Glass frit sealing method for macroscopic defects in Pd-based composite membranes with application in catalytic membrane reactors

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Abstract

A method of sealing defects in thin-film Pd-alloy composite membranes using commercially available glass frit powder is detailed. This technique involves application of a low melting point glass frit and in situ firing in inert gas to seal defects on the order of 1 mm in diameter. In this case, a glass frit with a melting point of 560 °C was found to produce stable seals at 520 °C during a 150 h stability test under pure hydrogen. Changing the feed mixture to 50 % H₂, 25 % Ar and 25 % steam, however, caused softening and subsequent seal failure at 520 °C. However, stable operation was achieved with water gas-shift mixtures when the temperature was reduced to 400 °C. The seal is demonstrated to be very robust within ammonia decomposition membrane reactors. Even though the frit seal had direct contact with the catalyst bed, it was observed to be stable in an ammonia decomposition reactor at 520 °C. The catalytic membrane reactor obtained 98 % conversion, producing above 99 % purity hydrogen with a flux of 0.11 mol m⁻² s⁻¹ for 150 h with no signs of seal degradation.

Keywords: Palladium (Pd) composite membrane; Defect repair; Glass frit seal; Ammonia decomposition; Catalytic membrane reactor

1. Introduction

Palladium and its alloys have garnered significant interest in the field of hydrogen separations for decades due to the ability of palladium to selectively transport hydrogen while maintaining good structural integrity. Although other metals, including vanadium, niobium and tantalum, have also been studied as hydrogen transport membranes [1–3], these metals are susceptible to severe hydrogen-induced embrittlement that is much more easily avoided in Pd-alloy systems [4,5]. Yet, implementation of palladium as a wide-scale hydrogen separation system has been hindered because of the metal's natural scarcity combined with its desirable catalytic properties, which make it one of the most expensive metals.

In an effort to reduce costs and increase the hydrogen productivity, the last few decades have focused heavily on the creation of thin films that are typically supported on a porous support for enhanced structural strength [6,7]. Synthesis techniques for these thin films essentially involve a method of growing the Pd film onto the support, including electroplating, electroless plating, chemical vapor deposition, physical vapor deposition, and sputtering [8]. Reducing the Pd thickness is desirable to increase flux and reduce cost, but these techniques often produce defects

in the final film that decrease purity by allowing non-hydrogen gas species to permeate through the resultant structure. The Pd thickness required to produce a leak-free membrane scales with the morphology of the underlying support, and using electroless plating Mardilovich et al. observed that the minimum thickness is 3 times the diameter of the largest pore within the support [9]. In addition, supported Pd membranes are susceptible to defect formation during handling or extreme operation that render a membrane useless. Thus a long standing goal in the community has been to develop efficient techniques to repair defects introduced during fabrication or after subsequent use.

One method used for defect repair is based on the osmosis plating technique developed by Varma and coworkers [10,11]. In this technique, a solute, such as sucrose or a chloride salt, is cycled through the interior of the support being plated while the Pd plating solution is exposed to the outer surface. This causes an osmotic pressure gradient that forces water with the Pd plating reagents into the pores of the Pd film, resulting in plating within these defects and subsequently a more dense and leak-free Pd layer [12]. Li et al. employed the osmosis technique to repair a Pd/ α -Al₂O₃ membrane and decreased the leak to 0.5 % of its initial value from $6.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $2.9 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ [13]. The thickness of the membrane, however, also increased from 7.6 μm to 10.3 μm , suggesting that this method should be considered for the initial membrane fabrication and preferably not any final repair.

To reduce the amount of palladium plated while simultaneously plating within defects, Zeng et al. repaired Pd membranes by separating the Pd precursor and reducing agents to opposite sides of the Pd film [14]. This idea, also described within a patent by Way and Hatlevik [15], is similar in nature to the osmosis technique because a higher rate of reaction will be observed within the defects in the membrane, but has the benefit of only plating in the defects because the reducing agent only meets the Pd precursor within these pores. Even though the palladium thickness did not increase, Zeng et al. obtained a decrease in nitrogen leak rates in their Pd film to 6 % of the initial value giving a final nitrogen leak permeance of $2.8 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. Based on initial and final images of the Pd film, defects on the order of ca. 100 μm were completely closed after repair plating.

Ryi et al., on the other hand, developed a polishing technique to repair Pd-based composite membranes fabricated via magnetron sputtering [16]. One sample membrane was sputtered to a thickness of ca. 4 μm on a planar porous nickel support (PNS) and initially observed to have a helium leak permeance of $3.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. Upon polishing this film with a fine grit alumina powder, the helium leak rate was reduced to less than $4.5 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. However, polishing methods are limited to planar supports where an equal and steady pressure may be applied. Tubular substrates would require significant effort to polish without uneven wear due to imperfect tubular shapes and/or limitations with most polishing equipment.

For larger scale defects, Lu et al. used metallic diffusion bonding to repair a Pd-based foil membrane [17]. They cut a 10 mm incision into their planar 25 μm thick Pd-25Ag foils and repaired this fabricated defect by pressing a small Pd-25Ag foil piece over the incision and annealing in hydrogen at 600 °C for ca. 60 h. Although this completely repaired the defect, it would be difficult to apply to a tubular design and requires significant palladium addition to

repair a membrane. In light of the fact that thin film Pd membranes are less than 10 μm thick, a significantly thinner foil would be required to keep costs of repair low.

Thus, the work detailed here is meant to offer one more tool for membrane repair – and particularly to fill a gap in the current techniques. The aforementioned techniques are able to cover either small defects ($\leq 100 \mu\text{m}$ in diameter) or defects above this size but only on planar membranes. This leaves a gap in the currently published database on how to repair defects greater than 100 μm on tubular supports, which may potentially be caused either by large defects in a ceramic or metallic filter support or by accidental scratches during handling of a fully fabricated film. By implementing a glass frit sealing strategy, we show that defects on the order of 1 mm can be effectively sealed for thin film Pd membranes supported on ceramic substrates. The thermal stability of these seals was evaluated for a number of industrially relevant membrane reactor environments including water-gas shift (WGS), steam methane reforming (SMR), and catalytic ammonia decomposition.

2. Experimental

2.1. Membrane fabrication

Tubular, asymmetric yttria-stabilized zirconia (YSZ) supports purchased from the Praxair Corporation were cleaned, characterized and plated using the electroless deposition method described in our recent publication [18]. Briefly, these supports had an average pore size of ca. 300 nm and were cleaned in ethanol and acetone solutions before plating. The supports were then activated with a Pd-acetate solution by spray coating with an airbrush until a uniform gold color was obtained. This Pd-acetate was then calcined in air using an open atmosphere oven at 350 $^{\circ}\text{C}$ for 30 min and reduced in hydrazine solution before Pd was deposited using a carbon-free electroless deposition bath. Multiple plating cycles were conducted until either the desired thickness or an acceptable nitrogen flux (non-hydrogen leak rate) was achieved at 20 $^{\circ}\text{C}$. An acceptable non-hydrogen leak permeance at room temperature is considered less than $10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, but initial values are occasionally higher than this after heating (e.g. M1). Membrane thicknesses were determined both gravimetrically and via X-ray fluorescence spectroscopy (XRF) using a Fischerscope X-Ray XDLM-C4 PCB spectrometer with a Ni filter operating at an accelerating voltage of 50 kV. A summary of the fabricated membranes and initial permeance values at 520 $^{\circ}\text{C}$ can be found in Table 1.

Table 1 Membrane data.

Membrane ID		M1	M2	M3
Active Area (cm^2)		11.6	10.7	23.6
Thickness (μm)	Gravimetric	4.5	4.8	8.8
	XRF	4.5	4.9	8.7
H_2 permeance at 520 $^{\circ}\text{C}$ ($\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$)		2.3×10^{-3}	2.0×10^{-3}	1.3×10^{-3}
N_2 permeance at 520 $^{\circ}\text{C}$ ($\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)		2.4×10^{-9}	9.4×10^{-10}	4.4×10^{-10}

2.2. Membrane sealing technique

The sealing strategy within this work consisted of three primary steps: fabricate a defect, apply a frit coating, and fire the frit to seal the defect. Although the eventual goal is to locate and seal natural defects in the plating process, this study attempted to show the viability of the seal on well-controlled samples. As such, defects needed to be fabricated on leak-free surfaces so the ability of the seal to effectively eliminate gas leaks could be determined. To fabricate the defects, a hole was created by twisting a blade tip on the surface of the palladium film until a hole of approximately 1 mm diameter was formed. This created a well within the surface that extended into the ceramic substrate, appearing similar in size and shape to the *Fabricated Defect* label in Figure 1.

Figure 1 Sample image showing the fabricated defect (left), applied but unfired frit (middle), and the seal after firing (right).

After creating the defect, a glass frit sealing solution of 1 g ml⁻¹ glass frit in deionized water was mixed. The manufacturer supplied material properties of the glass frit used in this study can be found in Table 2. Because this frit solution was only a mixture of particles in water without a binder to help maintain the suspension, the solution was always vigorously mixed immediately before application. Moreover, because the frit was only mixed with water, a dried solution could easily be recovered and re-used to minimize waste of the glass frit. To apply the frit to the defect, a thin-tipped paint brush was dipped into the solution and then lightly applied to the defect. Quick touches to the defect allowed the glass frit to wick onto the support, and after one to three quick applications, the pure white frit covered the defect in an appearance similar to the *Applied Frit* label in Figure 1.

Table 2 Glass frit properties.

Company	Nippon Electric Glass Co., Ltd.
Product ID	GA-12/325
Specific Surface Area (cm ² g ⁻¹)	5423
Mean Diameter (μm)	3.8
Density (g cm ⁻³)	2.94
Coefficient of Expansion (°C ⁻¹)	7.17×10^{-6}
Transition Point (°C)	464

Softening Point (°C)	559
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The final step involved firing of the applied frit for 90 min at the stated softening point of 560 °C to produce a sealed hole similar in appearance to the *Fired Frit* label in Figure 1. This was done under flowing nitrogen gas with a heating and cooling rate of 5 °C min⁻¹. By performing in situ nitrogen leak measurements, it was apparent during our initial testing that some frit applications completely sealed the defect within 30 min, whereas others did not fully seal the defect until ca. 70 min. Thus, a safe and so far 100 % effective time of 90 min was chosen for the final tests included in this study.

It is important to note that this technique did not use any organic binders within the frit and water mixture, making the firing step possible under a pure nitrogen environment. Although groups that have exposed Pd films to air saw no increase of non-hydrogen gases at 300 °C [19,20], exposure to 400 °C has shown that oxidation can increase defect size in thin Pd films and thus reduce hydrogen selectivity [21,22]. Whereas oxidation is only a near-surface effect, it remains possible that heavy oxidation and subsequent reduction can expand defects that already exist; and because this effect appears to become worse with increasing temperature, it can be presumed that the 560 °C required to melt the frit would cause irreparable damage to the Pd film. Regardless, it remains easy and effective to simply mix the glass frit with deionized water, making an oxygen (or otherwise heavily reducing) environment unnecessary.

2.3. Membrane reactor operation and analysis

Once synthesized, 1.0 cm outer diameter (OD) membranes were sealed onto 1/4 inch OD stainless steel piping using custom-made graphite ferrules from Chromalytic Technology and stainless steel compression fittings from Swagelok. The sealed membranes were then placed within a 1 inch OD stainless steel pipe and placed in one of two Lindberg MiniMite tube furnaces, as discussed next, for temperature control. The feed gas entered on the shell side of the membrane and the hydrogen that permeated the membrane was collected from the tube side. Neither sweep gas nor vacuum condition was applied for any experimental result presented in this study; all permeate gases were collected at local atmospheric pressure (ca. 82 kPa). A schematic of the testing module can be found in Collins and Way [23].

For the catalytic membrane reactor experiments (ammonia decomposition and steam methane reforming), a 0.5 % by mass Ru/Al₂O₃ reforming catalyst (Strem Chemicals) was packed around the annular space of the aforementioned membrane module and held in place by two SS mesh discs (100 mesh). The catalyst was crushed and sieved to a -30+40 mesh (425 µm to 600 µm) and a final volume (mass) of 30 cm³ (25 g) was used. Finally, the catalyst was activated in flowing hydrogen at 520 °C for 24 h before beginning any experiment.

Two permeation systems were used for the experiments included in the following sections. The permeation system for the pure gas thermal stability and ammonia decomposition experiments consisted of individual Porter Instruments mass flow controllers supplying H₂ (99.9 %), N₂ (99 %) and/or NH₃ (99.999 %) to the feed side, as well as mass flow meters to measure both the permeate and retentate flow rates. All flow data was recorded to a computer using a Visual Basic code running in Microsoft Excel. Internal temperature was measured via an Omega type K

thermocouple inserted through the permeate line with the tip near the inside center of the membrane. For mixed gas conditions, the permeate and retentate compositions were recorded via an SRI Instruments 8610C GC equipped with a 10' Hayesep D column and thermal conductivity detector (TCD) using H₂ as the carrier gas. The purity was measured and recorded every 20 min, with the time interval determined by the elution time of ammonia through the column. Based on results from a diluted calibration gas, the TCD and Hayesep D column combination is suggested to have lower detection limits of ca. 0.02 % nitrogen and ca. 0.05 % ammonia in hydrogen.

The permeation system for the WGS, SMR, and steam tolerance experiments was the same as in our recent SMR publication [24]. It consisted of individual Brooks 5850i mass flow controllers supplying Ar (99.98 %), CH₄ (99.97 %), CO₂ (98 %), CO (99 %), and/or H₂ (99.9 %) to the feed side, as well as a mass flow meter measuring the permeate flow rate. Steam was generated by metering deionized water into a pre-heater using a high-performance liquid chromatography (HPLC) pump controller (Teledyne Isco 500D). After exiting the reactor, both permeate and retentate streams passed through water-cooled tube-in-tube heat exchangers to condense the steam. All flow data, as well as internal temperature and pressure, was recorded to a computer using a DATAQ Instruments recorder. Internal temperature was measured via an Omega type J thermocouple inserted through the permeate line with the tip near the inside center of the membrane. For mixed gas conditions, the permeate and retentate compositions were recorded via a SRI Instruments 8610C GC equipped with a 6' Hayesep D column and TCD using H₂ as the carrier gas. The purity was measured and recorded every 10 min, with the time interval determined by the elution time of CO₂ through the column. Based on results from a diluted calibration gas, the TCD and Hayesep D column combination is suggested to have a lower detection limit of ca. 0.02 % for CH₄, CO and CO₂.

3. Results and discussion

3.1. Thermal stability of the seal

To obtain a good understanding of the thermal stability of this sealing technique, two tests were conducted: thermal cycling (Figure 2) and long-term operation (Figure 3). The thermal cycling test was conducted on M1 and consisted of a total of 20 heating and cooling cycles using a rate of 10 °C min⁻¹ between ambient temperature (ca. 20 °C) and 520 °C with a 1 h dwell. A nitrogen permeance was measured at ambient temperature before and after the heating cycle, and the plotted nitrogen permeance is the average of any overlapping measurements (Figure 2).

Figure 2 Nitrogen permeance measurements at ca. 20 °C between thermal cycling to 520 °C on M1.

Initially, the as-fabricated membrane was subjected to 5 thermal cycles, wherein stable nitrogen permeance between cycles was observed. A defect was then introduced into the Pd film before subjecting M1 to an additional 5 thermal cycles. At this point, the defect had increased the nitrogen permeance from an average of $2.5 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $1.3 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, but was still stable between thermal cycles. The defect in M1 was then sealed and subjected to the final 10 thermal cycles. Upon sealing, the nitrogen permeance was completely reduced to its original value of $2.5 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and was not observed to increase, suggesting this sealing method is robust and capable of withstanding any thermal cycling during operation in pure hydrogen and nitrogen.

It is interesting to note that the coefficients of thermal expansion (CTEs) for these materials were not identical, suggesting that perhaps the small size of the seal prevents any issues due to CTE mismatch. The CTE for Pd has been reported as $12.65 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 30 °C and 950 °C [25], which is slightly higher than the CTE values for a mole fraction of 3 % to 8 % YSZ of $10.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ to $10.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 600 °C [26]. The frit in this study, however, was stated to be $7.17 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 30 °C and 380 °C (Table 2), which is significantly lower than that of Pd. Yet, the high tolerance to thermal cycling without any apparent adhesion issues suggests that matching CTE values is not a critical requirement for maintain the integrity of the seal. Additionally, changes in the membrane materials, such as the use of a Pd-alloy or alumina supports, are not hypothesized to affect the success of this sealing technique.

The second thermal stability test consisted of long-term operation of membrane M3 at various temperatures with the intention of finding a maximum operating temperature for the applied frit. This test consisted of exposure to continuously flowing hydrogen at ca. 50 kPa except when changed to nitrogen for the permeance measurements shown in Figure 3. The temperature range of 520 °C to 600 °C was chosen specifically to straddle the frit softening (and firing) temperature of 560 °C.

Initially, the as-fabricated film was tested for one week at each temperature to obtain a baseline measurement of potential nitrogen permeance growth, plotted as circles in Figure 3. The nitrogen permeance growth rates for the as-fabricated film were very similar to those observed for un-

annealed pure Pd membranes on the same supports in our previous work [27,28], with the growth rate being 1.2×10^{-12} (mol m⁻² s⁻¹ Pa⁻¹) h⁻¹ at 520 °C and 8.7×10^{-12} (mol m⁻² s⁻¹ Pa⁻¹) h⁻¹ at 600 °C. Guazzone and Ma [29] also observed an increasing leak growth rate with temperature, reporting that the temperature dependence followed an Arrhenius relationship with an activation energy similar to the self-diffusion of Pd.

Figure 3 Nitrogen permeance over time at several temperatures for M3 soaked in 50 kPa H₂ between measurements. Circles represent data before sealing, whereas diamonds represent data after the defect was fabricated and sealed.

After obtaining the baseline data up to 600 °C, M3 was cooled and a defect was fabricated and subsequently sealed as before. The membrane was then re-tested beginning at 520 °C, whereat the initial nitrogen permeance was about equal to the last data point at 600 °C and a nitrogen permeance growth of 8.6×10^{-13} (mol m⁻² s⁻¹ Pa⁻¹) h⁻¹ was observed. This slightly lower growth rate compared to before sealing may be attributed to the 600 °C annealing period before sealing, as we found in our previous annealing work [28]. More importantly, upon raising the temperature to 560 °C, the nitrogen permeance began to grow significantly and the frit seal appeared to fail completely within the week of testing. This suggested that a clear transition in operating stability will occur when the membrane temperature approaches the softening point of a glass frit – most likely due to the glass frit becoming mobile and wicking or dripping out of the defect. In other words, the upper temperature limit for practical operation is dictated by the softening point of the glass frit.

3.2. WGS environments

The water gas shift reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, is an important process in hydrogen production and conversion is equilibrium limited. By extracting H₂ membrane reactors can enable this reaction to proceed to completion [30]. In an effort to demonstrate the potential benefits of sealing ca. 1 mm diameter defects, membrane M2 was subjected to three days of WGS tests at 400 °C and a trans-membrane pressure of 1.0 MPa. The gas mixture used in this instance consisted of the mole fractions 50 % H₂, 19 % H₂O, 27 % CO₂ and 4 % CO, with a total flow of 1.0 SLPM for the duration. Figure 4 shows the results of the WGS test, wherein the membrane was heated and tested for three separate 24 h periods.

The first 24 h period was performed as a baseline on the as-fabricated membrane, meaning no defect or seal had been applied. This test maintained a constant permeate purity of 99.6 %, but observed a declining hydrogen flux. Hydrogen flux inhibition due to CO has previously been reported in the literature for pure Pd membranes[31–33], so it remains a potential reason for the decline. It is also possible that the initial decline was due to grain growth and annealing of the fresh Pd film. More important to this study, the glass frit application accounts for less than 0.7 % of the membrane area and is thus unlikely to alter hydrogen flux in any significant manner.

After the first day, a defect was introduced that caused a drop in hydrogen purity to ca. 91 % throughout the second day of testing. Hydrogen flux began slightly higher than the end of the first day but continued to decline for the duration. The membrane was then cooled and the defect sealed with frit before testing for the third day. This caused the hydrogen permeate purity to regain its initial 99.6 % value, and, interestingly, the hydrogen flux stopped declining after the first several hours of operation. A stable hydrogen flux was found to be $0.14 \text{ mol m}^{-2} \text{ s}^{-1}$ during the final 13 h, suggesting that the CO adsorption on the Pd surface had come to an equilibrium for the given gas mixture after three days of exposure. Moreover, the complete recovery of the initial hydrogen purity shows that the seal was completely effective in blocking a defect that was able to lower purity by nearly 9 %.

Before each day of testing, a nitrogen leak permeance was measured for M2 at room temperature (ca. 20 °C). These values were $1.0 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ initially, $2.7 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ after creating the defect, and finally $9.2 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ once the defect was sealed. Post testing analysis of the frit seal included a visual leak check by applying a soap film to the outer surface of the membrane and pressurizing the inside up to 400 kPa to look for bubbles, but no indication of any leak near the glass frit was observed. With the results of this test, it was concluded that the frit seal appeared stable under WGS conditions at 400 °C and 1.0 MPa trans-membrane pressure.

Figure 4 H_2 flux and purity under WGS atmosphere at 400 °C and 1.0 MPa trans-membrane pressure before and after sealing M2.

3.3. SMR membrane reactor

A second important industrial reaction is steam methane reforming. The issue with SMR is that this endothermic reaction is limited by thermodynamics at the temperatures required to generate sufficiently fast kinetics [34]. However, catalytic membrane reactors can overcome this conflict because the simultaneous removal of hydrogen is able to increase thermodynamic conversion to completion [35]. To test the performance of the glass frit seal in an SMR environment membrane M2 was remounted with Ru/alumina catalyst, as described in Section 2.2, and run as a SMR membrane reactor. Because thermal stability testing suggested safe operation of the frit at 520 °C, this was chosen as the operating temperature for the furnace. The reactor conditions were similar to that of our previous work [24], with a steam-to-carbon ratio (SCR) of 3, trans-membrane pressure of 2.9 MPa, and a methane gas hourly space velocity (GHSV) of 184 h⁻¹. Although the furnace temperature maintained an outer temperature of 520 °C, the internal thermocouple measured a permeate temperature of ca. 505 °C due to the endothermic nature of the reaction.

Unfortunately, as Figure 5 shows, a significant quantity of impurities quickly began to permeate the membrane, causing a rapid decrease in the hydrogen purity. The purity declined to below 90 % within one day and was only 80 % at the end of the 170 h test. Additionally, this decline in purity was coupled with an increase in permeate flux and thus hydrogen recovery. The hydrogen flux was observed to increase from 0.10 mol m⁻² s⁻¹ to 0.15 mol m⁻² s⁻¹ at the end. It was initially hypothesized that the Pd film may have failed, similar to the long-term test of Sarić et al. [36], wherein purity declined to 81 % after 900 h of testing. However, once cooled and removed from the module, it was found that the glass frit seal on M2 had dislodged from the membrane defect and appeared a chalky white similar to the unfired glaze. In other words, the glass frit seal had completely failed under the SMR environment.

Figure 5 SMR results for M2 with a methane feed of 0.092 SLPM (GHSV of 184 h⁻¹) and SCR of 3. Reactor operated at 520 °C and a trans-membrane pressure of 2.9 MPa.

3.4. Instability due to steam

Due to the failure of the seal under SMR conditions, it was hypothesized that the glass frit was unstable under steam environments. It was thus decided to re-seal M2 and test under a simplified steam atmosphere to verify. The gas mixture was chosen to contain mole fractions of 50 % H₂, 25 % Ar and 25 % H₂O. It must be noted that, lacking a calibration gas for the Ar, purity was instead measured by assuming argon would give a similar signal as CO by the TCD. These gases have similar elution times, but the higher thermal conductivity of CO does mean the measured purities have some error. Instead, it is simply the qualitative change in purity that is important.

This test was run at similar conditions to the WGS experiment, with a total flow of 1.0 SLPM at 1.0 MPa trans-membrane pressure, except that the temperature was increased to the 520 °C of the SMR experiment. The results of this test are shown in Figure 6, wherein it is clear that a sudden drop in purity occurred around the 50 h mark. An initial nitrogen leak permeance was obtained before heating of $3.0 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and was observed to increase by a factor of 3 to a value of $9.0 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ after 110 h of exposure to the steam environment. This represented a drop in an ideal H_2/N_2 selectivity from 490 to 190, and was verified at room temperature to be due to a leak emanating from around the frit seal.

One hypothesis to explain the lesser degradation versus the SMR experiment is the lack of a catalyst bed. During SMR, it is hypothesized that the frit softened due to water exposure and was subsequently able to wick onto the alumina catalyst particles. This would pull the frit from the membrane defect and possibly quicken its failure, as measured by hydrogen purity. However, in the argon and steam environment, the glass frit could not be removed due to wicking because no catalyst bed was present. Yet, even without a catalyst bed, the presence of steam was found to significantly affect the stability of the glass frit seal when operated at temperatures close to its softening point.

Figure 6 Flux and purity over time for membrane M2 exposed to 50 % H_2 , 25 % Ar, and 25 % H_2O feed, with a 1.0 SLPM total flow at 520 °C and trans-membrane pressure of 1.0 MPa.

Although the seal did not completely detach as it had during the SMR test, it had visibly altered in color and was found to be leaking significantly. This may have suggested a change in the outer composition of the glass and is hypothesized to have led to a loss of adhesion with the YSZ and/or Pd. Changes in the composition of outer layers of glass is a well-known topic in the nuclear waste management community, with compositional variations due to hydration known for several glasses including borosilicates [37], zirconolites [38] and SON68 [39]. Ebert et al. [37], for example, studied the exposure of a borosilicate in steam and found that exposure at 200 °C caused the release of alkali metal ions and boron from the near-surface, resulting in the formation of a solid reaction layer on the outer layer of the glass.

Martin et al. [38] observed that the initial hydration and ion exchange mechanism led to an increase in surface area of the zirconolite, which could help explain how the seal in the current work failed. Our work has suggested that the glass frit does not adhere well to the Pd, which is

why the hole into the YSZ must be formed. It is hypothesized that the contact with the YSZ is what creates the adhesion necessary to form a durable leak-tight seal. Yet, a small adhesion is probably necessary with the Pd, otherwise gas might be able to seep under the frit/Pd layer and make its way through the support. Thus, one hypothesis for the failure seen here is that a change in the surface roughness of the frit caused a loss of adhesion to the Pd, which then allowed gas to seep through the defect and cause a loss in purity. Although the nature of this degradation is not intended to be a primary topic of the current work, it would certainly be of importance should this method of sealing membranes be used in an environment where steam is necessary.

3.5. Ammonia decomposition membrane reactor

Among hydrogen storage materials, ammonia has the advantages of a high hydrogen density, a well-developed technology for synthesis and distribution, and easy catalytic decomposition [40]. Membrane reactors are attractive for onboard H_2 delivery, providing decomposition and purification in a compact footprint. To further test the limits of the proposed sealing strategy, the stability of the glass frit seal was evaluated in the reactive reducing environment of an ammonia decomposition membrane reactor. The frit seal on M2 that failed during the steam exposure was removed and subsequently replaced with a new application to once again re-seal the initially fabricated defect. Then, M2 was remounted in a new shell using the same Ru/ Al_2O_3 catalyst recovered from the SMR experiment and subjected to a 150 h ammonia decomposition membrane reactor test (Figure 7).

In a continued effort to push the thermal stability limits, the temperature of the reactor was once again set to 520 °C. The trans-membrane pressure, however, was reduced to 0.4 MPa due to vapor pressure limitations of the feed ammonia coupled with a necessary pressure drop for stable MFC operation. The feed was fixed at a GHSV of 360 ml g-cat⁻¹ h⁻¹ (300 h⁻¹), which provided a 98 % conversion, as seen in Figure 7. Under these conditions, the membrane was able to continuously recover 66 % of the hydrogen produced with a flux of 0.11 mol m⁻² s⁻¹. Alternatively, one could consider the overall reactor productivity as 3.6 mol m⁻³ s⁻¹ if the total catalyst and membrane volume are included together.

Figure 7 Ammonia decomposition CMR results for membrane M2, operated at 500 °C with a trans-membrane pressure of 0.4 MPa and feed of 0.15 SLPM (GHSV of 300 h⁻¹ or 360 ml g-cat⁻¹ h⁻¹).

These results compare well to literature values from Zhang et al. [41] and Israni et al. [42] who both used similar thin-film Pd-based CMR designs without the use of a sweep gas in the permeate stream (Table 3). In this comparison, each reactor was operated at ca. 500 °C and 400 kPa trans-membrane pressure, producing similar hydrogen purities above 99 %.

Table 3 Comparison of ammonia reactor results with the literature at similar conditions.

	Zhang et al. [41]	Israni et al. [42]	This study
Temperature (°C)	500	500	520
Pressure (kPa)	400	400	400
Catalyst GHSV (ml g-cat ⁻¹ h ⁻¹)	2000	250	360
Membrane GHSV(ml cm ⁻² h ⁻¹)	640	910	850
Purity (%)	99.6	99.4	99.2
Conversion (%)	99	91	98
Recovery (%)	91	74	66
Flux (mol m ⁻² s ⁻¹)	0.11		0.11
Productivity (mol m ⁻³ s ⁻¹)		3.4	3.6

The comparison with Zhang et al. [41] shows that although the ammonia conversion, hydrogen purity and hydrogen flux were nearly identical, the hydrogen recovery was 91 % for Zhang et al. but only 66 % for the current study. This can be attributed to the difference in the membrane area-based GHSV, along with differences in the pure hydrogen membrane permeance. Within Table 3, the catalyst GHSV is the traditional metric for describing a reactor throughput; this shows that Zhang et al. used a GHSV ca. 5.5 times larger than the current study. However, membrane area is also an important factor when using a CMR. If the membrane area is used instead of the volume of catalyst, one can obtain the membrane GHSV shown in the table. This shows that the current study fed 33 % more ammonia than Zhang et al. [41], which may explain the 25 % reduction in recovery for our CMR. Additionally, Zhang et al. had a significantly higher pure hydrogen permeance at 500 °C of ca. $5 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$, compared to the $2.0 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$ at 520 °C of the current study. It is quite possible that differences in hydrogen recovery are due more to membrane permeance limitations rather than catalyst kinetics.

In terms of the slightly lower hydrogen recovery of 66 % here versus the 74 % by Israni et al. [42], this may potentially be due to differences in the reactor module design and total utilization. Overall, Israni et al. had a significantly longer and thinner module design, using a 1.52 cm ID shell with a 30.5 cm long membrane. This is in contrast to the 2.4 cm ID shell and 10.7 cm long membrane used here. Although their membrane was also significantly thinner at 2 mm OD versus 1.0 cm OD here, these differences may account for significantly different flow patterns within the reactor that helped them achieve a higher hydrogen recovery. Additionally, a slightly higher recovery is in contrast to their slightly lower overall reactor productivity of $3.4 \text{ mol m}^{-3} \text{ s}^{-1}$ versus $3.6 \text{ mol m}^{-3} \text{ s}^{-1}$ in this study. Although very similar, one can argue that a higher productivity will likely be linked to worse concentration polarization effects, even if the reactors were the same design. Finally, Israni et al. [42] did state that they observed severe concentration polarization effects for some conditions that limited their hydrogen recovery and overall reactor productivity, and it is reasonable to assume that the CMR in the current study suffered from similar issues.

The reported conversion in this study was slightly higher than the equilibrium value of 97.8 % at 520 °C and 0.5 MPa. However, this can be attributed to a small shift in equilibrium due to the constant removal of hydrogen through the membrane, similar to results observed for other ammonia decomposition CMR studies [43,44]. Ammonia decomposition is known to be an exception to Le Châtelier's principle, but this is only true for the addition of nitrogen to the system [45]. In essence, removal of hydrogen can be viewed similar to addition of nitrogen, which above a critical value actually causes more nitrogen to be formed. Thus, any CMR design that removes hydrogen has the capability to drive the reaction to completion.

Finally, the pure nitrogen permeance at the end of testing was $3.0 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, which is identical to the value reported for the argon and steam test of Section 3.4. This permeance gave an ideal H_2/N_2 selectivity of 540 at 100 kPa and showing that the seal had not degraded during operation. It is interesting to note that only a slightly lower hydrogen purity was observed in this study, yet Zhang et al. [41] reported an ideal selectivity above 5000 and Israni et al. [42] reported 6600. Even with an order of magnitude increase in the ideal selectivity, it seems that only very minor improvements to purity were obtained.

4. Conclusions

In this study, we introduced a method of sealing defects in thin-film Pd-alloy composite membranes using commercially available glass frit powder with a 560 °C melting point. This technique involves application of a low melting point glass frit without the use of a binder, allowing for in situ firing in inert gas. The absence of an organic binder prevents the required use of oxygen during firing that would otherwise heavily oxidize the Pd membrane. This method was used to seal defects on the order of 1 mm in diameter, and was observed to be stable during the 150 h pure hydrogen test at 520 °C, as well as impervious to thermal cycling between room temperature and 520 °C. Yet, the nitrogen leak rate was observed to increase rapidly when tested at 560 °C, suggesting that an upper temperature limit for the glass frit can be estimated based on its melting point.

Steam, however, was observed to soften the frit and cause seal failure within a couple of days even when operated below the melting point of the frit. Visual inspection suggested that steam was able to absorb into the previously fired frit and revert it to a chalky substance similar to a wet, but unfired, frit. This caused a loss of adhesion to the Pd film and ceramic support, leading to the failure of the seal. Thus, for applications in steam containing environments, such as WGS or SMR, the operating temperature must be reduced significantly below the frit melting point. For the frit in this study, stable operation for WGS was observed at 400 °C, or 160 °C below the melting point.

Alternatively, the seal was demonstrated to have excellent performance in reducing environments such as ammonia decomposition membrane reactors. Even though the seal had direct contact with the catalyst bed, the frit seal was observed to be stable in an ammonia decomposition CMR at 520 °C for 150 h of continuous testing. This suggests that reducing environments act similarly to pure hydrogen from the perspective of frit stability, and thus operating temperature can be predicted directly from the frit melting point. Here, the CMR obtained 98 % conversion, producing above 99 % purity hydrogen with a flux of $0.11 \text{ mol m}^{-2} \text{ s}^{-1}$

for 150 h with no signs of seal degradation. These reactor conditions were compared to the literature and shown to be similar to other CMR studies.

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