II.C.5 Advanced Water-Gas-Shift Membrane Reactor

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Objectives

- Identify a suitable Pd-Cu tri-metallic alloy membrane with high stability and commercially-relevant hydrogen permeation in the presence of carbon monoxide and trace amounts of sulfur.
- Identify and synthesize a water-gas-shift (WGS) catalyst with a high operating life that is sulfur and chlorine tolerant at low concentrations of these impurities.

Introduction

This project is an effort to conduct atomistic and thermodynamic modeling studies to identify a Pd-Cu tri-metallic alloy membrane with high stability to provide commercially-relevant hydrogen permeation rates in the presence of trace amounts of carbon monoxide and sulfur. The project effort will also seek to identify and synthesize a WGS catalyst with a high engineering and operating lifetime, which will also be sulfur and chlorine tolerant at low concentrations of these impurities.

Tables 1 and 2 list the targets that the project will attempt to meet during its implementation.

TABLE 1. Technical Targets: Ion Transfer Membranes for Hydrogen Separation and Purification.[a]

Performance Criteria	Units	2003 Status	2005 Target	2010 Target	2015 Target
Flux Rate	scfh/ft^2	60	100	200	300[b]
Cost	$/ft^2	200	150	100	<$100
Durability	Hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	100	200	400	400-1,000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity	% of total (dry) gas	>99.9	>99.9	>99.95	99.99

[a] Targets are derived from Table 3.1.5. from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, Sep. 2005
[b] Flux upper limit for ion transport membranes

TABLE 2. Technical Targets for the Water Gas Shift Reaction[c]

Performance Criteria	Units	Current Status	2005 Target	2010 Target	2015 Target
Reactor Type	-	Multiple fixed beds	To be determined		
Catalyst Form	-	Pellets	To be determined		
Active Metal	-	Cu/Zn or Fe/Cr or Co/Mo	To be determined		
Temperature	°C	200-550	300-450	300-500	200-600
Pressure	psia	450-1150	450	750	>1,000
Approach to Equilibrium	°C	8-10	10	6	<4
Min Steam/CO Ratio	Molar	2.6	3.0	2.5	<2
Sulfur Tolerance	-	Varies	Low	Moderate	High
Chloride Tolerance	-	Varies	Low	Moderate	High
Water Tolerance	-	Varies	Low	Moderate	High
Stability/Durability	Years	3-7	3	7	>10
Reactor Cost Reduction	%	-	-	>15 %	>30%

[c] Targets are derived from Table 6 of the Hydrogen from Coal RD&D Program, Sep. 2005

Approach

- Identify, through a combination of atomistic and thermodynamic modeling, a suitable Pd-Cu tri-metallic alloy membrane that displays high stability and produces a commercially relevant hydrogen permeation rate under 42 atm of H_2, CO, CO_2, and H_2O containing ~8.8 atm partial pressure of carbon monoxide and 0.004 atm partial pressure H_2S (~100 ppm) in the presence of at least 24 atm of steam.

- Identify and develop a WGS catalyst with robust qualities and high operating life times through a combination of atomistic modeling to identify target catalyst structures, catalyst synthesis to realize these structures, micro-reactor kinetics determination and >1,000-hour life testing. The target catalyst activity is a projected precious metal turnover frequency of 0.5 moles CO/moles total precious metal/sec at ~400°C after 45,000 hours of operation under 42 atm of cleaned, oxygen-blown coal gas with a H_2O/CO ratio of ~3 and containing about ~100 ppm sulfur species.

Accomplishments

Completed screening and down-selected from six to two transition metal (TM) substituents for Pd-Cu-TM alloy candidates demonstrating the best potential to enhance stability of the ordered, beta body cubic center Pd-Cu phase over an extended alloy composition and temperature range.

Future Directions

- Complete deployment of atomic and thermodynamic predictions to identify the unique properties of the ordered beta body cubic center Pd-Cu phase that impart high hydrogen permeability.
- Complete selection of four, ordered, ternary Pd-Cu-TM compositions based on the results of solid-state, thermodynamic, and hydrogen diffusivity parameter predictions.
- Select a final Pd-Cu-TM composition through virtual refinement of phase stability, hydrogen permeability, and resistance to sulfide formation. Complete evaluation of the synthesis and testing of the first set of five WGS catalyst candidates for performance in the presence of 0.004 atm H_2S.