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

## QUARTERLY TECHNICAL PROGRESS REPORT

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| REPORTING PERIOD START DATE: | 9/09/03 (PROGRAM START) |
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| OTHER TEAM MEMBERS: | COLORADO SCHOOL OF MINES<br>IDATECH |
| SUBMIT TO: | NETL AAD DOCUMENT CONTROL<br>U.S. DEPARTMENT OF ENERGY<br>NATIONAL ENERGY TECHNOLOGY LABORATORY<br>BUILDING 921<br>626 COCHRANS MILL R0AD<br>P.O. BOX 10940<br>PITTSBURGH, PA 15236-0940 |

SOUTHWEST RESEARCH INSTITUTE®
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APPROVED:

James H. Arps, Manager
Surface Engineering Section

# DISCLAIMER

# ABSTRACT

Extending upon development efforts last quarter to produce "free-standing", copper and palladium alloy films, the goal this quarter has been to produce pinhole-free, Pd-Cu alloy films up to 5 × 5" in area (1 - 3 microns thick) using both magnetron sputtering and e-beam evaporation on PVA (Solublon) and polystyrene backing materials.  A set of experiments were conducted to assess processing methods/solutions chemistry for removing the polymer backing material from the Pd-Cu film.  For all of the alloy films produced to this point, we were unable to produce pinhole-free films on plastic although we were able to produce free-standing Pd-Cu films at less than 0.5 microns thick with minimal intrinsic stress.  Subsequently, to evaluate gas permeation and leakage across the films, two films were sandwiched together on top of a porous Monel support disc (25 mm in diameter) and then tested in a leak test apparatus.  Using two Cu films (10 micron thickness total) in the sandwich configuration, leak rates were about 20% of the background leak rate.

# TABLE OF CONTENTS

## 1.0 EXECUTIVE SUMMARY

Extending upon development efforts last quarter to produce "free-standing", copper and palladium alloy films, the goal this quarter has been to produce pinhole-free, Pd-Cu alloy films up to 5 × 5" in area (1 - 3 microns thick) using both magnetron sputtering and e-beam evaporation on PVA (Solublon) and polystyrene backing materials. A set of experiments was conducted to assess processing methods/solutions chemistry for removing the polymer backing material from the Pd-Cu film. For all of the alloy films produced to this point, we were unable to produce pinhole-free films on plastic although we were able to produce free-standing Pd-Cu films at less than 0.5 microns thick with minimal intrinsic stress. Subsequently, to evaluate gas permeation and leakage across the films, two films were sandwiched together on top of a porous Monel support disc (25 mm in diameter) and then tested in a leak test apparatus. Using two Cu films (10 micron thickness total) in the sandwich configuration, leak rates were about 20% of the background leak rate.

## 2.0 EXPERIMENTAL

***<u>Pd-Cu alloy Vacuum Deposition</u>***: Pd-Cu alloy films were deposited onto both PVA (Solublon) and polystyrene backing materials using magnetron sputtering and e-beam evaporation. In the case of magnetron sputtering, Pd-Cu films were deposited from a Pd-Cu target (power density of 0.24 – 1.25 $W.cm^{-2}$, sputter pressure of 1.0 mtorr, and no active cooling) onto a plastic backing material in a batch, planetary configuration; whereas, in the case of evaporation, Pd-Cu alloy films were deposited onto plastic backing materials in a drum (web) coating configuration. A design of experiments approach was implemented in the case of the evaporation experiments in the web coater to better evaluate the large number of parameters; i.e., metal deposition rates (1 – 4 nm/sec), web speed (0 - 0.2 m/sec), drum temperature, (0 - 60°C), plastic backing film (Solublon, polystyrene), and others.

*<u>Plastic Backing Removal:</u>* Pd-Cu alloy coated plastic samples were first cut into discs 75 mm in diameter, sandwiched together with a porous metal disc (Monel) between two microscreens and then clamped (refer to schematic in Figure 1). To remove the plastic backing material, the samples are then lowered horizontally, coated polymer discs up, Monel mesh down, into the appropriate solvent; hot water (60 - 80°C) for Solublon and chloroform (room temperature) for polystyrene. Polymer dissolution (removal rate) was evaluated as a function of temperature and time. Nominal times were 30 seconds for the Solublon and 600 seconds for the polystyrene. Upon dissolution of the polymer backing material, samples were removed from the solvent, carefully disassembled and then dried.

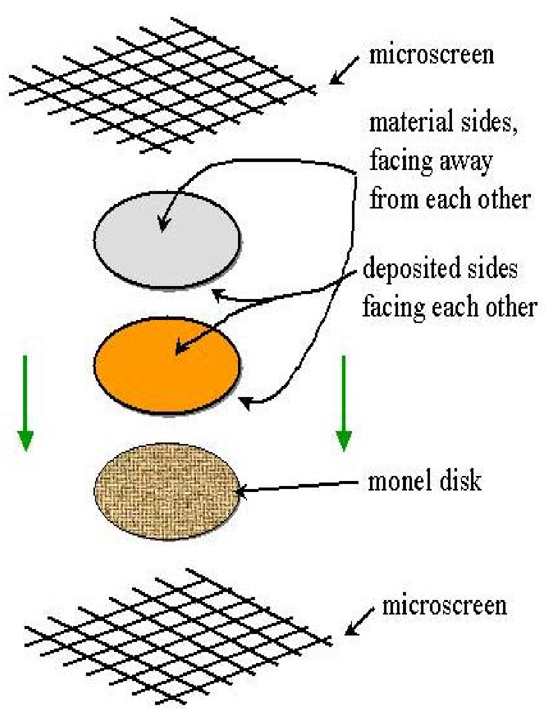


Figure 1. Schematic of sandwich configuration.

*Inert gas (He) Leak Test*: A system was put together quickly to characterize the leak rate of the metal film samples sent to CSM at room temperature. A schematic of the simple leak test apparatus is given in Figure 2 below. The heart of the apparatus is a 25 mm diameter, stainless steel membrane holder manufactured by Millipore. The test procedure was to pressurize the feed side of the membrane cell to a moderate pressure, 50 - 100 psig, and then measure the time necessary for the feed pressure to decay. A simple material balance expression is used to estimate the leak rate of the sample gas, which is then normalized by the membrane area (19 mm diameter area available for permeation = 2.8 $cm^2$ = 2.8 • $10^{-4}$ $m^2$). Before testing the foil samples sent by SWRI®, a baseline leak test was run on the apparatus using a relatively thick Al foil sample, assumed to be leak free. This test was to ascertain the leaks in the plumbing and the o-ring seal in the Millipore membrane holder. The baseline leak rate, using He, was 3•$10^{-8}$ mole/s with the Al foil sample in the cell. The baseline leak is then subtracted from the He leak rate of the Cu foil samples.

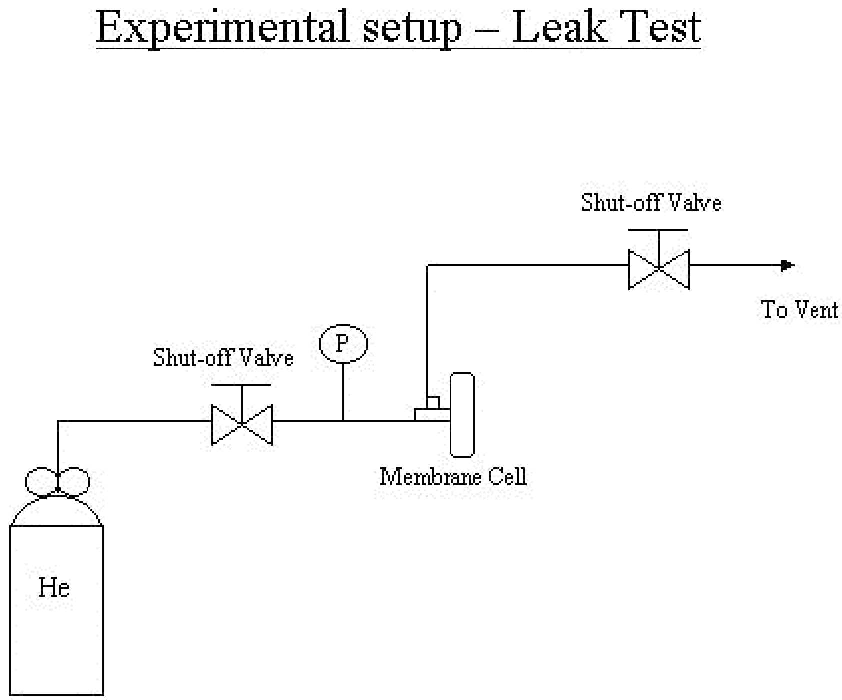


Figure 2. Schematic of CSM inert gas leak test apparatus.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Progress

#### *3.1.1 Pd-Cu Alloy Deposition*

*Magnetron Sputtered*: Pd-Cu alloy films were sputtered from a 60/40, Pd/Cu alloy target onto 6” × 6” Solublon and polystyrene films and the resulting compositions of the as-deposited film was 62.5 wt.% palladium, 37.5 wt.% copper. Since as-deposited films appear to be slightly Pd-rich, future films could be produced with higher copper/palladium ratios by placing a proportionate amount of copper pieces onto the target surface.

Without having the ability to actively cool the polymer backing film during the sputtering process, however, the resulting films contained high stresses as the polymer backing materials softened with temperature. Rather than continue with the existing configuration, the approach will be to re-configure our drum coating system to accommodate the Pd-Cu target material.

*Co-evaporation (e-beam):* Pd-Cu alloy films were formed on polymer backing materials in the 12” wide drum or web-coating system shown in Figure 3. Deposition rates of palladium and copper were independently controlled using crystal quartz monitor of electron impact emission spectroscopy (EIES). After having established uniformity profiles and elemental distribution across the deposition zone, a design of experiments (DOE) approach was conducted to correlate processing parameters (i.e., deposition/web feed rates, drum temperature, polymer pre-treatment, etc.) with final properties (response) of the Pd-Cu alloy films (i.e., composition, defects, strain). From the initial DOE tests conducted on PVA (Solublon), we observed excessive film strain and corresponding delamination at total deposition rates greater than 2 nm/sec and for web feed rates < 0.001 m/sec. The goal for these initial trials were to define rates such that Pd-Cu alloy films could be produced with minimal defects and strain. Since total thickness of the films were kept low (< 250 nm) in order to rapidly screen processing conditions, the resulting films were too thin to remove the backing polymer material. We are currently in the process of producing thicker films in order to evaluate the free-standing properties (i.e., permeability) of the films. In addition, we currently evaluating techniques to pre-treat or functionalize the polymer surface (increase surface energy, decrease roughness) in order to increase wetting/planarization of the Pd-Cu alloy film and reduce pinhole-type defects.

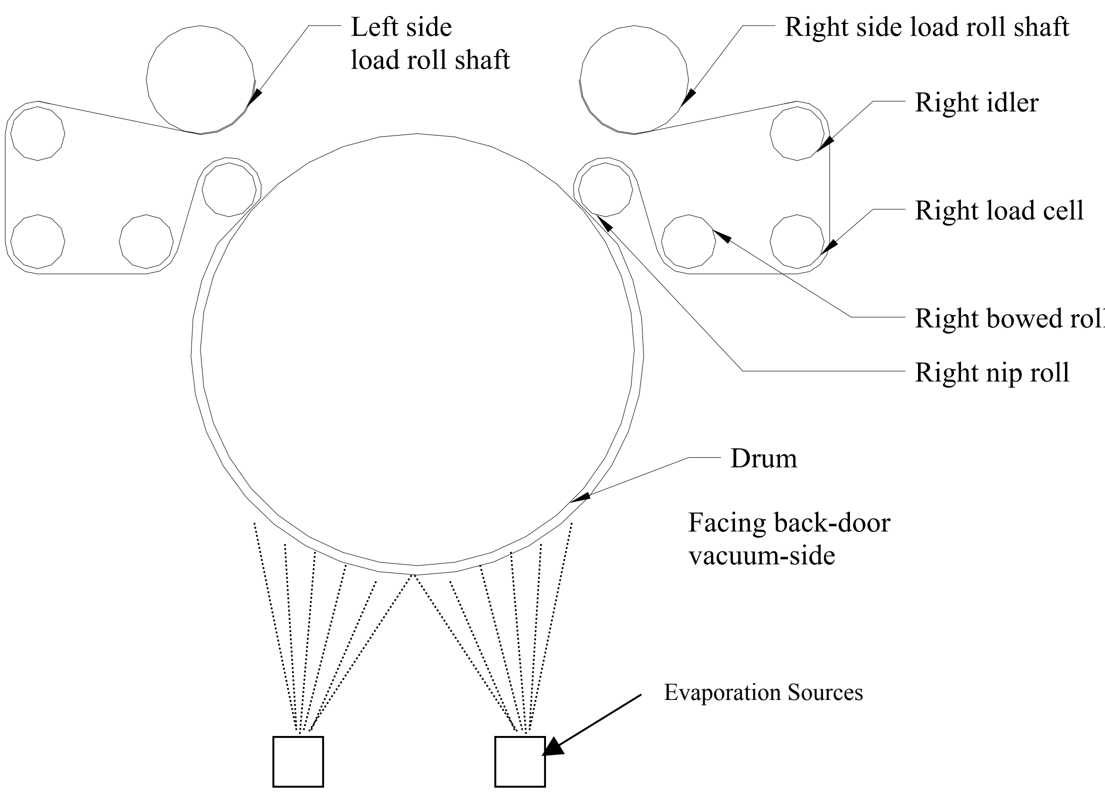


Figure 3. Schematic of web roll coater with evaporation sources.

### *3.1.2 Plastic Backing Removal*

Both polystyrene and PVA (Solublon) represent unique challenges in the development of procedures for removing or separating the Pd-Cu film from the plastic. A first order effect on the properties of the final Pd-Cu alloy film is the intrinsic strain or stress in the film. At the one extreme, too much stress in the film can lead to total fragmentation of the thin film as the supporting polymer material is dissolved away. Extrinsic stress can form due to thermal expansion differences between the metal and polymer. For example, a fully dense, contiguous metal layer (i.e., wetting) at the polymer surface is less compliant and with the thermal expansion differences between the metal film and the polymer backing material, excessive strain can build up in the film and promote fragmentation in the backing removal process.

Using the procedures outlined in the experimental section, a number of metal films were successfully removed from the polymer backing material (both PVA (Solublon) and polystyrene) and retained on the porous Monel grid material. Although the procedures and corresponding fixtures were representative of a batch type process, the established methodology can be transitioned to a large-scale, continuous processing format. Based on our efforts to date, both polystyrene and Solublon materials will be carried forward in subsequent alloy membrane development tasks.

### *3.1.3 Preliminary Gas (He) Leak Testing*

As per the procedures outlined in the experimental section, the leak rate of the metal foils was characterized. Since our current single metal films contain defects across a 25 mm area, we sandwiched two films together in order to evaluate the leak test apparatus. Sample films exhibited leak rates between five times the background He leak rate and 20% the background. For comparison, when composite Pd and Pd alloy membranes made by electroless plating are leak tested, the $N_2$ leak rate is typically $\leq 10^{-4}$ mole/m$^2$•s before annealing (Roa et al., 2003). Annealing at temperatures above 300°C typically reduces the leak rate further. Typical pure hydrogen fluxes for our composite Pd alloy membranes of micron thickness are in the range of 0.1 – 0.5 mole/m$^2$•s for a 50 psig feed gas.

## 3.2 Problems Encountered

As reported above, pinhole defects in the single layers can create short circuit flow paths in the membrane, and therefore, efforts are currently in progress to alleviate the pinhole defect issues in the films. The current issue of pinholes will not affect the near term milestones although it can have an impact on the long-term implementation of the membranes.

## 3.3 Plans for The Next Reporting Period

- Implementation of methods to minimize defect formation in large area, Pd-Cu alloy films in addition to development of methods to seal defects in membranes once formed;
- Complete initial series of leakage and purification tests at CSM on SwRI-fabricated membranes in an effort to further optimize processing parameters;

## 4.0 CONCLUSION

Pd-Cu alloy films up to 5 × 5" in area (1-3 microns thick) were created using both magnetron sputtering and e-beam evaporation on PVA (Solublon) and polystyrene backing materials. In the case of co-evaporation in a web coater, uniformity profiles and elemental distribution were established across the deposition zone in addition to conducting a design of experiments (DOE) to correlate processing parameters (i.e., deposition/web feed rates, drum temperature, polymer pre-treatment, etc.) with final properties (response) of the Pd-Cu alloy films (i.e., composition, defects, strain). A set of experiments were also conducted to assess processing methods/solutions chemistry for removing the polymer backing material from the Pd-Cu film. Using two Cu films (10 micron thickness total) in a sandwich configuration, leak rates were measured to be about 20% of the background leak rate.

## 5.0 REFERENCES

Roa, F. Way, J. D., McCormick, R. L. and S. N. Paglieri, "Preparation and Characterization of Pd-Cu Composite Membranes for $H_2$ Separation," *The Chemical Engineering Journal*, 2003. 93(1): p. 11-22.