Novel Hydrogen Purification Device Integrated with PEM Fuel Cells

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Abstract

A prototype device containing twelve membrane tubes was designed, built, and demonstrated. The device produced almost 300 scfh of purified hydrogen at 200 psig feed pressure. The extent of purification met the program target of selectively removing enough impurities to enable industrial-grade hydrogen to meet purity specifications for PEM fuel cells. An extrusion process was developed to produce substrate tubes. Membranes met several test objectives, including completing 20 thermal cycles, exceeding 250 hours of operating life, and demonstrating a flux of 965 scfh/ft² at 200 psid and 400°C.
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Executive Summary

A membrane test successfully completed 20 thermal cycles without membrane failure.

The hydrogen flux test facility was upgraded to enable tests at 200 psid. This allows testing at the targeted differential pressure and generally improved the ability to characterize the membranes. Further, this enables testing seals at high differential pressure, which is important for defining performance of industrial-scale reactors.

The highest hydrogen flux observed in testing was 965 scfh/ft² at 200 psid and 400°C. This membrane was a Pd alloy membrane. The alloy is expected to significantly improve the tensile strength of the membrane, allowing for thinner membranes to have sufficient strength and ability to bridge the pores of the substrate.

An extrusion process to manufacture membrane substrates was developed. Extrusion allows for larger quantities of larger tubes to be produced at a lower cost than is possible by isostatic pressing. Although large tubes are not vital to producing a prototype hydrogen purifier, they are essential to large-scale hydrogen production plants, such as those that would make hydrogen from coal. Improvements made to the extrusion process produced substrates with larger bulk pores and smaller maximum surface pores than previous substrate tubes. Larger bulk pores provide less resistance to flow and are less likely to limit the hydrogen flux. Smaller surface pores enable thinner palladium alloy layers to cover the pores and produce leak-free membranes. Thinner films have higher hydrogen flux and will require less membrane area to produce the same quantity of purified hydrogen.

Alloys were tested and showed no decrease in hydrogen flux due to other gases in the mixture, including up to 3% CO. This result is particularly important for applications where the feed gas is a mixture, such as syngas.

An annealing technique heating the membrane to high temperature for an extended time under H₂ was applied to a Pd alloy tube and H₂ flux increased by a factor of 2.5 with a significant increase in leak rate. To minimize damage to the tube, a milder condition was tried and H₂ flux increased by a factor of more than 2 with a minor increase in leak rate after treatment.

The theoretical research involved the development of a one-dimensional model which, given fundamental material properties such as hydrogen diffusivity through a bulk alloy and the energy of dissociative
desorption/desorption, allows hydrogen permeability to be calculated. Density functional theory was then used to determine these fundamental properties, both for pure palladium and palladium alloys.

The prototype device was operated with a full load of twelve tubes. Tests results showed H₂ permeate flow rates of about 180 scfh at 135 psid and about 275 scfh at 185 psid. In all tests, the membranes showed sufficient selectivity to reduce CO₂ concentrations from 10 ppm to less than 1 ppm.
**Project Objectives**

The primary objective of the project was to develop a novel polishing device to produce ultra-high purity hydrogen that could be integrated with a PEM fuel cell. The device is based on palladium alloy membranes developed by Praxair and the Colorado School of Mines. The goal is to ensure that the device enables the stringent hydrogen purity requirements for PEM fuel cells can be met using standard-grade industrial hydrogen. Point-of-use purification will provide the added benefit of eliminating harmful impurities regardless of where they are introduced in the hydrogen production, distribution, and supply system.

To facilitate integration with the fuel cell, another objective of the project is to develop palladium membranes that operate at lower temperature than they are typically used (300-600°C). Although internal combustion engines operate at very high temperature, fuel cells do not. A typical palladium membrane operates above about 300°C. This level of waste heat is not available from a fuel cell. Lower operating temperature will also reduce thermal stress.

Figure 1 shows a coal gasification process to produce hydrogen [1]. Hydrogen produced from large-scale coal-based processes using conventional large-scale purification methods, such as pressure swing adsorption (PSA) will not meet the purity requirement for use in a PEM fuel cell. The widespread utilization of PEM fuel cells will depend on providing hydrogen to the fuel cell at sufficient purity. For optimum fuel cell performance, hydrogen must be exceptionally pure, free of harmful components such as carbon monoxide, formic acid, formaldehyde, and sulfur compounds that can damage the fuel cell. The hydrogen must also be free of particulates and organic substances such as oils and long chain compounds. Furthermore, inert gases such as helium, nitrogen, and argon can reduce fuel cell performance and require additional purging. The novel device developed in this program will enable standard, industrial-grade hydrogen produced in large-scale plants based on coal or natural gas to be distributed using the existing network and then dispensed to PEM fuel cell vehicles or stationary fuel cells for power production.
The device will be utilized at the point of use of the fuel cell. It is based on a palladium alloy membrane, which is perfectly selective to hydrogen over other species and can have a very high flux under the proper operating conditions. Because purification is at the point of use, any impurity introduced anywhere in the distribution system can be removed before it reaches the fuel cell. Furthermore, the loss of pressure caused by the membrane is not a problem at the fuel cell because hydrogen must be stored at pressure on the vehicle, but its pressure is reduced before entering the fuel cell. If the membrane were used anywhere else in the distribution chain, product compression would be required because high-pressure storage would be necessary, adding to the cost of hydrogen. Purifying at the point of use eliminates the need for compressing the purified hydrogen because it is used at low pressure and storage is not required.

Integration with the fuel cell is important. Figure 2 shows a diagram of the system comprising the device. In this design the membrane is designed for 99% hydrogen recovery. Hydrogen gas (100-500 psig) coming from the gas storage tank or other storage system such as liquid, hydride, or adsorbent, is supplied to the system. The inlet hydrogen is initially heated against the permeate stream headed to the fuel cell. This heat exchanger is expected to have a $\Delta T$ less than about 100°F. The additional heat is provided by burning the retentate hydrogen. Currently, about 1% of the hydrogen fed to the fuel cell is vented. Venting some of the hydrogen is required to eliminate impurities and inerts in the feed stream. Likewise, the impurities and inerts need to be removed in this system, but in this case, instead of purging the feed
side of the fuel cell, the removal occurs through the retentate stream. If 1% of the hydrogen is left in the retentate, burning it provides more than enough heat to get the hydrogen feed up to the membrane temperature. Obviously, higher recovery is preferred, but the advantage would be small. As proposed, this system uses the same amount of hydrogen as the existing fuel cell system because the blow down would be eliminated. For startup, electric heat could be provided directly to the membrane. The fuel cell vehicles of the future are likely to be hybrids and the membrane area will be small, so there will be sufficient electrical power available to heat the initial hydrogen feed.

![Process Flow Diagram for the Device](image)

**Figure 2. Process Flow Diagram for the Device**

**Introduction**

Praxair is producing porous ceramic substrates using isostatic pressing and extrusion. These substrates have graded porosity so that the surface of the substrate to be coated has very fine pores while the rest of the tube has open porosity with minimal resistance to flow.

CSM and Praxair coated the tubes using electroless plating to deposit a Pd or Pd alloy layer. A seeding procedure had to be performed prior to the palladium plating in order to ensure adhesion between the metallic film and the ceramic surface. That step involves impregnation of the ceramic support using an organic Pd salt solution, followed by calcination and reduction, leaving Pd nanocrystallites on the surface. The presence of Pd crystallites on the support surface also catalyzes the Pd deposition by electroless plating. Previous research has shown that ethylenediaminetetraacetic acid (EDTA), a common stabilizing
agent in Pd plating baths, tends to remain in the membrane, producing carbon contamination and compromising performance. CSM has recently removed EDTA from the plating solution in an effort to reduce or eliminate carbon contamination.

CSM also modeled hydrogen transport through the membrane. All steps of the entire process are considered in the model, which is used to determine the rate-determining step for different membrane compositions and thicknesses. This model provided guidance for alloy selection and for optimizing membrane properties.

Praxair built a prototype multi-tube hydrogen purifier. Demonstrating prototype performance was the major task of the final phase of the program.

**Experimental Methods**

**Pure Gas Flux Test**

A palladium tube was loaded in a reactor (2” O.D. Haynes tube) and heated in a furnace under N2 stream at a ramping rate of 1°C/min. When a desired temperature was reached, the feed side of the reactor was pressurized up to 200 psid using a back pressure regulator with a permeate side at atmospheric pressure. Flow to the reactor was controlled by a series of mass flow controllers. A gas flow rate through the tube was measured by a mass flow meter and flux was calculated by dividing the gas flow rate by the surface area of the tube. During temperature cycle tests, a ramping rate was kept at 1°C/min.

**Mixed Gas Flux Test**

Mixed gas tests were carried out using a feed stream containing 3% CO, 14% CO2, 56% H2, and 27% H2O. A vaporizer was used to generate process steam and water was introduced to the vaporizer using a metered water pump. The feed side was pressurized from 20 to 125 psid. Retentate and permeate streams were sent to a gas chromatograph to analyze the composition of each stream. The GC had molecular sieve 5A and PPQ columns attached to a thermal conductivity detector.

**Electroless Plating of Palladium Tubes**

Palladium tubes were prepared by electroless plating of pure palladium. Tubes produced by extrusion were cut into 8- 10“ lengths to serve as substrates for plating. Electroless plating consisted of two main steps denoted as activation and plating steps. In the activation step, palladium seeds were deposited on the surface of a substrate by dip-coating with a palladium acetate solution. The activated substrate was
then heated in air to burn off organics and reduced in a solution containing N$_2$H$_4$. In the plating step, the substrate was placed in a flow-plating system circulating a plating solution at a speed of about 3 cm$^3$/s and plating continued for 4 hours at room temperature. Plating was repeated until a reasonably low leak rate was observed from the plated tube.

**Start-Up of the Hydrogen Purifier Pilot System**

With a permeate backpressure controller set to 20 psig, the retentate backpressure controller set to 150 psig and the bypass valve open, pilot start-up was initiated by establishing nitrogen. Once N$_2$ flow was established, process heating was initiated. The pre-heater was energized, set to 380°C with a ramping rate of 4°C/min. The reactor cartridge heater was then energized, set at 350°C with a ramping rate of 1.5°C/min. Hydrogen feed was initiated after the system was at an appropriate temperature. The H$_2$ feed was blended while simultaneously decreasing the N$_2$ flow, maintaining an overall flow of about 150-175 scfh. Once the flow was completely switched over to H$_2$, flux tests began.

**Flux Tests in the Hydrogen Purifier Pilot System**

The retentate backpressure controller setting was decreased, in steps, to 20 psig while the permeate backpressure controller setting was increased to 25 psig to create an approximately balanced flow between permeate and retentate sides. After the bypass valve was slowly closed, the retentate backpressure controller setting was increased to 40 psig. Once the retentate side was stabilized, the retentate backpressure controller setting was incrementally raised to the first desired value (50, 75 100 psig, etc.). Once the desired retentate backpressure was set, the feed flow was adjusted to maintain about 40-45 scfh flow through the retentate side. This was necessary to maintain temperature stability in the reactor. To meet testing criteria and measure selectivity, CO$_2$ was added to the feed as necessary while maintaining a 40-45 scfh retentate flow. Pre-heater and cartridge heater settings were adjusted as necessary to maintain about 390°C in the middle of the reactor.
Results and Discussion

Task 1 - Membrane Development

1.1 Electroless Plating

CSM used electroless plating to apply Pd and Pd alloy films to Praxair porous ceramic supports. After the membranes were characterized by capillary flow porometry, they were coated by a solution of Pd acetate in chloroform. The supports were then fired in air, which decomposed the palladium salt, leaving Pd oxide nanocrystallites firmly adhered to the membrane surface. Immediately prior to plating, the membranes were reduced in a dilute solution of hydrazine to convert the Pd oxide to metallic $Pd^0$. In the actual plating reaction, Equation 1, these $Pd^0$ crystallites catalyze the decomposition of hydrazine, promoting heterogeneous plating on the membrane surface instead of homogeneous plating throughout the bath.

$$2Pd(NH_3)_4^{++} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + 8NH_3 + N_2 + 4H_2O$$ (1)

Typical commercial plating baths require an organic complexing agent, such as ethylenediaminetetraacetic acid (EDTA), to stabilize the Pd ions in solution. This can be problematic, as EDTA tends to deposit small amounts of carbon in the film which can depress permeability and promote leak formation in oxidizing or carburizing gas mixtures. By raising the bath pH, CSM has developed stable plating solutions without any organic compounds. Figure 3 shows these baths produce membranes with equivalent hydrogen permeability to cold-rolled or sputtered Pd.
Electroless plating can be performed on any appropriately activated surface that can tolerate the plating conditions, allowing for membranes to be produced on diverse substrates or even as self-supported foils. It can also be modified to produce Pd alloys. In electroless coplating, additional metallic ions are added to the plating bath. In sequential plating, the secondary metal is applied using a separate bath. Figure 4 is a display of membranes at different stages of the plating process.
1.2 Membrane Repair Techniques

In general, substrate pores should be less than 10-20% of the film thickness to enable coating. Sometimes, there are a few isolated defects in the substrate and the rest of the substrate is good. In these instances, it is important to develop a method to seal the holes and produce a usable membrane. As long as the area of the defects is small, the loss of membrane area and hydrogen permeation can also be small. Therefore, some potential defect repair techniques including preplating glaze, preferential plating, and diffusion-induced repair were attempted. Diffusion-induced repair has been developed as an improvement over preferential plating for smaller defects. Preplating glaze can be used to mask off large defects that are readily apparent in the substrate, but sacrifices potential active area. A protocol for deciding when to use each technique was developed based on the measured properties of the substrate and the quality of the deposited film.

Preplating Glaze

Substrates are tested for pore size and flow. If a substrate has good flow properties, and generally good pore size characteristics with only a few large pores, preplating glaze can be used to repair the substrate. In this case, a glaze is applied to the defective area of the substrate before plating. The tube is heated to sinter the glaze and the substrate is retested after glazing. Provided that the glaze repaired the defective area sufficiently, the tube can then be plated. Only the unglazed area will have sufficient porosity to
transport hydrogen. Preplating glaze can repair defects, but it results in the loss of potential active area on
the substrate.

In one case, a tube with significant defects in the cap of the substrate was coated using a ceramic glaze to
seal the cap. The substrate was coated with a 2.9 µm thick film Pd alloy with no visual leaks from the
body when pressured internally to 20 psi. The membrane showed high flux and selectivity in permeation
testing.

**Preferential Plating**

After plating, if there are defects in the palladium alloy film, these can be repaired using preferential
plating or diffusion-induced repair. Tubes have been successfully coated with Pd and Pd alloy films
despite significant defects in the substrate. One tube was coated with approximately 5.7 µm of Pd, but a
defect in the metal film was still detectable by visual inspection, indicating a large leak. Further plating
of the membrane was unsuccessful at sealing the defect area, and a preferential plating technique was
employed to cover the defects. The defective areas were exposed while the rest of the tube was masked
using PTFE tape. The tube was then plated with Pd to cover the defective areas. This repair technique
deposited an additional 4.5 µm of Pd on the unmasked areas, bringing the total thickness at the unmasked
areas to 9.3 µm. This technique successfully sealed the film. The preferential plating treatment has
proven effective in sealing defects, but sacrifices the high flux potential of a small part of the membrane
due to the thicker film covering the affected areas of the support.

The additional processing step adds cost to membrane production. However, the cost of additional
precious metal is small. Pd currently costs about $750/oz, but because the additional film is quite thin
(about 5 µm) and because the additional plating area is very small, the additional cost of palladium is
negligible. The cost of palladium is about $25/square foot/micron thickness. In other words, a 5-micron
film that covered an entire square foot of area would cost about $125. In preferential plating, the area
coated is often less than a square inch. Figure 5 shows the different membrane repair techniques.
Figure 5. Membrane Repair Techniques
Diffusion-Induced Repair

A proprietary diffusion-induced repair technique [4] has been used to repair small defects without sacrificing a large layer to cover the defects. Diffusion of the N$_2$H$_4$ from the lumen of the substrate to the surface of the film where it is met with plating solution diffusing from the surface of the membrane can also be used to fix defects. In this case, the plating chemicals can mix only in areas where there is a leak, and form a film in those areas when they mix. This technique can be used to reduce the N$_2$ leak rate, but not eliminate it, most likely because the solutions do not penetrate very small pores and leaks. The procedure is still being developed and will hopefully lead to a more stable membrane without sacrificing the high flux obtained from thin films.

Alternatively, diffusion-induced repair can be used during the plating process instead of at the end, before large defects form in the film, patching small defects and producing better results. This may be due to the creation of very thin repair sections which form before the entire film is deposited. Then, when these sections are plated over, it is unlikely that these repaired defects will line up, and there will be no defect in the final film.

1.3 Palladium-Alloys for Improved Properties

In order to produce advantageous properties, such as increased hydrogen permeability or improved resistance to contaminating species, Pd can be alloyed with a wide range of other metallic elements. Since the pioneering work of McKinley[5] in the 1960’s, it has been known that up to 20 wt% Au (Au), up to 35 wt% silver (Ag), and 60 wt% copper (Cu) can improve permeability, while 40 wt% Au alloys are far more tolerant to H$_2$S than Pd, Pd-Cu, or Pd-Ag alloys as seen below.
Palladium-Gold (Pd-Au) Alloys

CSM developed an electroless plating bath to apply Au to Pd via a combination of normal plating and displacement plating, in which Pd ions from the surface are interchanged with Au ions from the plating solution. The initial formulation of this process involved applying multiple layers of Pd to the support to obtain a leak-free film, followed by applying a layer of Au on top of this. The Au plating process is catalyzed by Pd, and self-terminates when no available Pd sites remain and the surface is evenly coated with Au. Hydrogen and nitrogen fluxes for this type of membrane are shown in Figure 7.
While membranes made in this manner are of high quality and resistant to contaminating species such as CO and H₂S, they tend to have somewhat depressed fluxes, as the thick Au surface layer is impermeable to hydrogen and may never fully alloy with the base Pd layer at test temperature.
Figure 8. High Temperature XRD Images of a Pd-Au Self-Supported Membrane Showing Alloying to Produce a Au-Enriched Surface Layer over a Pure Pd Core

To compensate for this, CSM has developed a procedure in which thin Pd and other metal, for example, Au, layers are alternated, followed by a shorter, low-temperature annealing step prior to testing. These thinner layers more readily alloyed, and by renewing a Pd surface with each plating cycle, the content of the other metal can be increased over the traditional method. A typical membrane produced using this process is shown in Figure 9.
Thermal Cycles

One of the major goals of the program was to demonstrate thermal cycling. This was a particular concern because the membrane and substrate are different materials. In previous programs, differential thermal expansion was an important issue and led to membrane stress and failure. Figure 10 shows the temperature profile of the thermal cycling test. After ten thermal cycles were completed, the tube was treated with air for a short time to increase the flux. As shown in Figure 11, the air treatment increased the hydrogen flux by about 30%. The tube had a pinhole leak. After ten cycles, the tube was pressurized on the inside to find the leak. Ceramic glaze was used to cover the leak and the tube was heated to 600ºC to solidify the glaze. As shown in Figure 11, this attempt was not entirely successful because the nitrogen flux increased slightly. This was mainly due to a seal leak, but the defect repair was not entirely effective.

All thermal cycles were done in nitrogen. Nitrogen flux was measured at different pressures at 300ºC to measure the leak. Hydrogen was introduced at 300ºC and the hydrogen flux was measured at 10, 20, 40, and 70 psi in each cycle. The hydrogen flux increased over the first 100 hours of testing and then remained stable over the rest of the first ten thermal cycles. The air treatment increased the flux and the
flux increase remained over the next ten thermal cycles. The test was stopped after 20 thermal cycles and the tube was removed intact.

Figure 10. Thermal Cycling Test Temperature Profile for a Pd Alloy Tube
H₂ Stability Test

A life test for a Pd alloy tube was completed. Establishing long life for these membranes is important to their potential use. Figure 12 shows the H₂ stability test performed for a Pd alloy tube (ID: 081908-3) at 300°C and 20 psi. These conditions were chosen to minimize the number of hydrogen cylinders required and number of cylinder changes. The membrane showed excellent stability for over 250 hours under H₂ with no observable defects found after the test. The test was stopped after reaching the 250-hour goal with the tube and seal still working well.
Mixed Gas Test

A new Pd alloy tube was prepared. The tube (ID: 100608-1) was first annealed to 400°C under N₂ flow and tested for pure H₂ and N₂ fluxes from 300 to 400°C and at 20 to 200 psi as shown in Figure 13. A H₂ flux of 318 scfh/ft² with a H₂/N₂ selectivity of 275 was observed at 300°C and 200 psi. No observable defects were found throughout the test confirming a stability of the membrane.
Curves shown are for the best fit equation for flux using a modified Sievert’s Law equation. The data follow a consistent pattern throughout the pressure and temperature range studied.

In addition to a pure gas test, a mixed gas test including CO(3%), CO₂(14%), H₂(56%), and H₂O(27%) was fed to the membrane at 400°C and feed pressures up to 125 psi. Low CO concentration was chosen to simulate exit stream concentrations after a water-gas shift reaction. The test results are shown in Figure 14 and compared to those shown in Figure 13, which was a pure gas test. The H₂ flux data were very consistent with those obtained in the pure gas test. Once again, no observable defects were found in the membrane throughout the test.
The hydrogen recovery, defined as the ratio of permeated H$_2$ to fed H$_2$, is shown in Table 1. Higher recovery was observed at higher pressure with the highest recovery of 80% at 125 psi. This approaches the 2010 hydrogen recovery target of >80%, which is based on a feed pressure of 400 psi.

Table 1. Hydrogen Recovery for a Pd Alloy Tube at 400°C

<table>
<thead>
<tr>
<th>P (psid)</th>
<th>20</th>
<th>40</th>
<th>70</th>
<th>100</th>
<th>125</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ recovery (%)</td>
<td>10</td>
<td>24</td>
<td>45</td>
<td>65</td>
<td>80</td>
</tr>
</tbody>
</table>

Recovery increased with increasing pressure because hydrogen flux increased with pressure. All tests were done at the same flow rate. It is possible to increase hydrogen recovery by decreasing flow rate.
Low Temperature Test

Figure 15 shows the test results for a palladium alloy tube. The tube was tested from 300-400°C initially. After those tests were complete, testing was repeated at 300°C with no significant change in performance. The temperature was then decreased to 275, 250, and 225°C to get results at lower temperatures because membrane operation at lower temperatures is an important goal of the program. The tube failed at 200°C with some defects on the surface of the tube. The tube most likely failed due to a phase change in the alloy that happens as the alloy is cooled in hydrogen. This is a common failure mechanism for Pd and Pd alloys at lower temperatures.

![Figure 15. Flux Test Results for a Pd Alloy Tube (020508-1)](image)

A Pd alloy tube (ID:60209-B5) was prepared from an extruded tube and tested for H₂ flux at a temperature range of 300-400°C and a pressure range of 20-200 psi as shown in Figure 16. The H₂ fluxes at 200 psid were 477 and 597 scfh/ft² at 300 and 400°C, respectively. The H₂ fluxes were well fitted using a modified Sievert’s law with pressure dependence of 0.64 and an activation energy of 7.7 kJ/mol. No observable defects were found throughout the test.
Because a pure palladium membrane undergoes embrittlement in a hydrogen environment at temperatures below 300°C due to its phase change, alloying it with other metals has been tried as one possible solution to this. To study the effect of alloying on the performance, the Pd alloy membrane was tested for H₂ flux at temperatures below 300°C. As shown in Figure 17, the membrane failed at 250°C and at high pressures over 175 psid. Another Pd alloy membrane (ID:62309-C8) also failed at the same condition. To improve the performance at lower temperature, improved palladium alloys need to be developed.
Figure 17. Flux Test Results for a Pd Alloy Tube (ID: 60209-B5) at 250-400°C

The apparent increase in flux show at 250°C and pressures above 175 psi is because of a leak in the membrane that developed during testing. The membrane failure is because of problems that have previously been observed at low temperatures with these membranes.

Palladium Alloys for High Strength Membranes

CSM prepared Pd alloy membranes using a novel, electroless coplating bath, which were subsequently tested at Praxair. Cold-rolled membranes made of Pd alloy have been shown in the literature to have several advantages over pure Pd in hydrogen separation applications, including enhanced tensile strength and resistance to hydrogen embrittlement at low temperatures, as well as catalytic activity for relevant reactions such as the water-gas shift [6,7,8]. An organic-free, electroless codeposition bath was developed that produced highly selective composite membranes. Films consist of two phases at room temperature, but are expected from the phase diagram to form a single phase at typical test temperatures [9]. The
deposited composition is slightly Pd-enhanced over the bath composition. Pure-gas permeation testing shows H₂ permeabilities similar to those of pure Pd.

Although the electroless plating process does not produce samples appropriate for tensile testing, CSM has indirectly demonstrated increased tensile strength of the Pd alloy by nanoindentation hardness testing. Indent hardness of a material is the resistance of a material to permanent and plastic deformation due to mechanical stress on the object. It is measured by using a probe of known mechanical properties and a known load to make an indentation in the sample, and then measuring the indentation’s area or depth. The harder a material is, the smaller the indentation will be. Nanoindentation testers use very small probes and only indent a few hundred nanometers into the surface of a sample, allowing for samples with thicknesses less than 2.5 microns to be compared to thicker materials. Eight materials were tested in this way and the results are plotted in Figure 18.

![Figure 18. Indentation Hardnesses for CSM Pd and Pd Alloy Compared to Literature Values for A: Coarse-Grained Vacuum-Pressed Pd[10], B: Cold-Worked Pd[11], C: Nanocrystalline Vacuum-Pressed Pd[10], D: Nanostructured Pd Produced by PVD [12], E: Cold-Worked Pd75Ag25 [11], and F: Cold-Worked Pd90Y10 (wt%) [13].](image)

The Pd alloy tested in this fashion was 80% harder than an equivalent pure Pd film, and both films compare favorably to Pd alloys produced by other methods. Hardness in Pd has been demonstrated to be
approximately four times higher than the ultimate tensile strength, assuming no porosity in the ultimate sample [14]. Theoretically, the Pd alloy membrane described in Figure 18 could be expected to have a yield strength of 940 MPa. Harder material is more likely to be able to bridge a pore of a given size without failure under pressure conditions. This has been demonstrated, with a single Pd alloy plating cycle reducing nitrogen permeability by an average of 74%, versus 28% for a pure Pd cycle. This is true even though a given Pd alloy plating cycle applies only 50-75% of the film thickness that a pure Pd cycle applies.

**Flux Test Results**

The highest hydrogen flux observed for a Pd alloy tube was 965 scfh/ft² at 200 psid and 400°C, as shown in Figure 19. The permeate pressure in Figure 19 was 1 atm. This particular membrane was thinner than most membranes tested, possibly because its high tensile strength enabled a thinner membrane to cover the substrate pores and be leak tight, while a weaker material at the same thickness cannot bridge all the pores. Several different binary alloys and some ternary alloys were tested at different times in the membrane development program.
Palladium Alloys for Low Temperature Applications

Synthesis of Pd alloy composite membranes via electroless plating is traditionally done with the bath stabilizer EDTA due to the sensitivity of most Pd alloy co-plating baths to temperature and light [15,16,17]. EDTA has been shown to remain in the membrane and cause contamination during mixed gas testing [18,19]. A novel process for the co-plating of Pd alloys has been developed that does not include EDTA in the electroless plating baths. This process involves the sequential plating of a Pd alloy layer followed by a pure Pd layer on top of the ceramic support.

The plating sequence is repeated until the film has a room temperature nitrogen leak rate of less than 1.5 mL/min at 20 psi. The Pd layer can be added in a variety of ways, the standard plating bath [3], a repair technique, or re-activation. In the diffusion induced repair process, the hydrazine reducing solution is
segregated within the tube lumen, while the Pd plating solution is on the outside of the tube. By this method, large holes are preferentially plated, reducing the leak rate without a significant increase in membrane thickness. When neither the standard plating bath nor the repair technique is working, a reactivation procedure is used. Using this novel plating method, membranes were made and tested at CSM. Pure gas permeation testing showed promising results. Figure 20 is a comparison between the Pd alloy films and pure Pd films on the same support.

![Graph showing flux vs. thickness for different Pd alloy membranes.]

Figure 20. Preliminary Pd Alloy Hydrogen Flux Data Compared with Pure Pd

Given the same testing conditions, all of the Pd alloy membranes had a higher flux than a pure Pd membrane of a similar thickness. All three of these membranes were annealed differently, but included anywhere from 4 to 20 hours at high temperature (550 °C) under hydrogen. The annealing procedure originally adapted from Bhandari and Ma [16] proved to be too harsh for our films, which included 20 hours at 550°C. The long time at high temperatures increased the H₂ flux, however the selectivity decreased due to an increasing N₂ leak rate. As more membranes were made, the annealing time at 550°C was decreased to maintain higher selectivities.
For further proof of concept, membranes C8#1 and SW3 were compared with other Pd alloy membranes in the literature of similar thickness and composition. Figure 21 shows this comparison at 400°C to a membrane previously reported by Uemiya [20].

![Figure 21. CSM Pd Alloy Films Compared with Literature](image)

Figure 21 is encouraging because the fabrication technique is able to produce membranes that seem to be annealed based on the comparison of flux values to the literature. This promising beginning of synthesizing Pd alloy membranes without EDTA led us to try to gain a better understanding of the plating kinetics.

**Optimization of Synthesis**

Our objective was to identify plating conditions where the co-plated Pd alloy film deposited has the same composition as the plating bath. Two questions were examined in order to try to understand how the electroless plating conditions affect the amount of Pd in the film.

1.) How does the length of plating time influence the amount of Pd in the film?
2.) Does the surface structure and/or chemistry affect the outcome of film quality and composition?
To address the first question dealing with time, two plating times were chosen: 40 minutes (the original plating time) and 2.5 hours (the longer plating time). The plating time had been increased to reduce the number of plating cycles needed for appreciable film thickness. The longer cycles lead to a thicker film per cycle. Table 3 shows a summary of the Energy Dispersive Spectroscopy (EDS) results.

<table>
<thead>
<tr>
<th>Bath (% Pd)</th>
<th>Plating Time</th>
<th>Film (% Pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>40 minutes</td>
<td>79</td>
</tr>
<tr>
<td>80</td>
<td>2.5 hours</td>
<td>78</td>
</tr>
<tr>
<td>70</td>
<td>40 minutes</td>
<td>61</td>
</tr>
<tr>
<td>70</td>
<td>2.5 hours</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 2. Pd Composition Measured by EDS as a Function of Plating Bath and Time

Although Table 2 may not be the best representation of what is happening with the plating baths, it is clear that the longer cycles seem to put less Pd in the film than intended. Scanning electron microscopy (SEM) was used, in conjunction with EDS, to look at the surfaces of the film for structural differences instead of the composition only. Figure 22 shows the difference in the structure of the plated films depending on bath times for both co-plating baths.
The Pd content, estimated by EDS, of the plated films decreases with plating time for both baths. From the SEM images it is clear that as the Pd content decreases, the structure of the film changes. The film goes from low, bubbly, and connected (high Pd) to high, spiney structures with voids (low Pd). The structures with lower Pd content need more metal layers for the $N_2$ leak rate to be testable.

From average EDS compositions and SEM images, the 80% Pd bath seemed to be more reliable to use to address the question about the effect of the surface layer on plating. 40 minute plating cycles were used as they provided the least amount of deviation in the plated film composition. Due to the sequential plating process used to make these films, the layer preceding the Pd alloy is a pure Pd layer. The Pd layer can be made or modified in the following ways:

1.) Activation: this is the first step in making electroless Pd films in which the sites for nucleation are deposited.

2.) Standard Pd plating cycle, dried normally at 130 °C.
3.) Reactivation: a step where an activation solution is sprayed on the membrane surface and dried at 250°C.

4.) Standard Pd plating cycle, dried at 250°C. The higher temperature should “roughen” the surface due to the formation of Pd oxide.

Table 3 shows the EDS average composition and thickness results for the 80% Pd co-plating bath on each of the surface layers mentioned above.

<table>
<thead>
<tr>
<th>Surface Preceding PdAg Layer</th>
<th>Avg. EDS Comp (% Pd)</th>
<th>Total Avg. Thickness for 40 min cycle (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation</td>
<td>80</td>
<td>0.60</td>
</tr>
<tr>
<td>Pd (130°C)</td>
<td>81</td>
<td>0.24</td>
</tr>
<tr>
<td>Reactivation</td>
<td>82</td>
<td>0.29</td>
</tr>
<tr>
<td>Pd (250°C)</td>
<td>77</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 3. Average Pd Composition Measure by EDS and Thicknesses for Pre-Pd Alloy Layer

**Flux Test Results**

Using the plating process mentioned above, four additional Pd alloy membranes were synthesized and tested in hydrogen. These films had much lower permeability than was expected based on thickness and composition estimations as seen in Figure 23.
Figure 23. Pd Alloy Films with Thicknesses Estimated by Weight Gain Compared with Pure Pd Films

After testing, most of the membranes were cut in half to examine the extent of annealing in the cross section. Figure 24 shows an example of one of the EDS/SEM scans at 2000x. The orange line on the picture on the left side matches up with the orange line on the bottom of the picture of the right side.
As seen on the right hand side, the ceramic support counts drop dramatically at the membrane-support interface. The Pd and alloy metal lines rise sharply as the ceramic drops off and are almost on top of each other. This provides strong evidence that the membrane is annealed. The estimated thickness of this membrane based on weight gain during plating cycles was less than 5 microns. However, as seen by the Pd and alloy metal lines in the scan and looking at the SEM micrograph the actual thickness seems to be almost twice the original estimate. Upon closer inspection, all of the cross sections examined showed thicker membranes than what is estimated by weight gain with some more extreme than others. A new comparison plot with SEM corrected thicknesses can be seen in Figure 25. The adjustment of thickness moves most of the Pd alloy points above the pure Pd line. However, some of the fluxes still are not as high as expected.
A Pd alloy tube (ID: 916C8) was prepared from an extruded tube by combining pure and co-plating methods. The tube was then annealed in a reducing environment. The H₂ flux increased by a factor of more than 2 at all pressures up to 200 psid as shown in Figure 26. After annealing, a minor increase in N₂ leak rate was observed compared to a significant increase seen after annealing under different conditions as shown in Figure 27. This membrane showed lower H₂ fluxes due to a thicker palladium layer compared to the Pd alloy membrane (ID: 916B8-2).
Figure 26. Effect of a Mild Annealing Condition for a Pd Alloy Tube (ID: 916C8) at 400°C.

Figure 27. The Change in N2 Leak Rate after Annealing at Different Conditions of 500°C for 7 Hours (ID: 916C8) and 550°C for 20 Hours (ID: 916B8-2)
The membrane was then tested for H₂ flux at different temperatures as shown in Figure 28 and also tested for durability at low temperatures below 300°C. A significant increase in the N₂ leak rate was observed at 150°C and a visual leak test confirmed that some defects were formed on the membrane surface.

This tube survived testing at 200°C, which is a lower temperature than any previously tested tube in the program. Operating at low temperature has several advantages because it reduces the heat duty, reduces heat loss, and improves efficiency. The disadvantage of lower temperature is that the flux is lower, so more membrane area or higher pressure is required for the same production rate. Furthermore, it appears that this particular tube has lower flux than expected at higher pressures.
Ternary Alloys for the Primary Advantage of Each Binary Alloy

A ternary Pd alloy tube, which might be able to provide the benefits of two alloying metals, was synthesized and tested. Figure 29 shows pure H\textsubscript{2} flux data for a ternary alloy membrane (ID: 100308-2) at a temperature range of 300-400°C and a pressure range of 20 to 200 psi. Respective H\textsubscript{2} fluxes of 150 scfh/ft\textsuperscript{2} and 194 scfh/ft\textsuperscript{2} at 200 psi were observed at 300°C and 400°C. These fluxes are lower than the fluxes for either binary alloy under the same conditions. However, the ternary composition has not been optimized, so it is likely that finding a better composition will increase the flux. The H\textsubscript{2} fluxes were well fitted using a modified Sievert’s law with pressure dependence of 0.67 and activation energy of 8.8 kJ/mol.

![Figure 29. Flux Test Results in a Pure Gas for a Ternary Pd Alloy Tube](image)

A mixed gas test was also carried out for the membrane at 400°C at a feed pressure up to 125 psi. The composition of the feed stream was 3% CO, 14% CO\textsubscript{2}, 56% H\textsubscript{2}, and 27% H\textsubscript{2}O. Figure 30 shows the test results and a comparison between pure and mixed gas tests. The H\textsubscript{2} flux in the mixed gas tests was
consistent with the flux in pure gas tests at a feed pressure up to 100 psi. The higher \( \text{H}_2 \) flux observed at 125 psi (70 psi \( \text{H}_2 \) partial pressure) was due to a leak that developed during the test. Like a binary Pd alloy membrane, the ternary alloy showed the same flux at the same hydrogen partial pressure. In this case, the ternary alloy was able to maintain the advantage shown earlier by the binary alloy.

![Figure 30. Flux Test Results in a Mixed Gas for a Ternary Pd Alloy Tube](image)

Tests with another ternary alloy tube showed significant improvement in flux, as shown in Figure 31. All results are for hydrogen feed. The flux compares well with the best binary alloy membranes, such as the results shown in Figure 19. For example, the maximum flux (at 400°C and 200 psid) was 965 scfh/ft² for the Pd binary alloy (Figure 19) and 809 scfh/ft² for the Pd ternary alloy (Figure 31). Obviously, the number of potential compositions for a ternary alloy is much larger than for a binary alloy and optimizing the composition is a more difficult task. However, this membrane represents a significant improvement over earlier ternary membranes and provides important information for improving membrane performance.
Task 2 - Substrate Development

2.1 Membrane Production

The separation layer consists of dense palladium or palladium alloy, which is infinitely selective to hydrogen. The flux through the membrane is inversely proportional to the separation layer thickness, so thin separation layers are important to increase flux and reduce required membrane area and cost. This is particularly important considering that palladium is a very expensive material. Reducing film thickness reduces the cost of each square foot of membrane and also reduces the area required, so if the thickness can be reduced to half, the cost of palladium will be reduced by a factor of four because only half as much palladium is used on each square foot and only half the area is required to purify the same amount of hydrogen at the same conditions. However, thin layers lack sufficient mechanical strength.

This problem is overcome by depositing thin separation layers on relatively thick porous ceramic substrates, which provide strength without limiting flux or selectivity. Methods to produce substrates include isostatic pressing and extrusion. The separation layer can be deposited by electroless plating, which is a series of chemical reactions to produce a dense thin film of palladium or palladium alloy. The progress made in membrane production is described in the following section.
Substrate Manufacturing

Early in the program, all substrates were made using isostatic pressing. Isostatic pressing is a batch process and is difficult to scale up to mass production of membranes. One of the most economical methods to produce large quantities of ceramic tubes is to use extrusion. Therefore, it is important to produce substrates using extrusion that are equivalent or better than those made by isostatic pressing. Praxair had experience making dense ceramic tubes by extrusion and this experience was applied to producing porous tubes. The initial attempt to produce porous substrates by extrusion made tubes that were structurally sound. The pore structure was examined by SEM. Both the cross section and surface images of the extruded tubes looked similar to tubes made by isostatic pressing, but the surface pores were too large to produce an effective membrane. Further improvements made to the extrusion process produced tubes with sufficient strength and sufficient pore size control to be coated without significantly limiting the possible hydrogen flux. In general, this means that the largest surface pores are smaller than 1 μm, and preferably less than 0.5 μm, and that dry nitrogen flow at 70°F is at least 100 sccm/cm² at 20 psid. Dry nitrogen flow at room temperature is a good approximation for hydrogen flow at process temperatures because the viscosity of nitrogen at room temperature is similar to the viscosity of hydrogen at 400°C. This is particularly important for scaling up manufacturing to larger tubes and to larger quantities of tubes.

Mix & Extrusion

Each mix is capable of producing 16-20 tubes of 18 in length, or a larger quantity of shorter tubes, or fewer longer tubes. Mixes and resulting extrusion paste were characterized by ease of mixing, consistency, time to paste, extrudability (via extrusion pressure), sinter shrinkage, and final porosity after sintering. The extrusion die was designed to obtain a final sintered OD of 0.375 +/- 0.010”.

Sintering

A shuttle kiln is used for final sintering. The shuttle kiln refractory has been built to accept up to 8 tubes per muffle. The kiln exhibits a six muffle capacity. To make sure that the outside surface is not compromised by contact during firing, tubes are hang fired. Hang firing also aids in final straightness and reduces ovality.
QC

Tube inspection after firing comprises dimensional and visual techniques. An optical microscope is implemented to view the tube surface and identify surface imperfections. Addition of a light fiber placed inside the tube during inspections helps identify minute cracks and pinholes. Capabilities available include a proof test fixture which can determine tube strength and crude bubble leak tester which may further help identify larger pinholes not discovered during visual testing.

Sealing

Work was done to develop a reliable metal-ceramic seal based on proprietary seals and seal designs developed for other membranes at Praxair. The other membranes operate in oxidizing environments at a different temperature range. Although we use a similar design, different materials are required for hydrogen transport membranes because they operate at lower temperatures and in reducing environments. Initial attempts to duplicate the seal were not successful because of the temperature and environmental mismatch. The seal material that was stable in the oxidizing environment decomposed in a reducing atmosphere. Although the seal and seal design translate well to hydrogen transport membranes, the seal material had to be changed.

2.2 Substrate Characterization

An optimized porous support for electroless plating of Pd must have several desirable properties. As the plated film must bridge the pores, both the mean pore size and the largest pores on the support surface must be as small as possible. As a rule of thumb, in order to coat a given pore with a dense layer of Pd, the Pd thickness must be 10x the pore diameter. These small pores must be balanced with the need to minimize support resistance to gas transfer and the mechanical strength to endure test conditions. To determine the suitability of a given membrane for testing, a capillary flow porometry protocol was developed. Capillary flow porometry is based upon the Young-Laplace equation, which states that the size of a pore in a porous medium is inversely proportional to the pressure needed to expel a wetting liquid from that pore. This equation takes the form:

\[ r_p = \frac{2\gamma}{\Delta P \cos \theta} \]  

where:
- \( r_p \) = pore radius
- \( \gamma \) = the surface tension of the interface between air and the wetting liquid
- \( \theta \) = the contact angle between the surface and the wetting liquid
Because this angle cannot be measured in a pore, we choose liquids that wet the surface well, and assume \( \theta = 0 \) and thus \( \cos \theta = 1 \). Membranes were then mounted with Ultratorr™ fittings in a shell-and-tube stainless steel flow housing as seen in Figure 32.

Membranes are first tested dry, and flow rates are measured across a range of gas pressures. The membranes are then removed from the housing saturated with the soaking liquid, typically water or an ethanol/water mixture of known surface tension. The saturated membrane is remounted in the housing, and flow is measured at the same pressures as previously, starting at the lowest pressure in order to determine when each pore begins to expel its liquid. The percentage of a membrane’s pores that are of a given size is calculated by averaging as follows:

\[
\%DifferentialFlow = 50 \left( \frac{F_{w}}{F_{d \, i+1}} - \frac{F_{w}}{F_{d \, i-1}} \right)
\]

\( F_{w} \) = flow through the saturated tube
\( F_{d} \) = flow through the dry tube
\( i+1 \) = the pressure increment above the given pore size
\( i-1 \) = the pressure increment below the given pore size.
The tubes have comparable pore size to commercially available symmetric porous ceramic supports, but have far less resistance to gas transport as seen in Figure 33.

![Figure 33. Comparison of Pore Size and Dry Gas Flux for Program Tubes (Praxair) and Commercial Symmetric Alumina Supports](image)

**Task 3 - Computer Modeling**

### 3.1 One-Dimensional Hydrogen Permeation Model

CSM has successfully produced a one-dimensional hydrogen flux simulator for the permeation of hydrogen through an unsupported, pure Pd membrane. It is a continuum model based on the work of T.L. Ward and T. Dao [21]. The simulator, implemented as a Mathematica program, is comprised of the intrinsic forward and reverse rate equations for each part of a seven-step permeation process: (1) molecular gas transport from bulk gas to gas adjacent to the surface of the membrane; (2) dissociative adsorption onto the surface; (3) movement of atomic hydrogen from the surface of the membrane into the
bulk; (4) diffusion of atomic hydrogen through the bulk; (5) bulk to surface transition of atomic hydrogen on the permeate side; (6) recombinative desorption from the surface of the metal; and, (7) molecular gas transport away from the surface.

Our continuum flux simulator requires that the user provide a set of physical properties for the membrane to be studied along with the temperature, feed pressure and targeted permeate pressure. The simulator then starts with an initial guess for membrane flux and uses it to sequentially solve the forward and reverse rate equations from the high pressure side to the low pressure side. At each step, concentration is determined and the result of the last stage calculation is a permeate pressure. This pressure is compared with the targeted value and used to automatically adjust the guess for flux. The entire process is then repeated until permeate pressure is within the tolerance.

Figure 34 illustrates the capability of the simulator by showing the atomic hydrogen flux over a range of temperatures for two pressure sets with the same driving force. The simulator also delivers hydrogen surface coverage on either side of the membrane as well as the amount of hydrogen in the interstitial sites below each surface. As shown, bulk diffusion of hydrogen is the rate-limiting step for hydrogen flux at temperatures from about 250-750°C, the temperature range of interest for Pd membranes. Most previous tests have studied Pd membrane performance at temperatures above 400°C, with a few looking at temperatures approaching 250-300°C. These results indicate that bulk diffusion is the rate-determining step for a 10-µm thick membrane at any typical temperature of interest.

Figure 34. H₂ Flux vs. Temperature for Two Different Pressure Sets
The simulator is able to identify limiting fluxes and hence the processes most hindering permeation. In Figure 35, for instance, the limiting fluxes which are most prevalent for the conditions shown are desorption and diffusion (blue and red curves, respectively) for a thin pure Pd film.

![Figure 35. Rate Limiting Fluxes vs. Temperature for Pure Pd Unsupported Membrane](image)

It is important to note that both Figure 34 and 35 are derived from experimental values gathered by Ward and Dao [21]. The purpose of this theoretical work is to generate the input values for the one-dimensional hydrogen flux simulator with density functional theory (DFT). The end goal is to be able to compare to current experimental results and then use as a predictive tool for alloying metals. Figure 36 is an example of this, where the hydrogen flux for different thicknesses as predicted by the simulator is compared with CSM experimental values. We are currently conducting a sensitivity analysis to quantify the impact of each rate parameter on the discrepancy with the experimental data of Figure 36. Figure 37 shows one example of the sensitivity analysis where the permeate pressure was increased to one atmosphere to account for pressure drop in the system outlet, including a flow meter. Decreasing the driving force by increasing the permeate pressure less than 0.2 atm significantly improves the accuracy of the model predictions, especially for thinner membranes.
Experimental Data

**Conditions**

- $P_{\text{feed}} = 1.3609$ atm
- $P_{\text{perm}} = 0.8122$ atm
- $T = 673$ K

**Figure 36.** Experimental and Model Fluxes vs. Membrane Thickness

**Figure 37.** Experimental and Model Fluxes vs. Membrane Thickness at Increased Permeate Pressure
Figures 36 and 37 were generated with rate parameters derived from experimental input. The first objective was to generate adsorption and desorption energies for pure Pd membranes in order to make direct comparisons with the literature values. The long-term objective, though, is to use this approach to estimate the performance of new alloys.

### 3.2 Reproducing Numbers for Model with DMol³

The DFT program being utilized by CSM is DMol³ which is part of the Materials Studio package. We have performed calculations to find these energies via ab initio, so our model would not need any experimental input. We examined a five-layer Pd crystal slab with the bottom two layers fixed as seen in Figure 38. The energies were calculated using a GGA PW91 level of theory and are as follows with our energy first and the experimental energy in parenthesis: surface-to-bulk energy 11.5 kcal/mol (13.3 – 15.3 kcal/mol), diffusion energy 1.9 kcal/mol (5.3 kcal/mol), bulk-to-surface energy 1.5 kcal/mol (5.3 kcal/mol), and desorption energy 12.3 kcal/mol (10 – 12 kcal/mol).

![Figure 38. Example of a Five-Layer Pd Crystal](image)

Using all of the DFT calculated values in the model to compare with experiments, there was a large deviation. Although the diffusion and bulk-to-surface energies are the furthest from experimental values, the model was most sensitive to the surface-to-bulk and desorption energies. This can be seen in Figures 39 and 40, which compare experimental data with the model now predicting fluxes with DFT input. Figure 39 uses the experimental numbers and our desorption energy, while Figure 40 uses the experimental numbers and our diffusion energy.
Figures 39 and 40 show the extremes in sensitivity: the hydrogen flux model is very sensitive to desorption energy while not as sensitive to the diffusion energy. Focus is shifting to understanding how to gain more accuracy with respect to the desorption energy barrier.
While working out the kinks with the pure Pd system, CSM examined the effect of putting alloying atoms different places in our surface structure. We began by placing different metal atoms on the surface of the Pd crystal slab to see the affect on the desorption energy. The values of these calculations can be seen in Table 4.

<table>
<thead>
<tr>
<th>% on surface (0% corresponds to pure Pd)</th>
<th>Desorption Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% M1</td>
<td>12.3</td>
</tr>
<tr>
<td>25% M1</td>
<td>11.8</td>
</tr>
<tr>
<td>50% M1</td>
<td>16.4</td>
</tr>
<tr>
<td>100% M1</td>
<td>16.4</td>
</tr>
<tr>
<td>0% M2</td>
<td>12.3</td>
</tr>
<tr>
<td>25% M2</td>
<td>6.8</td>
</tr>
<tr>
<td>50% M2</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 4. Effect of Surface Composition on Desorption Energy

As seen from Table 4, adding a little bit of metal M1 to the surface lowers the desorption energy a little, but adding M2 lowers the desorption energy a lot. When there is too much M2 on the surface (more than 50%), adsorption is no longer favored, so the optimized structure will not even have hydrogen on it.

The next thing CSM looked at was seeing where the metal preferred to be in the crystal surface slab. To do this, M2 was randomly placed in the top layer, second layer, and third layer and a geometry optimization was performed. M2 in the top layer gave the lowest energy and this was confirmed with experimental observations when the Pd-M2 system was annealed at high temperatures.

The next steps in our work involve understanding cluster expansion (CE), a tool which is used to find the minimum energy structure as a function of composition within the bulk of the alloy via a minimal amount of DFT calculations. We are first examined Cu-Au, which is a well studied alloy. Once we are able to reproduce the Cu-Au energy as function of composition plot, we gained confidence in our technique and moved on to Pd alloys, which are not characterized as thoroughly. With the bulk structure known, we can calculate some of the input parameters for our model via DFT.
3.3 Gaining Understanding of Cluster Expansion

CE is a technique to find the lowest energy configuration of a binary alloy. It allows one to calculate the energy of any configuration from parameters derived from a few DFT. A (B) atoms in AₓBᵧ alloy are assigned a spin value of +1 (-1). CE expresses the total energy of a lattice as a linear combination of characteristic figures such as pairs, triangles, etc. in an Ising expansion as in Equation 4.

\[ E = J_0 + \sum_i J_i \sigma_i + \sum_{ij} J_{ij} \sigma_i \sigma_j + \sum_{ijk} J_{ijk} \sigma_i \sigma_j \sigma_k + \ldots \]  

\[ E = \text{the energy of any configuration} \]
\[ J_i = \text{the energy of the characteristic figure} \]
\[ \sigma_i = \text{the spin value of the atom occupying site } i \]

The untruncated form of Equation 4 is exact, but unrealistic for one to calculate. So the question of where to truncate is one that has been investigated. The contribution to the total energy of characteristic energies of pairs of atoms gets less important as atoms are farther away (i.e. the nearest neighbor is more important than the 5th nearest neighbor) and the same goes for the interactions involving more atoms as the interaction is spread out further.

In order use CE effectively, there are five steps:

1.) Calculate the energies of ~10 arbitrarily chosen input structures via DFT.
2.) Solve for the interaction energies.
3.) Calculate the energy of the new structure (not included in the original 10) with both DFT and CE.
4.) If \( \left| E_{\text{DFT}} - E_{\text{CE}} \right| \leq \text{tolerance} \), enough input structures have been included for a quality cluster expansion. If not, then go back to step one and repeat steps 1 – 3 with more input structures.
5.) Use Monte Carlo (MC) simulations to find the lowest energy structure as a function of temperature.

We have been able to look at Ag-Au binary alloys, which are more thoroughly characterized than Pd alloys, as a proof of concept to check if we were able to utilize CE equations and calculate \( J_i \)'s. Figure 41 shows a CE with the minimum amount of input structures compared with other work.
The Ag-Au system has been chosen due to the similar lattice sizing of Au and Ag, which makes the mathematical procedure simple. A MC code is being developed and at this point CSM has a rudimentary code for a two dimensional version for a simple cubic structure. The next step in the process is to extend this to a three dimensional, face-centered cubic (fcc) lattice structure. The input equations are being developed, and with a quality cluster expansion for the Ag-Au system, we will be able to obtain information about the bulk properties as a function of temperature.

3.4 MC Code to Understand Diffusivity in Addition to CE
The MC code for an FCC crystal lattice is complete and has been debugged with experimental input. Bulk DFT calculations to find the diffusional parameters such as the activation energy for diffusion and the pre-exponential for diffusion are needed to supplement the code for becoming completely derived from computation. The first step in achieving this is to define a rate for hopping between interstitial sites. Figure 42 demonstrates how a hydrogen proton (red) moves between interstitial sites of an fcc crystal lattice.
As seen above, the hydrogen moves from site to site via transition states. Using DFT, the nudged elastic band method can be used to find the transition state. Quantum-corrected harmonic transition state theory allows us to define the hopping rate from an octahedral to a tetrahedral site as in Equation 5.

\[
k_{OT} = \exp\left(\frac{-E_a}{k_b T}\right) \prod_{i=1}^{3} \nu_{O,i} f\left(\frac{h\nu_{O,i}}{2k_b T}\right) \prod_{i=1}^{2} \nu_{TS,i} f\left(\frac{h\nu_{TS,i}}{2k_b T}\right)
\]

(5)

\(k_{OT}\) = rate

\(E_a\) = activation energy for diffusion

\(\nu_i\) = frequency of the hydrogen at site \(i\)

\(h\) = Planck’s constant

\(k_b\) = Boltzmann’s constant

\(T\) = temperature

\(f(x)\) is defined by Equation 6

\[
f(x) = \frac{\text{Sinh}(x)}{x}
\]

(6)

The hopping rate from a tetrahedral site to an octahedral site is defined in a similar manner. Once the hopping rates have been established, a few protons are inserted in the interstitial sites of the lowest energy
structure (as found above). The atomistic proton hopping domain is illustrated in Figure 43, where metal lattice (purple) are shown along with octahedral interstitial sites (green), and tetrahedral interstitial sites (red).

Figure 43. 3D View of MC Code FCC Lattice

The MC code chooses one of the hydrogen atoms at random and “traces” it as it moves through the metal lattice. In the simulator, protons are placed in random interstitial sites. These protons are then allowed to hop with a probability based on lattice vibration, temperature and the energy barriers encountered from DFT analysis. The diffusivity of the proton can be found via Equation 7.

\[
D_s = \lim_{t \rightarrow \infty} \left( \frac{1}{6Nt} \sum_{i=1}^{N} \langle (R_i(t) - R_i(0))^2 \rangle \right) \quad (7)
\]

The self-diffusivity, \(D_s\), is obtained for many temperatures and an Arrhenius plot, as in Figure 44, is used to find the diffusion pre-factor and activation energy. The diffusion pre-factor and activation energy for proton diffusion is obtained using Equation 8:

\[
D_s = D_0 \exp \left( \frac{-E_{a,eff}}{k_bT} \right) \quad (8)
\]
Density Functional Theory (DFT) was used at the quantum mechanical level to generate proton hopping data for pure Pd.

### 3.5 Switch from DMol³ Vienna Ab-Initio Simulation Package (VASP)

After spending many hours to understand why the DFT input values were inaccurate, the data obtained using the code DMol³ was deemed not sufficiently accurate in comparison with literature values. With the one-dimensional simulator for modeling hydrogen flux and a kinetic MC complete for proton hopping, we returned to the DFT analysis and decided to implement a more accurate code called VASP. This code is much more computationally demanding and so we now rely on our high performance supercomputer for all calculations. A sensitivity analysis was performed on the hopping rates, which are dependent on oscillations of the interstitial proton, and the activation energies provided to the code. The main conclusion of this analysis was that the octahedral frequency is very important when obtaining values close what is expected based on experiment. In order to feel confident in results obtained, a convergence study with respect to the Pd-H system was done. DFT calculations were performed to find convergence of the O frequency based on input parameters. The following figures show a few of the parameters investigated.
Figure 45. Convergence of O-Site Frequency for Different K-Point Meshes and Smearing Values

Figure 46. How Number of Atoms in Frequency Calculation Affects the Outcome of Frequency
Figure 45 shows how increasing the kinetic energy cutoff (ENCUT) affects the zero point vibrational frequency of the H atom. An increase in this parameter amounts to using more plane waves to describe the system, and increasing ENCUT beyond 400 eV has no impact on the accuracy of the result. Figure 46 illustrates two main points: first, the lattice spacing has a large effect on the calculated frequency, and second, that including the metal atoms nearest to the interstitial H does not significantly change the vibrational frequency of the H atom in an O-site compared to the frequency obtained when all of the atoms are included in the calculation. The all atom calculations take the longest, so it was decided that only the H-atom and nearest neighbor (NN) metal atoms would be included in these calculations. These results have helped us to understand where the greatest sensitivity lies as well as allowing us to set our parameters so as to cut down on the computational expense of each simulation without loss of accuracy. Specifically, we now know what ENCUT (energy range to use), the appropriate lattice sizing (3.95 – 3.96 Å yielded the lowest energy), and which atoms to include in the frequency calculation. These were just two of the parameters needed to develop a DFT analysis that gives a reasonable estimate of the vibrational frequency. After all of the convergence work, the diffusional parameters obtained by CSM can be compared to published literature and experimental values as seen in the table below.

<table>
<thead>
<tr>
<th></th>
<th>D&lt;sub&gt;0&lt;/sub&gt; (m&lt;sup&gt;2&lt;/sup&gt;/s)</th>
<th>E&lt;sub&gt;a,eff&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sholl [22]</td>
<td>7.57E-08</td>
<td>0.234</td>
</tr>
<tr>
<td>Wilcox [23]</td>
<td>1.04E-07</td>
<td>0.227</td>
</tr>
<tr>
<td><strong>CSM</strong></td>
<td><strong>1.8E-07</strong></td>
<td><strong>0.224</strong></td>
</tr>
<tr>
<td>Alefeld [24]</td>
<td>2.9E-07</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 5. Comparison of Pre-Exponential and Energy Barrier for Diffusion

Table 5 provides valuable insight to how closely CSM compares to other theoretical work as well as experiments. As the DFT results with pure Pd become converged, CSM moved back towards alloying beginning with Pd<sub>94.3</sub>Au<sub>5.7</sub> (in weight percent), which is a system with 1 Au atom and 31 Pd atoms. The expanded lattice parameter due to the addition of the larger Au atom was found to be 3.965 Å, which is an expansion of 0.12% compared with Pd. This lattice parameter is very close to other theoretical values in the literature. Alloying DFT work focuses on two fronts: alloying of Au into the bulk Pd; and a preliminary analysis of hydrogen dissociation on a (1 1 1) surface.

In order to estimate the effect of Au on diffusivity, vibrational analyses and energies of interstitial H for octahedral (O), tetrahedral (T), and transition states (TS) are required. The modified diffusivity function, fitted to be a function of Au fraction, will be applied within the one-dimensional flux model. Using DFT,
we examined how the energy changes with the addition of an Au atom for different configurations of neighboring hydrogen atoms. The preliminary results show that Au atom affects the binding sites of H by creating larger energy wells than in pure Pd when it is in the nn-shell for either an O- or T-site. As the Au atom is moved further away from an O-site, it seems to create a more energetically favorable site, which is the opposite effect for a T-site.

The second facet of our computational work has focused on the interaction of hydrogen with membrane surfaces. The objective here is to quantify the barrier to dissociation as a function of Au content. We considered a five-layer structure with one atom per layer. This structure has been replicated into a 20-atom structure in order to more clearly indicate the surface adsorption sites. The 20-atom structure will also be used to consider the effect of systems with lower Au content. Both structures are given in Figure 47.

![Figure 47. Five-Layer Surfaces Examined: Five Atoms (Left); and 20 Atoms (Right)](image)

The first step was to establish the (1 1 1) structure and energies of pure Pd in the five-layer structure. The purpose of using only five-atoms is to obtain an idea of input parameters before undertaking a larger,
more time consuming cell. With the bottom two layers fixed to represent the bulk, the top three layers are allowed to expand and contract. Once pure Pd calculations were complete, additional calculations were completed with one Au atom per layer. The results are summarized in Table 6.

<table>
<thead>
<tr>
<th># layers fixed</th>
<th>Pure Pd</th>
<th>Pd$<em>{68.4}$Au$</em>{31.6}$</th>
<th>Pd$<em>{68.4}$Au$</em>{31.6}$</th>
<th>Pd$<em>{68.4}$Au$</em>{31.6}$</th>
<th>Pd$<em>{68.4}$Au$</em>{31.6}$</th>
<th>Pd$<em>{68.4}$Au$</em>{31.6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td># of atoms</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Position of Au</td>
<td>n/a</td>
<td>top</td>
<td>second</td>
<td>middle</td>
<td>fourth</td>
<td>fifth</td>
</tr>
</tbody>
</table>

Table 6. Effect of Au on Energy of Surface Slab

Table 6 shows that the lowest energy five-layer structure occurs when the Au atom is in the top layer. We focused on the 20-atom structure to see how the energy changes with an Au atom present in different layers. It is expected to follow a similar trend to what is seen with the smaller structure, where the lowest energy position is in the top layer. An additional purpose of doing these energy calculations with a larger cell is the optimized geometry is used as part of the input in the presence of hydrogen.

**Task 4 – Design Membrane Test Unit**

The membrane test apparatus is shown schematically in Figure 48. The membranes are evaluated by conducting permeation tests with pure and mixed gases, including steam. The hydrogen flux test facility was upgraded to enable tests at 200 psid. This allows testing at the targeted differential pressure and generally improves the ability to characterize the membranes. Further, this enables testing seals at high differential pressure, which is important for defining performance of industrial-scale reactors.
Task 5 – Economic Evaluation

The goal of this program is to develop a purification device that can provide hydrogen with sufficiently high purity to the PEM fuel cell. A part of this goal is to develop a system that produces the purified hydrogen at a pressure that it can be used without further compression because impurities are more likely to be introduced at lower pressure and additional compression requires significant energy input. A palladium alloy membrane is one way to accomplish this goal and will do so without sacrificing hydrogen utilization on the vehicle.

An alternative purification method would be to liquefy the hydrogen before it is dispensed as pumped liquid. Liquid pumping requires much less energy than gas compression and liquid hydrogen is so cold that any impurity would probably solidify before it could leak into the system.

There is no adsorption-based process developed today that can remove helium from hydrogen. This is an essential separation to meet the purity requirements set by SAE for hydrogen produced from natural gas that contains a relatively high amount of helium, which is common in the Midwest and Rocky Mountain states. Adsorption could become an attractive alternative if, and only if, the purity requirements for PEM
fuel cells are relaxed. This is an area of current research, but there has been limited progress regarding changing the specifications to date.

Hydrogen liquefaction produces hydrogen that has sufficient purity to meet the current specifications developed by SAE and ISO. The 2012 DOE goal for power consumption from the Multi-Year Research, Development, and Demonstration Plan is 11.11 kWh/kg for a small (30 tons/day) liquefier. Currently, a 30 TPD liquefier would be one of the largest in the world. Developing a small liquefier operating at a fueling station that could meet the same efficiency is very unlikely, and doing it at no capital cost would be impossible. Current fuel cell vehicles in the DOE demonstration program are getting less than 50 miles/kg, but 50 miles/kg is a goal that could be achieved. These assumptions were used for the comparison case to develop a target based on an unobtainable zero-capital-cost version of liquefaction. If this benchmark can be reached, the on-board purifier will clearly be more economical than liquefaction.

| Vehicle miles over the life of the vehicle | 250,000 miles |
| Vehicle mileage | 50 miles/kg |
| Hydrogen usage over the life of the vehicle | 5000 kg |
| On-site liquefier power consumption | 11.11 kWh/kg H₂ |
| Liquefaction power consumed | 55,550 kWh |
| Power cost | 0.08 $/kWh |
| Liquefaction power cost over the life of the vehicle | $4,444.00 |

If the final cost of the purifier(s) is less than $4,444.00, the on-board purifier will have a cost advantage over using hydrogen liquefaction for purification. This ignores the time value of money, which would make the liquefier more attractive, but if the capital cost is included, the total cost would be substantially more.

We have demonstrated our target flux of 400 scfh/ft² at 200 psid on several different membranes. This means that only one square foot of membrane area would be required to produce 1 kg of purified hydrogen in an hour. Using our target flux, instead of the actual results, which have exceeded the target, produces the following results:

| Maximum vehicle miles per hour | 75 miles per hour |
| Vehicle mileage | 50 miles/kg |
| Maximum hydrogen consumed per hour | 1.5 kg |
| Projected membrane flux | 1 kg/ft²/hr |
| Total membrane area required | 1.5 ft² |
Membrane thickness     5 µm  
Palladium cost      750 $/oz  
Silver cost      35 $/oz  
Total precious metal cost for purifier $113.60

Producing substrate tubes by extrusion significantly reduces the cost of mass production when compared to isostatic pressing. The material cost of the substrate is small; there are no precious metals in the substrate. The major cost of the substrate will be manufacturing it because there are many steps involved. The starting material needs to be made into a powder, mixed with pore formers, extruded, cut, and sintered. Then, the palladium alloy must be deposited on the substrate, introducing another set of processing steps due to electroless plating. However, if substrates are mass produced, the cost of processing for any particular tube will be minimized.

Even if we assume that the cost of manufacturing and packaging is so high that the cost of palladium is only 20% of the total device cost, the device would cost $568.00. This compares very favorably to the cost of hydrogen liquefaction, which is the most reliable alternative to provide sufficiently pure hydrogen for fuel cells. The cost of power alone for liquefaction over the life of the vehicle, $4444.00, is almost 40x the cost of palladium for the purifier. This ignores the capital cost necessary to build a liquefier, which is likely to be at least as large as the liquefier operating cost on a per kg basis, especially for a small liquefier such as one that would located at a fueling station.

The life of the purifier, and particularly the membrane tubes, is a key issue. Figure 49 shows the economic analysis results for different vehicle and purifier lifetimes. In this analysis, an initial installation cost of $20 and a replacement installation cost of $100 were assumed for the purifier. This is because the initial installation would be done as part of the initial vehicle assembly as part of the manufacturing process while subsequent replacements would need to be done one at a time without other work and with less access to the purifier.
Two lines are shown for the liquefier cost. The lower cost line completely ignores capital and maintenance costs for the liquefier. The higher cost line assumes that the contribution of capital is $0.55 per kg of hydrogen, as explained below. This is based on targets for a 30 TPD liquefier. In actuality, the targets set by DOE are very challenging. Furthermore, a smaller system, which will have a higher relative capital cost, is more likely to be realistic and delivery costs are ignored in this analysis, so the line shown is below the actual expected cost. In many small-scale applications, the capital cost can be larger than the operating cost. Currently, we have no design for a liquefier small enough to fit into a fueling station, so there is no capital cost estimate. In fact, it would not be surprising if the actual capital cost contribution for a small liquefier were more than the power cost. The stepwise curves represent the purifier cases for different purifier lifetimes.

The actual contribution of capital cost can be estimated as follows. The 2012 DOE target for capital cost for a 30 TPD liquefier is $40 million. The H2A Model [25] calculates a capital recovery factor of 0.117 assuming a 20-year life and a 10% after-tax internal rate of return. Assuming depreciation and a 38.9% tax rate, this leads to a real fixed charge rate of 0.150 [25]. Multiplying this by the total capital cost, $40 million, and dividing by the total number of kg produced in a year at 100% utilization, 365 days/year
*30,000 kg/day = 10,950,000 kg/year, leads to a capital cost contribution of $0.55 per kg. Multiplying this by the number of kg consumed over the vehicle lifetime, 5000 kg, leads to a capital cost contribution from the liquefier of $2750.

The purifier lifetime is a significant factor in assessing economic viability because of the number of devices that will be used over the lifetime of the vehicle. For example, if the vehicle lifetime is 250,000 miles, and the purifier lifetime is only 25,000 miles, the owner will need to buy 10 purifiers over the life of the vehicle. This is likely to be an unacceptable scenario for the vehicle owner and the overall cost of hydrogen purification over the vehicle lifetime becomes quite high. The target lifetime for the purifier based on this analysis is 50,000 miles, which closely approximates the power cost for liquefaction. Any lifetime greater than 50,000 miles produces purified hydrogen at a similar cost to just the power cost of liquefaction. At an average driving speed of 40 MPH, this represents a 1250-hour life for the membranes. In this program, we have already demonstrated membranes with several hundred hours of operating life, but have not tried to achieve 1250 hours on any single membrane. Currently, we expect that we could achieve 1250 hours with current membranes, but have not demonstrated it. The large number of thermal cycles required and road vibration are more likely to be important issues than the membrane life under laboratory test conditions.

**Task 6 – Prototype Design and Testing**

**6.1 Prototype Design**

One of the primary goals of the project was to build the hydrogen purification section of a stationary multi-tube hydrogen purifier based on designs disclosed in U.S. Patent 7,628,842 [26]. The prototype device includes heat exchange, but uses electric power to generate additional heat instead of combustion. This was done to simplify the design, reduce device cost for a single one-of-a-kind unit, and still demonstrate hydrogen purification. Most of the tests were conducted with 1% CO₂ in the hydrogen feed so that a low cost analyzer could measure the amount of impurity in the permeate stream and results could be extrapolated to approximate performance using industrial-grade hydrogen. This significantly simplified and reduced the costs of product purity analysis. Praxair completed the design of the device using the results of the membrane testing. Laboratory tests demonstrated the target flux, so 1 ft² of membrane area will allow 1 kg/hr of purified hydrogen to be produced at 200 psid and 300°C. The membrane tubes are 3/8” diameter, and the device holds 12 tubes, so the tubes need to have an active length of 10.2” to provide 1 ft² of membrane area. This is only one of many possible configurations that could easily fit into a small cylinder. A feed/product heat exchanger using microchannels could also fit...
into a small volume. The final design used a tube-in-tube heat exchanger, which is readily available at a low cost from commercial suppliers. The current cost of microchannel heat exchangers was prohibitive for a single prototype unit. The total heat transferred to a 60°F feed to heat it to 300°C is about 1.13 kW. Assuming an average temperature difference of 20°C, and a heat transfer coefficient of 200 W/m²K, the required area is only 0.28 m².

Heated crude hydrogen is fed at approximately 200 psig to the outside of the tubes and purified hydrogen at slightly above atmospheric pressure flows through the inside of the membrane tubes. In current fuel cell operation, a small purge flow is removed from the retentate side of the PEM membrane to eliminate impurities from the system. Our design removes that same stream, but takes it from the retentate side of the purifier membrane instead of from the PEM membrane. The actual tests used a larger purge flow than the design case. This enabled increased feed flow and significantly improved temperature and pressure control of the system. The heart of the assembly is the HTM tube, shown in Figure 50, located in the center of the assembly. A ceramic plug is used on one end of the tube to allow for thermal expansion and reduce the total number of seals required compared to open ended tubes, which would require two seals each.

Figure 50. Tube Assembly
Figure 51 shows the manifold assembly. This is used to combine the purified hydrogen flow produced from each tube into one stream. Compression fittings were used to connect the metal attachment tubes to the manifold. In production units, the compression fittings would most likely be replaced with welded connections. Tube isolation devices could be located in the tubes to close off tubes that developed leaks. Extra membrane area could be added by using longer tubes or extra tubes so that the device could continue to produce sufficient hydrogen even after one or more tubes failed. This would also increase the life of the device and reduce replacement costs over the life of the vehicle. The components of the manifold assembly were vacuum brazed to ensure that connections are leak tight. Vacuum brazing of manifold assemblies for high temperature applications has been used successfully on other projects.
Figure 52 shows the membrane module assembly. The required tube area is about 1 ft², assuming that the target flux can be achieved. In reality, some extra area will be added to the final device to account for possible performance decay due to contamination or even the failure of one of the tubes. The current design features 12 tubes that are 3/8” diameter and have an active length of 10.2”. This is one of the many possible configurations that could be used to produce a module with 1 ft² of membrane area. An insulated cylindrical shell (not shown) envelopes the entire assembly to contain pressure and heat within the unit.

6.2 Test Results

The prototype device was operated with 4-12 membrane tubes. Three demonstration tests were conducted. The first two tests were shut down when atmospheric monitors detected flammable gases leaking outside the system. There was no membrane failure in either case. Figure 53 shows the results of the November 2010 test.
The top line shows the CO₂ concentration in the permeate stream in ppm. The feed concentration for this test was about 1%, or 10,000 ppm. The maximum CO₂ concentration in the permeate was 384 ppm, which represents a 96% reduction in CO₂ concentration compared to the feed. Although this is not perfect selectivity, most likely because of small leaks through the membrane seals, it is sufficient to reduce the CO₂ content in a typical industrial hydrogen stream from 10 ppm to less than one half ppm, or from unacceptable for most PEM fuel cells to exceeding the current purity specification set by the Society of Automotive Engineers (SAE) or the International Organization for Standardization (ISO).

The next line shows the hydrogen feed. This was kept constant at 200 scfh for most of the test and raised to 210 scfh for the final few hours. Interestingly, the increase in feed rate did not change the permeate flow significantly, but it significantly increased the hydrogen concentration on the retentate side, and consequently, significantly reduced the CO₂ concentration on the permeate side because the CO₂ content of the leak dropped. This shows that permeate purity is very sensitive to how the system is operated and can be increased by taking a small loss in hydrogen recovery. Conversely, if very high recovery is required, the retentate concentration of impurity will be magnified significantly and will have a negative impact on product purity if there is a leak and will also reduce flux through the membrane because the feed side hydrogen partial pressure will be lower.
The next line down shows the permeate flow. This ranged from about 175 scfh to about 185 scfh during the test. The increase is due to a slight increase in the leaks through the seals and a slight increase in operating temperature over the length of the test.

The next line shows the differential pressure across the membrane during the test. This was kept constant at 135 psi with a feed pressure of about 150 psig and a permeate pressure of about 15 psig. The permeate pressure was higher than used in the design condition and the feed pressure was lower than the design feed pressure.

The bottom line shows the retentate flow in scfh. This was set to achieve approximately 90% hydrogen recovery during the test. Accepting lower recovery will lead to higher flux and product purity as discussed above.

Repairs were made to the system including replacing a leaky valve that caused the system shutdown at the end of the November run.

The second test, which was conducted in December 2010, is shown in Figure 54.

Figure 54. Prototype Device Test Results (Second Test)
The CO₂ concentration in the permeate varied greatly during the test. Over the first two days of the test, the retentate flow was decreased, increasing hydrogen recovery, but also increasing CO₂ concentration in the permeate from about 90 ppm to about 230 ppm. Next, the feed flow and retentate flow were both increased while the permeate flow stayed relatively constant. This caused the CO₂ concentration in the permeate to drop to about 170 ppm where it stayed until the feed concentration was increased from 1% to 2%, causing the CO₂ in the retentate and permeate to essentially double to about 390 ppm in the permeate. Then, the CO₂ feed was shut off and the permeate concentration dropped to 0. The final CO₂ concentration was 1% and the permeate concentration increased to about 210 ppm, up from 170 ppm earlier at the same feed concentration. This is because the hydrogen feed was lower, 225 scfh compared to 275 scfh in the earlier portion of the test.

The hydrogen feed was varied from a low of 150 scfh at the beginning of the test to a high of 300 scfh for a short time in the middle of the test. Increasing hydrogen feed flow generally has a small impact on permeate flow by increasing the hydrogen partial pressure on the feed side and a larger impact on hydrogen recovery with recovery dropping as feed flow increases.

The permeate flow increased significantly from about 110 scfh to about 180 scfh when the hydrogen feed flow was increased from 150 scfh to 210 scfh. The permeate flow did not change significantly when the feed flow increased beyond 210 scfh. As expected, increasing the CO₂ feed concentration reduced permeate flow while decreasing CO₂ concentration increased permeate flow.

The differential pressure was generally kept constant at 135 psi for most of the test. However, feed pressure could not be maintained at 150 psi at the lowest hydrogen feed flow of 150 scfh early in the test. The higher pressure could be maintained only when the feed flow was increased to 210 scfh. This shows that the system is very sensitive to pressure and feed and that the two cannot be controlled separately in all cases.

The retentate flow is the difference between the feed flow and the permeate flow. The maximum retentate flow that we can measure is 50 scfh. Much of the December test run was done with relatively low hydrogen recovery and a retentate flow that was more than 50 scfh.

The third test, conducted in February 2011 is shown in Figure 55.
Changes were made to the reactor system to enable testing at 200 psig. This is the highest pressure at which the system was operated. At least one tube developed a leak or a bad seal before the test started that became worse during the test. Pinholes were found in some tubes after they were exposed to an oxidizing environment. Previous experience with oxidizing treatments has shown that flux can be improved, but one risks damaging the tubes. In this case, it is likely that the oxidizing treatment compromised the integrity of the membrane. The CO₂ concentration in the permeate increased during the test, but was always higher than in the other two tests. The CO₂ concentration in the feed was 1% for the duration of the test.

The higher pressure led to increased hydrogen permeation, about 275 scfh compared to less than 200 scfh for most of the other tests. The increased CO₂ in the permeate is an indication of higher flow through leaks in the membranes or seals. The hydrogen flow rate permeating through the membrane is a more important result for future reactor design, so the permeated flow rate must be estimated. This can be done as follows:
At the end of the test, the following flows and compositions were measured:

- Hydrogen Feed Flow = 310 scfh
- CO₂ Feed Flow = 3.1 scfh
- Total Permeate Flow = 270 scfh
- Total Retentate Flow = 43 scfh
- CO₂ Concentration in the Permeate = 725 ppm

A mass balance leads to the following results:

- CO₂ Permeate Flow = 725/1000000 * 270 = 0.196 scfh
- H₂ Permeate Flow = 270 – 0.196 = 270 scfh
- CO₂ Retentate Flow = 3.1 – 0.196 = 2.9 scfh
- H₂ Retentate Flow = 310 – 270 = 40 scfh
- CO₂ Concentration in the Retentate = 2.9/(2.9+40) = 6.76%
- H₂ Concentration in the Retentate = 40/(2.9+40) = 93.24%

Once the retentate gas composition is known, the leak can be estimated. The hydrogen concentration is 99% on the feed side inlet and 93% at the outlet. The linear and log mean average concentration is 96%, so assume that the average gas composition at a leak is 96% hydrogen. This means that the leaking gas will contain 24 times more hydrogen than it contains CO₂ based simply on composition. However, hydrogen is smaller than CO₂ and therefore, more likely to leak through very small openings. Assuming that Knudsen diffusion applies, each gas leak will be inversely proportionally to the square root of its molecular weight, so Equation 9 can be used to calculate the ratio.

\[
\frac{F_{H_2}}{F_{CO_2}} = \sqrt{\frac{MW_{CO_2}}{MW_{H_2}}} = \sqrt{\frac{44}{2}} = 4.69
\]  

\(F_{H_2}\) = flow of hydrogen through the leak  
\(F_{CO_2}\) = flow of CO₂ through the leak  
MWᵢ = molecular weight of species i

The hydrogen flow through leaks can be calculated by taking the CO₂ flow, multiplying it by the concentration factor, 24, and the Knudsen diffusion factor, 4.69. This leads to a total hydrogen flow due to leaks of 0.196 scfh x 24 x 4.69 = 22 scfh, or about 8% of the total hydrogen flow. The permeated hydrogen flow rate through the membranes is estimated to be 270 – 22 = 248 scfh. This is still a much higher flow rate than was seen in the other tests. The accuracy of this estimate is limited by the accuracy of the measurements, but it is an indication that more than 90% of the hydrogen in the permeate stream came through the membrane instead of coming through a leak.
Task 7 – Program Management
General program management and reporting were done throughout the project period.

Conclusions
A thermal cycling test, which is one of the major goals of this program, was successfully carried out with a Pd alloy tube between 25 and 300°C. The hydrogen flux remained stable for 20 thermal cycles.

Binary and ternary palladium alloys showed high H2 fluxes and the highest H2 flux of 965 scfh/ft² at 200 psid and 400°C was observed for a binary alloy tube. A comparable H2 flux of 809 scfh/ft² at the same condition was observed for a ternary alloy tube. These alloys were tested in a mixed gas condition (CO(3%), CO2(14%), H2(56%), and H2O(27%) ) and showed no decrease in hydrogen flux at the same hydrogen partial pressure. This is a particularly encouraging result because other alloys have shown a decrease in flux in mixed gas tests, which are particularly important to processes where the membrane would be used to separate hydrogen from syngas.

A new annealing technique has been developed and applied to a Pd alloy tube. After annealing, H2 flux increased by a factor of 2.5 and N2 leak rate also increased significantly possibly due to a harsh annealing condition. Therefore, a milder annealing condition at lower temperature and shorter time was applied to another Pd alloy tube and a similar H2 flux increase was observed with only minor N2 leak rate increase.

A manufacturing technique for producing substrates by extrusion was developed to enable large-scale substrate production. The process reduced pore size and enabled plating with thin membranes without limiting hydrogen flux. This process enabled us to produce larger tubes and produce them in larger quantity and lower cost than we could by using isostatic pressing.

A one-dimensional mathematical model which breaks hydrogen transport through a membrane down into seven fundamental steps was developed. Using density functional theory (DFT), the energies of each of these steps may be calculated for a palladium alloy, and the permeability of that alloy may be predicted at various experimental conditions. Using the 1-D model, it was determined that for thin films at low temperatures, hydrogen desorption on the low-pressure permeate side tended to be rate limiting, while at higher temperatures hydrogen diffusion is rate limiting. The 1-D tool can be used to help understand why alloys may have higher or lower hydrogen permeation based on composition.

The prototype device with 12 palladium tubes demonstrated about 180 scfh of hydrogen permeation at 135 psid. This is below the expected design point because the feed pressure was lower and the permeate
pressure was higher than originally expected. A design change was made to enable the device to reach 200 psig. This increased the hydrogen permeation to about 275 scfh, which was still below the design point because the permeate pressure remained higher than expected. Future designs will require either a higher permeate pressure design point, or less gas handling of the permeate to reduce pressure at the membrane surface.

Acknowledgments
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Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CE</td>
<td>Cluster Expansion</td>
</tr>
<tr>
<td>CSM</td>
<td>Colorado School of Mines</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic Acid</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
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<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
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<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer Electrolyte Membrane</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly-tetrafluoroethylene</td>
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<tr>
<td>SAE</td>
<td>Society of Automotive Engineers</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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References