# II.D.4 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, VA

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Project End Date: March 31, 2010


## Objectives

- Develop and construct hydrogen 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 hydrogen permeance of 25 $m^3 m^{-2}$ $atm^{-0.5}$ $h^{-1}$ 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 Hydrogen, Fuel Cells and Infrastructure 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, hydrogen 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" hydrogen selective separators will be completed. The progress toward achieving the U.S. Department of Energy's (DOE) technical targets based on the atomistic modeling predictions and experimental data is shown in Table 1.

**TABLE 1.** Progress Toward the Hydrogen Separation Technical Target

| Metric | 2010 DOE Target | Current Porject Status | Notes |
|---|---|---|---|
| Hydrogen Flux | 200 $ft^3 ft^{-2} h^{-1}$ | 61 $ft^3 ft^{-2} h^{-1}$ (P+E alloy)<br>200 $ft^3 ft^{-2} h^{-1}$ (UTRC alloy prediction) | • P+E alloy at 600°C; 100 psig $H_2$<br>• UTRC alloy predicted to be 200 $ft^3 ft^{-2} h^{-1}$ by atomistic modeling at ≅475°C with current tube thicknesses |
| 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)<br>9 ppmv $NH_3$ (P+E alloy) | • Demonstrated with P+E alloy at 450°C<br>• Demonstrated 487±4 ppmv for 4 hours<br>• Demonstrated 9 ppmv $NH_3$ for 175 hours |
| ΔP operating Capability | Up to 400 psi ΔP | 280 psig | • Facilities and current separator design limited to 20.7 atm (290 psig) testing |
| 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<br>• CO < 1 ppm, S < 15 ppbv desired for fuel cell applications |

## Accomplishments

- Constructed 10 commercially manufactured hydrogen separators for evaluation.
- Produced five of the separators with the UTRC ternary alloy composition.
- Completed advanced membrane property simulations by atomistic and thermodynamic modeling calculations.
- Performed atomistic modeling calculations to show sulfur and coke resistance of separator alloys.
- Completed 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 carbon monoxide (CO), carbon dioxide ($CO_2$), nitrogen ($N_2$), and water ($H_2O$) on $H_2$ permeability. Achieved DOE sulfur targets:
  - 26 scfh/ft$^2$ stable flux with 20 ppmv $H_2S$ at 200 psig (100 psig $_{H2}$) at 450°C.
  - Operated >100 hours with 33-78 ppmv $H_2S$ with no loss in flux.
- Completed initial technical and economic modeling.

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## Introduction

This project is focused on increasing the technology readiness level of Pd-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 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 Pd-silver (Ag) 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 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 has been performed to examine performance characteristics, such as resistance to carbon formation. In parallel with the modeling, a new test rig for high pressure separator evaluation has been constructed while separator units of both the Power+Energy and UTRC alloys are manufactured by Power+Energy.

The experimental efforts are 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 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 logistic fuel into syngas (hydrogen and CO) 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-hour to 2,000-hour 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 and delivered to UTRC. Five of these separators contained membrane tubes made with UTRC's ternary bcc PdCuTM 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 to be resistant to sulfur concentrations in excess of 100 ppmv. Four separators have been evaluated. 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 $NH_3$. In addition to the 10 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 phase transition diagram and electron backscatter diffraction (EBSD) phase map for binary alloy on surface of ternary alloy. X-ray diffraction confirmed formation of bcc PdCu as predicted. EBSD on an individual tube indicates the presence of a binary Pd alloy covering the surface of membrane. This surface alloy layer was estimated to be 500 Å to 700 Å thick by microprobe analysis. Heat treatments to desegregate/homogenize alloys result in limited improvement.

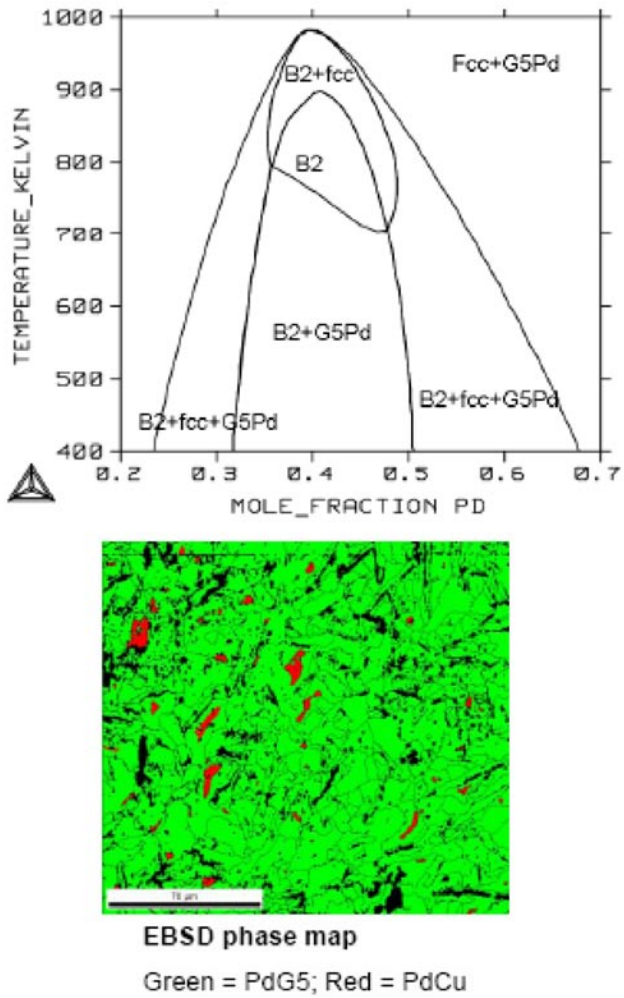


**FIGURE 1.** The Phase Transition Diagram and EBSD Phase Map for Binary Alloy on Surface of Ternary Alloy

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, the bulk composition and structure of the alloy tubes were confirmed to be acceptable.

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. The dotted curve is the original model predicted hydrogen flux for the UTRC ternary alloy which shows that it has the potential to exceed DOE's

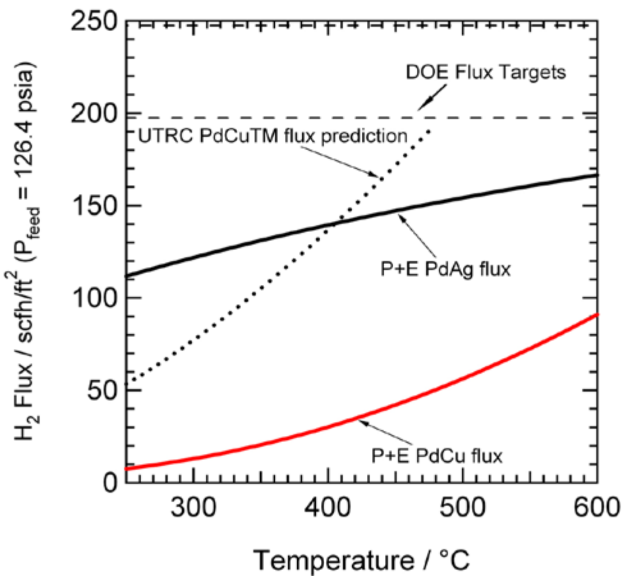


**FIGURE 2.** Predicted and Experimentally Derived Hydrogen Fluxes of the Various Alloys

flux targets above temperatures of approximately 450°C and have a flux performance comparable to PdAg with the sulfur resistance of PdCu at temperatures above 400°C.

PdCu alloy separators were tested for >200 hours with 20 to 90 ppmv $H_2S$ at 410°C to 450°C. Sulfur concentrations at temperatures of 400°C to 500°C have little or no impact on membrane performance. Operation at pressures of 290 psig causes failures in defective membrane tubes. Figure 3 displays hydrogen flux and permeability data for the fcc PdCu alloy.

The best flux of 61 scfh/ft$^2$ was measured for pure $H_2$. Flux for hydrogen gas mixture with >20 ppmv $H_2S$ was identical to sulfur-free flux. Some variations in separator performances were observed. Separator tubes failed at temperatures of 400°C to 770°C and 290 psig pressure. Lowering pressure to <250 psig mitigates the failure.

When the UTRC alloy separators were evaluated to determine their hydrogen permeabilities and fluxes, their performance were found to be lower than that of the Power+Energy alloy. Using a combination of 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 Pd and the ternary stabilizing element. This surface layer was estimated to be approximately 500 Å to 750 Å in depth. Figure 2 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 that contains a PdCu phase. Essentially, the binary alloy acts as a diffusion barrier for

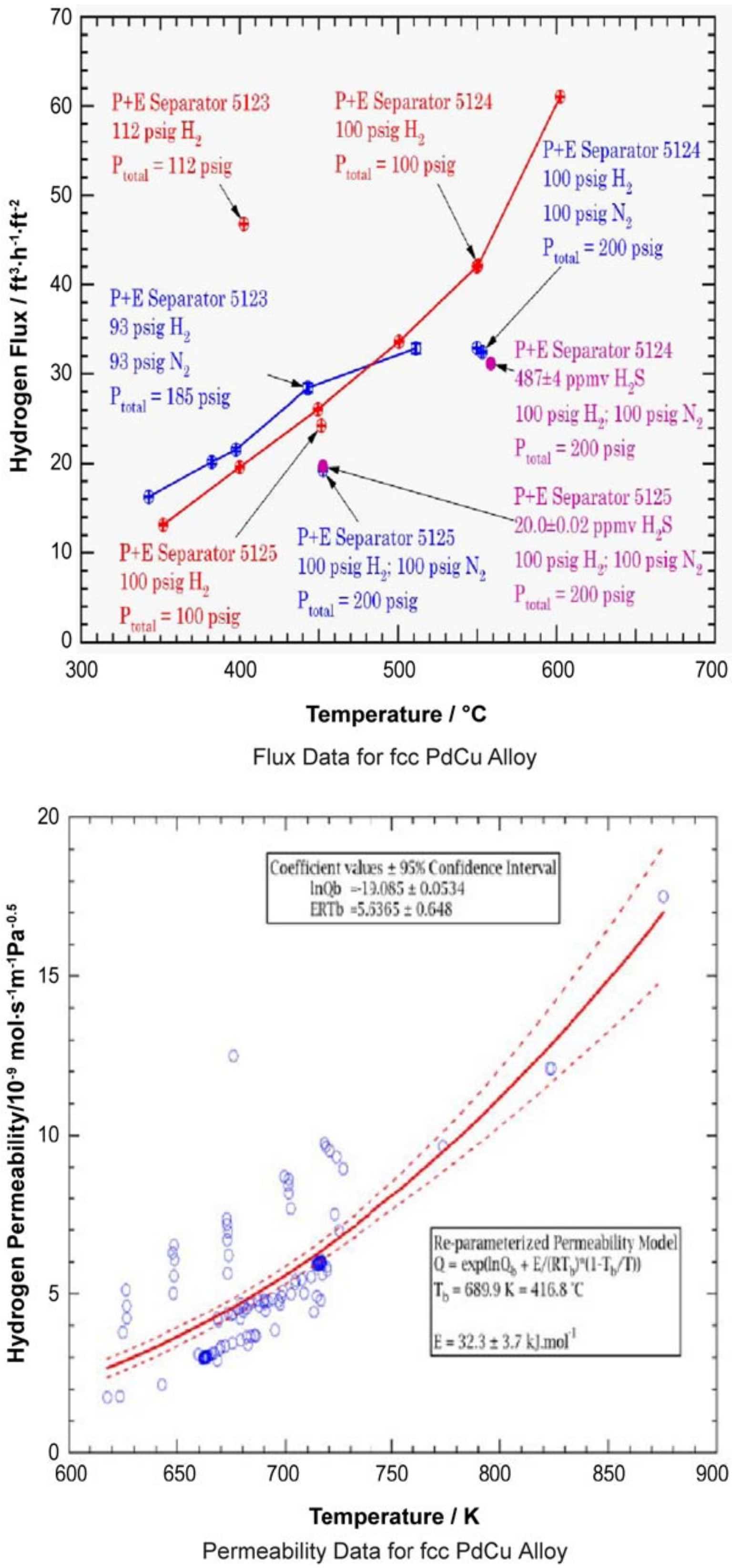


**FIGURE 3.** Hydrogen Fluxes and Permeability of Different Power+Energy PdCu Alloy Separators

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 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.

Low pressure laboratory experiments were performed on the Power+Energy alloy. A total of 123 different experimental conditions with different combinations of hydrogen, nitrogen, CO, $CO_2$, and $H_2O$ 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. The effect of $H_2S$ was added to the model based on some of the data shown in Figure 3. The effect of $H_2S$ was found to be orders of magnitude greater than CO which is an order of magnitude stronger adsorber than the other gases.

## Conclusions and Future Directions

Ten separators have been successfully constructed with five separators containing the UTRC ternary alloy composition and the other five 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.

A new batch of ternary PdCu alloy tubes was produced by Power+Energy with a slightly reduced concentration of the ternary element. The tubes were found to be in the fcc phase as received and showed no trace of a binary phase diffusion barrier on the surface. High temperature X-ray diffraction experiments and a heat treatment at 410°C showed that it is possible to convert these new alloy tubes to the bcc phase, although they may be susceptible to oxidation during high temperature heat treatments. Work is in progress to modify Power+Energy's proprietary heat treatment processing to prevent oxidation by using a hydrogen background gas.

Construction of the high pressure (>10 atm) testing rig using the logistic fuel reformer was completed. More than 300 hours of testing was completed on one separator with three separators evaluated in the testing rig. The DOE has introduced a new testing protocol 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 delivered through a house supply system and not via gas bottles. Thus, the low pressure rig was modified to perform 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 above.

Future work will focus on the fabrication and testing of at least two additional ternary PdCuTM alloy separators. Durability of separators in the presence of $H_2S$, $NH_3$, and HCl will be tested and evaluated. Durability for 500 to 2,000 hours will be demonstrated.