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Role of Gadolinia-Doped Ceria Interlayer Microstructure and Orientation on the Cation Diffusion Behavior in LSCF/GDC/YSZ Model Heterostructures Jeffrey C. De Vero¹, Katherine D. Bagarinao¹, Do-Hyung Cho¹, Haruo Kishimoto¹, Katsuhiko Yamaji¹, Teruhisa Horita¹ and Harumi Yokokawa^{1,2}; ¹National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ²Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

The stability of gadolinia-doped ceria (GDC) as a diffusion barrier between porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode and polycrystalline yttria-stabilized zirconia YSZ electrolyte plays a key role in understanding cation diffusion towards improved performance of LSCF cathodes at the required operating temperatures. However, GDC interlayer microstructure in porous LSCF/GDC/poly-YSZ heterostructure is complicated by the extreme reactivity of LSCF to YSZ, and the electrochemical reaction conditions. For this purpose, ~ 1.0 μm -thick GDC interlayers were prepared by pulsed laser deposition on single crystal YSZ substrates with termination planes (100) and (111), which were subsequently pre-annealed at 1300°C for 5h, and finally deposited with ~ 0.35 μm -thick dense LSCF layers. The samples were then annealed between 800°C and 1000°C starting from 168 hours up to 731 hours. We found that the resulting microstructure and crack density in LSCF/GDC/YSZ heterostructures after annealing depended strongly on the GDC interlayer orientation. Sr and Zr surface diffusions along the cracks or crack-walls of GDC interlayer were found to be relatively fast in LSCF/GDC/YSZ(100) compared to LSCF/GDC/YSZ(111), which exhibited significantly different crack densities. We also made systematic comparison with dense LSCF films on GDC/polycrystalline YSZ substrates to elucidate the possible contribution of grain boundaries as well as the influence of density of microcracks in GDC interlayer on cation diffusion. This result highlights the importance of GDC interlayer microstructure in understanding cation diffusion in LSCF/GDC/YSZ heterostructures.

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The Utility of Model Electrodes for the Separation of Current Pathways in Solid State Electrochemistry Alexander K. Opitz, Markus Kubicek, Stefanie Taibl, Tobias Huber, Gerald Holzlechner, Herbert Hutter and Juergen Fleig; Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Austria.

Micro-patterned thin film electrodes offer a powerful tool for the separation and investigation of different reaction pathways and rate determining reaction steps on electrodes in solid state electrochemistry, since they allow well-defined electrode geometries and direct access of the electrochemically active zones to surface analytical tools. In this work, the usefulness of model-type electrodes is exemplified by platinum electrodes on yttria stabilized zirconia (Pt/YSZ) as well as mixed conducting electrode materials such as $(\text{La,Sr})\text{MnO}_3$, $(\text{La,Sr})\text{FeO}_{3-\delta}$, and $(\text{La,Sr})\text{CoO}_{3-\delta}$.

On Pt electrodes two different parallel reaction pathways were identified under equilibrium conditions in air: A diffusion limited path along Pt grain boundaries dominating at lower temperatures, and an electrode surface path with oxygen incorporation at the three phase boundary at higher temperatures. An additional electrolyte surface path with electron transfer via the YSZ electrolyte can be activated by applying a strong cathodic polarization. The electrochemically active zone of this electrolyte surface path was visualized by ^{18}O tracer incorporation experiments in combination with time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis.

This tracer incorporation technique also enabled a separation of surface and bulk path on $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) electrodes by applying different cathodic overpotentials. On the mixed conducting electrode materials $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) the limitations of the tracer method are demonstrated. Due to the low polarization resistance of LSC electrodes the ^{18}O incorporation is determined by the current distribution in the electrolyte (i.e. the primary current distribution) and thus the electrochemically active zone of LSC cannot be visualized. The effect of changes of the electrode's electronic conductivity caused by cathodic polarization is demonstrated for LSF.

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Rapid Measurement of Chemical Diffusion in Oxide Thin Films by Color Front Motion Tracking Jae Jin Kim¹, Stuart N. Cook¹, Di Chen¹, Sean R. Bishop¹ and Harry L. Tuller^{1,2}; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan.

The direct quantification of ionic conductivity in mixed ionic-electronic conductors (MIECs) is of tremendous importance in developing novel materials for applications such as solid oxide fuel/electrolysis cell (SOFC/SOEC) electrodes. In MIECs the level of ionic conduction is typically significantly lower than that of the electronic contribution and its measurement is therefore more complex. Perhaps the most common technique is the quantification of the oxygen kinetics, i.e. the diffusion coefficient, which can be related to ionic conduction by the Nernst-Einstein relationship. This is typically performed by relaxation or isotopic tracer measurement techniques.

In order to measure the oxygen migration kinetics via relaxation, the material of interest must have a measurable property that depends on the oxygen defect concentration, for example electronic conductivity or lattice parameter, and a means of rapidly changing this concentration, such as temperature or oxygen partial pressure. The technique must therefore be tailored to individual materials. An additional complicating factor lies in the inherent convolution of the surface exchange and diffusion coefficients, that needs to be resolved in subsequent fitting of the relaxation curve.

Oxygen isotope tracer measurement allows the clear deconvolution of these two fitting parameters using quenched in diffusion profiles, however it is time consuming, utilizes expensive equipment and is typically a destructive technique.

In this work we demonstrate a novel technique to overcome the limitations of these methods by taking advantage of the previously demonstrated redox-state dependent color change in Pr doped ceria (PCO). This color change arises from the Pr (3+/4+) transition and can therefore serve as a means of quantifying the equilibrium Pr oxidation state and, in turn, the oxygen stoichiometry. Upon subjecting a thin film of PCO to a rapid change in $p\text{O}_2$, the change in oxygen stoichiometry is limited by the kinetics of oxygen surface exchange and diffusion. In order to track this diffusion over reasonable timescales, we limit the region exposed to the atmosphere using a blocking surface layer, so that the oxygen must diffuse laterally through the film. The diffusion profiles can therefore be optically recorded, in-situ, as the motion of a color front and evaluated by fitting to appropriate solutions to the diffusion equation to enable extraction of the oxygen surface exchange and chemical diffusion coefficients.

The results for PCO films over a range of partial pressures and temperatures are reported and contrasted with those determined by other methods. The potential application of this technique to other materials systems is also discussed, taking into account both its strengths and limitations.

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TraceX: Isotope Exchange Data Analysis, Back-Diffusion Simulation and Profile Fitting Samuel J. Cooper, Mathew Niania and John A. Kilner; Department of Materials, Imperial College London, London, United Kingdom.

Isotopic exchange has been well established as a technique to determine the diffusivity and surface exchange coefficients of ceramic materials for over two decades. The mass specific image data obtained, often through Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), requires some data analysis before a meaningful depth profile can be extracted. Factors such as sample alignment, correct surface location and the exclusion of porous regions must all be determined before a profile is generated [1].

The following work describes a new graphical user interface (GUI), based in the widely used MATLAB® environment, that offers image data analysis and curve fitting, as well as generating *back-diffusion* profiles through a finite difference simulation.