



	<b>Experiment title:</b> Hydrogen Absorption in Pd Nanoparticles in a Polymer Electrolyte Fuel Cell	<b>Experiment number:</b> CH6230
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 31.03.2022 to: 03.04.2022	<b>Date of report:</b> 24.01.2023
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## Report:

X-Ray measurements were carried out using a 5 cm<sup>2</sup> fuel cell along with its test station, allowing the control of the temperatures, voltage, gas pressures, gas flow rates and humidity level. The cell was operated in proton pump mode, i.e. H<sub>2</sub> is fed at the anode while the cathode is constantly flushed with N<sub>2</sub>.

### 1. Coexistence of the $\alpha$ -PdH and $\beta$ -PdH phases

Measurements have permitted to experimentally confirm the stable coexistence of the  $\alpha$ -PdH and  $\beta$ -PdH phases in a limited voltage range (around 0.05 V at 30 °C). Fig. 1 (a) shows without ambiguity that the Pd (220) peak is constituted of two major contributions, centred at 6.68 ° and 6.50 °, corresponding to  $\alpha$ -PdH and  $\beta$ -PdH respectively. Thanks to the high time resolution brought by the extremely brilliant source of X-rays, the transition from one phase to another was followed outside of the coexistence window, i.e. from 0 V to -0.4 V. Again, a short period of coexistence of the two phases was determined without ambiguity, whose duration lasts from about 1 s at 0 V to only 150 ms at -0.4 V (cf. fig 1 (b)).

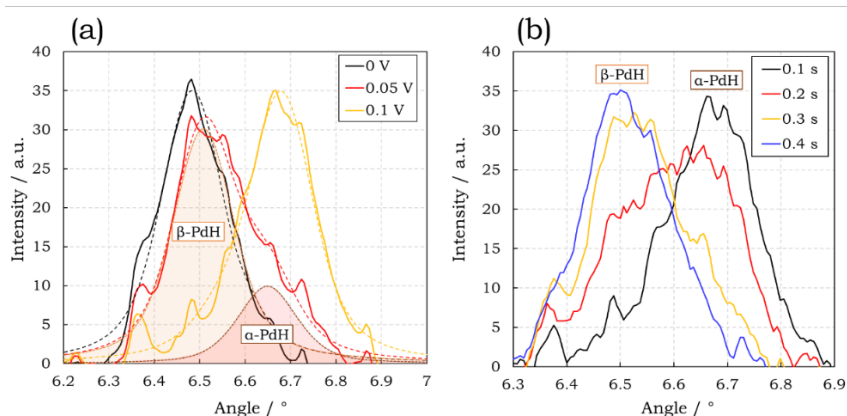


Figure 1: Shift of the Pd (220) peak with the cell voltage after 60 s of loading (a) and with the loading duration at -0.1 V (b). Plain lines correspond to the experimental data, dashed lines correspond to the fits. The coloured areas represent an example of the contributions from the coexisting  $\alpha$ -PdH and  $\beta$ -PdH phases. H<sub>2</sub>/N<sub>2</sub> 100 mL.min<sup>-1</sup>, RH 100%.

### 2. Influence of the cell voltage, temperature and the loading duration on the hydrogen absorption

The temperature of the cell has been shown to have a significant impact on the H absorption in Pd. With the increase in temperature, from 30 °C to 60 °C, three main aspects were noticed (fig. 2 (a)): (i) a decrease of the

maximum number of H absorbed, i.e. H/Pd decreases from 0.58 to 0.52; (ii) a larger proportion of H dissolve in the  $\alpha$ -PdH; and (iii) a shift of the  $\alpha$ -PdH to  $\beta$ -PdH phase transition towards lower cell voltages, from approx. 0 V to -0.1 V. All these results are in accordance with the literature. Some perturbations in the catalyst response started to appear around 60 °C due to cell flooding.

The expansion of the Pd lattice parameter and the PdH<sub>x</sub> composition was followed *in operando* during the insertion of H under constant potential (fig. 2 (c-e)). The time interval between two successive data points is 100 ms above -0.2 V and 20 ms at -0.2 V and below. As the voltage is quickly changed from +0.4 V (metallic Pd) to the value of interest, i.e. between 0.05 – -0.5 V, the Pd lattice parameter expands until reaching a maximum, whose value depends on the applied voltage. With a decrease in voltage, the expansion of the Pd lattice gets faster, from approx. 4 s at 0 V to 0.2 s at -0.5 V (30 °C). Also, after reaching a stable state, long loading durations do not enhance further the H absorption, the limit is only set by the applied cell voltage. This last result is of particular interest for further applications of PdH systems.

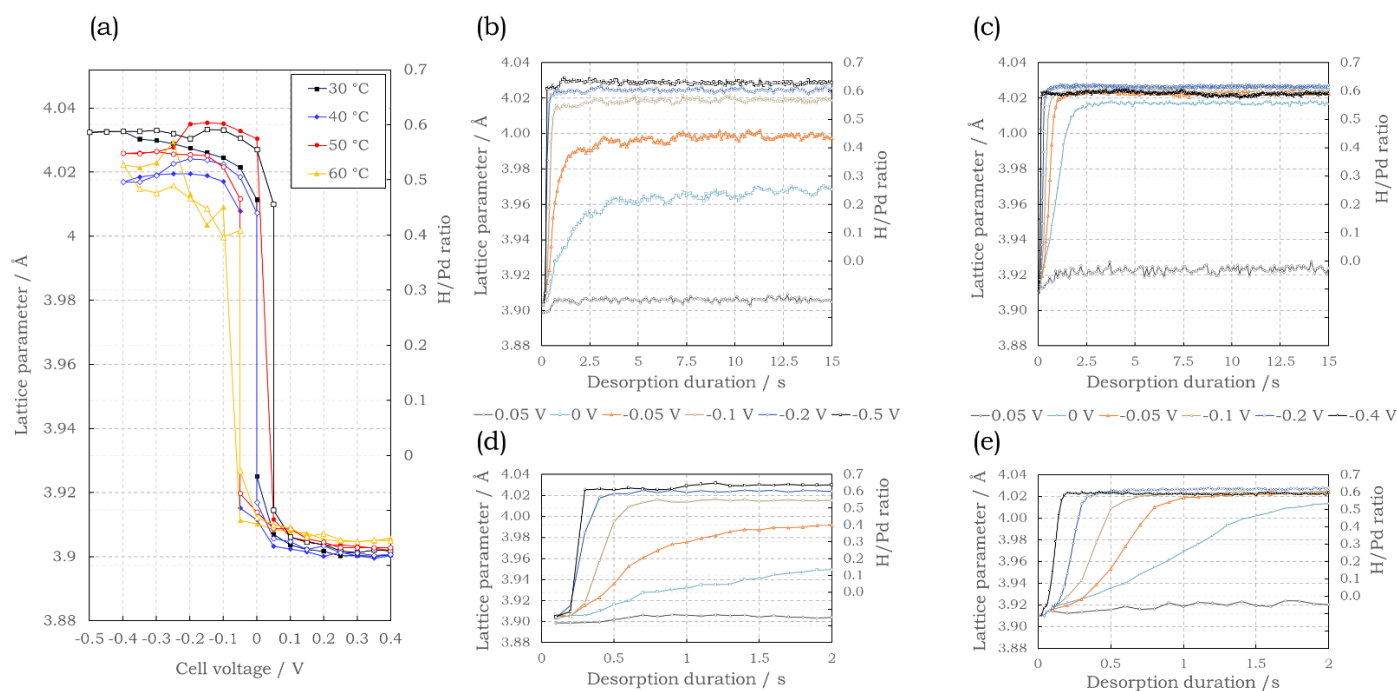


Figure 2: PdH<sub>x</sub> lattice parameter and composition as a function of the loading duration at temperatures ranging from 30 – 60 °C (a), and at constant cell voltage in the range 0.05 – -0.5 V, at 30 °C (b) and 40 °C (c). Graphs (d) and (e) are close-ups of graphs (b) and (c) respectively. H<sub>2</sub>/N<sub>2</sub> 100 mL.min<sup>-1</sup>, RH 100%.

### 3. Investigating the Pd particle size and the isotope effect

Investigations were carried out on two Pd nanoparticle sizes,  $3.8 \pm 0.6$  nm (Premetek, 20 wt-% Pd on Vulcan XC-72) and  $6.9 \pm 2.2$  nm (laboratory-made). Both samples behave in very similar manners, but a few aspects were noted, nonetheless. The commercial sample was able to dissolve a larger number of H in the  $\alpha$ -PdH phase, as expected in the literature. The transition from the  $\alpha$ -PdH to the  $\beta$ -PdH phase shifted towards lower cell voltages for the laboratory-made sample, which might be due to an opening of the hysteresis between the insertion and desinsertion of H, or the presence of surfactant on the Pd nanoparticles.

Additionally, our study emphasized on investigating the isotope effect, i.e. the change in behaviour brought by using two different isotopes (H<sub>2</sub> and D<sub>2</sub>). The X-ray signals observed with D<sub>2</sub> were in general very low, making difficult an in-depth analysis of this parameter. However, we were still able to extract some general trends. First, the maximum number of D atoms inserted in Pd is lower than the one of H atoms, i.e. 0.53 vs 0.58. This might be linked to the larger atomic diameter of D compared to H. A very pronounced shift of the  $\alpha$ -PdH to  $\beta$ -PdH transition towards lower cell voltages was observed with D<sub>2</sub>, indicating that more energy is required to introduce D into the Pd lattice.