Analysing the influence of H$_3$PO$_4$ as a catalyst poison in High Temperature PEM Fuel Cells using XAS

S. Kaserer$^1$, A. Schoekel$^1$, B. Peter$^1$, D. Dixon$^1$, K. Caldwell$^2$, D. E. Ramaker$^2$ and C. Roth$^1$

$^1$Institute for Materials Science, Technische Universität Darmstadt, Petersenstr. 23, D-64287 Darmstadt, Germany.

$^2$Dept. of Chemistry, The George Washington University, Washington, D.C. 20052, USA.

Introduction

Compared to normal low temperature PEM and DMFC fuel cells with a working temperature of 90°C, it is predicted that high temperature PEM fuel cells (HT-PEMFCs) offer some benefits. At a working temperature of about 180°C the kinetics of the electrochemical processes are enhanced, water management and cooling is simplified and lower quality reformed hydrogen may be used as the fuel. Apart from these advantages of high temperature operation, there are still some challenges of operating HT-PEMFCs.

At temperatures above 100°C the established Nafion® membrane does not work and instead phosphoric acid (H$_3$PO$_4$) imbibed polymer electrolyte membranes ensure the proton conductivity. However, not only the harsher conditions of the acid environment are problematic for the fuel cell materials, it is also discussed whether the phosphoric acid and its derivatives effectively adsorb at the platinum surface and block electrochemical active surface. The adsorption behaviour of phosphoric acid at platinum surfaces was analysed before under laboratory conditions using infrared spectroscopy [1]. However, the electrochemical environment in a real operating fuel cell is quite different from that even in an electrochemical half-cell setup and this difference may have an influence on the catalyst behaviour. Therefore, realistic studies should be as close to in operando as possible. To accomplish such measurements a special full cell with a beam window was designed and manufactured by our group.

Experimental

A new cell hardware, which resists the higher temperature and the presence of phosphoric acid, was designed. For the flow fields, which are in immediate contact with the membrane electrode assembly (MEA), chemically stable graphite was used. These were mechanically stabilised by alumina plates holding the heating elements. For measuring XAS in transmission mode, stepped slits (smallest 13 x 3mm) were drilled into all parts of the fuel cell and covered with Kapton® foil. To ensure gas leak tightness at 180°C, high temperature resisting silicon was used as a glue to fix the foil.

The measurements with the HT-PEM assembly took place at the beam line X1 at HASYLAB at DESY in Hamburg. X-ray absorption spectra of the Pt L$_3$ edge were recorded in-situ during fuel cell operation. To analyse the potential dependent adsorption of phosphoric acid on the Pt catalyst, only the cathode of the fuel cell was investigated at different points of an i/V curve shown in figure 1. Simultaneously with the sample a Pt metal foil was measured and later used as reference for energy calibration and data alignment. The data were analysed using Athena [2].

To analyse the adsorbates on the catalyst surface, the delta µ XANES technique was chosen. By this technique, the difference between a reference without adsorbate coverage and the actual spectrum is taken. It was shown previously that the signature is characteristic for adsorbates such as CO, OH, O, and H [3]. To identify the specific signature of H$_3$PO$_4$ theoretical FEFF8 calculations were obtained and can be compared with the measured results. For identifying the dependence
between cell voltage and adsorbed species the $\Delta \mu$ values of the different signatures are plotted versus the cell voltage. As a result, a plot like figure 2 is obtained.

![Graph](image1.png)

**Figure 1:** XAS measurement points with respect to a normal i/V curve.

![Graph](image2.png)

**Figure 2:** Plot of the $|\Delta \mu|$ magnitudes vs. cell potential for the indicated adsorbate species (H, red dots; O(H), blue triangles; PO$_4^{3-}$, black squares) at 180°C.

### Results

Figure 2 shows the $|\Delta \mu|$ magnitudes of different adsorbates (H, H$_{(3-n)}$PO$_4^n$, OH) on Pt in the cathode vs. the fuel cell potential. The $\Delta \mu$ technique cannot distinguish between the different phosphate anions (i.e. different n in H$_{(3-n)}$PO$_4^n$), so they are referred to collectively as PO$_4^{3-}$. At low potentials (< 200 mV), adsorbed H is noticeable coming from H$_2$O activation and the strong acid environment at the cathode, and the PO$_4^{3-}$ coverage decreases with H coverage. A similar trend is observed at potentials above 800 mV where PO$_4^{3-}$ decreases with O(H) coverage. In the potential region immediately above the H and below the O(H) adsorption, significant PO$_4^{3-}$ coverage is evident, however, it appears to go through a minimum in the intermediate potential region (300-600 mV). This suggests that at 180°C, PO$_4^{3-}$ anions do not adsorb in an ordered arrangement or in registry with the Pt surface, making them invisible to the $\Delta \mu$ technique. As soon as the H or OH adsorbs, the PO$_4^{3-}$ anions are forced to adsorb in specific ordered sites and become visible in the $\Delta \mu$. A similar behaviour was observed previously for HSO$_4^-$ anions at room temperature in H$_2$SO$_4$ [4]. It should be noted that at RT, the PO$_4^{3-}$ anions do not behave like HSO$_4^-$, but remain visible at all potentials, revealing the effect of temperature on the anion adsorption. Also, the adsorbed PO$_4^{3-}$ significantly alters the onset of the O(H) adsorption, shifting it to higher potentials.

### References