



Hydrogen purification of synthetic water gas shift gases using microstructured palladium membranes



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HIGHLIGHTS

- Microstructured Pd membrane shows high flux in synthetic water gas shift mixtures.
- Hydrogen flux is linear with pressure, indicating a deviation from Sieverts Law.
- Hydrogen to helium selectivity of over 5000:1 is attained at pressure below 1.0 MP.
- Membrane produced with mass production and automation friendly processes.

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ABSTRACT

Novel microstructured palladium composite membranes are fabricated using microfabrication technologies. The membranes have a thickness of 1 micron, and are supported by a microstructured nickel lattice 10 micron in thickness. The membranes' flux versus hydrogen partial pressure are evaluated, and a linear correlation found, indicating a deviation from Sieverts Law due to their relative thinness. The permeance of the membrane are found to be approximately $3 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. The membranes are tested under Department of Energy specified synthetic water gas shift mixtures at temperatures of 320 °C and 380 °C and exhibited fluxes between 0.2 and 0.4 $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}$ at 275 kPa_g (40 psig). The membranes have stable performance at 320 °C, while alloying of the palladium and nickel support slowly occurs at 380 °C, causing a decline in flux. A permeance selectivity of 458:1 H₂:He is observed at a pressure gradient of 1.37 MPa_g (205 psig) and 380 °C, however a true 'burst pressure' is unable to be determined due to the maximum output limitations of the pressure regulator. Hydrogen sulfide reduces membrane performance, as expected of a pure palladium membrane.

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1. Introduction

Pure hydrogen gas is a valuable chemical commodity, due to its use in refinery processes such as hydrodesulfurization [1–5], and as a feedstock for ammonia synthesis via the Haber–Bosch process [6–9]. In addition, it is a potential energy carrier for power sources such as fuel cells, or as a form of energy storage for intermittent renewable power [10–12].

Hydrogen is currently produced primarily through the reformation of fossil fuels, typically natural gas. Steam reforming is the most industrial relevant method of reformation, but catalytic partial oxidation and autothermal methods are also possible [13–15]. The reformation process converts the fossil fuel into a mixture of hydrogen, carbon dioxide, carbon monoxide and water. Additional

impurities may be produced depending on the fossil fuel feedstock. For example, hydrogen sulfide is produced if the feedstock contains organosulfur compounds [16].

While some applications such as combustion [17–19] are able to use the reformat gas mixture directly, other applications require high purity hydrogen. In the case of low temperature fuel cells, such as those being developed for mobile power, hydrogen purity of 99.99% or greater is desired [20]. The existing method to produce hydrogen of this purity is through pressure swing absorption (PSA) [21,22]. PSA is highly successful at the refinery-scale, it is not clear if the technology is the correct choice for mobile applications, due to its relative complexity and high energy requirements. A competing purification technology is dense palladium metal membranes. Palladium membranes are largely passive systems, requiring only a hydrogen partial pressure gradient to achieve separation. They operation though a chemical mechanism, where hydrogen gas is

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dissociated to atomic hydrogen on the surface of the upstream (feed) side of the membrane, followed by diffusion through the metal lattice, which eventually recombines into molecular hydrogen on the downstream (permeate) membrane surface and desorbs [23–25]. Due to this chemical separation mechanism, infinite selectivity is theoretically possible. Pure palladium membranes are typically operated at 300 °C or above, because of the well documented phase transition issue [26–30], as well as improved chemical kinetics of the hydrogen dissociation and recombination reactions. Further technical information on palladium membranes are found amongst the review articles on the subject [31–33].

Despite these advantages, palladium membranes have seen limited implementation, primarily due to the high material cost of palladium metal (presently at nearly \$30/gm, \$800/oz). This cost limits palladium membrane separators to niche applications. One pathway to commercial viability is to minimize the amount of palladium required by minimizing membrane thickness. Cold rolled membranes exist in thicknesses as thin as 5 microns [34]. Thinner cold rolled membranes are challenging due to the mechanical stability of such thin films. However, membranes below 5 microns thickness are possible if a support material is used to provide mechanical support to a thin palladium layer. Currently, two different support structures are seeing widespread research and development [35]. The first class of support is porous ceramics, typically α -alumina. The primary advantages are its tightly controlled small pore size resulting in minimal amounts of palladium to completely coat the support and avoid pinholes, and the metal/ceramic interface which prevents unwanted alloying of the palladium and the support. A disadvantage is the mechanical stresses placed on the brittle ceramic support during thermal cycling, as well as sealing of the supported membrane in reactor housings without cracking of the support. The second general type of support structures is porous stainless steel. An entirely metallic membrane demonstrates good thermal cycling behavior, and easy sealability within reactor housings. Unfortunately, they lack the pore uniformity of alumina, resulting in thicker layers of palladium to avoid pinholes, and there is risk of palladium/stainless steel alloying at operating temperatures. Fortunately, barrier layers may be introduced between the palladium and the stainless steel support that minimize or even eliminate the alloying issue [36]. A recent review provides a good comparison of the technologies [35]. In the majority of cases, the supported palladium membrane technology is developed with high pressure, stationary applications in mind – such as industrial scale methane steam reforming or coal to hydrogen. An additional drawback to these supported methods is that the mechanical support is often significantly more expensive than the cost of the palladium it is supporting, which does little to improve economic viability [37].

To address some of the drawbacks of the current state of the art supported membranes, a novel membrane architecture is developed at the Army Research Laboratory (ARL). An initial proof-of-concept design shows technical feasibility [38]. The architecture utilizes physical vapor deposition techniques to deposit a thin (1 micron) palladium layer on a starting silicon wafer substrate. Using photolithographic techniques followed by electroplating, a nickel support grid is grown from the palladium film. The palladium/nickel composite membrane is then delaminated from the silicon wafer, leaving a purely metallic membrane. Economic savings are potentially realized in both the low usage of palladium, and also in the high-throughput, high automation fabrication techniques employed in the membrane construction process.

The ARL membrane is optimized for portable high purity hydrogen production for fuel cell power. Due to the desire for portability, the reformate gas is likely to be supplied at lower pressures than traditional steam reformers. This is because high

pressure reactors require thicker and heavier walls, which reduce mobility, slows startup time (increased thermal mass) and introduces a pressure hazard for the user. In this work, the ARL membrane architecture is evaluated under synthetic reformate at pressures up to 410 kPa. Results show excellent selectivity and flux at all pressures tested, and at temperatures up to 380 °C. Stability, rate limiting reaction steps, influence of nickel support grid and maximum membrane pressure tolerances are discussed.

2. Experimental

2.1. Palladium composite membrane fabrication

The general fabrication procedure is found in earlier work done at ARL [38]. To summarize, a silicon wafer (Addison Engineering Inc.) starting substrate is placed in a thermal evaporator (Kurt Lesker PVD75) and brought under high vacuum. A 20 nm layer of chrome is deposited to act as an adhesion layer. Next, a 1000 nm layer of palladium is deposited, without breaking vacuum. This physical vapor deposition process allows for production of dense, highly precise and reproducible palladium films, with less than 1% variability palladium thickness across the surface, and wafer–wafer thickness variability of less than 10 nm.

The wafer is then removed from the evaporator, and a 10 micron photoresist (AZ9245, Microchemicals Co.) is applied to the palladium surface. The wafer is then exposed to UV light using a Karl Suss MA6 contact aligner and a contact mask containing a grid pattern. The exposed photoresist is removed using AZ 400K developer. The remaining photoresist acts as a mold for a nickel electroplating which builds the mechanical support grid for the palladium film. A nickel sulfamate solution (Nickel plate SN-10, Transene Co.) is used as the nickel plating solution, with depolarized S-Nickel rounds (Inco) acting as the anode. The electroplating bath is held at 50 °C. The process shares many similarities to the well-known LIGA process developed for MEMS applications, however in this case an easily removed photoresist is used as the mold, instead of the more chemically inert SU-8 polymer, since complete removal of the mold is critical to a well-functioning membrane.

After electroplating, the photoresist mold is removed with acetone, and further cleaned using an oxygen plasma (Metroline M4L Plasma System) etch to remove residual organic scum. The palladium/nickel composite membrane is released from the silicon starting substrate by dissolving the silicon in a hot (70 °C) potassium hydroxide solution. Finally, the chrome adhesion layer, which is still present on the surface of the palladium following silicon etch, is selectively etched using a chrome etchant (Chromium Cermet Etchant TFE, Transene Co.). The resulting membrane is completely metallic, planar in geometry, and contains less than $1.2 \text{ mg} \cdot \text{cm}^{-2}$ palladium metal loading.

2.2. Gas permeation measurements

Permeation measurements are conducted using a permeation cell, similar to that used in earlier work [38]. A palladium composite membrane is placed within the permeation cell, and a perforated stainless steel disc is placed on the permeate side of the membrane. This 200 micron thick disc provides additional mechanical support to the palladium/nickel composite, preventing bending under higher pressure loads. A gas tight seal is established between the membrane, disc, and permeation cell housing using graphite gaskets. The atmospheres on both the feed and permeate sides of the membrane are controlled by mass flow controllers (MKS M100B) and control software (LabView, National Instruments). Membrane temperature is controlled by placing the entire permeation cell into a single zone tube furnace (Carbonlite HZS).

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