Preparation of High Stability Pd/Ceramic/Ti-Al Alloy Composite Membranes by Electroless Plating

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High stability Pd/ceramic/Ti-Al alloy composite membranes were prepared by electroless plating. Ceramic membranes fabricated by an in situ oxidation method were used as an inter-diffusion barrier between the Pd layer and the Ti-Al alloy support of the membranes to prevent intermetallic diffusion. The stabilities of the ceramic membranes at high temperatures in an H2 atmosphere were investigated. The permeation performances and stabilities of the Pd/ceramic/Ti-Al alloy composite membranes were also studied. The results showed that the thickness, pore size, and microstructure of the ceramic membranes did not change significantly after the treatment in an H2 atmosphere at high temperatures, indicating that the ceramic membranes prepared by the in situ oxidation method were stable in an H2 atmosphere at high temperatures. The thickness of the Pd layer was ∼13 µm. The hydrogen permeability and H2/N2 selectivity of the Pd composite membranes at 773 K were 2.13 × 10⁻³ mol m⁻² s⁻¹ Pa⁻⁰·⁵ and 600, respectively. In addition, the H2 flux, N2 flux, and H2/N2 selectivity of the composite membranes remained nearly constant over three heat cycles (under the same conditions), indicating that the structures of the Pd/ceramic/Ti-Al alloy composite membranes were stable.

Keywords: in situ oxidation, Ti-Al alloy, ceramic, Pd composite membrane, hydrogen separation

INTRODUCTION

Recently, hydrogen has gained immense attention as a clean energy carrier for various industrial applications, especially for the development of fuel cells (Lemus and Duart, 2010; Vesborg et al., 2015; Sengodan et al., 2018). Pd membranes are widely used for hydrogen production and separation because of their high permeance and excellent selectivity for hydrogen (Keuler et al., 2002). The thickness of the Pd membrane is inversely proportional to the permeability. Hence, Pd-based membranes are usually prepared in the composite form, consisting of a thin, dense Pd top layer on a porous support (Zhang et al., 2006). Ti-Al alloys are considered promising porous supports for Pd membranes because of their higher specific strength, lower density, good oxidation resistance at higher temperatures, and similar thermal expansion co-efficient to that of Pd (Ma et al., 2007). However, although Ti-Al alloy averts the diffusion at temperatures lower than 873 K, the metal element diffusion phenomena occur between Pd and Ti-Al alloys after heat treatment at 973 K for 40 h in the presence of pure hydrogen (Zhang et al., 2011).

An effective approach to prevent intermetallic diffusion is to develop an inter-diffusion barrier layer between the Pd membrane and the metal support. However, the inter-diffusion barrier layer must be stable under high-temperature oxidation and reduction atmospheres. Huang and Dittmeyer (2006) used TiO2, YSZ, and ZrO2 as a diffusion barrier between the Pd layer and the
sintered-metal support of composite membranes. They indicated that YSZ was the most promising inter-diffusion barrier and showed better intermetallic diffusion prevention than ZrO$_2$ and TiO$_2$. Zhang et al. (2009) used two different methods (in situ oxidized metal and sol-gel-derived YSZ) to prepare intermetallic diffusion barriers between Pd layer and PSS support of Pd composite membranes. They found that both the inter-diffusion barrier layers showed effective intermetallic diffusion prevention and the membranes were stable at temperatures in the range of 773–873 K. However, only the YSZ inter-diffusion barrier layer could prevent diffusion at temperatures higher than 873 K. Mardilovich et al. (1998) carried out an in situ oxidation reaction prior to plating Pd/PSS membranes to form an oxide membrane layer on porous stainless steel to act as a diffusion barrier between Pd and PSS. They found that the membranes were stable to heat treatment at 623–723 K for 6,000 h. Shu et al. (1993) employed sputtering to prepare an ultrathin intermediate layer of titanium nitride between a Pd/Ag alloy membrane and a PSS substrate. The results showed that the membranes were stable at temperatures higher than 973 K. Zhang et al. (2012) fabricated TiO$_2$ membranes as a diffusion barrier on a Ti-Al alloy support to avoid intermetallic diffusion and to smooth the Ti-Al alloy support. The electron probe microanalysis (EPMA) and energy-dispersive X-ray spectroscopy (EDX) cross-sectional line scans showed that the TiO$_2$ layer was an effective inter-diffusion barrier and was stable after 40 h of heat treatment at 973 K in the presence of pure H$_2$. However, the adhesion between the TiO$_2$ layer and Ti-Al alloy supports at high temperatures should be improved.

In this study, the high-temperature stability of the ceramic/Ti-Al alloy support was investigated by the gravimetric method.

### TABLE 1 | Percent of weight gain of ceramic/Ti-Al alloy composite membrane after treatment in H$_2$ atmosphere at different temperatures for 20 h.

| Sample | 1#   | 2#   | 3#   |
|--------|------|------|------|
| m$_{fresh}$/g | 5.45 | 5.72 | 6.19 |
| Oxidation condition | 750°C/2 h | 750°C/2 h | 750°C/2 h |
| m$_{oxidizer}$/g | 6.33 | 6.57 | 7.24 |
| Reduction condition | 500°C/H$_2$/20 h | 600°C/H$_2$/20 h | 700°C/H$_2$/20 h |
| m$_{reduction}$/g | 6.33 | 6.57 | 7.24 |
| $\Delta m$ (m$_{reduction}$-m$_{oxidizer}$/g | 0    | 0    | 0    |

### TABLE 2 | Percent of N$_2$ flux change of ceramic/Ti-Al alloy composite membrane after treatment in H$_2$ atmosphere at different temperatures for 20 h.

| Sample | 1#   | 2#   | 3#   |
|--------|------|------|------|
| $\Delta P$/MPa | 0.03 | 0.03 | 0.03 |
| $J_{oxidizer}$/m$^3$.m$^{-2}$.h$^{-1}$ | 239.58 | 258.66 | 260.78 |
| Oxidation condition | 750°C/2 h | 750°C/2 h | 750°C/2 h |
| $J_{reduction}$/m$^3$.m$^{-2}$.h$^{-1}$ | 24.59 | 33.50 | 23.75 |
| Reduction condition | 500°C/H$_2$/20 h | 600°C/H$_2$/20 h | 700°C/H$_2$/20 h |
| $J_{reduction}$/m$^3$.m$^{-2}$.h$^{-1}$ | 20.35 | 36.04 | 20.35 |
| $\Delta J$ ($J_{reduction}$- $J_{oxidizer}$)/m$^3$.m$^{-2}$.h$^{-1}$ | -4.24 | 2.54 | -3.40 |

**FIGURE 1** | (A) Oxidized at 750°C/2 h X300. (B) 700°C/H$_2$/20 h X300. (C) Oxidized at 750°C/2 h X1200. (D) 700°C/H$_2$/20 h X1200. Surface SEM micrographs of the ceramic/Ti-Al alloy composite membrane in H$_2$ atmosphere at different temperature for 20 h.
gas flux measurements, EDX, X-ray diffraction, and scanning electron microscopy (SEM) in a hydrogen atmosphere. Then, Pd membranes were prepared on the surface of the ceramic/Ti-Al alloy support, and their morphologies, permeabilities, selectivities, and stabilities were investigated in detail.

EXPERIMENTAL

Preparation of Pd/Ceramic/Ti-Al Alloy Composite Membranes

Ti-Al alloy discs with a diameter of 34 mm, a thickness of 2.5 mm, and an average pore size of 6 µm were used as the support for preparing the thin Pd composite membranes. The porous Ti-Al alloy discs were prepared using the method reported by He et al. (2007).

Prior to preparing the membranes, the supports were cleaned with acetone in an ultrasonic bath for 2 h to remove surface dirt and grease and were then dried overnight at 423 K. The ceramic membranes were prepared on Ti-Al alloy discs by sintering the Ti-Al alloy discs under a static air atmosphere at 1,023 K for 2 h in an electric furnace at the heating and cooling rate of 2 K/min. The procedure for the preparation of ceramic membranes has been described in detail in Zhang et al. (2015).

Electroless plating was used to deposit the Pd membranes on porous ceramic/Ti-Al alloy supports (Alique et al., 2016). Prior to the preparation of the palladium membranes, the surface of the Ti-Al alloy supports was activated and sensitized to seed Pd nuclei (Keuler et al., 2002). The deposition of Pd membranes was carried out at 313 K, and the plating bath was changed after every 60 min until dense Pd membranes with an ideal thickness were obtained. Deionized water was applied to clean the surface of the palladium membranes immediately after electroless plating to remove the impurities adsorbed on the surface and pores of the Pd layer. The composite membranes were then dried overnight at 423 K for 12 h (Zhang et al., 2012).

Characterization of the Composite Membranes

An electronic balance (Sartorius BS2202S, Germany) was used to monitor the weight of the ceramic membranes. XRD (Bruker D8 Advance diffractometer, with Cu- radiation) was used to examine the phase composition of the ceramic/Ti-Al alloy composite membranes. EDX (JSM, 5600, LV, Japan) was used to analyze the composition of the ceramic membrane surface. The surface and cross-section of the palladium and ceramic membranes were investigated by SEM (Quanta 200, Philip, USA). The gas permeation of the composite membranes at high temperatures was measured using a permeability apparatus. The ceramic/Ti-Al alloy composite membranes were placed in a stainless steel permeator. The permeate side was maintained at atmospheric pressure, while the retentate side was fed with H2 or N2.
RESULT AND DISCUSSION

Stability of Ceramic/Ti-Al Composite Membranes

The ceramic membranes were prepared on Ti-Al alloy supports by an in situ oxidation method at 1,023 K for 2 h in an air atmosphere followed by their heat treatment in an H₂ atmosphere for 20 h at 773, 873, and 973 K, respectively. The stability test results of the membranes are summarized in Table 1. From the table, it is clear that the weight of the ceramic/Ti-Al alloys did not change when the heat treatment was carried out at temperatures lower than 973 K. This indicates that the oxide layers were stable at temperatures lower than 973 K. As can be seen from Table 2, the change in the N₂ flux of the ceramic/Ti-Al alloy composite membranes after the heat treatment was negligible. This indicates that the heat treatment did not destroy the pore structure of the ceramic membranes and that the ceramic layers were stable at high temperatures.

The surface SEM images of the ceramic/Ti-Al alloys are shown in Figure 1. The oxidation layer was evident, and no surface damages were observed even after the heat treatment at 973 K for 20 h in an H₂ atmosphere. Hence, the ceramic layer prepared by in situ oxidation was stable in an H₂ atmosphere. This is consistent with the weight and N₂ flux measurement results.

In order to investigate the effect of heat treatment on the elemental composition of the surface of the Ti-Al alloy support,
an EDX analysis of the membranes was carried out. As shown in Figure 2, oxygen was present on the support surface even after the heat treatment at 973 K in an H₂ atmosphere for 20 h, indicating that the ceramic layer prepared by in situ oxidation was stable at higher temperatures in an H₂ atmosphere.

The XRD patterns of the ceramic/Ti-Al alloy membrane are shown in Figure 3. The characteristic peak keeps constant even after the heat treatment in an H₂ atmosphere for 20 h at 773, 873, and 973 K, indicating that the ceramic/Ti-Al alloy composite membranes were highly stable to high temperatures in an H₂ atmosphere. These results are consistent with the EDX results shown in Figure 2.

The results of gravimetric, gas flux, SEM, EDX, and XRD analyses show that the ceramic layer prepared by the in situ oxidation method is a promising inter-diffusion barrier for Pd/ceramic/Ti-Al alloy composite membranes.

**Characterization of Pd/Ceramic/Ti-Al Alloy Composite Membranes**

The cross-sectional and surface SEM images of the Pd/ceramic/Ti-Al alloy composite membranes are shown in Figure 4. Figure 4A shows that the surface of the Pd membrane was not very smooth and homogeneous (mainly because of the high surface roughness of the ceramic/Ti-Al alloy support); however, no pinholes or cracks were observed. Although the images show smaller areas of the membranes, the gas leak test results further confirmed that the membranes had no defects at room temperature. Figure 4B shows that the thickness of the Pd membranes was uniform and was ∼11–14 µm, which is consistent with the value determined by the gravimetric method (average thickness = ∼13 µm).

**Gas Permeation of Pd/Ceramic/Ti-Al Alloy Composite Membranes**

Single gas permeation is an effective and simple method to measure the N₂ and H₂ permeation of palladium composite membranes. The pressure dependence of the hydrogen flux of the Pd composite membranes at various temperatures is shown in Figure 5. The H₂ permeation flux increased with an increase in the pressure difference ($ΔP_{H₂}$). The temperature also had an obvious effect on the H₂ permeation flux. These phenomena can be caused by the solution-diffusion mechanism.

Figure 6 shows the H₂/N₂ selectivity of the Pd composite membranes at different pressure and temperature. The results show that the selectivity increased with an increase in the temperature from 673–773 K. The H₂/ N₂ selectivity was found to be within the range of 200–700 under the operating conditions. This can be attributed to the thin Pd layers and the high surface roughness of the support.

**TABLE 3 | Comparison of the membrane prepared in this study and similar studies in the literatures.**

| Membrane | Pore size of support (µm) | Thickness (µm) | Temperature (°C) | $n$ | $F$ mol m⁻² s⁻¹ Pa⁻¹ | Separation factor | References |
|----------|---------------------------|----------------|-----------------|----|---------------------|-----------------|------------|
| PSS/GeO₂/Pd | 0.2 | 13 | 500 | 0.5 | $1.27 \times 10^{-3}$ | ∞ | | Tong et al., 2005 |
| PSS/Oxide/Pd | 0.2 | 21.3 | 450 | 0.5 | $1.43 \times 10^{-4}$ | ∞ | | Rothenbergera et al., 2004 |
| PSS/WO₃/Pd | 0.2 | 12 | 500 | 0.5 | $2 \times 10^{-3}$ | 10,000 | | Zahedia et al., 2009 |
| PSS/NaAZ80/Pd | 0.2 | 19 | 450 | 0.5 | $1.1 \times 10^{-3}$ | 608 | | Bosko et al., 2009 |
| PSS/Al₂O₃/Pd | 0.2 | 5 | 450 | 0.5 | $2.48 \times 10^{-3}$ | ∞ | | Li et al., 2007 |
| Ti-Al/TiO₂/Pd | 0.28 | 14 | 500 | 0.5 | $1.07 \times 10^{-3}$ | ∞ | | Zhang et al., 2012 |
| Ti-Al/ceramic/Pd | 0.44 | 13 | 500 | 0.5 | $2.13 \times 10^{-3}$ | 600 | | This work |

**TABLE 4 | Comparisons of activation energy of different palladium membranes.**

| Membrane | Thickness (µm) | Activation energy (kJ/mol) | Temperature (°C) | References |
|----------|----------------|---------------------------|-----------------|------------|
| Pd foil | 50 | 11.4 | 350–600 | Jung et al., 2000 |
| Pd/PSS | 20 | 16.38 | 350 | Mardilovich et al., 1998 |
| Pd/Al₂O₃ | 15 | 10 | 350 | Dittmeyer et al., 2001 |
| Pd/Al₂O₃ | 2.4–6 | 12.7–18.5 | 330–450 | Keuler et al., 2002 |
| Pd/TiO₂ | 0.3–0.4 | 21.27 | 500 | Wu et al., 2000 |
| Pd/TiO₂/Ti-Al | 14 | 13.65 | 350–500 | Zhang et al., 2012 |
| Pd/ceramic/Ti-Al | 13 | 13.86 | 400–500 | This work |
Table 3 shows a comparison of the membranes prepared in this study with those reported previously. The previously reported membranes had a thickness of $\sim 20\, \mu\text{m}$ and a hydrogen permeance coefficient of $\sim 10^{-3} \cdot 10^{-4}\, \text{mol m}^{-2}\, \text{s}^{-1}\, \text{Pa}^{-0.5}$. On the other hand, the hydrogen permeance coefficient of the membranes prepared in this study was of the order of $10^{-3}\, \text{mol}$.
m$^{-2}$ s$^{-1}$ Pa$^{-0.5}$. Hence, the selectivity of these membranes should be improved further.

Activation energy (E) is another critical parameter affecting the membrane permeability. The relationship between the hydrogen permeance of membranes and temperature can be shown by the Arrhenius equation as:

$$Q = Q_0 \exp \left(-\frac{E_a}{RT}\right)$$

The Arrhenius relation between temperature and the hydrogen permeance is shown in Figure 7. The average activation energy for $H_2$ permeation of the palladium composite membranes was calculated to be 13.86 kJ mol$^{-1}$ from 673–773 K, which is in agreement with the previously reported value. Table 4 lists the apparent activation energy of various membranes. These apparent activation energies were quite dispersed, due to various factors such as temperature, pressure, membrane structure, and other factors. Although the thicknesses of the Pd membranes were similar, different Pd membranes had different compositions, physical and chemical structures, and apparent activation energies.

**Hydrogen Permeation Stability**

The long-term stability of Pd composite membranes is crucial for practical applications. To investigate the effect of temperature variations on the $H_2$ permeation of the composite membranes, temperature cycling was performed. Figures 8–10 show the hydrogen flux, nitrogen flux, and $H_2/N_2$ selectivity of the Pd/ceramic/Ti-Al composite membranes operating in three heat cycles of 673 K $\rightarrow$ 723 K $\rightarrow$ 773 K $\rightarrow$ 723 K $\rightarrow$ 673 K (at $\Delta P = 0.1$ MPa). Under the same operating conditions, the $H_2$ flux, the $N_2$ flux, and $H_2/N_2$ selectivity of the Pd/ceramic/Ti-Al composite membranes showed no significant changes during the three heat cycles from 673–773 K, indicating that the Pd/ceramic/Ti-Al composite membranes possessed good thermal stability. This also shows that the ceramic layers were stable and could effectively avoid the inter-diffusion of metals.

**CONCLUSIONS**

Ceramic membranes fabricated on porous Ti-Al alloy supports by an in situ oxidation method were used as the barrier layer between a palladium layer and a Ti-Al alloy disc to avoid intermetallic diffusion. The stabilities of the ceramic/Ti-Al alloy at high temperature were investigated in an $H_2$ atmosphere, using gravimetric analysis, gas flux measurements, SEM, EDX, and XRD. The results showed that the thickness, pore size, and microscopy structure of the ceramic membrane were stable, even after heat treatment for 20 h at temperatures ranging from 773–973 K in an $H_2$ atmosphere. This suggested that these ceramic layers are promising inter-diffusion barriers. Pd membranes were prepared on the ceramic/Ti-Al alloy substrates by using the electroless plating method. The average thickness and permeability of the membranes were $\sim13 \mu m$ and $2.13 \times 10^{-3}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-0.5}$, respectively. The activation energy for $H_2$ permeation was 13.86 kJ mol$^{-1}$ from 673–773 K. Heat cycling was performed to examine the stability of the composite membranes. The $H_2$ flux, $N_2$ flux, and $H_2/N_2$ selectivity of the membranes showed no observable changes after three heat cycles from 673–773 K, indicating that the Pd composite membranes had good thermal stability.

**DATA AVAILABILITY STATEMENT**

All datasets generated for this study are included in the article/supplementary material.

**AUTHOR CONTRIBUTIONS**

DZ and YF: conceptualization. JZ: data curation. PY: investigation. YC and JZ: methodology. DZ: writing and editing. All authors have read and agreed to the published version of the manuscript.

**FUNDING**

This work was supported by the National Nature Science Foundation of China (No. 21206065; No. 21666018).

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer YJ declared a shared affiliation, though no other collaboration, with one of the authors YF to the handling editor.

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