Improvement of experimental tools for investigating individual electrodes of solid oxide cells

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Investigating electrochemical processes at single electrodes of solid state electrochemical cells is far from trivial since additional contributions to the cell resistance (ohmic resistances, counter electrode resistance) have to be eliminated before the true working electrode (WE) properties can be analyzed. Essentially, two main approaches are common for minimizing or eliminating the resistance of counter electrodes (CE). Either microelectrodes are used as WE, thus increasing their resistance compared to the extended CE, or three-terminal measurements (i.e. use of reference electrodes, RE) are employed. Both approaches suffer from shortcomings and problems and a further improvement of experimental setups or methods is desirable to make these kind of measurements better applicable in solid state ionics.

This presentation summarizes recent developments for improving the experimental designs and sample geometries for both approaches and shows examples to give an overview of new capabilities.

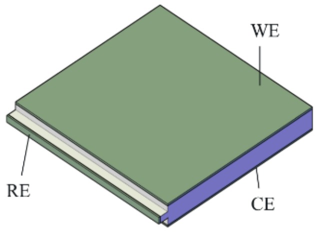

Fig. 1 „Wing Geometry“

i) Three-terminal measurements suffer from several difficulties including the problem of properly positioning the RE. It is discussed that three potential error sources are particularly crucial: Asymmetric sample cells, short circuit currents across the RE, and capacitances between the three electrodes. The **“wing geometry”** is proposed (see Fig. 1) which minimizes the measurement errors significantly. This geometry is applied to YSZ based electrochemcial cells and test measurements are discussed.

Fig. 2 Laser heated UHV and ambient pressure XPS stage

ii) Microelectrodes exhibit the advantage that their small size maximizes the polarization resistance and thus mainly the electrode processes at the measured microelectrode are visible in impedance spectra. Still several shortcomings are present. For example, samples with microelectrodes are mostly asymmetrically heated on a heating table in order to enable contacting by a tip from the top. Here, we show by examples that the application field of microelectrodes or microstructured electrodes can be extended by several experimental improvements: Symmetrically heated micro-contact stations for avoiding temperature inhomogeneities, sample holders enabling contacts of up to four individual microelectrodes in parallel and long time measurements over weeks with remote control of temperature, gas and bias, use of **microelectrodes in synchrotron facilities** to perform **in-situ measurements**, investigation of microelectrodes in a broad p(O2) range (< 10^{-30} mbar) enabled by a zirconia based oxygen pump, and current-voltage measurements in **^{18}O tracer gas atmosphere** with specially designed sample geometries.

Fig. 3 Sym. heated micro contacts

ii) In situ experiments The novel measurement and electrode designs are also implemented in novel setups for in situ experiments in **near ambient pressure XPS** (see Fig. 2) and **PLD chambers**.

PLD: Instead of chemical post-analysis of degraded thin films, the thin film electrode surface can be deliberately changed by depositing defined amounts of its constituents. These surface modification are simultaneously monitored by in situ impedance spectroscopy during pulsed laser deposition.

XPS: The common tools for in situ modifying the properties of oxides in solid state ionics are based on variations of oxygen partial pressure, temperature and applied voltage inducing changes of defect concentrations and thus modify electrochemical properties. Combined with a test interface (Fig. 2) allowing to contact the novel Wing Geometry (Fig. 1) such modifications can be performed in situ in a near ambient pressure XPS.