SSI-19

Program

The 19th International Conference on Solid State Ionics

June 2–7, 2013

Kyoto, JAPAN

Cosponsored by

Japan Society for the Promotion of Science

Commemorative Organization for the Japan World Exposition '70

International Institute for Carbon-Neutral Energy Research Kyushu University

The Murata Science Foundation

The Electrochemical Society of Japan, Kansai Branch

The Committee of Battery Technology The Electrochemical Society of Japan

Organized by

The Solid State Ionics Society of Japan

Under the auspices of

ISSI INTERNATIONAL SOCIETY FOR SOLID STATE IONICS

FACTORS INFLUENCING THE OXYGEN EXCHANGE KINETICS OF PEROVSKITE-TYPE THIN FILM ELECTRODES

J. Fleig[1], M. Kubicek[1], B. Yildiz[2], Z. Cai[2], W. Ma[2], H. Hutter[1], G. Rupp[1], A. Limbeck[1], S. Huber[1], S. Kogler[1], A. Nenning[1], A. Opitz[1]

[1] Inst. of Chem. Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria

[2] Dept. of Nuclear Sci. and Eng., Massachusetts Institute of Technology, 77 Mass. Av., Cambridge MA 02139, USA

Email: j.fleig@tuwien.ac.at

Keywords: MIEC electrodes, thin films, impedance spectroscopy, tracer diffusion, chemical analysis

Introduction

Perovskite-type oxides are of paramount importance as electrode materials in SOFCs/SOECs, not only on the oxygen side but increasingly relevant also under reducing conditions. Optimization of such electrodes considerably benefits from an in-depth understanding of the electrochemical surface, interface and bulk properties. Numerous factors influence these properties including microstructure, segregation, strain and the species involved in the oxidation or reduction reaction. However, it is frequently far from trivial to interpret empirical kinetic data in terms of elementary processes (surface gas exchange, ion transport, etc.) and factors affecting each of them (strain, segregants, etc.). Simplifying the system is a possible way to take a step forward, for example by investigating thin films or thin film microelectrodes. Combination of different tools in kinetic measurements and several methods for chemical / structural analysis then allows novel insights into the mechanisms governing gas exchange kinetics. This will be exemplified in this talk.

Experiments

Thin films of three materials ($La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), $La_{1-x}Sr_xFeO_{3-\delta}$ (LSF), $SrTi_{1-x}Fe_xO_{3-\delta}$ (STF)) were prepared by pulsed laser deposition (PLD) on either ion conducting (YSZ) or insulating ($SrTiO_3$, $LaAlO_3$) single crystalline substrates. For cation diffusion experiments also hetero-layers were deposited. ^{18}O tracer as well as cation tracer profiles were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Films on YSZ were further analyzed by impedance spectroscopy.

Results and Discussion

Emphasis is put on the following factors influencing gas exchange kinetics of thin film electrodes:

i) Strain

Epitaxial LSC layers (20 nm thin) exhibiting tensile or compressive strain were deposited on $SrTiO_3$ and $LaAlO_3$, respectively. The layers were exposed to $^{18}O_2$ atmosphere at elevated temperature. The profiles in Fig. 1 show that lattice strain has a strong effect on the oxygen exchange kinetics as well as on the tracer diffusion coefficient.

ii) Cation motion and segregation

Surface segregation of cations and its effect on the electrochemical properties of LSC was analyzed in a study combining inductively coupled plasma optical emission spectroscopy (ICP-OES) of chemically etched near-surface film regions and impedance spectroscopy.

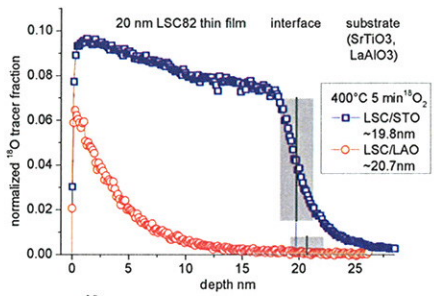

Fig. 1: ^{18}O tracer diffusion profiles obtained at 400°C for LSC on $SrTiO_3$ and $LaAlO_3$.

This allowed correlation between segregants and their effect on gas exchange kinetics. Moreover, cation mobility in thin films was investigated by Sr isotope diffusion and several cation diffusion couples. Grain boundary and bulk diffusion coefficients could be extracted at temperatures as low as 600°C.

iii) Gas species

The effect of the involved gas species on the reaction mechanism and the rate limiting step of gas exchange reactions was investigated for LSF and STF thin films: Their impedance was analyzed in oxidizing as well as in H_2/H_2O atmosphere. A special type of microelectrode was developed which allowed an analysis of surface-related polarization resistance, ionic conductivity, electronic conductivity, interfacial resistance and chemical capacitance of one and the same material in a single experiment (see Fig. 2).

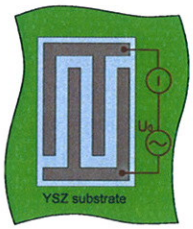

Fig. 2: Special type of a rectangular-shaped thin film microelectrode on YSZ including two interdigitally arranged Pt electrodes for analysis of kinetic properties by two measurement modes (in plane and electrochemical mode).

Conclusions

Investigation of the electrochemical properties of perovskite-type thin film electrodes can strongly benefit from complementary tools for kinetic measurements and defined variation of the decisive chemical and microstructural factors.