

Novel Measurement Approaches on Microelectrodes for Solid State Ionics exemplified by Bias enhanced oxygen exchange and diffusion kinetics of grain boundary engendered LSM thin films

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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). Microelectrodes are commonly used in the field of solid state electrochemistry owing to the fact that minimizing the size maximizes the polarization resistance. Moreover, meaningful DC measurements can only be obtained when applying a reversible counter electrode, or a three electrode arrangement. Both approaches are highly non-trivial in solid state electrochemistry due to difficulties in finding the right material combination or positioning the reference electrode. However, by using microelectrodes only the influence of the measured electrode is therefore seen in impedance spectra and the counter electrode acts as a reference electrode.

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] on symmetrically heated microelectrodes [3][4] 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). In order to facilitate these experiments, several new measurement set-ups were designed and constructed to extend the experimental prospects, to combine existing measurement techniques, analytical methods and experimental tools.

^{18}O incorporation/exchange experiments

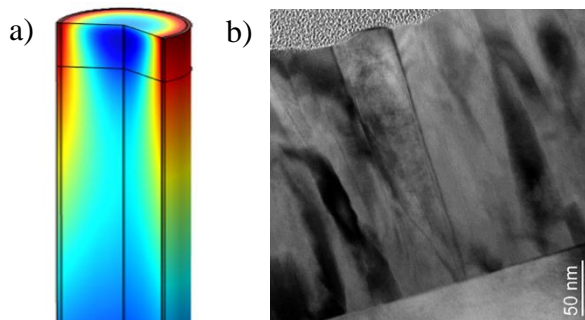


Fig. 1: a) Sketch of the 3D finite element model. b) Bright-field TEM image of a LSM thin film with columnar structure grown on single crystal YSZ.

Geometrically well-defined and dense, columnar grown thin film electrodes with well-defined microstructure on YSZ (100) single crystals (Fig. 1b) were annealed with and without polarization in ^{18}O tracer gas atmosphere. Additionally the micro structure was varied by changing the PLD deposition temperature (T_{dep}). After ^{18}O incorporation, the electrodes were quenched and analyzed by ToF-SIMS to obtain depth profiles of the ^{18}O incorporation (Fig. 2). 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.

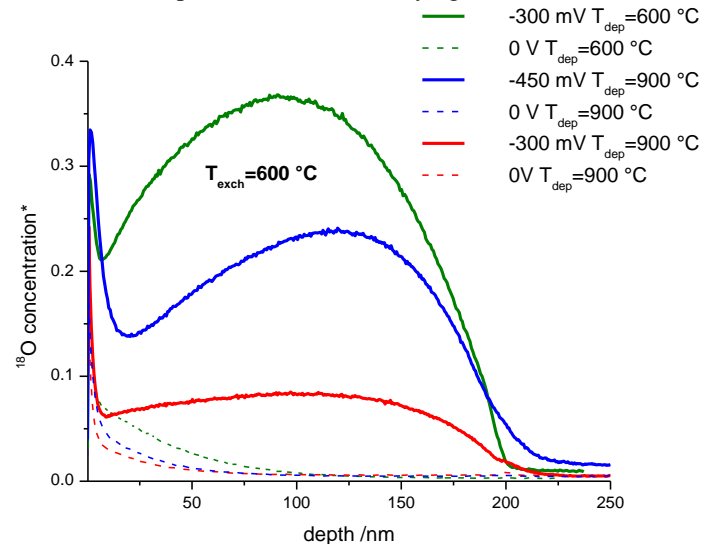


Fig. 2: ^{18}O concentration profile obtained by voltage driven tracer incorporation on a LSM thin film microelectrode for different currents and different microstructures (green curve: small grained with much grain boundaries, blue and red curve: big grains with less grain boundaries, dotted curves show only temperature annealed electrodes on the same samples).

Grain boundary diffusion and surface exchange values for non-polarized LSM thin films obtained from the measurements were approximately three orders of magnitude larger than those of the grains [1]. By applying cathodic bias surface exchange is additionally enhanced and diffusion coefficients are increased as a function of depth, according to the gradient of chemical potential. Due to the applied voltage, a Wagner-Hebb type polarization creates a depth dependent increase in transport properties leading to an apparent uphill diffusion in the depth profiles (Fig. 2). This behavior is also computable with the 3D finite element model.

References

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