



# Morphological and Elemental Analyses of Supported Palladium (Pd)/silver (Ag) Composite Membranes

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Supported palladium (Pd)/silver (Ag) composite membranes have been investigated for hydrogen separation mainly in order to avoid hydrogen embrittlement, improve hydrogen permeance and reduce membrane cost. The electroless method is recommended for the co-plating of Pd and Ag on a substrate surface. However, Ag precursor has a higher redox potential than Pd and, thus, Ag is preferentially deposited, which compromises the membrane selectivity to hydrogen. Here we investigated the morphology and elemental composition of supported palladium (Pd)/silver (Ag) composite membranes produced by different methods. The first membrane was produced from a plating solution of 80 wt% of Pd and 20 wt% of Ag. The membrane surface presented several large dendritic crystals that not grown in a direction to form a dense metallic film. According to EDS results, the membrane surface presented similar Pd and Ag composition, which confirms the preferential Ag deposition. At room temperature, this membrane presented a nitrogen flux of  $0.35 \text{ mol m}^{-2} \text{ s}^{-1}$  at 200 kPa of transmembrane pressure. Thus, the formed membrane is not suitable for hydrogen separation. The second membrane was formed by adding small amounts of Ag to the plating solution during the electroless process. The final plating solution contained 75 wt% of Pd and 25 wt% of Ag. The membrane thickness was 2  $\mu\text{m}$ , but the membrane morphology was not totally dense. According to EDS results, the Ag composition was greater than the Pd composition, especially at the membrane top surface. This membrane also presented high nitrogen permeance probably due to the holes formed on the membrane surface. Thus, although the controlled addition of Ag is recommended to form dense membranes, the Ag was preferentially deposited over the Pd when starting with the highest rate of Ag addition. Adding lower Ag rates at the beginning could be helpful to avoid the preferential Ag deposition.

## 1. Introduction

Hydrogen has been proposed as a proper energy carrier since hydrogen burn does not generate toxic gases <sup>[1]</sup>. The current production of hydrogen involves the steam methane reforming reaction, in which several other gases are produced <sup>[2]</sup>. Pure hydrogen can be obtained with conventional pressure swing adsorption or with membrane separations. Palladium (Pd) based membranes enable the production of ultrapure hydrogen due to its high selectivity for hydrogen <sup>[3]</sup>. However, self-supported palladium membranes present above 20–30  $\mu\text{m}$  thick, and therefore they have high costs and low hydrogen permeation.

Thus, thin Pd-based membranes are supported on porous substrates in order to provide mechanical stability <sup>[4]</sup>. Asymmetric ceramic hollow fibers have suitable characteristics for depositing a metal film due to the formation of microvoids through the fiber extension, so that the gas permeation through the substrate is not depressed <sup>[5]</sup>. Also, a thin sponge-like layer with lower porosity is formed on the substrate outer surface for a proper metal film deposition. Palladium (Pd)/silver (Ag) alloy composite membranes have been proposed in order to avoid hydrogen embrittlement, improve hydrogen permeance and reduce membrane cost <sup>[6]</sup>. Hydrogen permeability through Pd/Ag alloy composite membranes with 23 wt% of silver and 77 wt% of palladium is about 1.7 times higher than through pure palladium membranes <sup>[7]</sup>.

The electroless plating method is frequently used for the preparation of supported Pd/Ag composite membranes, which includes sequential and simultaneous depositions. Separated Pd and Ag layers are formed in the

sequential deposition and a long thermal annealing process are necessary to form a homogeneous alloy phase <sup>[8]</sup>. In the co-plating method, a single Pd/Ag solution is prepared for the electroless plating method, which includes the palladium- and silver-complex sources along with the reducers. However, Ag precursor has a higher redox potential than Pd and, thus, Ag is preferentially deposited at the early stages of plating. The preferential silver deposition causes non-uniformity in the alloy composition and formation of large dendritic crystals that impair the desired dense structure of the membranes <sup>[9]</sup>. Some improved co-plating procedures have been suggested in the literature to overcome these issues. Zeng et al. <sup>[10]</sup> developed an Ag-controlled co-plating method in which the feed rate of Ag to the Pd bath was progressively changed. Melendez et al. <sup>[11]</sup> improved the co-deposition of Pd and Ag by tuning the chemical composition of the plating solution. However, elemental distributions should be investigated to better understand the silver addition rate dependence. Here we evaluated the morphology and the elemental composition of Pd/Ag composite membranes which were co-deposited on asymmetric alumina hollow fibers by two different procedures.

## 2. Material and methods

Asymmetric alumina hollow fibers were produced by the phase inversion/sintering technique according to the procedures described in our previous work <sup>[12]</sup>. The fibers were then subjected to the steps presented in Figure 1 for the final gas permeation tests.

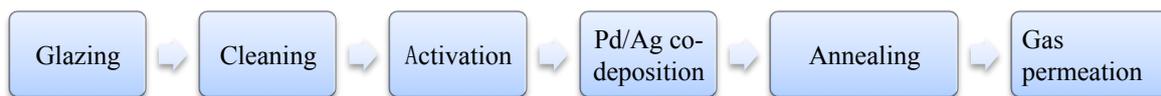


Figure 1. Steps for preparing the ceramic substrate.

In the glazing step, the length of the fiber that will not be covered by the metallic membrane was covered by a gas-tight glaze (Liquid Ceramic Enamel, Gel TAC017, Brazil). A length of 4 cm was left for depositing the metallic membrane. One end of the fiber was closed with the glaze and the other end was left open for gas permeation. A scheme of the glazing step is presented in Figure 2. After glazing, the fibers were sequentially washed with water and isopropyl alcohol in an ultrasonic bath to remove all dirtiness from the fiber surface. Then, the fibers were dried in an oven at 110°C for at least 30 min.

Before Pd-Ag co-deposition, sequential baths of SnCl<sub>2</sub> (1 g L<sup>-1</sup>), pure deionized water, PdCl<sub>2</sub> (0.1 g L<sup>-1</sup>), HCl (0.01 M), and pure deionized water were used to seed a layer of palladium nuclei (activation step). The fibers were sequentially dipped in the sensitization-activation baths of SnCl<sub>2</sub> for 5 min, deionized water for 5 min, PdCl<sub>2</sub> for 5 min, HCl for 2 min, and deionized water for 3 min. Air was bubbled in all baths to ensure a homogenous deposition of palladium seeds on the fiber surface, as suggested by Prasetya et al. [13]. This sensitization-activation treatment was repeated 5 to 8 times until the surface of the fiber was dark brown.

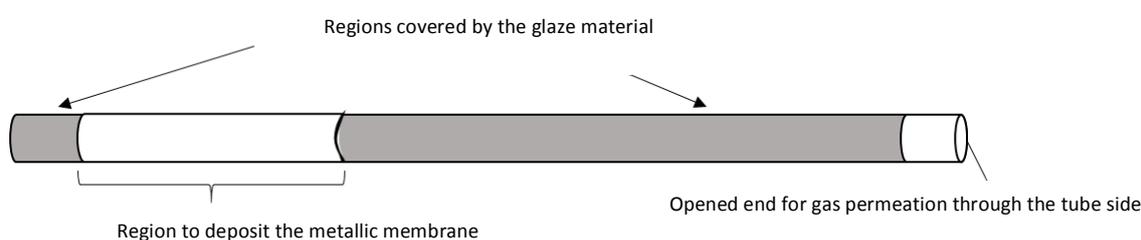


Figure 2. Scheme of the substrate after the glazing step.

The electroless plating procedure was applied for the Pd-Ag co-depositions. The plating solution was magnetic stirred and the solution volume corresponded to 3.5 mL per cm<sup>2</sup> of the fiber surface area, as suggested by Mardilovich et al. [14]. The plating solution was placed in a test tube, which was placed in a water bath for temperature maintenance, as presented in Figure 3.

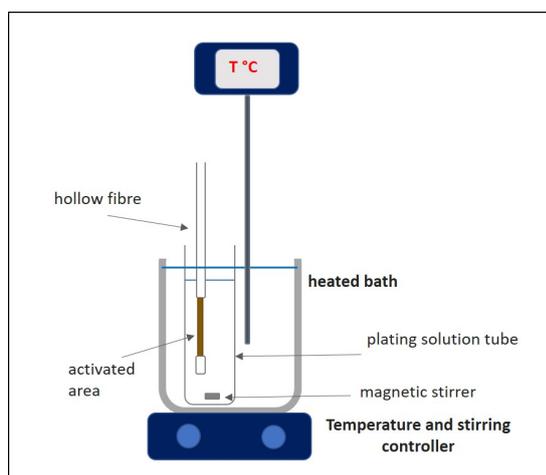


Figure 3. Scheme of the plating procedure.

The M1 membrane was prepared from a plating solution at concentrations presented in Table 1, as proposed by Foletto et al. [15]. After the plating solution temperature reached 50°C, the fiber was immersed in the plating solution containing PdCl<sub>2</sub>, AgNO<sub>3</sub>, NH<sub>4</sub>OH, and EDTA. Then, a hydrated hydrazine solution was added to the plating bath to act as the reducing agent. The plating procedure for the M1 composite membrane was carried out for 1 h, as suggested by Foletto et al. [15].

Table 1. Compositions of the plating solution for preparing the M1 membrane.

Compound	Concentration unit	Concentration value
PdCl <sub>2</sub>	g L <sup>-1</sup>	1.85
AgNO <sub>3</sub>	g L <sup>-1</sup>	0.44
Na <sub>2</sub> EDTA·2H <sub>2</sub> O	g L <sup>-1</sup>	16.14
NH <sub>4</sub> OH (28 vol%)	mL L <sup>-1</sup>	184
N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O (1 M)	mL L <sup>-1</sup>	13.26

The M2 membrane was prepared according to the procedure suggested by Zeng et al. [10]. Two individual Pd and Ag baths were prepared. The Pd bath was prepared by dissolving all the precursors into deionized water to form an aqueous solution containing 3.9 mmol/L PdCl<sub>2</sub>, 5 mol/L NH<sub>4</sub>OH and 0.12 mol/L Na<sub>2</sub>EDTA. The Ag bath was prepared by dissolving 5.1 mmol/L AgNO<sub>3</sub>, 5 mol/L NH<sub>4</sub>OH and 0.12 mol/L Na<sub>2</sub>EDTA. In a typical process, 60 mL Pd bath was loaded into a glass tube and 15 mL Ag bath was sucked into a syringe. The Pd bath was kept at 330 K and mildly magnetically stirred while the Ag bath was fixed on a programmable syringe pump. The activated supports were vertically placed inside the Pd bath, and thereafter the Ag bath was fed into the bottom of the Pd bath by the syringe pump. Immediately, 0.45 mL N<sub>2</sub>H<sub>4</sub> solution (1 mol/L) was added to the Pd bath and well mixed. The AgNO<sub>3</sub> solution was gradually added to the plating solution, as presented in Table 2. The total reaction time of the M2 plating procedure was 5 h. The final bath contained 75 mL solution of 3.1 mmol/L PdCl<sub>2</sub>, 1.0 mmol/L AgNO<sub>3</sub>, 5 mol/L NH<sub>4</sub>OH, 0.12 mol/L Na<sub>2</sub>EDTA, and 6 mmol/L N<sub>2</sub>H<sub>4</sub>. After plating, the fibers were washed with deionized water and dried at room temperature (approximately 25°C).

Table 2. The feed flow rate of AgNO<sub>3</sub> solution in the M2 plating procedure.

Reaction time (min)	Feed flow rate of AgNO <sub>3</sub> solution (mL min <sup>-1</sup> )
0	0.0350
45	0.0320
75	0.0281
105	0.0250
135	0.0210

165

0.0180

For annealing and gas permeation tests, the composite membranes were glued with Araldite<sup>®</sup> to a stainless steel holder which was connected to a stainless steel tube. This tube was assembled in the furnace (Carbolite MTF 1200) equipped with a temperature controller. The gas line (nitrogen and hydrogen) was connected to the stainless steel tube. The gas was fed to the shell side of the membrane and the permeating gas was collected from the membrane inner side. The pressure of the feed gas was adjusted using a pressure regulator (Omega<sup>®</sup>, model PRG101) and monitored using a manometer. The flow of permeating gas was measured with a bubble flow meter. The temperature was increased up to 340°C at 3°C min<sup>-1</sup> under a nitrogen purge. At this temperature, the N<sub>2</sub> gas was replaced by H<sub>2</sub> and the temperature was further increased up to 550°C at 3°C min<sup>-1</sup> under hydrogen purge. Then, the system was kept at 550°C for 3 h under hydrogen purge for the membrane annealing. After that, the temperature was decreased up to 450°C at 3°C min<sup>-1</sup> under the nitrogen purge. Nitrogen permeations were measured at different transmembrane pressures (from 40 to 200 kPa) and different temperatures (450, 400, 350, and 300°C). Morphological and compositional analyses (quantitative and qualitative) of the prepared composite membranes were carried out using a scanning electron microscopy (SEM, Carl Zeiss model EVO MA 10) equipped with an electron dispersive spectrometry (EDX, INCA X-ray microanalysis system model 51-ADD0048, OXFORD Instruments) for both qualitative and quantitative analysis.

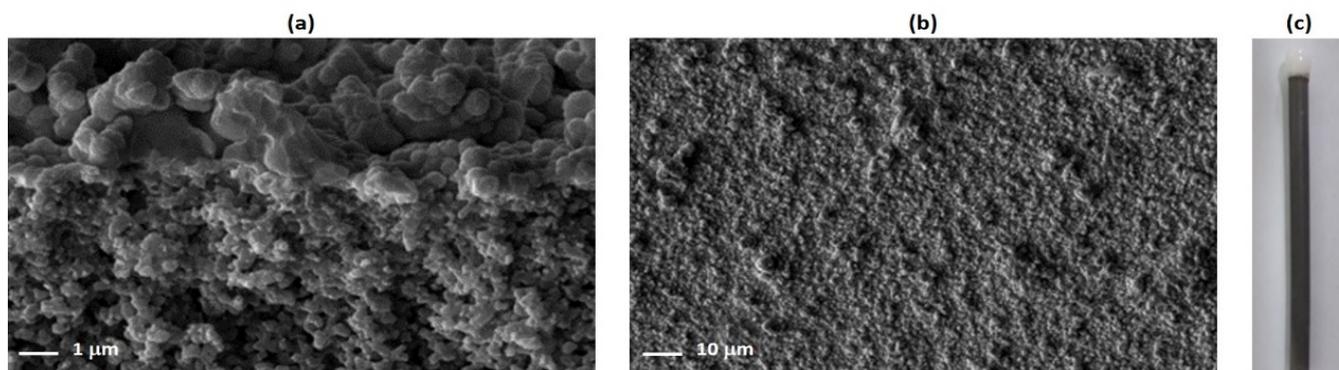


Figure 4. Cross-section (a) and outer surface (b) SEM images and (c) picture view of the M1 composite membrane.

The elemental composition of the M1 membrane is presented in Figure 5. According to EDS results, aluminum and oxygen were detected on the membrane surface, which suggests the Al<sub>2</sub>O<sub>3</sub> substrate was not completely covered by the metallic membrane.

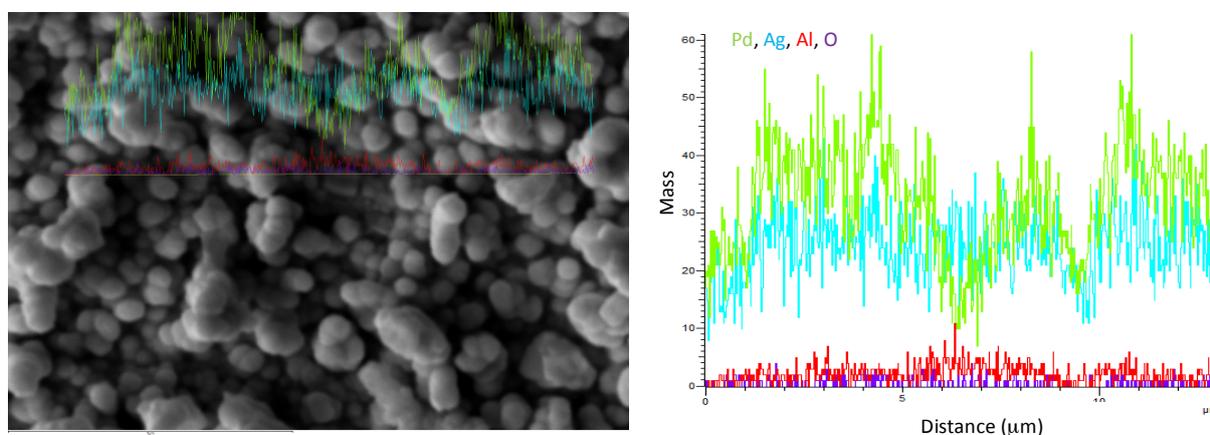


Figure 5. Elemental composition on the outer surface of the M1 composite membrane.

Figure 6 presents nitrogen flux through the membrane M1 at room temperature (approximately 25°C). The relatively high nitrogen flux

The EDX system was equipped with a silicon drift INCA PentaFET-Precision detector. An accelerating voltage of 20 kV and a current of 3.0 nA were used. In order to prevent sample charging, all samples were coated with a layer of gold using sputtering equipment (LEICA Metallizer EM SCD 050) under vacuum for 120 s at 50 mA. Elemental composition analyses (line mapping and point & ID) were performed with the INCA software.

### 3. Results and Discussion

Scanning electron microscopy (SEM) images show that a continuous and fully dense metallic layer was not formed in the M1 membrane (Figure 4). The membrane morphology observed in Figure 4 can be explained by the different deposition behaviors of Pd and Ag. The Ag precursor has a higher redox potential than Pd, which leads to a mismatched deposition rate between Ag and Pd. The uneven deposition of silver causes not only non-uniformity in the alloy composition but also leads to large dendritic crystals that impair the desired dense structure of the membranes. Thus, the metallic film exhibits dendritic morphology and highly nonuniform growth and tends to grow in the vertical direction on the Pd membrane surface, with poor lateral growth or pore coverage. The membrane presented a mat aspect (Figure 3(c)) since the metallic deposited layer was not dense and flat.

The plating bath contained 80 wt% of Pd and 20 wt% of Ag. However, the Pd composition was similar to the Ag composition due to the preferential Ag deposition.

confirms that a proper metallic layer was not deposited on the substrate surface and, thus, a selective membrane to hydrogen was not achieved.

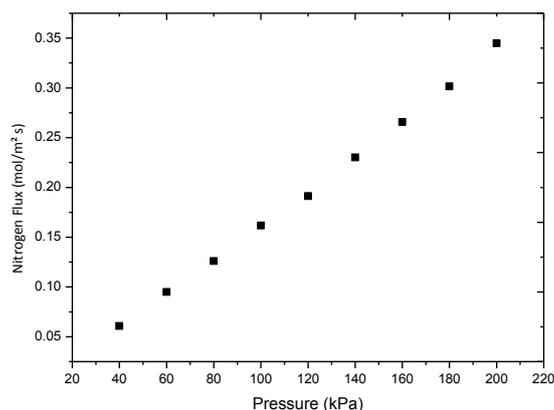


Figure 6. Nitrogen flux through the membrane M1 at room temperature.

Figure 7 presents the morphology of the M2 membrane, which was produced by controlling Ag addition during the electroless plating. A metallic layer of approximately 2 μm thick was deposited on the substrate outer surface. However, the deposited Pd/Ag membrane was

not totally dense and, thus, the membrane selectivity may be compromised. The membrane presented a mat silver color (Figure 7(b)).

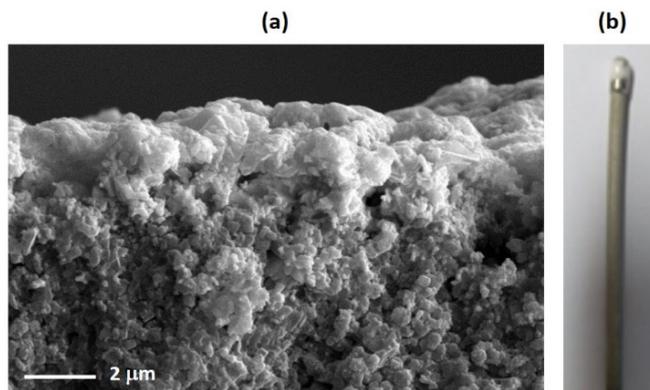


Figure 7. Cross-section (a) SEM image and (b) picture view of the composite membrane M2

Figure 8 shows the EDS composition profile through the cross-section of the M2 membrane. Aluminum and oxygen were detected at a low concentration up to a distance of approximately 6 μm of the membrane outer surface. Thus, the Al<sub>2</sub>O<sub>3</sub> substrate was not entirely covered by the M2 membrane. The silver composition was up to 40 wt%, while the Pd composition kept below 10 wt%. Thus, the silver deposition was favored even with controlled silver addition in the plating bath during the plating procedure. The plating bath presented a final composition of 75 wt% of

Pd and 25 wt% of Ag. However, the initial high rates of Ag added to the plating bath may have also favored silver deposition. Silver composition presented a pronounced decreased through the fiber cross-section up to a distance of approximately 2 μm, which corresponds to the membrane thickness. The M2 membrane presented a high nitrogen flux so that it was not tested for hydrogen permeation.

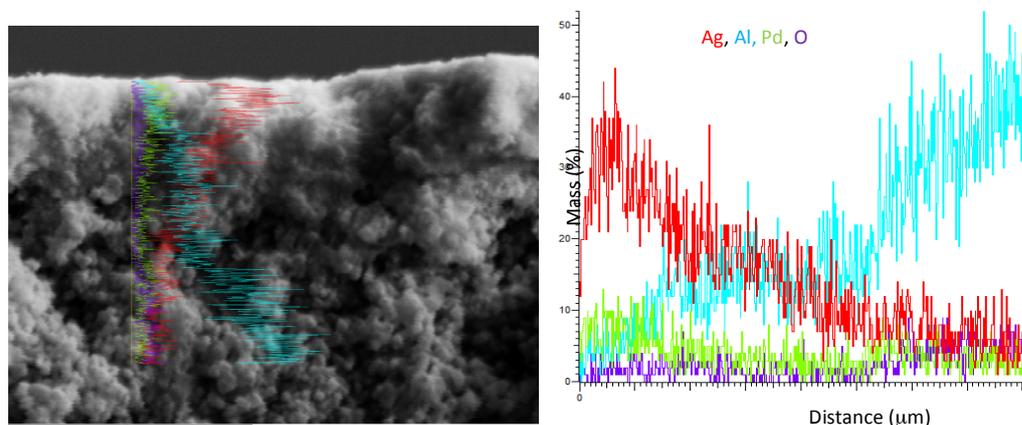


Figure 8. Elemental composition on the cross-section of the composite membrane M2.

#### 4. Conclusion

Two different co-deposition methods were evaluated to produce Pd/Ag composite membranes. A conventional co-deposition electroless plating procedure was applied from a plating bath containing 80 wt% of Pd and 20 wt% of Ag. However, the produced membrane presented similar Pd and Ag compositions due to the preferential Ag deposition. The large Ag deposition produced a non-uniformity membrane with large dendritic crystals that compromised the membrane selectivity to hydrogen. Alternatively, silver was added to the plating bath at regular intervals to prevent preferential Ag deposition. However, the plating bath presented a final composition of 75 wt% of Pd and 25 w% of Ag. However, the produced membrane presented a high silver concentration at the beginning of plating, thus, silver deposition was still favored and the membrane did not present the required selectivity to hydrogen. Further studies are suggested by starting with a lower rate of Ag addition.

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#### Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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