

	<b>Experiment title:</b> In situ time resolved EDE studies of hydrogen absorption by Pd electrocatalysts	<b>Experiment number:</b> CH-1064
<b>Beamline:</b> ID-24	<b>Date of experiment:</b> from: 27/6/2001      to: 1/7/2001	<b>Date of report:</b> 25/2/2002 <i>Received at ESRF:</i>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Sofia Diaz-Moreno	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Andrea E. Russell*, Abigail Rose*, Oliver South* Department of Chemistry, University of Southampton Highfield, Southampton, SO17 1BJ, UK Ian Harvey* CCLRC Daresbury Laboratory, Warrington, WA4 4AD, UK		

## Report:

Carbon supported Pd electrocatalysts and Pd electrode materials have become of more interest recently as hydrogen storage materials and oxidation catalysts in fuel cells, specifically low temperature PEM and alkaline fuel cells [1, 2]. As a hydrogen storage media, Pd is interesting in that hydrogen is not restricted to the surface or near surface of the metal particles. It may be absorbed, occupying the interstices of the metal lattice. A Pt/Pd catalyst has recently been shown to have increased stability over the more traditional Raney Ni materials for alkaline fuel cells [3].

In the work described in this report, Energy Dispersive EXAFS (EDE) at the Pd K edge was used to investigate the adsorption and absorption of hydrogen (H or D) on/by carbon supported Pd electrocatalyst materials. This system is an ideal test case for in situ EDE of electrocatalyst materials, as it is the Pd-Pd distance that changes significantly upon hydrogen adsorption rather than a change in coordination number.

Poly-tetrafluoroethylene bound electrodes were prepared from 40 wt% Pd/C (XC72), supplied by ETEK, spread on to carbon paper. The electrodes were mounted in a custom designed electrochemical cell for the EDE measurements [4] with a Pt gauze counter electrode and a Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode. All potentials have been corrected to the RHE scale for clarity. The electrolyte was either 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> prepared using 18 MΩ cm H<sub>2</sub>O or 1 mol<sup>-1</sup> D<sub>2</sub>SO<sub>4</sub> prepared using D<sub>2</sub>O (Aldrich). An analogue potentiostat (Bank Electronics) and waveform generator (HiTek) were used to apply the potential steps to the electrodes. The EDE data was recorded as a function of time following the potential step with a time resolution of 0.25 s.

The quality of the EDE data obtained is demonstrated in Figure 1(a). The data was useful out to  $k = 13.5 \text{ \AA}^{-1}$ . The data were fitted using one Pd-Pd distance and representative results in both  $k$  and  $r$  space are shown in Figure 1.

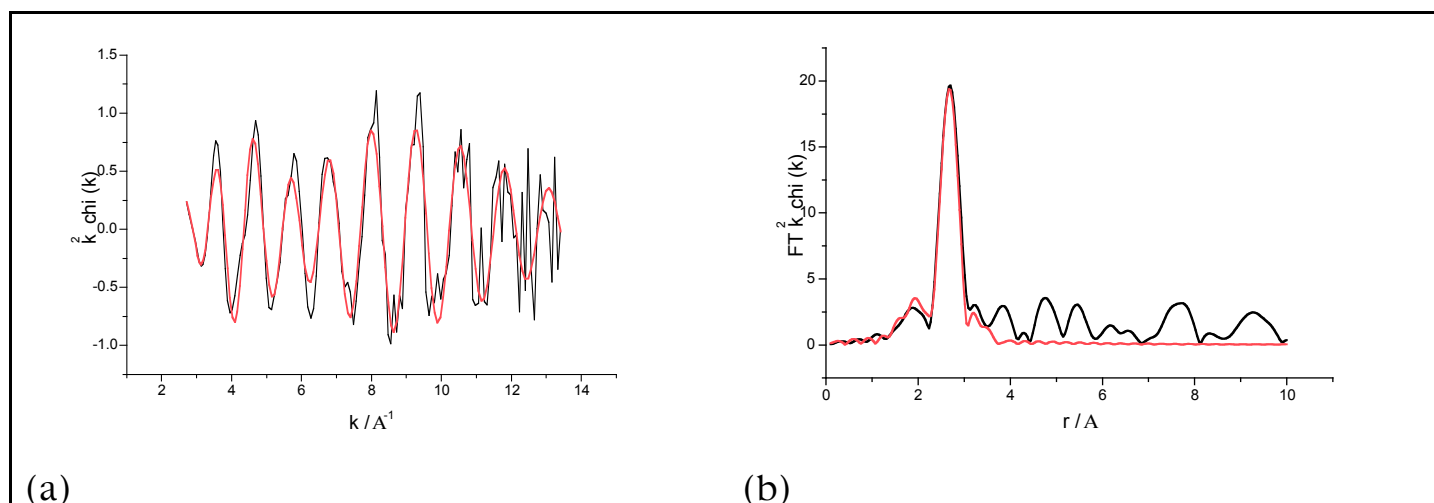


Figure 1. (a)  $k^2$  weighted experimental data (black line) and fit (red line) b) Fourier Transform plot (black line) and fit (red line) for step from 0.654 to -0.096 V vs. RHE. Scan at 23 s after step.

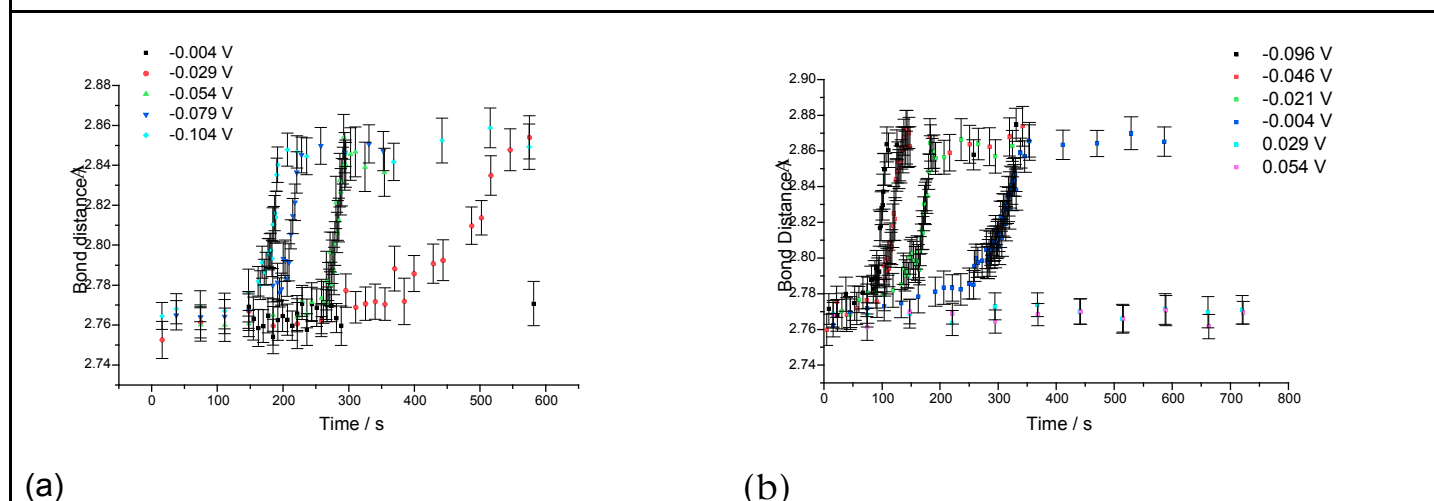


Figure 2. Plots of bond distance as a function of time following potential step from 0.654 V vs. RHE in (a) 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and (b) 1 mol dm<sup>-3</sup> D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O.

The lattice expansion on absorption of hydrogen, formation of the hydride phase, as a function of the step potential is shown in figure 2. The 3.9% lattice expansion in H<sub>2</sub>O corresponds to the formation of the  $\beta$ -hydride [5]. A slightly smaller expansion is observed in D<sub>2</sub>O, reflecting the smaller amount of deuterium absorbed by the Pd particles. The current transients collected at the same time as the EDE

data may be interpreted in terms of a moving boundary layer model [6]. Integration to obtain the charge shows that the total charge passed at the inflection point of the lattice expansion plots is constant. Together with the EDE data, the results suggest that the lattice expansion is a diffusion controlled process limited by the local concentration of the H or D species at the surface of the metal particle.

Data was also collected for a 20 wt% Pd/C catalyst (not shown), which has a smaller particle size than the 40 wt% catalyst. Analysis of these data is in progress. A detailed kinetic model of the formation of the  $\beta$ -hydride phase will then be developed. Future work will investigate the effects of the adsorption of surface poisons which alter the H adsorption : H<sub>2</sub> evolution branching ratio on the rate of the lattice expansion.

1. P.L. Cabot, E. Guezala, M.T. Garcia, J. Casado, *J. Electrochem. Soc.*, **147** (2000) 43.
2. T.F. Otero, M.T. Bireben, *Proc. 2<sup>nd</sup> Int. Fuel Cell Symp., Montreal*, (1997) 894.
3. Y. Kiron, S. Schwartz, *J. Power Sources*, **87** (2000) 101.
4. S. Maniguet, R.J. Mathew, A.E. Russell, *J. Phys. Chem. B*, **104** (2000) 1998.
5. J.A. McCaulley, *J. Phys. Chem.*, **97** (1993) 10372.
6. P. Millet, M. Srouf, R. Faure, R. Durand, *Electrochem. Com.*, **3** (2001) 478.