

Analysing the catalyst degradation in High Temperature PEM Fuel Cells using XAS

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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 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. For example, at higher temperatures also the degradation of the engineering materials and the gas diffusion electrode is increased [1]. Especially for the behaviour of carbon supported platinum nanoparticles, which were used in fuel cell electrodes, XAS is one of the few methods which can be used during operation. By analysing the EXAFS spectra, important information about the particle geometry and oxidation level can be obtained.

Another difference between low and high temperature PEMFCs is the used membrane. At temperatures above 100°C the established Nafion® membrane does not work and instead phosphoric acid (H_3PO_4) imbibed polymer electrolyte membranes ensure the proton conductivity. But not only the harsher conditions of the acid environment are problematic for the fuel cell materials, it is also discussed if the phosphoric acid and its derivatives effectively adsorb at the platinum surface and thus hinder the electrocatalytic reaction. To prove this, the delta μ XANES technique is chosen. By this technique, the difference between a reference without adsorbate coverage and the actual spectrum is taken. It has been shown previously that the signature is characteristic for adsorbates such as CO, OH, O, and H [2]. And it is assumed that H_3PO_4 also has such a characteristic signal.

Experimental

Before testing high temperature membrane electrode assemblies (MEAs) at a XAS beamline, a new cell, which resists the higher temperature and the presence of phosphoric acid, was designed. For the flow fields, which are in immediate contact with the MEA, chemically stable graphite was used. These were mechanically stabilised by alumina plates holding the heating elements. The endplates, which were also used to fix the whole cell to the Teflon® base, were made of a high temperature resisting composite material. For measuring XAS in transmission mode, stepped slits (smallest 13 x 3mm) were drilled in 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 glue to fix the foil. An drawing of the cell is shown in Fig. 1.

The first measurements with the HT-PEM assembly took place at the beamline X1. X-ray absorption spectra of the Pt L₃ edge were recorded ex-situ and in-situ on the anode side during

fuel cell operation. The cell was operated at different temperatures up to 180°C with hydrogen on the anode and synthetic air on the cathode side. To distinguish the information from the two electrodes with their different environments, each sample has in the beam window region only the catalyst at one side of the membrane. 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 and Artemis [3].

Results

Preliminary measurements were carried out to see, if transmission spectra without any artefacts from the higher temperature, the silicon glue and the different environment were feasible. In Fig. 2 the XANES region of the first results is shown and no unusual behaviour could be observed.

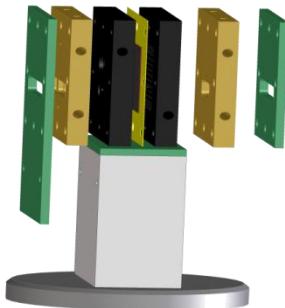


Figure 1: HT-PEM fuel cell (yellow: MEA, black: graphite flow field, gold: alumina plates, green: composite material, white: Teflon[®])

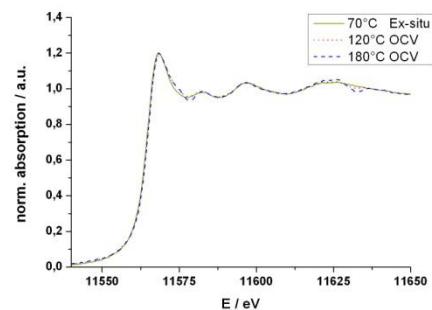


Figure 2: XANES region of the Pt L₃ edge at different temperatures and working conditions.

Analysing the EXAFS (Tab. 1) for the Pt L₃ edge shows, that with increasing sample temperature the Debye-Waller factor is also increasing. Due to the fact that the observed catalyst was used on the anode side of the fuel cell, the increase in the number of nearest Pt neighbours can be attributed to the reduction of the Pt nanoparticles, when hydrogen is present. A particle growth dependent change in N could be excluded because of the small time scale between the measurements.

Table 1: EXAFS results of HT-PEMFC anode catalyst at different temperatures.

	N _{Pt-Pt}	R _{Pt-Pt} [Å]	E ₀	σ ²
70°C Ex-situ	7,2	2,74	7,8	0,0050
120°C OCV	7,7	2,75	7,2	0,0058
180°C OCV	8,3	2,76	7,9	0,0061

Acknowledgment

The kind support of A. Webb and M. Herrmann at X1 is gratefully acknowledged.

References

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