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Comparison of Composite Pd-Ag and Pd-Cu Membranes over PSS Supports for Hydrogen Separation

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1 Introduction

Nowadays, technologies to produce hydrogen are growing up due to it is considered a clean energy vector suitable for the substitution of actual fossil fuels based economy [1]. In particular, pure palladium based membranes and membrane reactors have been widely studied for hydrogen purification and its simultaneous production and purification due to its extremely high selectivity and good permeability [2]. However, the industrial application of these membranes retains some limitations, mainly the high cost of palladium and efficiency loss by hydrogen embrittlement [3]. For this reason, a growing attention has been focused to develop composite membranes with a thin active layer of precious metal over ceramic or metallic supports, achieving good mechanical stability and an important reduction in fabrication costs [4]. Moreover, it is possible to reduce and even eliminate the membrane embrittlement by preparing alloys of palladium with metals such as silver, copper or gold. In addition, some of these Pd based alloys can present high hydrogen permeability, better mechanical properties and sulfur resistance than those prepared with pure Pd [5]. Among a large number of preparation methods for composite membranes, a chemical process denoted as electroless plating (ELP) is the most widely used technique for the incorporation of Pd, Ag and Cu. This method is known for its simplicity of application, the possibility of achieving uniform deposition on supports with complex shapes, the easy of scale-up and the low cost of the process since electrical current is not required [6].

In this context, the present work is focused on the preparation and characterization of composed membranes of alloys of both Pd-Ag and Pd-Cu over porous stainless-steel supports. Both solutions used for the coating by ELP and the conditions of the thermal treatment carried out to obtain $Pd_{77}Ag_{23}$ and $Pd_{60}Cu_{40}$ alloys have been studied in detail.

2 Experimental

Tubular stainless steel supports with a porosity of ca. 20% and media grade of 0.2 μm (which means that 95% rejection of particles with a size greater than the grade is guaranteed) were provided by Mott Metallurgical. The supports have a thickness of 1.9 mm, external diameter of 12.9 mm and a length of 150 mm. Smaller PSS pieces were obtained by cutting the original substrates to 30 mm of length.

The preparation of alloys of Pd-Ag and Pd-Cu over PSS supports involves the next consecutive steps: chemical cleaning and surface activation of the support, metal deposition by ELP and obtaining the alloy by thermal treatment. Due to the presence of several contaminants on the surface of commercial supports such as oil, grease or dirt, it is necessary to carry out an appropriate cleaning. This process consists of consecutive

immersions in solutions of sodium hydroxide 0.1 M for 5 min, hydrochloric acid 0.1 M for 5 min and ethanol for 15 min. All washing steps were performed in an deionised water ultrasonic bath at 60 ºC with a rinsing between each immersion completing the process with a drying step at 110 ° C for 8 hours. After that, the activation of the PSS surface is necessary in order to initiate a homogeneous plating process with a relative low induction period. The process involves successive dip of the support in several acidic solutions of tin (1.0 g/L) and palladium (0.1 g/L) chlorides. Gentle rinsing with deionised water between both baths and one additional rising with dilute hydrochloric solution (0.01 M HCl) to prevent the hydrolysis of palladium ions fixed in the PSS supports were carried out. The immersions of PSS support in all baths were carried out at room temperature with a controlled vertical rotation (50 rpm) to ensure a suitable homogeneity. Moreover, the ends of the support were closed with Teflon tapes to keep out of solution at the internal surface of PSS support. The activation was repeated 6 times in order to achieve a homogeneous distribution of Pd nuclei. Next, metals were incorporated by electroless plating technique adding the reducing agent in several doses. The composition of the electroless plating baths and the deposition conditions are given in Table 1. The activated supports with the ends closed with Teflon tapes were immersed into 30 mL of the plating solution under vertical rotation at 60 ºC for Pd and Ag deposition and 25 ºC for Cu plating. Finally the membranes were rinsed with deionised water and dried at 110 ºC for 8 hours. The thickness and final composition for each alloy were controlled by using different number of inmersions in the plating solution of each metal. After that, the formation of the alloy occurs by thermal treatment under nitrogen atmosphere. Different procedures were carried out varying the temperature in the range 500-700ºC and the time of the process between 0-72 h.

Table 1: Composition of the electroless plating baths and the experimental procedure for Pd, Ag and Cu deposition.

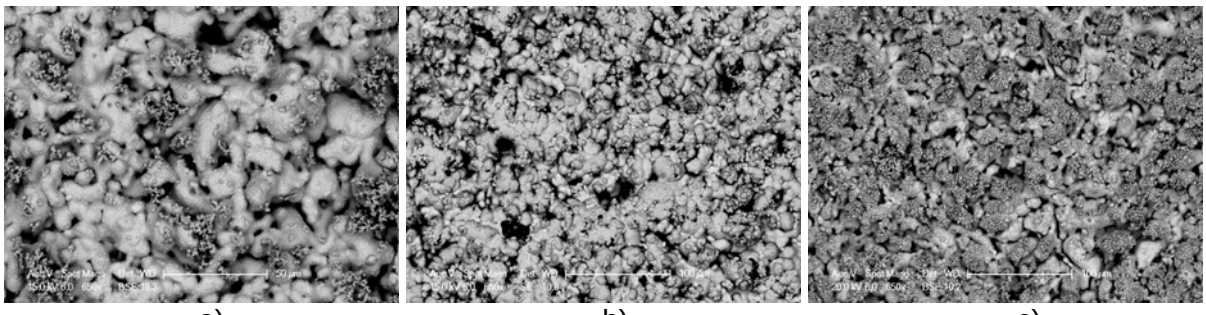
Components of the different plating baths	Composition of pure Pd plating bath	Composition of pure Ag plating bath	Composition of Pd-Ag plating bath	Composition of pure Cu plating bath
$PdCl_2$ (g/L)	5.4	-	5.40	-
$AgNO_3$ (g/L)	-	5.17	1.52	-
$CuNO_3 \cdot 3H_2O$ (g/L)	-	-	-	9.67
NH_4OH 32% (mL/L)	390	390	390	-
NaOH (g/L)	-	-	-	8.65
Na_2EDTA (g/L)	70	70	70	29.78
N_2H_4 (mL/L)	10	10	10	-
HCHO (mL/L)	-	-	-	50
Temperature (ºC)	60	60	60	25
Time (min)	90	90	90	90
* $V_{solution}/S_{plating\ area}$ (cm^3/cm^2) =2.47				

All prepared membranes were characterized by SEM, XRD, gravimetric analysis and ICP-AES (inductively coupled plasma atomic emission spectroscopy) to determine the effectiveness of the different steps undertaken.

3 Results and Discussion

Two of the most critical factors that influence the preparation of palladium based alloys over PSS supports are the composition of the plating baths and the experimental conditions (temperature and time) of the thermal treatment of the alloy. As previously mentioned, in this work two different types of membranes, Pd-Ag and Pd-Cu, were prepared for avoiding some of the main drawbacks of Pd pure membranes, mainly the embrittlement in presence of hydrogen.

Pd-Ag alloy membranes can be prepared by sequential plating of individual metals or by co-deposition, followed in both cases by thermal diffusion treatment. Palladium and silver plating over activated PSS surface is performed by using similar bath compositions (shown in Table 1) with an efficiency around 35-45%. In both cases the low values for the efficiencies are due to the generation and precipitation of waste byproducts in bulk solution, maintaining the content of both metals in spent solutions lower than 1 mg/L (measured by ICP analysis). Moreover, previous studies have showed the possibility of making the metal deposition of Pd and Ag in any order without extraction of previously incorporated metal analyzing the spent solutions by ICP-AES. This fact lets to achieve a theoretical composition in the membrane near of the suitable value for high permeation fluxes ($Pd_{77}Ag_{23}$) by adjusting with the proper amount of metal plating. In this work this has been carried out by using three successive immersions on Pd plating bath and a further one in Ag plating bath. Furthermore, since Pd and Ag baths are very similar it has been possible to carry out the co-deposition of both metals for preparing the alloy. In this case, only one immersion of PSS support in the Pd-Ag plating bath was used. This method have the advantage of a theoretically easy homogenization in the thermal treatment process but it was found very difficult to adjust the composition in solution for obtaining an appropriate plating rate of each metal with a 77:23 ratio by the preferentially incorporation of Pd. Figure 1 shows the SEM images of modified PPS supports after each metal deposition. As can be seen, the covering is very homogeneous for Pd and Ag in any conditions.



a) b) c)

Figure 1: SEM images of Pd-Ag composite membranes: a) Pd-Ag sequential plating, b) Ag-Pd sequential plating and c) co-deposition.

One of the most important factor which affects to the quality of the Pd-Ag alloy membranes is the conditions in which thermal treatment is carried out. In this work temperatures in the range 500-700 ºC under nitrogen atmosphere and times between 0 and 72 h have been employed. Figure 2 shows the XRD spectra for different temperatures and times of annealing over Pd-Ag membranes prepared by sequential and co-deposition plating. The figure shows the presence of typical metals diffraction peaks before annealing at 40º, 47º and 68º for Pd and 38º, 44º, 64º and 77º for Ag. As it can be seen, in the samples obtained by sequential step (Figure 2 a, b and c) thermal treatment of the samples provokes the presence of new signals between each diffraction peak of both metals due to the generation of a new phase: the Pd-Ag alloy (at 39º, 45º, 66º and 79º). Although the alloy was achieved for all cases, the behaviour of the Pd-Ag alloy is different depending on the temperature at which it is being treated. Thus, at 500ºC the peaks of the alloy are observed from 6 to 24 h of thermal treatment, but it disappeared at 48 h when and new peaks arose in the spectra. At 600ºC, peaks of the alloy appear from 6 h and remain up to 72 h, even growing strongly with time. And finally, at 700ºc it seems that alloy is achieved from 6 h of thermal treatment but at longer times peaks of Pd are also present. High temperature can increase the rate of intermetallic diffusion between the components of the PSS support and the membrane layer.

Moreover, the influence of preparing Pd-Ag membranes by sequential plating or co-deposition was evaluated. In Figure 2 are shown the results obtaining after thermal treatment at 600 ºC over these both membranes. As it can be clearly seen, in the XRD spectra of samples obtained by co-deposition method the alloy is not observed at any time, but also other several peaks different of Pd and Ag are shown. In these samples, other additional components (such as Na, Mg or Cl) are detected by EDX analysis, which are not detected in the sequential plating samples. The presence of additional components between Pd and Ag particles co-deposited may provoke unsuccessful annealing process with the appearance of unclear XRD spectra for the alloy. Moreover it is possible that both Pd and Ag can be deposited as isolated clusters in different areas with a reduced surface of contact between them. This fact can avoid the formation of a suitable alloy due to the difficulty for the homogeneous diffusion of both metals. According with all discussed results, 600ºC was selected for the thermal treatment of annealing on Pd-Ag membranes prepared by sequential plating.

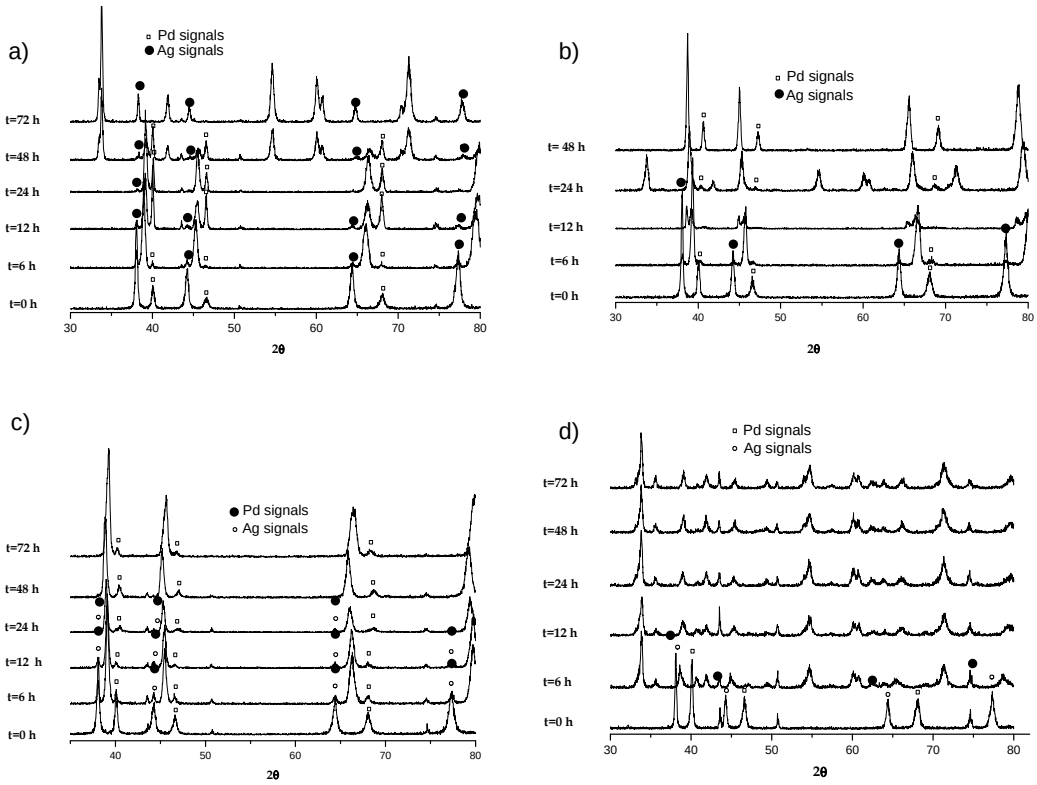
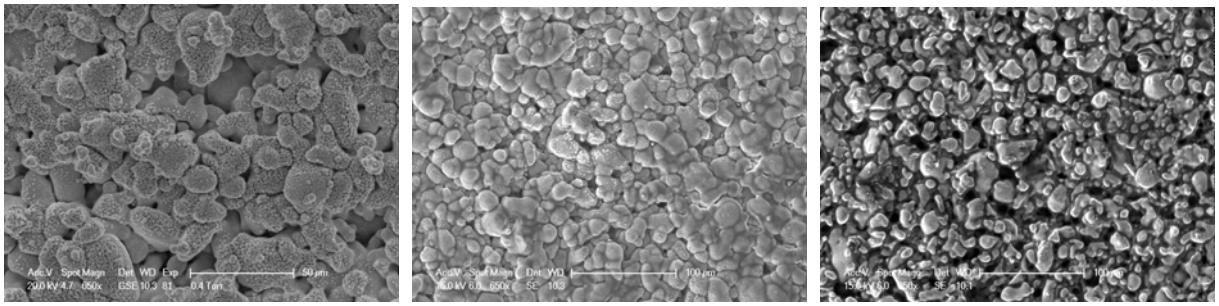


Figure 2: X-ray diffraction patterns of Pd-Ag membranes prepared in several conditions: Sequential deposition with thermal treatment at 500 ºC (a), 700 ºC (b), 600 ºC (c) and co-deposition with thermal treatment at 600 ºC (d).

Similar experiments were carried out for preparing Pd-Cu membranes over PSS supports. Figure 3 shows SEM photographs of the surface after sequential plating of Pd-Cu and Cu-Pd and simultaneous deposition of both (co-deposition). In this case, the composition of the plating baths of Pd and Cu are very different between them. This fact provokes that co-deposition of both metals was unfeasible being the sequential plating the most suitable alternative for the membrane preparation. Moreover, EDX analysis of the samples shows that Cu is extracted and re-dissolved by typical palladium plating baths. Thus, in this bimetallic alloy is necessary to incorporate first the palladium and then the copper. In this manner, it was found very difficult to achieve the suitable composition of alloy for maximize the permeation flux of hydrogen ($Pd_{60}Cu_{40}$).



a) b) c)

Figure 3: SEM images of Pd-Cu composite membranes: a) Pd-Cu sequential plating, b) Cu-Pd sequential plating and c) co-deposition.

Figure 4 shows the XRD spectra for each temperature at different times of thermal treatment over Pd-Cu membranes prepared by sequential plating. The spectra at t=0 h (before any thermal treatment) shows the diffraction peaks corresponding to pure metals at 40º, 47º and 68º for Pd and 44º, 51º, and 74º for Cu. As it can be clearly seen, temperature influences significantly in the annealing process in a major grade than Pd-Ag membranes. For Pd-Cu membranes thermal treatment at 500ºC is insufficient for obtaining the alloy until 24 h, although the presence of remaining amounts of Pd and copper even appear after 72 hours. At 600ºc the annealing process is improved, since the signals related to the Pd-Cu alloy between each diffraction peak of both metals appear at relatively low times. However, at higher temperature, as it was mentioned for Pd-Ag membranes, the migration of components of PSS supports to the selective layer of the membrane became relevant, which reduces the application of the membrane for a good hydrogen separation.

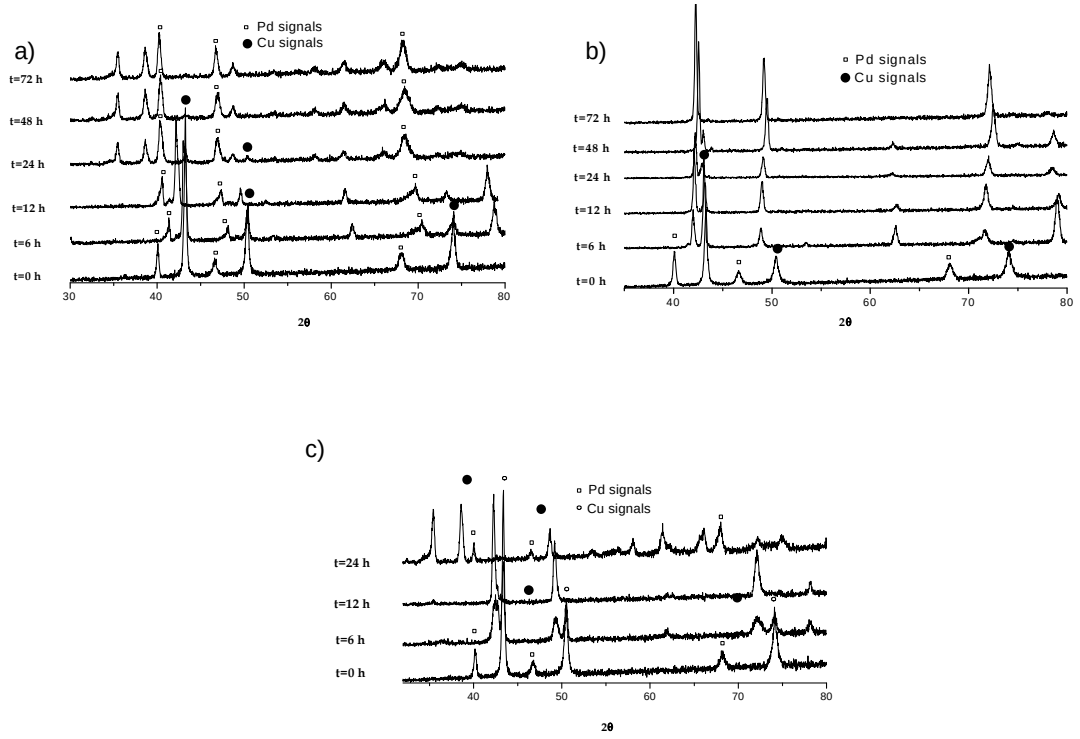


Figure 4: X-ray diffraction analysis of Pd-cu membranes prepared by sequential deposition followed by thermal treatment at 500 ºC (a), 600 ºC (b), 700 ºC (c).

4 Conclusions

Pd-Ag and Pd-Cu membranes can be prepared by electroless plating of these metals on porous stainless steel tubes followed by thermal treatment. Pd and Ag can be incorporated by both sequential plating and co-deposition (simultaneous deposition of both metals) methods, although the composition of the alloy can be adjusted better with the first technique. The homogeneity of the Pd-Ag alloy depends of the preparation method and temperature of the annealing treatment. The co-deposition provokes the generation of clusters of pure metals, reducing the area for contact between Pd and Ag and making the diffusion of metals difficult. Pd-Ag alloy was obtained for sequential plating of both metals although temperature influenced significantly in the time necessary for obtaining the Pd-Ag phase. After 6 h of thermal treatment, characteristic diffraction peaks of Pd-Ag alloy appear independently of the temperature of the process. However, at longer times this phase only was maintained at 600 ºC, appearing new diffraction peaks and/or re-appearing the signals due to both pure Pd and Ag. In this manner, the temperature of 600 ºC was selected for the thermal treatment of annealing on Pd-Ag membranes prepared by sequential plating. On the other hand, it has been determined that Pd and Cu only can be incorporated by sequential plating (firstly Pd and then Cu) making very difficult to achieve the suitable composition of alloy for maximize the permeation flux of hydrogen (60:40 respectively). For these membranes thermal treatment at 500ºC is clearly insufficient for obtaining the alloy until 24 h,

although the presence of remaining amounts of Pd and copper even appear after 72 hours. Higher temperatures improve the annealing process, appearing the signals related to the Pd-Cu alloy between each diffraction peak of both metals at relatively low times. However, very high temperatures can provoke the migration of components of PSS supports to the selective layer of the membrane, reducing their application for a good hydrogen separation. This fact provokes the generation of Pd-Cu alloy phase for long times at 600ºC (72 h) while it can be obtained after times lower than 12 h with thermal treatment at 700ºC. Nevertheless, longer times at this high temperature provoke the apparition of new signals due to several components different of searched alloy.

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