TITLE: COST-EFFECTIVE METHOD FOR PRODUCING SELF SUPPORTED PALLADIUM ALLOY MEMBRANES FOR USE IN EFFICIENT PRODUCTION OF COAL DERIVED HYDROGEN

REVISED QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD START DATE:	9/09/03 (PROGRAM START)
REPORTING PERIOD END DATE:	07/30/05
PRINCIPLE AUTHOR(S):	B. LANNING, J. ARPS
DATE REPORT WAS REISSUED:	08/31/05
DOE AWARD NUMBER:	DE-FC26-03NT41849
SUBMITTING ORGANIZATION:	SOUTHWEST RESEARCH INSTITUTE 6220 CULEBRA ROAD (78238-5166) P.O. BOX 28510 (78228-0510) SAN ANTONIO, TEXAS
OTHER TEAM MEMBERS:	COLORADO SCHOOL OF MINES IDATECH
SUBMIT TO:	NETL AAD DOCUMENT CONTROL BLDG. 921 U.S. DEPARTMENT OF ENERGY NATIONAL ENERGY TECHNOLOGY LABORATORY P.O. BOX 10940 PITTSBURGH, PA 15236-0940

SOUTHWEST RESEARCH INSTITUTE®

SAN ANTONIO HOUSTON WASHINGTON, DC

TITLE: COST-EFFECTIVE METHOD FOR PRODUCING SELF SUPPORTED PALLADIUM ALLOY MEMBRANES FOR USE IN EFFICIENT PRODUCTION OF COAL DERIVED HYDROGEN

REVISED QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD START DATE:	9/09/03 (PROGRAM START)
REPORTING PERIOD END DATE:	07/30/05
PRINCIPLE AUTHOR(S):	B. LANNING, J. ARPS
DATE REPORT WAS REISSUED:	08/31/05
DOE AWARD NUMBER:	DE-FC26-03NT41849
SUBMITTING ORGANIZATION:	SOUTHWEST RESEARCH INSTITUTE 6220 CULEBRA ROAD (78238-5166) P.O. BOX 28510 (78228-0510) SAN ANTONIO, TEXAS
OTHER TEAM MEMBERS:	COLORADO SCHOOL OF MINES IDATECH
SUBMIT TO:	NETL AAD DOCUMENT CONTROL BLDG. 921 U.S. DEPARTMENT OF ENERGY NATIONAL ENERGY TECHNOLOGY LABORATORY P.O. BOX 10940 PITTSBURGH, PA 15236-0940

APPROVED:

James H. Arps, Manager
Surface Engineering Section

DISCLAIMER

ABSTRACT

Efforts in this quarter were concentrated on developing vacuum processing procedures to produce thinner (<4 μm-thick), defect-free films over larger areas (>100 cm^2). We continued to test three different types of rigid supporting substrates, thermally oxidized silicon (10 cm diameter), polished borosilicate glass (10 cm diameter), and soda-lime glass (>100 cm^2 areas), each representing a different cost, surface roughness, and chemistry. Mechanical integrity, defect density, and release characteristics of the films, though similar for the oxidized silicon and borosilicate glass, were distinctly different for the inexpensive soda-lime (float) glass; i.e., more sensitive to surface impurities. In general, films less than 4 μm-thick were shown to be very sensitive to surface condition of the supporting substrate, particularly in the case of the soda-lime glass, to the point where surface strain overrode and dominated the intrinsic bulk stresses that are produced during the growth process. Therefore, in the near term (over the next quarter), large area films (>100 cm^2) will be produced at a minimum thickness of 5μm while further development will be conducted in subsequent quarters to reduce membrane thickness in large area films.

Continued hydrogen permeation experiments and characterization of 5 and 10 μm-thick, Pd-Cu films, with compositions near the 60/40 (Pd/Cu phase boundary) in combination with air oxidation treatments to improve performance. Pure hydrogen permeability for an as-received, 5 μm film at 400 ^oC was determined to be $1.3x10^{-4}$ $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg^{0.5}$ at steady state. Even a membrane ~ 10μm-thick, exhibited a steady state hydrogen flux of 32 $cm^3(STP)/cm^2min$ after air exposure, which, when normalized for DOE's Office of Fossil Energy's specified hydrogen flux with a ΔP of 100 psi and a permeate pressure of 50 psia, results in a flux of 155 $scf/h/ft^2$ (exceeding the 2007 target by 55% and 77% of the 2010 target).

Finally, on May 25, we presented a poster at the Hydrogen Program Review in Washington.

Table of Contents

1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pd-Cu alloy Vacuum Deposition –
Rigid substrates – Based on procedures reported previously for depositing and releasing Pd-Cu films from rigid silicon substrates, we extended this development to include larger silicon and glass substrates. In brief, processing parameters were optimized to produce films with poor adhesion and minimal electrostatic interaction forces using magnetron sputtering from an alloy target.

H_2 Testing – A membrane foil is first sandwiched between two circular supports, such as alumina paper, and then sealed with either a Kalrez O-ring (max. use to 315 ^oC) or Grafoil packing material (allowing a 650 ^oC upper use temperature in oxygen-free environments) in the 25 mm Millipore membrane cell. The membrane is then checked with helium to confirm a tight seal and that the membrane is defect (pinhole) free. Subsequently, the membrane is heated to operating temperature to begin permeation testing.

3.0 RESULTS AND DISCUSSION

3.1 Progress

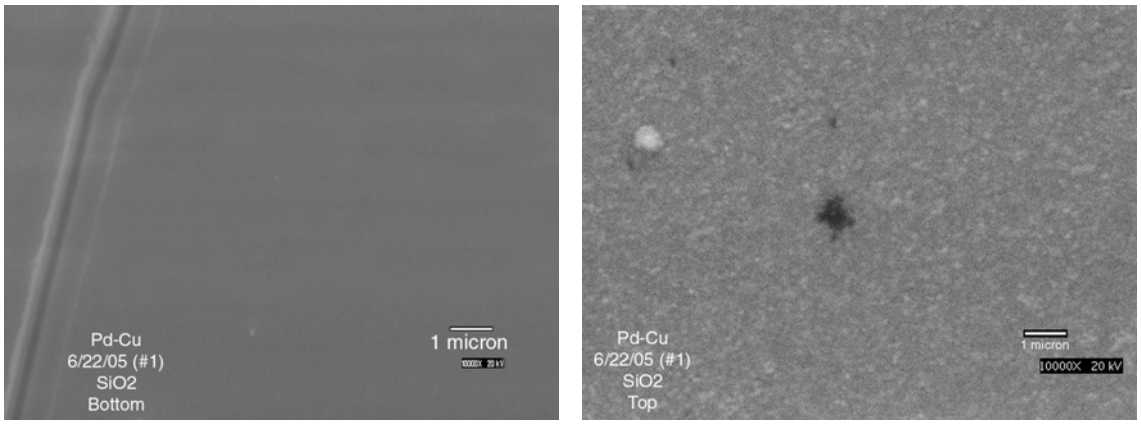
3.1.1 Optimization of Pd-Cu Membrane Formation

Rigid Substrates (silicon/glass)

Although procedures (processing parameters) were previously established for releasing 5 μm-thick films from 4" diameter (10 cm) rounds of oxidized silicon and polished borosilicate glass, the long term goal has been to produce thinner films with a larger surface area and with greater reproducibility. To accomplish this goal on a rigid backing substrate, we began developing procedures for releasing thinner films from inexpensive soda-lime glass. Different types of pre-cleaning procedures (both wet chemical and dry vacuum ion sputtering), in addition to pre-deposition of a thin release layer such as 10 nm-thick Al_2O_3, were investigated on the soda-lime glass in order to achieve consistency in film release and mechanical properties. Although 2.5 μm-thick films were consistently deposited onto the supporting soda-lime glass substrates (up to 230 cm^2 in area) without defects (as determined with "back-lighting" methods), defects were created in the films during the process of releasing the films from the glass substrate. Defect formation during release is directly attributable to surface contamination and variability in the cleaning procedure; alternative pre-treatment procedures are being implemented and their effect on film quality will be reported in the next quarter.

With the goal of understanding the release characteristics of the film, we have begun characterizing the interface between the glass substrate and the film after the film is released. In general, the side of the film that was in contact with the glass will then re-adhere to the glass when placed in contact with the glass. This attraction is primarily observed on the side that was in direct contact with the glass substrate during deposition; i.e., the top surface of the film (away from the substrate) does not exhibit any attraction to the glass substrate. This "Velcro" type effect is observed whenever the released side of the film is placed in contact with any surface that had been previously used for film preparation (i.e., a glass surface or even another metal surface). There appears to be a type of key-lock type of relationship between the various release surfaces.

The released metal surfaces were analyzed with Auger Electron Spectroscopy (AES) to check for trace elements and, other than the typical carbon and oxygen, we were not able to detect other trace elements, such as silicon. The "released" surface, as shown in the SEM image in Figure 1 (a), was essentially featureless at the magnification shown although the top surface (Figure (b)) exhibited some degree of texture (from profile measurements, the surface roughness was estimated to be less than 3 nm).



a) b)

Figure 1 – SEM image of Pd-Cu film at the a) release surface and b) top surface; films grown on (and released) from polished borosilicate glass.

3.1.2 H_2 Permeation Testing

Sputtered films on silicon – 5 μm-thick

Continued permeation experiments with a representative 5 μm-thick membrane, *SwRI-pg176*. Figure 2 shows the hydrogen flux behavior with time at 400 °C and 20 psi trans-membrane pressure and the influence of air oxidation treatments. The hydrogen flux at 20 psi achieved a steady state of approximately 28 cm^3(STP)/ cm^2 min relatively quickly. An in-situ air oxidation

was performed at 20 psig and 400 °C for 1 hour, upon which the hydrogen flux doubled to a steady value of approximately 59 cm^3(STP)/ cm^2 min. A second air oxidation was then performed where air was supplied to the foil at 20 psig and 400 °C for a period of 2 days. A jump in the hydrogen flux was observed followed by a gradual decrease to an even higher steady state of 78 cm^3(STP)/ cm^2 min. A subsequent oxidation resulted in a spike in the hydrogen flux, but eventually declined back to the previous steady state. The pure hydrogen permeability (measured at steady state after ~330 hours) was determined to be $1.3 \cdot 10^{-4}$ cm^3(STP)•cm/cm^2•s•$cmHg^{0.5}$. This permeability was calculated from the steady-state H_2 flux and a thickness of 5 μm (as determined with micrometer gauge). It is worth noting that this permeability corresponds to a flux of 187 ft^3(STP)/ft^2•h for a hydrogen partial pressure difference of 50 psi, which meets the DOE Fossil Energy flux target for 2007.

It should also be noted that this membrane displayed a helium leak that increased over time from about 3.7 to 9 cm^3(STP)/ cm^2 min. The hydrogen flux has been corrected for this leak. Analysis of the surface using SEM will be performed in addition to structure and composition analysis.

Wrought foils from Wilkenson – 25 μm-thick

We have been investigating the air oxidation effect further with our 25 μm control foil. See Figure 3 for a graph of hydrogen flow rate vs. time for *wilk_pg185*. This foil was heated in air ex-situ at 400 °C for 2 hours. This presumably cleans the surface of contaminants. The membrane was then mounted and heated to 400 °C in helium followed immediately by an in-situ air oxidation of the feed side. At this point, the membrane exhibited a slightly increasing hydrogen flow rate of about 110 cm^3(STP)/min. Next, the permeate side of the membrane was exposed to air at the same conditions. A hydrogen flux increase of ~50% was measured. This could support the hypothesis that the hydrogen flux increase is a result of surface effects. Another possibility is that carbon contamination inside the membrane (possibly from the fabrication procedure) is not completely removed after only the in-situ feed side oxidation. It could likely be a combination of these effects. As a control, the feed side of this membrane was exposed to air a second time to investigate its effect on hydrogen permeability. The flux marginally increased, indicating that the surface morphology did not change dramatically or that carbon contamination in the membrane was nearly completely removed after the second in-situ oxidation.

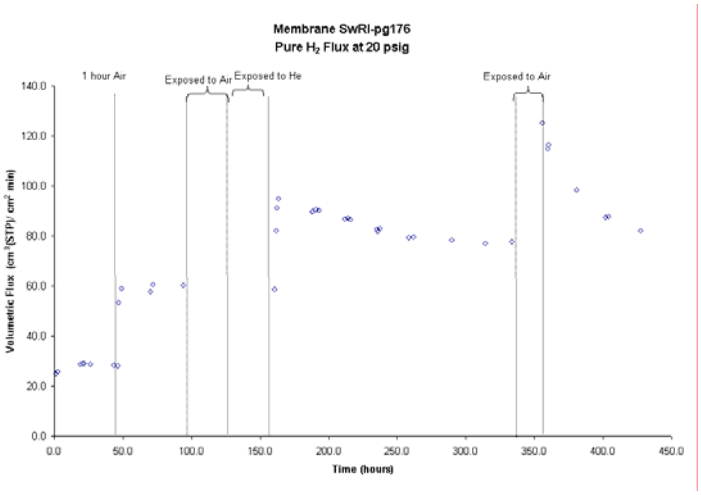


Figure 2. Influence of time and air oxidation on hydrogen permeation of membrane *SwRI-pg176* at 400 °C with a hydrogen feed pressure of 20 psig.

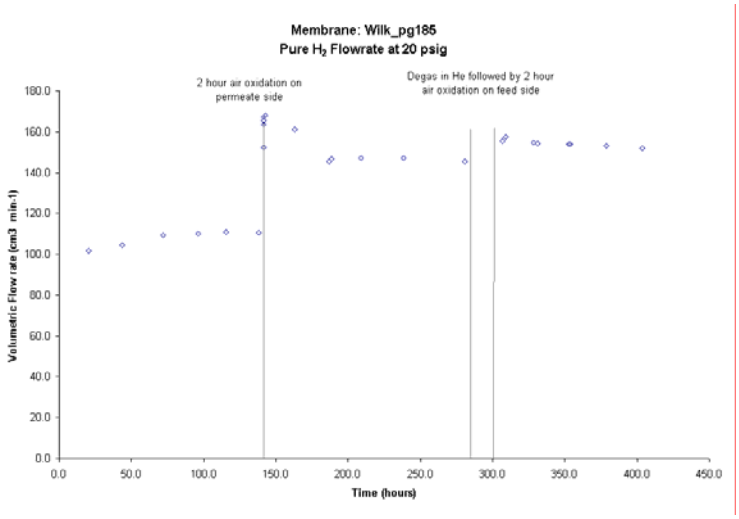


Figure 3. Influence of time and air oxidation on hydrogen permeation of membrane *wilk_pg185* at 400 °C with a hydrogen feed pressure of 20 psig.

Sputtered films on silicon – 10 μm-thick

Thicker membranes, up to 10 μm-thick, were also tested and results for a representative film, *SwRI_pg203*, are presented below. Initially, this membrane was heated to 250 °C in helium and subsequently tested for hydrogen permeation. After 15 hours of testing, there was essentially no hydrogen permeation through the membrane at 250 °C. With a 20 psi trans-membrane pressure, a hydrogen flux of only 0.3 cm^3(STP)/cm^2 min was measured. The temperature was then ramped to 400 °C, and the hydrogen flux began to increase yet remained lower than expected. Figure 4 shows the data set for this membrane after the temperature was increased to 400 °C. In light of recent results showing the influence of air exposure on these membranes, the feed side of this membrane was exposed to air at 10 psig for 2 hours at 400 °C in-situ. The time of the air exposure is marked on Figure 4 by the dotted vertical line at approximately 85 hours. As seen in the figure, the hydrogen flux rapidly increased to a steady hydrogen flux of 32 cm^3(STP)/cm^2 min after the air exposure.

Figure 5 shows the pure hydrogen flux vs. driving force once this steady value was achieved. From the data in this figure, the n-value was determined to be 0.59, indicating that the measured transport through the system may not be completely governed by solution diffusion in the bulk of the metal foil. However, the hydrogen/helium ideal separation factor at 20 psig and 400 °C was determined to be greater than 100,000. This reveals that the membrane was mostly defect free. Hence, Knudsen diffusion through the foil should not play a significant role in the transport mechanism and therefore is unlikely the reason for the deviation in the n-value. A possible reason for the slightly larger n value for this membrane could be contamination on the feed side such as carbon.

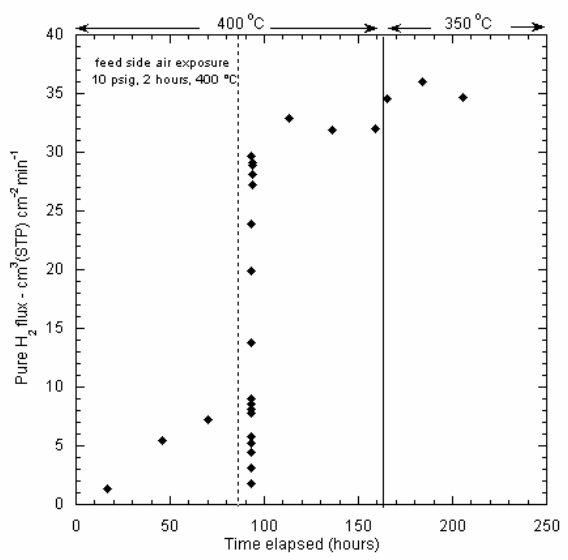


Figure 4. Influence of time and air oxidation on hydrogen permeation of membrane *SwRI-pg203* at 400 °C with a hydrogen feed pressure of 20 psig.

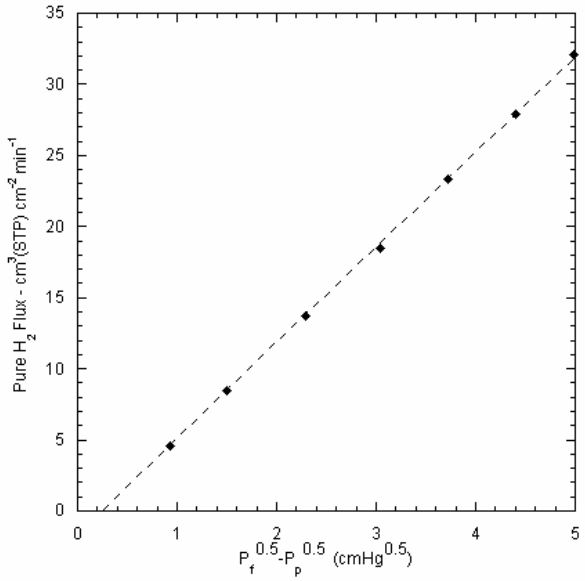


Figure 5. Pure hydrogen flux at 400 °C vs. driving force for membrane *SwRI-pg203*.

The DOE's Office of Fossil Energy specifies hydrogen flux with a ΔP of 100 psi and a permeate pressure of 50 psia. Based on the experimental measurements above, we can calculate the expected pure hydrogen flux for this membrane at these conditions to be 155 scf/h/ft^2. This membrane exceeds the 2007 target by 55 % and is 77 % of the 2010 target.

Based on SEM images of the cross-section of the foil (one of which is shown in Figure 6), an average membrane thickness was determined to be 9.7 μm. This is significant, in that it demonstrates that even a membrane approximately 10 μm thick can exceed the DOE's hydrogen flux target. Additionally, this value was used to calculate a pure hydrogen permeability of $1.1 \cdot 10^{-4}$ cm^3(STP)•cm/cm^2•s•cm Hg$^{0.5}$.

Crystalline structure analysis was performed using XRD after hydrogen permeation. The membrane was cooled relatively quickly from the last testing condition of 350 °C and it is presumed that the crystal structure reflects that temperature condition. The diffraction pattern is shown in Figure 7. It is interesting to note that there are prominent α and β-phase peaks observed. Based on the PdCu phase diagram, the α-phase is not expected at 350 °C given the composition of 60.25 wt% Pd mentioned above. Additionally, the hydrogen permeability of this membrane was relatively high, suggesting that the foil would be mostly or all in the higher permeability β-phase. EDS analysis was performed here to confirm the alloy composition. The composition measured here was determined to be 62.96 wt.% Pd. This is more consistent with the crystal structure determined by XRD, but less consistent with the high permeability measured that corresponds to an alloy composition at or very near to 60 wt.% Pd.

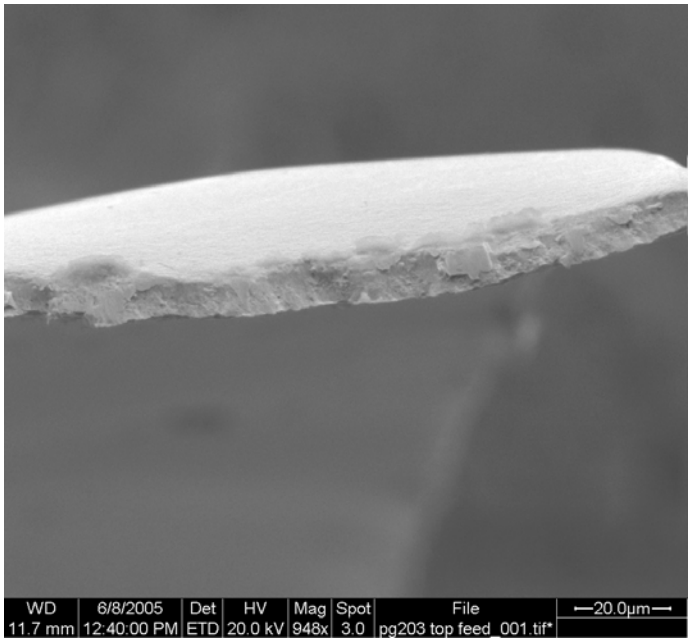


Figure 6. Cross-sectional image of membrane *SwRI-pg203*.

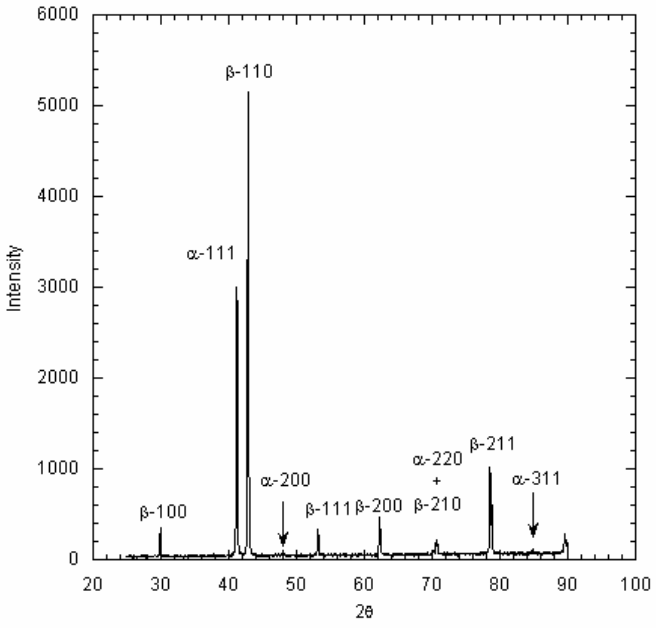


Figure 7. Diffraction pattern of membrane *SwRI-pg203* after permeation testing at 350 °C.

3.2 Problems Encountered:

As we have concentrated this last quarter on establishing procedures for producing thin, less than 5 μm-thick membranes without any pinholes, we have delayed fabrication of membranes to be delivered to IdaTech. We are still in the process of fabricating these films and will deliver to IdaTech upon completion.

3.3 Plans for Next Reporting Period:

- Complete fabrication of ~100 cm^2 membranes for delivery to IdaTech for incorporation into test module.
- Continue to develop procedures, such as oxygen pre-treatment, and develop processes for the incorporation of alloy additions, that will enhance hydrogen permeation.

4.0 CONCLUSION

We continued to test three different types of rigid supporting substrates, thermally oxidized silicon (10 cm diameter), polished borosilicate glass (10 cm diameter), and soda-lime glass (>100 cm^2 areas), each representing a different cost, surface roughness, and chemistry, with an overall goal to produce thinner (<4 μm-thick), defect-free Pd-Cu films over larger areas (>100

cm^2). Mechanical integrity, defect density, and release characteristics of the films, though similar for the oxidized silicon and borosilicate glass, were distinctly different for the inexpensive soda-lime (float) glass; i.e., more sensitive to surface impurities. In general, films less than 4 μm-thick were shown to be very sensitive to surface condition of the supporting substrate, particularly in the case of the soda-lime glass, to the point where surface strain overrode and dominated the intrinsic bulk stresses that are produced during the growth process. In thicker films (>5 μm), interface stresses are more adequately balanced by intrinsic bulk stresses such that the bulk stresses will control the release characteristics. Since bulk stresses are controlled by the growth characteristics (processing parameters), overall release characteristics and film properties are more easily controlled in thicker films. In the near term (over the next quarter), therefore, large area films (>100 cm^2) will be produced with a minimum thickness of 5μm while further development will be conducted in subsequent quarters to reduce membrane thickness in large area films.

Continued hydrogen permeation experiments and characterization of 5 and 10 μm-thick, Pd-Cu films with compositions near the 60/40 (Pd/Cu phase boundary) in combination with air oxidation treatments to improve performance. Pure hydrogen permeability for an as-received, 5 μm film at 400 ^oC was determined to be $1.3x10^{-4}$ $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg^{0.5}$ at steady state. Even a membrane ~ 10μm-thick, exhibited a steady state hydrogen flux of 32 $cm^3(STP)/cm^2min$ after air exposure, which, when normalized for DOE's Office of Fossil Energy's specified hydrogen flux with a ΔP of 100 psi and a permeate pressure of 50 psia, results in a flux of 155 $scf/h/ft^2$ (this flux exceeds the 2007 target by 55% and is a significant fraction (i.e. 77%) of the 2010 target).

Finally, on May 25, we presented a poster at the Hydrogen Program Review in Washington.

5.0 REFERENCES

N/A