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X-Ray Studies of Pd/Ag Membranes for Hydrogen Separation

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Abstract

The homogeneity of typical electrolessly plated Pd/Ag membranes for H₂ separation was investigated with XAFS and XPS depth profiling. Next the crucial mixing of the separate Pd and Ag layers, obtained after the two sequential plating steps, was followed *in situ* with XRD. The results show that some low temperature alloying procedures found in the field are insufficient for obtaining a well-mixed Pd/Ag alloy membrane.

Finally the Pd/Ag-H XANES was determined for the first time. In contrast to the Pd-H and Pd/Ag systems, shifts in electron density from the Ag or H atoms to the Pd could not satisfactorily explain the observed XANES. Not only is the intensity of the whiteline higher than expected, the shape and the intensity of the anti-bonding Pd 4d H 1s feature have also significantly changed. Local geometry is expected to account for these deviations.

1. Introduction

Thin Pd₇₇Ag₂₃ films on inert, porous supports such as α -Al₂O₃, Vycor glass or porous stainless steel are very important membrane materials [1–3]. Applications vary from separating H₂ from gas streams to use as a membrane reactor in hydrogenation or dehydrogenation reactions.

Electroless plating is the most suited technique for large scale production of these membranes. A typical electroless plating solution contains a metal salt, a strong reducing agent (here hydrazine), buffer reagents (here ammonia), water and a complexing agent (here Na₂EDTA). With electroless plating, in contrast to the electroplating technique, it is possible to deposit a metal film on a non-conducting support material such as Al₂O₃.

A Pd/Ag mixture is obtained by consecutively depositing a Pd and an Ag layer followed by a heat treatment to attain alloying. However there is no consensus on the required alloying treatment; temperatures vary from 450–900 °C, treatments last from a few hours to dozens of hours and finally both inert and H₂ atmospheres are used by different researchers [3–6].

Inadequate mixing is expected [4, 5] to seriously limit the performance and lifetime of the membranes. Therefore the homogeneity of the Ag distribution in typical electrolessly plated samples is studied in this paper with K-edge XAFS and XPS depth profiling. Furthermore the alloying of the Pd and Ag layers is studied *in situ* using XRD.

Finally the Pd/Ag-H system is studied as well; with L₃-edge XANES to learn more about the fundamentals of this system.

2. Experimental Section

The following samples were obtained with electroless plating: pure Pd on α -Al₂O₃, pure Ag on α -Al₂O₃ and samples with both a Pd (first) and an Ag layer (second) on α -Al₂O₃ (intended Ag content 23 at%). One of the Pd/Ag samples was alloyed at 500 °C

under 5% H₂/He for 150 hours, the others were alloyed during the *in situ* XRD experiments described below. Visual inspection with SEM confirmed that the samples were several μ m thick as intended.

A 750 nm Pd₈₀Ag₂₀ sample on a Si wafer (with 20 nm Ti adhesion layer) obtained with bi-sputtering, *i.e.*, the simultaneous sputtering of two pure targets to produce a binary alloy, was received from the MESA⁺ institute of the University Twente.

Pd and Ag K-edge XAFS measurements were performed with the electrolessly plated samples at the X1 beamline of the HASYLAB facility in Hamburg, Germany. All measurements occurred in transmission mode. The samples were first measured in vacuum at 77 K. This was followed by one hour of exposure to H₂ (100 ml min^{−1} flow) at room temperature, after which the cells were closed, cooled to 77 K and the samples were measured again.

The XDAP 2.2.2 program was used for the data analysis. For each measurement at least two scans were averaged. In the subsequent procedure the pre-edge and background were subtracted, as described in [7], before fitting the data. The fit parameters can be found in Table I and II.

At the E4 beamline of the HASYLAB facility the L₃ XANES of pure, electrolessly plated, Pd and of the Pd/Ag bi-sputtered sample in vacuum and H₂ atmosphere (1.5 bar) were determined. The measurements were performed at room temperature using a fluorescence detector. At least two scans were averaged for each measurement. The pre-edges and backgrounds were subtracted and the measurements were normalised at 50 eV beyond the edge. Some saturation was visible when comparing the results to the literature [8]. A numerical compensation was determined for Pd and Pd/Ag under vacuum, which was also applied to the hydrogen measurements.

XPS depth profiling of the Pd/Ag samples were performed in our laboratory. In regular steps the metal layer was removed by sputtering with Ar⁺ ions until the support material was detected. Unfortunately it is not possible to determine the amount of material removed with sputtering with our XPS set-up. Therefore, total thicknesses of the samples had earlier been determined with Rutherford backscattering with 2 MeV protons. Since the masses of the isotopes of Pd and Ag are too similar the two elements cannot be distinguished from one another with RBS. However the densities of the elements are also very similar so that there are no problems in determining the total thicknesses of the metal (alloy) layers. With the total thicknesses the rate of removal during XPS depth profiling could be calculated.

Co K-edge XRD ($\lambda = 1.78897 \text{ \AA}$) was used to study the alloying of the Pd and Ag domains *in situ* at temperatures from 400–600 °C in He. After the heat treatments the average Ag content was determined. For this purpose, a lattice constant vs. Ag content diagram was constructed using literature data [9, 10].

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Table I. Pd K-edge measurements, k^3 weighing, k range 2.5–15.69, fit range 2.0–3.0 Å.

Pd membrane			
Measurement	r (Å) (± 0.01)	ΔS^2	E_0
Vac, 77 K	2.74	0.0020	−0.17
H ₂ , 77 K	2.86	0.0031	−2.10
Pd/Ag membrane			
Measurement	r (Å)	ΔS^2	E_0
Vac, 77 K	2.77	0.0039	−0.12
H ₂ , 77 K	2.85	0.0011	−3.52

Table II. Ag K-edge measurements, k^3 weighing, k range 2.5–11.74, fit range 2.0–3.0 Å.

Ag membrane			
Measurement	r (Å) (± 0.01)	ΔS^2	E_0
Vac, 77 K	2.88	−0.0001	−0.93
H ₂ , 77 K	2.87	0.0038	0.18
Pd/Ag membrane			
Measurement	r (Å)	ΔS^2	E_0
Vac, 77 K	2.81	0.0022	2.27
H ₂ , 77 K	2.83	0.0009	1.85

3. Results

3.1. Homogeneity of the Pd/Ag mixtures

In Table I the Pd K-edge and in Table II the Ag K-edge fit results are shown. Fits were carried out with the coordination number (N-cor) fixed at 12 (typical for the fcc structure).

The behaviour of the pure Pd and pure Ag membrane on exposure to H₂ was as expected: the Ag membrane showed no significant change and the Pd-Pd distance changed from 2.74 to 2.86 Å. The Pd-Pd distance in bulk Pd at 25 °C is 2.7511 Å [11]. The lattice constant of bulk β -PdH_{0.6} at 25 °C is 4.025 Å [12], which corresponds to a Pd-Pd distance of 2.8461 Å. The Ag-Ag distance in bulk Ag at 25 °C is 2.8894 Å [11].

Also in case of the Pd/Ag sample the change in distance between the average Pd atom and its closest neighbours (Pd or Ag) on exposure to hydrogen corresponds with the literature values. However, the most interesting results are the Ag edge measurements of this sample.

The XAFS results suggest that on exposure to hydrogen a small change in distance to the nearest neighbour occurs, 2.81 to 2.83 Å, which can only be explained by the assumption that the average Ag atom has a relatively large number of Pd neighbours. Yet complete dissolution of atomic Ag in a true alloy of Pd and Ag is not achieved, seeing the large difference between the average Pd-X and Ag-X ($X = \text{Pd or Ag}$) distances. Either the Ag atoms are present in small clusters in a Pd sea or the metal layer consists mainly of Pd/Ag clusters (with different Ag contents).

The XPS depth profile of the Pd/Ag electrolessly plated sample showed an inhomogeneous Ag distribution; from 40 at% at the surface to 15 at% in the bulk and the bottom. Both microscopically and macroscopically the alloying is clearly incomplete.

In contrast; the Ag content of the bi-sputtered sample was very constant at 20 at% although the surface showed a small Ag enrichment (25 at%). This sample proves that a properly mixed Pd/Ag system can be synthesized. It is important to note that the result corresponds with the thermodynamic equilibrium [13, 14] and is therefore the most homogeneous Ag distribution obtainable.

With our XRD setup the alloying could be studied *in situ*. The reflections of the Pd and Ag domains present in the unmixed

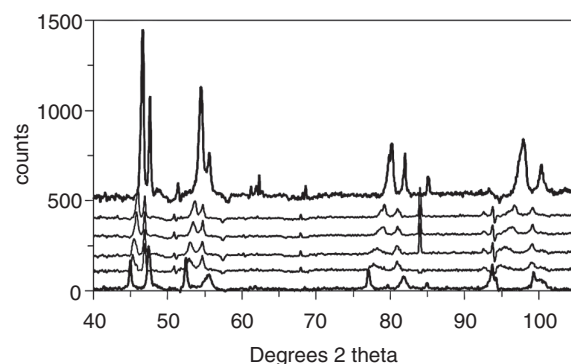


Fig. 1. From bottom to top: $t = 0$ (RT), $t = 3$ hours (375 °C), $t = 4$ hours (first measurement at 400 °C), $t = 18$ hours (400 °C), $t = 57$ hours (last measurement at 400 °C), $t = 60$ hours (RT).

electrolessly plated samples are nicely separated, as shown in figure 1. Beyond about 400 °C these reflections started to disappear and new Pd/Ag alloy reflections appeared. However even after 54 hours at 400 °C the reflections of the separate Pd and Ag domains were not completely removed.

Shorter periods of time (<20 hours) at 500 and 600 °C did completely remove these reflections. Yet the XPS depth profile of the sample alloyed at 500 °C (for a total time of 30 hours) showed that the thermodynamic equilibrium had not yet been reached and the sample was still quite inhomogeneous; the Ag content varied from 38 at% at the surface to 18 at% at the alumina support. Obtaining an Ag profile as homogeneous as the bi-sputtered sample requires a more intense treatment.

3.2. The Pd/Ag-H XANES

Figure 2a shows that the addition of Ag to Pd gives a lower white line, which is in agreement with results in the literature [8]. This

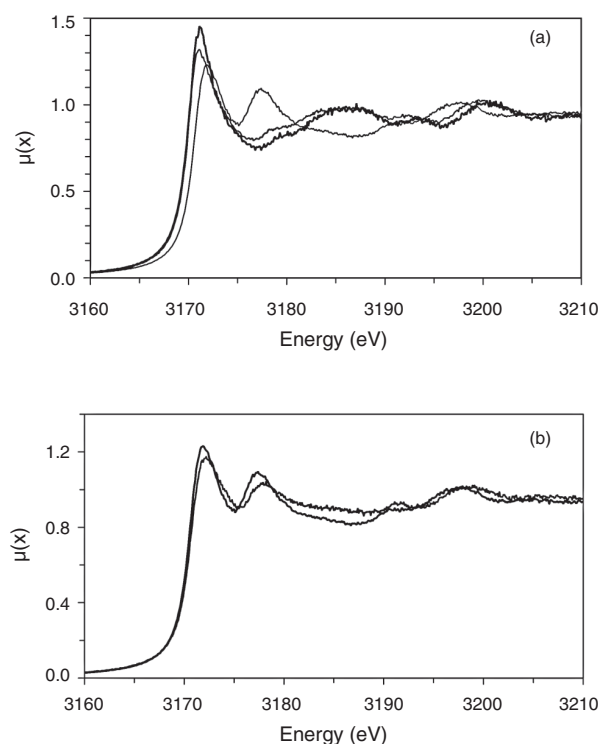


Fig. 2. (a) Pd in vacuum (black), Pd/Ag in vacuum (grey) and Pd in H₂ (thinner line). (b) Pd in H₂ (black) and Pd/Ag in H₂ (grey).

can be attributed to a decrease of the number of 4d holes in Pd, *i.e.*, to a shift of electron density from the Ag to the Pd metal. The peak at approximately 3200 eV is shifted to lower energy for Pd/Ag, indicating an increase in the lattice constant, in full agreement with the EXAFS analysis. In addition, figure 2a shows that dissolving hydrogen in Pd causes a decrease in whiteness intensity, a blue shift and a new peak at +7 eV from the whiteness [15]. This new feature is attributed to the unfilled Pd4d-H1s anti-bonding orbital and the decrease of the white line is expected because part of the empty Pd 4d states are now part of this anti-bonding orbital.

As far as we are aware of, the XANES of the Pd/Ag-H system has not yet been reported. Figure 2b, indicates that the Pd/Ag-H system is not a simple combination of the separate effects of Ag and H described above. Not only is the intensity of the whiteness higher than expected, the shape and the intensity of the hydrogen feature have also significantly changed. In our opinion these changes are a reflection of differences in the local geometry between Pd-H and Pd/Ag-H. Several effects can cause the more intense white line and broader anti-bonding state of Pd/Ag-H, for example: (1) a displacement of the H atoms from their normal octahedral position because of a preference for Pd atoms, (2) (some) clustering of Ag atoms within the Pd sea, (3) local deviations from the bulk lattice constants resulting in a range of slightly different storage sites for hydrogen atoms. The averaged local geometry obtained with XAFS cannot settle this discussion yet. At this time FEFF 8.0 calculations are performed to check whether changes in local geometry can explain our observations in more detail.

4. Conclusions

Alloying of Pd and Ag starts at low temperatures (400 °C), nevertheless achieving total bulk mixing is more problematic. Some low temperature alloying procedures found in the field most likely have resulted in inhomogeneous Ag distributions.

For the first time the Pd/Ag-H XANES was determined. The current model of electron density shift cannot completely explain the observed differences in the XANES of Pd-H and Pd/Ag-H. It is expected that local geometry has a strong influence as well, which is currently being researched with FEFF 8.0 calculations.

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