) Å with increasing Ga content, x, while the total valence electron number of Ti_{12-a}Ga_xBi_{3-x}O₁₀ was maintained at 117.1 by decreasing Ti defects, δ . Stella octangula is formed by sharing of the edges of four supertetrahedra composed of O-centered Ti tetrahedra and trigonal bipyramids (oxide part) (Figure 1). Another superpolyhedron is formed by sharing of the pyramidal planes of Ga/Bi-centered Ti mono-caped square antiprisms (intermetallic part). These two parts are incorporated in the structure. A polycrystalline bulk of a solid solution with x =2.01, $\delta = 0.67$ (a = 13.53772(13) Å) was synthesized by reaction sintering at 950 °C from the mixture of Ti, TiO₂, Bi₂O₃ and Ga₂O₃. The resistivities measured for the bulk were $2.2-2.4 \times 10^{-5} \Omega m$ in the temperature range from 10 K to 300 K.





occupancy											total number
multiplicity, Wyckoff letter	96 <i>j</i>	32f	8 <i>c</i>	4b	4 <i>a</i>		24e		48g ^{32j}		of valence electrons per
site (valence electron	Ti1 (4)	Ti2	Ti3	Ti4	Ti5 (4)	Ga (3)	Sn (4)Bi (5)	01	02	formula unit
<u>number)</u>	(.)	(4)	(4)	(4)					(6)	(6)	
Ti _{11.31} Sn ₃ O ₁₀ sc. ¹⁾	0.5	1	0.58	0.46	1	0	1	0	1	1	117.2
$Ti_{11.17}Sn_{2.45}Bi_{0.45}O_{10}\ sc.^{2)}$	0.5	1	0.518	0.309	1	0	0.85	0.15	1	1	117.1
Ti _{11.23} Ga _{1.42} Bi _{1.58} O ₁₀ sc.	0.5	0.818	1	0.909	1	0.472	0	0.528	1	1	117.1
Ti11.27Ga1.51Bi1.49O10 sc.	0.5	0.826	1	0.94	1	0.503	0	0.497	1	1	117.1
Ti _{11.37} Ga _{1.67} Bi _{1.33} O ₁₀ sc.	0.5	0.848	1	0.953	1	0.557	0	0.443	1	1	117.1
Ti _{11.38} Ga _{1.74} Bi _{1.26} O ₁₀ sc.	0.5	0.851	1	0.96	1	0.581	0	0.419	1	1	117.1
Ti _{11.33} Ga _{2.01} Bi _{0.99} O ₁₀ pd	0.5	0.836	1	0.966	1	0.67	0	0.33	1	1	116.3

Table 1 Site occupancies and total number of valence electrons for $Ti_{12-\delta}Sn_3O_{10}$ -type compounds.

sc: single crystal, pd: powder

References

1) Hillebrecht, H.; Ade, M., Synthesis and Crystal Structure of Ti₁₂Sn₃O₁₀. A Low Valent Oxide of Titanium with an Oxidic Network and Intermetallic "Islands". Z. Anorg. Allg. Chem. 1999, 625, 572-576

2) Yamane, H.; Amano, S., Synthesis of Suboxides, Ti₈(Sn_xBi_{1-x})O₇ and Ti_{11.17}(Sn_{0.85}Bi_{0.15})₃O₁₀, Using a Bi Flux and Their Crystal Structures. J. Alloys Compd. 2017, 701, 967-974.

NONSTOICHIOMETRY AND REACTIVITY OF LITHIUM SOLID ELECTROLYTES FOR SOLID STATE BATTERIES

Jürgen Janek, Institute of Physical Chemistry & Center for Materials Science, Justus Liebig University, Germany; BELLA, Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany juergen.janek@pc.jlug.de

Key Words: Lithium electrolytes, solid electrolyte, batteries, thiophosphates, SEI

Ideal solid electrolytes are ion-conducting phases with negligible nonstoichiometry – as any nonstoichiometry is usually related to unwanted changes in (electronic) transport properties. In solid-state batteries the solid electrolyte experiences extreme chemical boundary conditions, from very high chemical potential of Li at the anode side to very low chemical potential at the cathode side. Depending on the electrodes, the range of chemical potential can span more than 4 V (expressed as OCV). Under these conditions, the redox chemistry and the nonstoichiometry of solid electrolytes becomes decisive for the function of the batteries itself.

In this lecture, the redox chemistry of different types of solid electrolytes will be discussed, aiming for a better understanding of their degradation in contact with typical anode materials at different electrode potentials. Lithium thiophospates (Li-P-S and Li-M-P-S) will be discussed in more detail, oxides and phosphates will be discussed in brief. A combination of conductivity studies and XPS measurements shows that lithium thiophosphates indeed show a narrow range of nonstoichiometry and that decomposition into lithium-rich or lithium-deficient phases will occur easily under operating conditions of soli- state batteries.



Figure 1 – Oxidation of Li₃PS₄ solid electrolyte and structural/chemical changes due to lithium deficiency as origin of electrode degradation

The role of nonstoichiometry of solid electrolytes as source of (unwanted) reversible and irreversible additional cell capacity is also highlighted.

References

[1] Interfacial reactivity and interphase growth of argyrodite solid electrolytes at lithium metal electrodes, S. Wenzel, S. J. SedImaier, C. Dietrich, W. G. Zeier, and J. Janek, Solid State Ionics 318 (2018) 102-112
[2] Degradation Mechanisms at the Li₁₀GeP₂S₁₂/LiCoO₂ Cathode Interface in an All-Solid-State Lithium Battery, W. Zhang, F. H. Richter, S. P. Culver, T. Leichtweiss, J. G. Lozano, C. Dietrich, P. G. Bruce, W. G. Zeier, and J. Janek, ACS Appl. Mater. Interf. 10 (2018) 22226-22236

[3] Spectroscopic characterization of lithium thiophosphates by XPS and XAS – a new model to help monitor interfacial reactions in all-solid-state batteries, C. Dietrich, R. Koerver, M. W. Gaultois, G. Cibin, G. Kieslich, J. Janek, W. G. Zeier, Phys. Chem. Chem. Phys. 20 (2018) 20088-20095

ELECTROCHEMICAL PROPERTIES OF MICRO-BATTERIES WITH SINGLE NCM-111 SECONDARY PARTICLES AS CATHODE

Matthias T. Elm, Center for Materials Research, Justus-Liebig University Gießen, Matthias.elm@phys.chemie.uni-giessen.de Simon Burkhardt, Center for Materials Research, Justus-Liebig University Gießen Markus S. Friedrich, Center for Materials Research, Justus-Liebig University Gießen Julian Zahnow, Center for Materials Research, Justus-Liebig University Gießen Jürgen Janek, Center for Materials Research, Justus-Liebig University Gießen Peter J. Klar, Center for Materials Research, Justus-Liebig University Gießen

Key Words: Lithium-ion battery, single particle investigation, active cathode material, NCM111, impedance spectroscopy.

Although lithium ion batteries (LIB) are already used in numerous applications, e.g. as power source in portable devices, the optimization of the battery performance, such as life-time, cyclability and energy density, is of large interest for using LIBs in e.g. electrical vehicles or temporary storage systems for renewable energy sources. Typically, the performance of the cathode active material is investigated using composite electrodes. Advanced composite electrodes consist of a complex architecture with comparably large secondary particles (10 μ m - 30 μ m) of the active material built up from nanometer sized primary particles. Furthermore, they also contain additives influencing the electrochemical properties of the composite electrode. To avoid such influences and to further optimize the performance of the cathode's active material a detailed understanding of the impact of the cathode architecture on the ionic and electronic transport processes is necessary.

Here, we present the investigation of the ionic and electronic transport properties of single secondary particles of the active cathode material Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM-111) using electrochemical impedance spectroscopy. For this purpose, single NCM-111 particles have been arranged in traps on a glass substrate deposited with copper or gold as electrode using the meniscus force deposition method [1,2]. The traps on top of the metal film were prepared by patterning of a SU-8 resist films using photolithography. Using a specially designed electrochemical cell, the single secondary particles were contacted using a stainless steel cylinder. To determine the electronic conductivity of the single secondary particle the top electrode was coated with gold as ion blocking metal electrode. For measuring the micro-battery performance, the cell was assembled using a separator impregnated with liquid electrolyte (1M LiPF6 in 50:50 PC:DMC) and a cylinder with lithium foil as anode. Impedance measurements were performed with an amplitude of 50 mV in the frequency range between 10 mHz and 7 MHz..



The impedance measurements using gold as blocking electrodes for the ionic transport reveal two transport processes, which are attributed to a contact resistance and the electronic transport in the NCM-111 particle. By a systematic analysis of the results it was possible to determine the partial electronic conductivity of single secondary particles of mixed-ionic electronic conducting materials, which is in good agreement with values obtained from measurements on pressed pellets. Furthermore, by studying the impedance response of different cell arrangements, it was possible to identify the different transport processes visible in the impedance spectra of the micro-battery.

Figure 15–Nyquist- and Bode-plot of the impedance spectrum of a microbattery revealing several transport processes.

 Y. Cui, M. T. Bjrk, A. Liddle, C. Snnichsen, B. Boussert, and A. P. Alivisatos, "Integration of colloidal nanocrystals into lithographically patterend devices", Nano. Lett., 4, 1093 (2004).
 A. Fabian, M.T. Elm, D.M. Hofmann, and P.J. Klar, "Hierarchical structures of magnetic nanoparticles for controlling magnetic interactions on three different length scales", Appl. Phys. Lett., 121, 224303 (2017).

MECHANISM OF OXYGEN RELEASE FROM LI-RICH CATHODE MATERIAL FOR LITHIUM ION BATTERIES

Takashi Nakamura, IMRAM, Tohoku University takashi.nakamura.e3@tohoku.ac.jp Hongze Gao, Tohoku University Kento Ohta, Tohoku University Yuta Kimura, Tohoku University Yusuke Tamenori, JASRI Koji Amezawa, Tohoku University

Key Words: Oxygen release; Oxygen nonstoichiometry; Lithium ion batteries; Li-rich cathodes

For further wide spread of high energy density batteries, one of the most important technological challenges is preventing thermal runaway. For that, a key phenomenon is the oxygen release from cathode active materials, because released oxygen may react with the organic solvent and generate heat. Therefore, it is important to understand the mechanism of oxygen release to ensure safe battery operation. While the reaction of charged cathode material and organic solvent was investigated well [1], the mechanism of oxygen release from cathode material is not understood so far [2]. In this study, oxygen release behavior of Li-rich cathode material Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d} was investigated, and the mechanism of oxygen release was discussed based on defect chemistry and thermodynamics.

Li_{1,2}Mn_{0.6}Ni_{0.2}O_{2-d} was synthesized by a solid state reaction method from Li(OH)·H₂O and the Ni-Mn mixed carbonate precursor which was prepared by co-precipitation method. The mixed powder was sintered at 1173 K for 10 h and grounded in a mortar thoroughly. Oxygen nonstoichiometry of Li1.2Mn0.6Ni0.2O2-d was evaluated by a thermogravimetry and a coulometric titration. The absolute value of the oxygen content was determined by an iodometric titration. The crystal structure and electronic structure of the pristine and the oxygen extracted samples were investigated by XRD and soft X-ray absorption spectroscopy at BL27SU SPring-8, Japan. Figure 1 shows the relation between the oxygen content (O/M) and the equilibrium PO2 of Li1.2Mn0.6Ni0.2O2-d at 873 K. We successfully observed the oxygen release phenomena from Li-rich cathode material, $Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d}$. In this figure, O/M is the molar ratio of oxygen and cations. Therefore, O/M = 1.0 means the stoichiometric composition and O/M < 1 means the oxygen deficient composition. Until O/M = ca.0.97, the equilibrium PO_2 changes depending on O/M. This indicates that the oxygen vacancies are created in the oxygen sub-lattice of Li1.2Mn0.6Ni0.2O2-d while the original layered rock-salt structure was maintained. Namely, the oxygen deficient nonstoichiometry of Li1,2Mn0.6Ni0,2O2-d was observed in this region. On the contrary, when O/M is smaller than 0.97, the equilibrium PO₂ is invariant regardless of O/M. This indicates Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d} started to decompose at O/M = 0.97, and co-exist with the reduction decomposed phases. By XRD measurement, MnNi₆O₈ was detected when O/M became smaller than 0.97. From these results, the oxygen release reaction can be expressed as follows.



 $\begin{array}{l} 0.97 < O/M < 1: Li_{1.2}Mn_{0.6}Ni_{0.2}O_2 \rightarrow Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d} + d/2O_2 \\ (1) \\ O/M < 0.97: \ aLi_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d} \rightarrow bLi(Li,Mn,Ni)O_{2-d'} + cMnNi_6O_8 + O_2 \\ (2) \end{array}$

Detailed mechanism of the oxygen release was investigated by defect chemical and thermodynamic analyses. The crystal and electronic structural changes due to the oxygen release will be also discussed in the presentation.

Acknowledgements

This work was supported by Grand-in-Aid for Scientific Research (c), Grant number JP18K05288

Figure 1. Oxygen release behavior from Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2-d} at 873 K

References

^[1] A. W. Golubkow, *et al.*, RSC Adv., 2015, 5, 57171.
[2] S. Kim, *et al.*, *Energy Environ. Sci.*, 2017, 10, 2201.

NONSTOICHIOMETRY AND DEFECT STRUCTURE OF γ-Na_xCoO₂

Wonhyo Joo, Department of Materials Science and Engineering, Seoul National University, Seoul, Korea templerj@snu.ac.kr Han-III Yoo, Daegu-Gyeongbuk Institute of Science and Technology, Daegu, Korea

Key Words: γ-Na_xCoO₂, Oxygen nonstoichiometry, Electrical conductivity, Defect structure, Hole degeneracy

γ-Na_xCoO₂, has long been known to be the best ever p-type oxide thermoelectric, but its oxygen nonstoichiometry and defect structure remains unelucidated. In this work, we measured oxygen nonstoichiometry and electrical conductivity on the system of γ-Na_xCoO₂ against oxygen activity (a_{O2}) across its widest ever range below a_{O2}=1 for a fixed Na-content x=0.706 at different temperatures in the range of 773-973 K, and at a fixed temperature 973 K for x=0.664, 0.706 and 0.731, respectively. It has been deduced therefrom that as a_{O2} decreases, the majority disorder type shifts from [V_{Na}']≈p to either [V_{Na}']≈[Co_{Na}···] or [V_{Na}']≈[Co_i···], however, exhibiting a positive deviation from the ideal defect behavior. The latter is attributed to the positive deviation of holes due to their degeneracy. By taking into appropriate account of the activity coefficient of holes in terms of the Fermi-Dirac integral of order 1/2, the nonstoichiometry and electrical conductivity have been precisely and consistently depicted to evaluate the defect-chemical parameters including the effective mass and mobility of holes and the redox equilibrium constant. The phase-stability limit of γ-Na_xCoO₂ is also reported against temperature and Na-content.

DEVELOPMENT OF COMPLEX HYDRIDES FOR FAST IONIC CONDUCTION

Motoaki Matsuo, School of Science and Technology, Kwansei Gakuin University matsuo35@kwansei.ac.jp

Norihiro Matsubara, School of Science and Technology, Kwansei Gakuin University Noboru Katayama, School of Science and Technology, Kwansei Gakuin University Hayato Asano, School of Science and Technology, Kwansei Gakuin University Kengo Sawada, School of Science and Technology, Kwansei Gakuin University Shin-ichi Orimo, Advanced Institute for Materials Research, Tohoku University

Key Words: complex hydride, fast ionic conductor

Complex hydrides have been attracting much attention as solid-state fast ionic conductors since we reported the fast lithium ionic conduction in LiBH₄ [1]. The development of fast ionic conductors is important because of their potential applications as solid electrolytes in rechargeable batteries [2]. We have worked on the development of lithium ionic conductors as well as sodium ionic conductors of complex hydrides.

Na₂B₁₂H₁₂, composed of the [B₁₂H₁₂]₂- closo-borate anions shown in Fig.1, exhibits superionic conductivity on the order of 0.1 S/cm above its order-disorder phase-transition at about 530 K [3]. The rapid reorientational motions of the anions, evidenced by the NMR and QENS measurements, play an important role in the formation of the cation-vacancy-rich structures in the high-temperature disordered phase. In addition, three-dimensional conductivity of 0.01 S/cm over 380 K triggered by the rapid reorientational motions of the [B₁₀H₁₀]₂- anions [4]. From the application point of view, it is highly desirable to enhance the conductivities of Na₂B_nH_n at room temperature. In this study, we report combining Na₂B_nH_n with NaNH₂ is effective in modifying the conductivities of Na₂B_nH_n.



Figure 16 Crystal structures of $Na_2B_{12}H_{12}$ in orthorhombic LT phase and cubic HT phase.

Figure2 Temperature dependences of the sodium ionicl conductivity of complex hydrides.

References

M. Matsuo, Y. Nakamori, S. Orimo, H. Maekawa, H. Takamura, *Appl. Phys. Lett.*, 91, 224103 (2007).
 A. Unemoto, M. Matsuo, S. Orimo, *Adv. Funct. Mater.*, 24, 2267 (2014).

[3] T.J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A.V. Skripov, J.J. Rush, H. Takamura, S. Orimo, *Chem. Commun.*, 50, 3750 (2014).

[4] T.J. Udovic, M. Matsuo, W.S. Tang, H. Wu, V. Stavila, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, J.J. Rush, A. Unemoto, H. Takamura, S. Orimo, *Adv. Mater.*, 26, 7622 (2014).