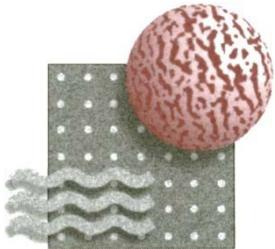


# Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

*DE-FG36-05GO15092*

PD 072



**Paul KT Liu**  
**Media and Process Technology Inc.**  
**1155 William Pitt Way**  
**Pittsburgh, PA 15238 - 1678**  
**June 7-11, 2010**

# Overview

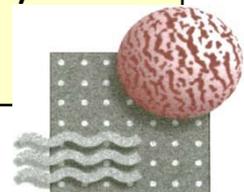
- Project Start Date**  
7/1/05
- Project End Date**  
6/30/11
- Percent Complete**  
70%

## 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.
- FY09:** \$0
- FY10 Plan:** \$100K
- No catalyst development activities due to funding limitation in the beginning of the project

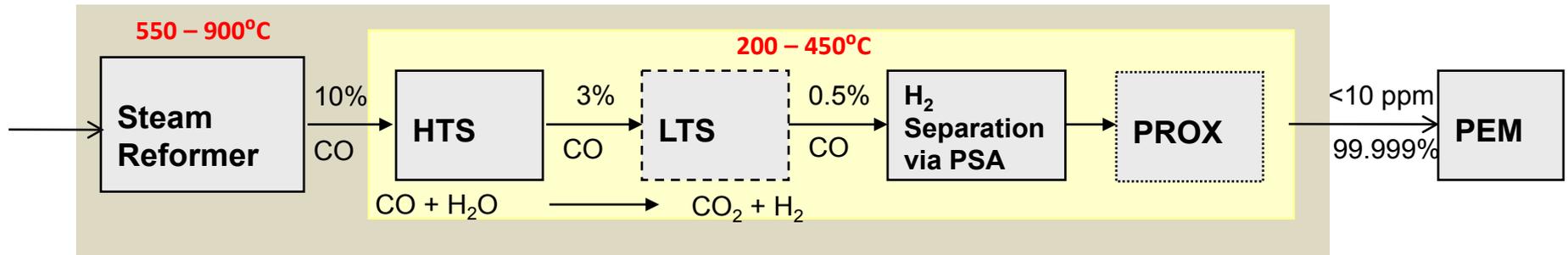
- Professor Theo T. Tsotsis**  
University of Southern California,  
Catalytic membrane reactor expert
- Dr. Babak Fayyaz-Najafi** Chevron ETC,  
End User Participant
- Dr. Hugh Stitt**, Johnson Matthey,  
Catalyst Manufacturer
- Dr. Pat Hearn**, Ballard Power Systems  
Fuel Processing End User



## 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 membranes/modules and conduct a field test for hydrogen separations

## 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).

Field Test on MR in Phase II

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



## Specific Objectives and Technical Approach for FY09-10

- **Fabricating the Field Test Module for H<sub>2</sub> Recovery (Barrier #1&2)**

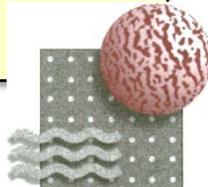
- improved the field test module design to minimize module leaking potential experienced in the 1<sup>st</sup> field test.
- performed the test to verify the thermal cycling stability and permeate flux of the improved field test module.
- pursued 2<sup>nd</sup> generation membrane/module development to meet cost vs performance criteria set by our commercialization partner.

- **Conducting the membrane reactor test using full-scale membrane tubes (Barrier #1)**

- experimentally verified the performance based upon process simulation.
- provided design basis for our field test unit in Phase II.

- **Performing field tests on H<sub>2</sub> recovery (Barrier #1&3)**

- conducting a field test using a 150 scfh H<sub>2</sub> separator in 2<sup>nd</sup> Q



# TECHNICAL ACCOMPLISHMENTS – FY09-10

## Balanced performance vs cost for our H<sub>2</sub> Selective Membrane

Through evaluation of a range of ceramic membrane substrates with various permeances, we have been successful in developing our H<sub>2</sub> selective membrane product to meet the low cost feature requested by our commercialization partner.

## Corrected leakage issue of the 1<sup>st</sup> generation module and ready for the field test

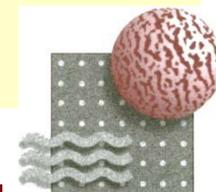
Our 1<sup>st</sup> field test failed due to module leakage. This leak of the 1<sup>st</sup> generation module has been corrected and the module is now ready for the field test scheduled in 2<sup>nd</sup> Q.

## Designed and fabricated the 2<sup>nd</sup> generation module using ceramic membrane bundles

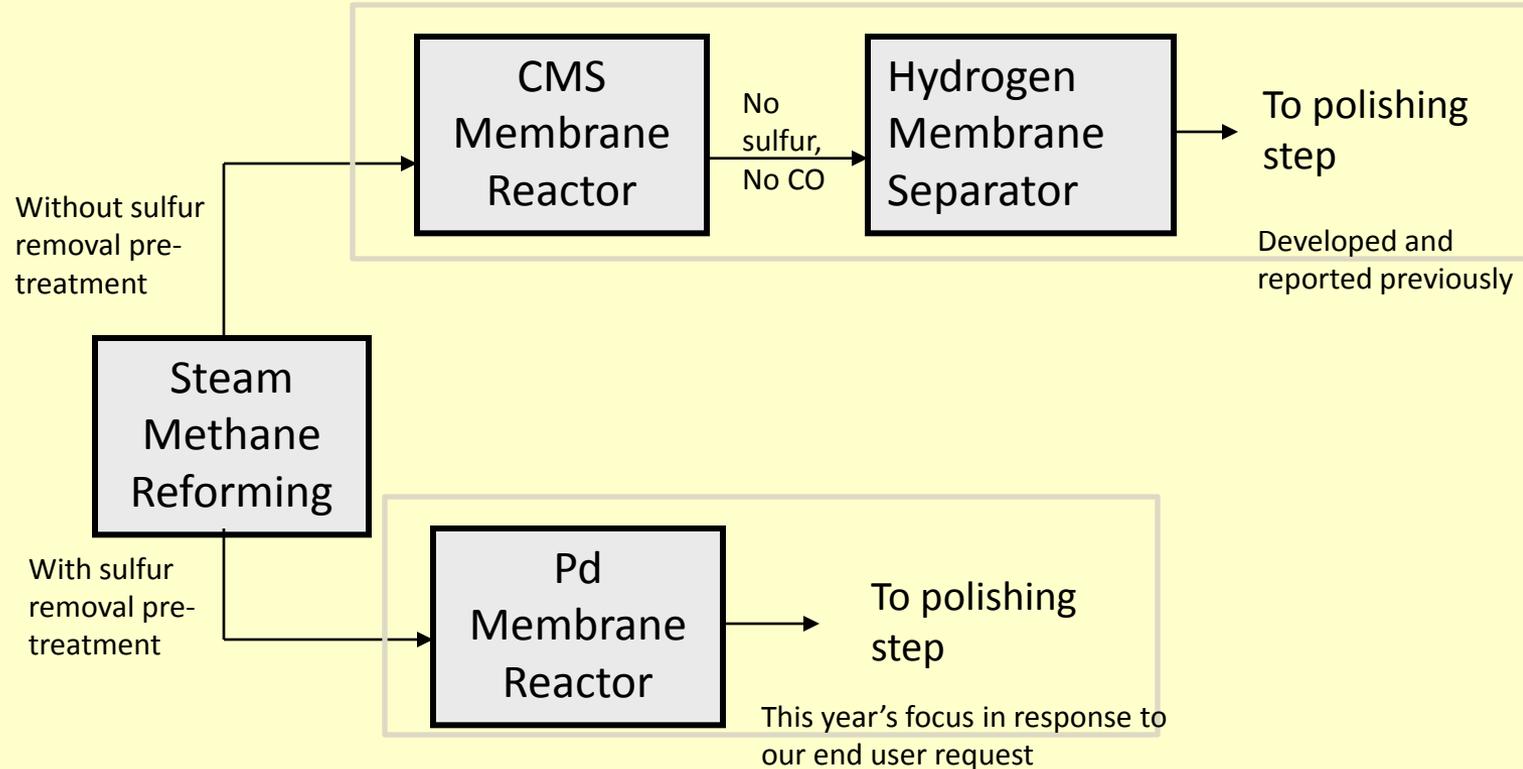
We have successfully developed the membrane bundle for our tubular H<sub>2</sub> selective membrane. This bundle approach can minimize module leak and reduce the module cost, and will be used for our field test in Phase II.

## Conducted membrane reactor test using our full-scale membrane tubes

The WGS-MR process we developed from a bench-scale unit previously has been verified experimentally using a full-scale tubular membrane. ~99% CO conversion, >83% H<sub>2</sub> recovery and >99.9% purity H<sub>2</sub> were achieved with this full-scale membrane reactor module.

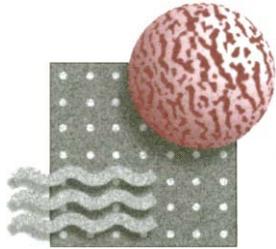


## M&P Membrane Reactor Schemes



### Unique Advantages of our Membranes/Membrane Reactors

1. Low temperature operation (WGS-LTS), thus, no exotic engineering/materials are required to develop for a membrane reactor and separator.
2. Our commercial low cost ceramic membranes/modules as platform ; thus, capital cost can be justified due to low permeate flux at a low temperature.



## 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

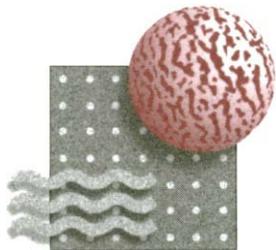
### Examples of Commercial Installations

- Oil filtration applications at 150°C and 80 psi
- Water vapor recovery from flue gas at ~75°C



### Proposed Applications

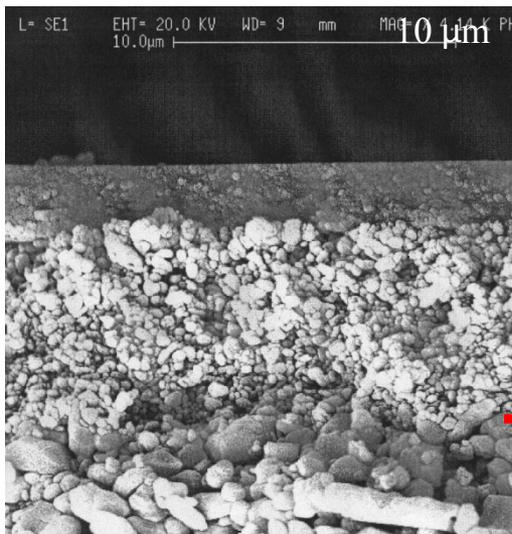
- Hydrogen recovery from reformat
- Water gas shift (WGS) membrane reactor at 200 to 350°C



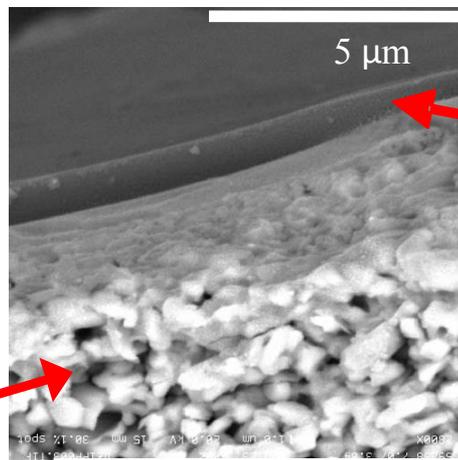
# M&P Emerging Inorganic Membranes

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

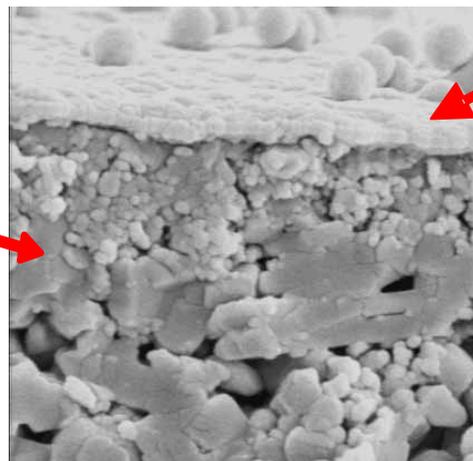
## Inorganic Substrate



Ceramic  
Substrate



Carbon  
molecular  
sieve  
(porous,  
sulfur  
resistance)



Palladium  
(dense,  
excellent  
selectivity)

## Unique features of Supported Membranes

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

# Cost Analysis for Stationary Power Generators:

## *Challenges for Membrane-based Processes*

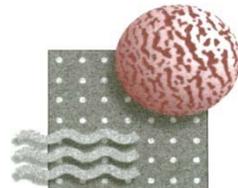
| Cost Allocations for A 5kW Fuel Cell Based Genset based upon a conventional diesel fuel reforming |  |              |              |
|---|--|--------------|--------------|
| Component   | Typical Equipment  | Cost [\$]    | \$/kW        |
| Stack   | Fuel cell stack  | +            | +            |
| Fuel Processor  | Reformer, fuel pumps, catalytic burner, air compressor   | +            | +            |
| Purifier  | Pd membrane*   | 400          | 80           |
| Other BOP   | Cathode compressor, gas to gas humidifiers, plumbing, wiring, heat exchangers, power/control electronics | +            | +            |
| Electrical  | Power and control electronics  | +            | +            |
| Packaging   | Chassis, insulation, sound proofing  | +            | +            |
|   | <b>Total</b>   | <b>5,250</b> | <b>1,050</b> |

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

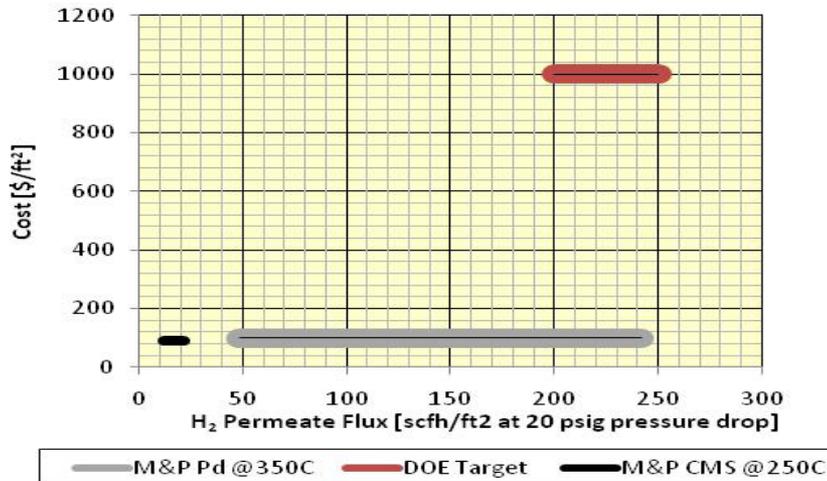
+ Proprietary information of our end user participant.

(Courtesy of Ballard Power Systems)

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# 1. Performance Characterization (typical)



## Membrane Cost for 5kW Genset

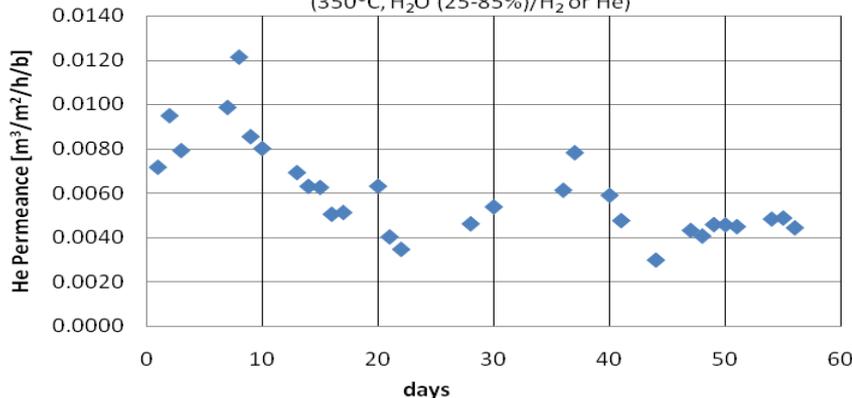
| Targets     | H <sub>2</sub> Flux* | Cost [\$/5 kW] |
|-------------|----------------------|----------------|
| DOE Target  | 250                  | 2,000          |
| M&P current | 121                  | 416            |

\* in scfh/ft<sup>2</sup> at 20 psig

# 3. Thermal/ Hydrothermal Stability

## Long Term Hydrothermal Stability Test of Hydrogen Selective Membrane

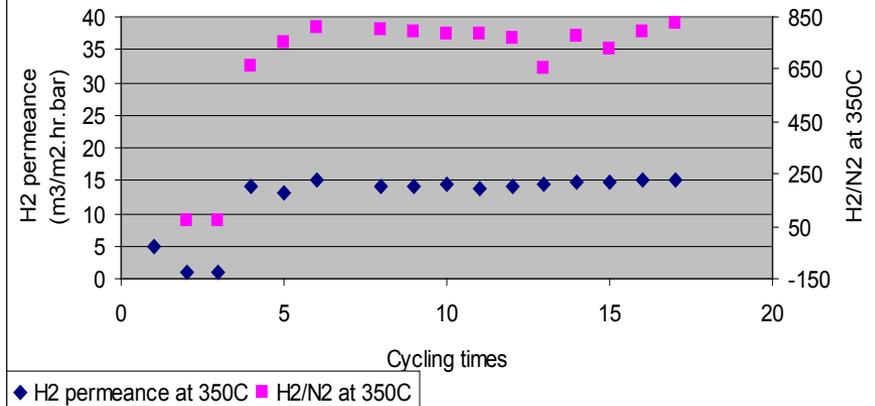
(350°C, H<sub>2</sub>O (25-85%)/H<sub>2</sub> or He)



# Evaluation of M&P Hydrogen Selective Pd Membranes: Results

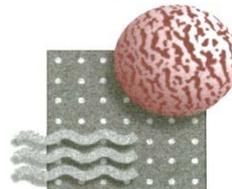
## 2. Thermal Cycling Stability

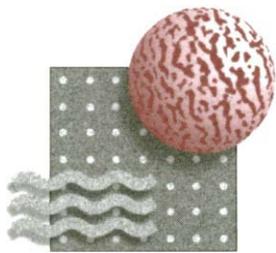
H<sub>2</sub> permeance and H<sub>2</sub>/N<sub>2</sub> selectivity at 350C for Pd-500-1



1. Our Pd membranes 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/ft<sup>2</sup> at 20 psig with \$100/ft<sup>2</sup> can meet the cost target set by our commercialization partner.

**Media and Process Tech In.**





## M&P H<sub>2</sub> Selective Pd Membranes

### *Effect of substrate on Permeance and Product Cost*

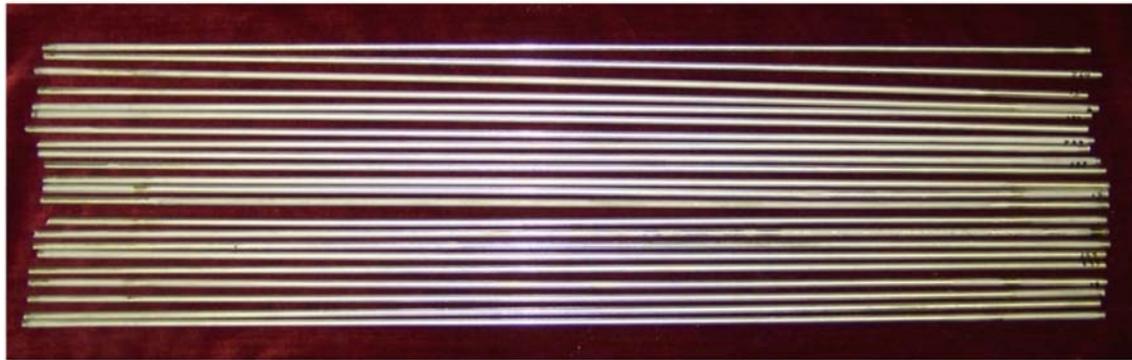
| M&P Substrate                         | Substrate N <sub>2</sub> Permeance [m <sup>3</sup> /m <sup>2</sup> /hr/bar] | Pd Permeance [m <sup>3</sup> /m <sup>2</sup> /hr/bar] | Selectivity [H <sub>2</sub> /N <sub>2</sub> ] |
|---------------------------------------|---|---|---|
| Early Stage                           | 50 to 70  | 3 to 5  | 800 to 2,000                                  |
| Current Standard                      | 50 to 70  | 10 to 15  | 1,000 to >10,000                              |
| Next Generation                       | 120 to 150  | 20 to 25  | 350 to 500<br>(need improvement)              |
| High Permeance Experimental Substrate | >790  | 40 to 50  | 40 to 100                                     |

| Substrate Configuration |                | Features for Pd Film Deposition   | Cost           |
|-------------------------|----------------|-----------------------------------|----------------|
| Symmetric               | Metallic foil  | Thicker film; lower flux          | very expensive |
| Asymmetric              | Porous Ceramic | Higher quality surface topography | low cost       |
|                         | Porous SS      | Requiring diffusion barrier       | expensive      |

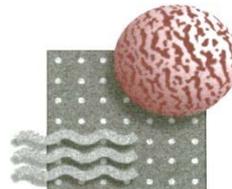
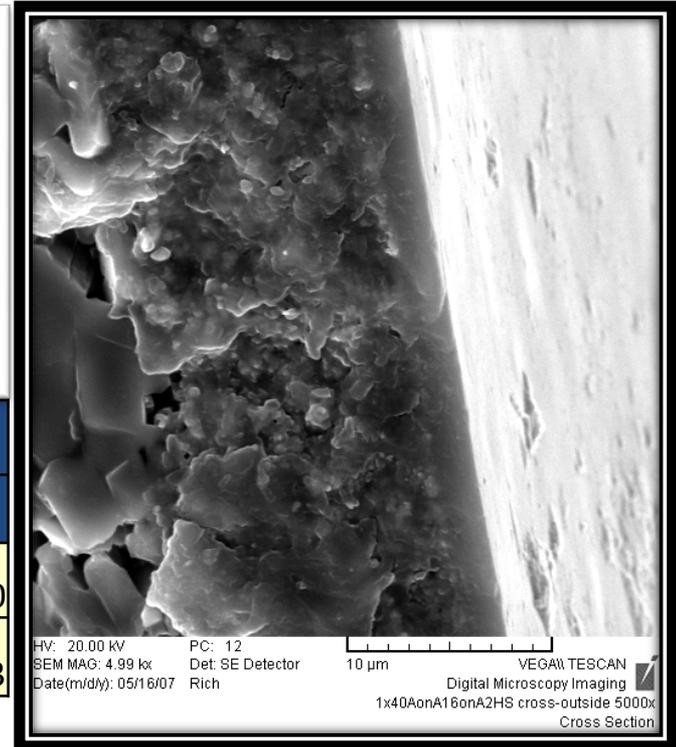
However, seal for the ceramic membrane to the metallic housing is considered complicated.

## Our Standard Full-scale Pd Membranes

*Pd Thin Film Coated on the Outside  
of Our Tubular Commercial Ceramic Membranes as Substrate*



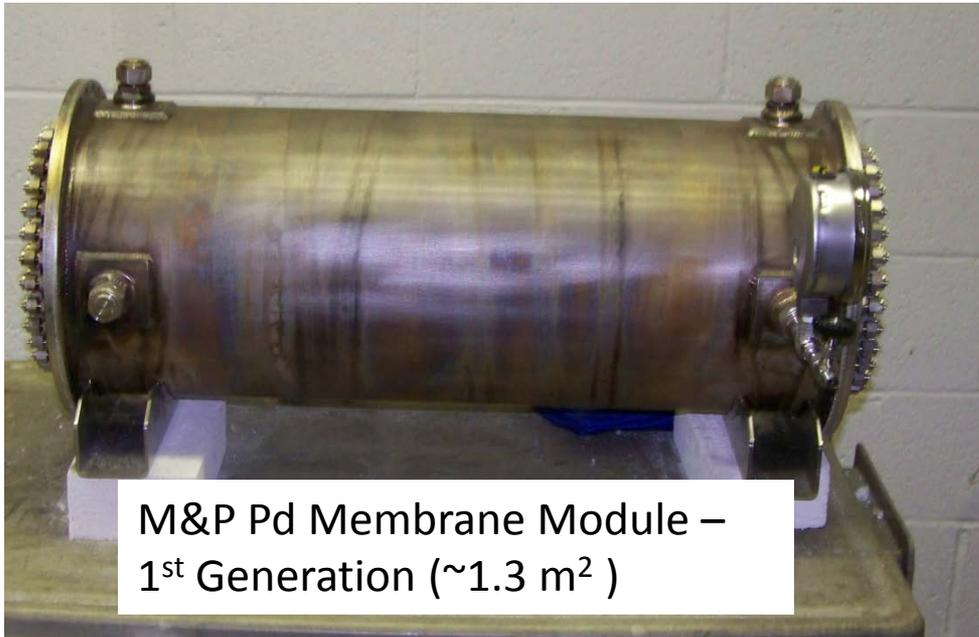
| Layer Location | Tube Diameter [cm] |      | Tube Length | Surface Area                | Surface Area |
|----------------|--------------------|------|-------------|-----------------------------|--------------|
|                | OD                 | ID   | [in]        | [m <sup>2</sup> /30"L tube] | Ratio [-]    |
| Inside         | 0.57               | 0.35 | 30          | 0.0084                      | 1.00         |
| Outside        | 0.57               | 0.35 | 30          | 0.0136                      | 1.63         |



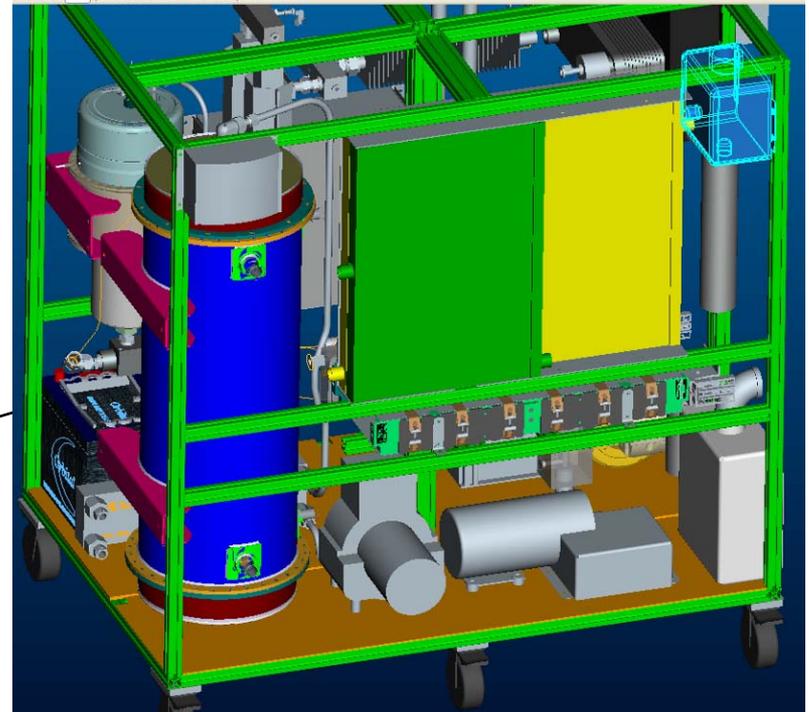
# Field Test Activities in FY09-10

M&P H<sub>2</sub> Selective Membranes for fuel processing to produce 152 scfh Hydrogen

Picture: Design of 5 kWh fuel-cell power generation unit (courtesy of Ballard Corp)



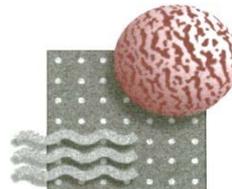
M&P Pd Membrane Module –  
1<sup>st</sup> Generation (~1.3 m<sup>2</sup> )



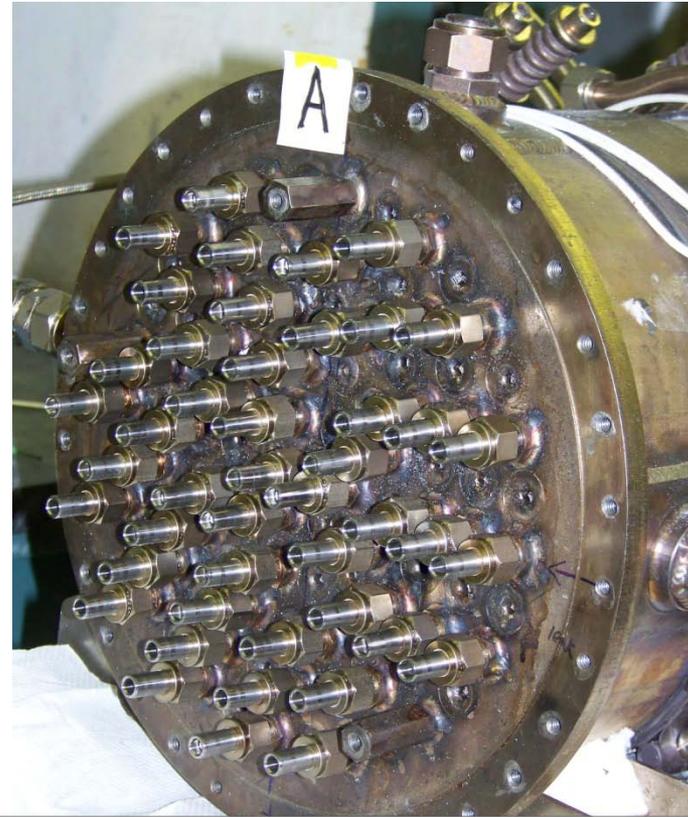
## Current Status:

Leak was encountered in the 1<sup>st</sup> test.  
scheduled to perform the 2<sup>nd</sup> test in 2<sup>nd</sup> Q 2010

**Media and Process Tech In.**

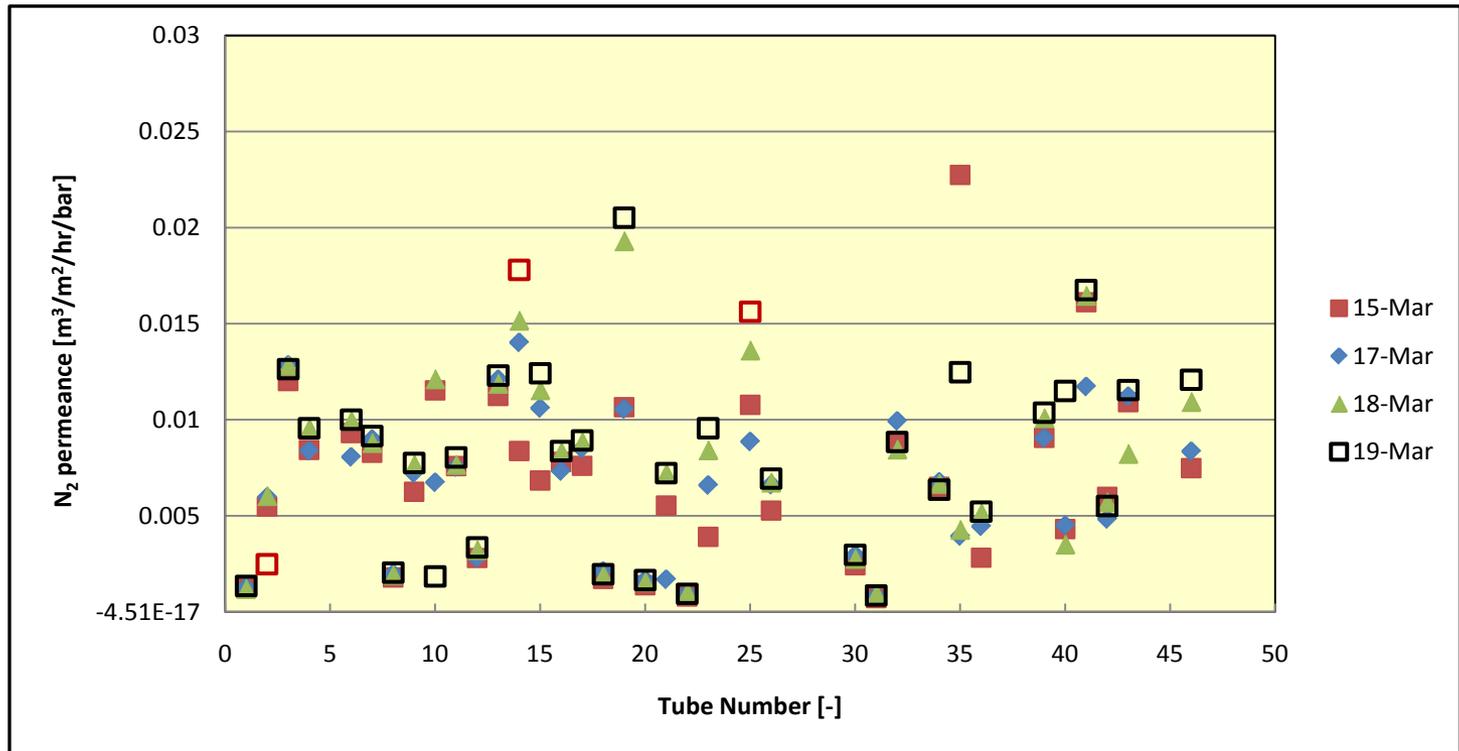


# 1<sup>st</sup> Generation M&P Membrane Module Over View and Membrane Tube Packing



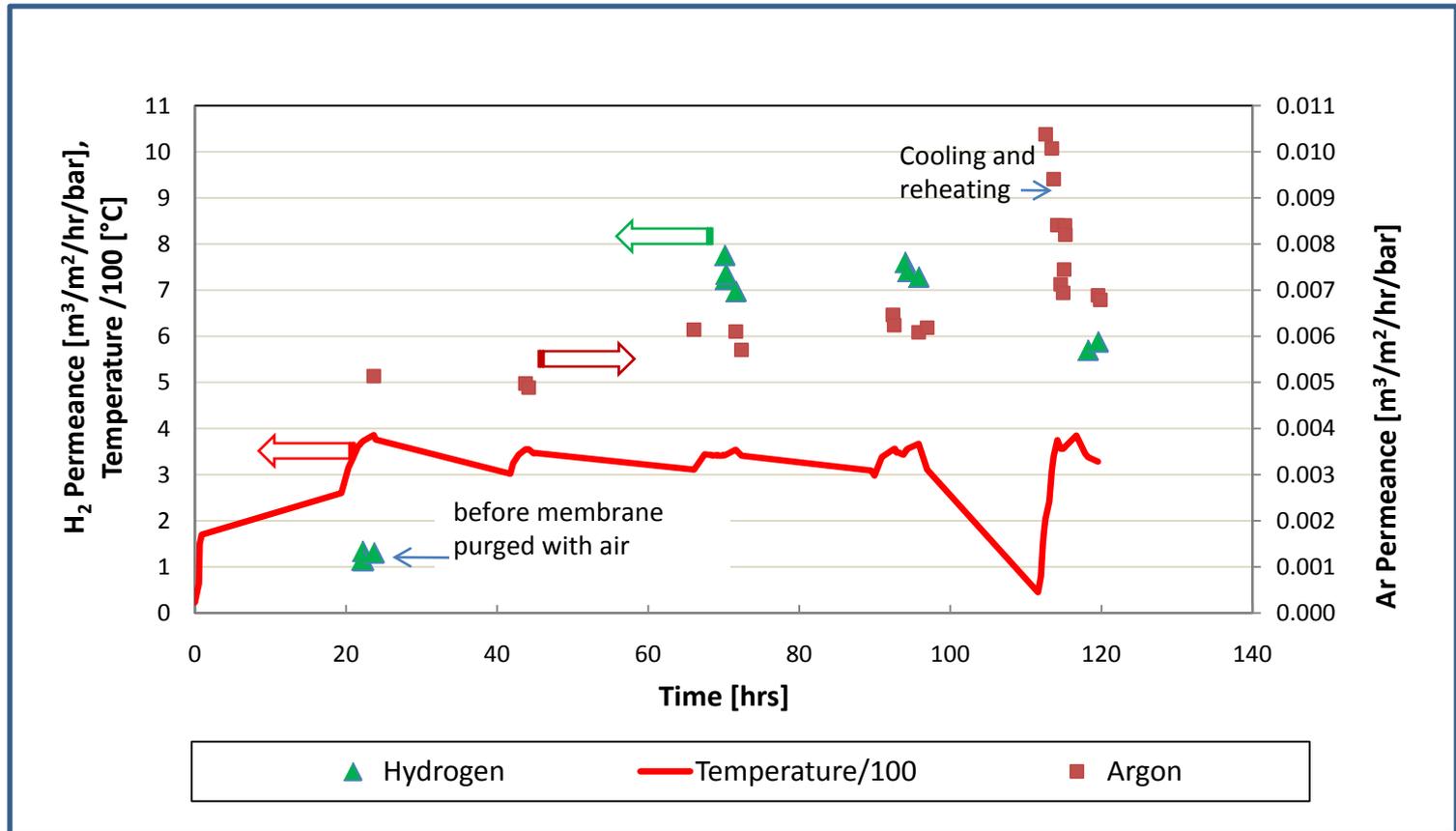
## Stability of the 1<sup>st</sup> Generation Module through Thermal Cycling

N<sub>2</sub> permeance measurement for each individual tube at room temperature after 25 to 350 C thermal cycling



- Since the leaking trend does not follow the sequence of thermal cycles for most tubes, we conclude that the tube seal is stable through multiple thermal cycles.
- N<sub>2</sub> measurement of ~0.08 m<sup>3</sup>/m<sup>2</sup>/hr/bar in average is equivalent to ~0.006 m<sup>3</sup>/m<sup>2</sup>/hr/bar at 350°C based upon Knudsen diffusion, which is consistent with the measurement on the module basis as shown in the next slide.

## Evaluation of the 1st Generation Field Test Module for H<sub>2</sub> Separation: hydrogen permeance, selectivity and leak potential through thermal cycling



- Hydrogen permeance of 7- 8 m<sup>3</sup>/m<sup>2</sup>/hr/bar was obtained, consistent with our measurement from single tubes.
- Selectivity of >1,000 was obtained, indicating leaking is acceptable.
- Combining the results from this and the previous slides indicates that the 1<sup>st</sup> generation module is acceptable in terms of stability and performance after improvement of packing.

# MEMBRANE BUNDLE AND HOUSING PREPARATION as 2<sup>nd</sup> Generation Module for Phase II Field Test

These membranes and modules were adapted from our existing commercial ceramic membrane products and modules.

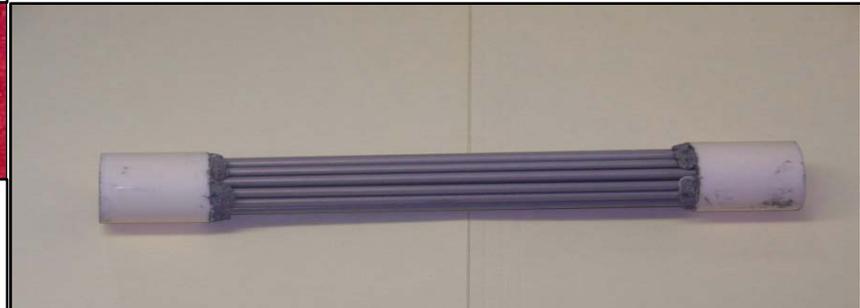


← Our full-scale ceramic membrane module (3 - 4" dia, prototype) for gas applications

## Pilot Scale Membrane Bundle and Housing for High Pressure Intermediate Temperature Applications



- 1.5" Dia Bundles (top & right) and Housing (bottom),
- 20 x 5mm Membranes in candle filter configuration for CMS membrane (above)
- 20 x 5mm Membranes in two-end mounted configuration for Pd membrane (right)
- Thermal cycling tested at 20 to 220°C
- Pressure cycling tested at 0 to 1000 psig

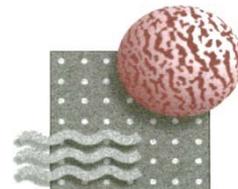


### Unique Features

- low cost
- existing engineering/materials know-how

### Our Accomplishments

- successfully thermal/pressure cyclic tested



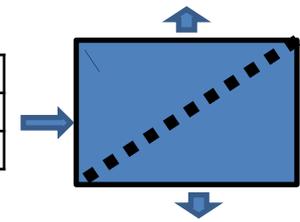
# Performance and Thermal Cycling Stability of The 2<sup>nd</sup> Generation Module: Pd Membrane Bundle

Pilot Test at M&P with Synthetic Mixture

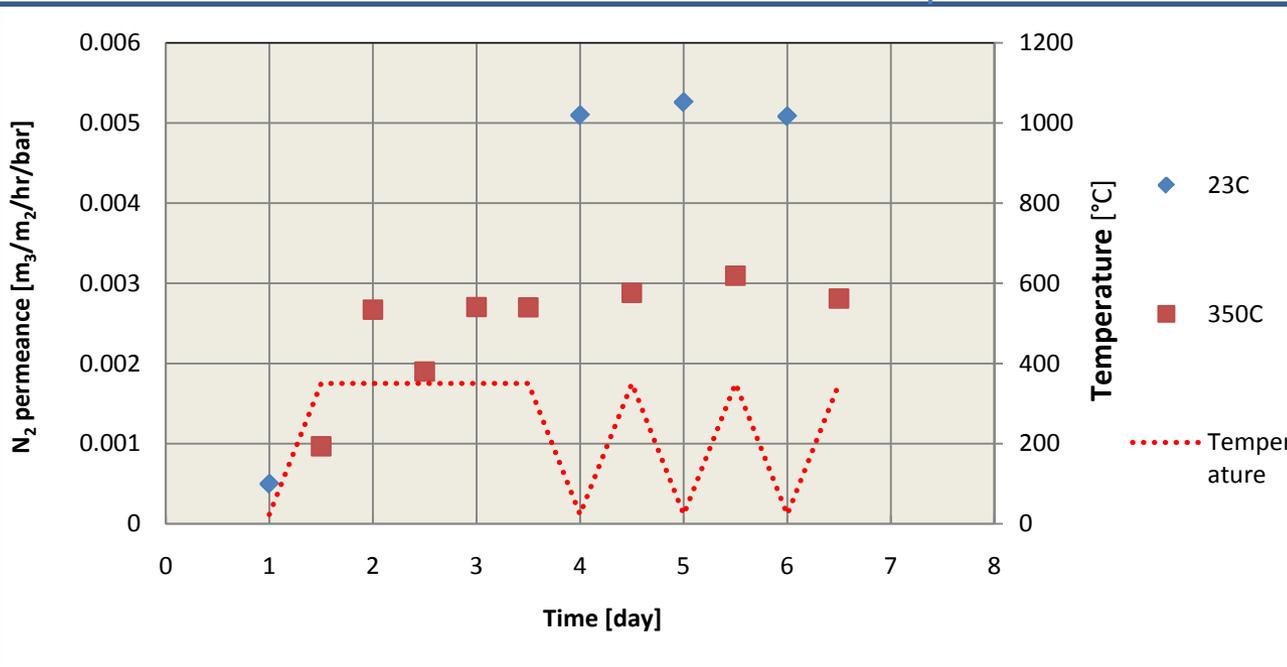
|                       |     |
|-----------------------|-----|
| Reject [liter/min]    | 2.0 |
| H <sub>2</sub> [vol%] | 68  |
| CO <sub>2</sub>       | 32  |

350°C, 14 psig, 4.5 liter/min

|                       |    |
|-----------------------|----|
| H <sub>2</sub> [vol%] | 80 |
| CO <sub>2</sub>       | 20 |

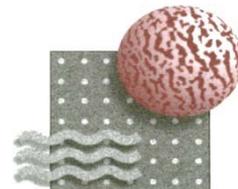


|                       |      |
|-----------------------|------|
| Permeate [liter/min]  | 2.5  |
| H <sub>2</sub> [vol%] | 99.9 |
| CO <sub>2</sub>       | 0.1  |



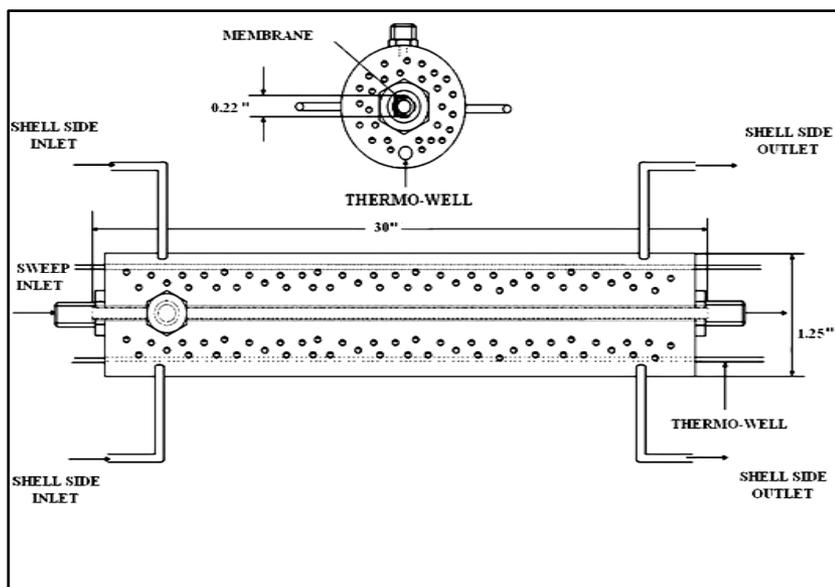
- Temperature Range: 25 to 350 C
- At 350 C, membrane was exposed to hydrogen
- At <350 C, membrane was exposed to nitrogen

- Bundle leaking is acceptable and stable through the multiple thermal cycling test.
- Pd bundle configuration for the 2<sup>nd</sup> generation module shown here will be used in the field test to be undertaken in Phase III.



# WGS-LTS Membrane Reactor Activities in FY09-10

**Objective: using a full-scale H<sub>2</sub> 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 <sub>2</sub> :CO:CO <sub>2</sub> :CH <sub>4</sub> :H <sub>2</sub> O | 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 [m <sup>3</sup> /m <sup>2</sup> /h/bar] | Seprn Factor |
|-----------------|---|--------------|
| H <sub>2</sub>  | 16.82   | 1            |
| CO              | 0.01  | 2,369        |
| CO <sub>2</sub> | 0.01  | 2,951        |
| Ar              | 0.01  | 2,474        |
| N <sub>2</sub>  | 0.01  | 2,548        |

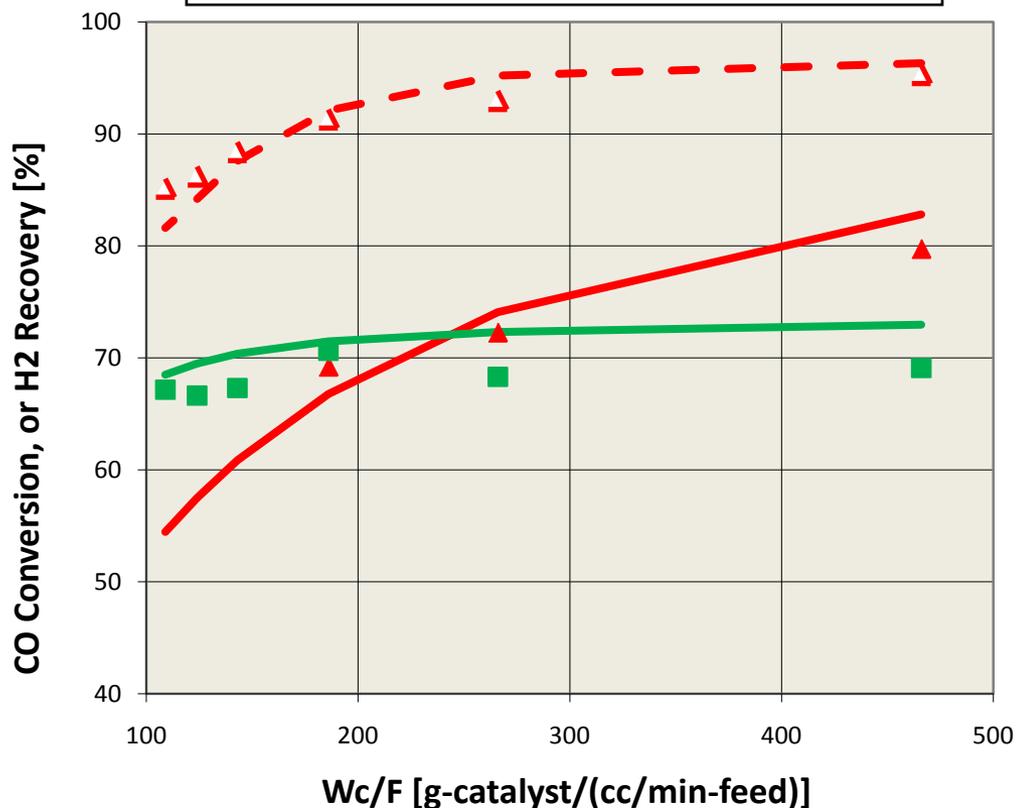
# WGS-LTS Membrane Reactor Activities in FY09-10

Experimental Results from operation *at 30 psig and with no sweep*

## WGS/MR Operating Conditions

Temperature: 300°C, Feed Pressure: 30 psig

Perm Pressure: 1 psig, Perm Sweep Ratio: 0.0

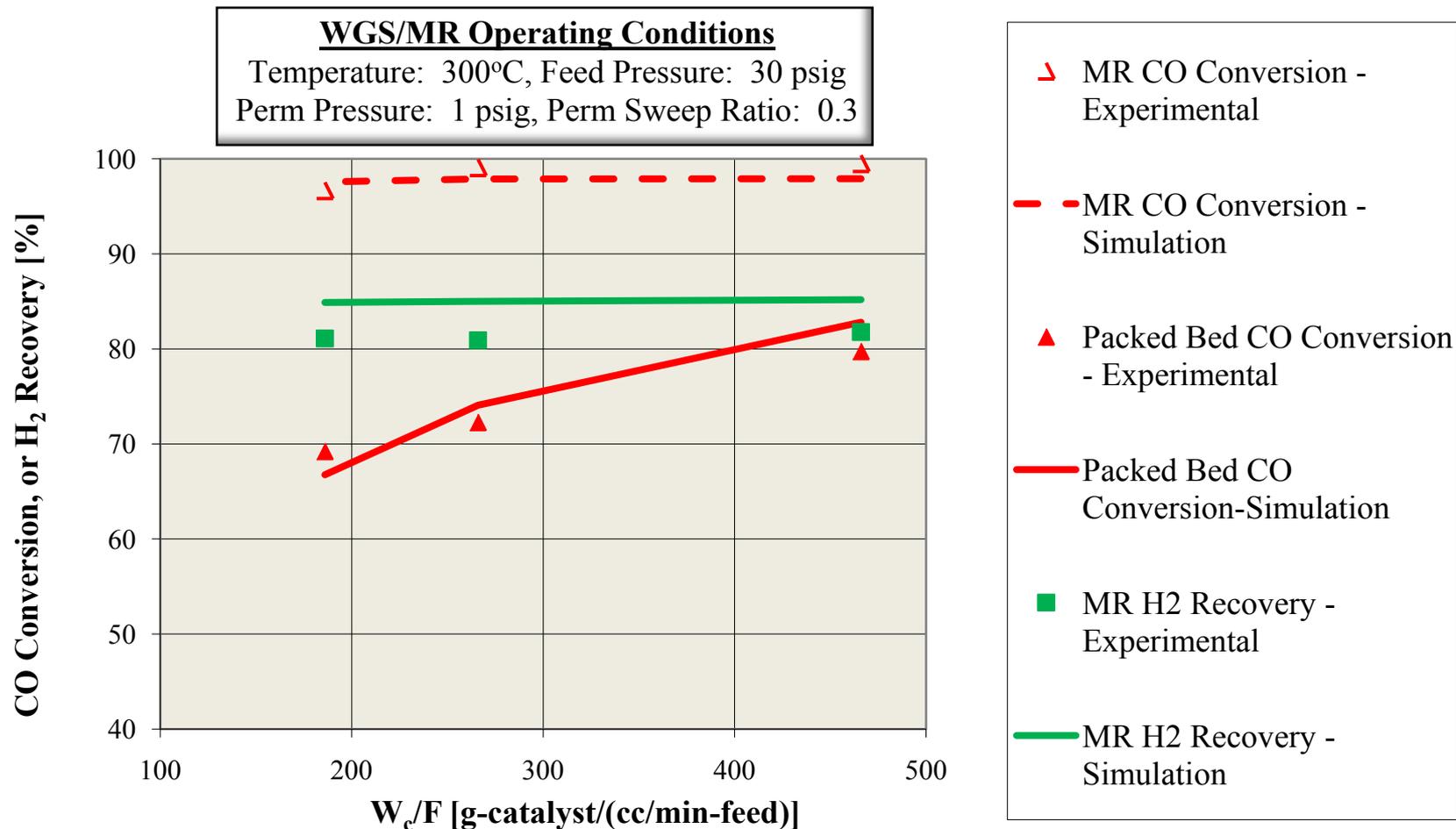


- MRr CO Conversion - Experimental
- MR CO Conversion - Simulation
- Packed Bed CO Conversion - Experimental
- Packed Bed CO Conversion - Simulation
- MR H2 Recovery - Experimental
- MR H2 Recovery - Simulation

CO concentration of <50 ppm and H<sub>2</sub> Purity >99.9% were obtained experimentally.

# WGS-LTS Membrane Reactor Activities in FY09-10

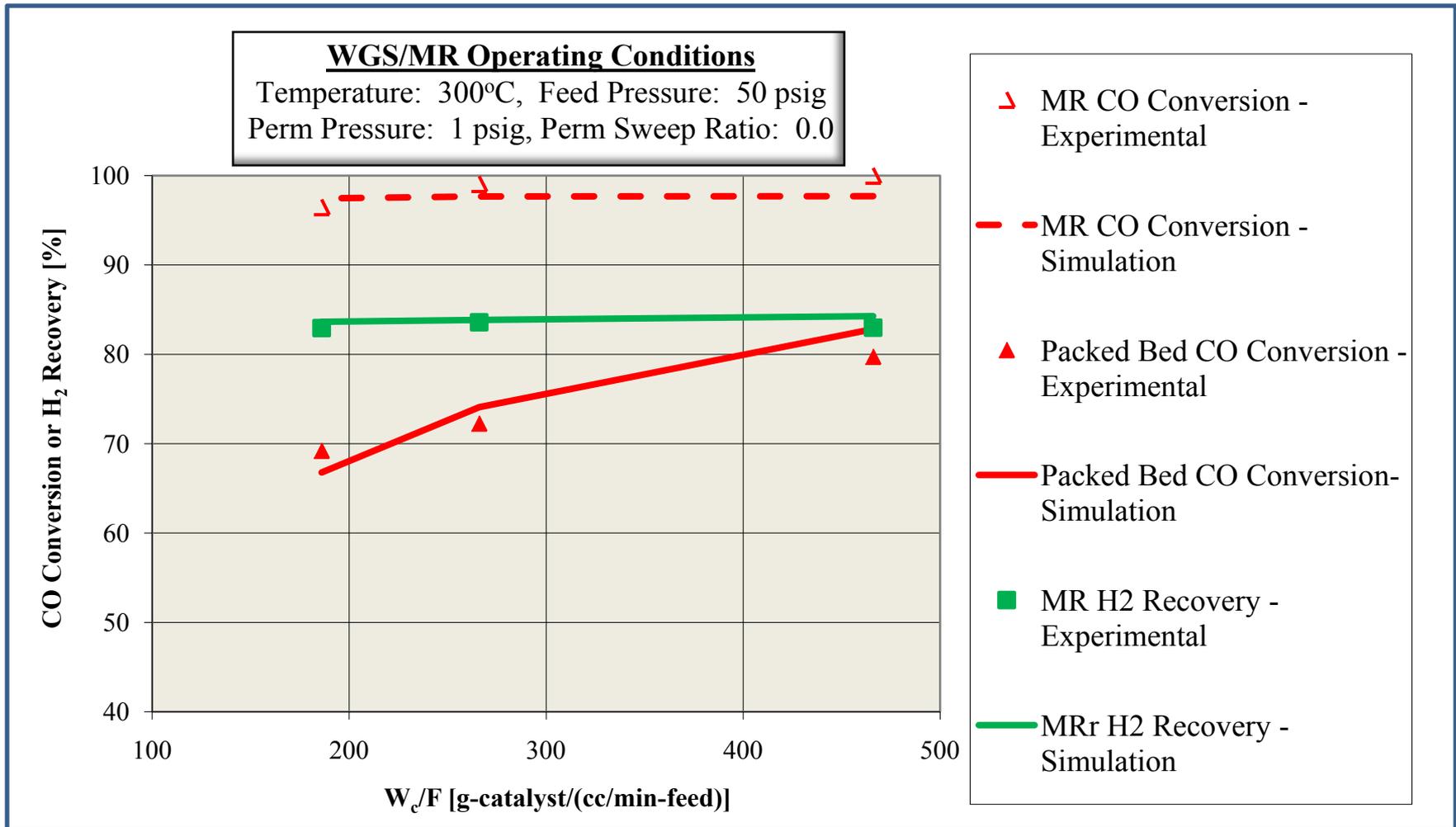
Experimental Results from the operation at 30 psig and sweep ratio = 0.3



>99% CO Conversion is possible; 20-30% additional conversion over the level by the packed bed was accomplished.

# WGS-LTS Membrane Reactor Activities in FY08-09

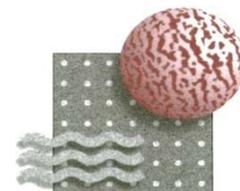
Experimental results from the operation *at 50 psig and with no sweep*



- ~83% H<sub>2</sub> recovery ratio at >99.9% H<sub>2</sub> purity were obtained experimentally.
- The experimental results shown in this and the previous two slides demonstrate >99% conversion and >99.9% purity at >83% hydrogen recovery is possible by our WGS-MR.

## Summary and Conclusions – FY09-10

- The low cost Pd membranes supported on our ceramic substrate were developed, which can meet the very stringent cost target set by our commercialization partner.
- We have improved the 1<sup>st</sup> generation module and successfully verified its stability (i.e., acceptable leak through thermal cycling) and performance, which is ready for the field test involving hydrogen separation (to be held in April 2010).
- The 2<sup>nd</sup> generation module, i.e., Pd membrane bundle, which is more economical and less prone to leak, has been developed and successfully tested. This module will be used for field test in Phase II.
- >99% CO conversion and >99.9% purity hydrogen at >83% hydrogen recovery ratio was demonstrated experimentally using a reactor packed with our full-scale Pd membrane and a commercial catalyst. We are now ready to move to the field test of the membrane reactor to be undertaken in Phase II.



## Work Plan for Rest of Project Period

### Phase I: Field Test on Membranes/Modules

1. Complete the field test for hydrogen separation at our commercialization partner site to demonstrate its commercial viability in the field (scheduled in April 2010).
2. Prepare the field test involving the WGS-Membrane Reactor (MR) with the 2<sup>nd</sup> generation module, which will be the focus of our Phase II project.

### Phase II: Field Test Activities

1. Prepare 2<sup>nd</sup> generation membrane/modules for use as a full-scale WGS-MR.
2. Design and construct the full-scale membrane reactor for field test at Ballard Power Systems.
3. Conduct field test at the participated end user site.

