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Surface Modification of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ by Nanometer-Thick Mixed Conducting Oxide Films Michael L. Machala, Burcu Oeguet, David N. Mueller and William C. Chueh; Stanford University, Stanford, California, United States.

The oxygen evolution and reduction reactions are ubiquitous in many energy conversion processes. Of particular interest are reactions that take place over the solid/gas interface of perovskite-structured (ABO_3) mixed ionic and electronic conductors (MIECs). In conjunction with a solid electrolyte, devices using MIEC electrocatalysts—such as solid oxide fuel cells and electrolyzers—can operate at elevated temperatures (500–800°C), leading to faster kinetics of oxygen exchange reactions.

To further enhance device performance, heterostructured electrocatalysts have been employed through extrinsic decoration of MIEC oxide surfaces with dissimilar materials. Here, we study dense, thin film $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) electrodes grown by pulsed-laser deposition. LSCF is a promising MIEC scaffold with high electronic and ionic conductivity but a moderate and unstable oxygen reaction rate. We deposited nanometer-thick layers of MIEC oxides on top of thin-film LSCF electrodes and investigated their effect on electrochemical activity and stability. Crystal structure and chemical composition at the nanoscale was also investigated by high-resolution transmission electron microscopy. The precise role of the nanometer-thick surface coating in modifying and stabilizing the oxygen exchange reactions will be discussed.

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Microstructural Effect to Thermal Stability and Cathode Performance by Nanoscale ZrO_2 Capping in Platinum Based-Solid Oxide Fuel Cells Kang-Yu Liu¹, Liangdong Fan¹, Chen-Chiang Yu² and Pei-Chen Su¹; ¹School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, Singapore; ²Interdisciplinary Graduate School, Nanyang Technological University, Singapore, Singapore.

Thermally-driven agglomeration of platinum electrode heavily induced the loss of effective triple phase boundary (TPB) densities as temperature increases and irreversibly deteriorates fuel cell performances. This work demonstrates the capping of a nanoscale zirconia on a nano-porous platinum cathode, which has effectively improved the chronically poor thermal stability of such porous metal electrode and at the same time obtained an unexpected cathode performance enhancement. An approximately 1.6 nm of zirconia capping deposited on platinum by atomic layer deposition (ALD) serves as a mechanical barrier to prevent the rapid thermally-driven agglomeration of platinum nanoparticles. The oxygen-rich zirconia nanoparticles deposited on platinum surface may possibly decreased the oxygen adsorption-desorption resistance and rendered the unexpected drop in cathode polarization resistance. The behavior of cathode enhancement is dependent on zirconia capping by using ALD with thickness below 10 nm. The nanometer-thin zirconia capping may lead to different microstructural effects on the cathode enhancement. These results point out the explicit phenomenon of improving both thermal stability and cathode polarization by decorating a nanoscale zirconia on metal electrode. It might be a trigger point of exploring wider usage of other metal electrode in solid oxide fuel cells. Further confirmation on the microstructural effect of the nanoscale zirconia on platinum and the rate limited step of the cathode polarization are undergoing to clarify the fundamental mechanism for the unexpected cathode performance enhancement observed in this work.

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Microstructure and Functionality of Cathode/Electrolyte Interfaces in SOFCs Virginia Wilde¹, Heike Stoecker¹, Julian Szasz², Florian Wankmueller², Ellen Ivers-Tiffée² and Dagmar Gerthsen¹; ¹Laboratory for Electron Microscopy (LEM), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; ²Institute of Materials for Electric and Electronic Engineering (IWE), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.

Future solid oxide fuel cells (SOFC) with long lifetime and high efficiency at low operating temperatures require a thorough selection of materials for the different SOFC components cathode, electrolyte and anode. $\text{La}_{1-x}\text{S}_x\text{Co}_y\text{Fe}_{0.3-4}\text{O}_{3-\delta}$ (LSCF) is a high performance cathode material, however, when directly applied to Yttria-stabilized Zirconia (YSZ) electrolyte, a Strontiumzirconate (SZO) blocking layer is formed. One option to prevent SZO formation is the insertion of a dense Gd-doped Ceria (GDC) layer between LSCF and YSZ. Yet, to achieve highly functional GDC interlayers, sophisticated processing is essential. The present study combines electrochemical characterization of LSCF-GDC-YSZ interfaces with detailed microstructural characterization at the nanoscale using conventional and analytical (scanning) transmission electron microscopy ((S)TEM). Symmetric cell samples were fabricated by screen-printing a 5 μm thick GDC layer on both sides of YSZ substrates, followed by sintering at different temperatures from 1100 °C to 1400 °C. The LSCF was also screen-printed and sintering at 1080°C was applied to all LSCF layers irrespective of the GDC sintering temperature. The study shows that the nature of the GDC barrier layer depends strongly on the GDC sintering temperature and controls the area specific resistance of the cathode. Detailed TEM investigations give new insights into material interactions at the YSZ/GDC and GDC/LSCF interfaces for different GDC sintering temperatures. The study focuses particularly on the effect of GDC sintering temperature on SZO formation and cation interdiffusion. The origin of secondary phase formation between LSCF, GDC and YSZ and the effects of the microstructural development on electrochemical SOFC performance is discussed.

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Bias Enhanced Fast Oxygen Exchange and Diffusion Kinetics of Grain Boundaries in LSM Thin Films Tobias M. Huber^{1,2,3}, Edvinas Navickas⁴, Daio Takeshi¹, George F. Harrington^{1,2,3}, Nicola H. Perry^{3,5}, Ghislain Rupp⁴, Walid Hetaba⁶, Michael Stoecker-Pollach⁶, Harry L. Tuller^{2,5}, Bilge Yildiz^{3,2}, Kazunari Sasaki⁵ and Juergen Fleig¹; ¹Mechanical Engineering, Kyushu University, Fukuoka, Japan; ²Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ³Department of Nuclear Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁴Institute of Chemical Technologies and Analytics, Research Division Electrochemistry, Vienna University of Technology, Vienna, Austria; ⁵International Center for Carbon Neutral Energy Research (I2CNER), Kyushu University, Fukuoka, Japan; ⁶University Service Centre for Transmission Electron Microscopy, Vienna University of Technology, Vienna, Austria.

Introduction

The kinetics of the oxygen reduction reaction on solid oxide electrolytes and electrodes has been widely investigated in recent years. Although it is one of the best studied reactions in solid state ionics, several questions remain including the actual site of the oxygen reduction reaction (ORR). Sr-doped lanthanum manganite (LSM) is the most commonly used cathode material in solid oxide fuel cells (SOFC). Recently attention has been focused on ORR on LSM thin films via the grain boundary dependent path [1]. An improved understanding of the role of grain boundaries in perovskite materials may lead to improved electrode kinetics. In this work the ORR was investigated on pulsed laser deposited (PLD) LSM thin films. Voltage-driven ^{18}O tracer incorporation [2] was investigated by time of flight secondary ion mass spectrometry (ToF-SIMS) and analyzed with a 3D finite element model. The micro structure of the thin films was analyzed by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM).

^{18}O incorporation/exchange experiments

Geometrically well defined and dense, columnar grown thin film electrodes with well-defined microstructure on YSZ (100) single crystals were annealed with and without polarization in ^{18}O tracer gas atmosphere. After ^{18}O incorporation, the electrodes were quenched and analyzed by ToF-SIMS to obtain depth profiles of the ^{18}O incorporation. Numerical analysis of the profiles allowed a quantification of the surface oxygen incorporation kinetics and diffusion coefficients. This method allows one to distinguish between oxygen transport and oxygen incorporation at grains and grain boundaries. Microelectrodes were additionally electrochemically characterized by impedance spectroscopy at different temperatures and with varying microstructures.