

Surface reaction mechanisms and transport kinetics of perovskite mixed conducting oxide thin films

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The oxygen exchange reaction on mixed ionic electronic conducting (MIEC) oxides is highly important for solid oxide fuel cells, sensors or oxygen permeation membranes. The reaction rates and diffusion characteristics of an MIEC oxide depends on many different parameters. In this contribution, surface composition, defect concentrations, lattice strain and humidity are discussed.

More specific, three different experiment types are presented which allow to investigate different aspects of MIEC oxides. *First*, a newly developed in-situ-combination of electrochemical impedance spectroscopy (EIS) and pulsed laser deposition (PLD) was used to investigate thin films while growing them. The technique gives direct insight into changes of MIEC thin films during growth, but also allows deposition of thin films with unique reproducibility between samples. These features together with EIS analysis makes it possible to measure even tiny changes of the surface, microstructure, strain or defect concentrations.

Second, the influence of lattice strain on thin films is discussed, which is imposed by growing epitaxially on different perovskite substrates. Here, earlier cross-plane diffusion experiments have been extended by additional measurements of in-plane diffusion coefficients. Comparison of diffusion in the two directions gives new insights on the influence of vacancy concentration (which remains the same in the two directions and the same strain state) vs. the individual hops (which happen *via* the elongated or *via* the shortened lattice direction for the two directions but the same strain state).

Third, a study on the influence of humidity on oxygen incorporation and diffusion is presented. Five commonly used MIEC materials were investigated in isotope exchange experiments. These were performed by using isotope labeled (^{18}O) and conventional (^{16}O) oxygen and water. By using different combinations of O_2 and or H_2O atmospheres, it was possible to investigate two different oxygen exchange mechanisms of which only one is electrochemically active. Huge differences in their utilization have been observed for the five different MIEC oxides. The extracted tracer exchange coefficients (k^*) were also compared with their electrical counterparts (k^q). In dried isotope gas k^q and k^* were rather similar ($k^*/k^q=1.5$), whereas in humid atmospheres the difference between k^* and k^q becomes tremendous ($k^*/k^q=1000$) for some materials.