

An ambient pressure photoelectron spectroscopy investigation of a membrane-electrode assembly of a high temperature PEM under potential control

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High temperature polymer electrolyte fuel cell (HT PEMFC) is a subkind of PEMFC that use phosphoric acid imbibed polymer membranes instead of sulfonated polymers like Nafion® or its analogs [1]. The advantage of a HT PEMFC is its operating temperature of 150 - 200°C which renders them much higher tolerance to contaminations and simpler water and heat management. Unfortunately, along the said advantages they suffer from slower, compared to a low temperature PEMFC, ORR kinetics usually attributed to the adsorption of phosphoric acid at the metal/electrolyte interface as well as to the low O₂ solubility in phosphoric acid [2]. Hence, an understanding of the state of the interface between catalytic Pt nanoparticles and the phosphoric acid-imbibed polymer membrane *in situ* under potential control is of paramount importance for the dissemination of this attractive technology.

Photoelectron spectroscopy (PES) is one of the most powerful techniques for surface studies since it is very sensitive to the composition and the oxidation state of components located on the surface and in the near-surface region of materials. However, application of PES requires ultra-high vacuum thus severely restricting the range of electrochemical systems which can be investigated.

Recent advances in vacuum and analyzer technologies have resulted in the development of specialized instruments at synchrotron facilities which allow performing the so-called Ambient Pressure Photoelectron Spectroscopy (APPEs) measurements in the pressure range of millibars [3]. Development of the APPEs has boosted *in situ* studies of various catalytic [4] and recently also electrocatalytic [5] systems. Recently, Zhang et al. [5] applied APPEs to study a single-chamber solid oxide fuel cell at 750°C in 1 mbar reactant gases. However, *in situ* monitoring of the metal/polymer electrolyte interfaces relevant to PEMFCs is still a challenge.

Here we will present the results of an *in situ* study of the interface between Pt nanoparticles and phosphoric acid imbibed polymer membrane under potential control. The measurements were performed at the BESSY synchrotron facility in Berlin (beamline ISISS, operated by Fritz-Haber Institute) which allows

measurements at pressures in the millibar range. MEAs were prepared by chemical deposition of ultrathin Pt layers directly onto the high temperature polymer membrane. The preparation technique provides highly extended three phase boundary between the membrane, the catalyst and the gas phase which is of key importance in this study.

We will show that the approach employed allows probing the potential distribution, as well as the observation of various potential-driven processes including Pt surface oxide formation, as well as migration of phosphoric acid in the catalytic layer.

Acknowledgement

Funding from the European Commission under the project DEMMEA (Project Number 245156) and from the International Center for Frontier Research in Chemistry (Strasbourg) is gratefully acknowledged.

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