Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

DE-FG36-05GO15092

PD 072

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Overview

- Project Start Date
  7/1/05
- Project End Date
  12/31/11
- Percent Complete
  90%

BARRIERS

#1 Testing/Analysis: few commercial scale membrane- and membrane reactor-based processes in operation

#2 Permeate Flux/Selectivity: cost vs performance target meeting our end user requirements

#3 Stability: lack of long term membrane and membrane reactor performance data under our target field conditions

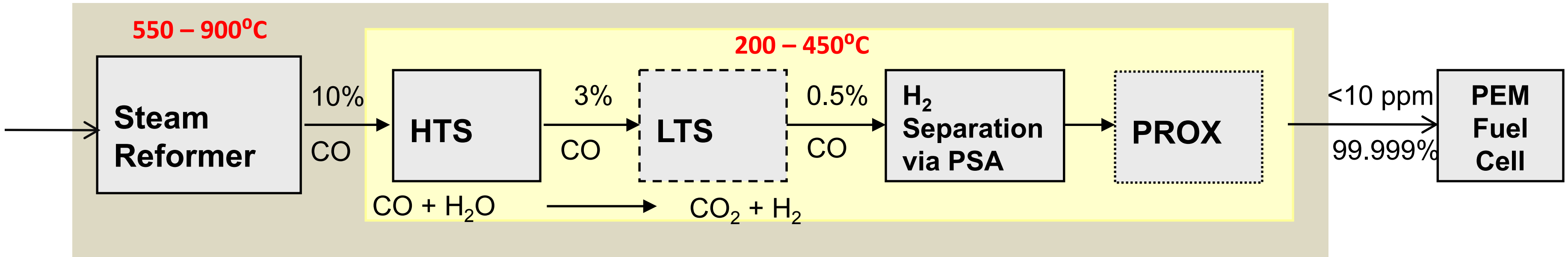
- **Total project funding**
  - DOE Share: $2,592,350.
  - Contractor Share: $648,087.
- **FY10:** $100K
- **FY11**: $481K
- No catalyst development activities due to funding limitation in the beginning of the project

- **Professor Theo T. Tsotsis**
  University of Southern California,
  Catalytic membrane reactor expert
- **Dr. Babak Fayyaz-Najafi** Chevron ETC,
  End User Participant
- **Dr. Hugh Stitt,** Johnson Matthey,
  Catalyst Manufacturer
- **Dr. Pat Hearn**, Ballard Power Systems
  Fuel Processing End User

Overall Project Objectives - Relevance

1. Develop, fabricate and demonstrate field implementable hydrogen selective membranes/modules
2. Intensify/improve conventional hydrogen production process via a membrane reactor
3. Prepare field test modules and conduct a field test for hydrogen production/purification

Example of Conventional Process - Steam Methane Reforming (SMR)



Overall Technical Approach

Objective #2

1. Reduce HTS/LTS reactors & inter-stage coolers into a single stage **LTS/MR** operation (Barrier #1)

Objective #1

2. Develop a cost acceptable **hydrogen selective membrane and module** for end users (Barrier #2 & 3).

Objective #3

3. Fabricate full-scale membrane/modules and perform field test for hydrogen separation (Barrier #1).

⇨ **Project Goal**

Field Test on Membrane Reactor

HTS: High Temperature Shift
LTS: Low Temperature Shift
PROX: Preferential Oxidation
PEM: Proton Exchange Membrane
MR: Membrane Reactor
PSA: Pressure Swing Adsorption

Specific Objectives and Technical Approach for FY10-11

- **Develop economic bundling technique for Pd membrane tubes**
- **Evaluate bundle performance**

Field Test H_2 Recovery (Barrier 1&2)

- ❑ Fabricate 2nd generation membrane/bundle to meet commercial partner's cost and performance criteria.
- ❑ Use pilot-scale gas separation test to compare bundle to single tube performance.
- ❑ Field test hydrogen recovery from reformate stream.

Design and fabricating full-scale membrane reactor for field testing (Barrier 1)

- ❑ Use bundles for WGS-LTS process in the full scale membrane reactor.
- ❑ Incorporate cooling coils for in-situ cooling.

Develop post-treatment technology to meet the CO level requirement (Barrier 1&3)

Develop 3rd generation membrane with cooling stability in the presence of H_2.

TECHNICAL ACCOMPLISHMENTS – FY10-11

- **Developed low cost potting technique for commercially viable Pd membrane tube bundles**

  Last year we successfully met our commercial partner's low cost request and this year we developed a commercially-viable potting technique that packages the Pd membrane tubes into bundles.

- **Prepared palladium membrane bundles and confirmed performance with field testing**

  We prepared membrane bundles for field testing; verified separation properties at our pilot plant and end user site; and prepared bundles to be packaged into the reactor for field testing.

- **Used a simulated application environment to test long-term thermal cycling stability of Pd membrane bundles**

  We tested long-term cycling stability of Pd membrane bundles using a simulated application environment for ~150 thermal cycles demonstrating stability in nitrogen between room temperature and 350°C.

TECHNICAL ACCOMPLISHMENTS – FY10-11

- **Developed a post-treatment strategy to meet the hydrogen product purity requirement of <<10ppm CO**

  Our membrane reactor work in FY 09-10 delivers 83% hydrogen recovery of 99.9% purity hydrogen with ~ 50ppm CO. Our bench-top post-treatment study this year shows the reduction of 300, 70 and 10ppm CO in H_2 to 16, 1.2 and 0.3ppm respectively.

- **Fabricated reactor module for field test**

  We designed the full-scale membrane reactor and are currently preparing membrane tube bundles and a built-in cooling coil for in-situ WGS-LTS heat transfer.

- **Developing Pd membranes with cooling stability in the presence of hydrogen**

  We conducted cyclic cooling tests to identify a potential alloy for upgrading our Pd membrane product with this cooling feature.

M&P CERAMIC MEMBRANES - Low Cost

for harsh environment applications

Developmental Work Required

1. Deposition of an additional thin film for hydrogen separation
2. Fabrication of bundle/housing suitable for working environment

Examples of Commercial Installations

- Oil filtration applications at 150^{o}C and 80 psi
- Water vapor recovery from flue gas at ~75 ^{o}C

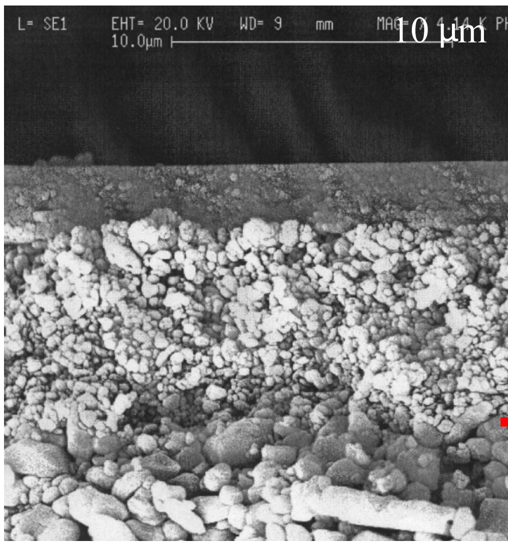
Proposed Applications

- Hydrogen recovery from reformate
- Water gas shift (WGS) membrane reactor at 200 to 350^{o}C

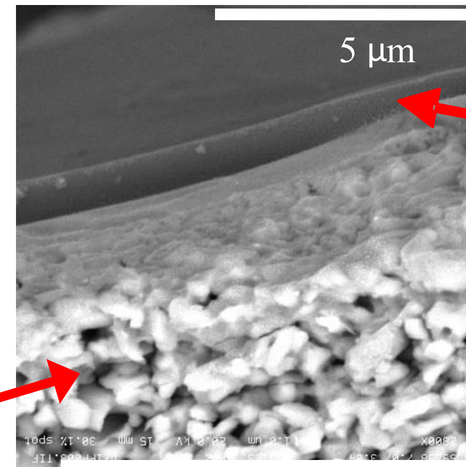
M&P Advanced Inorganic Membranes

M&P's Core Technology: Thin film deposition on porous substrates

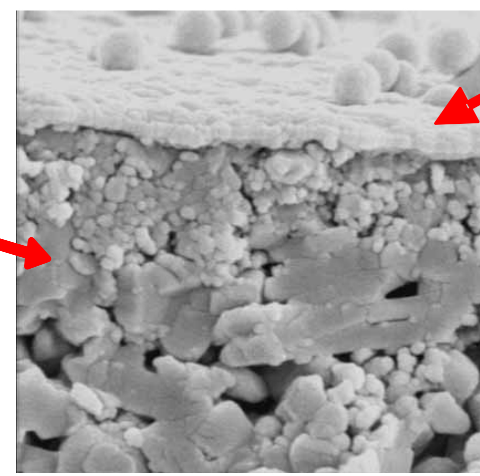
Inorganic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistance)



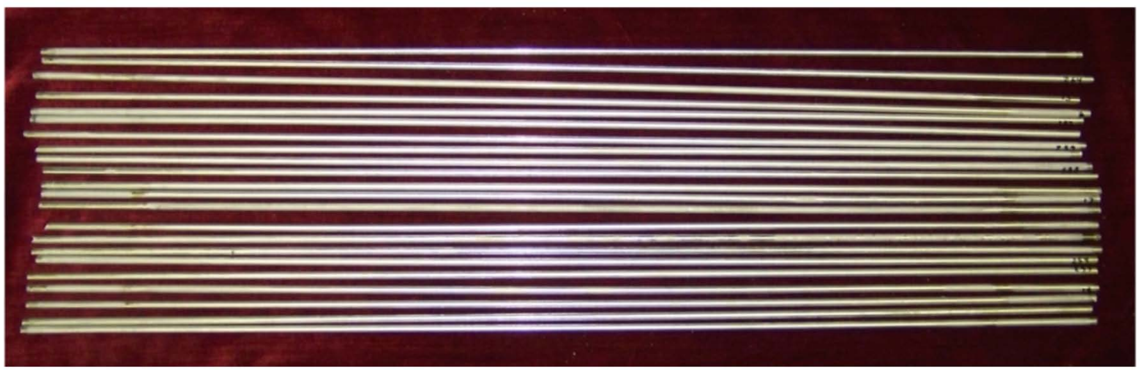
Palladium (dense, excellent selectivity)

Unique features of
<u>Supported Membranes</u>

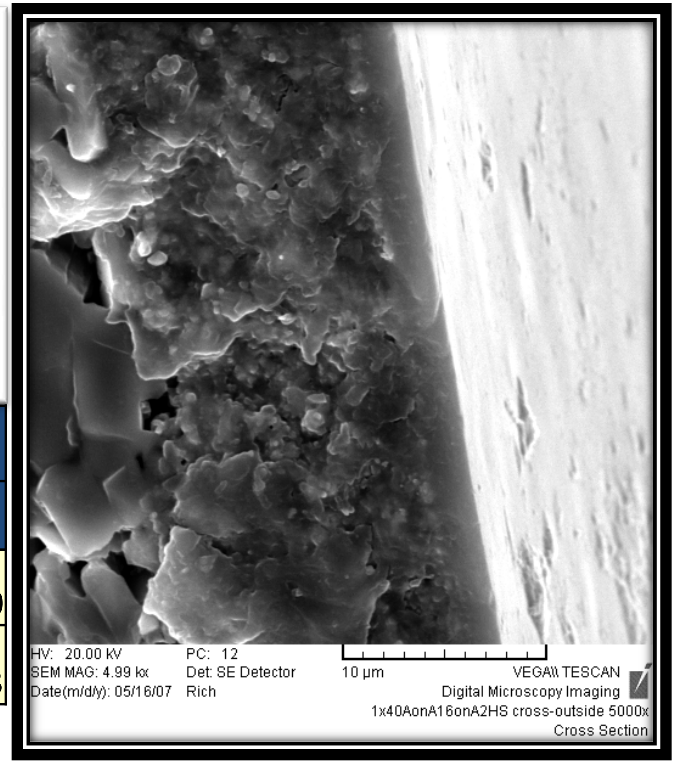
- Low cost, no Pd supply challenge
- Module/housing for high temperature/pressure use

Full-scale Pd Membrane Tubes

Pd Thin Film Coated on the Outside with a
Tubular Commercial Ceramic Membrane as Substrate



Layer Location	Tube Diameter [cm] OD	ID	Tube Length [in]	Surface Area [m²/30"L tube]	Surface Area Ratio [-]
Inside	0.57	0.35	30	0.0084	1.00
Outside	0.57	0.35	30	0.0136	1.63



Outside coated Pd membrane product is a preferred choice due to its >50% increase in surface area.

Full-Scale Ceramic Membrane Bundles for Gas Separation

Palladium Membrane Bundles for Portable Power Generation Applications for this project

<u>ACCOMPLISHMENT in FY10-11</u>

Used low cost potting technique to pot outside coated Pd membrane tubes to create commercially viable bundles.

Cost Target for Applications Stationary Power Generators:

Membrane-based Process Challenges

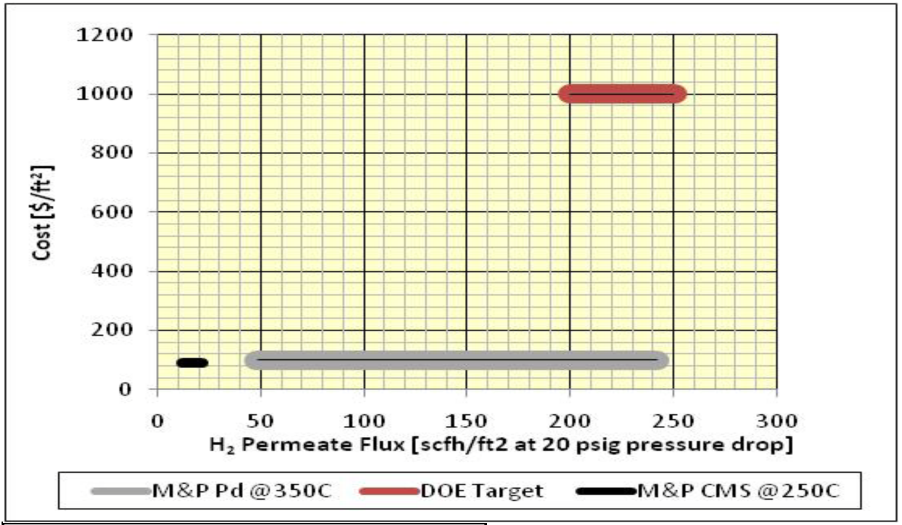
Cost Allocations for A 5kW Fuel Cell Based Genset based upon a conventional diesel fuel reforming			
Component	**Typical Equipment**	**Cost [$]**	**$/kW**
Purifier	Pd membrane*	400	80

•*The benefits offered by the membrane reactor were not taken into consideration in this analysis.*

(Courtesy of Ballard Power Systems)

Evaluation of M&P Pd Membranes/Bundles: Results

1. Performance Characterization (typical)



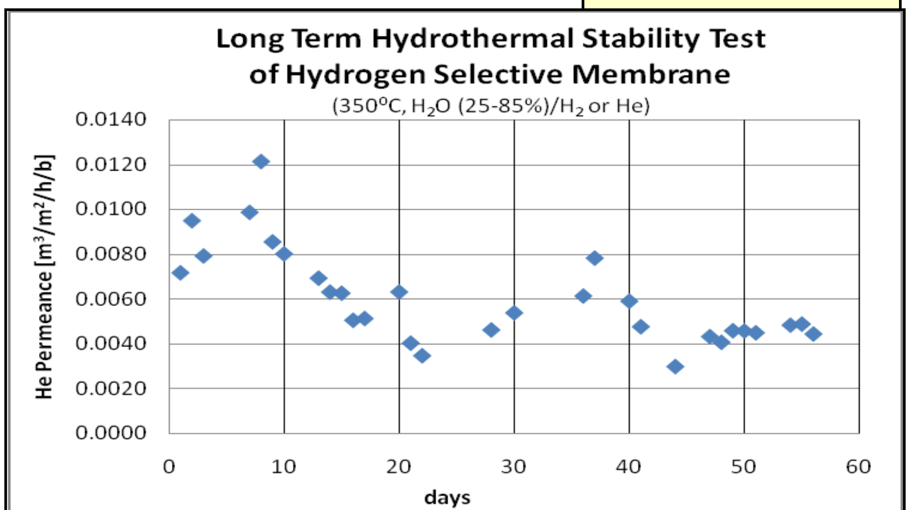
Membrane Cost for 5kW Genset		
Targets	H_2 Flux*	Cost [$/5 kW]
DOE Target	250	2,000
M&P current	121	416

* in scfh/ft² at 20 psig

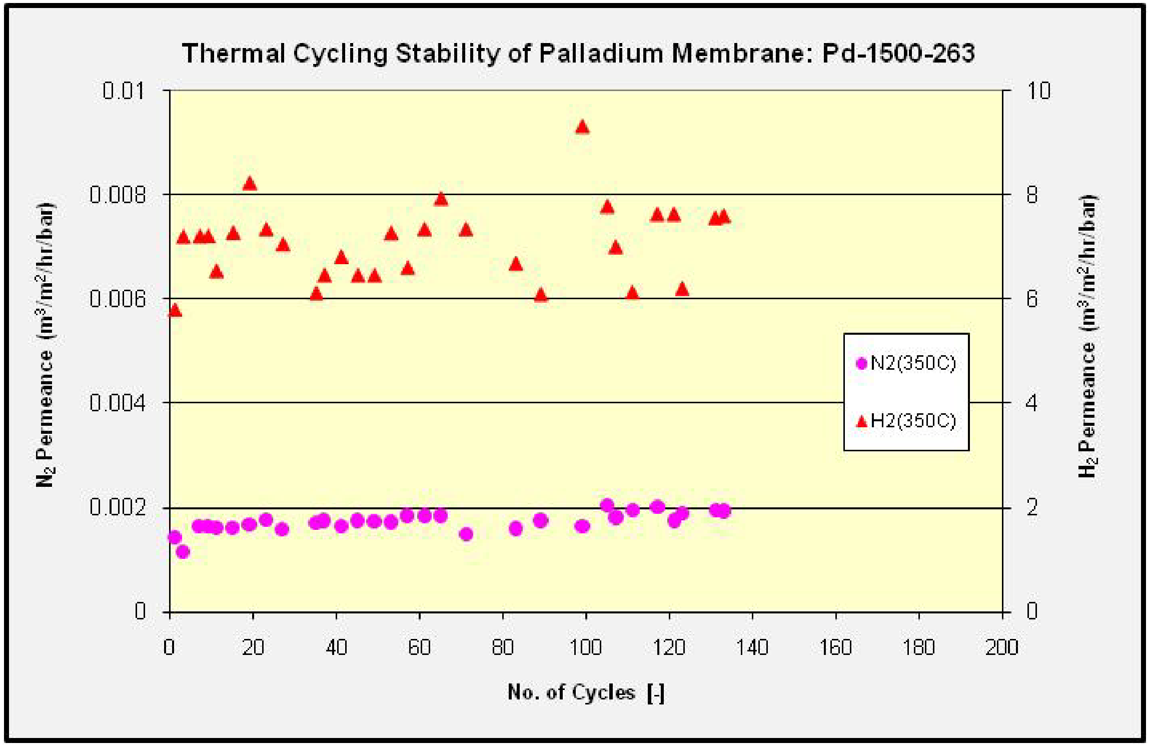
2. Thermal and Thermal Cycling Stability

- In FY 09-10, we presented our results on thermal and thermal cycling stability of our Pd membrane tubes.
- In FY10-11, we focused on the stability test for the membrane bundles. Extended thermal and thermal cycling stability test has been conducted in this period to verify its stability for the frequent start-up and shut-down requirement for our target application.
- See the following two slides for technical details.

3. Thermal/ Hydrothermal Stability

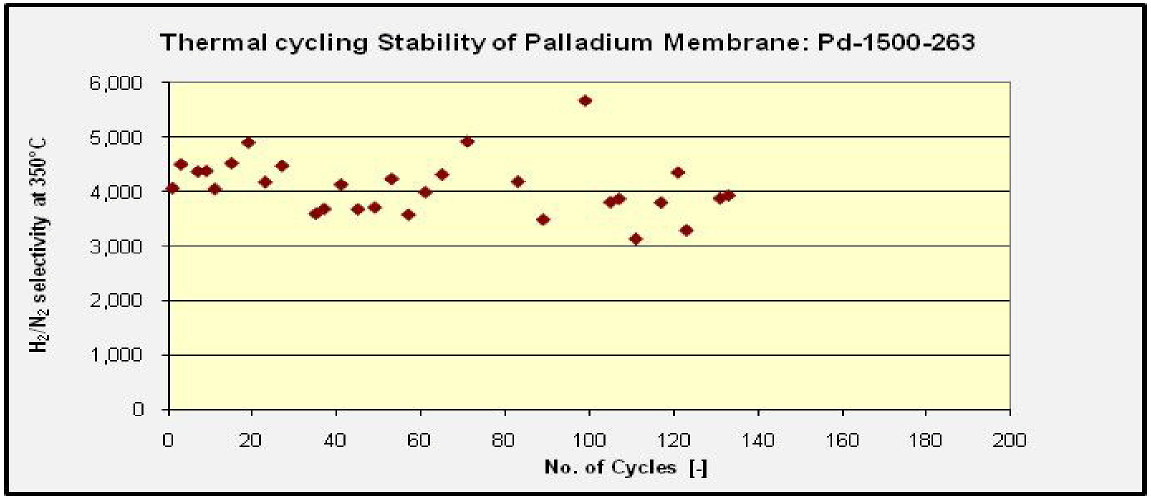


1. Our Pd membranes/bundles have been comprehensively evaluated under multiple temperature cycles and extended thermal/hydrothermal test.
2. Our cost/performance ratio meets/exceeds the DOE target. More importantly, the membrane is prepared on existing commercial ceramic membrane products.
3. 121 scfh/ft² at 20 psig with $100/ft² can meet the cost target set by our commercialization partner.



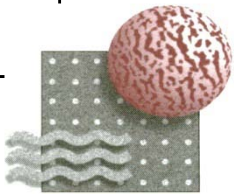
Accomplishment in FY10-11:

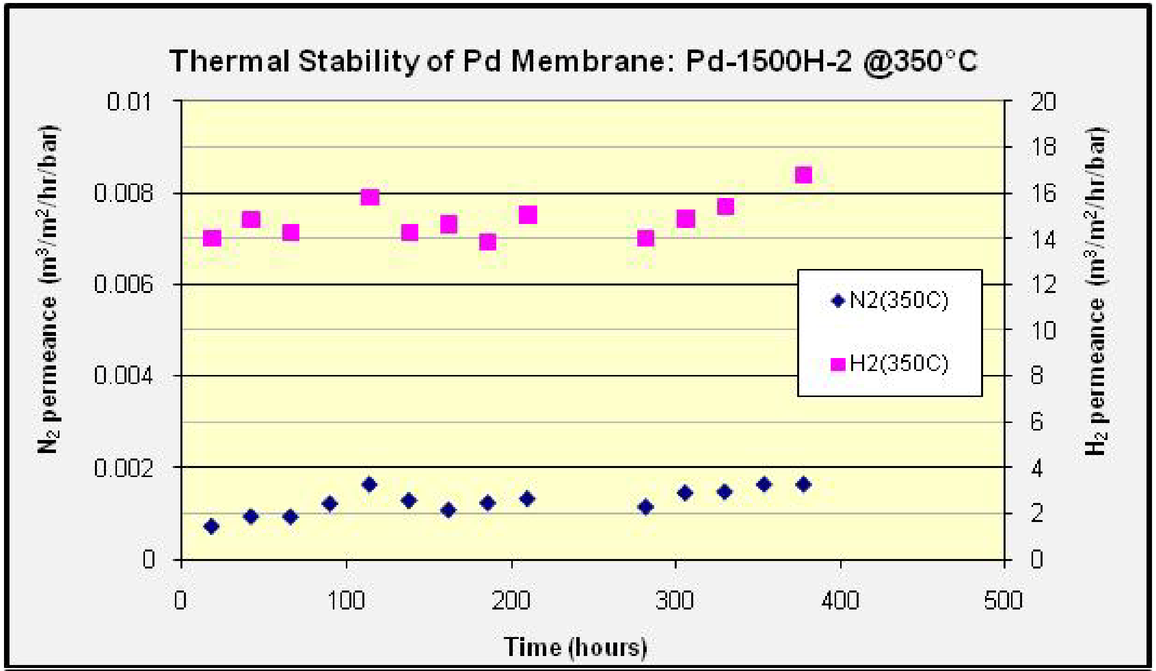
Demonstrated Thermal Cycling Stability of Palladium Membrane Bundles

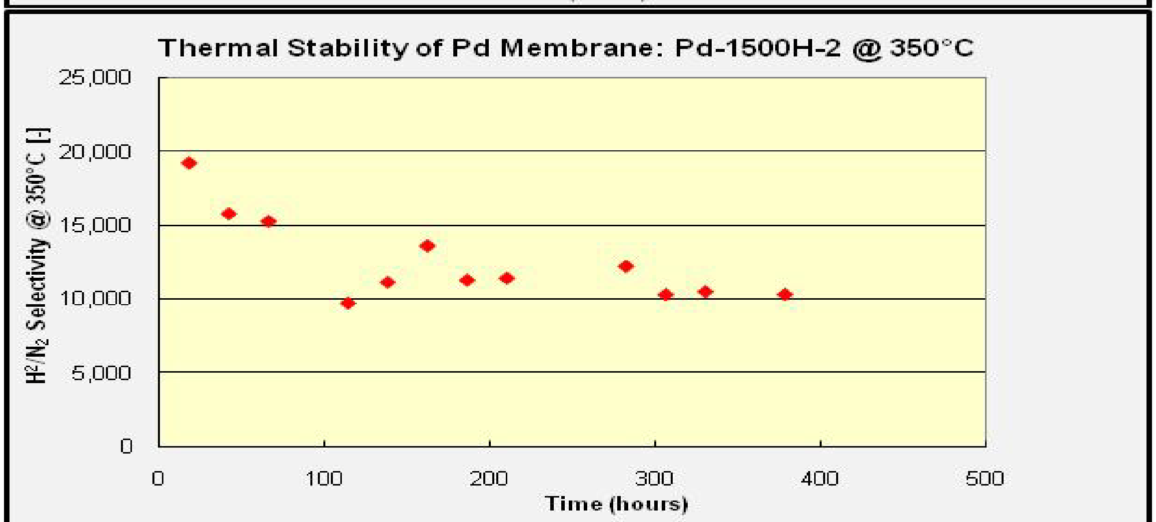


Test Protocol for Each Cycle

- 25 – 350 C in N_2 for 3 hrs
- 350 C in N_2 for 2 hrs
- 350 – 25 C in N_2 for 2 hrs







Accomplishment in FY 10-11:

Demonstrated Thermal Stability of Palladium Membrane Bundles

Test Condition
• 350°C in N_2

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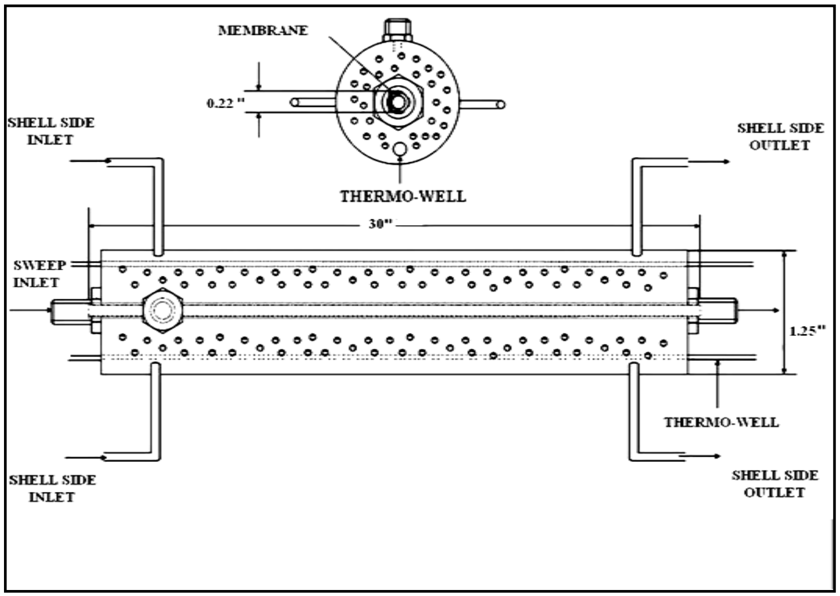
WGS-LTS Membrane Reactor Activities in FY09-10

Objective: using a full-scale H_2 selective membrane to demonstrate high CO conversion and high purity hydrogen product at a high hydrogen recovery ratio



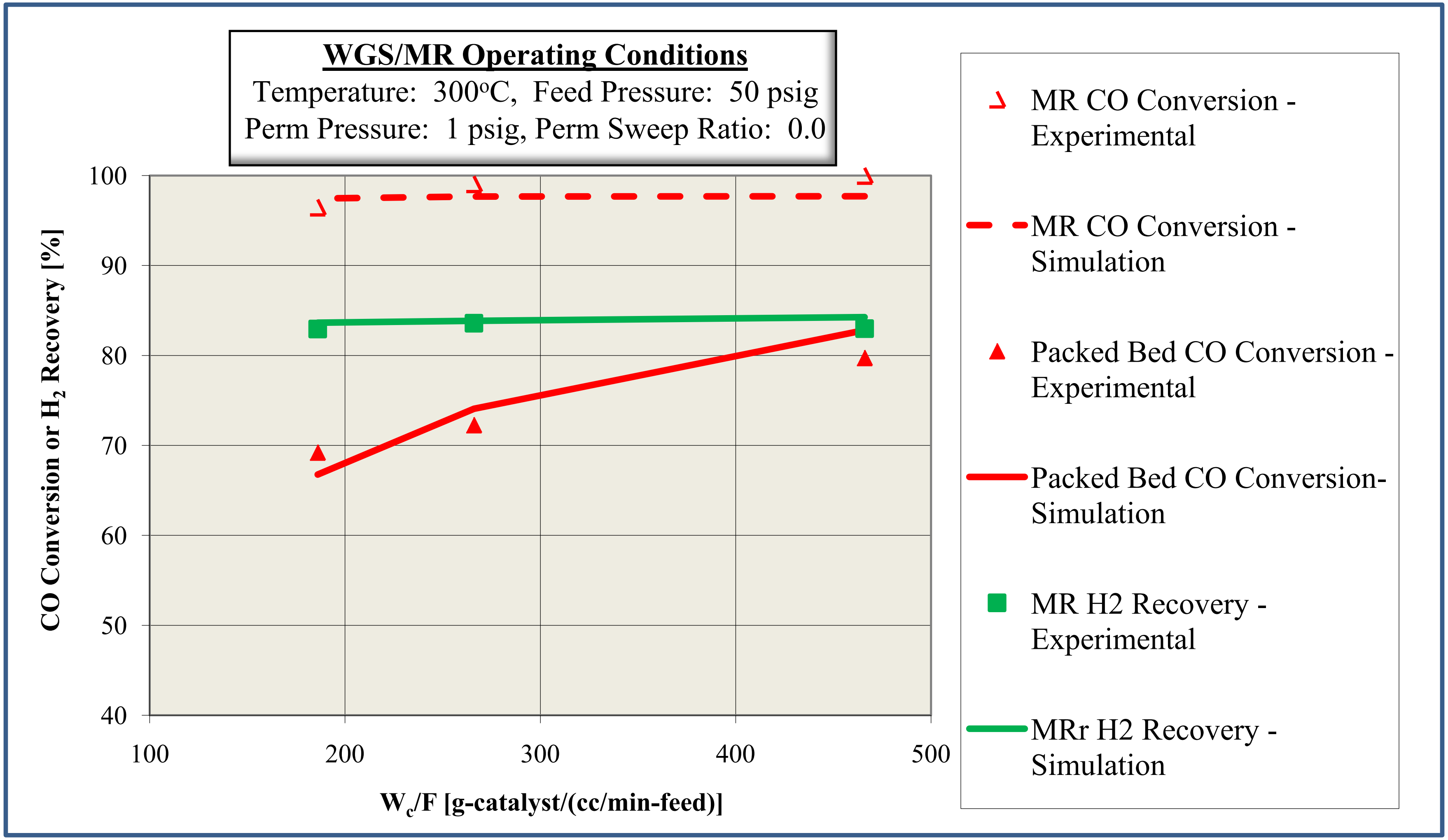
Physical Characteristics and Operating Parameters	
Pd Membrane:	30"L, 0.57cm OD
Temperature:	300°C
Catalyst:	30g of Cu/ZnO
Feed:	
H_2:CO:CO_2:CH_4:H_2O	5.22:1:0.48:0.22:2.8
Pressure:	30 to 50 psig
Sweep Ratio:	0 to 0.3

Membrane Performance Characteristics:
Single Component Gas Permeances at 300°C

Gas	Permeance [m3/m2/h/bar]	Sepn Factor
H_2	16.82	1
CO	0.01	2,369
CO_2	0.01	2,951
Ar	0.01	2,474
N_2	0.01	2,548

WGS-LTS Membrane Reactor Activities in FY09-10

Experimental results from the operation *at 50 psig and with no sweep*



The experimental results conducted in FY09-10 demonstrated <u>>99% CO conversion and >99.9% H_2 purity (~50 ppm CO) at >83%</u> hydrogen recovery was possible by our WGS-MR.

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Accomplishment in FY10-11
Post Treatment for CO Reduction for H2 Generated from WGS-MR

CO Contaminant in the Hydrogen Stream Produced from WGS-MR

As shown in our previous membrane reactor study, our palladium membrane has been able to deliver a hydrogen product stream with ~50 ppm CO using our standard Pd membrane as a reactor.

Our Proposed Solution to Reduce CO Contaminant Level

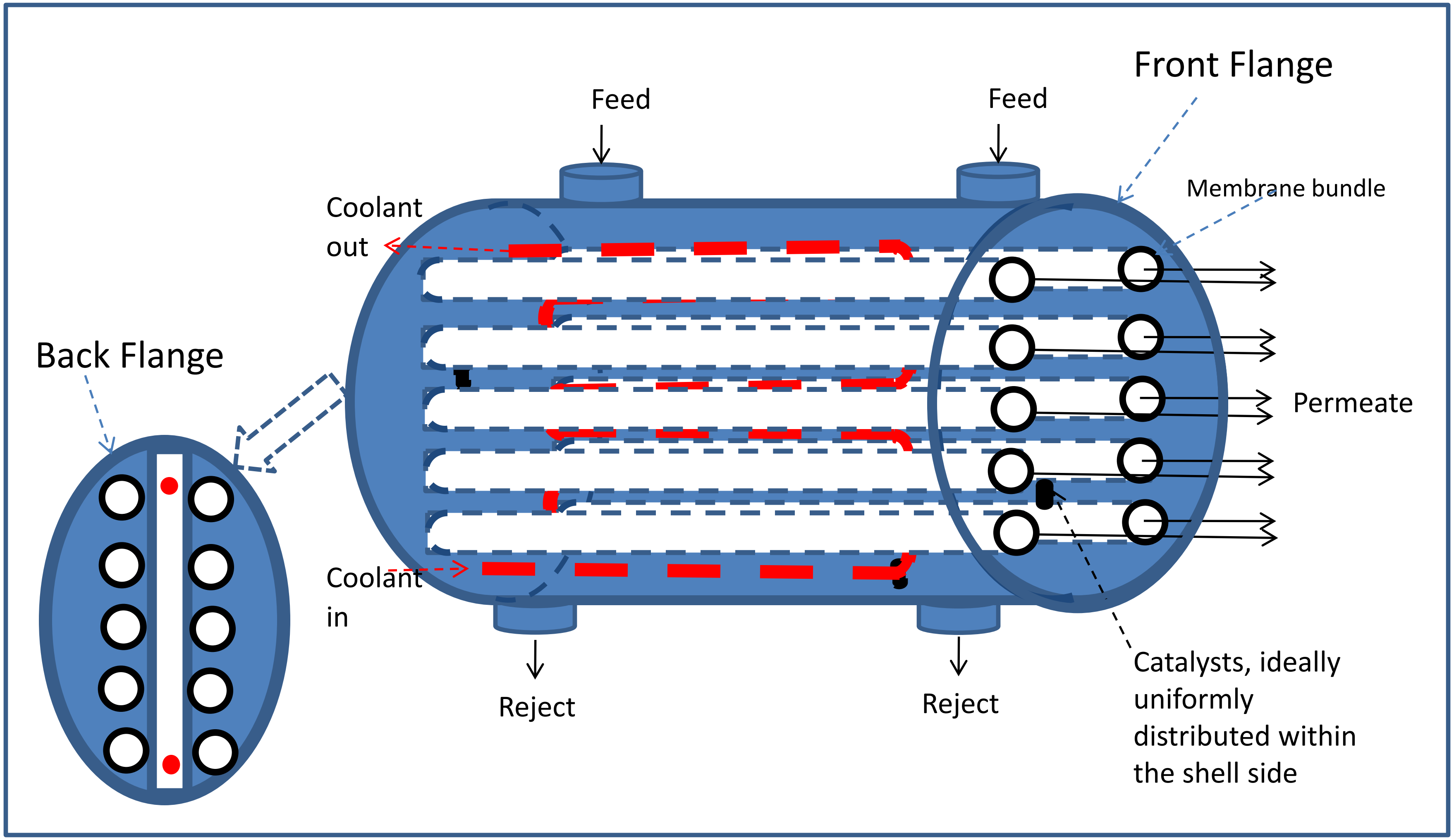
A post treatment strategy has been developed and experimentally demonstrated on the technical feasibility in reducing CO contaminant to an extremely low level, such as <10-1 ppm as shown below

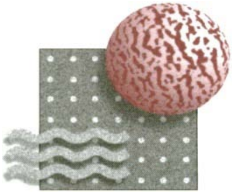
Concentration of CO in Feed [ppm]	Residual CO in Product [ppm]	W/F [g catalyst/(mol CO/hr)]
300	16	4,148
70	1.1	17,778
50	0.3	24,889

Activities Planned in 2011

- demonstrate this post treatment strategy in conjunction with our WGS-MR.
- further incorporate this post treatment into our WGS-MR as an integrated membrane reactor.

Conceptual Model for Catalytic Membrane Reactor using Pd Membranes



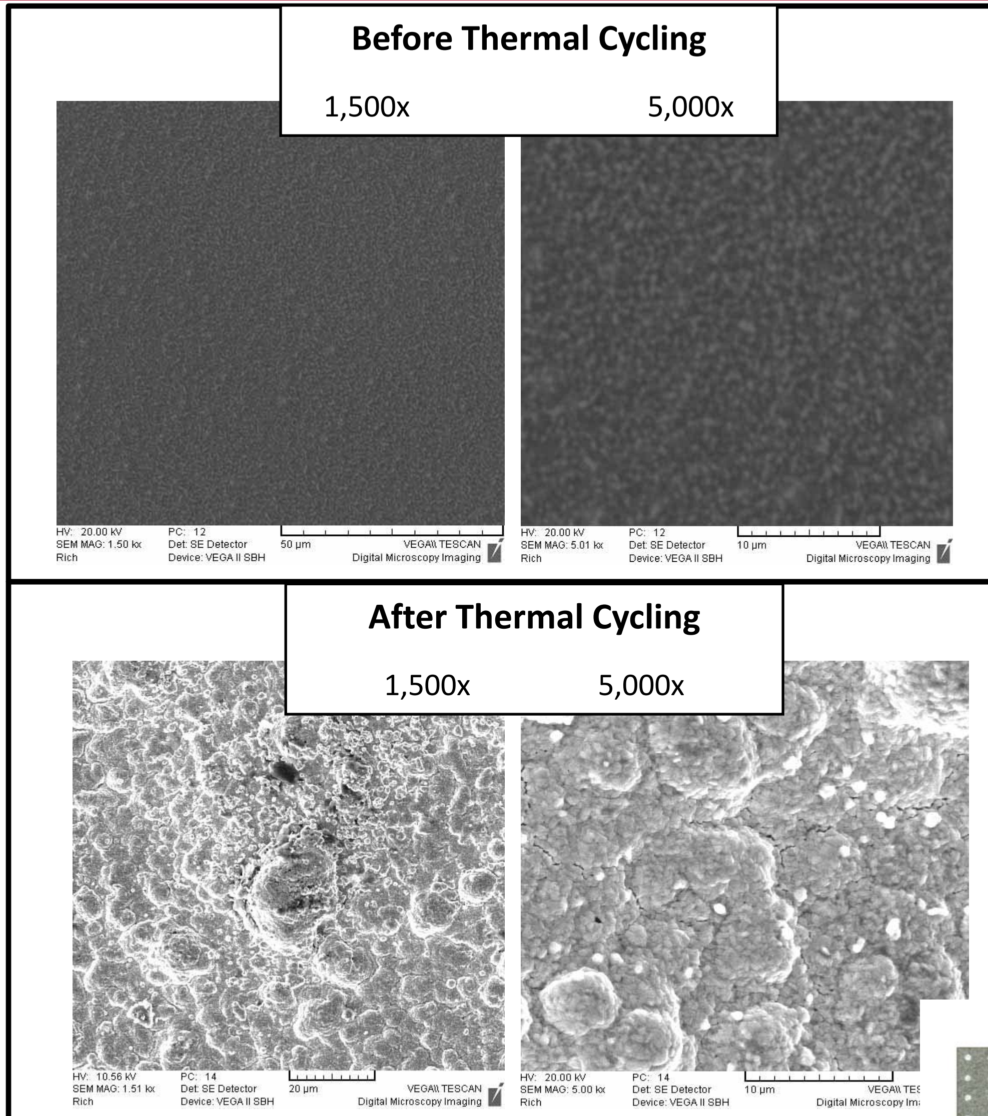


Accomplishment in FY 10-11
R&D on Stability of Cooling in the Presence of Hydrogen for Palladium Membranes

Treatment:
Thermal cycling of in the presence of H_2 from 350˚C to room temperature

Sample:
Our Pd membrane supported on commercial ceramic substrate

Results:
Our Pd membrane is not stable as shown in the morphological change after treatment (as most Pd membranes).



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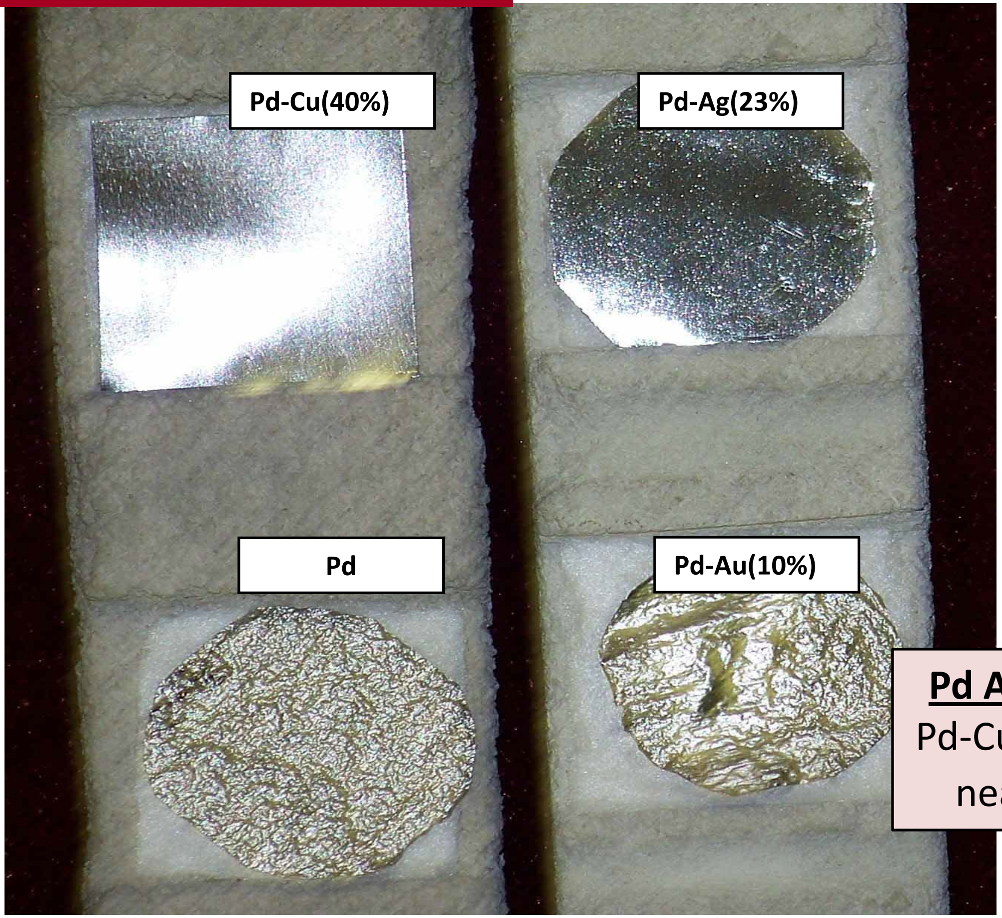
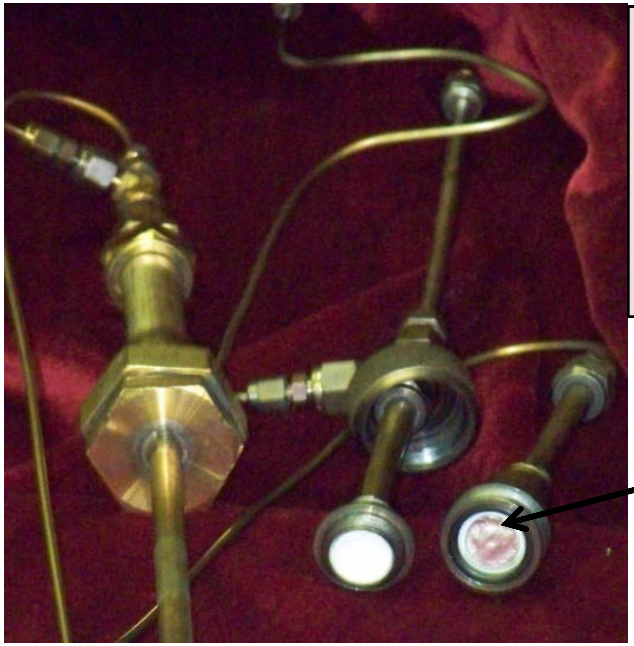
Evaluation of Commercially Available Pd Alloy Foils for Cooling Stability under H_2 Charged – As a guideline for our membrane material development

Pd-alloys		
Alloy Type Tested	**Size**	**Vendor**
Pd	25mm x 25mm x 0.025mm	Alfa Aesar (978)5216300
(77%Pd) / (23%Ag)	25mm x 25mm x 0.025mm	Alfa Aesar (978)5216300
(90%wtPd) / (10%wtAu)	25mm x 25mm x 0.025mm	Refining system, Inc (702)3680579
(60%wt)Pd / (40%wtCu)	25mm x 25mm x 0.025mm	Refining system, Inc (702)3680579



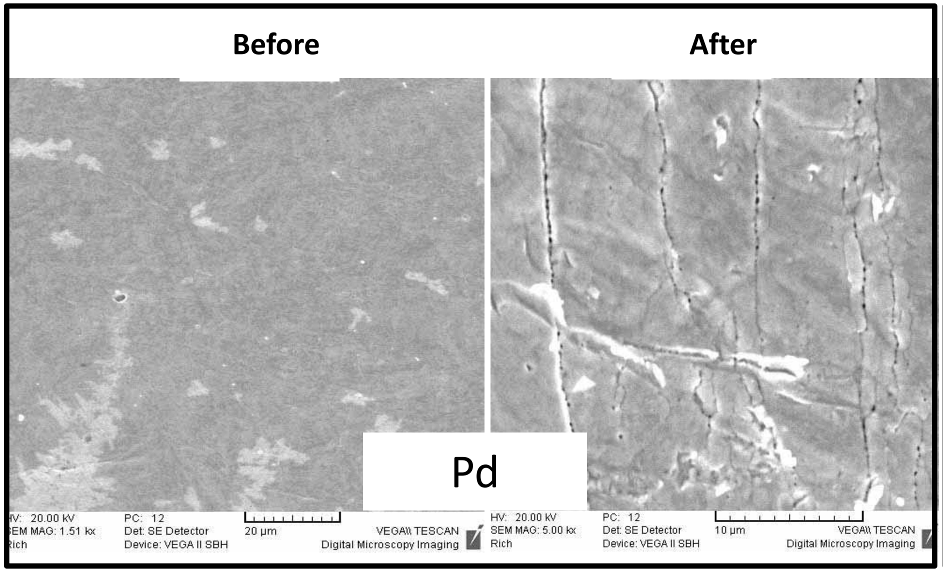


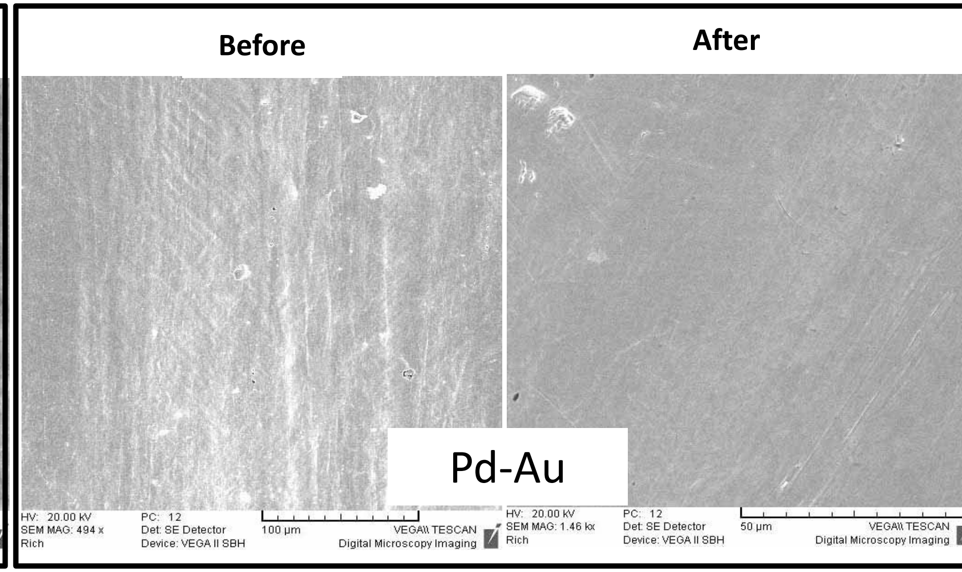
Test Cells for Pd Alloy Films

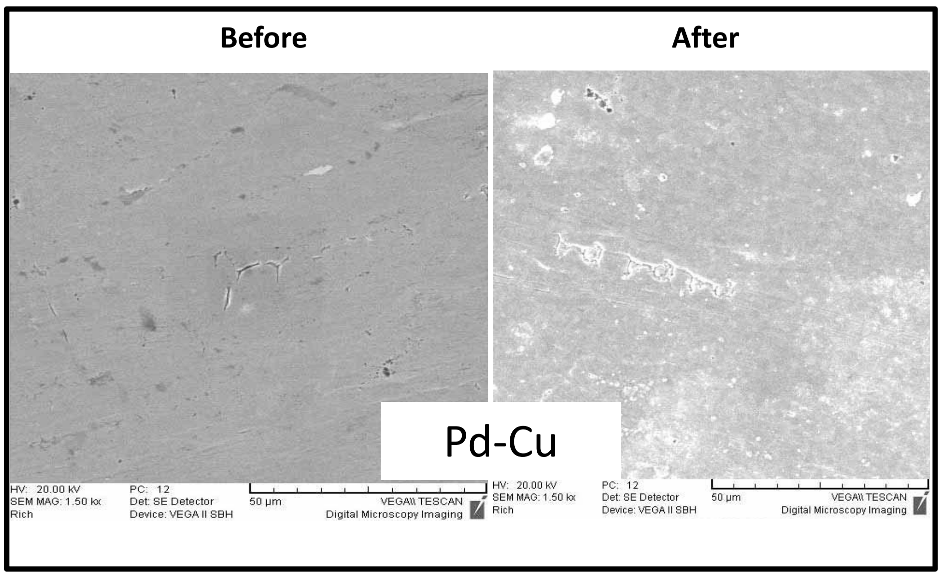
Pd alloy disc

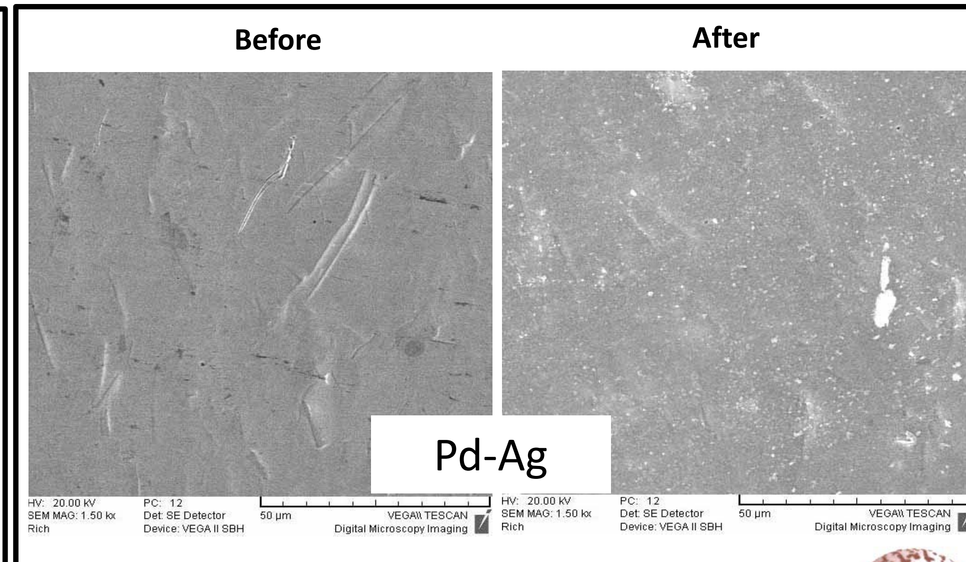
Pd Alloy Discs after 34 Cooling Cycles: Pd-Cu was intact, Pd-Ag showed wrinkle near the edge, Pd and Pd-Au failed.

SEM Examination of Various Palladium Alloys









Overall, visual and SEM inspection of the unsupported films following H_2 thermal cycling indicated that the film stability goes as Pd-Cu(40) ~ Pd-Ag(23) >> Pd-Au(10) >> Pd.

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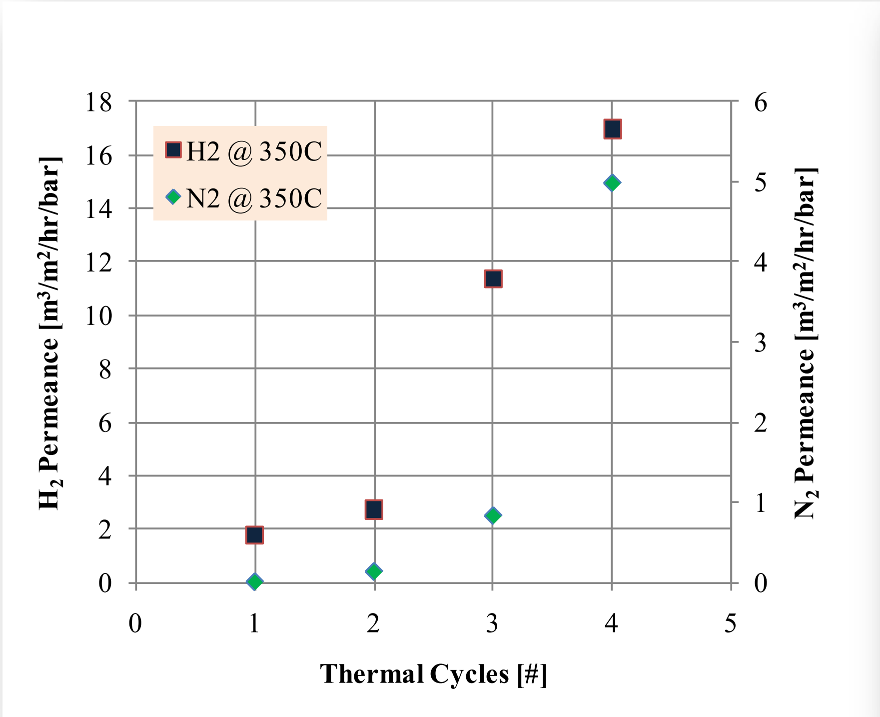
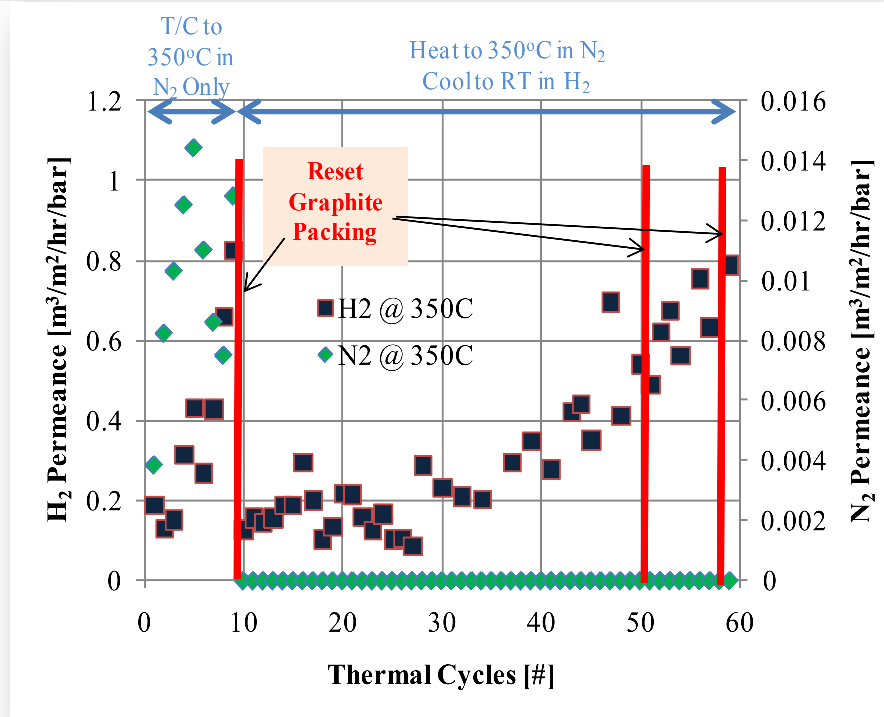
Permeation Measurements of Various Palladium Alloys

H_2 and N_2 permeances of the Pd-Ag(23%) alloy (left) and Pd-Cu(40%) alloy (right) flat disc membranes following thermal cycling between RT and 350˚C with cooling in hydrogen.





Conclusions of Our Evaluation Study on Cooling Stability of Pd Alloys

(i) Considerable damage to Pd and Pd/Au membranes throughout the cooling test.

(ii) The Pd-Cu and Pd-Ag alloys were stable throughout the cooling test under visual and SEM examination

(iii) No damage to Pd-Cu by the graphite packing was observed.

(iv) Damage to to the Pd-Ag alloy was observed in our recent test even without using graphite packing.

Development of Pd Alloy membranes with a imilar composition as the Pd-Cu foil is recommended.

Summary and Conclusions – FY10-11

- Potting technique has been developed to package our low cost Pd membrane tubes into commercially viable bundles while retaining the low cost feature. Further these bundles have demonstrated the thermal and thermal cycling study (~150 cycles), similar to the stability demonstrated previously for the Pd membrane tubes.

- Both pilot and field tests have confirmed the performance of our Pd membrane bundles, i.e., the separation efficiency of bundles ≈ membrane tubes

- >99% CO conversion and >99.9% purity hydrogen (containing ~50 ppm CO) at >83% hydrogen recovery ratio was demonstrated experimentally using a membrane reactor packed with a commercial catalyst in FY 09-10. During this period, we have developed a post treatment strategy which can further reduce the CO contaminant to << 10 ppm. A bench top study has demonstrated this technical feasibility.

- A full-scale membrane reactor packed with our Pd membrane bundles and equipped with internal cooling coils has been designed and is currently under fabrication for the field test to be conducted in 2011.

- Our evaluation study using commercially available Pd alloy foils has concluded that Pd-Cu alloy could potentially offer the cooling stability in the presence of hydrogen. This cooling stability would provide a desirable feature for our target application.

Work Plan for Rest of Project Period

1. Complete the fabrication of a full-scale membrane reactor packed with Pd membrane bundles and equipped with cooling coils for field test to be performed in 2011.
2. Integrate the post treatment strategy into the membrane reactor to deliver hydrogen product with << 10 ppm CO.
3. Conduct a field test with the use of the membrane reactor at the participated end user site.
4. Develop the 3rd generation Pd membrane with the cooling stability in the presence of hydrogen as a desirable feature for our target application.