Effect of aprotic solvent on characteristics of Al$_2$O$_3$ ceramic hollow fiber substrates prepared by phase inversion for hydrogen permeation applications

Edoardo Magnone, Seung Hwan Lee, Min Chang Shin, Xuelong Zhuang, Jae Yeon Hwang, Jeong In Lee and Jung Hoon Park

Department of Chemical & Biochemical Engineering, Dongguk University, Seoul, Korea

1. Introduction

Metal membranes made of palladium and palladium alloys are attractive candidates for high-purity hydrogen production and separation [1]. Because of their nearly complete hydrogen selectivity, great thermal stability, and mechanical resistance, hydrogen-permeable metal membranes constructed of Pd and related alloys have attracted academic and industrial interest [1]. Several research projects are underway to lower the cost of Pd-based membranes while also improving mechanical resistance and fabrication reproducibility [1,2]. Using a supported Pd membrane to reduce the amount of Pd necessary to generate a fully dense layer has been one of the most studied ways in recent years to reduce the cost of membranes [2]. The most common inorganic substrate materials are ceramic oxides [1,2], and dense Pd-based membranes are often made as thin dense layers on a tube [3] and flat disc [4] porous ceramic oxide substrate that offers mechanical support. Pd membranes deposited on aluminum oxide (Al$_2$O$_3$) substrates using the electroless plating approach [5–7] are viewed as the most promising technique for practical applications [6–11]. α-Al$_2$O$_3$ hollow fibers are a typical substrate for the production of Pd membranes [1,2,8,12–14]. Orakwe et al. [15] and Terra et al. [16] used an electroless deposition technique to produce thinner Pd layers on 77% alumina and 33% titania tubular ceramic oxide substrates and asymmetric alumina hollow fiber substrates, respectively. Coated Pd layers typically had thicknesses ranging from 1.4 µm [16] to around 5.0 µm [17], with thicknesses of up to 33.8 µm [18].

Ceramists and materials scientists are working hard to understand the properties of porous ceramic oxide substrates like Al$_2$O$_3$ ceramic hollow fiber substrate (AICHSF) for Pd layer deposition, as well as the various parameters and experimental factors that influence its final performance during phase inversion processing techniques. As a result, the ceramic oxide substrate macrostructure has been identified as a critical influencing factor [16,17]. According to earlier studies [3,5], the thickness of the metal layer and the type of the ceramic oxide substrate are the most important factors affecting the hydrogen permeation rate through the Pd-coated Al$_2$O$_3$ substrate. Aside from that, there are only a few studies in the literature that have attempted to increase the hydrogen permeability of Pd-coated Al$_2$O$_3$ substrates by calibrating the ceramic oxide substrate macrostructures. The influence of the ceramic oxide substrate properties on the characteristics of Pd supported membranes was investigated by Irfan Hatim et al. [17] and Mardilovich et al. [18], who came to the conclusion that the surface of the ceramic oxide substrate determines the morphology of the final Pd layer. Pd penetrated deeper into the pores of the ceramic oxide substrate than silver, according to Keeler et al. [19], with a depth of Pd of at least 3 ± 4 µm when deposited initially. By depositing silver first and then Pd,
on the other hand, coatings demonstrated extremely low pore penetration in the order of 1 μm [19]. Sun et al. [8] also demonstrated that the surface properties of ceramic oxide substrates have a significant influence on the thickness and surface morphologies of the Pd layer. Understanding how the AlCHFS ceramic oxide substrate macrostructures affect hydrogen permeation qualities is important not only for a fundamental understanding of the overall process but also for realizing the potential of these ceramic oxide materials.

AlCHFSs were developed in this study through a phase inversion process followed by a high-temperature sintering procedure. During the phase inversion procedure, aprotic solvents such as dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAC), and 1-Methyl-2-pyrrolidone (NMP) were utilized to investigate the relationship between solvent and non-solvent properties. Pd layers were deposited on the surface of various AlCHFSs using an electroless plating technique in a constant temperature water bath kept at 40°C. This temperature was chosen based on previous research [14]. In addition, the Pd-coated AlCHFSs were studied for hydrogen permeation behavior throughout a wide temperature range of 350°C to 450°C while keeping all other variables constant.

In brief, the following are the goals of this research work: (1) investigate the effect of aprotic solvents on the ceramic oxide substrate morphology prepared by phase inversion, and (2) establish connections between the ceramic oxide substrate characteristics and gas permeation performances in terms of hydrogen flux through Pd-coated AlCHFSs. The ultimate goal is to figure out which aprotic solvent-water correlation is required in a phase inversion method to maximize the ceramic oxide substrate’s nature for hydrogen permeation applications.

To our knowledge, this is the first study that shows that the characteristics of an aprotic solvent can be successfully employed to create improved ceramic oxide substrates, which can then be used to improve the final properties of a Pd-coated AlCHFS. In the field of polymeric hollow fiber membrane preparation by phase inversion, solubility parameters (i.e. total Hildebrand solubility, Hansen solubility, and fractional parameters) are fairly widely used, whereas there is no systematic information regarding the effects of aprotic solvents on the preparation of ceramic oxide substrates for advanced hydrogen productions [20–23].

2. Experimental

2.1. Al₂O₃ ceramic hollow fiber substrate (AlCHFS)

In this work, a two-step process involving phase inversion and high-temperature sintering was used to prepare α-Al₂O₃ hollow fiber substrates [24]. In particular, to prepare the AlCHFSs we used a mixture in equal parts of two different particle sizes of Al₂O₃ powders i.e. about 0.3 μm (99.9%, Kercoll Cell, Korea) and 0.5 μm (99.9%, Kercoll Cell, Korea) in diameter [25]. Polyethersulfone (PES, Ultrason® E6020P, BASF, Germany) as a polymer binder was used for preparing the starting solution. Polyvinylpyrrolidone (PVP, Sigma Aldrich, USA) was used as an additive with surfactant properties. In all preparations, the weight ratio of 0.3 μm Al₂O₃, 0.5 μm Al₂O₃, PES, and PVP on the dope solution is constantly equal to 30, 30, 5.75, and 0.75 wt.% to determine the composition of the dope solution, we use the results obtained in previous literature [26–28]. The remaining 33.5% of the dope solution is made up of aprotic solvent. We investigated three different types of aprotic solvents in this study; (1) Dimethyl sulfoxide (DMSO, 99.5%, Samchun Pure Chemical Co., Ltd, Korea), (2) N, N-Dimethylacetamide (DMAC, 99.5%, Samchun Pure Chemical Co., Ltd, Korea), and (3) 1-Methyl-2-pyrrolidone (NMP, 99.5%, Samchun Pure Chemical Co., Ltd, Korea). The DMSO, DMAC, and NMP solvents were selected to cover a wide range of Hansen solubility parameters like dispersion force component (δd), polar bonding component (δp), and hydrogen bonding component (δh) [29]. The total Hildebrand solubility parameter (δt) of aprotic solvents used in this work are calculated as follows:

\[ \delta t^2 = \delta d^2 + \delta p^2 + \delta h^2 \quad (1) \]

In addition, the corresponding fractional parameters are calculated using the following equations:

\[ 1 = f_d + f_p + f_h \quad (2) \]

Hansen solubility, total Hildebrand solubility, and fractional parameters are summarized in Table 1. The link between the respective fractional parameters associated with the aprotic solvents tested in this work is shown in Figure 1 as a Teas graph. These three aprotic solvents were chosen to see how solvents affected AlCHFS morphologies and then the hydrogen permeation properties of the Pd layer deposited on AlCHFS.

The prepared dope solution was stirred, degassed by a vacuum pump (IDP3, Varian, U.S.A.), and then extruded using a co-axial nozzle apparatus (External nozzle: inner diameter (ID): 3 mm; Internal nozzle: outer diameter (OD): 1.2 mm, ID: 0.5 mm) [28,30–32]. The N₂ pressure was supplied by a pump to obtain different extrusion pressures in the range from one to five bar. Table 2 summarizes the extrusion pressures.

| Table 1. Solubility and fractional parameters of the aprotic solvents used in this study. Water is reported for comparative purposes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | DMSO(CH₃)NO      | DMACC₂H₅NO      | NMPC₂H₃NO       | Water H₂O       |
| δd (MPa0.5)     | 18.4            | 16.8            | 18.0            | 15.6            |
| δp (MPa0.5)     | 16.4            | 11.5            | 12.3            | 16.0            |
| δh (MPa0.5)     | 10.2            | 10.2            | 7.2             | 42.3            |
| δt (MPa0.5)     | 26.7            | 22.7            | 21.5            | 47.8            |
| 100 fd          | 41              | 44              | 48.0            | 21              |
| 100 fp          | 36              | 30              | 32.8            | 22              |
| 100 fh          | 23              | 26              | 19.2            | 57              |
employed in this study. These conditions were chosen to investigate the effect of extrusion pressures on the nature of AICHFS in a given aprotic solvent (Sample 1, Sample 2, and Sample 3), as well as the effect of aprotic solvents at a given extrusion pressure (Sample 3 and Sample 5). The extrusion pressure for the Sample 4 was one bar instead of programmed three bar like Sample 3 and Sample 5. The lower extrusion pressure employed in Sample 4 compared to other samples is due to the fact that a low spinning speed allows enough time for the phase inversion process between the internal coagulant and the dope solution at the AICHFS lumenside. In our experiments, the spinning was performed at room temperature with a humidity of about 40%, and there was no apparent difference in viscosity between different samples so Sample 4 was also studied to determine its morphological properties and hydrogen permeation. The internal coagulant flow rate was kept constant at 10 cc/min and the air gap was kept at 20 cm. Water was used as a non-solvent coagulant.

AICHFSs prepared in various aprotic solvents were left in a water coagulation bath for 24 h at room temperature (20°C) to allow the phase inversion process to occur, following which they were gently removed and cleaned several times with deionized water. The AICHFSs were cut using a laboratory scalpel to a uniform length of 25 cm and then dried for a day at 80°C. Finally, all AICHFSs were sintered in a high-temperature furnace for 2.4 h at 1450°C (Multipurpose 1500°C Box Furnace, Thermo-Scientific Lindberg/Blue M, United States) [33]. Table S1 shows the experimental specifics of the sintering conditions (Supplementary material).

2.2. Pd-coated AICHFS

A two-step procedure was used to deposit a Pd layer on the surface of the prepared AICHFSs. The AICHFS surface was first activated by seeding it with Pd nuclei. A solution of 1.2 g of stannous chloride (SnCl₂, 99.9%, Sigma Aldrich, USA) and 0.3 mL of hydrochloric acid (HCl, 35/37%, Samchun Pure-Chemical Co. Ltd., Korea) in 120 mL of distilled water was used to activate the AICHFS surface. The AICHFS was maintained in the acid SnCl₂ solution for 30 min. It was then cleaned many times with distilled water before being dried in an oven at 80°C for 30 min. At this point, the AICHFS was dipped for other 30 min into a solution of 0.3 mL tetramine palladium nitrate (Pd(NH₃)₄(NO₃)₂, 99.99%, Sigma Aldrich, USA) in water (120 mL) and HCl (0.3 mL), the details of which were previously reported [14]. After reacting with tetramine palladium solution, the AICHFS surface was washed with distilled water, and dried in an oven at 80°C for 30 min. For each AICHFS, the activation process with acid SnCl₂ solution and acid tetramine palladium solution was repeated five times. A vacuum-assisted electroless plating procedure was used to

Table 2. Experimental parameters to obtain the AICHFSs by a combined phase inversion and sintering process.

| Sample | Aprotic solvent | Extrusion pressure (bar) |
|--------|-----------------|--------------------------|
| 1      | DMSO            | 5                        |
| 2      | DMSO            | 4                        |
| 3      | DMSO            | 3                        |
| 4      | DMAC            | 1                        |
| 5      | NMP             | 3                        |
deposit the Pd layer on the activated AlCHFS surface after the activation step. In this process, the Pd bath solution was constituted of 15 mL of ammonium hydroxide solution (NH₄OH, 28–30%, Samchun Pure Chemical Co., Ltd, Korea), 3.4 g of disodium ethylenediaminetetraacetate dihydrate (Na₂EDTA, 99%, Sigma Aldrich, USA), 0.33 g of palladium(II) chloride (PdCl₂, 99%, Sigma Aldrich, USA), and 0.06 mL of hydrazine hydrate (H₂N₂.O, 50–60%, Sigma Aldrich, USA) in 76 mL of distilled water. The pH of the prepared Pd bath solution was 11.5–12. The thickness of the Pd layer is inversely proportional to the bath temperature, as indicated in a previous work [14], and the hydrogen fluxes increase as the electroless plating temperature increases. In the present experiment, a thermostatic water bath was used to keep the Pd bath solution at a consistent temperature of 40°C. There were four steps to the deposition process, which took a total of 10 h. Because hydrazine has a high reactivity, it was divided into four additions by injecting it at different times: 0, 1, 2, and 3 h. On the lumen side of AlCHFS, vacuum was applied to assist the deposition of a Pd layer on the shell side.

2.3. Characterizations of the ceramic oxide substrate and Pd-coated AlCHFS

The as-prepared and Pd-coated AlCHFSs were characterized by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Tokyo, Japan) with energy-dispersive X-ray (EDS, S-4800, Hitachi, Japan).

2.4. Gas permeation measurements

The gas permeation performances of the AlCHFS were confirmed through a hydrogen gas permeation experiment (350–450°C). Before the hydrogen permeation test, all samples were annealed in pure hydrogen (Pₐ = 1 bar; Pₒ = 0 bar) for 2 h at 450°C [34]. Figure 2 shows a schematic diagram of the experimental setup. One end of the AlCHFS was sealed with a ceramic sealant (Aron Ceramic, Aron Alpha, Japan) and dried at 150°C for 2 h. The other end was connected to the pressurizing system. The gas (H₂, 99.999%) was supplied to the shell side of the AlCHFS and controlled by a pressure regulator so that the permeability according to the pressure difference between the shell side and lumen side was measured with a flow meter (Gilibraotr-2, Sensidyne, USA). Once the testing chamber reached the temperature of testing, a pressure of six bar was applied to the Pd-coated AlCHFS’ shell side using Argon (Ar, 99.999%) to evaluate its gas permeation capability from 450 to 350°C. The temperature was raised at a rate of 1.5°C min⁻¹. When there was no leak for 1 h, a hydrogen permeation measurement was performed. Permeated hydrogen was measured with hydrogen using a mass flow controller (MFM, model 5860E, Brooks Instrument, USA) and gas chromatography (GC-TCD, 7820A, Agilent Technology, USA). A back pressure valve (BPR) was used to manage the supply gas pressure.

The total gas permeability passing through the micropores of the AlCHFS can be expressed as the sum of Knudsen diffusion (Pₖ) and Poiseuille diffusion (Pₚ) as follows:

![Figure 2. Experimental setup for the measurement of gas permeation flux.](image-url)
$$P = P_b + P_r = \frac{2}{3} \left( \frac{8RT}{\pi NM} \right)^{0.5} \frac{1}{RT} \frac{r_p}{L_p} + \frac{8\mu RT}{L_p} P$$

(3)

where $P$ is the gas permeance (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), $P_b$ is the arithmetic mean of the inlet and outlet pressures (Pa), $r_p$ is the mean pore size (radius), $\frac{P}{RT}$ is the effective surface porosity, $R$ is the gas constant 8.314 (J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K), and $M$ the molecular mass of the hydrogen gas. Thus, it is clear from the above equation that,

$$P = K_0 + P_0 \rho$$

(4)

where $K_0$ and $P_0$ are the intercept and slope, respectively, of a liner extrapolation in a plot gas permeance versus mean pressures [35]. The mean pore size (μm) and the surface porosity (m$^{-1}$) of the AlCHFSs prepared by a combined phase inversion process in water and sintering process under different conditions were calculated from the intercept ($K_0$) and slope ($P_0$) as follows:

$$r_p = \frac{16}{3} \left( \frac{P_0}{K_0} \right) \left( \frac{8RT}{\pi NM} \right)^{0.5} \mu$$

(5)

$$\varepsilon = \frac{8\mu RTP_0}{r_p}$$

(6)

3. Result and discussion

3.1. Characterization of AlCHFSs

SEM pictures of cross-sections generated by fracturing the ceramic oxide substrates after sintering at high temperatures (1450°C, 2.4 h) are shown in Figure 3, permitting the AlCHFSs dimensions to be easily calculated. After sintering, the dimensions of Sample 1 are about 1.7 mm in diameter and 275 μm thick, compared to Sample 4 with 2.0 mm in diameter and 245 μm in thickness. The dimensions of Sample 2 and Sample 3 after the sintering process are in both cases 1.7 mm in diameter and 260 μm and 245 μm in thickness, respectively. According to these findings, the wall thickness of AlCHFS reduces significantly from 275 μm to 245 μm as the extrusion pressure decreases from five to three bar with DMSO aprotic solvent. The dimension of Sample 5 is about 1.7 mm as diameter and about 210 μm in thickness. These findings explain how the extrusion pressure affects the wall thickness of AlCHFSs. In fact, this suggests that the ceramic oxide substrate’s wall thickness can range from 210 μm to 275 μm, depending on the sort of application for which the AlCHFSs are utilized. The diameter of all AlCHFSs was found to be unaffected by the aprotic solvent type.

The second point to mention is that the choice of aprotic solvents during the phase inversion procedure in water had a substantial impact on the morphologies of AlCHFSs. The overall pore structure of Sample 1, Sample 2, and Sample 3 is an asymmetrical structure with a finger-like structure just on the lumen side and a pore structure on the shell side. This is consistent with the findings for flat disc ceramic membranes for potential use in water treatment [4]. For the three samples prepared by DMSO solvent with different extrusion pressures, the ratio between the size of the pore structure and the size of the finger-like structure was always about 60:40. Therefore, when DMAC and NMP solvents are used to prepare AlCHFSs, as shown in the SEM analysis image in Figure 3(d,e), a different type of morphology is observed. When DMAC and NMP solvent were used, the columniform pores with different diameters on the finger-like structures were formed both inside and outside of the AlCHFSs, where the pore structure was still observed in the middle of the cross-section (see Figure 3(d,e)). In detail, Sample 4 and Sample 5 had 32:28:40 and 55:12:33 ratios of finger-like structure on the lumen side, pore structure in the middle, and finger-like structure on the shell side, respectively. The diverse aprotic solvents utilized during the phase inversion process in water are the main cause of the morphological change. Accordingly, both dispersive interaction linked with the dispersion

Figure 3. Representative SEM images of the cross-sections obtained by the fracturing of the AlCHFS prepared by phase inversion process: (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, and (e) Sample 5.
force component ($\delta d$) and polar bonding interaction due to the polar bonding interaction ($\delta p$) between DMSO and water are bigger than DMAC/water and NMP/water, but the hydrogen bonding interaction of hydrogen bonding component ($\delta h$) is practically unchanged in the case of DMSO and DMAC. In conclusion, the overall Hildebrand solubility parameter is related inversely to the structural symmetry of finger-like structures in and out of the prepared AICHFS ($\delta t$) (See Table 1). The finger-like structure on the shell side expands toward the outer part as total Hildebrand solubility decreases from Sample 1, Sample 2, and Sample 3 prepared with DMSO solvent (26.7 MPa$^{0.5}$) to Sample 4 obtained with DMAC solvent (22.7 MPa$^{0.5}$). As total Hildebrand solubility decreased further, as in Sample 5 with NMP aprotic solvent (21.5 MPa$^{0.5}$), deeper finger-like structures appeared on both sides of the AICHFS, and the pore structure in the middle of the cross-section decreased.

Many parameters have been shown to play a role in the phase inversion process, including dope and bore solution flow rates, temperature, humidity, and the air-gap region between the spinneret and coagulation bath \cite{16,17,24–27,36,37}. The findings of this study suggest that the nature of an aprotic solvent can be successfully employed to influence changes and improve the properties of ceramic oxide substrates such as AICHFS. While several factors play a part in ensuring AICHFS quality, the nature of the solvent and the mutual affinity between solvent and non-solvent (water) is one of the most important. The finger-like structure on the shell sides became more pronounced as the aprotic strength was reduced. These results are consistent with previous research on polymeric hollow fiber membranes \cite{20–23}.

The gas permeance test for the AICHFS prepared by the phase inversion procedure is shown in Figure 4. The dashed lines indicate the best linear fits to the data. AICHFS has a pressure-dependent hydrogen permeance. With increasing pressure, the hydrogen permeances of the five AICHFS increase. Based on these findings, the hydrogen permeances are found to correlate with the extrusion pressure at a given aprotic solvent (i.e. DMSO). As the extrusion pressure is reduced, the hydrogen permeance increases in the following order: Sample 1, Sample 2, and Sample 3. Sample 4, with a ratio of 32:28:40 between finger-like structure on the lumen side of the AICHFS, pore structure in the middle, and finger-like structure on the shell side, has a larger hydrogen permeance than Sample 5 with a ratio of 55:12:33. In comparison to other cases, Sample 1’s linear fit to permeation data had a lower slope. This could be because the Knudsen flow contributed more to total gas permeation than the other samples, which could be due to the tiny pore size \cite{35}.

The mean pore size and surface porosity of the prepared AICHFS are estimated using the intercept and slope calculated from the linear fits to the permeance functions of Figure 4 and Equations (5–6) \cite{17,35}. Table 3 displays the results. The pore size value obtained with Sample 4 is half that of Samples 1, 2, and 3. This behavior can be attributed to a synergistic

![Figure 4](image_url)  

**Figure 4.** Permeance according to the mean pressure of the AICHFS prepared by phase inversion process in water.
Table 3. Mean pore size and surface porosity of AlCHFS.

| Sample | Mean pore size (µm) | Surface porosity (m⁻¹) |
|--------|---------------------|------------------------|
| Sample 1 | 0.157              | 10,737                 |
| Sample 2 | 0.165              | 14,530                 |
| Sample 3 | 0.166              | 16,748                 |
| Sample 4 | 0.083              | 53,966                 |
| Sample 5 | 0.152              | 16,241                 |

The effect between the extrusion pressure (see Table 2) and the effects of DMAC solvent during the phase inversion method for Sample 4. The obtained mean pore size values are consistent with recent publications on Al₂O₃ hollow fibers, which reported values ranging from 0.034 µm [17] to 0.88 µm [38]. The mean pore diameters of AlCHFS produced using an aprotic solvent such as DMSO are generally stable, with a little increasing trend from Sample 1 to Sample 2 and then Sample 3. When we look at the characteristics of sample 5, we can observe that the pore size and porosity are similar to those of the DMSO samples. This observation was supported by SEM investigation, which revealed that the aprotic solvent is a determining factor in determining particular AlCHFS characteristics.

The surface porosities measured were higher than those indicated by Irfan Hatim and colleagues [17], who suggested that the porosity of the ceramic oxide substrate should be at least 1000 m⁻¹ with a Pd layer thickness of less than 10 µm. The effects of the AlCHFS on hydrogen permeability are minor under these conditions, with a value of less than 5% [17].

3.2. Characterization of Pd-coated AlCHFS

The images of the cross-sections generated by fracturing the Pd-coated AlCHFS acquired by SEM examination are shown in Figure 5. Throughout all of the preparations, the experimental conditions were kept consistent. The cross-section images of Sample 1, Sample 2, and Sample 3 (see Figure 5(a-c)) demonstrate a Pd layer thickness of around 9.7 µm, indicating that the Pd layers are largely unchanged in the case of the DMSO solvent-based substrate. The observed Pd layer thickness agrees well with the value estimated by Li et al. [34]. The thicknesses of the Pd layers for each Pd-coated AlCHFS are reasonably consistent with one another and with other researchers’ findings [16,17]. Keeping all other experimental conditions constant, it is interesting to note that the same electroless plating testing settings can result in varied Pd layer thicknesses. The thickness of the Pd layer is inversely related to the electroless plating temperatures, as previously observed [14]. In this work, while maintaining all other experimental parameters constant, it can be concluded that not only the electroless plating temperature is an important variable to design the right Pd-coated AlCHFS [14] but that the Pd layer thickness can be influenced indirectly by the nature of the aprotic solvent used to prepare the ceramic oxide substrate.

A closer look at Figure 5(d) reveals that the Pd layer in Sample 4 had a wide thickness variability, ranging from 6.6 µm to 21.3 µm high peaks, which can be explained indirectly by the high surface porosity of Sample 4 created with DMAC solvent. This is supported by the fact that the coating layer on Sample 5 prepared with NMP solvent varied from 4.1 µm to 6.6 µm, and the columniform pores of the finger-like structure on the shell side were generally shallower than those on Sample 4. Surface porosity in Sample 1 was around 10,000 m⁻¹. Surface porosity values of around 16,000 m⁻¹ were found in Samples 3 and Sample 5, with Sample 4 having a relatively high value (50,000 m⁻¹). As a result, the aprotic solvent used in the phase inversion procedure had an effect on the columniform pores and surface porosities of finger-like structures on the shell side of ceramic oxide substrate. The above-mentioned process factors, in turn, can influence the deposited Pd layer properties. The thickness values of the Pd layer is compatible with the results of the EDS line-scanning analysis in the next section, as will be discussed.

The thickness of the Pd layer was also measured by EDS line-scanning, permitting the distribution of the Pd element to be confirmed throughout three
representative Pd-coated AlCHFS cross-sections. Figure 6 shows the EDS line-scanning results of the Pd layers deposited on Sample 2, Sample 4, and Sample 5. Sample 2 has a Pd thickness of approximately 9–10 μm. Corresponding values of Pd thickness, as determined from EDS line-scanning profile images of Sample 2, are satisfactory agreement with values measured by the SEM photographs in Figure 5(b). In more specific terms, as shown in Figure 6, the thickness values of Pd layers obtained by SEM and EDS line-scanning measurements are always highly correlated. In this regard, the EDS line-scanning analysis shows that the Pd element is not penetrated into the pore structure on the shell side of Sample 2, but is infiltrated on the finger-like structure of Sample 4. As a result, in the context of Sample 2, the coating bath solution did not penetrate the pore structure on the shell side, causing the Pd layer to appear as a homogeneous, constant-thickness structure. On the other hand, in the case of Sample 4, a small amount of Pd atoms penetrated the shell side finger-like structure. From the difference of the equivalent thickness of the Pd layer calculated from the weight gain after Pd loading and the measured values from the SEM images, Irfan Hatim et al. [17] concluded that the Pd layer was not only coated on the surface as a dense layer but it also penetrated the surface of the hollow fiber to some degree. Because the deposited Pd would infiltrate the pores of the Al₂O₃ substrate, the hydrogen permeation process via the Pd-coated AlCHFSs is much more complex than through pure Pd membranes, according to Irfan Hatim et al. [17]. Indeed, the hydrogen permeation process through the Pd-coated AlCHFSs is a complex process involving at least five physical-chemistry steps in succession, including (1) external gas transport from the bulk gas phase (H₂) to the deposited Pd membrane surface on the retentate side of Pd-coated AlCHFSs, followed by (2) permeation step in the surface-coated Pd membrane. As a result, the third stage consists of (3) gas permeation via the penetrated Pd membrane followed by (4) permeation in the porous substrate and, finally, the (5) external molecular transport from the penetrated Pd surface on permeate side to the bulk gas phase [17]. In particular, the authors showed that the hydrogen flux increases with the mean pore radius because the ceramic oxide substrate resistance to mass transfer is reduced as a portion of the deposited Pd penetrates the alumina substrate pores [17].

Mardilovich et al. [18] also observed that the thickness of the Pd layers was determined by the size of the pores present in the ceramic oxide substrate when all

Figure 6. Representative SEM imagine and EDS-line scanning results of the Pd-coated AlCHFSs prepared by phase inversion process with three different aprotic solvents followed by electroless plating method: (a) Sample 2, (b) Sample 4, and (c) Sample 5.
other variables were held constant. Our results for Sample 4 agree with previous research [19], which found deep Pd penetration into the pores of the ceramic oxide substrate. Sample 4’s thickness decreases by around 35% when compared to samples created utilizing a phase inversion approach in the presence of DMSO solvent. The findings of our study indicated that the AlCHFS’s shell-side nature has a considerable impact on Pd thickness. As shown in Figure 6(b), the Pd layer of Sample 4 with an effective surface porosity of 54,000 m⁻¹ was found to have a thinner thickness with a penetration degree of about 4–5 μm, which is at least two times lower than the thickness of Sample 2 prepared using DMSO solvent. All of these findings are in line with previous findings, which indicated that the thickness of the Pd layers and Pd penetration were influenced by the size of the surface pores in the ceramic oxide substrate [5,16–18].

The result of EDX mapping for Pd-coated AlCHFS prepared by phase inversion with three representative different aprotic solvents followed by electrolless plating (Supplementary material, Fig. S1) confirms that Sample 4 had an irregular and corrugated surface in comparison to Sample 3 and Sample 5 prepared with DMSO and NMP solvents, respectively. The Pd layer of Sample 4 has some visible larger clusters of defects. These clusters of defects can be as large as 10 μm in length. In line with prior research [39–42], these oval-shaped defects with a cauliflower-like shape were observed to be randomly distributed across the Pd surface.

### 3.3. Hydrogen permeation properties of Pd-coated AlCHFS

Within the temperature range of 350°C to 450°C, Figure 7 shows the measurement of hydrogen fluxes versus the difference of square root hydrogen partial pressures (Pa). According to the data in Figure 7, the permeated hydrogen increases in all cases when the temperature and hydrogen lumen pressure are increased, which is consistent with Sievert’s law. Increasing the temperature to 450°C, for example, increased the pure hydrogen flux to roughly 2.2 mol m⁻² s⁻¹ for Sample 1. These findings are in line with those found in the literature [14].

As can be seen in Figure 7, the aprotic solvent adopted in the phase inversion process has an indirect impact on hydrogen flux performance. The reported morphological properties of Pd-coated AlCHFSs can explain the differences in hydrogen flux capabilities. The results demonstrate that Sample 1 and Sample 2 have identical hydrogen flux behavior at 350°C, but Sample 3 has a distinct behavior only at high temperatures (400–450°C). As a generally speaking, hydrogen flux increases in the following order: Sample 1 < Sample 2 < Sample 3. Samples 4 and 5, on the other hand, had distinct hydrogen flux characteristics than the other samples. Sample 4 has slightly better permeating hydrogen properties than the other samples, reaching at about 0.25 mol m⁻² s⁻¹ at 400°C in the studied pressure range. Based on the findings of this study as well as studies of the morphology and penetration degree of the Pd layer on the ceramic oxide substrate in similar systems described in the literature [17,39–41], we argue that the superior hydrogen flux performance of Sample 4 can be attributed to a synergic effect of the following four factors: (1) the size of the surface pores in the ceramic oxide substrate prepared with an aprotic solvent with low total Hildebrand solubility (6t), (2) the depth finger-like structure on the support shell side, (3) smooth Pd surface porosity with a cauliflower-like shape randomly distributed across the Pd surface, and (4) the fact that a small amount of Pd penetrates in some points of the columniform porous structure up to 4–5 μm in depth.

The hydrogen permeance was measured at temperatures ranging from 350°C to 450°C to confirm our hypothesis. Table S2 in the supplemental material summarizes these findings. Hydrogen permeances tended to increase in the order of surface porosity in the following order: Sample 1, Sample 2, and Sample 3 (see Fig. S2). This finding cannot be attributed to Pd thickness because it remains relatively constant for the DMSO-prepared sample across the 9.8–9.6 μm Pd thickness range. As a result, other factors, such as increasing surface porosity of the AlCHFS from Sample 1 to Sample 3, must be to responsible indirectly for the increased hydrogen permeation performance. Instead, the hydrogen permeance of Sample 4 is found to be close to that for Sample 5. As a result of these findings, it is proposed that the close proximity of Sample 4 and Sample 5 results demonstrate that not only the thickness of the Pd film, but also the grade of Pd penetration on the shell-side finger-like structure of the ceramic oxide substrate structure can effectively control hydrogen permeated flux.

The Arrhenius plot of hydrogen permeance versus 1/T shown in Fig. S3 (see Supplemental Material) can be used to determine the activation energy of the processes. The linear trend in all plots indicates that the process is thermally activated in each sample. At temperatures between 350°C and 450°C, the activation energy for hydrogen transport through all samples is determined to be around 11.06–14.61 kJ mol⁻¹, which is similar to the value published in the literature [9,43,44]. Within the limits of the precision of the measurements, the activation energy was found to range from 11.06 kJ mol⁻¹ for Sample 1 to 12.99 kJ mol⁻¹ for
Figure 7. Hydrogen flux versus the square root difference of the hydrogen partial pressure of the Pd-coated AICHFSs at (a) 450°C, (b) 400°C, and (c) 350°C operating temperatures (hydrogen feeding flow rate = 60 cc min⁻¹; shell side).

Sample 2, with 14.61 kJ mol⁻¹ for Sample 3. In the inset of Fig. 53 (see Supplemental Material), the activation energy versus surface porosities of Sample 1, Sample 2, and Sample 3, is illustrated. The activation energy for the samples prepared with DMAC solvent increases linearly with increasing surface porosity of ceramic oxide substrate, indicating that not only the Pd characteristics, but also the surface porosity of the substrate, plays an indirect role in the Pd-coated AICHFS properties and, as a result, in controlling the permeated hydrogen characteristics. The obtained activation energies of the hydrogen permeance through the Pd-coated AICHFSs compare very well with that of 14.6 kJ mol⁻¹ of a thin (2–3 μm) Pd layer deposited on Al₂O₃ hollow fibers by electroless plating technique [9], 15.8 kJ mol⁻¹ of a thin (0.6 μm) Pd layer deposited on Al₂O₃ hollow fibers by a dip-coating process [43], and 12.3 kJ mol⁻¹ for Pd layer deposited on asymmetric porous α-Al₂O₃ tubes by the technique of electroless plating combined with osmosis [44], but smaller than that calculated from hydrogen flux through other types of Pd membranes prepared by different techniques, as 23–32 kJ mol⁻¹ for thin (0.1–1.5 μm) Pd and Pd/Ag alloy film deposited on a composite ceramic oxide substrate of α-Al₂O₃/γ-Al₂O₃ by Metallorganic Chemical Vapor Deposition (MOCVD) and magnetron sputtering [45], and 23 kJ mol⁻¹ for a thin (0.25–0.5 μm) Pd/Ag film deposited on a porous α-Al₂O₃ disc coated with a γ-Al₂O₃ layer by the sputter deposition technique [46].

More research is needed on the effect of aprotic solvent nature on dope solution viscosity, mutual affinity between solvent and non-solvent (water) in a phase inversion process, and obtained morphological ceramic oxide substrate. The findings of this study (1) demonstrated the importance of the chemical nature of the aprotic solvent used in this preparation technique, (2) provided an initial indication of the correlation between aprotic solvent and morphology of the ceramic oxide substrate, and (3) indicated how
4. Conclusions

Solubility parameters such as the Hildebrand solubility parameter (\(\delta t\)) have been widely used in the phase inversion process for the preparation of polymeric hollow fiber membranes, but few studies have started to look at the effects of solvent/non-solvent interactions on the preparation of ceramic oxides like Al\(_2\)O\(_3\) ceramic hollow fiber substrates (AICHFS).

The phase inversion technique can produce ceramic oxide substrates with a variety of morphologies and gas transport characteristics. In terms of hydrogen flux through Pd-coated AICHFSs, each stage in the phase inversion process must be optimized to provide ceramic oxide substrates for the deposition of the Pd layers.

As described in this paper, the morphologies of AICHFS can be easily calibrated and engineered by varying the affinity between aprotic solvent and non-solvent (water) during the phase inversion process. To obtain a better understanding of the effects of solvent/non-solvent interactions on the morphologies of the ceramic oxide substrate and the deposited Pd layer, three aprotic solvents were investigated.

A phase inversion procedure was followed by an electroless plating process to prepare Pd-coated AICHFSs. To investigate how the nature of an aprotic solvent impacted the morphological structure and hydrogen permeation characteristics of Pd-coated AICHFSs, AICHFSs were prepared with the following aprotic solvents: dimethyl sulfoxide (DMSO, \(\delta t = 26.7\) MPa\(^{0.5}\)), N,N-dimethylacetamide (DMAC, \(\delta t = 22.7\) MPa\(^{0.5}\)), and 1-methyl-2-pyrroli-done (NMP, \(\delta t = 21.5\) MPa\(^{0.5}\)). According to these findings, the structural symmetry of finger-like structures in and out of the prepared ceramic oxide substrate is inversely proportional to the total Hildebrand solubility, and the finger-like structure on the shell sides increased as the aprotic strength decreased. Furthermore, the results reveal that aprotic solvents affect the AICHFS’s mean pore size and surface porosity. The permeated hydrogen from a Pd-coated AICHFS prepared with an aprotic solvent with a low total Hildebrand solubility was higher than the permeated hydrogen from samples prepared with a solvent with a high value. Under optimal conditions, the Pd-coated AICHFS produces a hydrogen flux of approximately 0.24 mol m\(^{-2}\) s\(^{-1}\). The hydrogen permeability property was improved, indicating the ceramic oxide substrate’s positive impacts.

We also emphasize the necessity for more research in this field, particularly on the effects of different parameters on the phase inversion process, such as Hansen solubility parameters including dispersion force component (\(\delta d\)), polar bonding component (\(\delta p\)), and hydrogen bonding component (\(\delta h\)).

Acknowledgments

This work was supported by the Korea Electric Power Corporation under Grant number R21XA01-30.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Korea Electric Power Corporation (KR) [R21XA01-30].

References

[1] Habib MA, Harale A, Paglieri S, et al. Palladium-alloy membrane reactors for fuel reforming and hydrogen production: a review. Energy Fuels. 2021;35 (7):5558–5593.
[2] Cardoso SP, Azenha IS, Lin Z, et al. Inorganic membranes for hydrogen separation. Sep Purif Rev. 2017;47 (3):229–266.
[3] Santucci A, Borgognoni F, Vadrucci M, et al. Testing of dense Pd-Ag tubes: effect of pressure and membrane thickness on the hydrogen permeability. J Membr Sci. 2013;444:378–383.
[4] Lee M, Wang B, Wu Z, et al. Formation of micro-channels in ceramic membranes - Spatial structure, simulation, and potential use in water treatment. J Membr Sci. 2015;483:1–14.
[5] Seshimo M, Hirai T, Rahman MM, et al. Functionally graded Pd/y-alumina composite membrane fabricated by electroless plating with emulsion of supercritical CO\(_2\). J Membr Sci. 2009;342(1–2):321–326.
[6] Alique D, Imperatore M, Sanz R, et al. Hydrogen permeation in composite Pd-membranes prepared by conventional electroless plating and electroless pore-plating techniques over ceramic and metallic supports. Int J Hydrogen Energy. 2016;41(42):19430–19438.

[7] Yeung KL, Christiansen SC, Varma A. Palladium composite membranes by electroless plating technique: relationships between plating kinetics, film microstructure and membrane performance. J Membr Sci. 1999;159(1–2):107–122.

[8] Sun GB, Hidajat K, Kawi S. Ultra thin Pd membrane on α-Al₂O₃ hollow fiber by electroless plating: high performance and selectivity. J Membr Sci. 2006;284(1–2):110–119.

[9] Pan XL, Stroh N, Brunner H, et al. Pd/ceramic hollow fibers for H₂ separation. Sep Purif Technol. 2003;32(1–3):265–270.

[10] Okazaki J, Tanaka DAP, Tanco MAL, et al. Preparation and hydrogen permeation properties of thin Pd-Au alloy membranes supported on Porous α-alumina tube. Mater Trans. 2008;49(3):449–452.

[11] Yun S, Oyama ST. Correlations in palladium membranes for hydrogen separation: a review. J Membr Sci. 2011;375(1–2):28–45.

[12] Nair BK, Choi J, Harold MP. Electroless plating and permeation features of Pd and Pd/Ag hollow fiber composite membranes. J Membr Sci. 2007;288(1–2):67–84.

[13] Tanaka DAP, Tanco MAL, Niwa SI, et al. Preparation of palladium and silver alloy membrane on a porous α-alumina tube via simultaneous electroless plating. J Membr Sci. 2005;247(1–2):21–27.

[14] Magnone E, Lee SH, Park JH. Relationships between electroless plating temperature, Pd film thickness and hydrogen separation performance of Pd-coated Al₂O₃ hollow fibers. Mater Lett. 2020;272:127811.

[15] Orakwe I, Shehu H, Gobina E. Preparation and characterization of palladium ceramic alumina membrane for hydrogen permeation. Int J Hydrogen Energy. 2019;44(20):9914–9921.

[16] Terra NM, Lemos COT, da Silva FB, et al. Characterisation of asymmetric alumina hollow fibres: application for hydrogen permeation in composite membranes. Braz J Chem Eng. 2016;33(3):567–576.

[17] Irfan Hatim MD, Tan X, Wu Z, et al. Pd/Al₂O₃ composite hollow fibre membranes: effect of substrate resistances on H₂ permeation properties. Chem Eng Sci. 2011;66(6):1150–1158.

[18] Mardilovich IP, Engwall E, Ma YH. Dependence of hydrogen flux on the pore size and plating surface topology of asymmetric Pd-porous stainless steel membranes. Desalination. 2002;144(1–3):85–89.

[19] Keuler JN, Lorenzen L, Sanderson RD, et al. Characterization of electroless plated palladium-silica alloy membranes. Thin Solid Films. 1999;347(1–2):91–98.

[20] Buonomenna MG, Figoli A, Jansen JC, et al. Preparation of asymmetric PEEK/WC flat membranes with different microstructures by wet phase inversion. J Appl Polym Sci. 2004;92(1):576–591.

[21] Tasselli E, Diolli E. Tuning of hollow fiber membrane properties using different bore fluids. J Membr Sci. 2007;301(1–2):11–18.

[22] Li N, Xiao C, An S, et al. Preparation and properties of PVDF/PVA hollow fiber membranes. Desalination. 2010;250(2):530–537.

[23] Dahe GJ, Singh RP, Dudeek KW, et al. Influence of non-solvent chemistry on polybenzimidazole hollow fiber membrane separation. J Membr Sci. 2019;577:91–103.

[24] Smolders CA, Reuvers AJ, Boom RM, et al. Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids. J Membr Sci. 1992;73(2–3):259–275.

[25] Liu S, Li K, Hughes R. Preparation of porous aluminium oxide (Al₂O₃) hollow fibre membranes by a combined phase-inversion and sintering method. Ceram Int. 2003;29(8):875–881.

[26] Che JW, Lee HJ, Park JH. Preparation and characterization of α-alumina hollow fiber membrane. Membr J. 2016;26(3):212–219.

[27] Che JW, Lee HJ, Park JH. Preparation of alumina hollow fiber membrane with controlled pore structure for contactor process. Key Eng Mater. 2017;744:370–374.

[28] Lee HJ, Magnone E, Park JH. Preparation, characterization and laboratory-scale application of modified hydrophobic aluminum oxide hollow fiber membrane for CO₂ capture using H₂O as low-cost absorbent. J Membr Sci. 2015;494:143–153.

[29] Hansen CM. The three-dimensional solubility parameter and solvent diffusion coefficient [Dissertation]. Copenhagen (DK): The Technical University of Denmark; 1967. https://hansen-solubility.com/contents/HSP1967-OCR.pdf.

[30] Lee HJ, Park JH. Effect of hydrophobic modification on carbon dioxide absorption using porous alumina (Al₂O₃) hollow fiber membrane contactor. J Membr Sci. 2016;518:79–87.

[31] Magnone E, Lee HJ, Che JW, et al. High-performance of modified Al₂O₃ hollow fiber membranes for CO₂ absorption at room temperature. J Ind Eng Chem. 2016;42:19–22.

[32] Magnone E, Kim MK, Lee HJ, et al. Facile synthesis of TiO₂-supported Al₂O₃ ceramic hollow fiber substrates with extremely high photocatalytic activity and reusability. Ceram Int. 2021;47(6):7764–7775.

[33] Shi Z, Zhang Y, Cai C, et al. Preparation and characterization of α-Al₂O₃ hollow fiber membranes with four-channel configuration. Ceram Int. 2015;41(1):1333–1339.

[34] Li A, Liang W, Hughes R. Repair of a Pd/α-Al₂O₃ composite membrane containing defects. Sep Purif Technol. 1999;15(2):113–119.

[35] Mansourizadeh A, Ismail AF. Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO₂ absorption. J Membr Sci. 2010;348(1–2):260–267.

[36] Li L, Chen M, Dong Y, et al. A low-cost alumina-mullite composite hollow fiber ceramic membrane fabricated via phase-inversion and sintering method. J Eur Ceram Soc. 2016;36(8):2057–2066.

[37] Bell JG, Cavasin N, Knorpp AJ, et al. BaTiO₃-based thermistor hollow fibers prepared using a phase inversion spinning process for energy efficient gas sorption. J Eur Ceram Soc. 2022;42(8):981–992.

[38] Jiangsheng L, Lianjun W, Yaxia H, et al. Preparation and characterization of Al₂O₃ hollow fiber membranes. J Membr Sci. 2005;256(1–2):1–6.

[39] David E, Kopac J. Development of palladium/ceramic membranes for hydrogen separation. Int J Hydrogen Energy. 2011;36(7):4498–4506.
[40] Zhang X, Xiong G, Yang W. A modified electroless plating technique for thin dense palladium composite membranes with enhanced stability. J Membr Sci. 2008;314(1–2):226–237.

[41] Paglieri SN, Foo KY, Way JD, et al. A new preparation technique for Pd/alumina membranes with enhanced high temperature stability. Ind Eng Chem Res. 1999;38(5):1925–1936.

[42] Sari R, Yaakob Z, Ismail M, et al. Palladium–alumina composite membrane for hydrogen separator fabricated by combined sol–gel, and electroless plating technique. Ceram Int. 2013;39(3):3211–3219.

[43] Pan XL, Xiong GX, Sheng SS, et al. Thin dense Pd membranes supported on α-Al2O3 hollow fibers. Chem Comm. 2001;(24):2536–2537. 10.1039/b108395c.

[44] Li A, Liang W, Hughes R. Fabrication of dense palladium composite membranes for hydrogen separation. Catal Today. 2000;56(1–3):45–51.

[45] Xomeritakis G, Lin YS. Fabrication of thin metallic membranes by MOCVD and sputtering. J Membr Sci. 1997;133(2):217–230.

[46] Jayaraman V, Lin YS. Synthesis and hydrogen permeation properties of ultrathin palladium-silver alloy membranes. J Membr Sci. 1995;104(3):251–262.