The role (or lack thereof) of nitrogen or ammonia adsorption-induced hydrogen flux inhibition on palladium membrane performance

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Abstract

The potential impact of nitrogen and ammonia exposure on hydrogen permeance through thin palladium membranes (1.3 μm to 4.1 μm thick) fabricated by electroless plating was studied. Additionally, a robust approach is introduced to quantify the pressure exponent which accounts for contributions to Knudsen flow through defects present in very thin membranes. In sharp contrast to previously published results, no flux inhibition was observed due to nitrogen or ammonia exposure. Studies included 24 h exposures to both pure gases and equimolar hydrogen/nitrogen or hydrogen/ammonia mixtures at trans-membrane pressures ranging up to 1.0 MPa and temperatures of 598 K to 773 K. One membrane did exhibit significant flux inhibition after helium exposure, but this was attributed to changes in surface microstructure associated with hydrogen departing the lattice. This apparent hydrogen flux inhibition behavior was permanently eliminated by air exposure which roughens the surface, and it is suggested that this surface structure mechanism is a more probable explanation for flux inhibition than adsorption of nitrogen-based species.

Keywords: palladium (Pd) composite membrane; hydrogen (H_2) flux inhibition; ammonia (NH_3) adsorption; nitrogen (N_2) adsorption

1. Introduction

As a primary ingredient in the fertilizers which help sustain the world's current population, ammonia is arguably one of the most important chemicals produced in modern society [1]. However, a second and potentially equally important application for ammonia is that of an energy storage material. Ammonia has been suggested as a potential storage medium for hydrogen that is easier to transport, less costly to produce and has a higher energy density than that of compressed hydrogen gas [2–5]. This is because ammonia is easily compressed to a liquid state at room temperature and can thus be transported more efficiently than compressed hydrogen, especially across large distances that lack a gas pipeline.

Additionally, in recent advances in ammonia production, water, rather than hydrogen, is used as the feedstock for electrolysis which can also be performed at much lower pressures than the

traditional Haber-Bosch process [6,7]. If hydrogen were to be eliminated from the feed requirements, ammonia synthesis and decomposition would represent a complete carbon-free route for fuel cells with storage benefits over direct hydrogen production. However, once synthesized and transported, ammonia must be decomposed and separated for the hydrogen to be used efficiently in fuel cells [4,5].

A suggested means for decomposition and separation of ammonia has been the use of a membrane reactor consisting of a palladium-based alloy membrane surrounded by a catalyst [8–10]. As the ammonia reaches the catalyst it is decomposed into hydrogen and nitrogen. The hydrogen simultaneously permeates through the Pd membrane to produce a pure hydrogen stream for use in the fuel cell, while the nitrogen that is formed is exhausted into the atmosphere. Itoh et al. found that using this method could provide a kinetic enhancement to the decomposition and achieved 15% higher conversion than a conventional reactor as well as simultaneously capturing 60% of the hydrogen generated in a single pass [11].

Palladium is an excellent material for hydrogen permeation that provides high fluxes at moderate temperatures [12,13]. Many studies have reported its use as a separating agent [14–16] and in membrane reactors [17,18]. However, there have been suggestions that some species like hydrocarbons or CO can inhibit permeance by competitive adsorption on the Pd surface [19].

In considering membrane reactors for NH_3 decomposition/ H_2 purification, the question then arises as to whether either nitrogen or ammonia adsorption could potentially inhibit the hydrogen flux through Pd-based membranes. This would potentially be detrimental to the use of Pd membranes in such a system because any flux inhibition could lower productivity and thus affect their economic viability. According to a study by Sakamoto et al. [20], exposure to a 10% N_2 in H_2 feed stream at 523 K lowered the hydrogen flux by 9%, while exposure to a 10% NH_3 feed lowered the flux by 13%. This effect was found to decrease with increasing temperature until it became negligible at 723 K. Several years later, Wang et al. [21] reported that exposure of a Pd membrane to a 50/50 H_2/N_2 mixture for 10 h caused flux declines of 40% which took several hours to recover at 723 K in pure H_2 . This was a disturbing result, as N_2 has often been used as a reference gas in Pd membrane studies to ascertain the lack of defects.

The results of these membrane investigations, however, are inconsistent with the established understanding in the catalysis literature. For instance, King [22] reported nearly 50 years ago that although nitrogen gas adsorbed on palladium surfaces at 78 K and low partial pressures, it was nearly completely desorbed upon heating to 290 K. Kunimori et al. [23] confirmed that nitrogen did not adsorb at 298 K under ambient conditions, but exposure to a high energy electron beam for an hour resulted in dissociation of N_2 into $\text{N}(\text{ads})$ species. These $\text{N}(\text{ads})$ species were stable at 298 K and were not completely desorbed up to 473 K, but this was the maximum temperature tested. A recent theoretical study by the Nørskov group [24] showed that Pd has one of the lowest ammonia synthesis activities among transition metals because of its inability to dissociate nitrogen.

Al-Shammeri and Saleh [25] reported that ammonia adsorbed onto a palladium surface and formed NH_x ($x=0-3$) surface species at 193 K. Yet, no nitrogen desorption was detected from the surface during the experiment, nor could the adsorbed ammonia displace pre-adsorbed hydrogen

at 300 K. Although they reported that the $\text{NH}_x(x=0-3)$ species did not desorb by either pumping to vacuum or heating to 450 K, the lack of hydrogen displacement suggests that hydrogen flux inhibition would be unlikely for a palladium membrane. In addition, Kunimori et al. [23] found that while $\text{NH}_x(x=0-2)$ species formed from $\text{N}(\text{ads})$, no $\text{NH}_3(\text{ads})$ formation was observed, and it is important to remember that this only occurred when an outside energy source (an electron beam) was applied to dissociate the nitrogen.

The primary issue with the catalysis literature as it pertains to ammonia or nitrogen adsorption on palladium membranes is that most work is carried out under high vacuum at temperatures below 500 K. Efficient ammonia decomposition reactors are operated at temperatures of 523 K to 773 K and pressures ranging from 100 kPa to 800 kPa. The low end of this pressure window is a factor of 10^7 higher than the pressures used by King [22] or Kunimori et al. [23]. In fact, King suggested that higher partial pressures of nitrogen would likely lead to higher adsorption, but this did not take into consideration the competing nature of hydrogen and was merely directed at a pure nitrogen gas environment.

Basing their work on the studies of Wang et al. [21] on nitrogen inhibition of hydrogen permeance, Chantaramolee et al. [26] carried out density functional theory (DFT) calculations on N and H adsorption on palladium and suggested that $\text{N}(\text{ads})$ lowers the adsorption energy of $\text{H}(\text{ads})$ on nearby sites. However, the group did not discuss the potential for $\text{N}(\text{ads})$ formation in the first place. Alternatively, Herron, Tonelli and Mavrikakis [27] found that desorption of both $\text{N}_2(\text{ads})$ and $\text{NH}_3(\text{ads})$ is thermochemically preferred over decomposition of either molecule on the Pd(111) face, suggesting that formation of $\text{N}(\text{ads})$ is unlikely and therefore may not have significant coverage to affect hydrogen adsorption energies. In fact, Song and Hu [28] performed DFT calculations on ammonia synthesis over palladium and created a model suggesting that palladium would only have about 5% $\text{N}(\text{ads})$ coverage upon exposure to an ideal 3:1 $\text{H}_2:\text{N}_2$ mixture.

Essentially, not only is nitrogen dissociation on a Pd(111) surface not preferred over desorption, but the total coverage of either $\text{N}(\text{ads})$ or $\text{N}_2(\text{ads})$ may be too small to significantly impact hydrogen flux. At temperatures of interest N_2 desorption rather than decomposition is expected, in agreement with the fact that nitrogen dissociation has been considered the rate-limiting step in ammonia synthesis since the work of Emmett and Brunauer in 1934 [29]. Additionally, the ammonia desorption preference was confirmed in a separate DFT study by Jiang et al. [30], where they showed that the dehydrogenation of NH_3 to NH_2 and H is the rate-limiting step in ammonia decomposition.

However, calculations by Jiang et al. [30] showed that the most abundant surface species during ammonia decomposition is actually $\text{NH}(\text{ads})$, which may suggest that perhaps a slow decomposition of nitrogen in the presence of hydrogen could lead to a large coverage of $\text{NH}(\text{ads})$ species on a palladium membrane. This result would not conflict with the low $\text{N}(\text{ads})$ coverage predicted by Song and Hu [28] because they only considered the rate of N_2 dissociation under the assumption that this is the rate-limiting step in ammonia synthesis over the Pd(111) surface. Therefore, even though the rate of dissociation may be considered extremely slow, the hydrogen flux inhibition observed by Wang et al. may have been caused by a buildup of stable $\text{NH}(\text{ads})$ species.

Thus, the motivation for this study arises from a lack of experimental results to confirm or refute the work of Wang et al. [21]. In this work, we attempted to recreate the results of Wang et al. and then expanded the experiments to include not only co-existing nitrogen but also co-existing ammonia. In conflict with their results, the work here found no evidence of hydrogen flux inhibition by either species. Flux inhibition observed after helium exposure and subsequently corrected with oxygen exposure suggests that changes in the Pd surface structure, not competitive adsorption, are a more plausible explanation for inhibition in these systems.

2. Experimental

2.1. Membrane Fabrication

The supports used in this study were tubular, asymmetric ceramic cylinders made from yttria-stabilized zirconia (YSZ) purchased from the Praxair Corporation. The as-received supports were cleaned by soaking in ethanol and acetone for several hours to remove any remaining organic contaminants or loose ceramic particles. The supports were then rinsed with deionized water (DI) and dried overnight in air using an open atmosphere oven at 393 K. A pore size distribution was then collected using the flow porometry method defined by the ASTM F-316-3 Standard [31]. All membrane supports in this study conformed to a largest pore diameter of less than 800 nm with an average pore diameter of about 300 nm.

Once the support was properly characterized, the electroless plating technique was used to apply the thin palladium films on the outer surface of the substrates. The first step in the electroless method is activation of the surface with Pd crystallites to initiate the autocatalytic electroless plating process. In this method, a 0.16 M solution of palladium (II) acetate trimer (47% metal basis, Pressure Chemical Co.) in chloroform (AR grade, Macron Fine Chemicals) (33 g l^{-1}) was sprayed onto the support using an airbrush to obtain a uniform coating. The volume of solution sprayed was approximately 0.2 ml cm^{-2} , but is not exact since a large amount of the solution misses the support. Instead, the procedure was judged by appearance, where a uniform gold color was obtained when sufficient palladium acetate had attached to the support surface. The support was then fired at 623 K for 30 min in air using an open atmosphere oven, which is well above the decomposition temperature of the acetate ligand of 487 K [32]. At this point the procedure was repeated if the support was not a uniform dark gray color in appearance. This procedure deposited about 100 nm of palladium onto the support, as determined by gravimetric analysis.

After activating the surface with nanocrystalline palladium oxide particles, the oxide was reduced to form pure Pd crystallites by placing the support in a solution of 20 mM hydrazine (98%, reagent grade, Sigma-Aldrich) in water heated to 323 K for 20 min. The support was then rinsed in DI water to remove excess hydrazine before placing the support in the palladium electroless plating bath. The palladium plating bath used 4 M ammonia provided to the bath in the form of 30% ammonia in water, obtained by adding 260 ml l^{-1} of concentrated ammonium hydroxide solution (28% to 30%, ACS grade, VWR Analytical) to 740 ml l^{-1} DI water. To this solution, 1.8 g l^{-1} of palladium (II) chloride (60% metal basis, Pressure Chemical Co.) was added and allowed to sit for 24 h to obtain complete dissolution. An ultrasonic water bath was used to dislodge the nitrogen bubbles formed during plating in order to attain a more dense

microstructure. Multiple plating cycles were conducted until either the desired thickness or an acceptable argon flux (non-hydrogen leak rate) was achieved. The compositions of the activation, reduction and palladium plating solutions are given in Table 1.

Table 1: Membrane synthesis baths

Component (Chemical Formula)	Units	Activation	Reduction	Pd bath
Chloroform (CHCl ₃)	M	15.7		
Water (H ₂ O)	M		55.5	51
Ammonia (NH ₃)	M			4
Palladium acetate (Pd(OAc) ₂)	mM	160		
Palladium chloride (PdCl ₂)	mM			10
Hydrazine (N ₂ H ₄)	mM		20	10
Temperature	K		323	298
Time	min		20	60

When the desired palladium thickness was achieved, an argon leak rate was measured at 298 K to determine if the membrane quality was sufficiently high. An acceptable non-hydrogen leak permeance is typically less than 10^{-9} mol m⁻² s⁻¹ Pa⁻¹, but the thinnest membrane in this study could not achieve this criterion due to poor Pd plating over the large pore size of the supports used. In this case, it was decided that a higher leak would not adversely affect the primary goal of observing any potential hydrogen flux inhibition.

2.2. Experimental Apparatus

Once synthesized, membranes were sealed onto 1/4 inch outer diameter stainless steel piping using graphite ferrules from Chromalytic Technology and stainless steel compression fittings from Swagelok. Between the length that is lost due to the compression fittings and the potential for cracking a tube and re-sealing a shorter length, the active length of membranes varied from about 5 cm to 7 cm. The sealed membranes were then placed within a 1 inch outer diameter stainless steel pipe and placed in a Lindberg MiniMite tube furnace 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. A schematic of the testing module can be found in Collins and Way [33].

The permeation system for this project consisted of individual Porter Instruments mass flow controllers supplying UHP grade (purity above 99.999%) He, Ar, H₂, N₂ and/or NH₃ 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 Basics code running in Microsoft Excel. For mixed gas conditions, the permeate and retentate compositions were recorded via a SRI Instruments 8610C GC equipped with a 10' Hayesep D column and thermal conductivity detector (TCD). 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 calibration gas, the TCD and Hayesep D column combination is suggested to have lower detection limits of 0.02% nitrogen and 0.05% ammonia in hydrogen.

2.3. Membrane Characterization

Scanning electron microscopy images of the surface and cross-section of each membrane were obtained using a JEOL JSM-7000F FESEM at an accelerating voltage of 5 kV and magnifications up to 10,000x. Several images were taken for each membrane so that an average thickness could be estimated. In addition, membrane thicknesses were measured via X-ray fluorescence spectroscopy (XRF) with a Fischerscope X-Ray XDLM-C4 PCB spectrometer using a Ni filter with an accelerating voltage of 50 kV.

3. Results and Discussion

For this study, the results from three membranes will be discussed in detail (Table 2). These membranes were between 1.8 μm and 4.1 μm thick and showed a clear increasing hydrogen flux with decreasing thickness. Several SEM images of cross sections were taken to obtain an average thickness of each membrane, with an example of a surface and cross sectional SEM image for membrane M2 shown in Figure 1. It was also found that membranes M1 and M2 had permeance pressure exponents close to Sievert's law, whereas M3 was becoming thin enough to begin to see surface rate limitations. Sample properties from Wang et al. are given, showing that the membranes in the current study are of similar thickness with comparable hydrogen flux. The calculation and relevance of the pressure exponents will be discussed in Section 3.2.

Table 2: Summary of membrane properties.

Membrane ID		M1	M2	M3	Wang et al. [21]
Active Area (cm^2)		17.6	20.7	20.4	4.67
Thickness (μm)	Gravimetric	4.0	2.8	1.6	2-3
	SEM	3.9	3.1	1.8	
	XRF	4.4	3.2	1.9	
H_2 Flux at 673 K 100 kPa ($\text{mol m}^{-2} \text{s}^{-1}$)		0.21	0.29	0.60	0.29
H_2/N_2 Selectivity at 673 K and 100 kPa		2800	1100	176	3000
Pressure Exponent -n-		0.52	0.56	0.83	1

Figure 1: Surface (A) and cross-sectional (B) SEM images of M2 after testing. The surface shows a grain size of about 300 nm, whereas the cross section shows a dense film with a thickness of approximately 3.4 μm . Note that this image is one of several used to obtain the average thickness given in Table 2.

3.1. Hydrogen Flux Calculations

Membrane performance is typically interpreted through the use of the following expression:

$$J = \frac{\pi_H}{L} (P_{H_2,F}^n - P_{H_2,P}^n) \quad (1)$$

where J is the flux of molecular hydrogen, π_H is the hydrogen permeability, L is the total membrane thickness, and P_{H_2} is the hydrogen partial pressure in the feed (F) or permeate (P). One of the primary observable measurements on palladium membranes is the pressure dependence of the hydrogen flux. Thick Pd-based membranes often follow Sievert's law which states that the diffusion of hydrogen atoms in the bulk will control the process, leading to a theoretical pressure dependence of 0.5. Deviations from this, however, are common for thin supported membranes. If the palladium film is either thin enough or in the presence of poisons, limitations from either the surface kinetics (adsorption/desorption) or the external mass transport (support resistance) can become significant enough to increase the pressure dependence of the hydrogen flux toward 1.

Rather than assuming the value to be either 0.5 or 1, one can use a linear regression combined with a minimization of error technique to obtain the best pressure dependence value. In this technique it is desired to minimize the error in the permeance calculation, but the permeance

value will vary by several orders of magnitude using n -values between 0.5 and 1. This means that although the calculated error will also change by several orders of magnitude, it will not necessarily indicate a better fit at lower values. Therefore, the preferred method is to minimize the sum of the residuals given by the linear regression. Examples of residual curves for M1 and M3 are shown in Figure 2, where a clear minimum is achieved at one specific pressure dependence.

Figure 2: The residual sum of squares versus pressure exponent for a single sample permeance calculation for membranes M1 and M3. M1 has a minimum near the Sievert's regime of $n = 0.5$, whereas M3 has a minimum closer to the surface limited regime of $n = 1$.

For M1, where the membrane thickness was about $4.1 \mu\text{m}$, the pressure dependence was nearly the 0.5 expected for a bulk diffusion limited regime. This suggests that neither the support nor surface rate processes had significant effect on the flux of the membrane. More importantly, the fact that it was diffusion controlled offered a possible method for analyzing the cause for a change in hydrogen flux. For instance, if the surface of M1 were to become significantly covered by a non-hydrogen adsorbed species, one would expect the pressure dependence to increase from 0.5 toward 1 as the surface adsorption/dissociation of hydrogen became rate-limiting.

M3, however, had a dependence well above the diffusion dominated regime, indicating significant flow impedance by either the support or surface processes. A problem with M3, though, was the low ideal selectivity due to fabrication issues with such thin films. During the entire testing duration, membrane M3 fell from an ideal H_2/N_2 selectivity of 176 to only 90. The fall in selectivity was likely due to annealing effects such as an increase in grain size causing an agglomeration of pinhole defects, but more important to this study is whether this low selectivity could affect the pressure dependence calculation. To assess this possibility we corrected for the contributions of transport through pinholes and defects that are most often attributed to Knudsen flow.

For membrane M3, the flux of helium at 598 K and several pressures up to 200 kPa was measured to calculate a permeance that could then be used to estimate the Knudsen contribution for other gases. This approach was then validated by comparing the He-based predictions with experimental measurements of argon and nitrogen flow in the parity plot shown in Figure 3. It is observed that the estimated flow was within 10% for all values, but the measured flow was

always slightly below the estimate. This could potentially be due to some defects being small enough that they selectively transport helium due to its significantly smaller size than argon or nitrogen. The important message from Figure 3 is that, at least to an adequate approximation, Knudsen calculations could be used to estimate the contribution to hydrogen flow from the defects in the membrane.

Figure 3: Expected Knudsen flux versus measured flux for argon and nitrogen using helium as the basis. A good fit suggests that hydrogen flux due to leaks in the membrane can be calculated and removed from the total hydrogen flux to obtain a more accurate membrane-specific flux.

This knowledge allowed for the hydrogen flux in M3 to be corrected for both the initial and final selectivity of the membrane. Figure 4 shows the resultant pressure dependence calculations for one hydrogen flux measurement on M3 assuming either the initial (176) or final (90) selectivity to be accurate. A selectivity of 174 resulted in a negligible decrease in the pressure dependence of hydrogen flux, whereas a selectivity of 90 caused only a minor decrease from 0.84 to 0.82. Even this decrease, however, can be considered small and does not affect the argument that the hydrogen flux through M3 was not entirely diffusion controlled.

Figure 4: Residual sum of squares versus pressure exponent for M3 using both the measured hydrogen flux and two corrected values. The corrected values use the initial and final H_2/N_2 selectivity to reduce hydrogen flow assuming Knudsen flow through the defects.

Analyzing the rate-limiting step was considered important to this study because the primary goal was to determine whether surface effects, namely the inhibition of hydrogen adsorption due to nitrogen or ammonia species blocking surface sites, were significant. Ideally, the membranes tested would be thin enough to at least begin to see surface rate limitations so that any nitrogen-containing adsorbed surface species would inhibit the flow of hydrogen. Unfortunately, this requires membranes that are not only very thin, but lack any support resistance that might hinder the membrane flow. For instance, membrane M3, with a thickness of 1.8 μm , still had a hydrogen flux pressure dependence below unity. Additionally, the flux dependence may have been due to support resistances rather than surface rate processes in the hydrogen transport model. Nevertheless, the thickness below 2 μm offered the best opportunity for observing surface adsorbate effects on hydrogen flow given current membrane fabrication limitations.

3.2. Mixture Gas Experiments

Under any realistic operation condition, such as decomposition of ammonia, any nitrogen or ammonia would co-exist with hydrogen near the surface of the palladium membrane. Therefore, competitive adsorption between hydrogen, nitrogen and ammonia is critical to membrane operation. If either nitrogen or ammonia were to preferentially adsorb and block sufficient hydrogen adsorption and dissociation surface sites, the hydrogen flux would decline. This would affect the productivity of the membrane and suggest further study to be necessary at creating better materials with less inhibition.

Therefore, the first experiment looking for hydrogen flux inhibition was to expose membrane M2 to a binary gas mixture for an extended length of time. Membrane M2 was chosen for the mixture experiment over M3 due to its higher selectivity and therefore lesser chance of impurities in the permeate stream affecting the flux measurements. To understand the significance of the results of this experiment, the results of a similar experiment from the Wang et al. [21] study must be summarized. In a particular experiment, Wang et al. exposed a membrane to an equimolar hydrogen/nitrogen mixture at 673 K and a trans-membrane pressure of 160 kPa. After 10 h of exposure, they observed that the hydrogen flux had declined 28% under the mixed gas and a final pure hydrogen permeance indicated a decline of 58% from the original permeance. With such an extreme inhibition, it was expected during the experiment here that similar flux declines might be observed.

As shown in Figure 5, the first 24 h of exposure consisted of the binary hydrogen/nitrogen system at 673 K and trans-membrane pressure of 200 kPa with a total feed flow of 1.0 SLPM. However, where the results of Wang et al. observed a hydrogen flux decline within 10 h, no decline in a mixture or pure hydrogen flux was observed for M2 even after 24 h. It was then decided to increase the total trans-membrane pressure to 500 kPa and then 1.0 MPa to see if a higher pressure could create an effect, but again no flux declines were observed.

Figure 5: Permeation data for membrane M2 exposed to an equimolar H₂/(N₂ or NH₃) mixture at 673 K and various trans-membrane pressures. No decline in hydrogen flux was observed for any pressure/gas combination.

The experiment was then expanded to include three exposures to co-fed hydrogen/ammonia mixtures to see if ammonia might adsorb and/or dissociate easier to form the stable NH_x (x=0-3) surface adsorbates suggested in the literature. In this case, the highest possible trans-membrane pressure was 700 kPa because the vapor pressure of ammonia is approximately 800 kPa absolute.

It should be noted that although the flux appears to increase slightly for certain segments in Figure 5, this was always due to a slight increase in pressure over the 24 h period. To verify this, a pure gas hydrogen permeance was calculated between each 24 h period using three pressures between 0 kPa and 400 kPa. Because this pure gas permeance remained constant at 0.29 mol m⁻² s⁻¹ with $n = 0.56$ as indicated in Table 2, it was concluded that no inhibition (or flux increase) had occurred during any segment of the experiment.

3.3. Pure Gas Experiments

With a lack of adsorption in the mixed gas conditions, it was decided to conduct an experiment using the worst possible conditions given equipment and membrane synthesis technique limitations. For this reason, membrane M3 was fabricated as thin as possible at the expense of high selectivity. This was considered a reasonable tradeoff because error in the hydrogen flux measurements could be corrected by correlating the hydrogen flow through defects using Knudsen diffusion, as discussed in Section 3.1.

The entirety of the gas conditions and resultant hydrogen flux measurements are shown in Figure 6. The H₂ flux and the pressure exponent n were recorded at approximately 24 hour intervals after different pure gas exposures. Initially, membrane M3 was heated to 598 K and allowed to soak in 100 kPa hydrogen for 24 h. This was intended to be an initialization period to be certain that the flux would not change significantly under pure hydrogen. It can be seen that the flux did appear to decline slightly, but this was considered a small enough change that the experiment could proceed. Essentially, because the flux inhibition reported by Wang et al. was for permeance declines of more than 50%, a change of 5% can be considered insignificant - especially in light of the mixed gas experiment (Figure 5) showing no decline.

Figure 6: Permeation data for membrane M3 at a calculated pressure differential of 100 kPa. Exposure conditions for each gas state the absolute pressure.

After this initial day, M3 was exposed to 24 h periods of 1.0 MPa argon, 1.0 MPa nitrogen and 0.8 MPa ammonia at 598 K, 673 K and finally 773 K with hydrogen permeance measurements in between (the indicated points). Note that the soaking pressures used in this section are absolute rather than the trans-membrane, or gauge, pressures used in the mixed gas tests (Figure 5). This means the 0.8 MPa ammonia pressure here arises from the same vapor pressure limitation as the 0.7 MPa mixed gas condition shown previously. Although slight declines in flux were observed throughout the experiment, each individual decline never exceeded 5% of the previous flux and did not change between argon, nitrogen or ammonia exposures. In other words, the modest declines may plausibly be attributed to a form of palladium film rearrangement, such as surface smoothing or grain growth, rather than due to any specific adsorbed gas species.

It now becomes important to note that the experiments contained within this work do not specifically rebuke the hypothesis that some form of N₂ or NH_x (x=0-3) may adsorb onto the surface during these pure gas exposures. In fact, it is very likely that at least a portion of the surface becomes covered in diatomic nitrogen during pure nitrogen exposure, whereas a small amount of ammonia decomposition should result in a certain coverage of NH_x species. However, upon returning to a hydrogen rich atmosphere, it appears that most, if not all, of these adsorbed species desorb so rapidly that no noticeable hydrogen flux reduction is measured. The finding that H adsorption energies are reduced when N(ads) is present on the surface for Pd(111) [26] is likely due to conditions not relevant to permeation measurements, as it is not explained how the adsorbates are formed in the first place.

3.4. Apparent Flux Inhibition from Helium

While collecting data for the previous sections, a particular oddity in hydrogen permeance behavior was observed upon initial testing of membrane M1 after exposure to helium. Initially, membrane M1 was heated to 773 K and allowed to soak in 100 kPa hydrogen for a prolonged time. After this period the temperature was reduced to 673 K and the membrane was exposed to 1.0 MPa helium overnight (Figure 7). It was expected that this would not cause any hydrogen flux decline due to helium's inert nature, but surprisingly a significant flux decline was observed.

Figure 7: Permeation recovery results for M1 at 673 K after 18 h helium soak. Note the slow recovery at 0.1 MPa H₂ before pressure was increased to 1.0 MPa. A normalized hydrogen flux of 1 corresponds to 0.16 mol m⁻² s⁻¹ at 100 kPa.

Upon examination of Figure 7, it can be seen that soaking in helium not only caused the hydrogen flux to decline to 30% of its initial value, but also caused the pressure dependence to rise from 0.61 to 0.86. This suggests that after long term exposure to the inert gas, the membrane had become more surface rate limited than diffusion limited as it was initially. Additionally, although the flux failed to recover within 2 h at 673 K and 0.1 MPa hydrogen, raising the hydrogen pressure to 1.0 MPa initiated visible recovery, with the flux returning to 95% of the initial value within 5 h. Our initial hypothesis was that the He tank contained an impurity that was the source of this anomalous behavior. To test this possibility a second experiment was then immediately conducted using a new He cylinder, and the results are shown in Figure 8. In this experiment the helium soak was conducted at similar conditions (673 K and 1.0 MPa for 20 h), and again it was observed that the hydrogen flux declined significantly and the pressure dependence raised from 0.56 to 0.90. In this experiment the membrane was exposed to H₂ at 0.1 MPa, but at the higher temperature of 773 K rather than the 673 K of Figure 7. Under these conditions the hydrogen flux began to recover immediately, with the pressure dependence eventually returning to 0.56 and flux rising to 94% of the initial value after 20 h.

Figure 8: Permeation recovery results for M1 at 773 K after 20 h helium soak at 673 K. A normalized hydrogen flux of 1 correlates to 0.28 mol m⁻² s⁻¹ at 100 kPa.

The results of Figs. 7 and 8 thus offer a very peculiar result with similarities to the behavior observed by Wang et al. [21]. First, exposure to a non-hydrogen gas for several hours resulted in significant hydrogen flux loss. Second, this lost flux could be recovered when soaked in hydrogen, but the rate was sensitive to the conditions used with limited recovery observed at combinations of relatively low pressure and temperature. The primary difference of course is that whereas Wang et al. could ascribe their behavior to nitrogen exposure, this study shows that even helium exposure can induce similar behavior under certain conditions, and is offered as a possible alternative explanation for the results observed by Wang et al.

It is important to note that neither M3 nor M2 exhibited this behavior when tested as-fabricated, indicating the results were not easily reproducible by fabrication of new membranes. However, it is hypothesized that certain fabrication procedures may result in surface morphologies that are more prone to this type of behavior. In other words, the phenomenon shown here is suggested to be an issue with hydrogen uptake in the film. After long term exposure to any non-hydrogen gas, the palladium film becomes depleted in hydrogen. This can cause the palladium film to reconstruct and results in a subsequent slow hydrogen absorption rate when the film is re-exposed to a hydrogen source. The pressure dependence thus becomes surface rate limited to reflect this slow absorption rate, but returns to a diffusion controlled state after sufficient hydrogen has absorbed and swelled the palladium lattice.

Our hypothesis is that the odd behavior with helium observed with membrane M1 was caused by changes to the Pd microstructure that accompany the loss of hydrogen in an inert environment. To test this the microstructure was intentionally altered using air exposure. Previously it has been shown that the air exposure (or any oxygen-containing gas mixture) roughens the surface of palladium, increasing the rate of sorption into the film [34,35]. Specifically, M1 was exposed to helium for a third 20 h period at 473 K after the last data point in Figure 8, and a subsequent flux loss was again observed. This point becomes the first data point in the final set of experiments shown in Figure 9 with flux at 21% of the normalized value and an exponent of $n = 0.79$. Immediately after measuring the flux loss, M1 was exposed to 100 kPa air (grade zero, total hydrocarbon content less than 1 ppm) for 20 minutes, which caused an immediate recovery of hydrogen flux with the pressure dependence approaching the Sievert limit at 0.52. After this, the membrane was allowed to soak under 100 kPa hydrogen for 24 hours and the flux declined about 10%, but the pressure exponent was nominally unchanged. The membrane was then exposed to 24 hours of pure gas exposure to He, N₂, and NH₃. Yet, in contrast to the previous exposures, exposure to 1.0 MPa helium no longer caused any flux loss after exposure. In fact, after exposing the membrane to air, flux loss was not observed after long term exposure of helium, nitrogen or ammonia.

Figure 9: Permeation results for M1 at 773 K after a 20 minute air exposure. No flux decline was observed due to any specific gas after roughening the surface with air. A normalized hydrogen flux of 1 correlates to $0.24 \text{ mol m}^{-2} \text{ s}^{-1}$ at 100 kPa.

Similar behavior to that reported here was observed by Mejdell et al. [36] who used Pd-23Ag free-standing films and found that air exposure roughened the surface, increased hydrogen flux, and caused bulk diffusion to be rate-limiting even for films as thin as $1.3 \mu\text{m}$. This may suggest that the pressure dependence of both M3 ($1.8 \mu\text{m}$, $n=0.83$) of this study and that observed by Wang et al. ($2\text{--}3 \mu\text{m}$, $n=1$) [21] may have either been due to sorption rate limitations or viscous flow through the supports.

To summarize, the study here found that hydrogen flux in palladium membranes is not inhibited by adsorption of N_2 or NH_3 . The inhibition of the flux after helium exposure and subsequent rise after oxygen exposure is likely due to changes in the Pd surface structure, rather than competitive adsorption.

4. Conclusions

No evidence of hydrogen flux inhibition in Pd-based membranes due to nitrogen-containing adsorbed species was observed in this study based on exposure to both pure gases (N_2 , NH_3) and mixtures (H_2/N_2 , H_2/NH_3) for pressures up to 1.0 MPa and a temperature range of 598 K to 773 K. These results are proposed in sharp contrast to those published previously by Wang et al. where up to 75% inhibition of hydrogen flux was reported due to nitrogen exposure at 773 K [21]. One membrane did exhibit significant inhibition after He exposure, but this was attributed to changes in thin film microstructure that occurred when hydrogen departs the Pd lattice under hydrogen-depleted conditions. Strong support for this explanation was provided as this inhibition was permanently eliminated after exposing the membrane to air, which is known to roughen the surface and increase hydrogen sorption rate processes. It was also shown that Knudsen flow through defects and support resistance can increase the apparent pressure exponent, though the former may be corrected through appropriate calibrations. In conclusion, there is no inhibition in Pd membrane performance related to nitrogen species under conditions pertinent to ammonia decomposition.

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