

## Experiment Report Form

**Experiment title:**
**In situ XAS study of Carbon-supported core-shell  
electrocatalysts for oxidation of small organic molecules**
**Experiment  
number:**

01-01-777

<b>Beamline:</b> BM1B	<b>Date of experiment:</b> from: 29.11.2008                      to: 04.11.2008	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Hermann Emerich	<i>Received at ESRF:</i>

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### Report:

Catalytic and electrocatalytic processes are critical to many advanced energy conversion systems such as fuel cells, water-gas shift processes, PROX catalysts and NO<sub>x</sub> reduction. However, system level costs and/or performance criteria of the precious-metal based catalysts often limit the economic viability of these advanced energy conversion systems.

In catalysis and electrocatalysis core-shell bimetallic nanoparticles have gained much attention due their structure. The enhanced activity is related to the underlying interface between the core and shell metals in a bimetallic mechanism. Another advantage of this structure is that only surface atoms are active from the viewpoint of catalysis.

Bimetallic PtRu alloys offer a good efficiency and the best stability for oxidation of small organic molecules. Pt@Ru core-shell catalysts show a complete CO oxidation and hydrogen light-off below 30°C.

Bimetallic core-shell Pt-Ru/C, Pt-Au/C and Ru-Pt/C were synthesised at NTNU as well as mono-elemental standards and conventional bimetallic alloys. The particle size is in the range 2 - 4 nm and is not detected in conventional XRD. The prepared powders were tested ex situ (in dry state, diluted by carbon) and in situ in a electrochemical cell (see Figure 1).

For in situ experiment the powders were sprayed onto a carbon foil using a Nafion solution as binder. The foil was connected to a Gamry PCI4 potentiostat as the working electrode. Palladium mesh serves as the counter electrode. An Ag/AgCl reference electrode (or HYDROFLEX hydrogen electrode) in a Luggin capillary was used as a reference.

The electrodes were originally cycled in 0.5M sulphuric acid following addition of methanol (1M). After recording of cyclic voltammetry, steady state polarisation measurements were conducted. XAS measurements at 3 fixed potentials (before MeOH oxidation peak, at the peak maximum and after MeOH oxidation) were recorded at the Pt and Au L3 edges or at the Ru K edge.

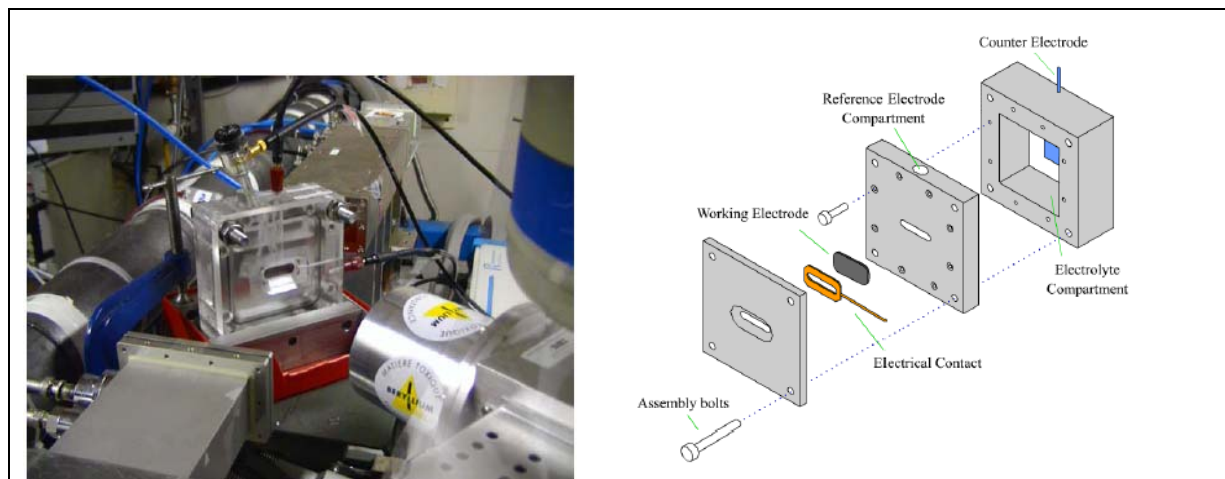


Figure 1. Photo and scheme of the in situ spectro-electrochemical cell

Polarisation measurements clearly indicate a principal difference in behavior of core-shell Pt and Ru depending on which element is creating a core and which element constitutes the shell.

The sample with Ru in the shell shows the highest activity in the electrochemical oxidation of methanol. Also, activity is higher in the case of thinner Pt shell on Ru.

Typical electrochemical results are presented in Figures 2 and 3.

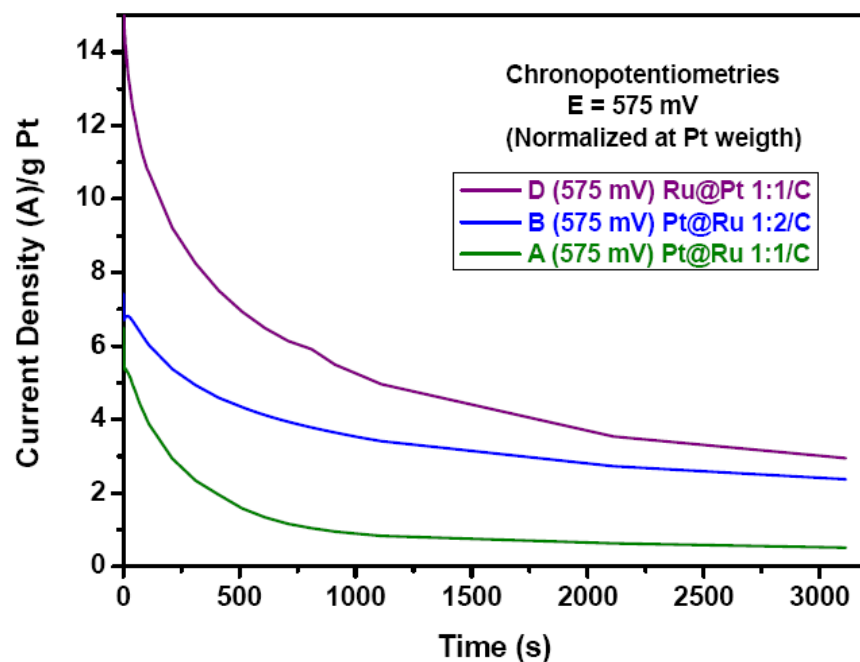


Figure 2. Chronoamperometrical curves for core-shell electrocatalysts

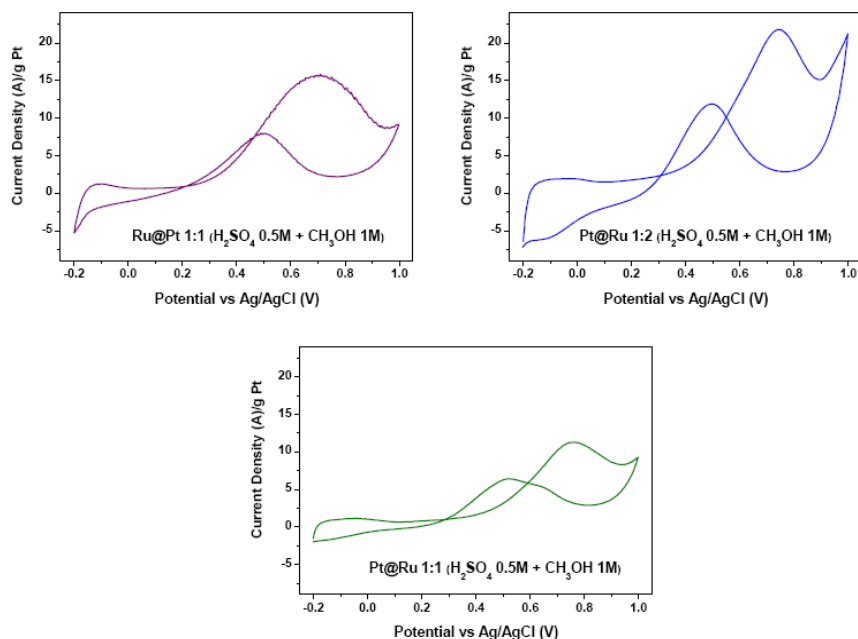


Figure 3. Cyclic voltammetry for the core shell electrocatalysts.

Data obtained from the XAS measurements show a difference between the samples with Pt in the core and in the shell, respectively. In figure 4 the radial distribution curve for the sample with Pt shell is shown. A change was observed in the sample with Pt shell during solvation. No similar effect was detected for the sample having Pt in the core. Detailed data analysis should be able to identify this difference in behaviour.

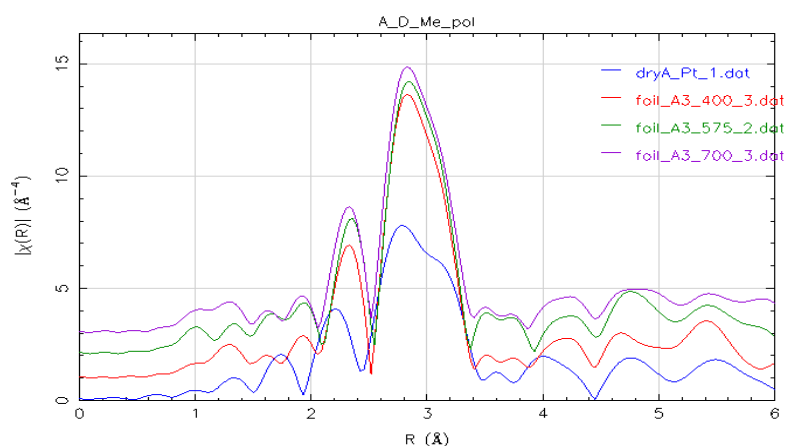


Figure 4. EXAFS FT Radial distribution function for sample Pt@Ru.