II.G.3 Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

Sean C. Emerson
United Technologies Research Center (UTRC)
411 Silver Lane
East Hartford, CT 06108
Phone: (860) 610–7524; Fax: (860) 660–9093
E-mail: emersosc@utrc.utc.com

DOE Technology Development Manager:
Daniel C. Cicero
Phone: (304) 285-4826
E-mail: daniel.cicero@netl.doe.gov

DOE Project Officer: Arun C. Bose
Phone: (412) 386-4467; Fax: (412) 386-4604
E-mail: arun.bose@netl.doe.gov

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Subcontractors:
- Power+Energy, Inc. (P+E), Ivyland, PA
- Metal Hydride Technologies, Inc., Burlington, VA

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Project End Date: June 14, 2009

Objectives

- Confirm the high stability and resistance of a palladium-copper (PdCu) trimetallic alloy to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia.
- Develop a sulfur, halide, and ammonia resistant alloy membrane with a projected hydrogen 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 PdCu trimetallic alloy membrane separators at feed pressures of 2 MPa (290 psia) in the presence of H_2S, NH_3, and HCl.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(K) Durability

(L) Impurities

(N) Hydrogen Selectivity

(P) Flux

Technical Targets

This project consists of three parts: atomistic modeling, hydrogen separator fabrication, and membrane separator experimental evaluation. The project has entered the second phase of work where the bulk of the experimental evaluation will take place. The current progress toward achieving the DOE's technical targets based on the atomistic modeling predictions as well as experimental data is given in Table 1.

TABLE 1. Progress Toward the Hydrogen Separation Technical Targets

Performance Criteria	Units	2012 Target	2008 Current Progress	Notes
Hydrogen Flux	$ft^3f^{t-2}h^{-1}$	200	256	P+E alloy at 530°C UTRC alloy predicted to be >400 $ft^3f^{t-2}h^{-1}$ by atomistic modeling
Temperature	°C	300–600	350–600	UTRC ternary alloy limited to 475°C
Sulfur Tolerance	ppmv	20	5	P+E demonstrated 800 h operation with 100 ppmv H_2S Plan to test with >40 ppmv H_2S, HCl; and 10 ppmv NH_3
ΔP Operating Capability	psi	Up to 400	290	Facilities & current separator design limited to 20 atm testing
Carbon Monoxide Tolerance	-	Yes	Yes	Demonstrated up to 13.3% CO at 90 psia total pressure
Hydrogen Purity	%	99.5	99.9999%	P+E manufacturing design and manufacturing ensures no leaks

Accomplishments

- Constructed ten commercially manufactured hydrogen separators for evaluation.
- Produced five of the separators with UTRC ternary alloy composition.
  - Phase segregation occurred on outer surface of membrane tubes.

  - Work is in progress to improve ternary separator performance.
  - Construction of two additional separators will address phase segregation issue.
- Performed atomistic modeling calculations to show sulfur and coke resistance of separator alloys.
- Performed experimental hydrogen solubility measurements on alloy tube samples and confirmed atomistic and thermodynamic modeling predictions within a factor of two.
- Evaluated performance of first face-centered-cubic (fcc) PdCu separator.
  - Quantified effect of CO, CO_2, N_2, and H_2O on H_2 permeability.
  - Commercial unit can meet DOE flux targets for temperatures >480°C.

Introduction

This project is focused on increasing the technology readiness level of palladium-based metallic membranes for hydrogen separation from coal-biomass gasifier exhaust or similar hydrogen-containing gas streams. Quantum mechanical atomistic modeling was performed in a previous contract to virtually 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 (bbc) phase of a PdCu binary alloy stable at WGSMR temperatures in the presence of high concentrations of poisons such as sulfur. As the bcc phase of PdCu has a much higher hydrogen permeability than the fcc materials, and the fcc materials have been shown to have good sulfur resistance, a stabilized fcc alloy should be able to obtain the high permeability of alloys like PdAg with the sulfur tolerance of fcc PdCu. Thus one of the major objectives of this work is to experimentally validate the UTRC PdCu ternary alloy performance. In addition, the best commercially available fcc PdCu alloy from UTRC's subcontractor, Power+Energy, will also be experimentally validated for meeting the DOE technical targets.

Approach

The basic concept for this project is to experimentally validate two different PdCu-based alloys for hydrogen separation. Additional atomistic modeling will be performed to examine additional characteristics, such as carbon formation resistance, that were not done under the previous DOE WGSMR contract. In parallel with the modeling, a new test rig for high pressure separator evaluation will be constructed while separator units of both the Power+Energy and UTRC alloys are manufactured by Power+Energy. Samples of the alloy tube separators will also be sent to Metal Hydride Technologies, to experimentally measure the hydrogen solubility of the manufactured material for model prediction validation.

The experimental effort is broken 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 low pressure (<10 atm) laboratory testing objective is to characterize the membrane separator hydrogen 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 will involve using an ambient pressure logistic fuel reformer to convert diesel fuel into syngas (hydrogen and carbon monoxide) which will be compressed and mixed with additional gas containing different concentrations of poisons (H_2S, HCl, and NH_3). The high pressure mixed gas will then be used in 500-h to 2,000-h durability tests to quantify the effect of poisons on the hydrogen permeability of both PdCu alloys.

Results

Ten leak-free hydrogen separators were constructed by Power+Energy at the end of 2007 and delivered to UTRC. Five of these separators contained membrane tubes made with UTRC's ternary alloy composition designed through modeling in a previous DOE contract. The other five separators were made with Power+Energy's best fcc PdCu alloy which has been demonstrated by the company to be resistant to sulfur concentrations in excess of 100 ppmv. Prior to the start of this project, UTRC had already internally evaluated the fcc PdCu alloy and shown it to be resistant to 5 ppmv sulfur and 11 ppmv ammonia. In addition to the ten separators, Power+Energy also delivered additional membrane alloy tube samples to UTRC for hydrogen solubility testing by Metal Hydride Technologies.

X-ray diffraction analysis was performed on the alloy tube samples to characterize their structures. Figure 1 shows the X-ray diffraction patterns for both types of alloy tubes. The Power+Energy alloy diffraction pattern in Figure 1 identifies the sample as an fcc structure while the UTRC alloy pattern was shown to be a bcc structure as predicted from modeling. The UTRC alloy also has a unit cell lattice parameter of approximately 2.99 Å, which is within 2% of the atomistic modeling predictions. Metal Hydride Technologies measured the hydrogen solubility of the tube samples and found the Power+Energy samples to have the solubility expected for that fcc composition. The UTRC alloy samples were found to have a hydrogen solubility of a little more than half that of the thermodynamic and atomistic model predictions. Thus,

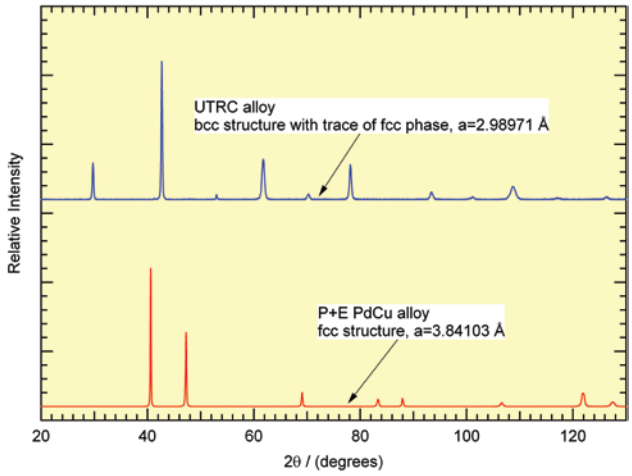

FIGURE 1. X-Ray Diffraction Patterns of Alloy Tube Samples

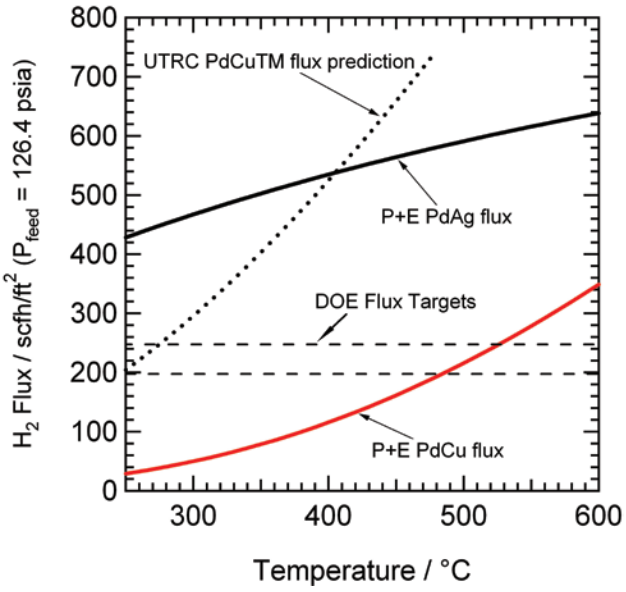

FIGURE 2. Experimentally derived and model predicted hydrogen fluxes of various membrane alloys as a function of temperature.

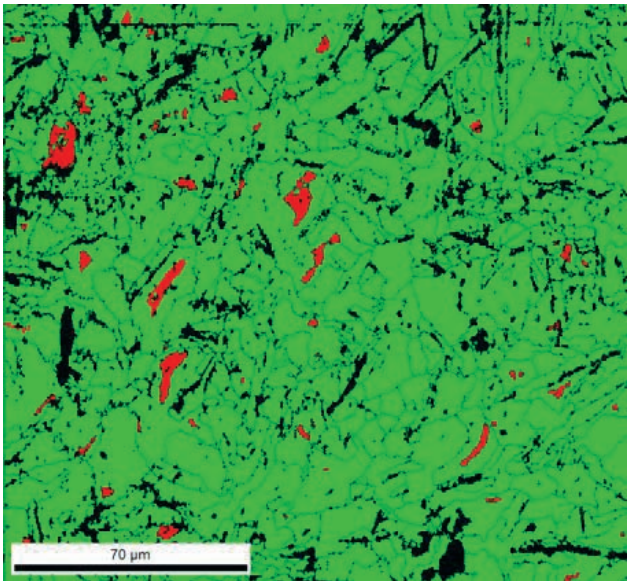

FIGURE 3. EBSD Phase Map of Part of the UTRC Alloy Sample Outer Surface

the bulk composition and structure of the alloy tubes were confirmed to be acceptable for this project.

Figure 2 shows predicted and experimentally derived hydrogen fluxes of the various alloys in this project as well as the experimentally derived fluxes for a Power+Energy PdAg separator for reference. The lower solid curve represents the experimentally derived flux of the Power+Energy fcc PdCu alloy as a function of temperature which shows that this alloy can achieve and exceed the DOE's hydrogen flux targets above a temperature of 480°C. The dotted curve is the original model predicted hydrogen flux for the UTRC ternary alloy which shows that it has the potential to exceed the DOE's flux targets above temperatures of approximately 250°C and have a flux performance comparable to PdAg with the sulfur resistance of PdCu at temperatures above 400°C.

When the UTRC alloy separators were evaluated to determine their hydrogen permeabilities and fluxes, their performance was found to be lower than that of the Power+Energy alloy. Using a combination of electron backscatter diffraction (EBSD) and microprobe analyses in a scanning electron microscope (SEM), it was determined that most of the surface of the UTRC alloy tubes was covered with a binary alloy of palladium and the ternary stabilizing element. This surface layer was estimated to be approximately 500 Å to 750 Å in depth. Figure 3 shows an EBSD phase map of part of the UTRC alloy sample outer surface. The green areas, which are the majority of the sample, are grains where the binary alloy was identified and the red areas are the <5% of the surface which contains a PdCu phase. The binary alloy essentially acts as a diffusion barrier for hydrogen and reduces the performance of the membranes. Additional SEM/EBSD characterization of the UTRC sample cross-section has shown that the ternary alloy identified by X-ray diffraction is present throughout the rest of the sample and that the binary phase is not present within the alloy tubes.

Thermal heat treatments in the presence of 6 atm of hydrogen have been unsuccessful in rehomogenizing or desegregating the UTRC alloy separators. The hydrogen flux of those separators continues to be below that of the Power+Energy alloy. As a result, UTRC will be performing experiments to use an appropriate etching solution to remove the surface barrier from the delivered separator units. UTRC and Power+Energy will also look

at ways to ensure the binary layer is not present in the final two UTRC alloy separators to be delivered later in 2008.

Low pressure laboratory experiments were performed on the Power+Energy alloy. A total of 123 different experimental conditions with different combinations of hydrogen, nitrogen, carbon monoxide, carbon dioxide, and water were used to evaluate separator performance. The results were quantified in a mathematical permeability model where the effect of each gas was represented by reversible adsorption. The model was tested against an arbitrary gas composition of 66.7% H_2, 7.7% CO, 7.7% CO_2, 7.7% H_2O, and 10.3% N_2 and the model was found to predict the effect of the gas mixture on hydrogen permeability within 5.2% of the experimental results. Figure 4 shows the comparison between experimentally obtained pure hydrogen and gas mixture permeabilities as well as the model prediction for comparison.

Conclusions and Future Directions

Ten separators have been successfully constructed with half the separators containing the UTRC ternary alloy composition and the other half containing the Power+Energy fcc PdCu alloy. The hydrogen permeability and effect of different gases have been quantified for the Power+Energy alloy. The UTRC alloy separators have yet to demonstrate the full potential of the ternary composition due to a binary diffusion barrier layer present on the outer surfaces of the alloy tubes. As thermal treatments in hydrogen have been unable to mitigate the effect of this barrier layer, work will proceed with in situ etching to try and improve the hydrogen permeability of the ternary separators. Two additional separators will be constructed with the UTRC ternary alloy composition later in 2008 and steps will be taken to ensure that the barrier layer is not present in those separators.

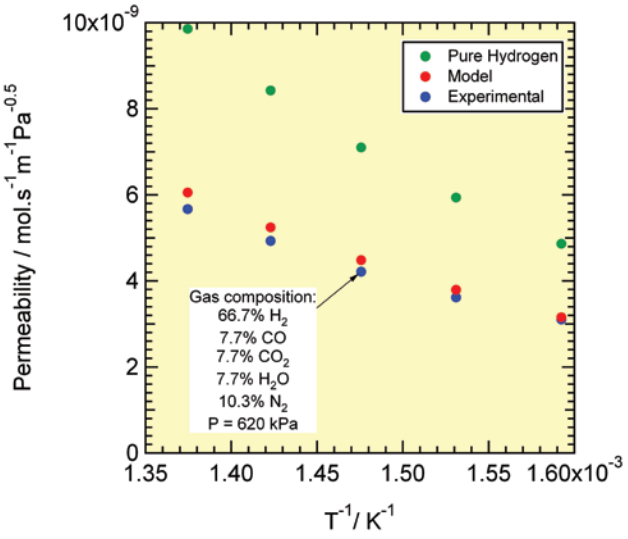

FIGURE 4. Comparison of permeability model prediction versus experimental data for a 66.7% H_2, 7.7% CO, 7.7% CO_2, 7.7% H_2O, 10.3% N_2 mixture as a function of temperature. Also shown for reference is the pure hydrogen permeability as a function of temperature.

Construction of the high pressure (>10 atm) testing rig using the logistic fuel reformer is entering its final stages. In addition, the DOE has introduced a new testing protocol in April for all hydrogen membrane projects. This testing protocol requires somewhat higher pressure testing, particularly for the hydrogen partial pressure, than the UTRC low pressure rig was designed for, as hydrogen and nitrogen are not delivered via gas bottles but through a house supply system. Thus, the low pressure rig is being modified to perform the DOE's new testing protocol on both types of alloy separators. Once these construction activities are complete, the experimental program will proceed to evaluate the separators' performance as outlined in the Approach section.

FY 2008 Publications/Presentations

1. S.M. Opalka, S.C. Emerson, Y. She, T.H. Vanderspurt, W. Huang, D. Wang, T.B. Flanagan, and O.M. Løvvik, "PdCu Ternary Alloy Development for Hydrogen Separators," presentation at the MH2008 International Symposium on Metal-Hydrogen Systems, Reykjavik, Iceland, June 24-28, 2008.

2. S.C. Emerson, J.T. Costello, Z. Dardas, T. Hale, R.R. Hebert, G.C. Marigliani, S.M. Opalka, Y. She, and T.H. Vanderspurt, Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production, presentation at 2008 DOE Annual Merit Review, Arlington, VA, June 13, 2008.

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, April 2008.

4. S.M. Opalka, T. H. Vanderspurt, S.C. Emerson, W. Huang, D. Wang, T. Flanagan, and Y. She, "Modeling of B2 Phase PdCuTM Alloy Hydrogen Selective Membrane Performance," invited presentation at 2008 TMS Annual Meeting, New Orleans, LA, March 9-13, 2008.

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, January 2008.

6. 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 2007.

7. S.M. Opalka, W. Huang, D. Wang, T. B. Flanagan, O.M. Løvvik, S.C. Emerson, Y. She, and T.H. Vanderspurt, "Hydrogen interactions with the PdCu ordered B2 alloy," J. Alloys Compd., 2007, 446-447, 583.

8. W. Huang, S.M. Opalka, D. Wang, and T.B. Flanagan, "Thermodynamic Modeling of the Cu-Pd-H system," CALPHAD, 2007, 31, 3.

9. S.M. Opalka, R.C. Benn, S.C. Emerson, T.B. Flanagan, W. Huang, Y. She, D. Wang, T.H. Vanderspurt, "Modeling of a stable, high permeability, sulfur resistant B2 phase PdCuTM alloy," presentation at the 234th ACS National Meeting, Boston, MA, August 19-23, 2007.

10. 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 2007.

11. S.M. Opalka, W. Huang, D. Wang, T.B. Flanagan, O.M. Løvvik, S.C. Emerson, Y. She, and T.H. Vanderspurt, "PdCu B2 Hydrogen Interactions under Advanced Water Gas Shift Membrane Reactor Conditions," presented at the 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007.

References

1. DOE Office of Energy Efficiency and Renewable Energy. Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy: Washington, D.C., October 2007.