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

QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD START DATE:	9/09/03 (PROGRAM START)
REPORTING PERIOD END DATE:	7/30/06
PRINCIPLE AUTHOR(S):	J. ARPS
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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, LLC
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

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APPROVED:

Ben H. Thacker, Director
Materials Engineering Department

DISCLAIMER

ABSTRACT

In the past quarter, we have delivered additional full-size membranes, 2” by 8” in area and 4-6 microns thick, to Idatech for incorporation and use in their new large-area prototype modules. Two other significant activities were the focus of work at SwRI this past quarter; 1) the development of annealing methods to and convert the Pd-Cu membranes from α-phase to β-phase or mixed α + β phase and 2) initiation of a series of controlled experiments to produce Pd-Cu membranes with different Pd concentration from 57-65 at% Pd.

Colorado School of Mines has continued to test additional membranes including Pd-Cu-Ru and Pd-Cu-Rh samples. We are attempting to resolve some discrepancies between energy dispersive X-ray spectrometry (EDS) measurements conducted at SwRI and CSM. In general, CSM measurements typically indicate a lower Pd concentration (2-3 atomic percent) than measurements on the same material conducted at SwRI. CSM has also observed some apparent differences in membrane performance depending on pre-annealing conditions.

Idatech, LLC has begun to assemble modules utilizing membranes supplied by SwRI and will begin a final series of permeation tests in the upcoming quarter.

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1.0 EXECUTIVE SUMMARY

Refer to abstract

2.0 EXPERIMENTAL

2.1 Pd-Cu Membrane Deposition and Annealing Experiments

In order to provide Idatech with a sufficient inventory of membranes for use in their upcoming test assemblies, additional deposition runs were carried out on 12-inch diameter silicon wafers. One important finding this quarter was that after the membrane is deposited and removed, the wafers can be reused to make additional membranes with minimal additional pinhole defects if the substrate is properly cleaned.

Another study we initiated with CSM was an effort so examine the permeability of vacuum fabricated membranes as a function of Pd content. Specifically we wanted to determine if the structure of these membrane differed from conventional rolled material as a function of Pd-Cu stoicheometry. To achieve these compositions, additional small pieces of pure Pd were placed on top of a nominal 60-40 Pd-Cu sputter target. After a tooling run was conducted, the composition was measured by energy dispersive X-ray spectrometry (EDS) and adjusted by placing additional pieces or repositioning the pieces until the desired composition was obtained. Figure 1 show the target with several pieces of Pd added in an effort to create a Pd content of ~66at%. Membranes with 62-66 at Pd have now been produce and small samples will be shipped to CSM next month.

Figure 1. Sputter target modified to increase the membrane Pd content.

As has been previously reported, as-deposited membranes are usually in the fcc phase and transform to bcc or mixed fcc+bcc upon heating to 400°C. Because these membranes are very thin it may not be possible to assemble the membranes into a module while still in the fcc phase as the change in lattice parameter associated with the phase transformation can result in a slight contraction that could place significant stress on the membrane and cause it to rupture. Hence we began a series of annealing experiments to convert the membrane to the desired phase prior to assembly in a module. Figure 2 shows the arrangement we development. The membrane is held between two pyrex glass plates held together with simple binder clips which have been stripped of paint prior to use. Stainless steel lock wire is used to maintain a separation between the plates to limit air entrapment and allow the membrane to expand or contract more freely without curling. After mounting, the membrane samples were placed in a tube furnace purged with a continuous flow of Ar at annealed at 450°C for 12 hours.

Figure 2. Photograph of fixture used to hold membranes flat during annealing.

2.2 Testing and Characterization at CSM

CSM has continued hydrogen permeation testing of SwRI fabricated membranes while investigating methods to anneal samples and bond samples together to seal pinholes. A list of samples that CSM has attempted to test over the past three months are listed in Table 1. Selected samples were also characterized using XRD, SEM, and EDS in the past quarter.

Table 1. Samples tested at CSM, N/A indicates the sample tore or developed a leak during testing.

Date	Maker Pd %	EDAX Pd %	Max Flux @ 400C & 20psi [$cm^3/cm^2 \cdot min$]	CSM Thickness [microns]	Source	Maker Thickness	Permeance @ 400C [$cm^3(STP)/cm^2 \cdot s \cdot cmHg^{0.5}$]	Permeability @ 400C [$cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$]
04/10/2002	59.14	---	N/A	---	SwRI	5.78	N/A	N/A
04/10/2002	59.14							
04/26/2002	Ternary	---	15.10	5.00	SwRI	5.00	0.05040	2.52E-05
04/13/2002	Ternary	---	1.48	5.00	SwRI	5.00	0.00491	2.46E-06
04/13/2002	Ternary	---	2.11	5.00	SwRI	5.00	0.00703	3.52E-06
04/26/2002	---	---	N/A	6.00	SwRI	6.00	N/A	N/A
05/09/2002	---	---	N/A	6.00	SwRI	6.00	N/A	N/A
05/25/2002	59.50	57.00	20.65	8.80	SEM	---	0.0691	6.08E-05
05/25/2002	59.50	57.00	10.41	8.80	SEM	---	0.0348	3.06E-05
06/11/2002	59.50	57.00	20.8	8.80	SEM	---	0.0692	6.09E-05
06/11/2002	59.50	57.00	12.13	8.80	SEM	---	3.56E-05	3.13E-08
06/27/2002	59.50	57.00	N/A	8.80	SEM	---	N/A	N/A

3.0 RESULTS AND DISCUSSION

3.1 Pd-Cu Membrane Annealing Trials

Figure 3 shows full-size membranes before and after annealing. Invariably, some degree of wrinkling was observed in the foil after annealing, although the foils tended to lay more flat suggesting that the heat treatment had relieved much if not all of the residual stress present in the as-deposited membrane. Several of the annealed membranes were inspected for the presence of pinholes with passing samples supplied to Idatech.

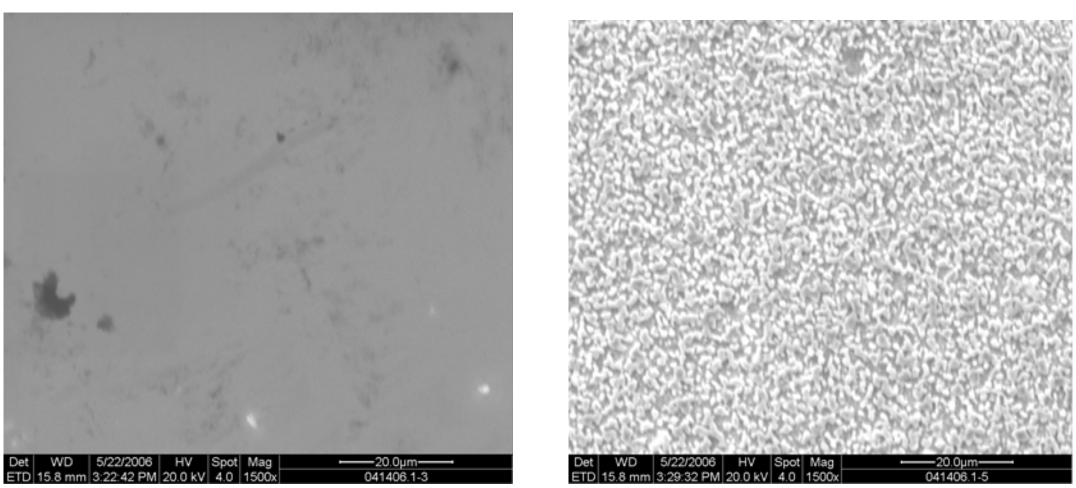
Figure 3. Full-size membranes before (foreground) and after (background) annealing in argon for 12 hours at 450^{o}C.

An extensive number of trials were carried out in an effort to produce low-stress pinhole-free membranes with Pd concentration from 60-66 at%. Even though several pieces of Pd were added to the target, no significant increase in the Pd content of the membrane was observed. After several iterations, a setup was established that allowed us to obtain the desired composition.

3.2 Membrane Permeation Testing and Characterization

Membrane 031406#2 was a ternary alloy with rhodium. The thickness was found to be 7.47 μm. After testing at 400^{o}C, the sample was heated to 525^{o}C for 10 hours to anneal the membranes. The hydrogen flux through a 1-inch diameter sample did not change after annealing. The final value was 1.48 cm^3(STP)/cm$^{2}\cdot$min at 400^{o}C and 20 psi. For a 2-inch sample, the hydrogen flux increased from 4.16 to 9.06 cm^3(STP)/cm$^{2}\cdot$min at 400^{o}C and 20 psi. This is an increase of a factor of 2 after annealing. The helium flux also increased by a similar factor (0.408 to 0.880 cm^3(STP)/cm$^{2}\cdot$min at 400^{o}C and 20 psi). The corresponding hydrogen permeability for the 2 inch sample was 3.5 • 10^{-6} cm^3(STP)cm/cm$^{2}\cdot$s$\cdot$cmHg$^{0.5}$.

Figures 4a and 4b show a significant change in the surface structure of the before and after samples based on SEM examination. The sample was not annealed before testing, but an air purge was run during testing. EDAX of the surface found a slight increase in the palladium composition after testing. The compositions were 43.62%Cu, 50.56%Pd, and 5.83%Rh and 41.68%Cu, 52.06%Pd, and 6.26%Rh before and after testing, respectively.



a **b**

Figure 4. Before (a) and after (b) testing SEM surface images of membrane 031406#2

Sample 030206#1, a Pd-Cu-Ru membrane, was tested for 11 days. The pure hydrogen flux reached 15.1 cm^3(STP)/cm^2·min at 400°C and 20 psi, but over the course of testing a substantial nitrogen leak developed. Therefore, the hydrogen flux and corresponding permeability are somewhat suspect. Roughening of the surface after testing was observed similar to the Pd-Cu-Rh sample. However, the surface of the Ru-doped membrane showed a significant change in composition. Before testing, the membrane was 44.61%Cu, 52.32%Pd, and 3.07%Ru. The palladium composition rose significantly after the testing and the final feed surface composition was 7.11%Cu, 90.57%Pd, and 2.32%Ru.

SEM, XRD, and EDAX analysis was done on selected samples from batch 051206#1 (Pd-Cu alloy). The XRD results showed that the as-received membranes were in the pure alpha phase while the annealed samples were purely beta (Figure 5). SEM images indicated that the membrane was unchanged during the annealing process.

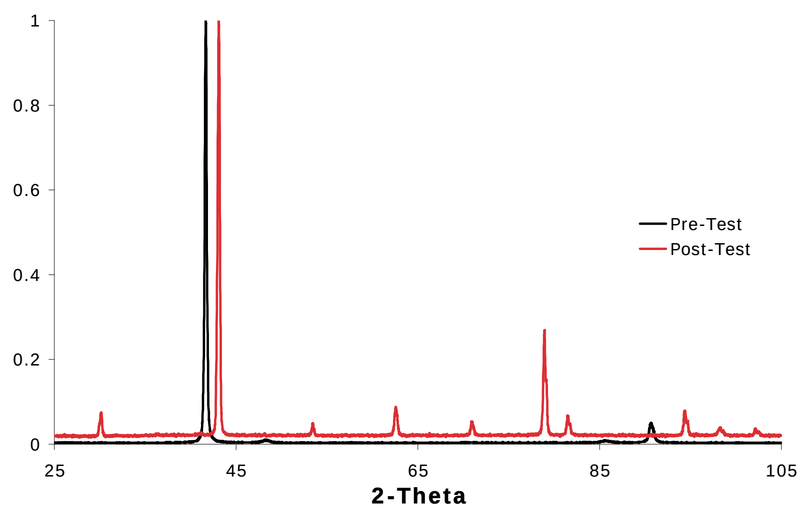


Figure 5. XRD spectrum of 051206#1 before and after testing

The membrane as-received was measured by EDX to be 57%Pd and 43%Cu which differed from SwRI measurement of 59.5%Pd and 40.5% Cu. Two membranes from batch 051206#1 are being tested. One was annealed at SwRI and the other is an as-received membrane from the same batch. The current fluxes at 20 psid and 400°C are 10 cm^3(STP)/cm^2·min and 24 cm^3(STP)/cm^2·min for the annealed and as-received membranes, respectively. These values are estimates since the area of the membrane is not known until the test is complete. This is the second test of samples 051206#1 where an as-received and an annealed sample are run simultaneously. The first test showed similar fluxes at the same conditions. The annealed membrane reached a flux of 10 cm^3(STP)/cm^2·min and the as-received sample had a maximum flux of 20 cm^3(STP)/cm^2·min at 20 psid and 400°C.

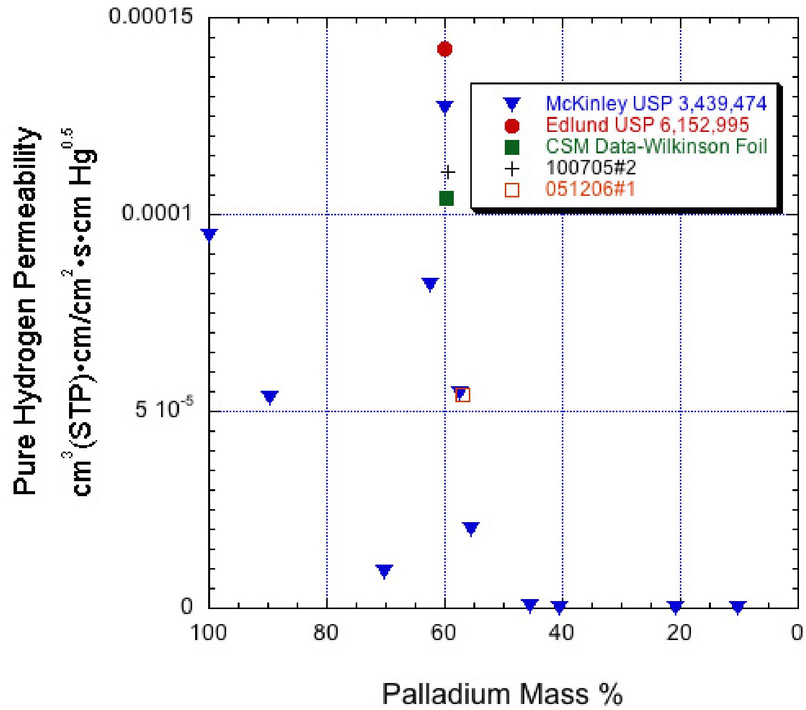


Figure 6. Comparison of permeability of the as-received 051206#1 (assuming 57% Pd) to published values at 350°C from McKinley (U. S. Patent 3,350,845, 1967)

The permeability of the as received samples of 051206#1 was at the expected value for its measured composition, as shown in Figure 6. In this plot, we compare SWRI membranes 100705#2 and 051206#1 to permeability data from the McKinley patent. The agreement with the literature is excellent. The annealed samples had a permeability of approximately $3 \cdot 10^{-5}$ $cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$ which is half the permeability of the as-received samples.

In an effort to for fully understand the effect of annealing on these Pd-Cu membranes, a 2-inch un-annealed sample of 051206#1 and a 1-inch sample of the Wilkinson 25 micron thick, $Pd_{60}Cu_{40}$ standard foil were annealed at 400^{o}C for 8 hours. The atmosphere was set to forming gas, but as has been seen before the membrane samples were oxidized. The two samples were then loaded into the test cells with no helium leak at room temperature. The furnace was ramped at 3^{o}C per minute to 400^{o}C where the helium flux remained zero throughout heating. The membranes remained under helium at 400^{o}C for 24 hours with no permeation of helium. The membranes were then exposed to hydrogen. Upon hydrogen exposure, the Wilkinson standard started with a low flux (1.61 $cm^3(STP)/cm^{2} \cdot min$) at 400^{o}C and 20 psid while the SwRI sample tore. The Wilkinson foil reached a flux of 2.98 $cm^3(STP)/cm^{2} \cdot min$ at 400^{o}C and 20 psig and was then purged with air. At the same conditions, the flux reached 13 $cm^3(STP)/cm^{2} \cdot min$.

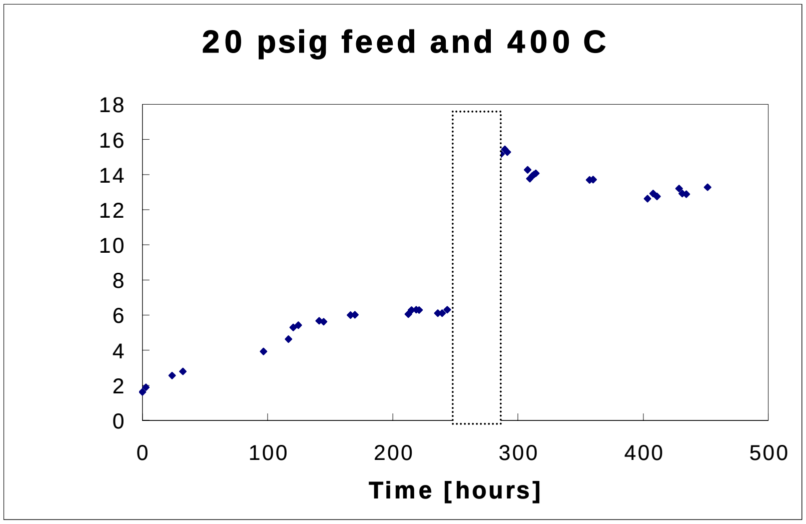


Figure7. Wilkinson foil flux over time at 400°C and 20 psid.

The air purge, denoted by the box in Figure 7, significantly raised the flux of the Wilkinson membrane. This has also been observed previously with the SwRI membranes. The final flux corresponds to a permeability of 1.1×10^{-4} $cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$ at 400°C. This is in good agreement with the data for Wilkinson foil samples from previous measurements at CSM.

One of the samples from batch 051206#1 that was annealed at SwRI was sprayed with palladium acetate, oxidized, and then reduced. This process added palladium to the membrane which raised the composition from 57%Pd to 60%Pd. From Figure 6, it was suggested that the current samples of 051206#1 were lower than expected in palladium composition. We hope to show that the spraying process increased the Pd composition which should raise the permeability. This test is scheduled to be completed in August.

3.3 Reporting

The project PI (Dr. Arps) and Bill Pledger, Chief Engineer at Idatech, gave a joint presentation at NETL-Pittsburgh on July 21st. Project activities and accomplishments were reviewed and discussed along with prospects for scale-up of the technology and demonstration on a pilot level.

3.4 Plans for Next Reporting Period:

- Idatech will complete pressure and purification testing of at least one SwRI-manufactured membrane and test it in a prototype module assembly.
- CSM will complete testing of remaining membranes fabricated at SwRI

- SwRI will complete a preliminary cost analysis for the pilot-scale production of thin membrane material which will be included in the final report.

4.0 CONCLUSION

Pending the successful assembly and testing of a full-scale membrane at Idatech, all major milestones for the project will have been achieved. We are producing membranes on a routine basis although efforts to optimize composition, minimize pinholes, and control stress and microstructure before and after annealing or exposure to feed streams at elevated temperatures are an ongoing process.