II.D.5 Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

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Subcontractors:
- Power+Energy, Inc. (P+E), Ivyland, PA
- Metal Hydride Technologies, Inc., Burlington, VT
- Pall Corporation, Cortland, NY

Project Start Date: June 15, 2007
Project End Date: June 30, 2010

Objectives

- Develop and construct hydrogen (H_2) membrane separators using sulfur-resistant palladium (Pd) alloys and membrane separators using proprietary palladium copper transition metal (PdCuTM) alloys.
- Establish the stability and resistance of proprietary PdCuTM trimetallic alloys to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia (NH_3).
- Develop a sulfur-, halide-, and NH_3-resistant alloy membrane with a projected H_2 permeance of 25 m^3m^{-2} $atm^{-0.5}$ h^{-1} at 400°C and capable of operating at pressures of 12.1 MPa (≈120 atm, 1,750 psia).
- Construct and experimentally validate the performance of 0.1 kg/day H_2 PdCuTM trimetallic alloy membrane separators at feed pressures of 2 MPa (290 psia) in the presence of hydrogen sulfide (H_2S), NH_3, and hydrogen chloride (HCl).

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability
(L) Impurities
(N) Hydrogen Selectivity
(P) Flux

Technical Targets

This project consists of three parts: atomistic modeling, H_2 separator fabrication, and membrane separator experimental evaluation. The project has entered the final phase of work where the testing and evaluating of "best of class" H_2 selective separators will be completed. The progress toward achieving the DOE technical targets based on the atomistic modeling predictions and experimental data is shown in Table 1.

Accomplishments

- Developed an atomistic modeling screening approach to evaluate materials for susceptibility to sulfur attack.
- Evaluated the performance of face-centered cubic (FCC) PdCu separators under the DOE testing protocol.
- Confirmed the sulfur resistance and stability of the PdCu alloy.
- Produced single tube separators with the UTRC ternary PdCuTM composition with doubled performance versus early 2009 results.
- Identified a polishing process to remove the surface barrier produced during manufacture of PdCuTM tubes.

Introduction

This project is focused on increasing the technology readiness level of Pd-based metallic membranes for H_2 separation from coal-biomass gasifier exhaust or similar H_2-containing gas streams. Quantum mechanical atomistic modeling was performed in a previous contract to develop a ternary PdCu alloy for a water-gas shift membrane reactor (WGSMR) in a coal gasifier system. The alloy was based on the concept of making the body-centered cubic (BCC) phase of a PdCu binary alloy stable at WGSMR temperatures in the presence of high concentrations of poisons such as sulfur. The

TABLE 1. Progress toward the Hydrogen Separation Technical Target

Metric	2010 DOE Target	Current Project Status	Notes
Hydrogen Flux	200 $ft^3ft^{-2}h^{-1}$	61 $ft^3ft^{-2}h^{-1}$ (P+E alloy) 45 $ft^3ft^{-2}h^{-1}$ (P+E alloy)	• P+E alloy at 600 °C; 100 psig H_2 • P+E alloy at 450 °C; 200 psia H_2
Temperature	300–600 °C	350–600 °C	• UTRC ternary alloy limited to 475 °C
Sulfur tolerance	20 ppmv	78 ppmv H_2S (P+E alloy) 9 ppmv NH_3 (P+E alloy)	• Demonstrated with P+E alloy at 450 °C • Demonstrated 487±4 ppmv for 4 hours • Demonstrated 9 ppmv NH_3 for 175 hours
ΔP operating capability	Up to 400 psi ΔP	200 psig	• Current tube thicknesses limited to ≈200 psia
CO tolerance	Yes	Yes	• Demonstrated up to 13.3% CO at 90 psia total pressure; >9% CO at 304.7 psia
Hydrogen purity	99.5%	99.9999%	• P+E manufacturing design and manufacturing ensures no leaks • CO < 1 ppm, S < 15 ppbv desired for fuel cell applications

BCC phase of PdCu has a much higher H_2 permeability than the FCC materials and the FCC materials have been shown to have good sulfur resistance. Thus, a stabilized BCC alloy should be able to obtain the high permeability of alloys like PdAg with the sulfur tolerance of FCC PdCu. One of the major objectives of this work is to experimentally validate the UTRC PdCu ternary alloy performance. An additional objective is to experimentally evaluate the best commercially available FCC PdCu alloy from Power+Energy for meeting the DOE technical targets.

Approach

The approach for this project is to experimentally validate two different PdCu-based alloys for H_2 separation. Additional atomistic modeling has been performed to examine performance characteristics, such as resistance to carbon formation and sulfur poisoning. In parallel with the modeling, separator units of both the Power+Energy and UTRC alloys were manufactured by Power+Energy and tested for their H_2 separation capabilities at UTRC.

The experimental efforts were divided into two distinct parts: (1) low pressure laboratory screening to quantify basic membrane performance and (2) high pressure testing to quantify durability and poison resistance of the two alloys. The objectives of the low pressure (<10 atm) laboratory testing were to characterize the membrane separator H_2 permeability as a function of temperature and to quantify the effect of different gas species (CO, CO_2, H_2O, and N_2) on the permeability. The high pressure (>10 atm) testing involved testing with gases containing different concentrations of poisons such as H_2S and NH_3, including DOE membrane testing protocol conditions. The high pressure mixed gas was used in the >500-hour durability tests to quantify the effect of gas mixtures and poisons on the H_2 permeability of the PdCu separators.

Results

Although irreversible corrosion product formation (i.e. Pd_4S) has been reported on a number of Pd-based alloys exposed to sulfur (S)-bearing atmospheres [1,2], S adsorption has been observed at UTRC to be reversible on PdCu alloys with recoverable H_2 permeability at higher temperatures. This finding motivated a systematic, first principles, atomic modeling study to pinpoint alloy characteristics that control the reversibility/irreversibility of S interactions on a range of Pd-based alloys. This understanding could then be used to develop a predictive tool to guide the development of S-tolerant alloys for dense metallic H_2-selective membranes.

Figure 1 provides a graphical representation of a useful approach to evaluate Pd-alloys for their susceptibility to irreversible sulfur attack. On the abscissa is plotted the reaction enthalpy for S absorption. The reaction enthalpy for Pd segregation and Pd_4S formation upon S absorption is plotted on the ordinate. A positive value on the abscissa implies that sulfur absorption on the surface is not favorable, while a negative value suggests the material can incorporate sulfur into the subsurface lattice structure. If sulfur is incorporated into the structure, a negative value on the ordinate predicts the material should undergo sulfur corrosion. For example, pure FCC Pd (111) and FCC Pd_3Ag (111) surfaces, both known to be sulfur intolerant

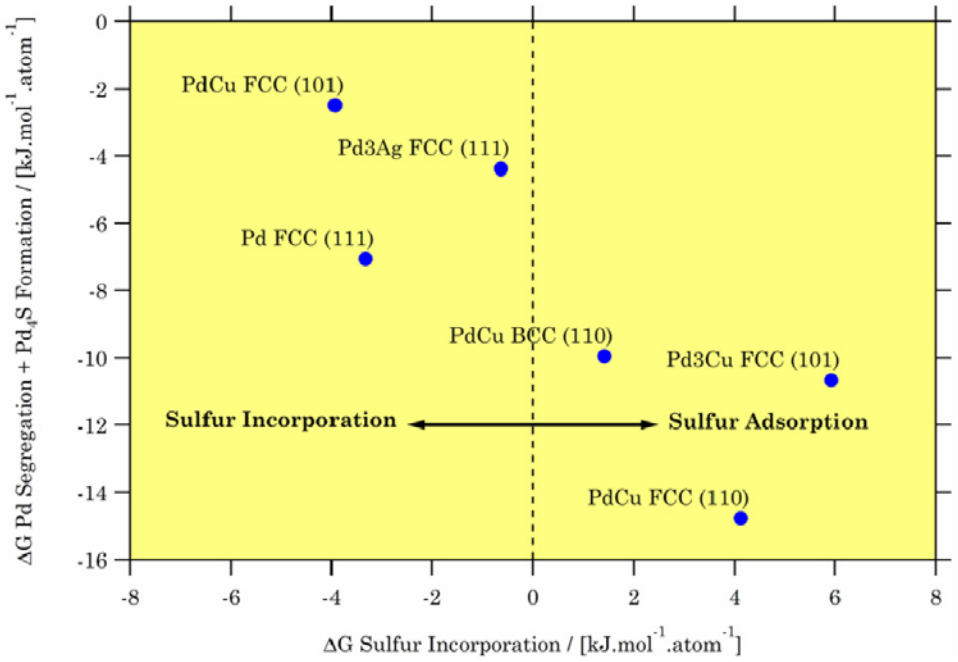

FIGURE 1. The analysis of reaction enthalpy for Pd segregation and Pd_4S formation upon S absorption versus the change in enthalpy for S incorporation by absorption relative to S adsorption. This serves as a predictive tool to delineate irreversible from reversible S interactions.

materials, have negative values for both the abscissa and ordinate, in agreement with experimental observations.

UTRC has previously demonstrated the reversible sulfur tolerance of PdCu alloys. After the project inception, the DOE developed a testing protocol for evaluating membrane performance [3]. Figure 2 shows the results of DOE test protocol testing on an FCC PdCu membrane produced for this project which lasted 527 hours. The testing was performed under pure H_2 as well as test conditions 1, 2a, and 2b. The data in Figure 2 show that under the specific test conditions, the pure H_2 flux of this separator was 45±2 $ft^3ft^{-2}h^{-1}$

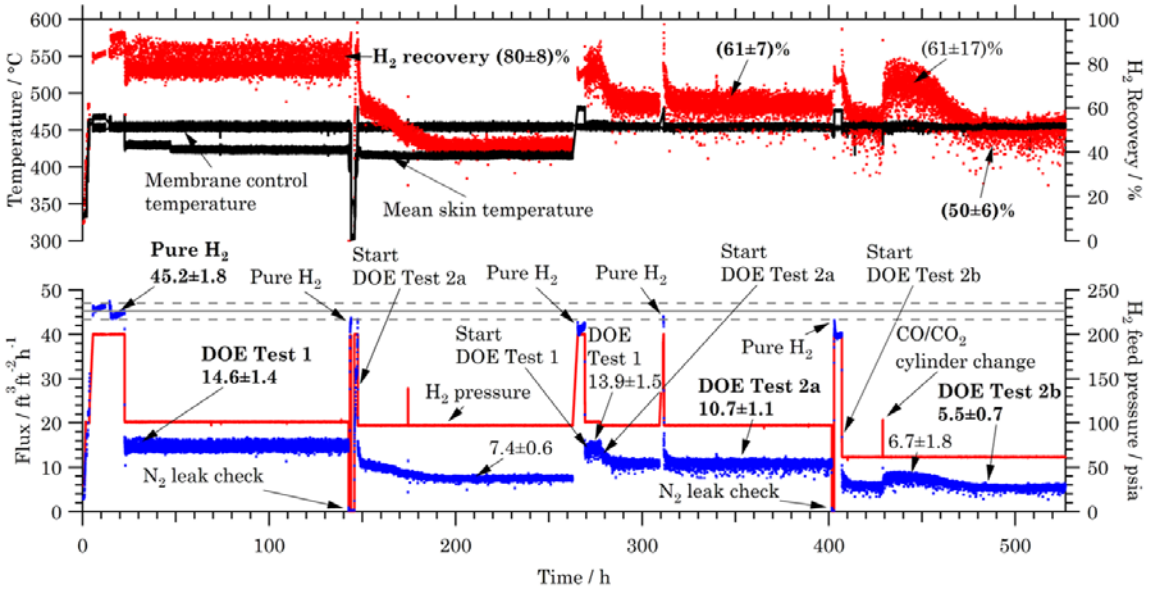

FIGURE 2. DOE protocol test data for an FCC PdCu separator which had been tested for 527 hours at DOE protocol test conditions 1, 2a, & 2b at 450°C.

with a H_2 recovery of >80% at 450°C and 200 psia. Upon exposure to the DOE test 1 conditions, this flux decreased to 14±2 $ft^3ft^{-2}h^{-1}$ with a similar recovery. When 20 ppmv H_2S was introduced during test 2a conditions, the flux was further reduced to 11±1 $ft^3ft^{-2}h^{-1}$ with a corresponding decrease in recovery to (61±7)%, however, membrane performance remained stable during the 100+ hours at each condition. Finally, when the H_2 concentration was decreased and the sulfur level increased to 40 ppmv, the flux was reduced to 6±1 $ft^3ft^{-2}h^{-1}$ with a H_2 recovery of (50±6)%. The decrease in H_2 flux due to composition effects was completely reversible based on measurements taken with pure H_2 between each of the gas compositions and also the fact that the membrane did not leak. This further supports the conclusion that FCC PdCu is sulfur resistant and not susceptible to sulfur corrosion.

Development of the UTRC ternary PdCuTM alloy resulted in a permeability performance in July 2009 that was similar to that of the FCC PdCu alloy (see Figure 3). Further characterization was performed to determine the root cause of the lower than expected performance. An unwanted TM-oxide surface scale forms during manufacturing of the separator tubes and requires removal. The separator performance in July 2009 was measured after chemical etching which resulted in selective dissolution of the Cu, leaving the surface Pd-rich. It is known from the literature [4,5] that a PdCu alloy with greater than ≈50 at% Pd has a rather poor permeability compared to pure Pd. As a result, a mechanical polishing technique was developed to remove the surface oxide scale without affecting the surface PdCu composition. The data for the polished separator tubes, measured in April 2010, is also given in Figure 3 and shows that the performance was improved by a factor of two.

A technical and economic modeling analysis was performed for the FCC PdCu dense metallic membranes. Similar assumptions to those used in the DOE test protocol [3] were used in the calculations. A mean flow rate of 6.425×10^5 $kg.h^{-1}$ was used for membrane sizing calculations based on different gasifier systems operating in the range of 520 MW to 640 MW [6]. For the purposes of the analysis, the gas was assumed to be at the DOE protocol test 1 composition (50% H_2, 1% CO, 30.0% CO_2, and 19.0% H_2O). Figure 4 shows the H_2 recovery as a function of membrane surface area at 450°C. The recovery curves are presented as a function of the membrane feed pressure. Higher feed pressures result in higher fluxes and thus a reduced area for the same H_2 recovery.

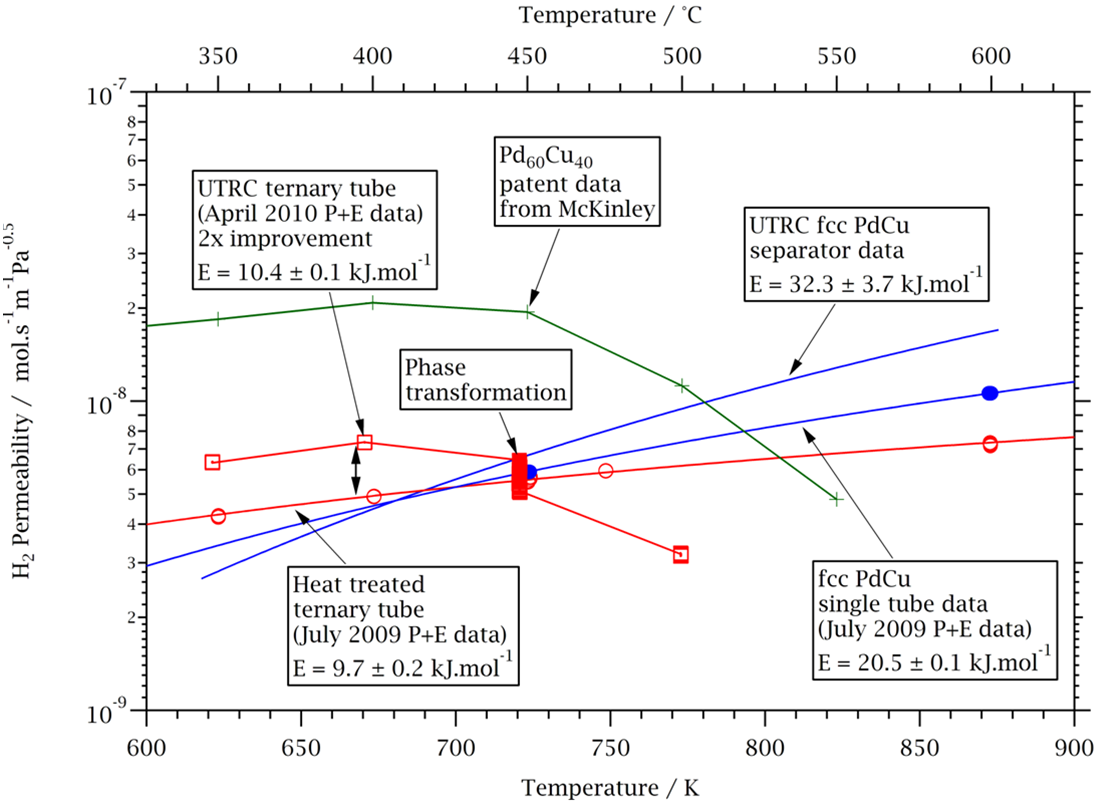

FIGURE 3. Permeability of FCC PdCu and single-tube ternary alloy separators compared to data from McKinley [5] for BCC PdCu.

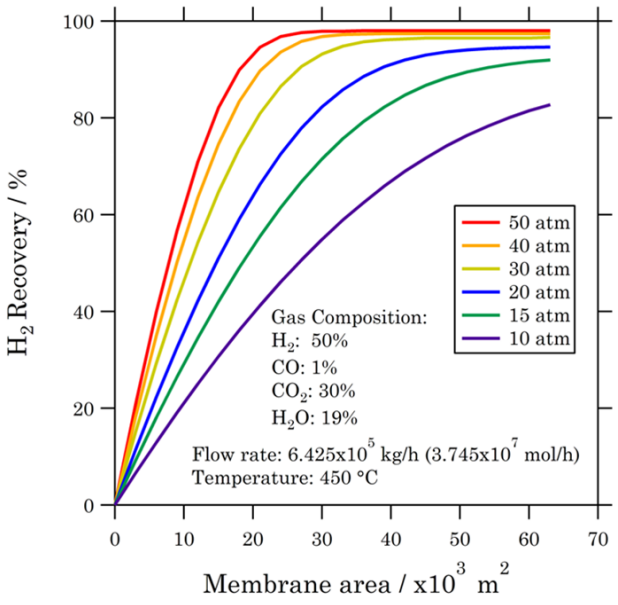

FIGURE 4. Impact of H_2 recovery on FCC PdCu membrane surface area for a 520–640 MW gasifier system operated at 450°C.

For a high H_2 recovery, a dense metallic PdCu membrane for this size system would require an area approaching 60,000 m^2 and the metal would cost on the order of $200,000,000. However, one advantage of the dense metallic membranes is that the raw materials can be recycled and the Pd cost can be significantly reduced by a lease and recycling strategy. In addition, the very high H_2 purity achievable by dense metallic membranes, along with their higher technology readiness level, makes the dense metallic approach a viable path forward for H_2 separation while other, longer-term, low-cost technology paths are further developed.

Conclusions and Future Directions

- An atomistic modeling screening approach for evaluating susceptibility to irreversible sulfur attack was developed that could assist other development projects on H_2 separation membranes.
- Dense metallic FCC PdCu separators can operate under the DOE testing protocol conditions and maintain their stability. In addition, the impact of poisons, such as sulfur, has been found to be reversible.
- Single tube separators with the UTRC ternary PdCuTM composition showed doubled performance versus early 2009 results after an improved polishing process was identified to remove the surface barrier produced during manufacturing of the PdCuTM tubes.
- No additional work is planned on the current project.
- Future work in this area should move in the direction of larger scale demonstrations with real gasifier exhaust.

FY 2010 Publications/Presentations

1. Emerson S., J. Costello, Z. Dardas, D. Goberman, T. Hale, R. Hebert, G. Marigliani, S. Opalka, Y. She, C. Thibaud-Erkey, T.H. Vanderspurt, R. Willigan Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, presentation at 2010 DOE Annual Merit Review, Washington, D.C., June 8, 2010.

2. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, DOE Award Number DE-FC26-07NT43055, United Technologies Research Center: East Hartford, CT, April 2010.

3. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, DOE Award Number DE-FC26-07NT43055, United Technologies Research Center: East Hartford, CT, January 2010.

4. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, DOE Award Number DE-FC26-07NT43055, United Technologies Research Center: East Hartford, CT, October 2009.

5. Emerson, S.C.; Vanderspurt, T.H. Quarterly Progress Report: Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, DOE Award Number DE-FC26-07NT43055, United Technologies Research Center: East Hartford, CT, July 2009.

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1. Morreale, B.D. *The influence of H_2S on palladium and palladium-copper alloy membranes.* Ph.D. Thesis, University of Pittsburgh, 2006.

2. Morreale, B.D.; Howard, B.H.; Iyoha, O.; Enick, R.M.; Ling, C.; Sholl, D.S. *Experimental and computational prediction of the hydrogen transport properties of Pd_4S.* J. Membr. Sci. 46 (2007) 6313-6319.

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4. McKinley, D.L. *Metal Alloy for Hydrogen Separation and Purification.* U.S. Patent 3,350,845, 1967.

5. McKinley, D.L. *Method for Hydrogen Separation and Purification.* U.S. Patent 3,439,474, 1969.

6. Klara, J.M. *Cost and Performance Baseline for Fossil Energy Plants*; DOE/NETL–2007/1281; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, October 2007.