

Mechanisms of electrochemical oxygen exchange on mixed conducting model electrodes in H₂-H₂O atmosphere

Abstract:

Solid oxide cells are on the verge of commercialization, but still much research is attributed to optimizing long term stability, for example by decreasing the operating temperature significantly below 800°C. For this goal, new electrode materials with high activity for oxygen exchange at intermediate temperatures are searched for. Mixed ionic and electronic conductors (MIECs) are a promising class of electrode materials, because all species (oxygen ions, electrons and atmospheric oxygen) necessary for electrochemical oxygen exchange are accessible on the entire surface area. While already much research effort was dedicated to the investigation of mixed conducting oxygen electrodes, fundamental investigations of the fuel side electrodes are rather scarce and only ceria-based materials have been studied on a detailed mechanistic level.

In this thesis, mixed conducting perovskite-type electrode materials are in the focus of research. The main goal was the development of methods and models to characterize mixed conducting acceptor doped perovskite-type materials in H₂+H₂O atmospheres. Electrochemical impedance spectroscopy (EIS) was used to quantify the area-specific resistance of the surface reaction, as well as electronic and ionic conductivity of mixed conductors. Additional analytic methods, such as ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and ¹⁸O isotope exchange with subsequent depth profiling were employed to gain a better insight into the mechanisms of electrochemical oxygen exchange at the surface.

For the impedance measurements, thin film model electrodes were deposited on YSZ substrates. As an experimental challenge, the electronic conductivity of acceptor-doped oxides in H₂+H₂O atmosphere is typically rather low, resulting in a complex interplay of electrochemical reactions and in-plane charge transport, which complicates the interpretation of impedance spectra. Therefore, a novel electrode design was developed, consisting of a mixed conducting thin film and metallic current collectors. Two interdigitating metallic current collectors are placed in a microelectrode, which allows in-plane measurements between the current collectors as well as electrochemical measurements versus a large counter electrode. Equivalent circuit models for quantifying the spectra of both measurement modes were developed and applied to simultaneously fit both spectra, using the same parameter set. In this manner, electronic conductivity as well as the area-specific resistance of the surface reaction and the chemical capacitance can be determined on a single microelectrode. This method together with in-plane measurements on microelectrodes on MgO substrates was employed to investigate the effect of the Fe content in SrTi_{1-x}Fe_xO_{3-δ} on the electronic and ionic conductivity as well as the area specific resistance of the surface oxygen exchange reaction.

The derived equivalent circuit models predict that the electrochemically active zone in weakly electron conducting materials is restricted to the vicinity of the current collectors. ¹⁸O Isotope exchange experiments were performed to map this zone on mixed conducting SrTi_{1-x}Fe_xO_{3-δ} and Ge_{0.8}Gd_{0.2}O_{1.9-δ} thin films with polarized current collectors in reducing H₂¹⁸O + H₂ atmosphere. Subsequent investigation of the ¹⁸O distribution revealed the electrochemically active areas where the ¹⁸O content depended on the polarization.

Further insight into the mechanisms of oxygen exchange was gained by simultaneously acquiring the electrical (k^q) and tracer (k^*) exchange coefficient of oxygen in three different atmospheres: dry ¹⁸O₂, H₂¹⁸O + ¹⁶O₂ and H₂¹⁸O + H₂. While good agreement of both coefficients is found in dry ¹⁸O₂, the tracer exchange coefficient is more than two orders of magnitude higher than the electrical one in humidified atmospheres. This huge difference can be explained by a fast equilibrium rate of water adsorption on surface oxygen vacancies and subsequent dissociation into two surface hydroxyl groups (and the reverse desorption of water), which enables ¹⁸O isotope exchange without an electron transfer. These results are highly important in oxidizing conditions, as they highlight how easily the electrochemical oxygen exchange activity can be over-estimated even when only traces of water are present in the atmosphere. In reducing conditions, the very high tracer exchange coefficient rules out the dissociation or desorption of H₂O to be rate limiting in the surface reaction.

Additional information on the surface chemistry in operating conditions was gained by ambient pressure XPS investigation of model cells with a thin film working electrodes of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC), $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) or $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (STF). This enabled very surface-sensitive chemical analysis near to technological operating conditions. The cells were investigated during well-defined electrochemical polarization in oxidizing (O_2) and in reducing ($\text{H}_2+\text{H}_2\text{O}$) atmospheres. In oxidizing atmosphere all materials exhibit additional surface species of strontium and oxygen. Switching between oxidizing and reducing atmospheres as well as electrochemical polarization caused reversible shifts in the measured binding energy. These shifts can be correlated to a Fermi level shift due to variations in the chemical potential of oxygen. Changes of oxidation states were detected on Fe, which appears as Fe^{III} in oxidizing atmosphere and as mixed $\text{Fe}^{\text{II/III}}$ in $\text{H}_2+\text{H}_2\text{O}$. Cathodic polarization in reducing atmosphere leads to the evolution of Fe^0 particles that can be reversibly oxidized and reduced by very small applied potentials. The current-voltage characteristics are very steep when metallic Fe is present and rather shallow without the presence of metallic Fe, which indicates a high catalytic activity of the formed Fe particles. The evolution of metallic Fe could be reproduced in a lab-based UHV XPS analyzer, which proves that the electrode bulk oxygen partial pressure is more decisive than the atmospheric conditions.