Analysing the effect of CO and water (co-)adsorption at the anode of High Temperature PEM Fuel Cells

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Introduction

The high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) with phosphoric acid as electrolyte offers various benefits compared to low temperature fuel cells. One of the advantages of this kind of fuel cell is their enhanced tolerance against carbon monoxide (CO) poisoning. With working temperatures between 160°C - 200°C total amounts up to 1-3% CO in the anode fuel can be tolerated [1]. This advantage makes HT-PEMFCs perfectly suited for steam-reformed hydrogen from petroleum gas and other fossil or bio fuels. The combination of reformer and fuel cell next to each other solves the problem of hydrogen storage. Moreover, the waste heat of the fuel cell can be used further enhancing the overall performance of the system (combined heat and power systems) [2]. But, although the higher temperature reduces the poisoning effects of CO on the platinum catalyst, it still adsorbs on its surface and blocks free adsorption sites, thus reducing the fuel cell performance.

To clarify the CO coverage of the fuel cell anode, in-operando XAS measurements and the Δµ XANES analysis are the perfect tool. With this fingerprint method, it is possible to follow the CO adsorption in varying operation conditions like different voltages, current densities and humidification levels. With this information, it is possible to identify a minimum in poisoning and thereby enhance the fuel cell performance.

Experimental

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 L₃ edge were recorded in-situ during fuel cell operation. To analyse the potential/humidification level-dependent poisoning of CO, only the anode of the fuel cell was investigated. For these measurements a new fuel cell hardware, which is described in detail in [3], was manufactured. 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 the IFEFFIT code [4].

To analyse the adsorbates on the catalyst surface, the Δµ XANES technique was chosen. By this technique, the difference between a reference without adsorbate coverage (CO free) and the actual spectrum (CO adsorbed) is taken. The characteristic Δµ XANES signature of CO was calculated and measured before [5] and used as comparison to the measured data. For a correlation between cell voltage/humidification level and CO coverage, the Δµ values of the signatures were plotted versus the cell parameters. As a result, a plot like figure 2 was obtained.
Results

The $\Delta \mu$ XANES analyses with changing cell voltage showed that the $\Delta \mu$ magnitudes of the CO signature, which are directly related to the CO coverage of the surface, do not change with the applied cell voltage within the limits of the method. Both positive (at ~7eV) and negative (at ~0eV) $\Delta \mu$ magnitudes of the CO signature were almost constant over cell voltage (not shown).

By adding water (35 mg/min) to the anode feed the $\Delta \mu$ XANES magnitudes also do not change much with the cell voltages and the difference between the measurements without water in the anode gas was also very small. We found that if there is a constant CO coverage present on the surface, the change in fuel cell voltage has almost no effect on this coverage, either with or without anode humidification. This is quite remarkable, since CO electro-oxidation should be possible at these elevated temperatures.

The analyzed $\Delta \mu$ XANES magnitudes (fig. 1) over CO concentration and humidification are shown in figure 2. With only CO in the anode feed, the positive and negative CO signature amplitude starts to increase dramatically compared to the first measurement without CO. By adding more water to the anode feed (10 and 29 mg/min) the CO coverage (CO $\Delta \mu$ XANES magnitudes, respectively) decreased at both constant current densities. By stopping only the CO flow, the Pt surface was able to regenerate and get back to its original state. Consequently, the measured $\Delta \mu$ XANES magnitudes are almost as low as in the first measurements without CO.

This behavior is an indication that the presence of water in the anode feed has an important role on the HT-PEM fuel cell performance, when CO is present in the anode feed. Water can help to clean the anode catalyst from adsorbed CO molecules. By providing hydroxy groups from the water activation it is possible to electro-oxidize adsorbed CO at high fuel cell current densities.

References