Oxygen tracer diffusion in Sr-doped LaFeO$_3$ investigated by ToF-SIMS and impedance spectroscopy

Sandra Kogler, Katharina Langner-Hansel, Herbert Hutter, Jürgen Faug
Institute of Chemical Technologies and Analytical, Vienna University of Technology, Vienna, Austria

Introduction

Sr-doped LaFeO$_3$ is a mixed ionic and electronic conducting perovskite. It is a promising electrode material in solid oxide fuel cells (SOFC) in both oxidizing and reducing atmosphere due to its high thermo-chemical stability over a wide oxygen partial pressure range [1, 2]. Therefore the transport and reaction kinetics of this material are of high interest. In this contribution we report the results from thermally driven $^{18}$O$_2$ isotope exchange experiments and subsequent Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis. These experiments provide two kinetic parameters, the tracer diffusion coefficient $D^*$ and the surface exchange coefficient $k^*$. A novel approach allowed comparison of $k^*$ and $D^*$ values under reducing and oxidizing conditions.

Methods

La$_{1.2}$Sr$_{0.8}$FeO$_3$ thin films of ~460 nm thickness were deposited on MgO single crystal by pulsed laser deposition (PLD). The deposited films were characterized by scanning electron microscopy (SEM). In a first experimental step, $^{18}$O$_2$ isotope exchange ($p(18O)=200$ mbar) was performed at 500°C for 20 min in order to fill the thin films with a monolayer tracer concentration, recorded by ToF-SIMS operated in CBA mode [3]. In a second step, oxygen release was performed at temperatures between 350 °C and 500 °C in oxidizing atmosphere ($p(18O)=200$ mbar) or in reducing atmosphere ($p(18O)+p(16O)=200$ mbar). Hence, $k^*$ factors of two different chemical reactions were probed. The resulting $^{16}$O$_2$ fraction diffusion profiles were again analyzed by ToF-SIMS operated in CBA mode.

Results and Discussion

The measurements revealed the strong dependence of the transport kinetics on the atmosphere. The two cases reflect the situations at the anode and the cathode in a SOFC. The diffusion profiles in oxidizing conditions were fitted with the finite element package COMSOL (COMSOL Multiphysics 4.3a) and deliver directly the tracer diffusion coefficient $D^*$ and the surface exchange coefficient $k^*$. Under reducing conditions, however the diffusion profiles are almost flat indicating high tracer diffusion coefficients due to the high oxygen vacancy concentration. Hence only the surface exchange coefficient $k^*$ can be determined.

Summary

A two-step tracer experiment and a subsequent ToF-SIMS investigation allowed the analysis of tracer exchange kinetics of Sr-doped LaFeO$_3$ thin films not only in oxygen but also in hydrogen atmosphere. The results show that the surface exchange in oxidizing and reducing conditions is of approximately the same magnitude but the diffusion coefficients differ drastically.

References


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