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Synthesis of pure and bimetallic Pd films supported in anodic alumina membranes by Solid State Reduction

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ABSTRACT

Films for commercial applications are usually obtained through deposition methods that are costly or produce reactant waste. In this work Pd, Pd/Ag and Pd/Pt films supported on anodic alumina membranes were obtained by Solid State Reduction (SSR). This synthesis occurs at room temperature, requires only standard laboratory equipment, and produces minimal reactant waste. Results show that SSR is effective at producing films of metals that have a high reduction potential and that the method is capable of forming alloys.

1. Introduction

Palladium (Pd) and palladium alloys (Pd/M) are materials of interest due to their high hydrogen (H_2) adsorption capacity. As films, they can be used as hydrogen sensors [1–5], H_2 separation membranes [6] membrane reactors for hydrogenation and dehydrogenation [7,8], among others [9–11].

Pure and multimetallic films for these applications are commonly obtained by vacuum processes such as sputtering [12–14], electron beam evaporation [4,15], chemical vapor deposition [16,17], and atomic layer deposition [18]. Through these techniques the film thickness, deposition rates, and microstructure can be controlled. However, these techniques require specialized equipment and consume substantial energy [19,20]. Films can also be obtained through more economical non-vacuum processes such as electrodeposition and electroless deposition, with which you also have control of the thickness and composition, but there is an excess of unreacted species that result from the process [21,22].

In this work Solid-State Reduction (SSR) [23,24] is explored as an alternative to obtain Pd and Pd bimetallic films supported in anodic alumina membranes.

2. Methodology

Synthesis: For the Pd films, 1.8 mg of palladium nitrate hydrate [$Pd(NO_3)_2 \cdot H_2O$ Alfa-Aesar] were dissolved in 30 μL of deionized water to obtain a metal loading of 5 wt% Pd. The solution was sonicated for 5 min and then it was added stepwise in intervals of 10 μL by impregnation over one side of a commercial Anodic Alumina Membrane (AAM) (Whatman® Anodisc 25 mm with a nominal pore size of 0.02 μm), air drying for 10 min after each impregnation. Metal reduction was attained by spreading a small pellet (~6 mg) of solid sodium borohydrate [$NaBH_4$ 98% mm-Alfa Aesar] with 2 μL of deionized water on the opposite side to the impregnation. All solid products and any remaining $NaBH_4$ were removed by dipping the membranes in cold deionized water three times for 30 min.

The bimetallic films were synthesized following the same steps detailed above. The mass of the precursor salts dissolved in the 30 μL of deionized (DI) water were calculated to maintain a 5 wt% total metal concentration and a 90:10 Pd:M ratio. The solution for the Pd/Ag, Pd/Pt and Pd/Ni films had 0.4 mg of silver nitrate [$AgNO_3$, Alfa Aesar] and 4.9 mg of $Pd(NO_3)_2 \cdot H_2O$, 0.8 mg of tetraammineplatinum(II) nitrate [$Pt(NH_3)_4(NO_3)_2$, Sigma Aldrich] and 4.4 mg of [$Pd(NO_3)_2 \cdot H_2O$ Alfa-Aesar],and 0.7 mg of nickel (II) nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6\,H_2O$, Alfa Aesar] and 5.2 mg of Pd $(NO_3)_2 \cdot H_2O$, respectively.

Characterization: The X-ray diffraction patterns of the Pd/M films were obtained on a Siemens D500 X-Ray Diffractometer, with a CuKα radiation. The morphology and homogeneity of the

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films were obtained on a JEOL-JSM – 6390 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer. X-ray Photoelectron Spectra (XPS) were obtained on a PHI 5000 Versa Probe using a monochromatic AlKα X-Ray Source. Binding energies where calibrated using as reference the Pd 3d 5/2 peak at 335.2 eV obtained from the spectrum of a pure Pd sample.

A KLA-Tencor Alpha-Step IQ Surface Profiler was used to study surface roughness and thickness using a scan length of 1000 μm, a scan speed of 5 μm/s with a sampling rate of 50 Hz, and a cut-off filter value of 250 μm.

3. Results and discussion

Fig. 1 shows that, with SSR, films are formed on either side of the AAM with different topologies: a coarser film on the impregnation side and a smoother film on the reduction side. This occurs for all the samples (Supplementary material). The films of the Pd sample have an average thickness of $\sim 1.02 \pm 0.70$ μm on the reduction side and $\sim 1.45 \pm 1.12$ μm on the impregnation side. The root mean squared (RMS) roughness of the film on the impregnation side is 0.213 ± 0.076 μm and 0.123 ± 0.042 μm on the reduction side.

Borohydrides react with water at room temperature to produce hydrogen as described in the reaction below [25].

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

Our results suggest that a rougher film is formed on the impregnation side because there is a higher water concentration such that the kinetics of the reaction is faster. A Pd sample was made where the precursor was added dry and films were also formed on both sides but the rougher film was formed on the reduction side where the water concentration was higher.

Although the effect of surface roughness on the permeability of hydrogen in palladium membranes is not clear [26], for applications involving an electrical current, such as hydrogen sensing, a rough film is desired as it increases the conductivity of the material [27,28]. Thus, only results of the film formed on the impregnation side are included.

EDS elemental mappings of Pd/M bimetallic films included in the Supplementary material shows a homogenous metal distribution on the surface of the films in all samples. The X-ray diffraction (XRD) patterns of the Pd and the three Pd/M samples (Fig. 2) have the characteristic Pd ⟨111⟩ and Pd ⟨200⟩ peaks evidencing that Pd was successfully reduced by SSR. For the Pd/Ag sample, the Ag ⟨111⟩ is shifted peak to $2\theta = 38.3^\circ$ which is characteristic of a solid solution of Pd in Ag. [29] This shift to higher angles is due to the shrinking of the Ag crystal lattice as consequence of the substitution of Ag atoms with Pd atoms, which have smaller atomic radius. However, the intense Pd peak is at theoretical values showing the presence of a pure Pd phase at a higher relative concentration than the Ag/Pd phase. No characteristic Ni or Pt peaks were observed for the Pd/Pt and Pd/Ni samples.

Full scan XPS spectra of all the samples (Supplementary material) did not show the presence of Boron, Sodium, or Nitrogen suggesting that the washing procedure is appropriate. Pd XPS spectra (Fig. 3A) shows that Pd is predominantly in its ground state (3d5/2 peak at 335.2 eV).[30] This spectra was characteristic of all the bimetallic Pd samples. The Ag XPS spectrum (Fig. 3B) has a low intensity 3d 5/2 peak at 368.3 eV that corresponds to pure Ag and a strong intense peak shifted by −0.6 eV that is characteristic of Pd/Ag alloys confirming the results observed with XRD that a partial Pd/Ag alloy is formed by SSR [31–35].

The Pt XPS spectrum of the Pd/Pt sample shows its characteristic ground state peaks (4f 7/2 and 4f 5/2 peaks at 71.1 eV and 74.5 eV, respectively) indicating that Pt was reduced by SSR without forming an alloy while the Ni XPS spectra of the Pd/Ni sample has a low intensity Ni 2p noisy peak at ~857 eV which roughly corresponds to $Ni(NO_3)_2 \cdot 6H_2O$ [36] suggesting that the Ni precursor was not reduced and that the washing process left a minimal amount of unreacted salt [37].

These results show that SSR is capable of reducing selected metal salts and can make alloys of selected metal combinations. This can be explained partially by the standard reduction potential (E°). The values of E° of Pt^{2+}, Pd^{2+}, and Ag^{1+} are 1.180 V, 0.915 V, 0.799 V, respectively, whereas for Ni^{2+} it is −0.236 V so the latter prefers to

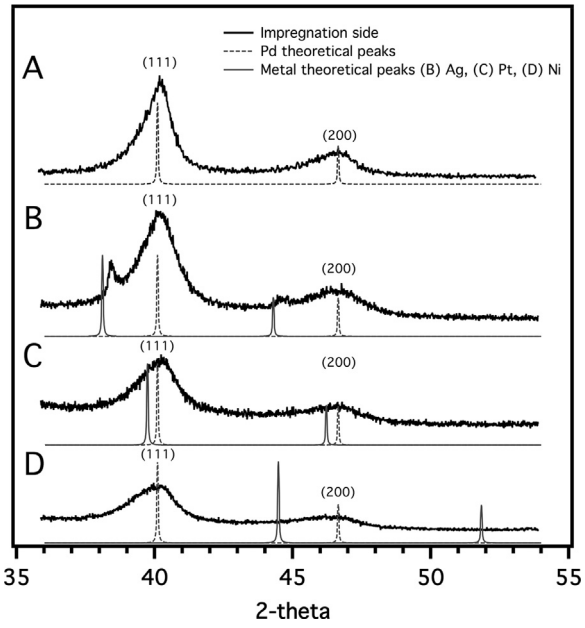

Fig. 2. XRD patterns of (A) Pd (B) Pd/Ag (C) Pd/Pt and (D) Pd/Ni films on the impregnation side.

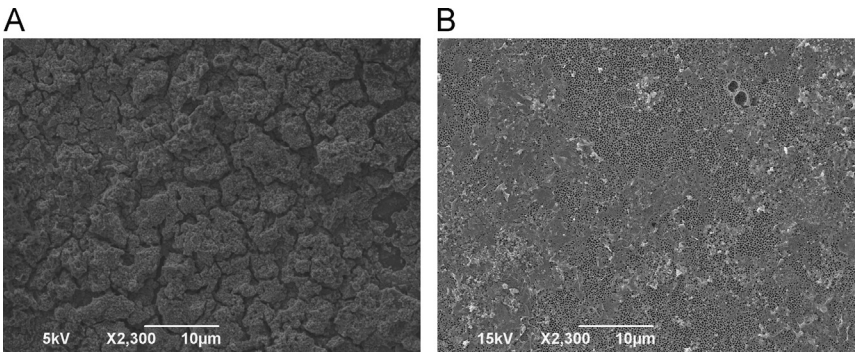

Fig. 1. SEM micrographs of the films formed on the (A) impregnation side and (B) on the reduction side of the Pd/Ag sample.