Defect and surface chemistry of porous La\(_{0.6}Sr_{0.4}FeO_3\)-\(\delta\) electrodes revealed by simultaneous three-electrode impedance and APXPS

Authors: Andreas Nenning(1), Harald Summerer(1), Raffael Rameshan(2), Lorenz Lindenthal(2), Stefan Reuter(1), Richard Schlesinger(3), Tobias Huber(1), Christoph Rameshan(2), Jurgen Fleig(1), Alexander K. Opitz(1)

Affiliations: (1) TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria (2) TU Wien, Institute of Materials Chemistry, Getreidemarkt 9/165, 1060 Vienna, Austria (3) ETH Zurich, Deptartment of Information Technology and Electrical Engineering, Physikerstrasse 3, CH-8092 Zurich

Resume: The performance of mixed conducting porous SOC electrodes depends on the concentration and mobility of electronic and ionic defects in the bulk, as well as the surface structure and chemistry, which determines the reactivity for oxygen exchange reactions. The simultaneous characterization of SOC electrodes with electrochemical impedance spectroscopy (EIS) and ambient pressure XPS (APXPS) delivers detailed insight into the reaction mechanism. Since the bulk and surface defect chemistry vary with atmosphere and overpotential of the investigated electrode, precise knowledge of these parameters is an important, but highly non-trivial experimental requirement, especially when the investigated electrode is porous and thus has a low polarization resistance. Therefore, combined EIS and APXPS studies were so far mostly performed on model cells with thin film electrodes. In the presented study we use a novel three electrode solid oxide cell design with three porous electrodes. This allows precise control of half-cell overpotentials and measurement of virtually artefact free half-cell impedance spectra in an APXPS chamber. We exemplify the strength of this design on porous La\(_{0.6}Sr_{0.4}FeO_3\) (LSF) electrodes. Equivalent circuit fitting of the half-cell impedance spectra reveals defect chemistry, surface reactivity and ion conductivity of the LSF phase, also when a DC bias is applied. Another important aspect of the cell design is the current collecting layer of the LSF electrode, which is realized in form a of a thin film Pt grid between electrode and electrolyte. Therefore, the LSF phase is accessible to ambient pressure XPS (APXPS) measurements at various bias and atmosphere conditions. The combination of these methods reveals a consistent picture about the relation of bulk and surface defect chemistry, mixed ion/electron conduction and redox kinetics. Specifically, we can show that in oxidizing atmosphere, overpotential drastically changes concentration of oxygen vacancies in LSF. By impedance fitting with a transmission line type equivalent circuit we find an according bias dependence of the ionic conductivity and chemical capacitance. Since oxygen vacancies are not directly detectable by APXPS, the surface chemistry depends only moderately on the overpotential. In reducing (H\(_2\)+H\(_2\)O) atmosphere, the vacancy concentration is high, irrespective of the applied overpotential. Still, the I-V curve is strongly asymmetric and much steeper in electrolysis direction. There, the overpotential has a strong effect on the oxidation states of Fe. We find Fe\(^{3+}\), Fe\(^{2+}\) and Fe\(^0\) states, depending on the overpotential. When cathodic bias is applied, metallic iron is present in form of exsolved nanoparticles, which explain the excellent H\(_2\)O electrolysis kinetics. Therefore we deliver direct proof that Fe exsolutions strongly accelerate the water splitting kinetics also on porous electrodes.