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23rd International Conference
on Solid State Ionics

PROGRAM GUIDE

July 17-22, 2022

BOSTON PARK PLAZA
BOSTON, MASSACHUSETTS



Mixed conducting oxides are important materials owing to their excellent performance as solid oxide fuel and electrolysis cell electrodes, for sensors, permeation membranes or iono-electronic devices. Due to their typically rather complex stoichiometry, thin films are often grown by pulsed laser deposition. Over the last years, we developed and optimized a technique for in-situ electrochemical characterization directly in the deposition chamber (i-PLD). This technique allows gaining deeper insight into several aspects that are relevant for enhancing the performance of materials and surfaces. Largest advantages of i-PLD vs conventional ex-situ measurements are the outstanding sample to sample reproducibility, the possibility to characterize a film layer-by-layer over its whole thickness, and the higher purity of surfaces and interfaces showing the true potential of certain materials. This enables detailed investigations of the oxygen incorporation and evolution reactions and also of the defect chemical situation inside a mixed conducting oxide thin film and at surfaces and interfaces. In addition to several other application examples of the method, sub-nanometer decoration layers deposited intentionally at the surface of mixed conductors will be discussed in more detail.

The surface of a mixed ionic electronic conductor is often the bottleneck for oxygen exchange, as several materials exist that combine high electronic with high ionic conductivity and therefore exhibit fast conduction and diffusion. The surface reaction on the other side is much more complex and requires among others: adsorption, breaking the O₂-bond, interaction with an oxygen vacancy, and electron transfer reactions. Additionally, the defect chemical situation at the surface may be further complicated by space charges, adsorbates, strain (release) or other effects. Experimentally it can be shown that tiny amounts of impurities may either activate or inactivate a surface with respect to the oxygen exchange reaction [1, 2]. While the latter is generally undesired and often described as degradation or poisoning, activation of surfaces offers great potential for improving existing materials. Measurements using (La,Sr)CoO_{3-δ} and (Pr,Ce)O_{2-δ} as mixed conducting oxides will be used as basis to discuss the effects of surface decoration layers from few % of a monolayer up to a full monolayer thickness. Different models in literature (space charge vs. surface acidity [3]) and their capabilities and limitations to explain the experimental results are discussed.

[1] Ghislain M. Rupp, Alexander K. Opitz, Andreas Nanning, Andreas Limbeck, and Jürgen Fleig. "Real-time impedance monitoring of oxygen reduction during surface modification of thin film cathodes" *Nature Materials* 16, 6, 640 – 645 (2017).

[2] Clement Nicollet, Cigdem Toparli, George F. Harrington, Thomas Defferriere, Bilge Yildiz, and Hally L. Tuller. "Acidity of surface-infiltrated binary oxides as a sensitive descriptor of oxygen exchange kinetics in mixed conducting oxides". *Nature Catalysis*. 3, 913–920 (2020).

[3] D. W. Smith. "An acidity scale for binary oxides". *J. Chem. Educ.* 64, 480-481 (1987).

2:30 PM DT14.02

Bulk and Surface Oxygen Transport Properties of Mixed Oxide-Ion and Electron Conductors Obtained by Combined Oxygen Permeation Cell and Oxygen Probe Method Kevin Huang; University of South Carolina System, United States

Surface exchange kinetics and bulk diffusion of oxygen are of paramount importance to the activity of oxygen electrocatalysis and performance of electrochemical devices such as fuel cell, metal-air batteries, and oxygen separation membranes. Conventional approaches to obtaining these transport properties are often limited to single property under a specific non-operational condition. Here we use a combined oxygen permeation cell and oxygen probe method to simultaneously attain rates of oxygen surface exchange and bulk conductivity/chemical diffusivity of three representative mixed oxide-ion and electron conductors, namely SrCo_{0.9}Ta_{0.1}O_{3-δ} (SCT), La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) and La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF), operated under a gradient of oxygen chemical potential. The results explicitly show that SCT exhibit the highest oxide-ion conductivity/chemical diffusivity, fastest rates of surface oxygen exchange kinetics, thus promising to be the best oxygen electrocatalyst. We have also mapped out the distribution of oxygen chemical potential gradient across the membranes and applied B-transport number concept to illustrate the rate-limiting steps in the overall oxygen permeation process.

2:45 PM *DT14.03

Relationship Between Acidity and Oxygen Exchange Kinetics in Mixed Conducting Oxides Clement Nicollet; Institut des Materiaux Jean Rouxel, France

In Solid Oxide Fuel Cells, oxygen electrode polarization related to electrochemical reactions at the gas/solid interface is often the dominant flux limiting mechanism. Accumulating surface impurities is known to lead to a reduction in long term durability. On the contrary, surface modification with selected metal oxides can also have a positive effect on the oxygen surface exchange rate¹. As there is no clear understanding as to why some elements poison oxide surfaces while others enhance their oxygen exchange kinetics, defining a general descriptor is highly desirable, and is the goal of this work.

In a previous study we used Pr-doped ceria as a model mixed ionic and electronic conductor and infiltrated it with binary oxides of various acidities². By comparing the evolution of the surface exchange kinetics with different infiltrated oxides, it was possible to define the acidity of the infiltrated oxide as a descriptor that allows one, on the one hand, to predict what will be the effect of a given oxide on the surface exchange kinetics, and on the other hand to tune the surface exchange coefficient over 7 orders of magnitude with great precision. In this presentation, we will explore the implications of these finding in terms of reactions mechanisms, and how can the acidity/surface exchange relationship be extended to other mixed conductors.

First, the protocol of infiltrating binary oxides to a mixed conductors is applied to perovskites oxides such as (La,Sr)CoO₃ and (LaSr)FeO₃, and characterized in terms of oxygen exchange kinetics, by conductivity relaxation and impedance spectroscopy. The influence of the infiltrated oxides is then discussed with respect to their acidity, and compared to our previous work on Pr doped Ceria.

Second, the Smith acidity factor³ is calculated for a variety of perovskite oxides, and data collected from the available literature for surface exchange kinetics is analyzed with respect to this new acidity factor. An attempt to use this factor as a complementary tool to describe oxygen surface exchange kinetics is discussed.

1. Tsvetkov, N., Lu, Q., Sun, L., Crumlin, E. J. & Yildiz, B. Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface. *Nat. Mater.* 15, 1010–1016 (2016).

2. Nicollet, C. *et al.* Acidity of surface-infiltrated binary oxides as a sensitive descriptor of oxygen exchange kinetics in mixed conducting oxides. *Nat Catal* 3, 913–920 (2020).

3. Smith, D. W. An acidity scale for binary oxides. *J. Chem. Educ.* 64, 480–481 (1987).

3:05 PM DT14.04

Characterization of LaNiO₃-PrNiO₃ Solid Solutions as Oxygen Electrode Materials for SOEC Aleksey Yaremchenko¹, Dzyana Boiba¹, Mikhail Patrakeev², Kiryl Zakharchuk¹ and Blanca I. Arias-Serrano^{1,3}; ¹University of Aveiro, Portugal; ²Institute of Solid State Chemistry UB RAS, Russian Federation; ³Leibniz Institute for Plasma Science and Technology, Germany

Ln₂NiO_{4+δ} (Ln = La, Pr, Nd) and its derivatives with Ruddlesden-Popper structure demonstrate high mixed ionic-electronic conductivity, moderate thermal and negligible chemical expansion, and, therefore, attract significant attention as prospective cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC). However, Ln₂NiO_{4+δ} are thermodynamically unstable at SOFC operation temperatures and slowly decompose to a mixture of higher-order Ln_{1+n}Ni_nO_{3n+1} (n = 2, 3) phases, perovskite-like LnNiO₃, and LnO_y. On the contrary, LnNiO₃ perovskites have limited stability at elevated temperatures under oxidizing conditions. In particular, LaNiO₃ decomposes on heating in air above ~1000°C. Cathodic polarization can also be expected to

induce the decomposition of the LnNiO_3 perovskite phase at lower temperatures characteristic for IT-SOFC operation. At the same time, redox changes imposed by anodic polarization (in solid oxide electrolysis cell mode) under oxidizing conditions should not be of risk for the phase stability of LnNiO_3 . Thus, the goal of the present work was the evaluation of LaNiO_3 - PrNiO_3 solid solutions as prospective oxygen electrode materials for solid oxide electrolysis cells.

$\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ ($x = 0, 0.2, 0.5$ and 1.0) solid solutions with perovskite-like structure were prepared by combustion synthesis with calcinations in oxygen at 800 - 1000°C . Porous ceramic samples were sintered in oxygen at 950 - 1050°C . The materials were synthesized and characterized by XRD, SEM/EDS, dilatometry, TGA, coulometric titration, and electrical measurements. All prepared $\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ perovskites were found to be oxygen-deficient with oxygen nonstoichiometry δ slightly increasing with Pr content. The cation composition was found to have a negligible impact on the low- $p(\text{O}_2)$ stability limits: all materials decompose at $\log p(\text{O}_2) \sim -3.5$ atm at 800°C . Increasing Pr content results in a decrease in p -type electronic conductivity: from ~ 460 S/cm for $x = 0$ - 0.2 to 220 S/cm for $x = 0.5$ and 115 S/cm for $x = 1.0$ at 800°C in air, but also reduces thermal expansion coefficient from 13.7 ppm/K for $x = 0$ to 11.8 ppm/K for $x = 1.0$ at 30 - 950°C in air. Comparative assessment of the electrochemical performance of $\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ -based electrodes in contact with $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (8YSZ) and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) solid electrolytes was performed in air at 600 - 800°C using symmetrical cell configuration.

3:20 PM DT14.05

Investigating the Oxygen Exchange Properties of Multilayered $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ | $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Thin-Film Electrodes via *In Situ* Impedance Spectroscopy During Pulsed Laser Deposition [Christin Boehme](#)¹, [Matthäus Siebenhofer](#)¹, [Sergej Raznjevic](#)², [Christoph Riedl](#)¹, [Zaoli Zhang](#)², [Juergen Fleig](#)¹ and [Markus Kubicek](#)¹; ¹Technische Universität Wien, Austria; ²Austrian Academy of Sciences, Austria

In-situ impedance spectroscopy during pulsed laser deposition (i-PLD) allows for electrochemical characterization of thin films during growth. To date the i-PLD technique has been utilized, for example, to investigate the electrochemical properties of pristine $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin films [1, 2] as well as the oxygen reduction pathways of several mixed ionic and electronic conducting materials [3].

In this work, we expand the i-PLD method to analyze the oxygen exchange properties of multilayered $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (STF) | LSC thin film electrodes grown epitaxially on single crystalline yttria-stabilized zirconia (YSZ). A particular focus is laid on elucidating if and how lattice strain between the single layers may influence the chemical capacitance (C_{chem}) and thus, the defect chemistry of the multilayered system. To achieve a dense and homogeneous multilayer morphology a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayer is deposited on top of the YSZ single crystal at the beginning of the i-PLD process, which enables epitaxial growth of the perovskite multilayer system. Individual layers of STF and LSC are grown in steps at 600°C and an oxygen partial pressure of 0.04 mbar to obtain thickness dependent values of the polarization resistance and C_{chem} . In addition to the i-PLD measurements, the structure and morphology of the STF | LSC multilayer system are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HR-TEM).

XRD reciprocal space mapping confirms epitaxial growth of the multilayer system. Additionally, HR-TEM measurements show that the cubic structure of STF is generally maintained throughout the multilayer system whereas for LSC changes of in-plane and out-of-plane lattice parameters are observable. Our i-PLD measurements furthermore show a fine structure in the chemical capacitance over the layer sequence. Most notably, an abrupt increase in the absolute values of C_{chem} within the first 2 nm for the STF layers can be observed. C_{chem} slopes evaluated in this range reveal that C_{chem} increases with a rate of ~ 9000 F/cm³, which is far above the expected values for STF and also by a factor of ~ 2 higher than explainable by a point defect model. Our model assumes a twofold impact of the stiffer STF lattice on the more elastic LSC: i) imposing strain on a growing LSC layer and ii) an impact of STF on LSC underneath while growing STF. Quantification of these two effects is discussed together with vacancy ordering, for which at least two different types were found in HR-TEM measurements.

References

- [1] Ghislain M. Rupp, Markus Kubicek, Alexander K. Opitz, and Jürgen Fleig. "In Situ Impedance Analysis of Oxygen Exchange on Growing $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Thin Films". In: ACS Applied Energy Materials 1.9 (2018), pp. 4522–4535.
- [2] Matthäus Siebenhofer, Tobias Martin Huber, Gemot Friedbacher, Werner Artner, Jürgen Fleig, and Markus Kubicek. "Oxygen exchange kinetics and nonstoichiometry of pristine $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films unaltered by degradation". In: Journal of Materials Chemistry A 8.16 (2020), pp. 7968–7979.
- [3] Matthäus Siebenhofer, Christoph Riedl, Alexander Schmid, Andreas Limbeck, Alexander Karl Opitz, Jürgen Fleig, and Markus Kubicek. "Investigating oxygen reduction pathways on pristine SOFC cathode surfaces by in situ PLD impedance spectroscopy". In: Journal of Materials Chemistry A (2021).

SESSION DT15: Polymer Electrolytes; Ca, Mg Conductors

Session Chair: Montse Casas Cabanas

Tuesday Afternoon, July 19, 2022

Mezzanine Level, Second Floor, Arlington

2:00 PM **DT15.01

Effect of Yield Stress on Stability of Solid Block Copolymer Electrolytes Against Lithium Metal Electrodes [Nitash Balsara](#); Lawrence Berkeley National Laboratory, United States

In the field of lithium-ion batteries, two critical factors that drive the research are energy density and safety.¹ Formation of irregular lithium protrusions during battery cycling has limited the development of new battery technologies.^{2,3} Understanding the factors that affect the growth of protrusions could enable successful implication of lithium metal anodes. In this context, solid polymer-based electrolytes, with high storage modulus, have been shown to significantly reduce the nucleation and growth of protrusions during cycling.⁴

We have studied the electrochemical properties of organic-inorganic hybrid diblock and triblock copolymers mixed with lithium bis(trifluoromethanesulfonyl)imide salt. Both the copolymers have similar molecular weights and conducting phase volume fractions. Although the ionic conductivity of the diblock copolymer was a factor of five higher than that of the triblock copolymer, the cycle life of Li/polymer/Li cells containing the triblock copolymer is almost a factor of 50 higher. The rigidity of polymer electrolytes was determined by studying shear modulus and yield stress. Although, both the copolymers exhibit similar storage shear modulus, the yield stress of the triblock copolymer is three times higher than the diblock copolymer. This was attributed to the presence of bridging polymer chains between the adjacent lamellae in the triblock copolymers. Such small difference in the yield stress resulted in difference in cell life time as well as the morphology of the lithium protrusions.

References

- Tarascon, J. M.; Armand, M. *Nature*, **2001**, *414*, 359.

SYMPOSIUM EI

Electrochemical Interfaces
July 18 - July 22, 2022

Symposium Organizers

Koji Amezawa, Tohoku University
WooChul Jung, Korea Advanced Institute of Science and
Technology
Jonathan Polfus, University of Oslo

* Invited Paper

SESSION EI07: Solid Oxide Cells
Session Chairs: Yoshitaka Aoki and William Chueh
Tuesday Morning, July 19, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

11:00 AM *EI07.01

Electrochemical Characterization of the Effects of Nanocatalyst Infiltration on the Air Electrode Reaction Kinetics Using the Transmission Line Model Jaewoon Hong^{1,2}, Hohan Bae¹ and Sun-Ju Song¹; ¹Chonnam National University, Korea (the Republic of); ²University of Maryland at College Park, United States

11:20 AM EI07.02 **WITHDRAWN**

Nanostructured LSC Thin-Film Electrodes with Improved Electrochemical Performance and Long-Term Stability Katherine Develos-Bagarinao¹, Ozden Celikbilek², Gwilherm Kerhervé³, Sarah Fearn³, Stephen J. Skinner³ and Haruo Kishimoto¹; ¹National Institute of Advanced Industrial Science and Technology, Japan; ²Centre National de la Recherche Scientifique, France; ³Imperial College London, United Kingdom

11:35 AM *EI07.03

Multi-Doped Stabilized Bismuth Oxides as Functional Interlayers and Oxygen Electrode Components for Reversible Solid Oxide Cells at Reduced Temperatures Kang Taek Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

11:55 AM EI07.04

Electrochemical Conversion of Methane to Ethylene Utilizing Highly Durable Barium Niobate Perovskites Kannan Ramaiyan, Luke Denoyer, Angelica Benavidez, Kyle Troche and Fernando Garzon; University of New Mexico College of Arts and Sciences, United States

12:10 PM **EI07.05

Recent Developments in Catalysts for Reversible Solid Oxide Cells Yucun Zhou, Nicholas Kane, Weilin Zhang, Zheyu Luo and Meilin Liu; Georgia Institute of Technology, United States

SYMPOSIUM DT

Defects and Transport Mechanisms in Solid Electrolytes and
Mixed Conductors
July 18 - July 22, 2022

Symposium Organizers

George Harrington, Kyushu University / MIT
Rotraut Merkle, Max Planck Institute for Solid State Research
Alexander Opitz, Technische Universität Wien

* Invited Paper

SESSION DT14: Surface Reaction
Session Chair: Matthias Elm
Tuesday Afternoon, July 19, 2022
Mezzanine Level, Second Floor, Georgian

2:00 PM **DT14.01

Electrochemical Characterization of Thin Films During Pulsed Laser Deposition Markus Kubicek; Technische Universität Wien, Austria

2:30 PM DT14.02

Bulk and Surface Oxygen Transport Properties of Mixed Oxide-Ion and Electron Conductors Obtained by Combined Oxygen Permeation Cell and Oxygen Probe Method Kevin Huang; University of South Carolina System, United States

2:45 PM *DT14.03

Relationship Between Acidity and Oxygen Exchange Kinetics in Mixed Conducting Oxides Clement Nicolle; Institut des Matériaux Jean Rouxel, France

3:05 PM DT14.04

Characterization of LaNiO₃-PrNiO₃ Solid Solutions as Oxygen Electrode Materials for SOEC Aleksey Yaremchenko¹, Dzyana Boiba¹, Mikhail Patrakeev², Kiryl Zakharchuk¹ and Blanca I. Arias-Serrano^{1,3}; ¹University of Aveiro, Portugal; ²Institute of Solid State Chemistry UB RAS, Russian Federation; ³Leibniz Institute for Plasma Science and Technology, Germany

3:20 PM DT14.05

Investigating the Oxygen Exchange Properties of Multilayered SrTi_{0.3}Fe_{0.7}O_{3-δ} | La_{0.6}Sr_{0.4}CoO_{3-δ} Thin-Film Electrodes via *In Situ* Impedance Spectroscopy During Pulsed Laser Deposition Christin Boehme¹, Matthäus Siebenhofer¹, Sergej Raznjevic², Christoph Riedl¹, Zaoli Zhang², Juergen Fleig¹ and Markus Kubicek¹; ¹Technische Universität Wien, Austria; ²Austrian Academy of Sciences, Austria

SESSION DT15: Polymer Electrolytes; Ca, Mg Conductors
Session Chair: Montse Casas Cabanas
Tuesday Afternoon, July 19, 2022
Mezzanine Level, Second Floor, Arlington

2:00 PM **DT15.01

Effect of Yield Stress on Stability of Solid Block Copolymer Electrolytes Against Lithium Metal Electrodes Nitash Balsara; Lawrence Berkeley National Laboratory, United States