



	<b>Experiment title:</b> <b>Short range order in PdCuAu membranes under hydrogen</b>	<b>Experiment number:</b> MA-2532
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 22/04/2015 to: 28/04/2015	<b>Date of report:</b> 11/04/2018
<b>Shifts:</b> 18	<b>Local contact(s):</b> Eduardo Salas-Colera	<i>Received at ESRF:</i>
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## Introduction

Pd membranes are an interesting option for H<sub>2</sub> purification in decentralized hydrogen production schemes where economics preclude the application of industrial technologies such as pressure swing adsorption [1]. However, Pd membranes can embrittle and fail rapidly at low temperatures because of a wide miscibility gap in the Pd-H phase diagram below 300 °C and H<sub>2</sub> pressures up to 20 bar [2]. The reason is the large lattice parameter discrepancy of the associated hydrogen-poor  $\alpha$  and hydrogen-rich  $\beta$  boundary hydride phases (3.895 Å and 4.025 Å, respectively, at room temperature) [3]. The width of the hydride phase miscibility gap can be significantly reduced and suppressed towards lower temperatures by alloying Pd with Cu and Au [3]. The resulting ternary PdCuAu alloys are promising new membrane materials for H<sub>2</sub> production from coal and biomass because Cu and Au also endow Pd with some sulphur tolerance [2].

Local ordering is another important aspect of these alloys because it affects hydrogen binding energies in interstitial lattice sites and thus hydrogen transport rates [4]. However, little is known about the local structure, whether element clustering occurs, or whether hydrogen induces such changes in multicomponent Pd alloys. An earlier study on PdAg membranes has shown that XAFS measurements are a sensitive tool for investigating such features [5]. The XANES region provided also insight into electronic features like filling of the anti-bonding Pd 4d-H 1s band [6]. Therefore we studied the local geometric and electronic structure via PdCuAu alloys via *in situ* XAFS at a typical membrane operation temperature (i.e. 350 °C) both with and without hydrogen present.

## Experimental

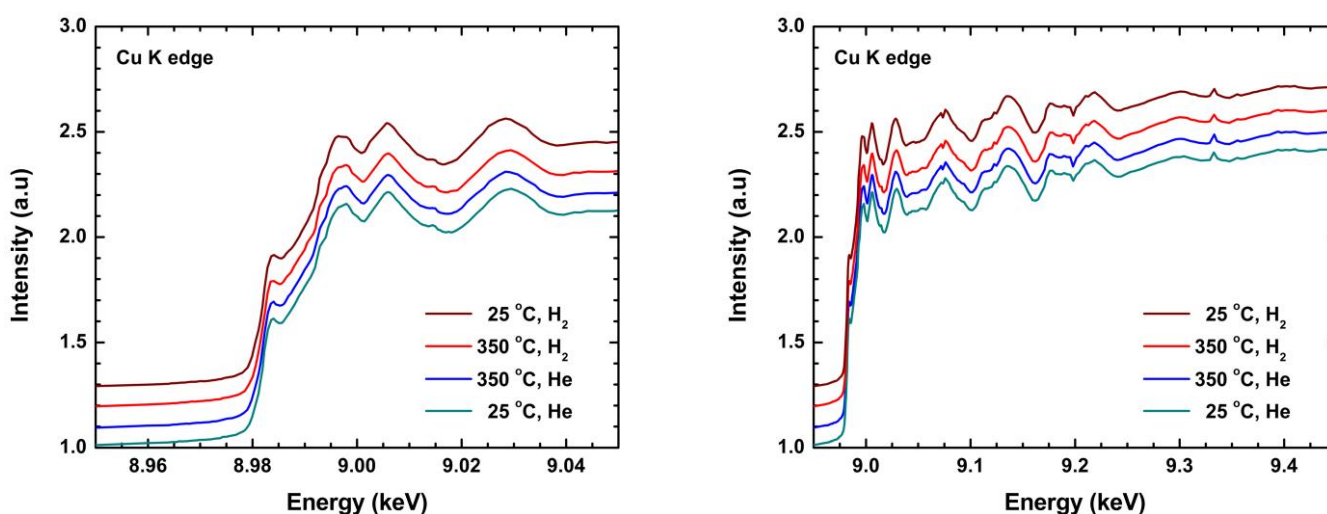
Three PdCuAu alloy films (PCA5 = Pd<sub>87</sub>Cu<sub>7</sub>Au<sub>6</sub>, PCA10 = Pd<sub>76</sub>Cu<sub>16</sub>Au<sub>8</sub>, PCA11 = Pd<sub>76</sub>Cu<sub>7</sub>Au<sub>17</sub>, all compositions in at.%) as well as a PdAu (PA2 = Pd<sub>93</sub>Au<sub>7</sub>) and a PdCu (PC2 = Pd<sub>78</sub>Cu<sub>22</sub>) alloy film were

studied at the X-ray absorption spectroscopy branch of the Spanish CRG beamline BM25 (SpLine). The alloy films were prepared via electroless plating on tubular ceramic substrates. The metals were deposited separately and subsequently alloyed through annealing under  $N_2$  at 873 K [7,8]. All five alloys exhibited face-centered cubic (fcc) structures just as pure Pd [2]. The obtained PdCuAu alloy films with thickness around 3  $\mu\text{m}$  were detached from the ceramic substrates, and ca.  $10 \times 1 \text{ mm}^2$  strips were inserted into 2 mm wide quartz capillaries for *in situ* XRD measurements under  $H_2$ .

X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements have been carried out at the Cu K (8981 eV), the Au  $L_{III}$  (11921 eV) and the Pd K (24351 eV) edges in transmission mode using a Si(111) double crystal monochromator. Two ionization chambers were used to measure the intensities of the incident and transmitted X-ray beam, and a third ionization chamber was used for energy calibration using a Cu, Au or Pd foil as standard, respectively. Four measurements were carried out with each sample in the following sequence: under He at (1) room temperature and (2) 350 °C and under  $H_2$  at (3) 350 °C and (4) room temperature, all at atmospheric pressure. The capillaries with the samples were heated with a gas blower (FMB Oxford) at a heating rate of 5 °C  $\text{min}^{-1}$ .

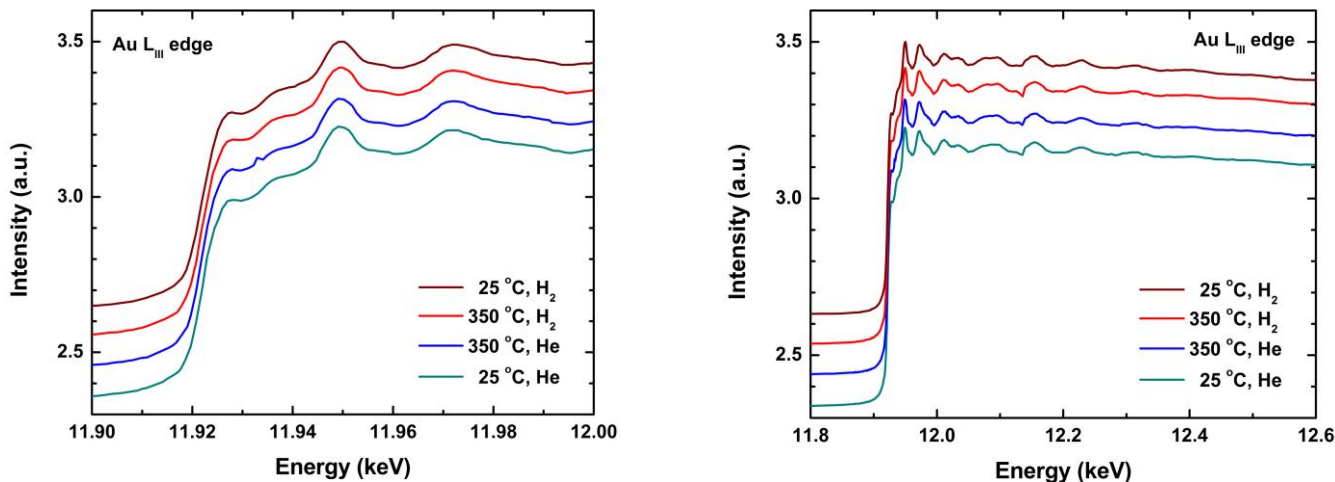
## Results and Discussion

Figures 1-3 show the XANES and EXAFS regions of the PCA10 alloy X-ray absorption spectra (XAS) at the Cu K, Au  $L_{III}$  and Pd K edges, respectively. Surprisingly, the XAS spectra did not change upon switching from He to  $H_2$  atmosphere nor when raising the temperature from room temperature to 350 °C. The same lack of sensitivity to temperature and gas atmosphere was observed for the XAS spectra of the other investigated binary and ternary Pd alloys. At first glance, this would suggest that the incorporation of hydrogen into the alloy lattices has a marginal effect on the metal-metal interaction and does not lead to changes in the local structure of these alloys at the employed  $H_2$  pressure and the time scale of our measurements.



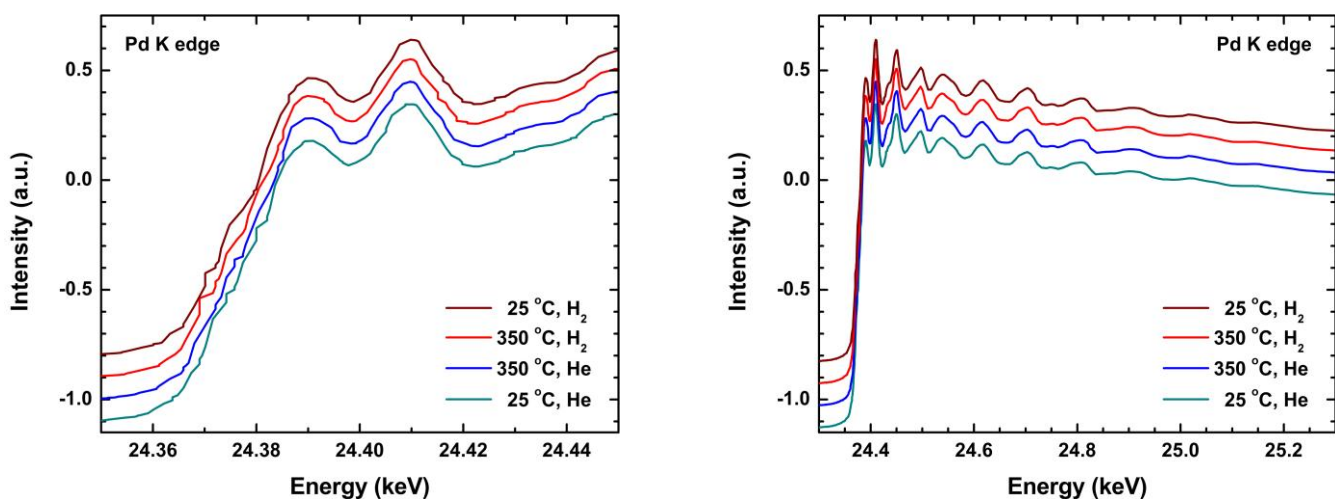
**Figure 1.** Copper K edge XANES (left) and EXAFS (right) spectra of alloy PCA10 recorded under He and  $H_2$  at atmospheric pressure at room temperature and 350 °C. The spectra are offset for clarity of display.

The PCA10 and PCA5 alloys have been also investigated by *in situ* XRD measurement under  $H_2$  at the X-ray diffraction branch of ESRF beamline BM25 SpLine [7-9]. The fcc structures were retained upon  $H_2$  exposure at pressures up to 1.3 bar but the XRD reflections shifted to lower angles because the alloy lattices expanded due to hydrogen incorporation. Indeed, at low temperatures a hydrogen-poor and a hydrogen-rich  $\beta$  hydride phase formed due to the persistence of the abovementioned miscibility gap in the Pd-Cu-Au-H phase diagram at the investigated ternary alloy compositions. Albeit, those miscibility gaps were significantly smaller in those alloys than in the Pd-H system, as expected [7]. Nevertheless, those XRD experiments confirmed that the ternary PdCuAu alloys studied here incorporate significant amounts of hydrogen into their lattices under the experimental conditions of the XAS measurements described at present.



**Figure 2.** Gold  $L_{III}$  edge XANES (left) and EXAFS (right) spectra of alloy PCA10 recorded under He and  $H_2$  at atmospheric pressure at room temperature and 350 °C. The spectra are offset for clarity of display.

Moreover, it is interesting to note that those *in situ* XRD experiments under  $H_2$  revealed a peculiar inhomogeneity of the PCA10 alloy [7,9]. Unexpectedly two  $\beta$  hydride reflections appeared upon exposure to 1.3 bar  $H_2$  despite that the XRD reflections of this alloy were rather narrow and symmetric in the absence of  $H_2$ . This indicated that this material consisted of a mixture of two stoichiometrically distinct alloys with practically matching lattice constants but disparate hydrogen solubility. Indeed, Pd, Cu and Au can form ternary alloys with differing composition but identical lattice dimensions because Cu addition leads to contraction while Au addition results in expansion of the Pd lattice. Thus, a series of ternary alloys with decreasing Pd content can be formed that have identical lattice parameters through careful balance of the Cu and Au content [10]. However, hydrogen solubility decreases substantially in these alloys with decreasing Pd content [10] so that the apparent lattice equality is lifted upon incorporation of hydrogen. Hence, the PCA10 membrane alloy does include the type of fluctuations in local atomic ordering that was hypothesized at the outset of this XAS experiment. Moreover, hydrogen uptake by the alloy lattice should facilitate the detection of such short range order variations.



**Figure 3.** Palladium K edge XANES (left) and EXAFS (right) spectra of alloy PCA10 recorded under He and  $H_2$  at atmospheric pressure at room temperature and 350 °C. The spectra are offset for clarity of display.

An earlier EXAFS analysis of the Pd K edge XAS spectrum showed that the Pd-Pd distance in Pd increased from 2.74 Å to 2.86 Å upon  $H_2$  exposure at an unspecified pressure in good agreement with the reported lattice constant of the hydrogen-rich  $\beta$  boundary hydride phase at room temperature [4]. Analogous EXAFS analyses of Pd and Ag K edge XAS spectra from a PdAg membrane alloy showed that the Pd-X (X = Pd, Ag) distance increased from 2.77 Å to 2.85 Å upon  $H_2$  exposure due to hydrogen incorporation into the alloy

while the Ag-X distance was only weakly enlarged from 2.81 Å to 2.83 Å [4]. This large difference between the average Pd-X and Ag-X distances was interpreted as an indication of inhomogeneity with either Ag atoms being present in small clusters or the existence of Pd/Ag clusters with varying Ag contents [4]. Thus it should be feasible to examine short range order variations in the binary and ternary Pd alloys investigated here in the same manner.

On the other hand, the hydrogen solubility in Pd alloys decreases rapidly with increasing Cu amount and in general also with increasing temperature [2]. In addition, in case of pure Pd the lattice constant of the hydrogen-rich boundary hydride phase is 0.130 Å larger than that of hydrogen-free Pd at room temperature while that difference amounted only to 0.045-0.055 Å for the PCA10 alloy [7]. Accordingly, the XAS spectra of the ternary PdCuAu alloys will be less sensitive to the incorporation of hydrogen than pure Pd and PdAg alloys, and the effects of hydrogen may be even more difficult to discern at higher temperatures.

Finally, the Pd L<sub>III</sub> XANES regions may be better suited for analyzing the impact of incorporated hydrogen on the electronic structure of Pd alloys. In case of Pd and a PdAg membrane alloy, a new feature appeared in the Pd L<sub>III</sub> XANES spectrum that was attributed to the unfilled anti-bonding Pd 4d-H 1s orbital [5]. Theoretical calculations showed that this XANES feature is very sensitive to the hydrogen content of the Pd alloy. Silver had only little influence on this new XANES feature while the Pd L<sub>III</sub> white-line intensity ought to vary significantly with Ag distribution within the alloy according to the modelling results [5].

## Conclusion

Three PdCuAu membrane alloys have been examined by X-ray absorption spectroscopy under He and H<sub>2</sub> at room temperature and 300 °C. Neither temperature nor atmosphere appeared to have a significant impact on the XANES and EXAFS spectra recorded at the Cu K, Au L<sub>III</sub> and Pd K edges of these alloys. Separate *in situ* XRD experiments under H<sub>2</sub> have shown that hydrogen is incorporated into these ternary alloys under the employed experimental conditions [7]. Those XRD experiments also revealed that some of these alloys included short range order variations as targeted. The apparent lack of sensitivity of the present XAS investigations may have been in part related to the relatively low hydrogen solubility in copper-rich Pd alloys.

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