Standard Project

Experimental Report template

Proposal title: In-situ Pd K-edge XAS study of the temperature and potential effect on hydrogen absorption in C-supported Pd catalysts		**Proposal number: 30-02-1094**
Beamline: FAME	**Date(s) of experiment:** from: 09.04.2015 to: 14.04.2015	**Date of report:** 10.08.2015
Shifts: 15	**Local contact(s):** Olivier Proux	*Date of submission:* *10.09.2015*

Objective & expected results (less than 10 lines):

The objective of the measurement was to study the absorption of hydrogen in the lattice of Pd nanoparticles, supported on Vulcan carbon, as a function of temperature and applied potential. For these experiments, we used an operating fuel cell and a small test station to supply the humidified reactant gases to the cell (H_2 at the anode and N_2 at the cathode electrode). The working electrode (Pd) was polarized at different potentials for 1h each, during which 2 consecutive EXAFS spectra were recorded, lasting 30min each, from which we determined the Pd-Pd nearest neighbour distance by fitting the EXAFS equation to the data. We expected to see a change of the absorption behaviour depending on potential and temperature, which could help us understand the poor activity of Pd in the hydrogen oxidation reaction. Finally, we extended these experiments to H_2 atmosphere (1 bar) on both electrodes, thus mimicking the conditions in a real fuel cell anode and investigated the hydriding behaviour at different potentials.

Results and the conclusions of the study (main part):

In the course of the beamtime, we were able to characterize 7 samples under different temperatures and gas atmospheric conditions. With this data, we first established pressure-composition isotherms by changing the applied electrode potential at different temperatures. Since the electrode potential is correlated with a partial pressure of hydrogen according to the Nernst equation, we were able to interpret the results also in terms of hydrogen pressure and compare it with data reported in the literature. As expected from our preliminary results, we observed the expected R_{Pd-Pd} of 2.74±0.01Å in the absence of the hydride phase, i.e. at a potential of 90mV (corresponding to a hydrogen pressure of 1mbar), which is in accordance with gas phase literature. With decreasing potential, we found first a slow linear increase of the H-Pd stoichiometry (corresponding to the formation of α Pd-H_x) as indicated by integration of the charge measured in the electrochemical experiment which did not lead to a significant chancge of the lattice parameter. However, at potentials negative of 50mV, we saw a steep increase in the lattice parameter due to an expansion of the Pd-Pd distance by about 3%, from 2.74±0.01Å to 2.83±0.01Å. This change is caused by the formation of β Pd-H_x. With increasing temperature, the transition plateau pressure of the α→β conversion shifts to more negative values due to destabilization of the hydride phase at higher temperatures. A thermodynamic analysis of this plateau pressure allows determination of the transition enthalpy and the value observed here is in good agreement with values reported in the literature. Finally, we extended these experiments to a configuration where hydrogen gas was present at a pressure of 1 bar on both electrodes, thus mimicking the operating conditions of a fuel cell anode. At the typical operating temperature of a PEMFC, 80°C, we observed the lattice parameter characteristic for Pd-hydride at all tested potentials leading to the conclusion that the hydriding behaviour is entirely controlled by gas phase hydrogen and the change of applied potential does not lead to significant changes. Lastly, we performed transient absorption measurements at different potentials to investigate kinetics of the hydriding process in Pd nanoparticles. Due to the excellent experimental support by the beamline scientist, Olivier Proux, we were able to record EXAFS data of very high quality which was important for the analysis.

Justification and comments about the use of beam time (5 lines max.):

Overall, we are more than grateful for being awarded so many measurement shifts which allowed us to perform many experiments which lead to a conclusive study. Without the help of synchrotron radiation, in-situ measurements on an operating fuel cell are not possible because a high intensity and high energy beam is needed to penetrate the cell. Ultimately, this beamtime was very successful and we are preparing 2 manuscripts at the moment.

Publication(s):

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