New Insight into the Surface Species During Water Electrolysis by in-situ AP-XPS

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Introduction and Objectives

Ambient pressure XPS (AP-XPS) is a well-established tool for the surface characterization of heterogeneous catalysts under reactive environment in the pressure range up to 0.5 mbar [1]. Such a technique is also suitable to investigate the electrode surface under the electrochemical activation of a molecule. In this work, we present a cell-concept, which allows to characterize the surface of a Pt/NAFION-based electrode for electrochemical water splitting by means of the AP-XPS end-station at the ISISS beamline (HZB/BESSY II), in the water total pressure range of 10^{-2} mbar. The NAFION membrane is sputter-coated on both sides by the electro-active element, functioning as cathode on one side and anode on the other side. The cell presents a reservoir for liquid, which is leak-tight sealed through the coated-NAFION membrane. The use of liquid water in the reservoir is two-fold: on one hand it supplies the reactant molecules to both the electrodes due to the permeability of the NAFION membrane to water, on the other hand it guaranties a good hydration of the membrane which is fundamental for achieving a significant current. The electrode directly in contact with the liquid water functions as counter electrode, while the electrode exposed to photons is the working electrode (we). The water transport through the NAFION membrane results in a total pressure up to 10^{-2} mbar in the XPS chamber. Sketch of the cell is reported in Figure 1. Electrochemical techniques such as cyclic voltammetry (CV) and chrono-amperometry (CA) under relevant polarization are combined with simultaneous XPS investigation of the O1s, C1s and Pt4f core levels. In particular, the chemical state of the electro-active Pt and the oxygen surface species are investigated during water surface chemisorption, O_2 evolution and H_2 evolution. The gas composition is continuously monitored by mass spectrometry (online MS).

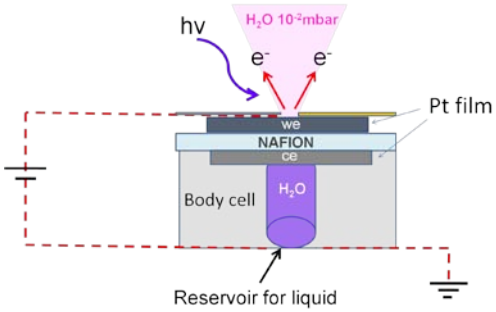

Figure 1: sketch of the cell for the in-situ XPS investigation

Results and Discussion

Figure 2 reports the cyclic voltammogram for the electrode/cell assemble in the in-situ XPS chamber. The gas phase analysis of the *m/z* 2 and *m/z* 32 MS traces at constant potential shows the response of the system when switching from open circuit condition to H_2 evolution or O_2 evolution condition. The current decreases when the liquid water in the reservoir is consumed and the pressure in the XPS cell decreases rapidly to 10^{-5} mbar.

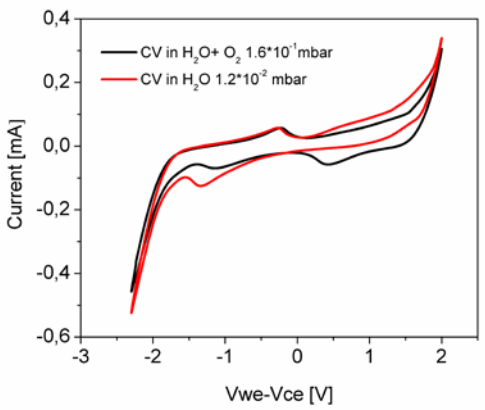

Figure 2: CV of the Pt/NAFION/Pt electrode in the cell.

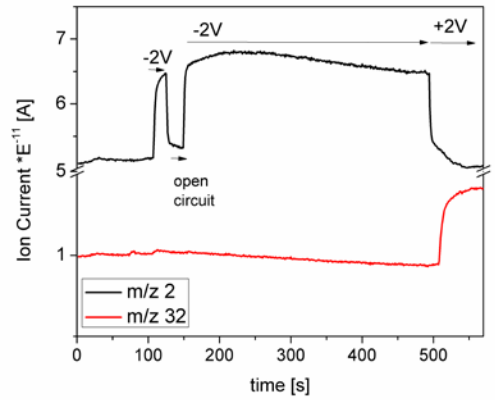

Figure 3: H_2 and O_2 profile during CA

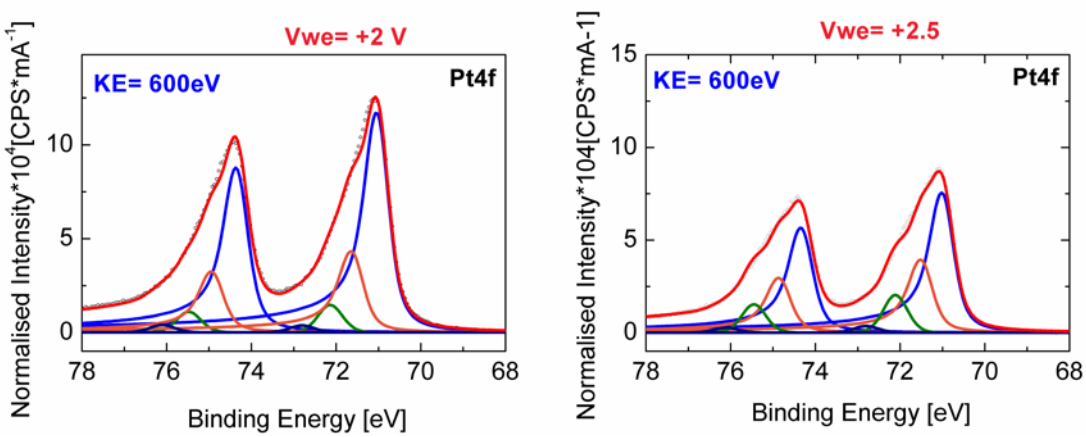

Figure 4: H_2 and O_2 profile during CA

Conclusions

The designed cell with the liquid reservoir was specially constructed to investigate by means of soft X-ray spectroscopy a Pt/NAFION electrode during in-situ electrochemical processes. The Pt4f shows that during OER, the Pt0/Pt+ ratio decreases indicating the progressive surface accumulation of Pt-O species. Such a system is suitable to be applied to investigate other electrocatalytic processes too.

References

[1] E. M. Vass, M. Hävecker, S. Zafeiratos, D. Teschner, A. Knop-Gericke, R. Schlögl
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