High-Performance, Durable, Palladium Alloy Membrane for Hydrogen Separation and Purification

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Project ID #PD 005

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Overview

Timeline

- July, 2005 start date
- Sept., 2011 end date
- 80% complete

Barriers

- Operational durability
- Compatibility to impurities
- Manufacturing cost

Budget

- $4 Million Project Total
  - $2.235M DOE share
  - $1.610M Contractor share
- FY10 Funding $500K
- FY11 Funding $220K

Partners

- Colorado School of Mines
- ORNL – High Temperature Materials Lab
- End user

Relevance- Objectives

The project objective is development, demonstration and economic analysis of a **Pd-alloy membrane** that enables the production of **99.99% pure H_2** from reformed ethanol at a cost **< $3/gge**.

The objectives from April 10 - March 11 were to:

- ✓ **Optimize** membrane alloy composition and thickness to maximize membrane performance in syngas/WGS reaction environment
- ✓ Conduct **long-term durability testing** of Pd-alloy membranes in **syngas/WGS** reaction environments **meeting Phase III goals**
- ✓ **Scale-up** the substrate and membrane synthesis to 12” elements
- ✓ **Design and fabricate multi-tube modules** minimizing concentration polarization effects at high hydrogen recoveries
- ✓ Work with end user to **compare cost/performance** of a membrane-based system to PSA and solvent-based systems for large scale hydrogen production with CO_2 capture.

Relevance - Addressing Barriers

- **Operational Durability**
  - Addressed through alloy and composite membrane structure
  - Demonstrated long-term (500 hr) **stable performance in aggressive syngas** environment with up to 20% CO in feed
  - Demonstrated stability against rapid **thermal cycling**
- **Compatibility to Impurities**
  - Evaluated effect of **CO and H_2O** on membrane performance
  - Determined acceptable **H_2O:CO ratio** for stable performance
  - Conducted limited tests with low concentration **H_2S** exposure
    - Observed reversible H_2 flux decline with H_2S exposure
- **Manufacturing Cost**
  - Target cost is estimated based on sales price to end user for membrane in a module
  - Manufacturing scale-up increases yield and reduces cost

DOE HFI Membrane Performance Targets*

Performance Criteria	2006 Status	2010 Target	2015 Target
Flux SCFH/ft^2 @20 psi ΔP H_2 partial pressure, 400ºC (Pure H_2 gas)	>200	**250**	300
Membrane Cost, \$/ft^2 (including all module costs)	1500	**1000**	<500
ΔP Operating Capability, system pressure, psi	200	**400**	400 - 600
Hydrogen Recovery (% of total gas)	60	**>80**	>90
Hydrogen Permeate Quality	99.98%	**99.99%**	>99.99%
Stability/Durability	<1 year	**2 years**	>5 years

* 2007 Technical Plan. Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification www1.eere.energy.gov/hydrogenandfuelcells/mypp

Approach - Overall Technical Approach

- **Develop a commercially viable Pd alloy membrane to enable the design of economical processes for hydrogen production**
  - Pd alloy composite membrane is shown to have both high flux rate and high separation factor for separating H_2 from ethanol/NG reformate gas
  - Commercial scale-up of high quality porous metal substrate along with alloy development, deposition methods and module design pursued
- **Increase the overall energy efficiency of a H_2 reforming system through use of membrane technology for process intensification**
  - Membranes with high operating temperatures can be heat integrated to reduce thermal loss within the system
  - Membranes with high separation factor can reduce system complexity, size and operating cost
  - Membrane reactors can reduce the cost of pressure vessels, reduce catalyst volumes and overall capital and operating cost

Approach – Progress FY 10/11

- **Membrane Development**
  - Modified DBS process to increase DBS surface roughness and eliminated potential film stresses and membrane film delaminations
  - Synthesis of membrane with varying thickness in 3 to 9 micron range and Pd-Au alloy composition in 0-30% Au range

- **Parametric Membrane Testing in Syngas Environment**
  - Typical syngas compositions were found not to be severe enough to cause decline in flux or purity over a couple of hundred hours
  - Developed a gas composition that was determined to be sufficiently aggressive to cause a decline in flux and purity in hundred hour time
  - Demonstrated membrane performance in aggressive Syngas/WGS reaction environments with up to 20% CO in the feed gas.
  - Testing is continuing to determine the optimal alloy composition and thickness for maximizing membrane performance

Approach – Progress FY 10/11 (cont.)

- **Module Development**
  - Scale-up substrate and membrane synthesis to 12” elements
  - Develop membrane module design concepts to overcome concentration polarization effects. Fabricated and tested module and confirmed hydrogen flux and recovery as predicted by model

- **Economic Evaluation**
  - Update costs based on membrane scale-up and module design
  - Estimate influence of operating parameters on the cost of hydrogen production guiding overall approach to minimize H_2 cost
  - Compare competing technologies (PSA and solvent scrubbing) to produce hydrogen by reforming of natural gas on a large scale with CO_2 capture and sequestration

Technical Accomplishments & Progress
Summary of Previous Accomplishments

- **Develop substrate process:** Porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 550ºC and 20 bar that can be made in longer lengths and ZrO_2 diffusion barrier fabrication process was scaled up to 12-inch lengths
- **Improve membrane deposition process:** Modified deposition methods to repeatedly produce thin Pd alloy membranes (≤2 microns) with high separation factors (greater than 20,000). Incorporated air oxidation and layering sequence to improve membrane performance
- **Fabricate test samples:** Produced various Pd-Au alloy tubular membranes 5-30% Au and thickness 1.0-3.5 microns and established inventory for parametric testing
- **Membrane performance** Analyzed the effect of alloy composition, process conditions and operational procedures on membrane performance
- **Design membrane for high ΔP:** Carried out tensile strength and strain at failure for Pd-alloy foils over the composition range of 0-38 mass % Au to determine high pressure operating capability for the functional membrane layer
- **Performed extensive testing in mixed gas streams:** Extensive testing has been carried out in mixed gas test streams to determine effect of major gas components
- **Estimated cost:** Module design, fabrication techniques and materials for a stand alone membrane separator device show that less than $1,000 per ft^2 of area cost to end user is achievable
- **Conducted techno-economic analysis:** Conducted preliminary H_2 production cost analysis using DTI's H2A based model and Pall provided costs. Results showed the cost of the separation device (PSA or membrane) is a small percent (<10%) of capital cost and is not the dominating factor. Greater membrane recovery however significantly reduces the cost of $H_{2,}$

Technical Accomplishments & Progress
Summary of Accomplishments for April 10 - March 11

- Continued optimization and characterization of the membrane formation process. A change in the substrate/DBS process was found to result in delamination of the membranes. The substrate/DBS process was modified to increase surface roughness thereby eliminating delaminations
- Pd-Au alloy membranes with varying thicknesses and alloy compositions are currently being evaluated for determining optimal membrane configuration for maximizing performance
- Conducted extensive testing of Pd-alloy membranes in pure gas streams and in methanol/NG reformate environments for parametric evaluation of their performance. The standard WGS composition was determined to be insufficient to cause a decline in flux or H_2 purity of most of the membranes for determination of the optimum alloy composition or thickness.
- An accelerated life test based on an aggressive variant of the WGS composition was therefore tested and determined to be sufficient to cause a decline in the H_2 purity and H_2 recovery in the 100 hour range.

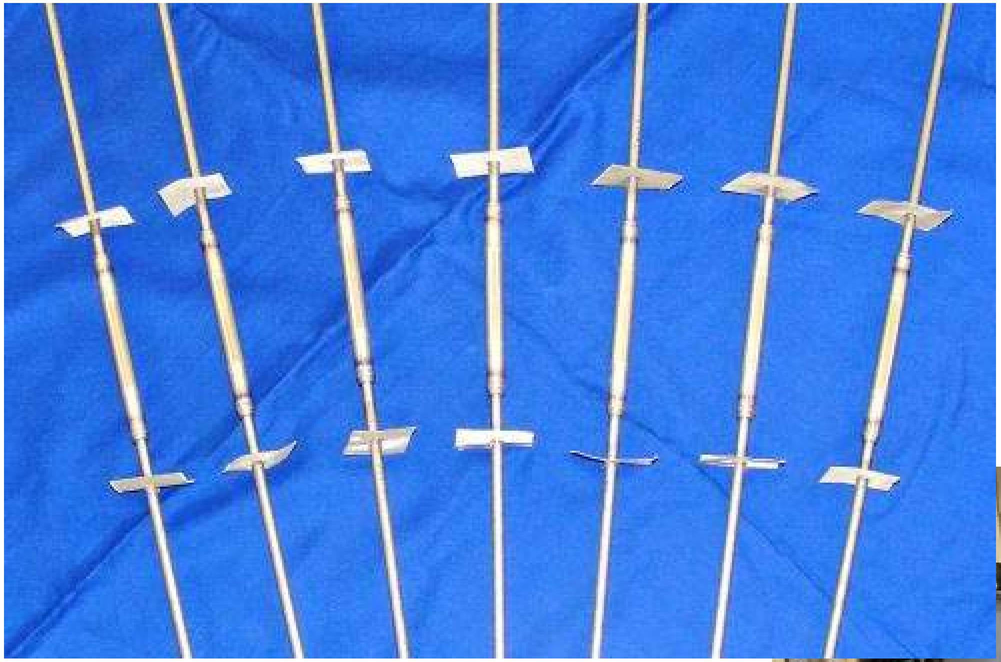
Significant progress towards establishing viability

Technical Accomplishments & Progress
Summary of Accomplishments for April 10 - March 11

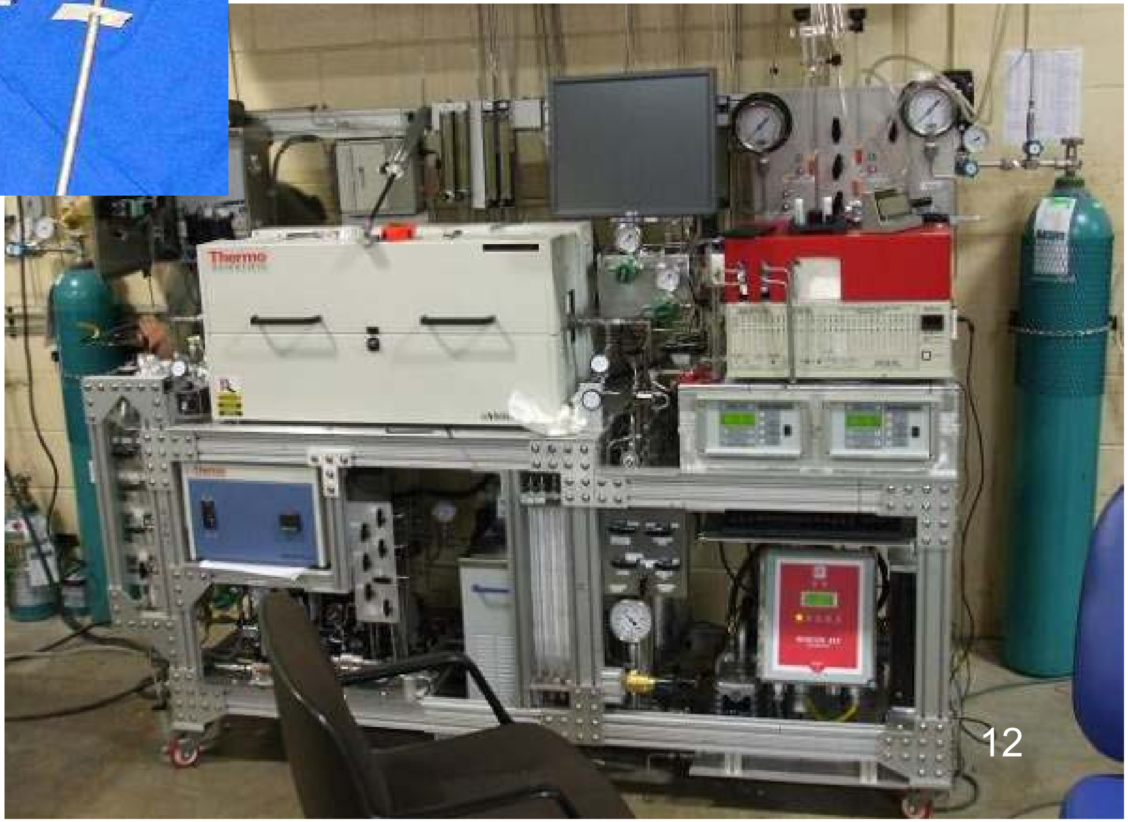
- Tests are proceeding on the determination of the best alloy composition and membrane thickness combination.
- Evaluated multi-tube membrane module design concepts to overcome concentration polarization effects. Fabricated and tested module and confirmed hydrogen flux and recovery as predicted by model
- Initiated techno-economic study in collaboration with an end user to compare Pd-membrane based process to competing PSA and solvent scrubbing-based processes for large scale hydrogen production (~36,000 kg/hr) from natural gas with CO_2 capture
- Provided estimates of membrane area and costs to the end user. A two-stage cascade of WGS reactor/membrane separator was found to be able to provide 90% H_2 recovery with 90% H_2 purity.
- ORNL – HTML is conducting an analytical study of the alloy phases developed and tested in this program

Significant progress towards establishing viability

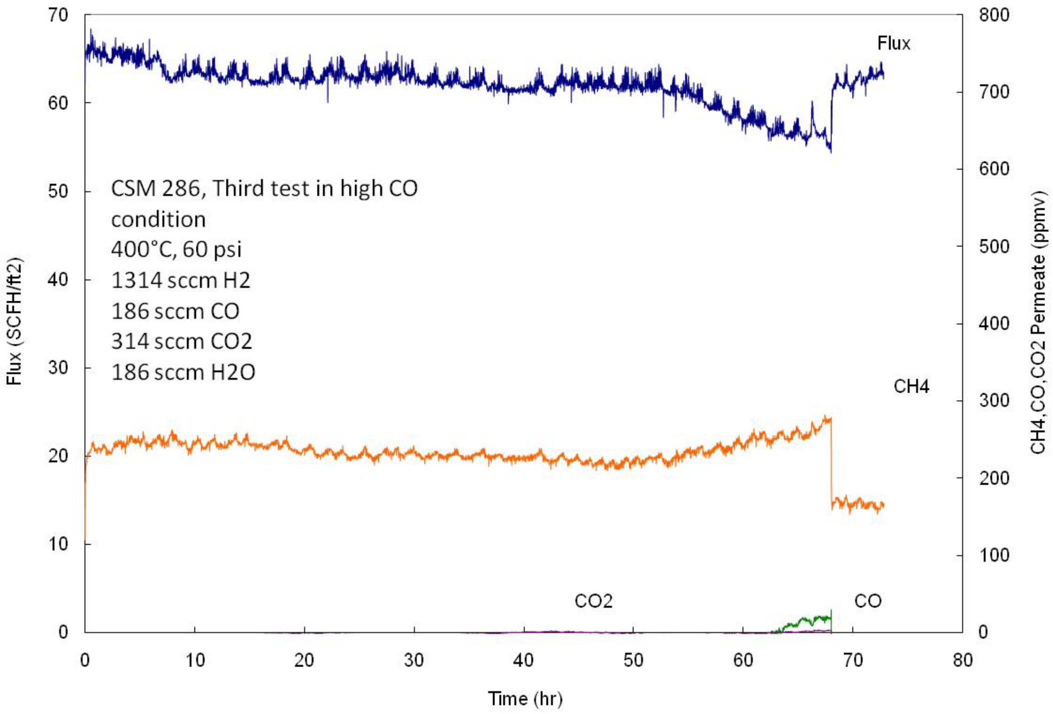
Technical Accomplishments Membrane Fabrication and Testing



Selection of tubes of varying Pd-Au alloys ready for testing on the automated water gas shift test stand



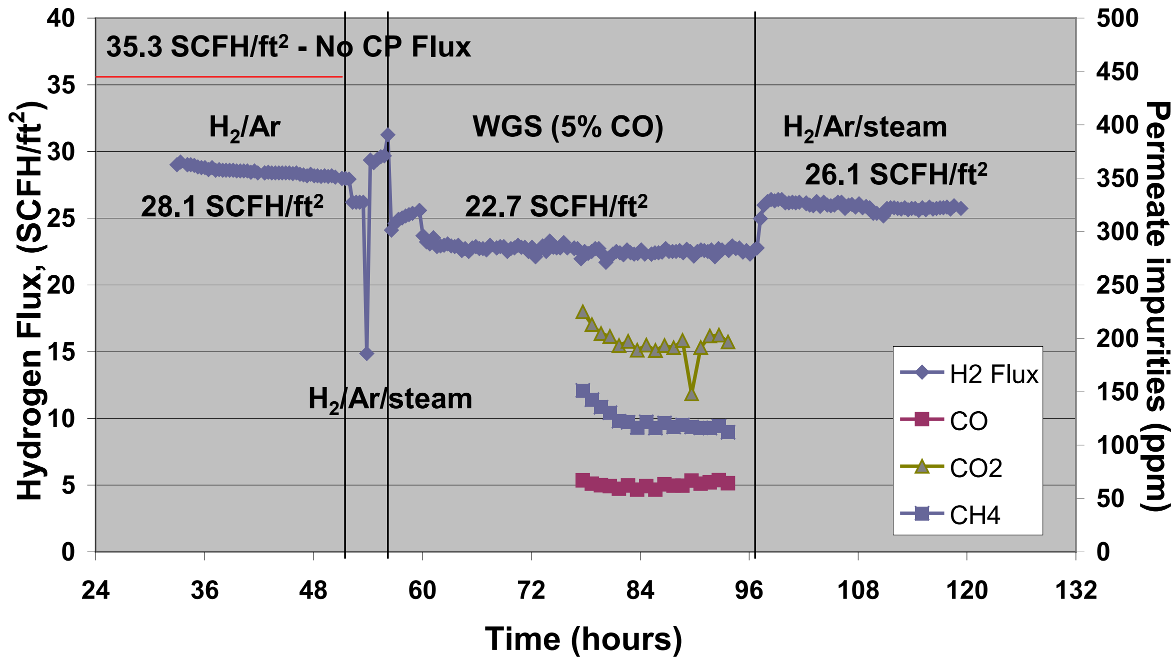
Pd-alloy Membrane test in High CO Feed Gas



- $Pd_{83}Au_{17}$ membrane 8.4 µm thickness
- Feed gas: Methanol reformate 65.7% H_2, 9.4% CO, 15.5% CO_2, 9.4% H_2O
- Feed flow rate = 2000 mL/min
- T = 400°C, P_{feed} - 5.0 bar (72 psia), $P_{permeate}$ - 0.8 bar (12 psia)
- Three startup/shutdown tests of 70 hr duration each – Third test shown above

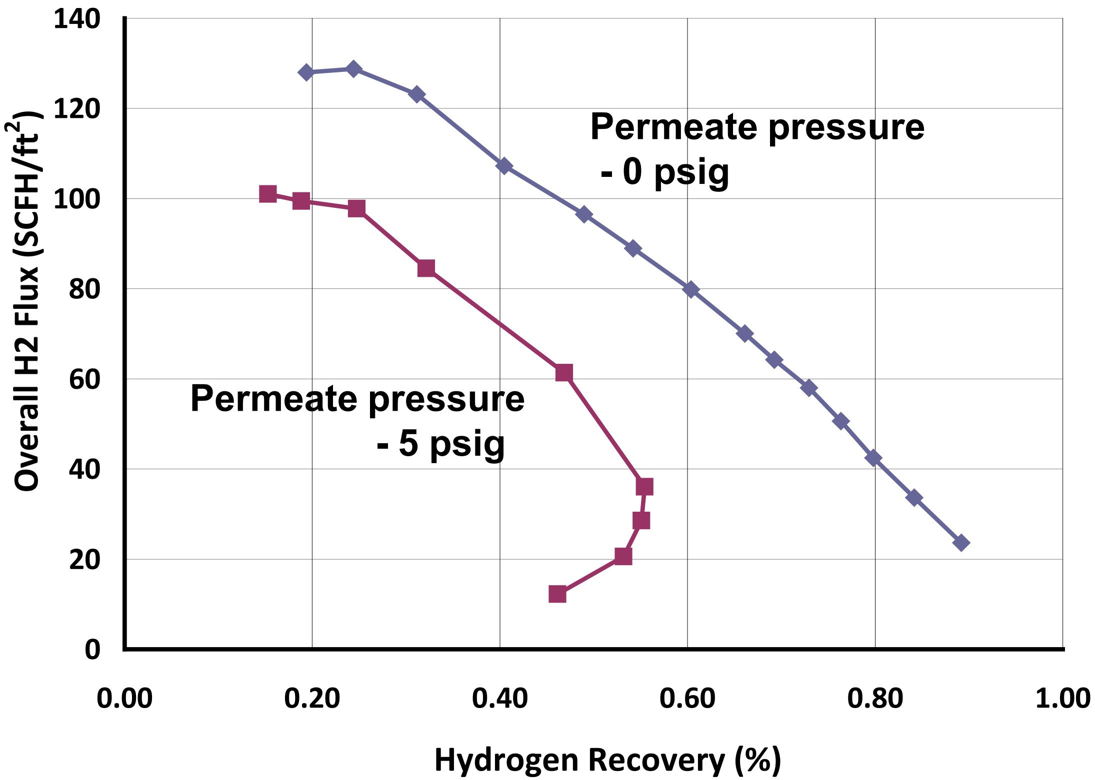
(Tests conducted by TDA research)

Effect of Concentration Polarization and CO



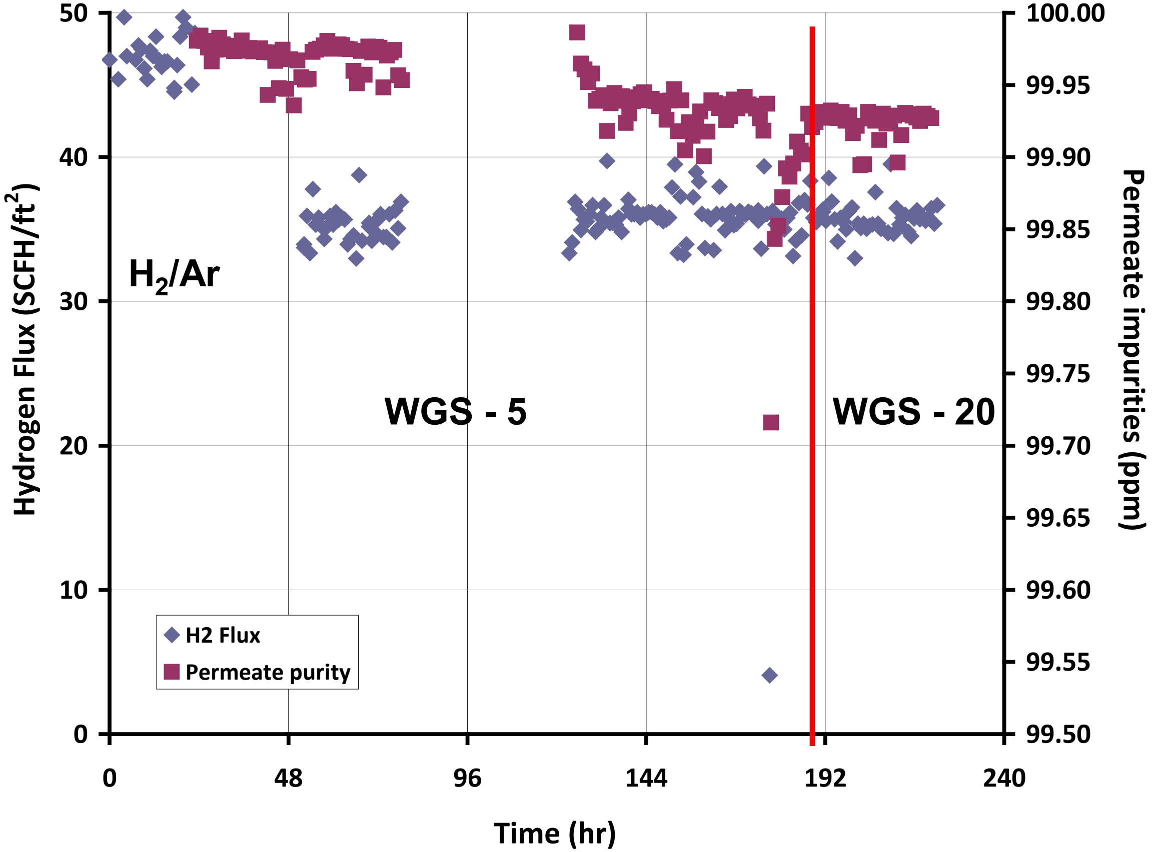
- $Pd_{95}Au_5$ membrane 8 µm thickness
- Feed gas: H2/Ar, H2/Ar/Steam and WGS (50% H2, 25%CO2, 20% H2O, 5%CO)
- Feed flow rate = 2000 mL/min
- T = 400°C, P_{feed} - 9.0 bar (132 psia), $P_{permeate}$ - 0.8 bar (12 psia)
- H_2 flux reduction - due to CP effect ~ 20%, due to CO ~ additional 20%

Overall H_2 flux as a Function of Recovery



- $Pd_{95}Au_5$ membrane 8 μm thickness
- T = 400°C, Feed Pressure - 9.0 bar (132 psia)
- Feed gas - 50% H_2, 50% Ar

Membrane Performance in WGS conditions



- $Pd_{90.7}Au_{9.3}$ membrane 1.8 µm thickness
- T = 400°C, Feed Pressure - 172 psig, Permeate Pressure – 5 psig
- WGS – 5 Feed Composition 50% H2, 25%CO2, 20% H2O, 5%CO
- WGS – 20 Feed Composition 50% H2, 10%CO2, 20% H2O, 20%CO

Test Conditions for Accelerated Degradation

- First accelerated test condition:
- Feed pressure ~182 psia
- Perm pressure ~ 17 psia
- Temperature - 400 C
- Flow rate 800 mL/min
- Feed Composition 50% H2, 10% CO2, 20% CO and 20% steam - **WGS - 20**
- Membrane CSM357 (1.8 micron, 9.3% Au) showed no flux decline or permeate purity decline over 150 hr of testing at these conditions.

- Second accelerated test conditions:
- Feed pressure ~182 psia
- Perm pressure ~ 17 psia
- Temperature - 400 C
- Flow rate 800 mL/min
- 50% H_2, 30% Ar, 20 % CO - **WGS – 20D**
- After stabilizing, the test showed a nominally steady decline in permeate purity of 32 ppm/day (0.0032%/day) over 100 hr.

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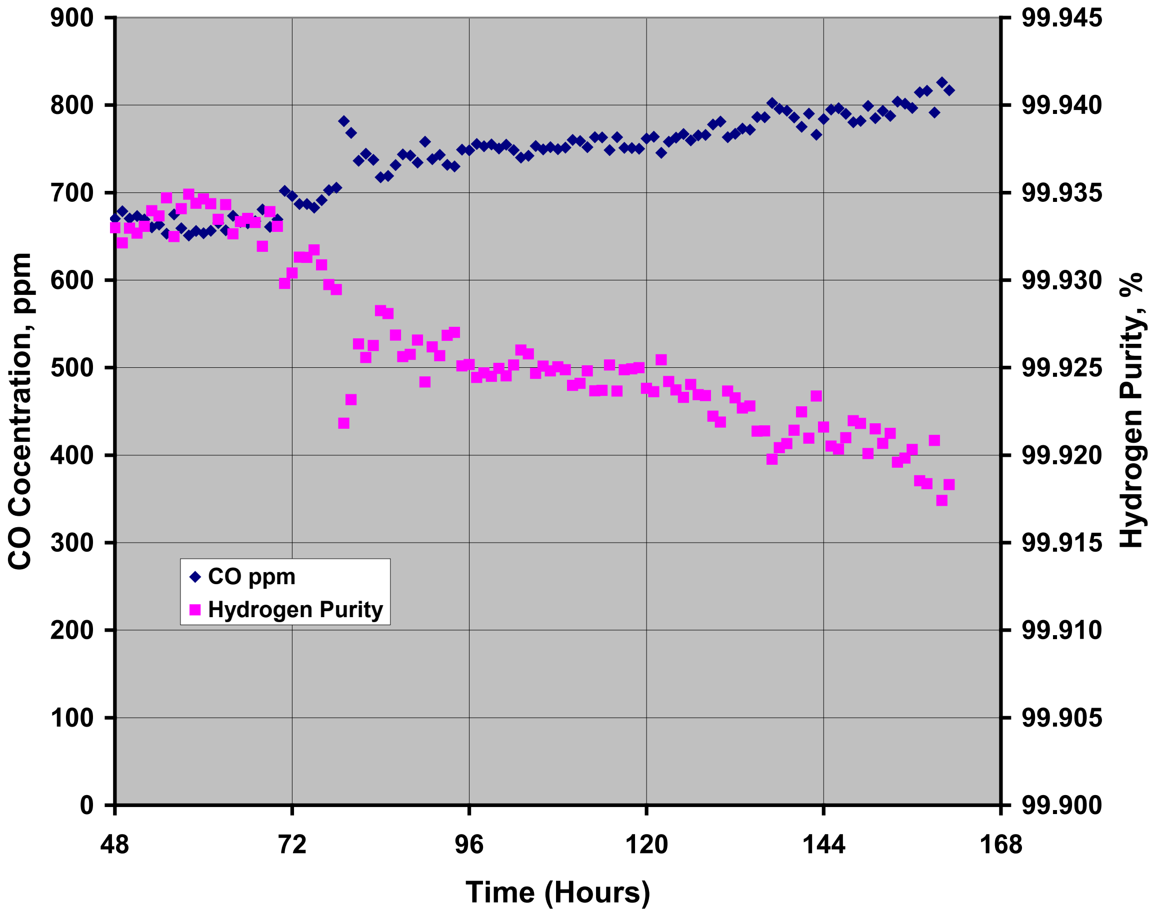
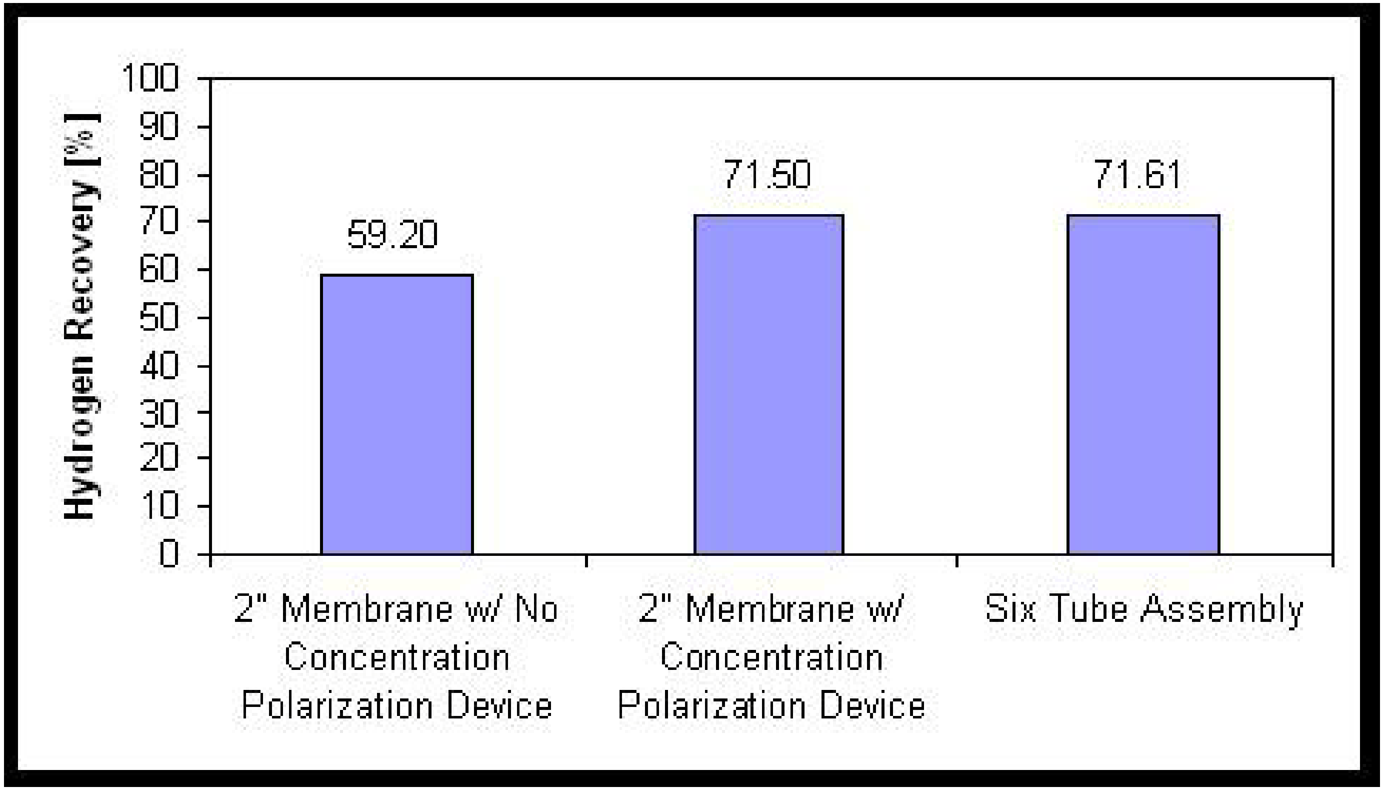
Membrane Performance in Accelerated Test



Pd90.7Au9.3 membrane 1.8 µm thickness, Flow rate 800 mL/min, Feed Pressure ~182 psia, Permeate pressure ~ 17 psia T = 400°C, Feed gas composition, 50% H_2, 30% Ar, 20 % CO – WGS – 20D

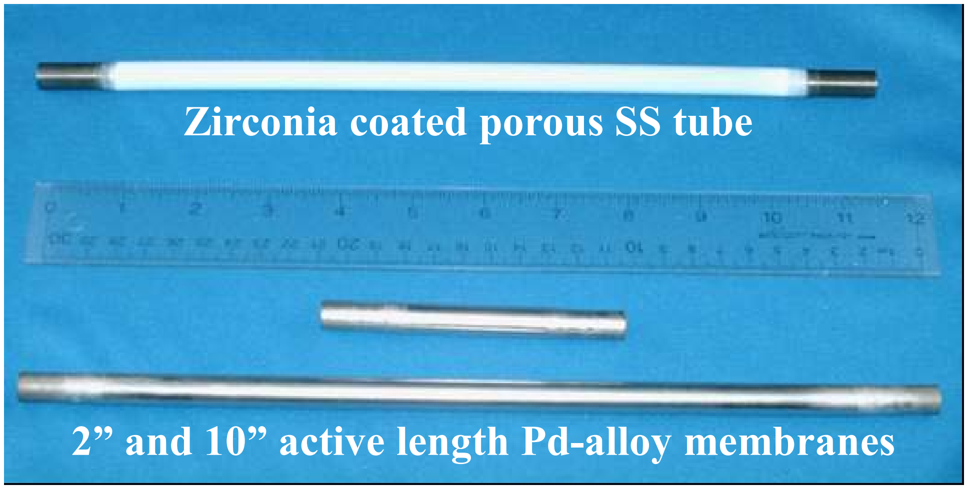
Module design - Comparison of the hydrogen recoveries

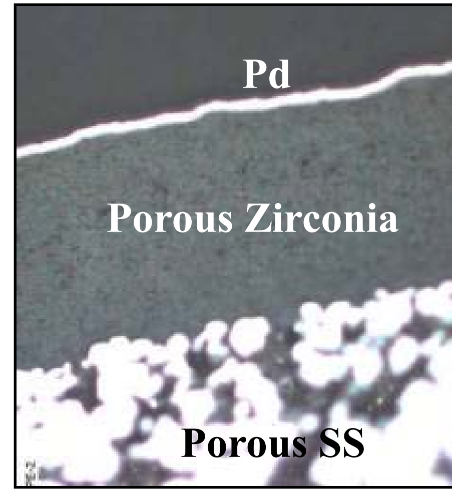


50/50 hydrogen/argon mixture at Pf = 170 psig, Pp = 5 psig and T = 400° C
2 SLPM for the single membrane vs. 12 SLPM for the six tube assembly

THE CP DEVICE AND THE MODULE WITH INHERENT CP DESIGN WERE DEVELOPED USING PALL FUNDS ON A SEPARATE PROJECT

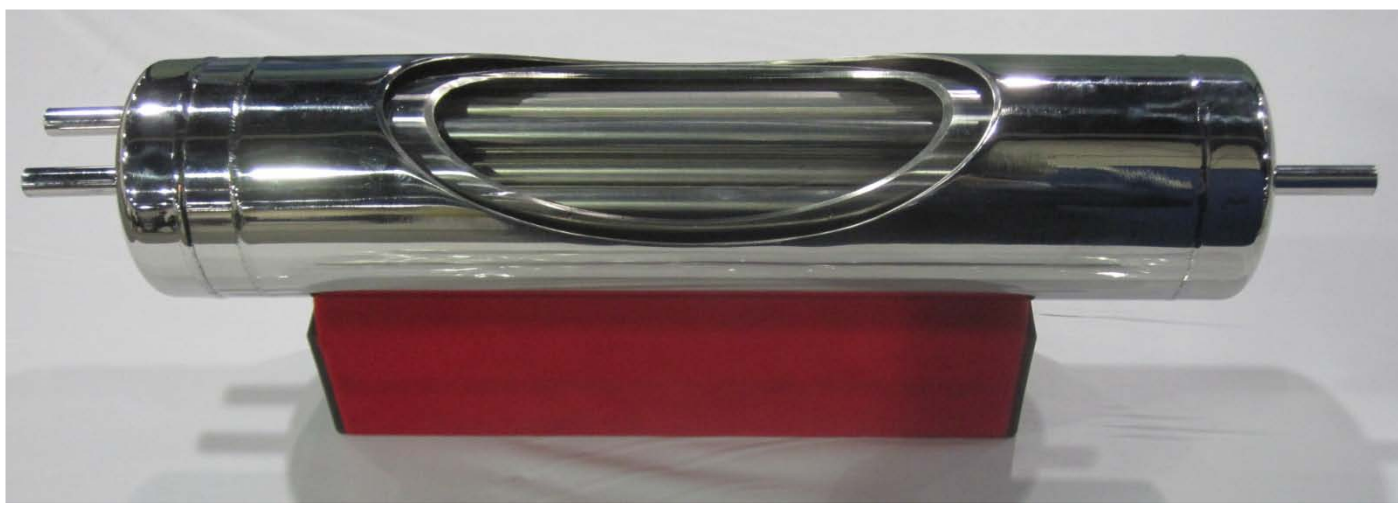
Membranes and Modules





Composite membrane structure

12-tube module with 12” elements for ~ 5 kW equivalent H_2 Production



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Collaborations

- **Pall Corporation:** Prime contractor responsible for porous substrate development, membrane testing, membrane scale-up, design/ fabrication of modules and development of production technology, technical and feasibility analysis and technology commercialization
- **Colorado School of Mines:** Sub-contractor focused on the material science. Responsibility includes selection of Pd-alloy compositions, fabrication of membranes and testing for compatibility.
- **ORNL-HTML:** Sub-contractor focused on the evaluation of material properties using unique test equipment and techniques. Includes mechanical properties and alloy structure at operating temperature.
- **Directed Technologies Inc.** Independent contractor to the DOE. Used module costs/performance to estimate H_2 cost by H2A model for an integrated membrane reformer/water gas shift reactor configuration.
- **H_2 producer – End User:** Conducting comparison of the membrane-based process with PSA and solvent scrubbing based processes for large scale hydrogen production with CO_2 capture.

Future Work (Phase III)

- Complete optimization of membrane synthesis steps, composition, and thickness for high flux, selectivity, and durability with short term testing (100-200 hours) using aggressive composition 50% H_2, 30% Ar, 20% CO **(WGS – 20D)** to determine the best alloy composition and membrane thickness for maximizing performance
- Conduct long term (>500 hours) durability testing with optimized membrane configuration to confirm membrane performance with respect to hydrogen flux rate and purity and membrane durability.
- Scale up membrane synthesis to 12" elements with testing to verify the membranes meet all Phase III performance goals set
- Fabricate 12 tube membrane modules with 12" length membrane elements for performance testing at TDA Research facilities
- With the end-user, complete techno-economic comparison of membrane-based process with competing PSA and solvent -based processes for large scale hydrogen production with CO_2 capture.

Establish overall economic viability for H_2 production via membrane based reforming

Summary
Technical Accomplishments Achieved This Year

- Improved **substrate/DBS process to eliminate delaminations and improve membranes**
- Scale-up to **Pd-alloy membranes to 12”** length is in process
- Determined that an **accelerated life test** was required to cause the membranes to decline in performance in a reasonable time to determine the best alloy composition and membrane thickness.
- **Optimization** of membrane alloy composition and thickness using the accelerated test and **verification** with long term testing is in process
- Initiated **techno-economic modeling** in collaboration with an end user to determine influence of membrane parameters (flux, recovery, cost) on cost of Hydrogen
- Provided **membrane module area/cost estimates** for large scale hydrogen production (36,000 kg/hr) to the end user for their cost comparison with PSA and solvent-based systems.

Summary - Performance Progress Against Targets 4-inch membrane module at 400°C

Performance Criteria	2010 Target	2015 Target	Pall Status 2010
Flux SCFH/ft² @20 psi ΔP H_2 partial pressure & 15 psig permeate side pressure	250	300	**270***
Membrane Cost, $/ft² (including all module costs)	$1,000	<$500	**<$1,000**
ΔP Operating Capability, system pressure (psi)	400	400 - 600	**400**
Hydrogen Recovery (% of total gas)	>80	>90	**>80****
Hydrogen Permeate Quality	99.99%	>99.99%	**99.99% *** **
Stability/Durability	2 years	>5 years	**TBD**

*Maximum observed flux in pure H_2/N_2. Average flux over more than 20 samples ~ 190 SCFH/ft². Economic analysis indicates separation factor rather than flux to be stronger determinant of cost of hydrogen production
** Measured on a 50% H2, 25%CO2, 20% H2O, 5%CO mixed gas WGS stream. The experimentally observed recovery is determined by chosen operating conditions and is not necessarily a limit of the membrane performance.
*** Projected purity based on H_2/N_2 ideal selectivity.