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
  12/31/12
- Percent Complete
  95%

BARRIERS

#1 Cooling Stability: Performance stability through cooling in H_2 is essential for portable power generation, and is desirable for distributed H_2 production.

#2 Cost vs Performance: meeting US DOE and our end user cost vs performance targets .

#3 Reactor Configuration: a membrane reactor equipped with an integral cooling device and reliable seals between ceramic bundles and metallic housing.

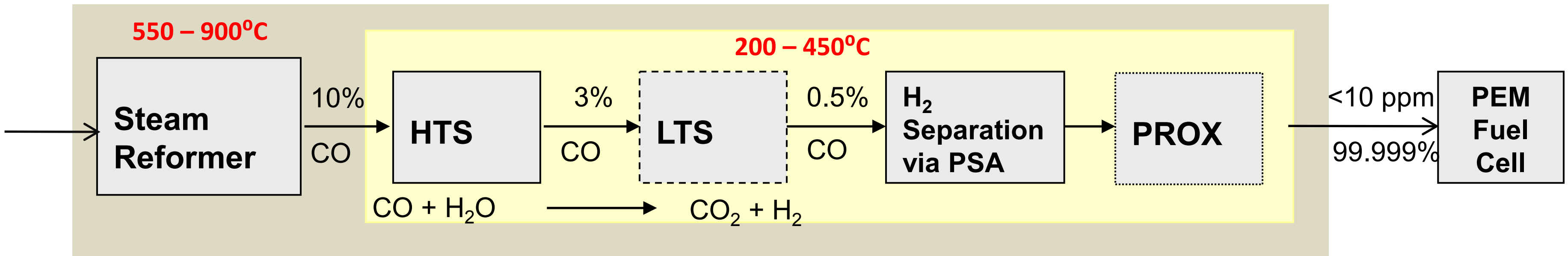
- **Total project funding**
  - DOE Share: $2,592,350.
  - Contractor Share: $648,087.
- **FY11:** $410K
- **Planned FY12**: $400K
- No catalyst development activities due to funding limitation in the beginning of the project

- **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
- **Mr. 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

Reduce HTS/LTS reactors & inter-stage coolers into a single stage **LTS/MR** operation (Barrier #3)

Objective #1

Develop a cost acceptable **hydrogen selective membrane** for end users, i.e., $100/ft^2 (Barrier #1 & 2).

Objective #3

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

Project Goal

⇨ Field Test

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 FY11-12

- **Develop improved palladium membranes with cooling stability in presence of H_2**
- **Design and fabricate a catalytic membrane reactor for field test**

Develop 3rd generation membrane with cooling stability in the H_2 charged environment (Barrier #1&2).

- ❑ Screen commercial Pd alloy foils to select a promising alloy exhibiting cooling stability.
- ❑ Deposit the thin film of the selected Pd alloy on our ceramic membranes as substrate.
- ❑ Evaluate the cooling stability of the Pd alloy membranes prepared.
- ❑ Optimize the Pd-Cu alloy membrane in terms of permeance vs selectivity.

Design and fabricate full-scale membrane bundles with the 3rd generation membrane as a membrane reactor (Barrier #3)

- ❑ Design and fabricate membrane bundles to accommodate (i) heat transfer requirement and (ii) the flexibility in catalyst volume/membrane surface area ratio for the WGS reaction.
- ❑ Fabricate membrane reactors with the above features for field test.

Prepare the test unit and system for field test (Barrier #3)

- ❑ Assemble a test unit for our membrane reactor.
- ❑ Conduct a field test.

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TECHNICAL ACCOMPLISHMENTS – FY11-12

- **Completed the foil evaluation to choose a promising palladium alloy for asymmetric membrane development.**

  Commercially available Pd-Cu, Pd-Ag, and Pd-Au foils along with the Pd foil (as control) were evaluated for their stability of cooling in hydrogen. The Pd-Cu foil shows structure stability through multiple cooling cycles in H_2 (i.e., >60 cycles), not Pd –Ag and Pd-Au.

- **Developed palladium-copper alloy membranes meeting the cost vs performance target set by US DOE.**

  Pd-Cu thin film (~5 μm) was successfully deposited on our commercial ceramic substrate with a H_2 permeance of 10-15 $m^3/m^2/hr/bar$ at 350°C (i.e., 50-75 scfh @ 20 psig) and the selectivity of H_2/N_2 of 200 to >1,000, meeting the DOE 2015 cost vs performance target.

- **Verified the cooling stability in the presence of hydrogen**

  More than 10 PdCu membranes are currently undergoing cooling stability testing, i.e., cooling from 350°C to room temperature in the presence of H_2. Several of them have experienced >85 cycles with no signs of performance degradation.

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TECHNICAL ACCOMPLISHMENTS – FY11-12

- **Designed and constructed membrane bundles which can accommodate (i) heat transfer requirement and (ii) flexibility in catalyst volume to membrane surface area ratio.**

  Our unique membrane bundling configuration permits a membrane reactor that can be integrated with internal cooling coils without significant modifications to the membrane housing and module for the exothermic WGS reaction. In addition, the bundling configuration allows flexibility in catalyst volume to surface area ratio.

- **Assembling a test system for the field test**

  We currently are assembling the test unit/system around the membrane reactor to perform the field test in the 3rd & 4th Quarter of 2012. The reformer and the membrane subunit have been fully tested to meet syngas productivity and separation and purification requirements (i.e., 16 liter/min syngas and <10 ppm CO).

- **Continuing the long term thermal stability test of the Pd and Pd-Cu membranes**

  Thermal stability testing of our Pd membrane bundle is continuing as part of the test requirement to verify that the DOE performance specification is met. Stability for $>$ 9,000 -10,000 hours at 350°C has been demonstrated for Pd and >600 hrs for PdCu membranes.

MPT CERAMIC MEMBRANES - Low Cost

for harsh environment applications

<u>Developmental Work Required</u>

1. Deposition of an additional thin film for hydrogen separation
2. Fabrication of bundle and housing suitable for the application environment

<u>Examples of Commercial Installations</u>

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

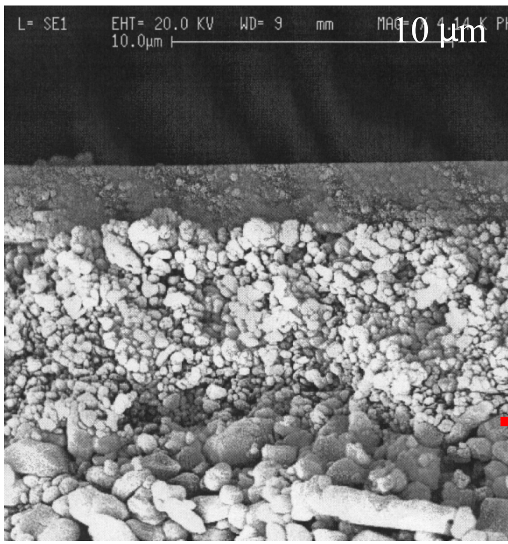
<u>Proposed Applications</u>

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

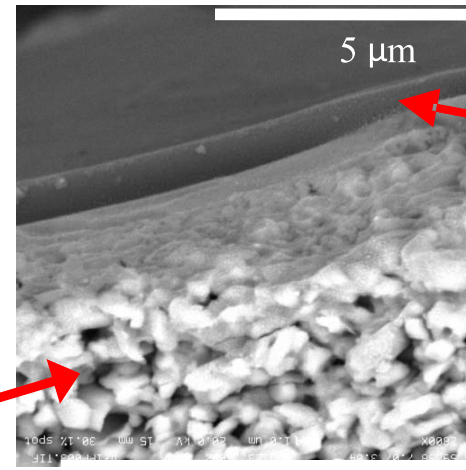
MPT Advanced Inorganic Membranes

Our Core Technology: Thin film deposition on porous substrates

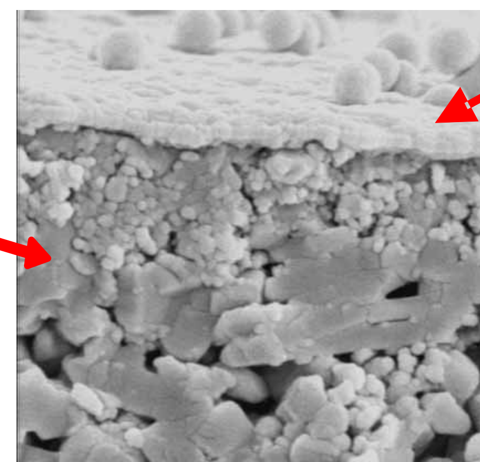
Inorganic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistant)



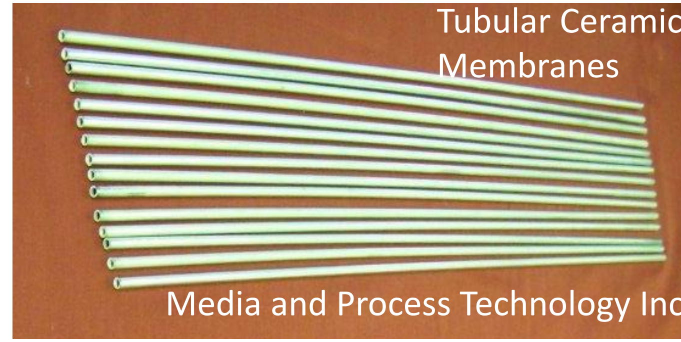
Palladium (dense, excellent selectivity)

Unique feature of
Supported Membranes

- Low cost, no Pd supply challenge

Ceramic Membranes as Substrate for Pd Membranes - Overview

Advantages of Ceramic Membranes:
- High temperature and chemical stability
- Well defined porous structure (in comparison with SS, or others)
- Low cost (at least 50% or more cheaper)



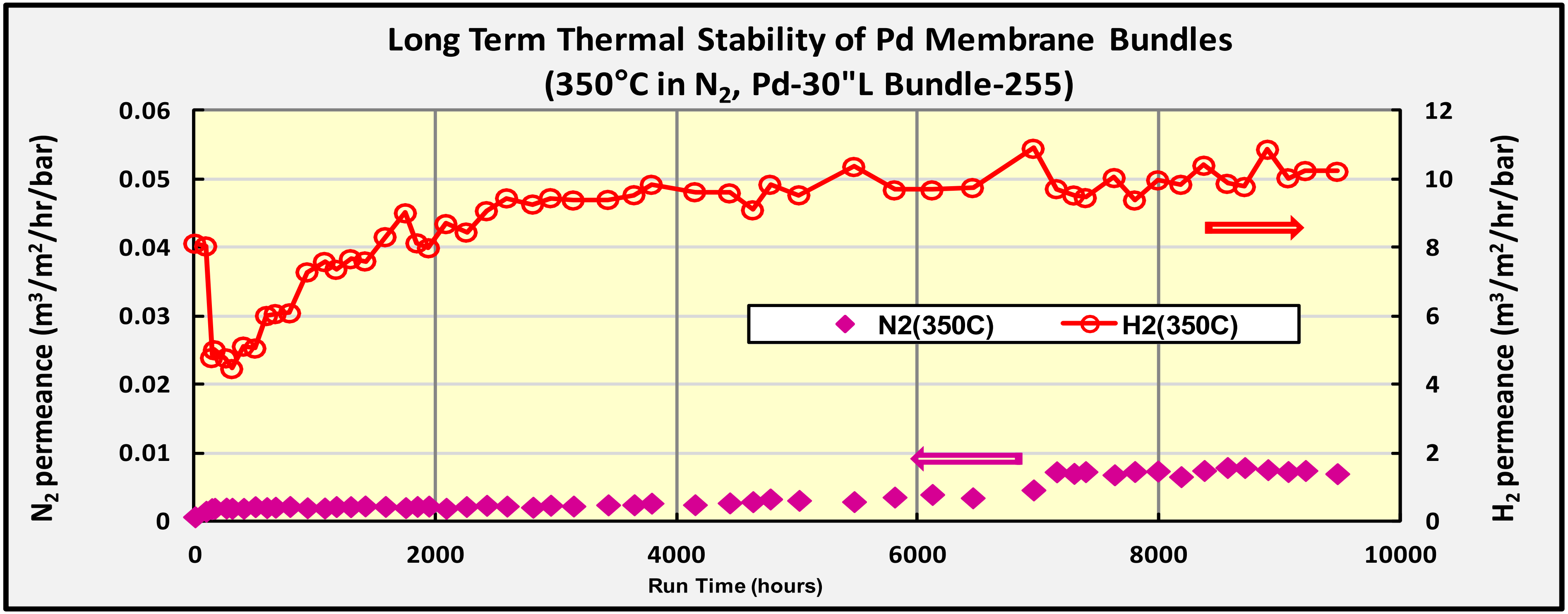
An ideal platform
for high temperature gas separations
e.g., H_2 separation and purification for H_2 production via reforming of hydrocarbons and biomass

Key Barriers:
- Effective and reliable **seal** between metallic housing and ceramic membranes, i.e., thermal mismatch (completed)
- Metallic thin film **cracks** from its ceramic substrate, in particular for palladium under cooling in H_2 charged environment (FY11-12)

A candle filter configuration to eliminate thermal mismatch between housing and membrane element

Accomplishments in FY 11-12:

Demonstrated Long Term Thermal Stability of Palladium Membrane Bundles



<u>Pd-Cu Alloy Thermal Stability</u>: Long term thermal stability testing of the MPT Pd-Cu membrane is currently underway. Over 600 hours of stable performance has been demonstrated.

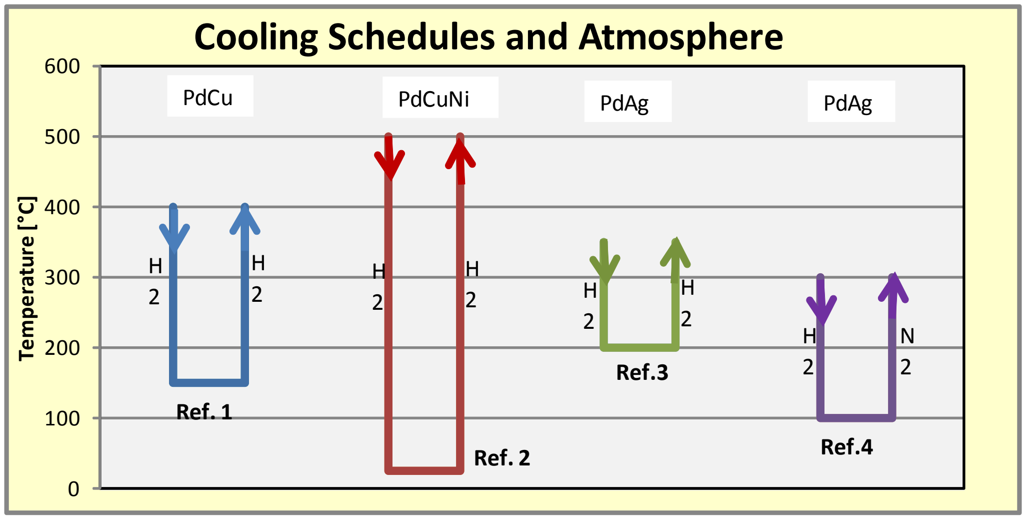
Literature Review: Cooling Stability of Existing Palladium Membranes
(Asymmetric Composite Membranes, Cooling in Hydrogen Charged Environment)

Reference	Alloy	PorousSupport	Preparation Method	Pd:X [%]	Atmosphere
1	PdCu	Alumina	Electroless plating	44 to 63:56to 37	H_2:cooling, H_2: heating
2	PdCuNi	Nickel	Sputtering	90:7:3	H_2:cooling, H_2: heating
3	PdAg	Alumina	Electroless plating	75:25	H_2:cooling, H_2: heating
4	PdAg	Alumina	Electroless plating	80:20 95:5	H_2:cooling, N_2: heating

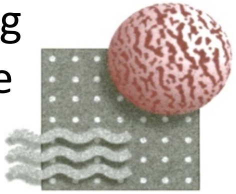
Reference	Temperature Cycling [°C]			No. of Cycles	Stable [Y/N]
1	400	150	400	1	Y
2	500	25	500	6	Y
3	350	200	350	10	Y
	300	150	300	10	N
4	300	100	300	5	Y
	300	100	300	5	N

References:

1. Acha, E., van Delft , Y.C., Overbeek, J., Arias, P.L., Cambra, J.F., "Copper deposition on Pd membranes by electroless plating", *Int. J. Hydrogen Energy* 36, 13114 (2011).
2. Shin-Kum Ryi; Jong-Soo Park; Sung-Hyn Kim; Dong-Won Kim; Jin-Wook Moon, "Long-term hydrogen permeation tests of Pd-Cu-Ni/PNS with temperature cycles from room temperature to 773 K", *J. of Memb. Sci., 306,* 261(2007).
3. Zeng, G., Goldbach, A., Shi, L., Hengyong Xu, "On alloying and low-temperature stability of thin, supported PdAg membranes", *Int. J. Hydrogen Energy in press,*(2012).
4. Okazaki, J., David A. Pacheco Tanaka; Margot A. Llosa Tanco; Wakui, Y., Mizukami, F., Suzuki, T., "Hydrogen permeability study of the thin Pd-Ag alloy membranes in the temperature range across the α-β phase transition", *J. Memb. Sci., 282,* 370 (2006).



<u>**No** supported Pd membranes have demonstrated stability</u> with an extended number of cooling cycles in H_2 charged environment, in particular with ceramic substrate. Nevertheless cooling stability is an important feature for small scale power generation.



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Development of Palladium Alloy Membranes with Performance Stability during Cooling in H_2 Charged Environment

- Performance of Our Existing Pd Membranes -

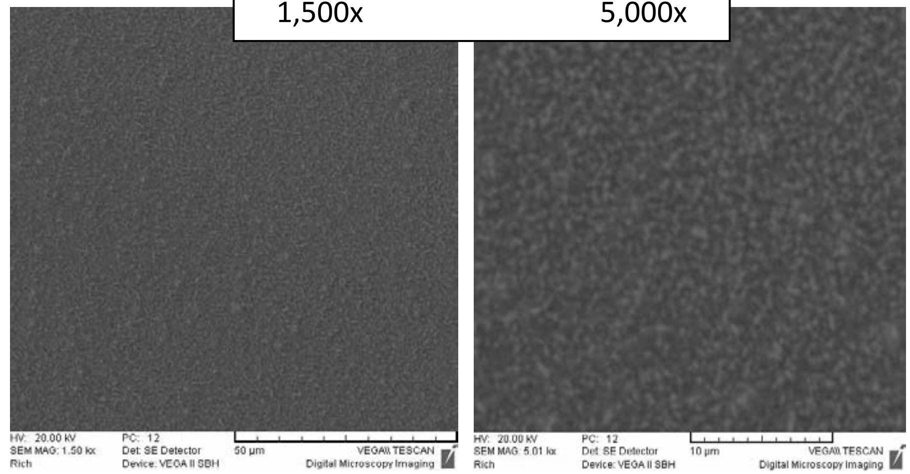
<u>Treatment</u>:
Cooling in the presence of H_2 from 350˚C to room temperature

<u>Sample</u>:
Our Pd membranes supported on commercial ceramic substrate

<u>Results</u>:
Our Pd membrane is **not stable** as shown by the morphological changes after treatment (**as most Pd membranes reported**). During FY 11-12, we have focused on the development of a Pd membrane that is stable during cooling in H_2.

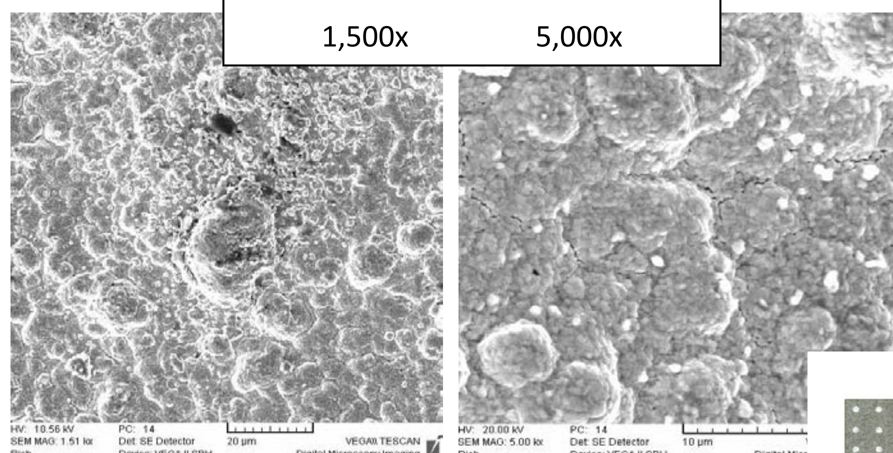
Before Thermal Cycling

1,500x 5,000x



After Thermal Cycling

1,500x 5,000x



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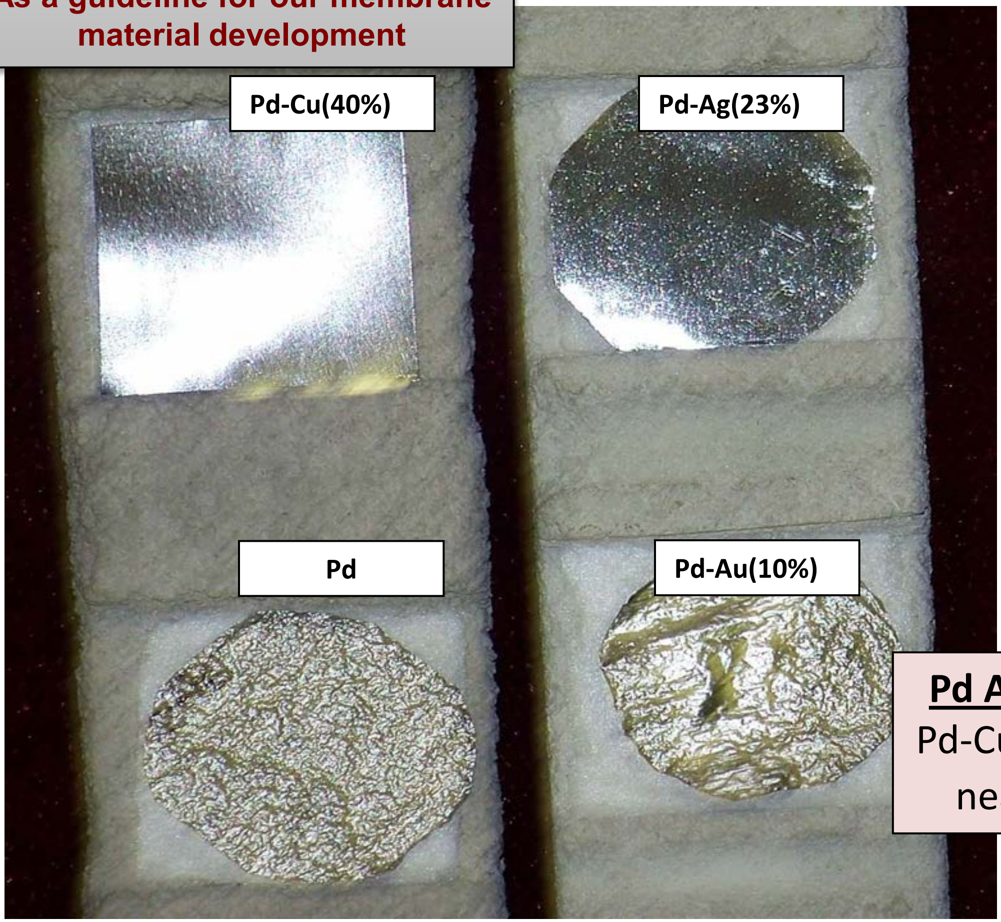
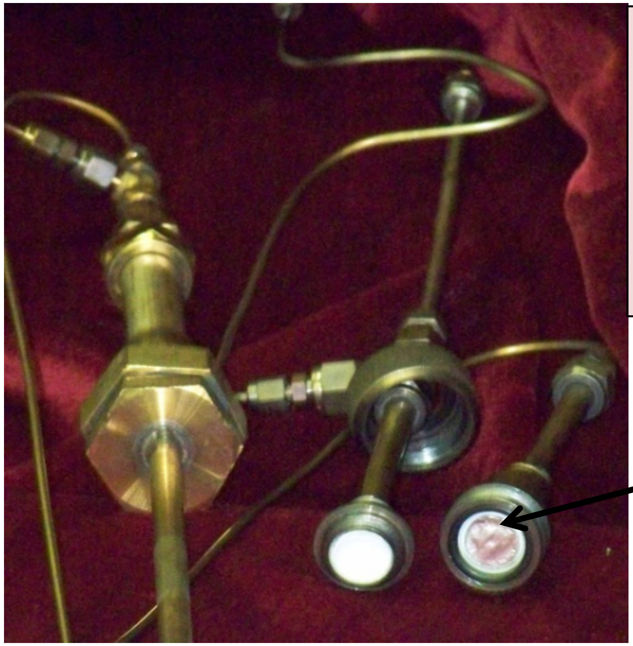
Our Approach
Evaluation of Commercially Available Pd Alloy Foils for Cooling Stability in H_2 Atmosphere

As a guideline for our membrane material development

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



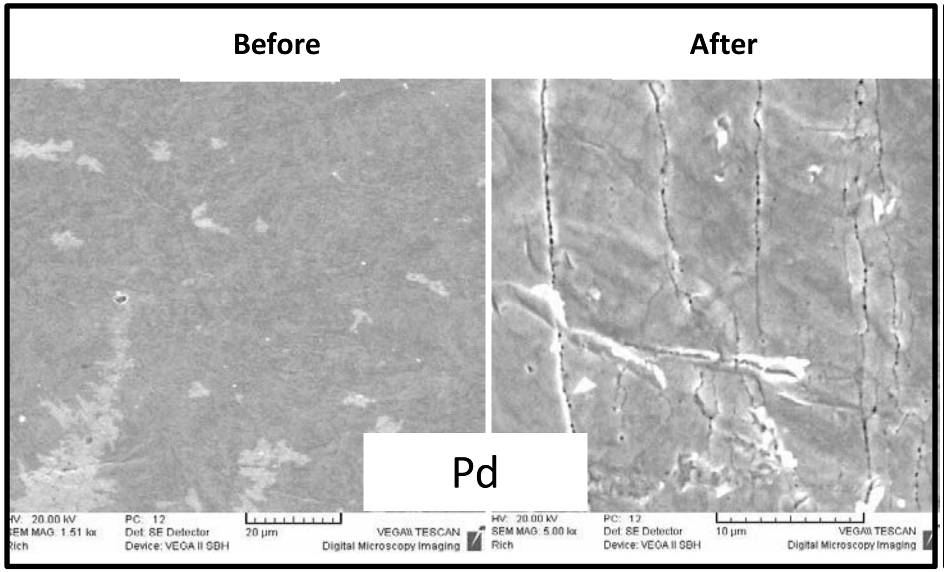


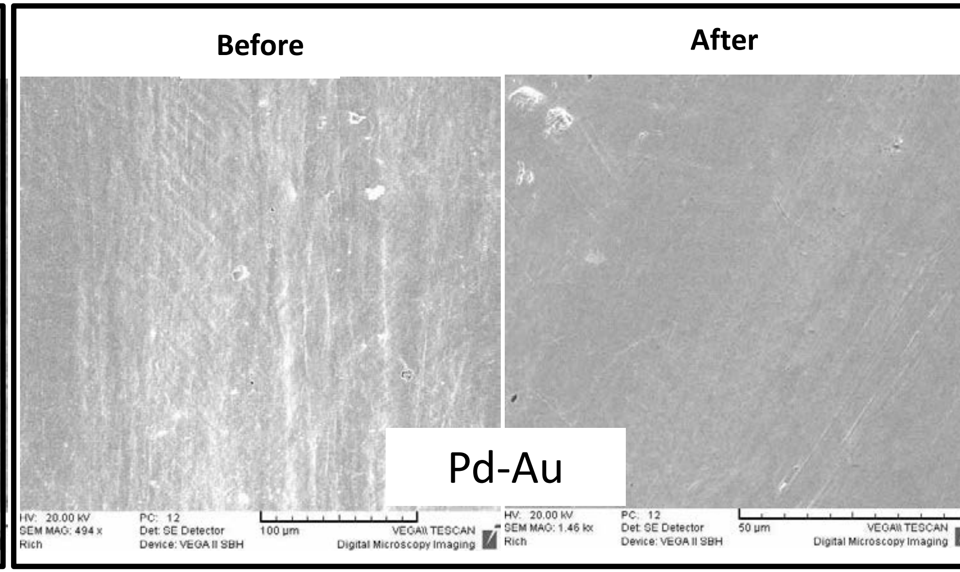
Test Cells for Pd Alloy Foils

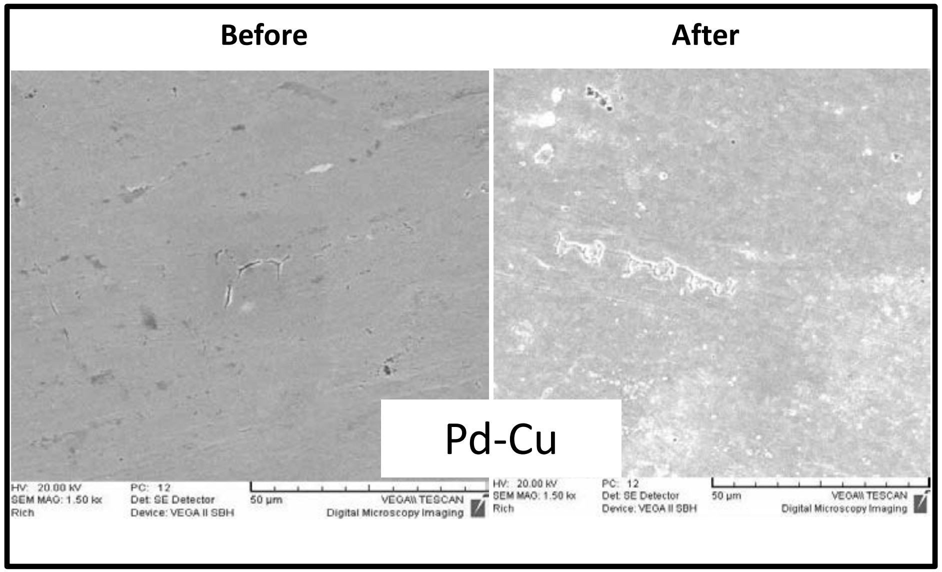
Pd alloy disc

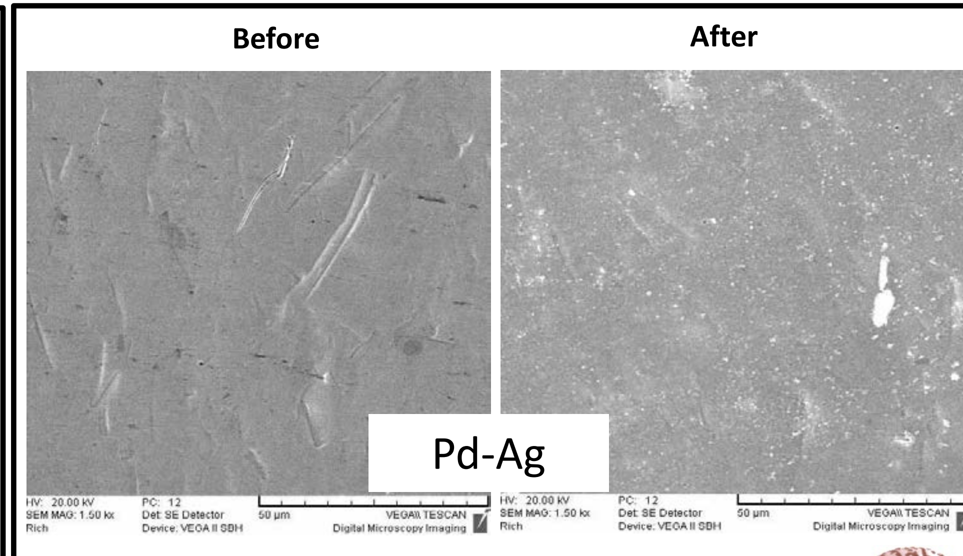
Pd Alloy Discs after 34 Cooling Cycles: Pd-Cu was intact, Pd-Ag showed wrinkle near the edge, Pd and Pd-Au failed.

SEM Examination of Various Palladium Alloys









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

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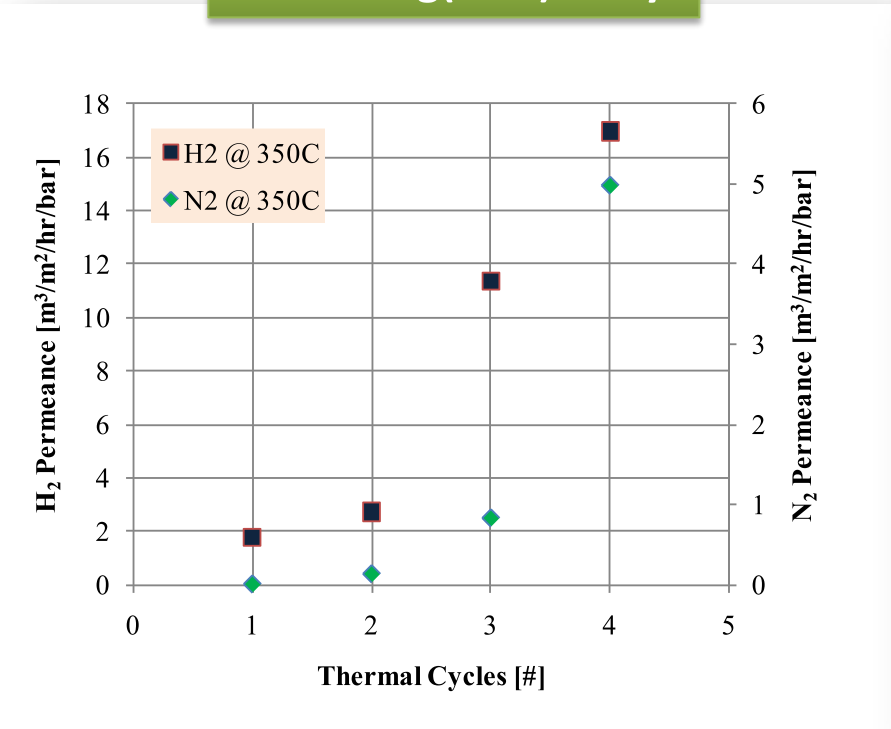
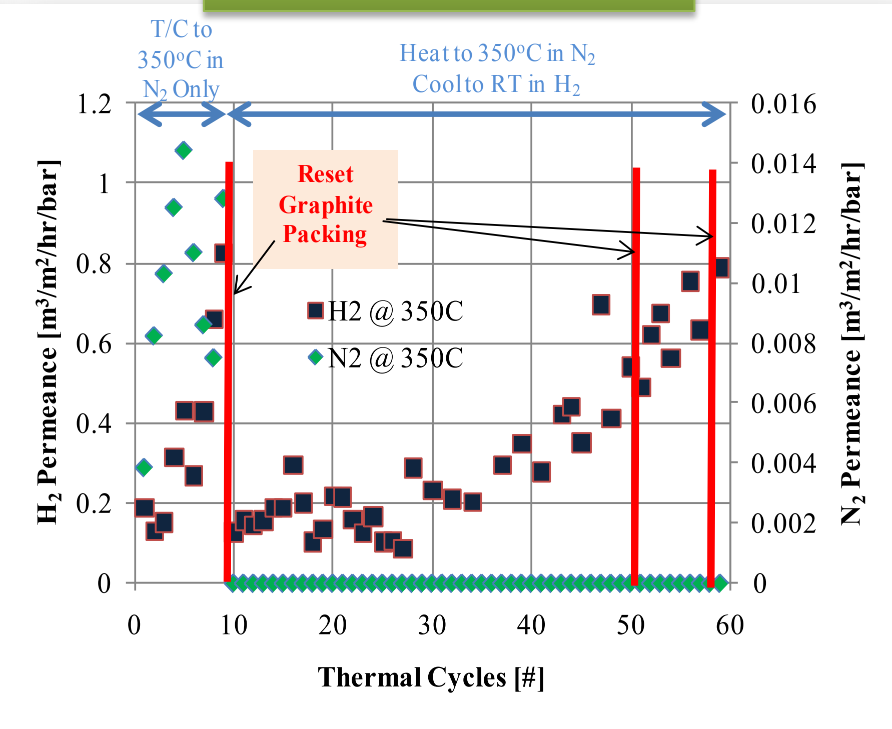
Cooling Stability in H_2 Charged Environment: PdAg vs PdCu

H_2 and N_2 Permeances vs thermal cycles

Foil: Pd-Ag(23%) Alloy



Foil: Pd-Cu(40%) Alloy



N2 increase, indicating membrane cracked

N_2 unchanged, indicating membrane intact

Test Protocol: flat disc membranes following thermal cycling between RT and 350˚C with cooling in H_2

Implication: Pd-Cu (~40%) alloy may deliver the cooling stability required.

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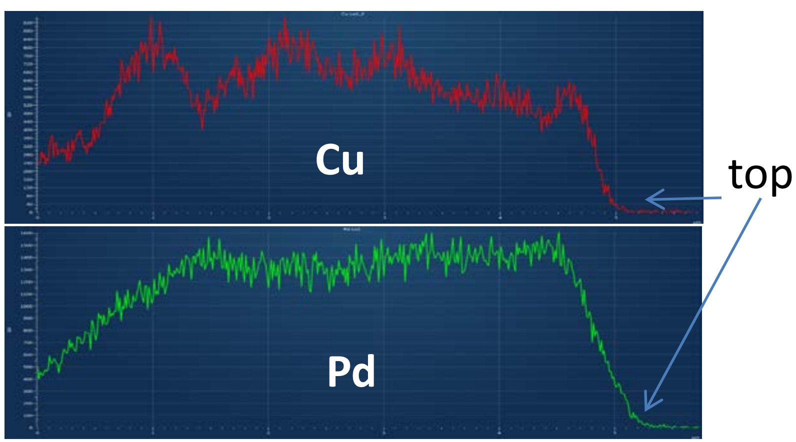
Accomplishments in FY11-12

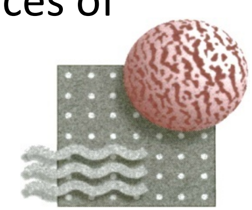
Summary of Some MPT Pd Alloy Membranes Prepared in FY11-12

Sample ID	Permeance [$M^3/m^2/hr/bar$] @350°C				Cu [wt%]	Thickness [µm]
	H_2	N_2	Selectivity	n^{th} Cooling Cycle		
PdCu-500-51	11.9	0.044	271	65	44.5	5.0
PdCu-500-52	10.3	0.075	138	65	45.3	4.7
PdCu-500-53	9.1	0.007	1,379	Fail	45.4	5.4
PdCu-500-54	11.4	0.008	1,354	Fail	43.3	3.8
PdCu-500-57	10.9	0.010	1,136	16	42.8	3.0
PdCu-500-58	11.5	0.053	219	16	44.3	5.1
PdCu-500-60	7.9	0.032	248	26	40.3	5.0
PdCu-500-62	6.2	0.010	616	6	41.5	
PdCu-500-63	10.6	0.015	695	3	43.2	
PdCu-500-64	15.4	0.038	403	3	45.0	

Distribution of Copper & Palladium throughout the Thin Film



We have successfully deposited the Pd-Cu (~44wt%) film on the ceramic substrate with permeances of 10-15 $m^3/m^2/h/b$ and selectivity up to >1,000 at 350°C.

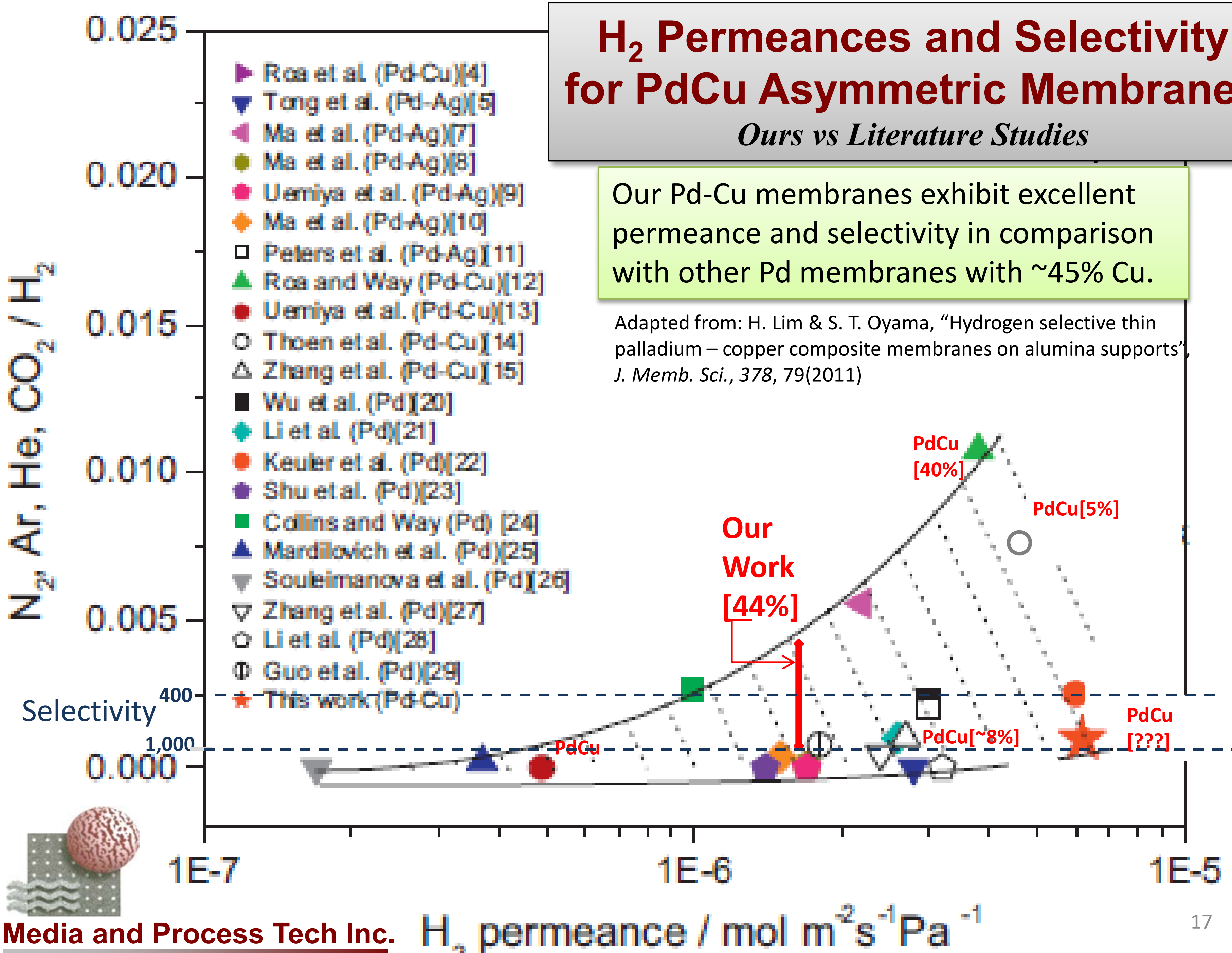


H_2 Permeances and Selectivity for PdCu Asymmetric Membranes

Ours vs Literature Studies

Our Pd-Cu membranes exhibit excellent permeance and selectivity in comparison with other Pd membranes with ~45% Cu.

Adapted from: H. Lim & S. T. Oyama, "Hydrogen selective thin palladium – copper composite membranes on alumina supports", *J. Memb. Sci.*, *378*, 79(2011)



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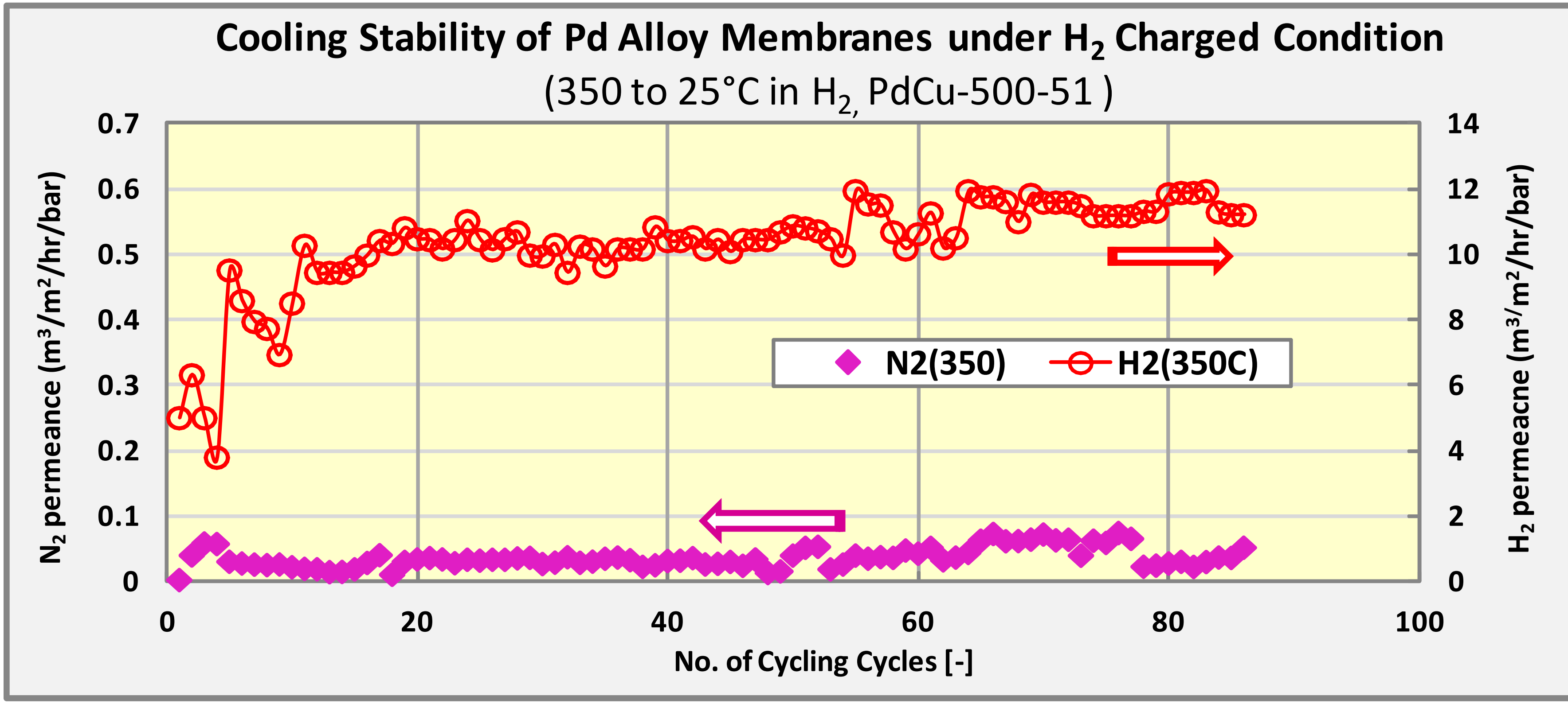
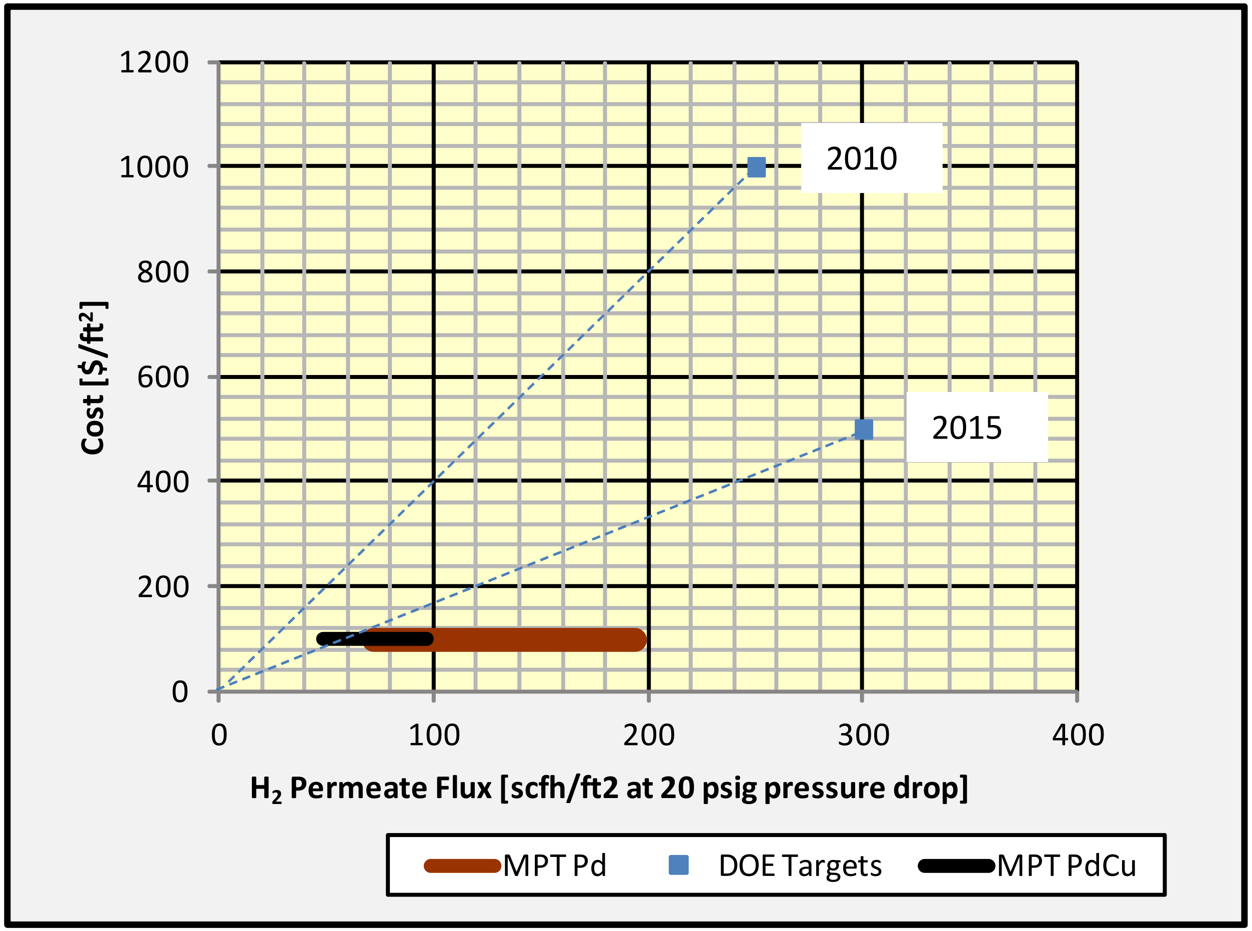
Accomplishments in FY 11-12:

Demonstrated MPT Pd-Cu Membranes with Cooling Stability under H_2 Charged Atmosphere



In comparison with the literature, this unique stability has not been reported for a Pd/ceramic asymmetric membrane.

Cost vs Performance: MPT PdCu Membranes



Our Pd-Cu membranes developed in FY11-12 meet the 2015 DOE cost vs performance target.

Use of low cost ceramic substrate as support for our Pd membranes is mainly responsible for meeting this cost vs performance target. On the other hand, through this project we have overcome the barriers associated with the use of ceramic substrate for high temperature gas separations.

Development of Catalytic Membrane Reactor for Water Gas Shift Reaction – Overview

Our previous laboratory study has demonstrated the performance potential of the membrane reactor for WGS reaction.

WGS-MR Results

>99% CO conversion
>99.9% H_2 purity
>83% H_2 recovery
<50 ppm CO
<3 ppm CO with post - treatment.

Key barriers associated with the ceramic membrane reactor and our accomplishments in FY 11-12 are presented below:

- **Lack of flexible means to accommodate catalysts vs. membrane surface area**
  Multi-tube membrane bundle with module (completed, prior to FY11-12);

- **Lack of simple means for in-situ heat transfer to remove exothermic heat**
  An innovative ceramic membrane reactor integrated with internal cooling coils has been developed. Thus, the in-situ heat transfer requirement can be accommodated without mechanical complication and cost increase(our focus in FY11-12).

Accomplishments in FY 11-12:

Engineering and fabricating a commercially viable membrane reactor which can accommodate in-situ heat transfer

Our Key Innovations:

Membrane reactors shown here are equipped with:

- **Cooling coils which can be easily integrated into the module.**

In addition, from our work in previous years, our candle filter configuration offers:

- **Flexibility in catalyst volume vs membrane surface area,**
- **Effective and reliable seal between metallic housing and ceramic membranes.**

In summary, a commercially viable ceramic membrane reactor has been developed successfully.

Field Test Unit Construction and Current Status

Reformer Subunit

Membrane Reactor Subunit
(inside the purging chamber)

Tests completed:

1. Syngas at 16L/min produced by the reforming subunit
2. Hydrogen purification with the palladium membrane subunit, delivering hydrogen with ≤ 10 ppm CO from reformate.

Units under Construction:

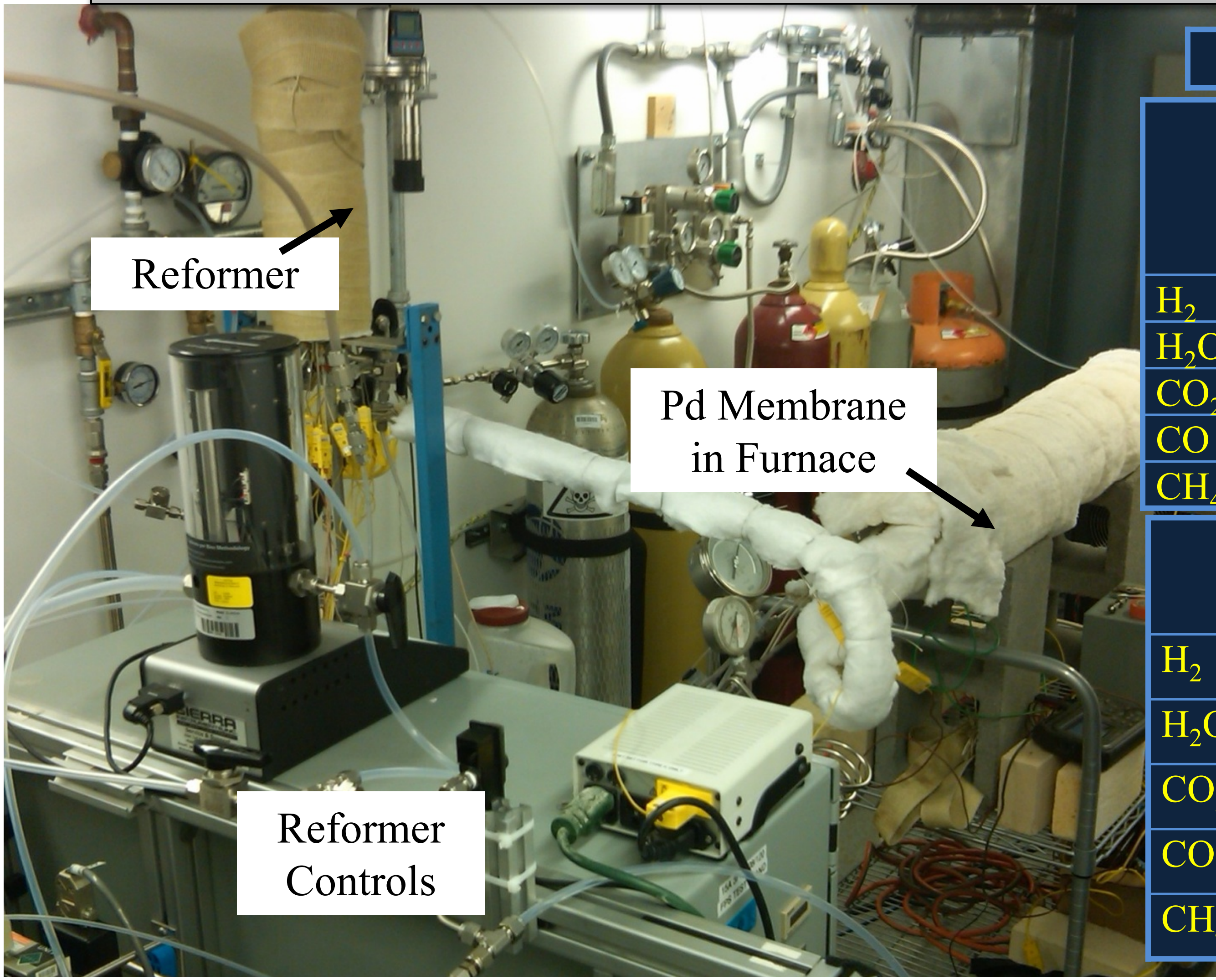
1. Membrane reactor subunit with integrated post treatment to further reduce CO.

Test to be completed by 3rd Q:

1. Water gas shift reaction and hydrogen separation via the membrane reactor.

Accomplishments in FY 11-12:

Reformer and Pd Membranes have been prepared/installed and fully tested.



Gas Compositions

	Reformate (Feed to Membrane)
H_2	61.6%
H_2O	19.0
CO_2	19.0
CO	0.3
CH_4	0.1

	Membrane Permeate
H_2	>99.9
H_2O	NA
CO_2	800 ppm
CO	<10 ppm
CH_4	ND

H_2separation and purification results from ***actual*** reformate are consistent with previous results obtained from synthetic mixtures. The membrane reactor will be installed and tested by 2[nd] Q ready for the field test in July 2012.

Summary and Conclusions – FY11-12

- Performance stability during thermal cycling in the presence of hydrogen is essential for the palladium membrane to be viable for portable power generation applications. Through a screening study with the commercially available Pd alloy foils, PdCu was identified as a promising alloy candidate. PdCu shows no sign of degradation for >60 cycles while PdAg shows degradation from the 2^{nd} cycle in our screening study.

- During this year, we have successfully deposited the PdCu alloy thin film (~5µm) on our commercial ceramic substrate as an asymmetric Pd alloy membrane in terms of performance, and thermal and cooling stability.

- The Pd alloy membrane thus developed meets the cost performance target set by US DOE for Yr 2015, i.e., 0.6 scfh @ Δp=20 psi/unit $ membrane cost. In general, the permeance is 10-15 $m^3/m^2/hr/bar$ with the selectivity of ≥~1,000 at 350°C.

- The Pd alloy membranes thus developed demonstrated performance stability during cooling from 350°C to room temperature in H_2 for >85 cycles as of today.

- A full-scale membrane reactor packed with our PdCu membrane bundle and equipped with an internal cooling device has been designed and is currently under fabrication. The reformer and the membrane subunits have been fully tested. The entire system is scheduled to be ready for field test by 2^{nd} Q 2012.

Work Plan for Rest of Project Period

1. **Complete the field test system assembly which is equipped with a full-scale PdCu membrane bundle and integrated with internal cooling coils by 2nd Q 2012.**

2. **Conduct a field test for 1 month (i.e., ~700 hrs) in 3rd Q 2012. The target performance is 99.999% purity and >83% recovery of H_2.**

3. **Upgrade the permeance of the 3rd generation Pd alloy membrane* we have developed by the end of 2012 to the level similar to our existing 2nd generation Pd membrane, i.e., H_2 permeance increase from 15 to 25 $m^3/m^2/hr/bar$.**

*with the cooling stability under the hydrogen charged environment