



	<b>Experiment title:</b> <b>Pt-contained nanosized electrocatalysts for fuel cells application</b>	<b>Experiment number:</b> 01-01-704
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## Report:

A new generation of polymer electrolyte fuel cells, operating at elevated temperatures, are very promising energy conversion systems for future clean energy plants. Such systems utilize polymeric membranes (e.g. polybenzimidazole, PBI), which in comparison with perfluorosulphonic acid ones (e.g. Nafion), can be operated at temperatures up to 200 °C. An increased operating temperature significantly increases the catalysts' tolerance towards contaminations in the fuel cell feed, especially CO [1], thus reducing the extensive and expensive pre-treatment of the fuel as required in low-temperature PEM fuel cells.

Unfortunately, stability of the catalyst and especially the catalyst support are not sufficient in such severe working conditions. The catalyst deactivates both by surface poisoning and by cluster reorganization. Another problem is partial oxidation of the carbon support. This leads to changes in the interaction between the active catalytic element and the support. In addition, products of the support oxidation process can affect the electrochemical behavior of the catalyst. The use of carbon nanotubes and nanofibres which are chemically and thermal more stable than activated carbon, improves the catalyst life-time and also gives better open circuit cell voltage.

Electrocatalysts prepared by the polyol method containing platinum supported on carbon are nanocrystalline or amorphous, with crystal sizes of a few nanometers [2]. X-ray diffraction investigations show phase changes and crystal growth after heat treatment, with the formation of solid solutions with different lattice parameters. However, the clusters are formed before the annealing stage, and the final composition and electrochemical behavior are strongly dependent on the preparation conditions.

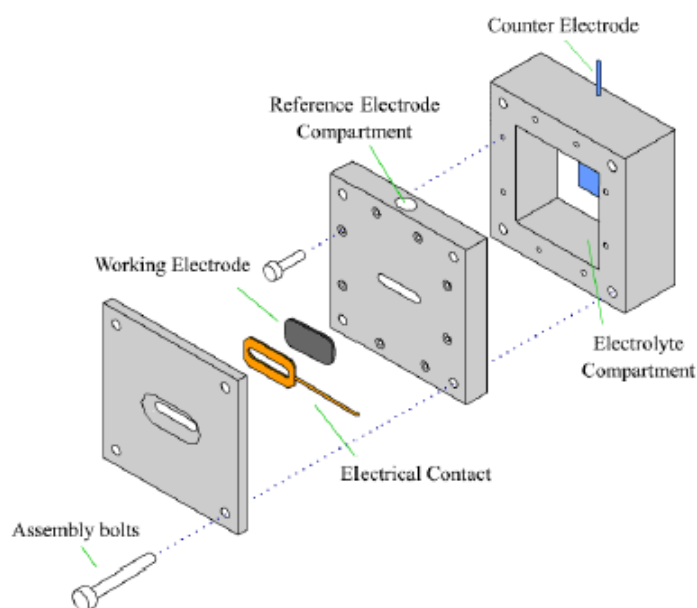
The powder samples were prepared in sealed sample holders and optimized for transmission EXAFS measurements. These powder samples consisted of Pt/C catalysts that had been heat treated in different atmospheres at several temperatures.

The colloid samples were synthesized in a reflux (polyol cell) reactor in the chemical lab at ESRF. The cell consists of a 3 neck bottle with reflux cooler. The reaction mixture was saturated with argon. Aliquots of the colloid (less than 0.5 ml) was removed from the bottle, cooled down and placed in the beam. The sample holder was a cuvette with Kapton windows (See photo of colloid cell).



**Figure1:** Picture of the cell used for measurements on Pt colloids.

To study electrocatalyst samples in-situ during electrochemical polarization, an in-situ Electrochemical /XAS cell developed for experiment 01-01-670 was used (Figure 2). In this cell the catalyst samples were coated (around  $0.5 \text{ mg/cm}^2$ ) onto graphite foil which acted as the electrical contact, catalyst support and X-ray window. This catalyst-graphite composite was then used as the working electrode for a series of electrochemical / XAS measurements. This was achieved by placing the catalytic layer in contact with an aqueous  $0.5 \text{ M H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  electrolyte, parallel to a platinum counter electrode which completed the electrical circuit. A reversible hydrogen electrode (RHE) was also placed in the electrolyte, with the potential of the working electrode measured and controlled relative to this reference potential, using a Zahner im6e potentiostat. The XAS measurements were made by aligning the incoming x-ray beam to centre of the working electrode. The resulting fluorescence signal was then recorded.



## Figure 2: in-situ Electrochemical /XAS cell

To study the Electrocatalysts in-situ during fuel cell operation, a fuel cell with PBI (saturated by phosphoric acid) membrane was used. The cell is a commercial fuel cell (EFC25-02SP) manufactured by **Electrochem Inc.** (<http://www.fuelcell.com/>). To obtain signal intensity from the catalytic layer, the fuel cell was modified by thinning the wall of the carbon housing. This cell design was adopted from experiments reported by the group of Andrea Russell at The University of Southampton [3]. The fuel cell experiments were conducted at 170°C using a MEA (Membrane Electrode Assembly) consisting of a catalytic layer of Pt catalyst on the working electrode and a Pd catalyst on the counter electrode. The electrodes were separated by a PBI membrane. The electrodes were supplied with 5% H<sub>2</sub> in He or pure O<sub>2</sub> (total flow rate 20 ml/min). The cell was heated with a resistant heating element and a type K thermocouple.

The EXAFS measurements were performed at the Pt L<sub>3</sub>-edge (11564 eV).

Kinetics of the colloidal precursor was investigated as well as behavior of the prepared electrocatalyst at different potentials. The fuel cell shows higher absorption, so some modification of the cell design is required. Data analysis is still on going.

### References

1. Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J., Fuel Cells 4(3) (2004) 147-159
2. Bonet, F.; Delmas, V.; Grugeon, S.; Urbina, R. Herrera; Silvert, P-Y.; Tekaiia-Elhsissen, K. Nanostructured Materials (2000), Volume Date 1999, 11(8), 1277-1284
3. Russell, Andrea E.; Rose, Abigail. Chemical Reviews (Washington, DC, United States) (2004), 104(10), 4613-4635