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In Situ XPS Study on the Electrochemical Nitrogen Incorporation in YSZ

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The electrochemical surface reactions of oxygen at the triple phase boundary electrode/solid electrolyte/gas phase have been studied extensively since long time. Both the heterogeneous surface kinetics of oxygen as well as the transport kinetics in oxides are now reasonably well understood. In contrast, the reactivity of nitrogen is by far less well studied. The main reasons are simple: On the one hand the dinitrogen molecule is much more stable than the dioxygen molecule, and it is less reactive. In fact, it is often used as an inert gas in chemistry and physics.

Recently we reported on the electrochemical nitrogen incorporation into yttria stabilized zirconia (YSZ) from nitrogen atmosphere. Based on the results of steady state polarization experiments we suggested a multi-step charge transfer mechanism with a rate limiting step $N_2^- + e^- = N_2^{2-}$ [1,2]. In the present study we investigated by *in situ* XPS (synchrotron radiation) with high spatial resolution the surface species created as a result of the electrochemical process of reduction of molecular nitrogen at the interface between an iridium micro-electrode and a (111)-orientated 9.5 mol-% doped YSZ singe crystal at 450 °C. We observed the N 1s peak corresponding to the N^{3-} oxidation state at a binding energy of 397.3 eV under cathodic potentials above –1.5 V, being reversible after switching off the external potential. The full set of XPS spectra, *i.e.*, Zr 3d, Y 3d, O 1s and N 1s peaks, collected at cathodic potentials of up to –3 V confirmed different nitrogen species upon polarisation.

Thus, we present the first unequivocal results on the electrochemical reduction of molecular nitrogen on solid electrolytes. The implications for an electrochemical activation of nitrogen in general and for the route to nitrogen electrochemistry are discussed.

References

[1] I. Valov, C. Korte, R. A. De Souza, M. Martin, J. Janek, Electrochem. Solid State Lett. 9 (2006) F23.
[2] I. Valov, J. Janek, Solid State Ion. 177 (2006) 1619.