II.D.2 Development of Robust Hydrogen Separation Membranes

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Objectives

The main objective of this research is the development of robust hydrogen separation membrane(s) for integration into coal conversion processes, including integrated water-gas shift (WGS) membrane reactor. Studies suggest that incorporating separation membranes into coal conversion processes can reduce costs by 8%.

Included in the primary project objectives are the definition of a H_2-membrane test protocol that:

- Will advance the technology towards application to coal conversion processes.
- Is consistent with overall Fossil Energy Program metrics.
- Yields a basis for an “apples-to-apples” comparison.

Research will be divided into two tasks: Task 1: Performance testing of external membranes and the “NETL H_2 Membrane Test Protocol” and Task 2: Robust Metal Membrane Development

Technical Barriers

This project addresses the following technical barriers from the *2008 Hydrogen from Coal Program: Research, Development and Demonstration Plan*.

(G) H_2 Embrittlement
(H) Thermal Cycling
(I) Poisoning of Catalytic Surface
(J) Loss of Structural Integrity and Performance

Technical Targets

The technical targets are DOE’s 2015 targets as shown in Table 1.

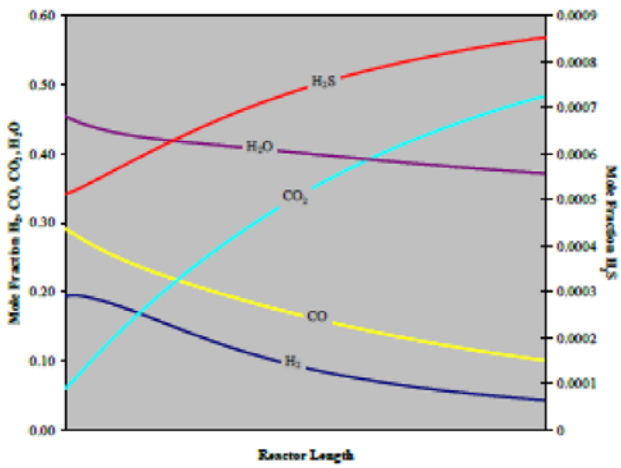
TABLE 1. DOE’s Hydrogen Membrane Performance Targets

Performance Criteria	Units	2007 Target	2010 Target	2015 Target
Flux [(a)]	sccm/cm^2	51	102	152.4
Temperature	°C	400–700	300–600	250–500
S Tolerance	ppmv	----	20	>100
Cost	\$/ft^2	150	100	<100
WGS Activity	-	Yes	Yes	Yes
ΔP Operating Capability [(b)]	psi	100	Up to 400	Up to 800 to 1,000
Carbon Monoxide Tolerance	-	Yes	Yes	Yes
Hydrogen Purity	%	95%	99.5%	99.99%
Stability/Durability	years	1	3	5

[a] For 100 psi ΔP (hydrogen partial pressure basis)
[b] ΔP = total pressure differential across the membrane reactor

Accomplishments

- Completed a survey to determine the effluent composition of a WGS unit (Figure 1).
- Developed COMSOL model to predict the influence of WGS reaction and/or H_2 removal on overall gas composition:
  - Identified the test conditions and gas compositions that are relevant to syngas conversion flowsheet options:
    - Test 1: Shifted syngas, with no sulfur
    - Test 2a: Shifted syngas with 20 ppm H_2S
    - Test 2b: Shifted syngas with ~50% H_2 removal
    - Test 2c: Shifted syngas with ~90% H_2 removal
- Moved the membrane test units to a new location:
  - Modified membrane units to accommodate the “test protocol”.
- Flow ranges and membranes to test:
  - Conducted detailed analysis of the flow requirements to test a variety of membranes being developed:
    - Disks, tubes
    - Performing at 2015 targets



	Test 1	Test 2a	Test 2b	Test 2c
H2	50%	50%	33%	5%
CO	1%	1%	1%	2%
CO2	30%	30%	40%	57%
H2O	19%	19%	25%	36%
H2S	0.0%	0.2%	0.3%	0.4%

Temp	300-600oC
P_{Ret}	200 psi
P_{Per}	atm

FIGURE 1. Effluent Composition of a WGS Unit

- Determined that for surface stability:
  - Pd-terminated surfaces are least stable.
  - S-Pd-terminated surfaces are most stable.
- Determined that for catalytic activity:
  - Incorporation of S into the Pd system decreases catalytic activity.
  - Pd-participation in the surface reaction allows rates high enough to meet DOE targets (either Pd-terminated or Sub-surface Pd).
- Hydrogen-Deuterium exchange study:
  - Modified quartz reactor system.
  - Developed kinetic model.
  - Initiated experimentation on Pd, Cu and 80Pd-CuThe 80Pd-Cu system is "more catalytic" than pure Pd in H_2.
- Synthesis of multi-layered membranes:
  - 25 µm PdCu substrate (corrosion resistance).
  - Synthesized continuous and dispersed overlayers.
  - Mono-layer Mo film:
    - Expected performance in H_2.
    - H_2S catalyzed the corrosion of PdCu substrate.
- Directly measured the H_2 permeability of Pd_4S:
  - In the presence of H_2, appears to follow Sievert's law.
  - Permeability of Pd_4S is ~10x less than Pd and consistent with face-centered cubic-phase 60Pd-Cu.
- Collaborations:
  - The research team conducting the work on the task consisted of participants from Carnegie Mellon University.
  - NETL Reaction Chemistry & Engineering Group.
  - NETL Computational Research Group (Dominic Alfonso).
  - Provide unbiased performance verification testing:
    - REB Research
    - Oak Ridge National Laboratory
    - Eltron Research
    - Western Research Institute

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Introduction

Hydrogen is viewed as the fuel source for the 21st century. The objective of this project is to support the development of test protocols to include more "commercially relevant" conditions

Approaches

- This project will apply an understanding of engineering principles, membrane technology and coal conversion processes to define a sequential protocol to test various membranes for an "apples-to-apples" comparison.
- The development of a multi-layered membrane system (Figure 2) that utilizes the catalytic activity shown with Pd_4S and the corrosion resistance of select PdCu alloys:
  - Use computational and experimental techniques to understand the catalytic activity at the gas-scale interface (Pd, Cu, Mo, Fe, Ni, Co, etc.).
  - Hydrogen transport properties of the layers and interfaces stability and growth scale.

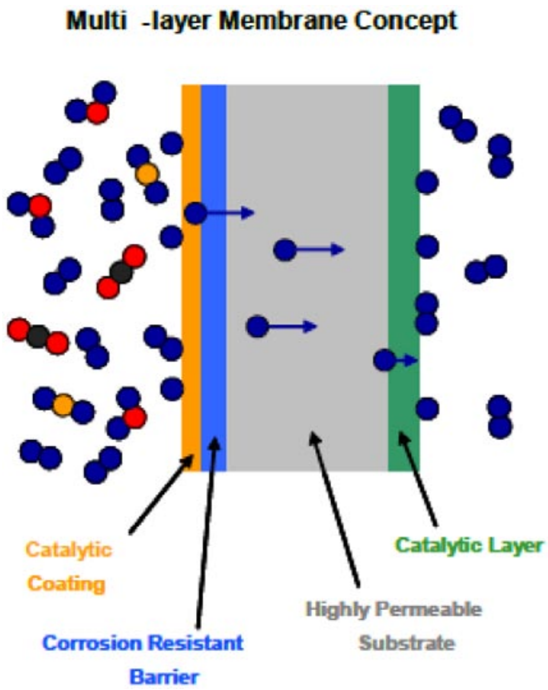

FIGURE 2. Schematic of Multi-Layered Membrane

Conclusions and Future Directions

Conclusions

- A test protocol has been developed and NETL's test systems have been modified to allow testing of various membrane geometries and performance levels.
- Evaluation of the catalytic activity of potential membrane catalyst layers has been initiated utilizing density functional theory, kinetic Monte Carlo and H2-D2 exchange in the presence of H_2. 80Pd-Cu appears more catalytic than Pd.
- Pd_4S shows catalytic properties for H_2 dissociation.
- Several multi-layered membrane systems have been fabricated using both continuous and dispersed catalysts. Thin catalyst layers appear to catalyze the corrosion of a corrosion resistance PdCualloy.
- The characterization of sulfide permeability has been initiated. Pd4S is approximately 10x lower than pure Pd.

Future work

- Continue to support the development of test protocols to include more "commercially relevant" conditions.
- Higher transmembrane pressure differentials.
- Contaminants other than H_2S.
- For example, Cl-and N-compounds for biomass co-feed.
- Integration of WGS reactor and membrane separator.

FY 2010 Publications/Presentations

1. "Gasification and Associated Degradation Mechanisms Applicable to Dense Metal Hydrogen Membranes", Inorganic Membranes for Energy and Fuel Applications, (2009) Springer.

2. "Structural Evolution of Sulfur Overlayers on Pd(111)"; (2009) Surface Science, 603, pp L82-L85.

3. "Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass", DOE/NETL-2009/1349 (2009).

4. "Hydrogen Dissociation on Pd4S Surfaces; (2009) Journal of Physical Chemistry C, 113(43), pp. 18800-18806.

5. "Inhibition of Hydrogen Transport through Palladium and Pd47Cu53Membranes by Hydrogen Sulfide at 350 ˚C"; (2010) Journal of Membrane Science, 349, pp. 380-384.

6. "Development of Membranes for H2-Separation: Pd-coated V-10Pd", submitted to Journal of Energy and Materials.

7. "Effect of H2S on the Performance of Pd4Pt Alloy Membranes", submitted to Journal of Energy and Materials.

8. "The Hydrogen Permeability of Pd4S", in preparation for Journal of Membrane Science.

9. "High-Throughput Characterization of Surface Segregation in CuxPd1-xAlloys", in preparation for Surface Science.

10. "Surface Characterization of Pd-Ag Composite Membranes After Annealing at Different Temperatures", submitted to Industrial and Engineering Chemistry Research.