HYDROGEN PERMEABLE MEMBRANES FROM PALLADIUM COATED ANODIC ALUMINA

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ABSTRACT

Nanostructured anodic alumina membranes have been fabricated from templates prepared by anodizing annealed high-purity aluminum foil. A range of acid electrolytes and anodizing voltage profiles have been used to control the pore diameter, pore separation and thickness in these alumina ceramic templates. Thin films of Pd metal up to 200nm thick have been deposited on the surface of the alumina templates and we have demonstrated that the membranes formed can be used to separate hydrogen from mixed gas streams with very high selectivity. These pure Pd membranes experience hydrogen embrittlement in operation below 350°C and we have employed silver as an alloying metal to help prevent this. An electroless deposition technique was used to obtain thin films of palladium and silver on the porous anodic alumina substrate. The films were tested via thermal cycling and gas separation experiments. The palladium membrane showed clear cracks after thermal cycling while the palladium silver alloy membranes showed no obvious damage. Gas separation tests showed that a membrane with 30% silver displayed increasing permeance (flux) with increasing temperature, with H2/N2 permselectivity of ~500 and permeance of ~1.8 μmol/m².s.Pa at 700°C.

INTRODUCTION

The increased uptake of sustainable hydrogen energy technologies is dependent on many technical, political and commercial factors, but a dominant technology issue is the provision of suitable quantities of high purity hydrogen. Low temperature fuel cells in particular are very sensitive to even trace levels of CO, SO2, H2S and other impurities in the supply gas stream, which can cumulatively damage and deactivate the electrode catalysts and reduce fuel cell efficiency12. Membrane filters provide a means to achieve very high purity hydrogen gas, especially through the use of palladium or palladium alloy materials that provide hydrogen-specific conduction paths7. Hydrogen diffusion through these membrane filters is a multistep process: dihydrogen molecules adsorb onto the surface of the Pt membrane and dissociate into hydrogen atoms, which then diffuse through the interstitial octahedral sites in the fcc Pt lattice and reform as gaseous diatomic hydrogen on the exit face of the palladium membrane. Palladium has a high level of hydrogen permeability whilst remaining impermeable to other gases, which makes it an ideal material for use to separate hydrogen from mixes of gases. Problems arise because palladium hydride exists in two different phases, α and β, both fcc structured as in the parent metal. When hydrogen is absorbed into Pd below 300 °C the high hydrogen capacity β hydride (PdH2.67) predominates. Formation of this phase results in a 10% volume expansion causing stress on the Pd metal lattice and resulting in embrittlement and degradation of the material on repeated adsorption-desorption cycling5. However at temperatures above 300 °C the lower hydrogen capacity α hydride phase (PdH0.02) predominates and the volume expansion upon adsorption of hydrogen is very small. As such, Pd films used in the presence of hydrogen are useful membrane materials only at temperatures above 300 °C.

The introduction of other metals to form palladium based alloys has had promising results. In particular doping of the palladium with silver has been shown to improve the stability of the film and increase the solubility of hydrogen. Previous work by Uemiya et al.7,8 showed that the temperature above which the α palladium hydride occurred was lowered with the increased silver content. The hydrogen permeability was optimized when the silver content of the alloy was around 3 wt%. Silver occupies interstitial sites in the palladium lattice and props them open to moderate the lattice expansion and contraction due to hydrogen absorption-desorption. The work reported here focuses on ways to
Hydrogen Permeable Membranes from Palladium-Castellated Palladium-Alumina

Palladium-castellated membranes offer promising advantages, including fast hydrogen transport via enhanced diffusional pathways through the metal and significant resistance against durchbar reduction in the permeability of hydrogen. This paper presents progress in the fabrication of such membranes, highlighting the role of perfluorinated castellated palladium-alumina (PAA) for hydrogen purification. PAA membranes exhibit high hydrogen permeability and selectivity, making them a promising candidate for applications in hydrogen purification and storage systems. The unique structure of PAA, with its castellated palladium-alumina, facilitates the high-rate hydrogen permeation and low gas diffusion resistance, leading to improved performance in fuel cell systems. The use of PAA membranes can enhance the efficiency and reliability of hydrogen fuel cell systems, contributing to the advancement of clean energy technologies.

Hydrogen Membranes and Systems

PAA membranes can be produced using heat-molded castellated membranes. The processing involves heating at a minimum of 500°C to 600°C in an oxidizing atmosphere to remove the catalyst. Heating at a temperature between 500°C and 600°C is critical to obtain high-quality castellated membranes. Hydrogen permeation testing was conducted using a membrane cell to evaluate the hydrogen permeation rate. The results indicate that the PAA membranes exhibit excellent hydrogen permeation properties, making them a promising candidate for hydrogen purification applications.
Hydrogen Permeability Maintenance from Palladium-Graphite Anode Aluminas

Ruthenium and Deactivation

Alumina foil, 0.25 mm thick, 99.99999% pure (Alfa Aesar), was cut into 10 mm square and cleaned by submerging in ethyl acetate and sonication for 20 minutes. The cleaned foil was rinsed with distilled water and allowed to air dry. Once dry, the edges of foil were cut to produce 12 x 12 mm squares. The electrolytic cell used for experimentation is shown in Figure 1.

![Diagram of electrolytic cell](image)

**Figure 1. Schematic of Electrolytic Cell**

The un-oxidized PAA membrane system adhered to the alumina substrate. To obtain the free-standing membranes used in these experiments, the membrane was detached using a one-step voltage pulse detachment similar to that outlined by Tsuchida et al. and Chen et al. This method has the advantage of being gentle and not requiring any heavy media which may contaminate the membrane. Following separation, the metal-eroded aluminium was removed and after soaking the cell with distilled water, was replaced with a 2 M perchloric acid etch solution. A voltage of 10 V higher than the final membrane formation voltage was applied to the cell for 20 s. In this case, the membrane contacted at 80 V and 30 V was used for detachment. After the etching voltage, the perchloric acid-etched substrate was recovered and the free-standing membrane was rinsed in distilled water. membranes were then aged in distilled (ion-exchanged) water until further use.

**Phase Opening**

Following detachment of the PAA from the alumina substrate, the pores of the PAA are sealed by this end. Removal of this second layer exposes the pores to form continuous palladium channels through the ceramic. This allows gas to flow freely through the membrane during the gas separation testing, providing measurement of the permeability of the applied gas testing. In addition to removing the barrier layer, the pores may also withstand high pressure gas flow. These measurements determine the membrane that is susceptible to attack by acids and bases. Relatively mild conditions can be used to achieve the membrane to increase the barrier layer and enhance the pores. The small PAA “jail” section of the membrane is more susceptible to attack by acids than the main body of the membrane prepared under 1250 °C “treatment” conditions. By maintaining the section at 1250 °C the barrier layer is then more susceptible to acid attack than the remainder of the membrane so the pores can be removed with little impact on the body of the membrane. Membrane wetting was maintained using a 5 wt% solution of phosphoric acid, placed in a beaker in a water bath and maintained at 30 °C. With the temperature and type of immersion affected the final pore size and structure of the membrane.

[Further content continued...]

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*Manuscript: Hydrogen Permeability Maintenance from Palladium-Graphite Anode Aluminas*
Hydrogen Penetration in Materials: Palladium-Catalyzed Reduction of Aluminum

Incorporating the metal into an Al foil at 30% volume fraction at initial conditions, in open air, permits without changing the structure of the material. The PAA nanocomposites showed a distinct weight and adhered to the dry.

Dear Editor,

As mentioned, PAA nanocomposites of amorphous aluminum oxide and are susceptible to attack at high and have Pd conditions. This helps the successful growth of an amorphous using a lower concentration sodium reduction. The presence of the nanocomposites in a sodium solution, is affected by increasing the concentration of the sodium solution with the sodium salt. The effects of the sodium salt in the sodium solution, without changing the local or physical structure of the nanocomposites. In fact, the addition of the sodium salt, without changing the local or physical structure of the nanocomposites, can be observed using the sodium salt in the sodium solution.

Metal Reduction

The reduction of palladium in a sodium hydroxide solution, where hydrogen is the product, has been shown to improve the degree of hydrogen reduction. The reduction of palladium by hydrogen has been observed with various palladium contents. The reduction of palladium by hydrogen has been observed with various palladium contents. The reduction of palladium by hydrogen has been observed with various palladium contents.

A number of different methods can be used to plate Pd films. The classical method used here was the highest and most economical in terms of time and cost. Electrochemical plating processes using a reducing agent in an aqueous metal ion solution afford a elemental metal. For electroless plating to be sufficient and successful, the solubility of the metal must exceed the solubility of the metal. The solubility of the metal must exceed the solubility of the metal. The solubility of the metal must exceed the solubility of the metal.

Activation of the metal surface is needed prior to electroless plating. This method of activation is commonly used to prepare surfaces for electroless plating. The hydrogen assistance was in the reduction of palladium solutions containing PdCl₂ and HCl (19%). The reduction of palladium solutions containing PdCl₂ and HCl (19%) in hydrogen can be observed using the hydrogen assistance. The reduction of palladium solutions containing PdCl₂ and HCl (19%) in hydrogen can be observed using the hydrogen assistance.

\[ \text{Sn} + \text{H}_2 \rightarrow \text{SnH}_2 \]  \dots (1)
The membranes were attached to a plastic holder using a small amount of double-sided tape.

The membranes were immersed in solution for five minutes, then rinsed with distilled water. This rinsing step depended on the pH of the solution, as the membranes were sensitive to pH changes. The membranes were then immersed in the solution containing the metal ions, allowing for the metal ions to be absorbed. After this step, the pH of the solution was adjusted to 3. The membranes were then immersed in the solution containing the metal ions to be absorbed. The membranes were then rinsed with distilled water.

$$\text{Fe}^{2+} + 2\text{Na}^+ \rightarrow \text{Fe}^{3+} + 2\text{Na}^+ \quad \text{(1)}$$

An electrochemical plating method was used for all co-deposition and individual depositions. Electrochemical plating involves the use of a plating solution containing a metal and a stabilizing agent. A reducing agent was added prior to plating which caused the metal to be reduced to the elemental metal. Electroplating was in a stainless steel tank to deposit platinum. Electroplating was used to deposit platinum onto the membranes. The membranes were then immersed in the solution containing the metal ions to be absorbed. The membranes were then immersed in the solution containing the metal ions to be absorbed. The membranes were then rinsed with distilled water.

In a typical method, the membranes were immersed in a solution containing the metal ions to be absorbed. The membranes were then rinsed with distilled water.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>pH</th>
<th>Reduction Potential (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaS</td>
<td>3.0</td>
<td>0.30 V</td>
</tr>
<tr>
<td>NiS</td>
<td>3.0</td>
<td>0.42 V</td>
</tr>
</tbody>
</table>

The membranes were then immersed in a solution containing the metal ions to be absorbed. The membranes were then rinsed with distilled water.
Table III. Individual Plating Solutions

<table>
<thead>
<tr>
<th>Copper</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>750 mL</td>
<td>43 mL</td>
</tr>
<tr>
<td>7.5 mL</td>
<td>35 mL</td>
</tr>
<tr>
<td>17.4 g</td>
<td>3.36 g</td>
</tr>
<tr>
<td>0.48 g</td>
<td>12.943 g</td>
</tr>
<tr>
<td>0.4956 g</td>
<td></td>
</tr>
<tr>
<td>9.77 mL (1 N)</td>
<td>4.7 mL</td>
</tr>
</tbody>
</table>
Figure 2. Schematic of Gas Separation Cell. PAA membrane is shown, for scale.

Table III. Gas Test Samples

<table>
<thead>
<tr>
<th>Test</th>
<th>Cu-Doped</th>
<th>Cu-doped NiAg</th>
<th>NiAg/30</th>
<th>NiAg/24</th>
<th>NiAg/22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>2 x 300 min.</td>
<td>25 min.</td>
<td>2 x 20 min.</td>
<td>2 x 30 min.</td>
<td>Agg 2 x 30 min.</td>
</tr>
<tr>
<td>Test 2</td>
<td>2 x 300 min.</td>
<td>25 min.</td>
<td>2 x 20 min.</td>
<td>2 x 30 min.</td>
<td>Agg 2 x 30 min.</td>
</tr>
</tbody>
</table>
Hydrogen Permeable Membranes from Palladium-Coated Aerogel Alumina.

Without Image...

...The final cleaning at 500 - 600°C was conducted using a steady heating rate for 30 h. The temperature schedule for the palladium-only membranes was also an exception to this program. As noted earlier, palladium molybdenum hydrogen catalytic membranes heated in a hydrogen containing atmosphere to a temperature greater than 500°C. However, the schedule for palladium isothermal heating to 500°C under a hydrogen atmosphere then switching to the H2SO3/H2SO4/H2O4 catalytic mixture. The molybdenum molybdenum catalysts were reactivated to their desired state and the following day the samples were heated between 300 and 500°C over 3 h. The sample was then cooled to 300°C overnight and heated back to 500°C. The sample was finally cooled to 100 °C under the hydrogen containing atmosphere.

The BA [18] also performed the same experiment...
Activation in Hot Process of PAA Membranes

Activation is usually used to seed the surface of the PAA membrane with palladium to enhance its selectivity for hydrogen. The techniques used depend on the nature of the PAA. During immersion in the activation solution, the palladium species reduces the palladium to palladium metal which then deposits on the surface of the membrane. The hydrogen exchange reaction occurs on the surface of the PAA after activation. The surface site of an activated PAA membrane is shown in Figure 1.

![Figure 1: Activated PAA membrane](image)

The deposition of Pd and Ag into the holes in a layer of impregnated Pd and Ag gauze, which are the membranes, is carried out in a solution of Pd and Ag aqueous, which are the alloy coating of 35% Ag and the most selective hydrogen permeability, and the lowest critical temperature. Experiments were carried out using a number of plating solutions with different Pd:Ag ratios. All solutions gave a coating coating of Pd and Ag. Experiments showed that 50:50 solutions resulted in a mixture which, when coated with 50% Ag appeared to be more selective in column 100% analysis, and an immersion plated for 60 minutes in solutions containing 50:50 Ag, 75:25 and 100:0 showed that the films had a higher Ag content than that of their precursor solutions, e.g., for the 75:25 solution the composition of the coating after 60 minutes was 65:35. This phenomenon has been previously reported and indicates that Ag in proportionally plated resulting in Ag enrichment. A Pd:Ag 80:20 salt solution resulted in a 80:20 Ag enrichment observed in a 600:60 film on a glass test tube after 60 minutes in a solution of 80:20. The inconsistency between the 80:20 solution and the test tube results cannot be due to the experiment with individual deposition. The 50:50 Ag purification showed another interesting trend. 100% mapping of the Pd and Ag coating in the film was performed on membranes plated for 30 and 60 minutes. Both samples showed uniform coating on the surface. The membranes were coated in an identical manner. The membranes coated in the same manner, except that the membranes were coated for 30 minutes. The membranes were then coated in an identical manner. The membranes were coated in the same manner, except that the membranes were coated for 60 minutes. These results suggest that Ag in deposition from solutions on the surface followed by a subsequent dip in the new solution resulted in the presence of Ag clusters on the surface. Hence, modifying the treatment of plating will reflect the evolution of Pd and Ag in the film.

Individual deposition was measured as a means to produce films with more controllable Pd and Ag ratios. The individual deposition requires immersion prior to deposition as with the co-deposition method. Initially only two layers were attempted, the first Pd and the second Ag. This was successful and the results of Pd and Ag could be exactly controlled. However, the resulting films were very thin and thus unreliable for use in laboratory measurements as they were more prone to breakage and degradation. Preservation of thicker films was accomplished by growing Pd then Ag then Pd. This produces structures that should provide longevity by minimizing the inter-metallic surface area. However, the second Pd deposition resulted in minimal weight increase indicating that deposition had not occurred. The initial Pd deposition requires a Pd standard surface, so it is likely that the lack of such a surface has prevented

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**Manufacturing and Processing**

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the second film deposition from occurring. The attachment was dried and weighed before and after each cycling step to gain quantitative assessment of the deposition on these porous unmodified colloidal Au-5Ag nanoparticles. This data in turn was instrumental in demonstrating that while adhesion grew more significant with exposure time than aged solutions, all greater samples were poorly adhering to modified metal substrates. The surface of the gold film after cycling for 30 min. is shown in Figure 6. The surface is smooth and even, but still shows some evidence of film thinning in the structure. Plating for longer than 30 min. decreased the film thickness and other defects.

Figure 5: Surface of a Palladium-only film after 30 min. deposition. Scale bar is 1 micron.

Alloying

Microstructural and chemical analysis employing techniques such as x-ray spectroscopy were carried out on a variety of samples from Au and Au-5Ag. The samples were prepared between 200-400°C and 50-800°C and were above the microstructural transition at ~200°C and ~600°C, while the Au-only and Au-5Ag samples only showed a microstructural transition at ~500°C. All alloying processes were performed with a low humidity. It was proposed that the transition was at 300°C due to the inability of the metal to oxidize at this temperature. Upon that change, alloying was conducted at 400°C for 1 h, initially in vacuum. However, alloying did not occur under those circumstances. Although ~300°C was sufficient for alloying, after heating for 1 h, the film determined melting in unsuitable low gas separation. This degradation was confirmed at ~200°C and ~600°C and appeared to be a result of using argon. When alloying was attempted in forming gas (5% H₂ to 95% Ar), no degradation was evident. Under forming gas the conditions were altered, allowing for 500°C for 12 h which is sufficient for alloying. The success of the film treatment were demonstrated by EDX as shown in Figure 2.

The "as-clad" area of a post-alloyed sample showed less peaks at oxygen, Au-5% Ag and Au-5% Ag due to Ag and Au respectively. The "alloyed area" area showed increased alloying as expected by a single phase appearance. Au-5% Ag. The position of the alloyed peaks can be used as a method to estimate the relative proportions of Ag and Au in the alloy, as demonstrated in the XRD profile in Figure 3.
The surfaces of two different samples after alloying are shown in the XRD images in Figure 8. These images were from samples treated at 550 °C for 2 h. The surface of the sample containing 10% Pd shows a peak at 44 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd. In contrast, the sample containing 50% Pd shows a peak at 48 °C, which is the peak of the Ag phase, indicating that the sample is pure Ag. The surface of the sample containing 75% Pd shows a peak at 46 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd. The surface of the sample containing 90% Pd shows a peak at 45 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd. The surface of the sample containing 10% Ag shows a peak at 44 °C, which is the peak of the Ag phase, indicating that the sample is pure Ag. The surface of the sample containing 50% Ag shows a peak at 48 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd. The surface of the sample containing 75% Ag shows a peak at 46 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd. The surface of the sample containing 90% Ag shows a peak at 45 °C, which is the peak of the Pd phase, indicating that the sample is pure Pd.
Heterogeneous Membrane Reactor: A Novel Decision-Making Framework

Figure 9. SS316 images of membrane surfaces after alloying.

A diagram illustrating the membrane surfaces after alloying shows significant changes in the microstructure. The images reveal a uniform distribution of alloy elements, indicating a successful alloying process. The surface texture appears smoother compared to the untreated membrane, suggesting improved stability and durability.

Figure 10. SS316 images of membrane surfaces after thermal cycling. The images show the effects of thermal cycling on the membrane's integrity. After thermal cycling, the membrane exhibits a slight change in color, indicating possible stress-induced damage. The images also show variations in the surface texture, suggesting potential microstructural changes due to thermal cycling.

Graph Representation:

A graph demonstrating the relationship between membrane performance and operating conditions is presented. The x-axis represents the operating temperature, while the y-axis shows the membrane's permeability. The data points indicate a positive correlation between temperature and permeability, suggesting that increasing temperatures lead to improved membrane performance. However, at higher temperatures, the permeability begins to decline, indicating a potential thermal limitation.
and 300 °C on the membranes were tested under a 10% Hz atmosphere. In this temperature window, no significant change was observed. Above 300 °C, the Hz flux (permeance) increases significantly, while the Hz and CO2 fluxes remain at a minimal level.

The 10% Ag:80% Ni-coated specimen was sealed effusively with minimal leaks. Though there is some variability in the data (plotted in Figure 1D), overall, the Hz flux increases with increasing temperature, while the flux of both Hz and CO2 remains stable at a minimal level, essentially at the detection limits of the mass spectrometers. Up to ~300 °C, the Hz permeate phase with membrane and nanowires shows that above 300 °C there is a more rapid increase in Hz flux through the membrane with accelerated transport through the phase. This increase in Hz flux above 300 °C is consistent with the results for the Ag-only membranes (Figure 1C), indicating that increasing the Ag content to ~30% (by 10% increase in Hz selectivity).

Figure 11. Gas Separation Results for Palladium only Membrane

Figure 12. Gas Separation Results for 10% Ag:80% Ni Membrane
Both the Pd-Ag 90:10 and 95:5% co-deposited samples did not show any significant differences in the AES data. These samples had higher background levels of C but lower N levels. Although the data is not 100% accurate, a decrease in the intensity of the 88 Ag without a shift in the element positions. The higher Ag concentration reached 90% but the Pd-Ag ratio decreased. This resulted in a slight decrease in the C concentration but not a significant change in the N concentration. The AES data showed that the Pd-Ag co-deposited samples had higher background levels of C but lower N levels.


