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Study of Electrochemical Interface Processes by Locally Resolving Photoelectron Spectroscopy and Microscopy

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The mechanistic understanding of electrochemical processes at electrodes requires the combination of phenomenological (electrochemical) techniques with spectroscopic and microscopic methods – if possible – under real *in situ* conditions. Whereas this is still a major problem in the case of buried interfaces between two condensed phases, gas electrodes on solid electrolytes offer favorable conditions for experimental access by surface-analytical tools. These tools have been developed primarily for the study of heterogeneous catalysts and surface reactions thereon, but find recently increasing application also in electrochemistry. However, the number of examples is still relatively small, and major advances have still to be expected once real *in operando* techniques at atmospheric pressure conditions become available.

Here, we summarize and discuss the results of UV and X-ray photoelectron-based studies on solid state electrode kinetics. All of the known studies report on electrode processes on YSZ (yttria-stabilized zirconia), which is sufficiently stable at high temperature and under strong photon irradiation. In detail, the following examples are briefly discussed:

a) Pt(O_2)/YSZ: The Pt(O_2) electrode is the most prominent electrode system in solid state ionics and provides a number of questions on the influence of electrode microstructure and impurity content. Scanning photoelectron microscopy (SPEM) and photoelectron emission microscopy (PEEM) experiments help to gain information of the so-called spillover process under anodic conditions.

b) Au(N_2)/YSZ: Under strongly reducing (cathodic) conditions dinitrogen can be electrochemically activated and incorporated into YSZ. SPEM experiments offer information on the intermediates.

c) LSM(O_2)/YSZ: The perovskite-type electrode LSM (Lanthanum Strontium Manganate) represents the prototype oxide electrode and is today widely used as cathode in solid oxide fuel cells (SOFC). SPEM experiments give a first spectroscopic insight into the reactive processes occurring under polarization.

All examples show that it is crucial to design model-type electrodes which offer well defined geometrical and chemical conditions. In all cases, either thin film electrodes prepared by PLD (pulsed laser deposition) or microelectrodes are used.

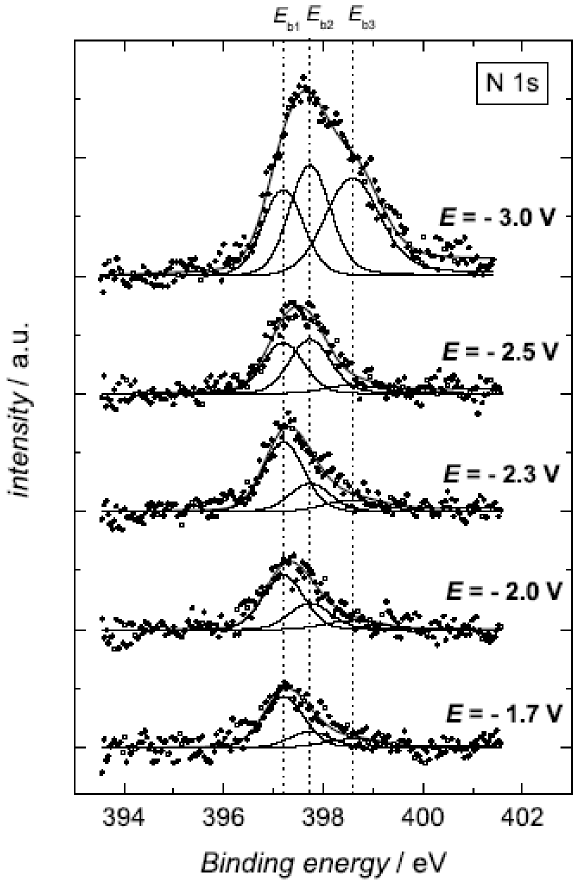

Fig. 1 The intensity of the N 1s line in high temperature μ-ESCA (SPEM) experiments at a $Au(O_2)$/YSZ microelectrode.

The results give valuable information on the electrode processes: In the case of the $Pt(O_2)$ electrode, oxygen spillover can be detected and its spatial distribution can be imaged. In the case of the nitrogen electrode, the spatial distribution of reaction products around the electrode and intermediates are detected. And in the case of the LSM electrode the reversible and irreversible segregation of electrode components can be imaged with spatial and temporal resolution.

References

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