II.D.3 Advanced Palladium Membrane Scale Up for Hydrogen Separation

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Subcontractors:
- Power & Energy, Inc., Ivyland, PA
- Energy & Environmental Research Center, University of North Dakota, Grand Forks, ND

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Project End Date: December 31, 2011

Fiscal Year (FY) 2011 Objectives

- Construct, test, and demonstrate a PdCu metallic tubular membrane micro-channel separator capable of producing 2 lb/day of H_2 at ≥95% recovery when operating downstream of an actual coal gasifier.
- Quantify the impact of simulated gas composition and temperature on separator performance.
- Compare the performance and durability of a surface-modified, higher H_2 flux PdCu membrane with the baseline PdCu tubular membrane.
- Evaluate various materials of construction for the separator's non-Pd structural parts to ensure durability under harsh gasifier conditions.
- Perform an engineering analysis using National Energy Technology Laboratory (NETL) guidelines of the separator design based on gasifier test performance for the co-production of electric power and clean fuels.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Separations section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(K) Durability

(L) Impurities

Technical Targets

The focus of this project is to construct, test, and demonstrate a PdCu separator capable of producing 2 lb/day H_2 operating downstream of a coal gasifier. As such, the emphasis is on achieving progress against the DOE technical targets pertaining to impurities (sulfur and CO tolerance) and durability. The current progress toward the DOE's 2015 technical targets for hydrogen separation is given in Table 1.

TABLE 1. Technical Progress for the Project as Measured Against the DOE's Technical Targets for Hydrogen Separation

Performance Criteria	Units	DOE 2015 Target	Current Status
H_2 Flux	$ft^3h^{-1}ft^{-2}$	300	125 (500°C, enhanced PdCu) (200 psia feed pressure, 185.3 psid)
Temperature	°C	250–500	250–600
Sulfur tolerance	ppmv	>100	618 h at 5–39 ppmv S (0.008 psia S) >24 h at 236–963 ppmv S (0.0104–0.0425 psia S) [8 h at 236 ppmv S (0.0104 psia S)] [5 h at 472 ppmv S (0.0208 psia S)] [4 h at 708 ppmv S (0.0312 psia S)] [7.5 h at 963 ppmv S (0.0425 psia S)] With reversible, low impact on permeability
Cost	$/ft^2	<100	400–500 (metal cost, without recycle & leasing strategy)
ΔP operating capability	psi	800–1,000	400
CO tolerance	–	Yes	13.3% CO at 90 psia >9% CO at 204.7 psia
H_2 purity	%	99.99	99.9999
Stability/ Durability	Years	5	1,031 h

FY 2011 Accomplishments

- Demonstrated negligible impact of gas species for temperatures ≥400°C and pressures ≤200 psia. Sulfur partial pressures up to 0.008 psia and CO partial pressures up to 2 psia do not affect H_2 flux for temperatures ≥400°C.
- Identified potential non-membrane materials of construction superior to SS-316.
- Constructed four laboratory-scale separators and two pilot-scale separators capable of separating >2 lb/day H_2.
- Compared the performance and durability of a surface-modified, higher H_2 flux PdCu membrane with the baseline PdCu tubular membrane.

Introduction

Advancements in hydrogen (H_2) membrane separation are critical to allow the development of a viable H_2 economy based on coal/biomass processing with CO_2 capture. United Technologies Research Center (UTRC), in collaboration with Power+Energy, Inc. (P+E) and the Energy & Environmental Research Center at the University of North Dakota (EERC), therefore proposed to demonstrate palladium (Pd)-based membrane separation of H_2 from coal-derived syngas at the pre-engineering/pilot scale.

In Phase I, the objectives are to: (1) construct, test, and demonstrate a PdCu metallic tubular membrane micro-channel separator capable of producing 2 lb/day of H_2 at ≥95% recovery when operating downstream of an actual coal gasifier; (2) quantify the impact of simulated gas composition and temperature on separator performance; (3) compare the performance and durability of a surface modified, higher H_2 flux PdCu membrane with the baseline PdCu tubular membrane; (4) evaluate various materials of construction for the non-Pd separator structural parts to ensure durability under harsh gasifier conditions; (5) perform an engineering analysis using NETL guidelines of the separator design based on gasifier test performance for the co-production of electric power and clean fuels; and (6) select a gasification facility partner for Phase III.

Approach

This project is a continuation of the UTRC-led team's approach to increase 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. The current project is aimed at demonstrating at the pre-engineering/pilot scale the separation of H_2 from coal-derived syngas using a proprietary, surface-modified, palladium-copper (PdCu) tubular membrane separator. It will include testing of separators capable of producing 2 lb/day of H_2 and, in follow-on phases, separators capable of producing 100 lb/day of H_2.

UTRC's subcontractor, P+E will manufacture the separators and EERC will test the separators downstream of a coal gasifier. The main objective of the first phase (Phase I) of the project is to construct, test, and demonstrate a PdCu dense metallic tubular membrane separator capable of producing 2 lb/day of H_2 at a minimum 95% recovery when operating downstream of an actual coal gasifier. The project will also acquire engineering data to reliably scale up PdCu membrane separators to a size of 4 tons per day (tpd) of H_2 and assess the combined effects of coal gas constituents and trace contaminants on membrane performance and durability. The data will be evaluated against the DOE's 2015 targets for H_2 membrane separation and used in an engineering analysis of the separation and production method using NETL guidelines.

Results

By the end of June 2011, P+E had delivered four out of six laboratory-scale (≈0.1 ft^2) separators as well as two out of six pilot-scale (≈1.5 ft^2) separators. Based on the information from preliminary corrosion tests, as well as the availability of alloys in the forms needed for fabrication, it was decided that all remaining separators to be delivered in Phase I of the project would be made out of C-22 and/or C-276. As a result, two of the laboratory-scale separators and both pilot-scale separators were made using these alloys. Due to manufacturing delays, the first two pilot-scale separators were made with non-surface enhanced PdCu alloys. All future pilot-scale separators will be made with the enhanced PdCu membranes.

Seven separators (identified as 5265, 5266, 5276, 5277, 5290, 5291, and 5297) have been evaluated for their hydrogen separation capability. An Arrhenius plot of the pure hydrogen permeability for each of the separators versus temperature is given in Figure 1. All but two separators (5266 & 5297) demonstrated similar performance, which was greater than that of conventional PdCu, although not as high as the original target for the enhanced PdCu.

Separator 5266 was a single-tube membrane separator from a previous DOE contract (DEFC2607NT43055) that was sent to EERC for gasifier testing and returned to UTRC. The data obtained at UTRC for separator 5266 indicated that the separator was leak tight and that performance of the membrane was equivalent to conventional PdCu after gasifier testing. Separator 5266 was used to establish reproducibility between EERC's and UTRC's testing hardware and will be characterized to determine the impact of gas contaminants on its materials of construction.

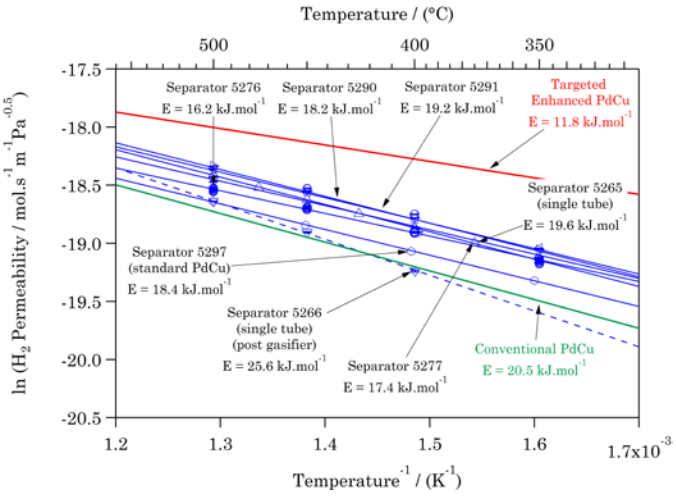

FIGURE 1. Arrhenius plot of the pure hydrogen permeability versus temperature for the PdCu separators tested so far on this project. Shown for reference are the hydrogen permeability curves for conventional PdCu membranes as well as the target performance for the surface modified, enhanced PdCu membranes.

Separator 5276 was tested for 1,031 hours, including 618 hours of hydrogen sulfide (H_2S) exposure with no signs of performance degradation. The impact of non-sulfur gas contaminants on hydrogen permeability for temperatures greater than or equal to 400°C appeared to be negligible when compared to pure hydrogen experiments as shown in Figure 2. Furthermore, the addition of H_2S to the same gas mixtures also had a negligible effect on the hydrogen permeability as shown in Figure 3. One objective of the sulfur tests was to determine the length of time required for the membrane performance to come to a steady state upon exposure to H_2S. Preliminary durability data suggested that the separator needed to be equilibrated for at least 100 hours before stable gas contaminant testing could be measured.

Separator 5297 is a pilot-scale separator that was tested with pure H_2 and H_2/N_2 mixtures at feed pressures of 44.1 psia and 88.2 psia, respectively, to verify separator performance with UTRC's separator model. The separator was also tested with H_2S in H_2 to verify its ability to withstand gasifier poisons. The maximum H_2S concentration used was 963 ppmv at 44.1 psia, approximately five times the maximum sulfur partial pressure used for testing separator 5276. At 500°C, the reduction in H_2 permeation from the 0.043 psia H_2S was approximately 50% but the H_2 performance fully recovered after exposure to pure H_2. Separator 5297 was also pressure checked at 400 psia and found to be leak free. The separator was exposed to four thermal cycles in H_2/N_2 from 200°C to 500°C with no performance degradation and no leaks. Separator 5297 was shipped to EERC after a total of 356 hours of testing at UTRC to serve as the test article for a coal gasifier test before the end of September.

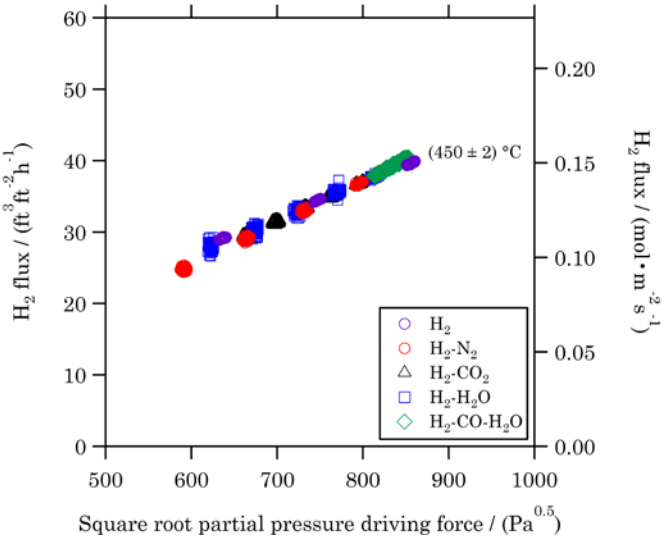

FIGURE 2. Hydrogen flux at (450 ± 2)°C versus the square root hydrogen partial pressure driving force for separator 5276 for different gas mixtures, not including H_2S. The separator was tested at feed pressures varying from 29.4 psia to 200 psia with different binary and ternary gas mixtures.

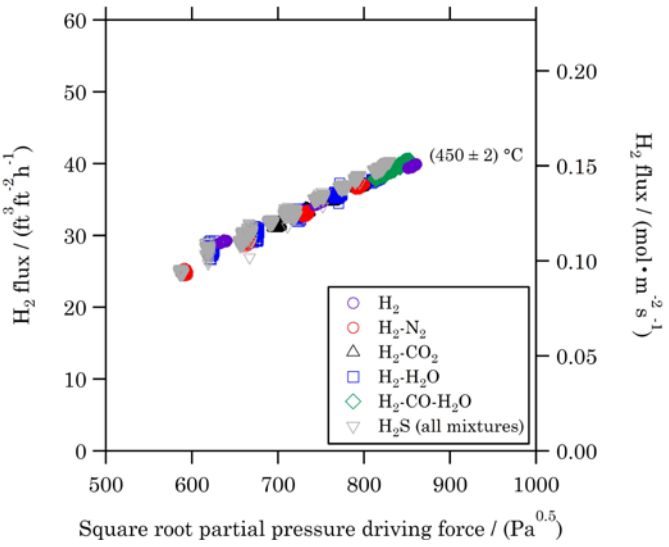

FIGURE 3. Hydrogen flux at (450 ± 2)°C versus the square root hydrogen partial pressure driving force for separator 5276 for different gas mixtures, including H_2S. The separator was tested at feed pressures varying from 29.4 psia to 200 psia with different binary and ternary gas mixtures. The H_2S gas concentration was varied from 5 ppmv to 39 ppmv.

UTRC began preliminary corrosion testing under a slightly modified DOE test 2A condition at 500°C in February. Initial Round 1 coupon tests were performed for 474 hours with samples of SS-316, SS-309, C-22 and C-276. After 474 hours of testing, it was observed that SS-309, C-22, and C-276 had weight gain constants that were two orders of magnitude lower than SS-316. This was likely due to their improved resistance to H_2S compared to SS-316. Some coupons exhibited crevice corrosion where the metal samples sat in a ceramic "dee-tube." Thus, a new fixture was designed for Round 2 testing in which samples hang from an alumina rod to minimize this effect.

The Round 2 corrosion test included two Oak Ridge National Laboratory alloys (OC-10 and OC-11) as well as HR-120 and SS-310. Corrosion testing of these alloys is currently in progress, with more than 1,500 hours of accumulated run time. Round 2 corrosion testing will continue until approximately 2,000 hours of total run time has been achieved, after which the Round 1 coupon tests will be repeated for approximately 2,000 hours.

In addition to lab-scale tests performed at UTRC, a total of 24 samples were prepared for exposure testing under actual gasifier conditions at the National Carbon Capture Center (NCCC) in Alabama. The coupons were made of eight different alloys (SS-316, SS-309, SS-310, HR-120, C-22, C-276, OC-10, and OC-11) and were sent to NCCC in late March.

Conclusions and Future Directions

- Dense metallic, PdCu membranes can fully tolerate the DOE test protocol conditions for pressures up to 200 psia and temperatures between 400°C and 500°C.
- The impact of H_2S for partial pressures <0.008 psia on H_2 permeability was insignificant for temperatures between 400°C and 500°C, although exposure to partial pressures as high as 0.043 psia H_2S showed a reduction in permeability up to 50% which was completely reversible.
- The surface enhanced PdCu membranes show higher hydrogen permeability than the conventional PdCu, particularly at lower temperatures (<450°C).
- Several non-membrane materials of construction have been identified that have superior corrosion resistance to the DOE protocol conditions compared to SS-316.
- Samples of the non-membrane materials of construction were sent to the NCCC in Alabama for exposure testing under real gasifier conditions.
- A single-tube separator was exposed to coal gasifier exhaust and will be characterized to determine the impact of gas contaminants on the materials of construction.
- A pilot-scale separator will be tested at 400 psia downstream of a coal gasifier at EERC by September to evaluate the impact of real gasifier exhaust on membrane performance.

FY 2011 Publications/Presentations

1. Emerson, S.C. Advanced Palladium Membrane Scale-up for Hydrogen Separation, invited presentation at Advancing the Hydrogen Economy Action Summit III, University of North Dakota EERC's National Center for Hydrogen Technology, Grand Forks, ND, September 13–15, 2010.

2. Emerson, S.C. Quarterly Progress Report: Advanced Palladium Membrane Scale-up for Hydrogen Separation, DOE Award Number DE–FE0004967, United Technologies Research Center: East Hartford, CT, January 2011.

3. Emerson, S.C. Quarterly Progress Report: Advanced Palladium Membrane Scale-up for Hydrogen Separation, DOE Award Number DE–FE0004967, United Technologies Research Center: East Hartford, CT, April 2011.

References

1. DOE Office of Energy Efficiency and Renewable Energy. Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy: Washington, D.C., 27 April 2007.