

## Abstract

Solid oxide fuel cells (SOFCs) are expected to substantially contribute to tomorrow's electrical energy production and may become an important technology to ease the transition from fossil fuels to renewable resources such as biomass. Current applications include combined heating and power (CHP) systems for companies or housing complexes as well as portable power supply and typically operate at 700 – 1000 °C. The high operating temperatures restrict the choice of materials used, complicate production, decrease the durability of the components because of undesired side reactions, and therefore hamper a broad commercialization. However, realization of intermediate temperature SOFCs operating at 400 – 600 °C demands cathode materials that are highly active for the oxygen reduction reaction (ORR). Several mixed ionic electronic conductors (MIECs) including  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  (LSC) prove suitable for this task but suffer from degradation of the electrochemical kinetics when subjected to operating temperatures, even on short-time scales (hours, days). This degradation is correlated to changes of the surface composition and structure and its analysis requires methods that are specifically adapted to the underlying complex chemical phenomena.

In this thesis, relationships between surface cation composition and the kinetics of the ORR of LSC model thin films are revealed. A combination of low energy ion scattering (LEIS) measurements and an innovative approach for determination of the surface stoichiometry of solids by on-line inductively coupled plasma – mass spectrometry (ICP-MS) allowed quantitative determination of the surface termination of these thin films. These experiments showed that formation of a Sr-rich surface layer is an equilibrium property of LSC and that significant Sr diffusion takes place above 550°C. Further, a new tool was developed to manipulate thin film electrode surfaces by deposition of different oxides while in-situ measuring the ORR activity: In-situ Impedance spectroscopy inside a pulsed laser deposition chamber (IPLD). Thus, key parameters influencing the ORR kinetics were found and insights into the degradation mechanism of LSC thin films were gained. Particularly, it could be shown that even a single laser pulse applied to a SrO target, i.e. growth of a 4% fraction of a SrO monolayer on an LSC surface, severely decreases the ORR kinetics. This indicates that only a few sites of as-prepared LSC films are highly active for oxygen exchange and additional Sr cations do not randomly cover the surface but specifically deactivate those active sites. Further, a strong enhancement of the ORR kinetics was found, when decorating the surface with Co-oxides.

As an alternative cathode material  $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$  (LBC) was investigated. An extraordinarily high catalytic activity for the oxygen exchange was discovered and an in-depth impedance analysis revealed the influence of the dopant size ( $\text{Ba}^{2+} > \text{Sr}^{2+}$ ) in  $\text{LaCoO}_{3-\delta}$  on the oxygen exchange activity, chemical capacitance and electronic conductivity.

Finally, the electrochemical properties of a single crystal of  $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}$  (LSGM), one of the most promising electrolyte materials for intermediate SOFC, were analyzed by AC experiments with ion blocking electrode. The excellent agreement between equivalent circuit model and experimental data allowed determination of the ionic and electronic conductivity, the chemical capacitance and the oxygen chemical diffusion coefficient from a single impedance spectrum.