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**
  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**

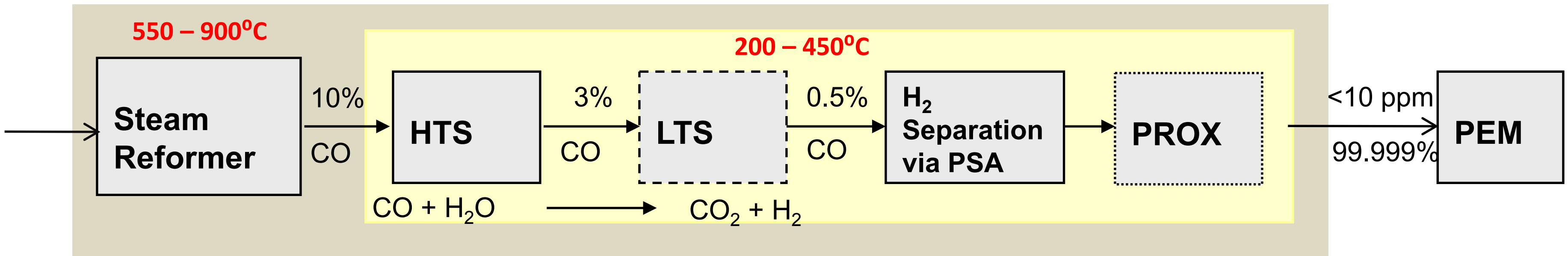
- **Total project funding**
  - DOE Share: $2,592,350.
  - Contractor Share: $648,087.
- **FY09:** $0
- **FY10 Plan:** $100K
- No catalyst development activities due to funding limitation in the beginning of the project

- **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_2 Recovery (Barrier #1&2)**
  - ❑ improved the field test module design to minimize module leaking potential experienced in the 1st field test.
  - ❑ performed the test to verify the thermal cycling stability and permeate flux of the improved field test module.
  - ❑ pursued 2nd 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_2 recovery (Barrier #1&3)**
  - ❑ conducting a field test using a 150 scfh H_2 separator in 2nd Q

TECHNICAL ACCOMPLISHMENTS – FY09-10

- **Balanced performance vs cost for our H_2 Selective Membrane**

  Through evaluation of a range of ceramic membrane substrates with various permeances, we have been successful in developing our H_2 selective membrane product to meet the low cost feature requested by our commercialization partner.

- **Corrected leakage issue of the 1^{st} generation module and ready for the field test**

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

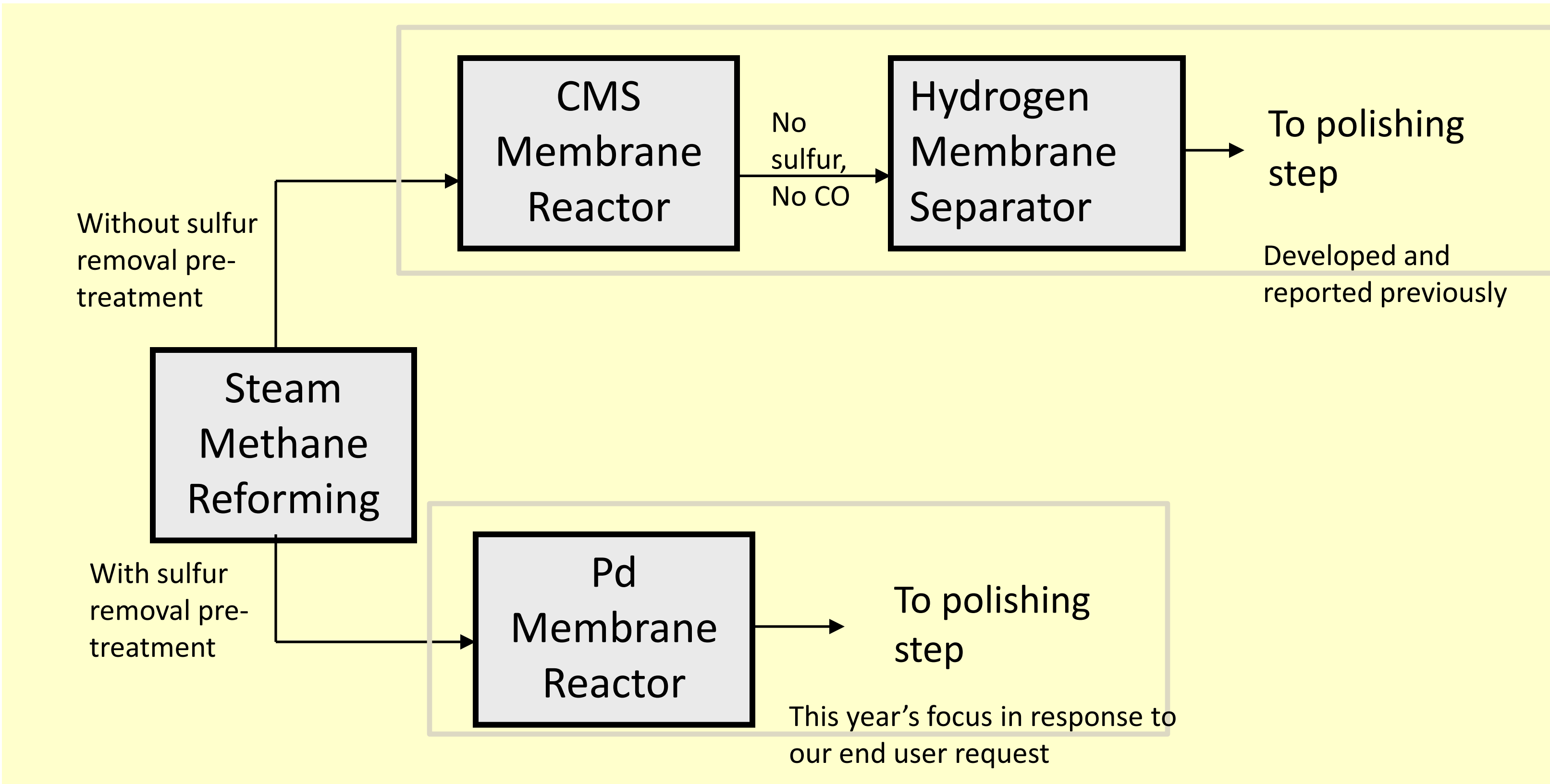
- **Designed and fabricated the 2^{nd} generation module using ceramic membrane bundles**

  We have successfully developed the membrane bundle for our tubular H_2 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_2 recovery and >99.9% purity H_2 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

<u>Developmental Work Required</u>

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

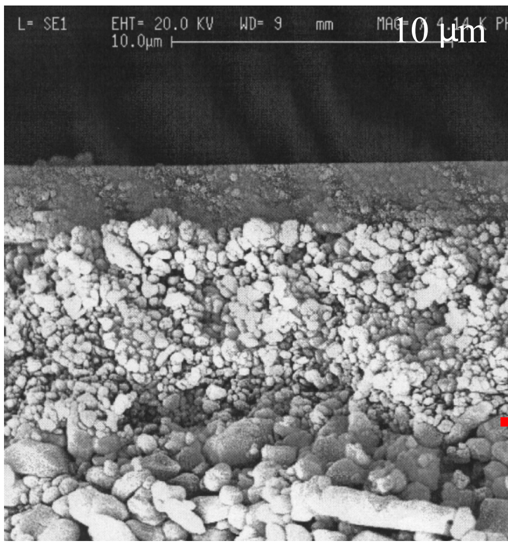
<u>Proposed Applications</u>

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

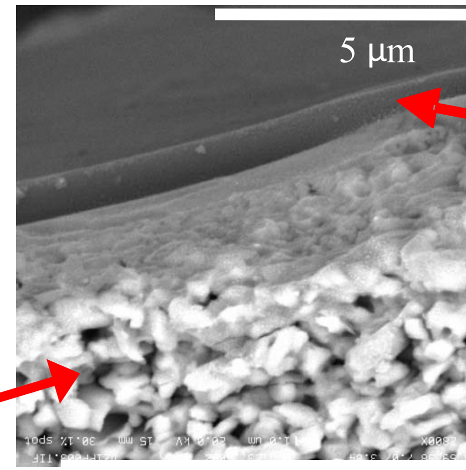
M&P Emerging Inorganic Membranes

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

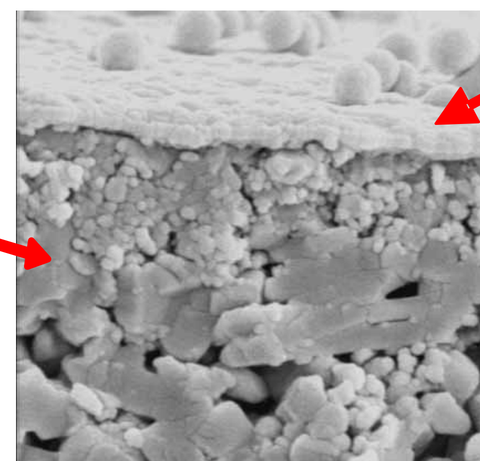
Inorganic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistance)



Palladium (dense, excellent selectivity)

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

- 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	+	+
	Total	**5,250**	**1,050**

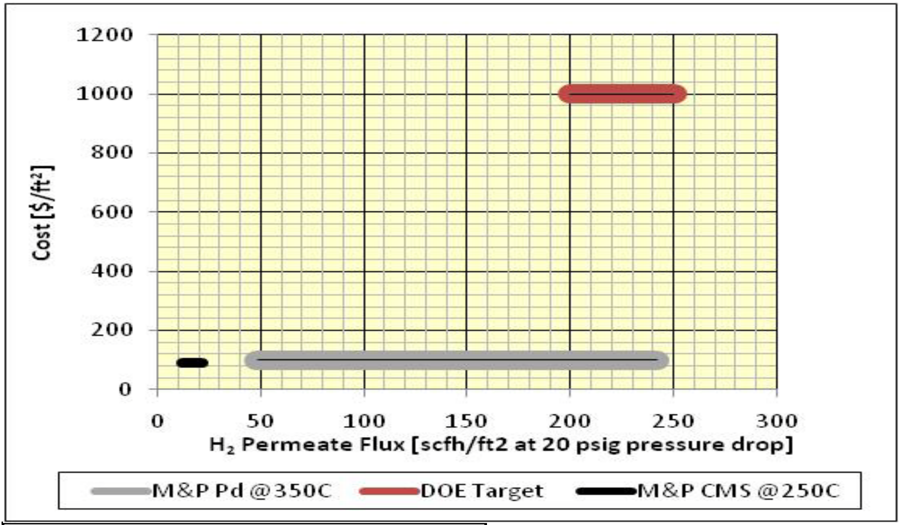
•The benefits offered by the membrane reactor was not taken into consideration in this analysis.

+ Proprietary information of our end user participant.

(Courtesy of Ballard Power Systems)

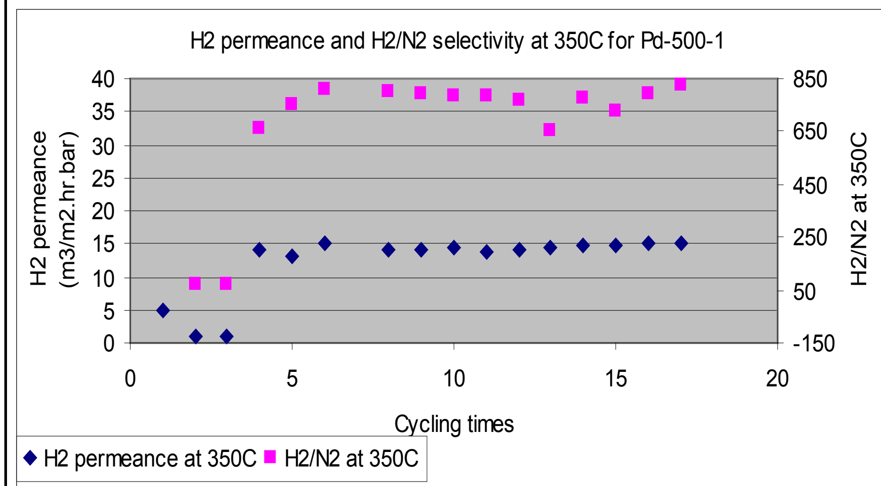
Evaluation of M&P Hydrogen Selective Pd Membranes: Results

1. Performance Characterization (typical)

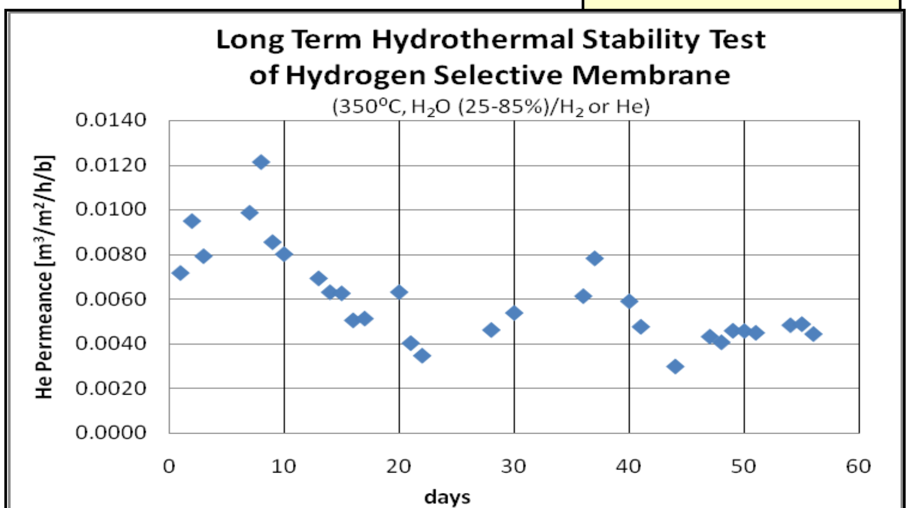


Membrane Cost for 5kW Genset		
Targets	H_2 Flux*	Cost [$/5 kW]
DOE Target	250	2,000
M&P current	121	416
* in scfh/ft² at 20 psig		

2. Thermal Cycling Stability



3. Thermal/ Hydrothermal Stability



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/ft² at 20 psig with $100/ft² can meet the cost target set by our commercialization partner.

M&P H_2 Selective Pd Membranes

Effect of substrate on Permeance and Product Cost

M&P Substrate	Substrate N_2 Permeance [$m^3/m^2/hr/bar$]	Pd Permeance [$m^3/m^2/hr/bar$]	Selectivity [H_2/N_2]
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 (need improvement)
High Permeance Experimental Substrate	>790	40 to 50	40 to 100

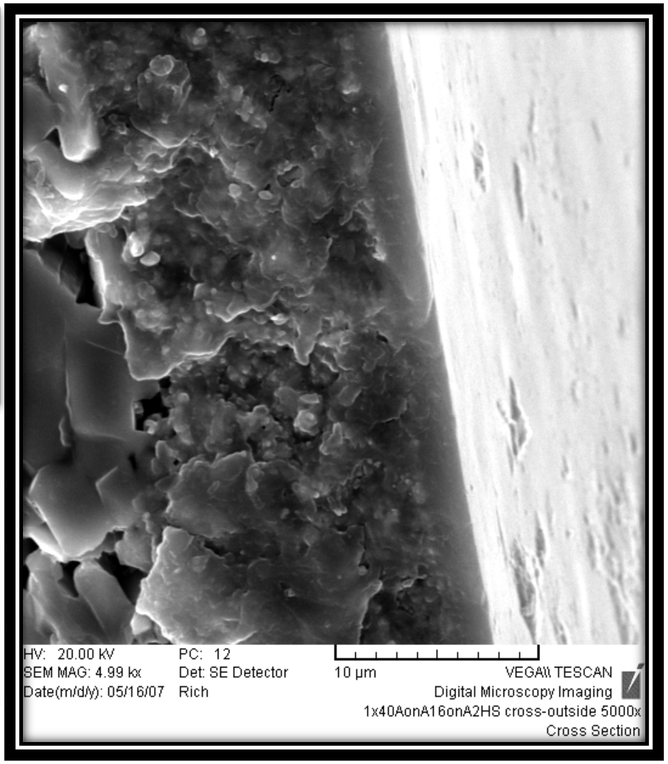
Substrate Configuration		Features for Pd Film Deposition	Cost
Symmetric	Metallic foil	Thicker film; lower flux	very expensive
Asymmetric	Porous Ceramic	Higher quality surface topography	low cost
	Porous SS	Requiring diffusion barrier	expensive

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

Our Standard Full-scale Pd Membranes

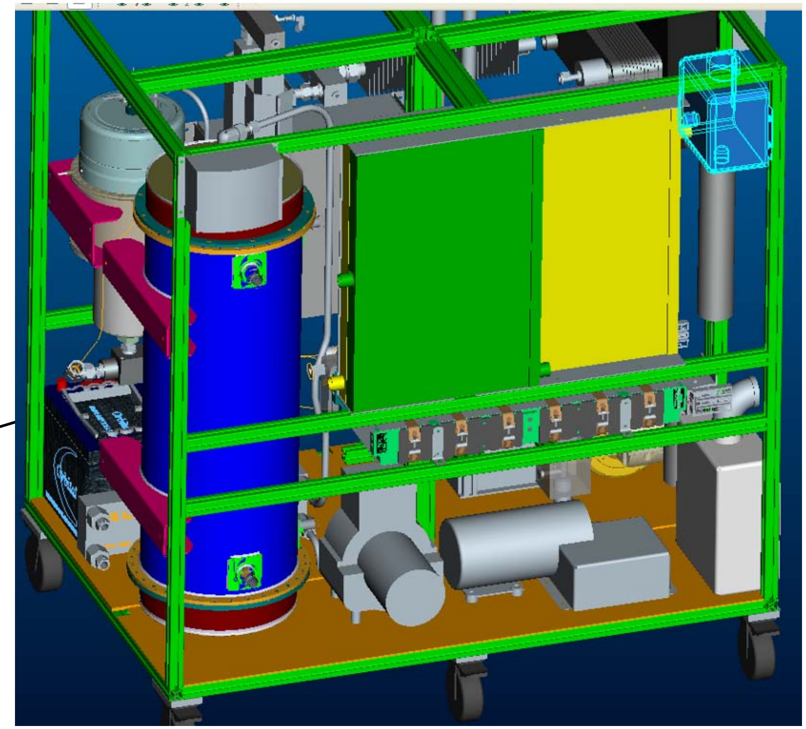
Pd Thin Film Coated on the Outside
of Our Tubular Commercial Ceramic Membranes as Substrate

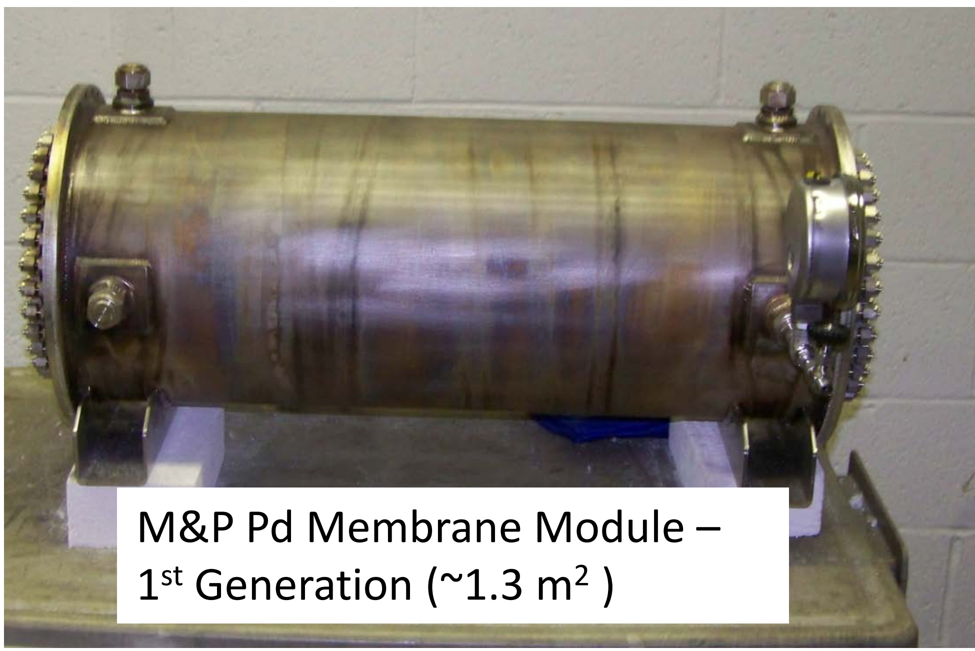
Layer Location	Tube Diameter [cm]		Tube Length	Surface Area	Surface Area
	OD	ID	[in]	[m²/30"L tube]	Ratio [-]
Inside	0.57	0.35	30	0.0084	1.00
Outside	0.57	0.35	30	0.0136	1.63



Field Test Activities in FY09-10

M&P H_2 Selective Membranes for fuel processing to produce 152 scfh Hydrogen
Picture: Design of 5 kWh fuel-cell power generation unit (courtesy of Ballard Corp)



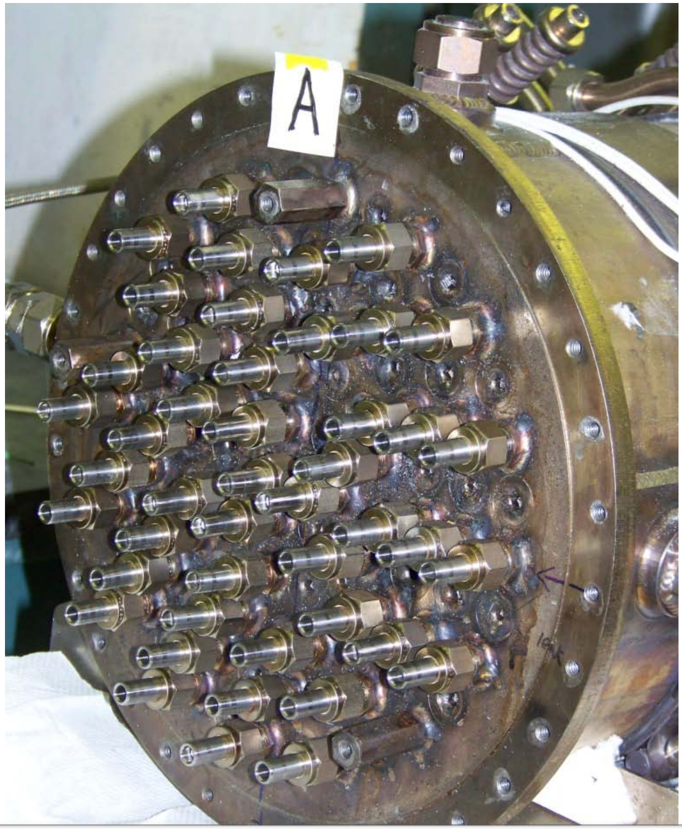


M&P Pd Membrane Module – 1st Generation (~1.3 m^2)

Current Status:
Leak was encountered in the 1st test.
scheduled to perform the 2nd test in 2nd Q 2010

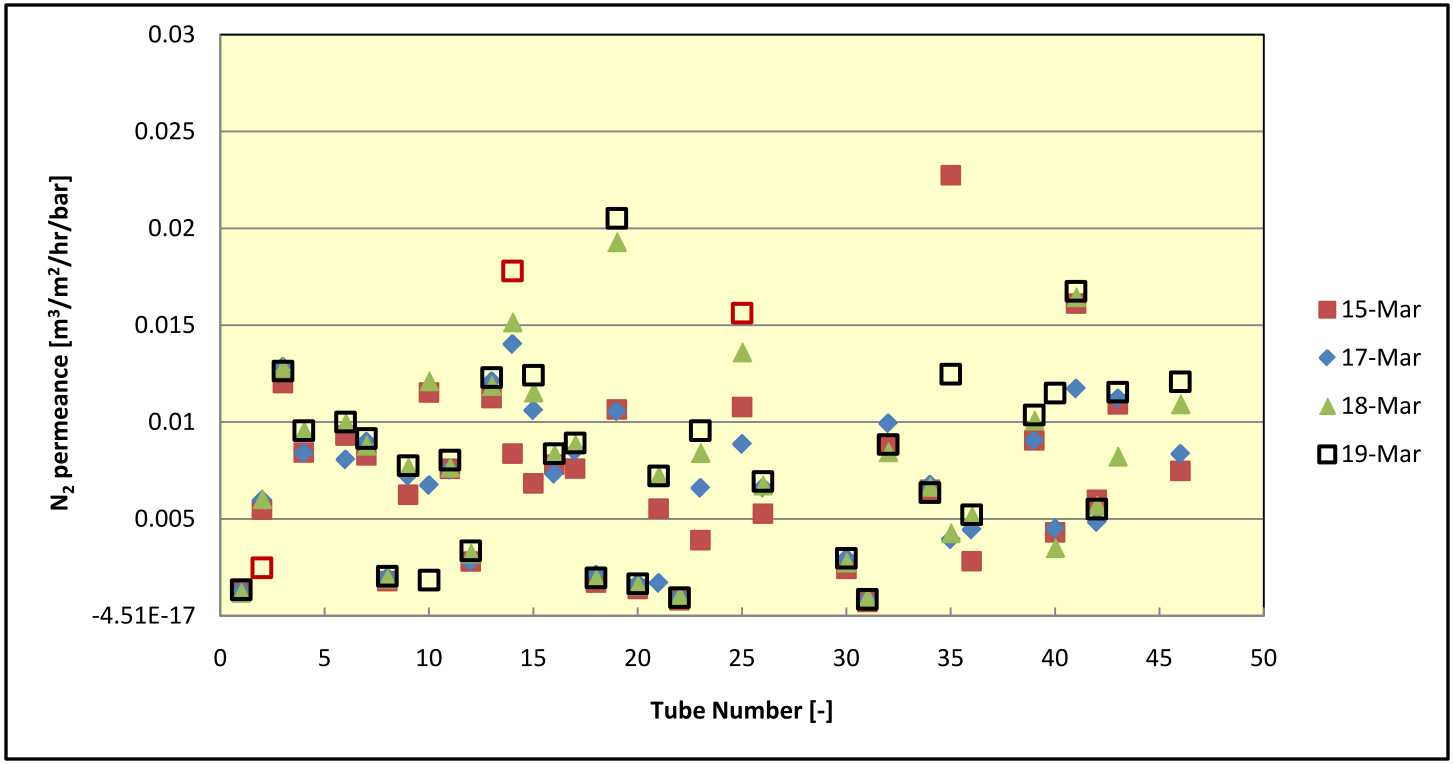
Media and Process Tech In.

1st Generation M&P Membrane Module Over View and Membrane Tube Packing



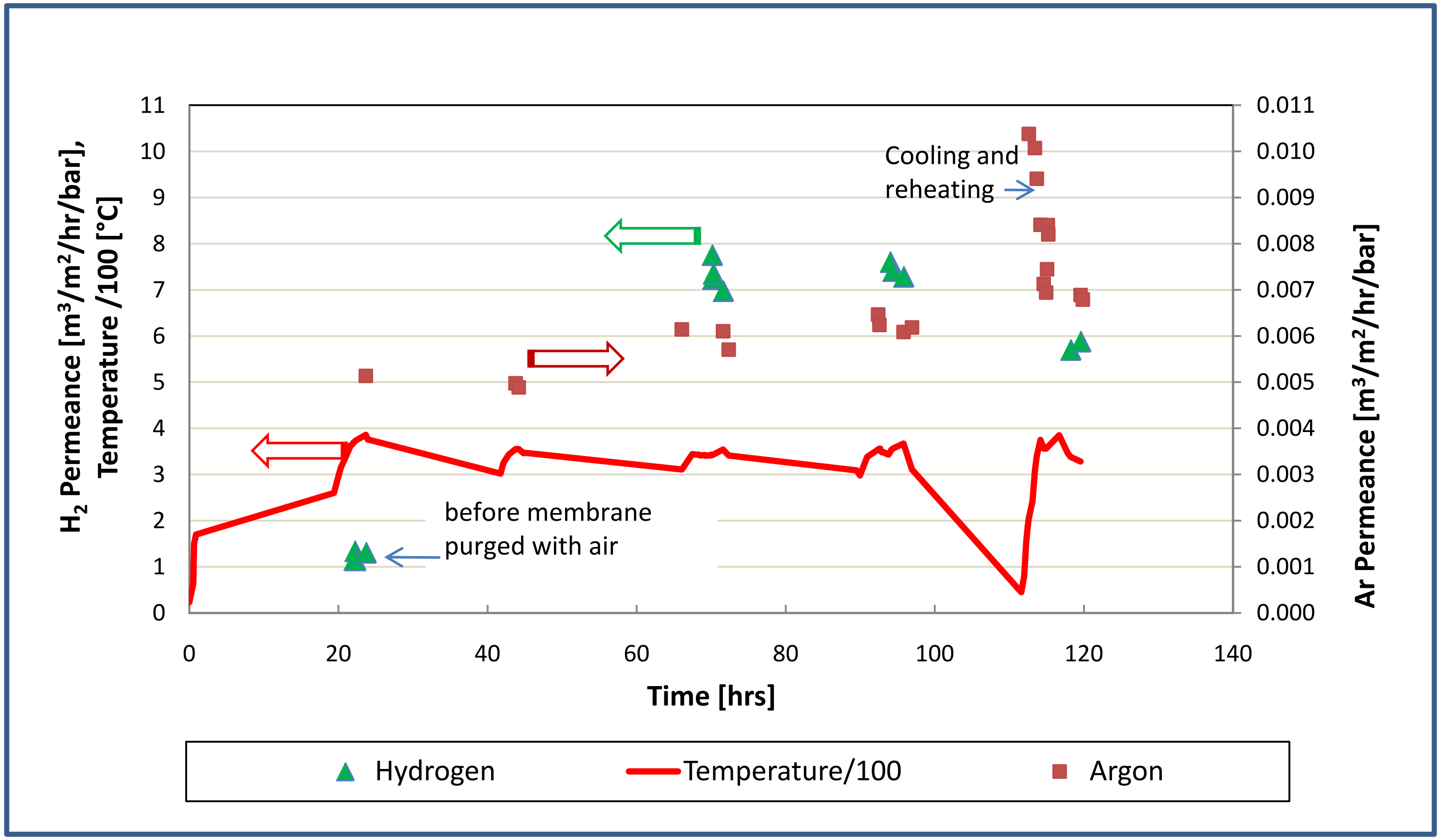
Stability of the 1st Generation Module through Thermal Cycling

N_2 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_2 measurement of ~0.08 $m^3/m^2/hr/bar$ in average is equivalent to ~0.006 $m^3/m^2/hr/bar$ 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_2 Separation:
hydrogen permeance, selectivity and leak potential through thermal cycling



- Hydrogen permeance of 7- 8 $m^3/m^2/hr/bar$ 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 1st generation module is acceptable in terms of stability and performance after improvement of packing.

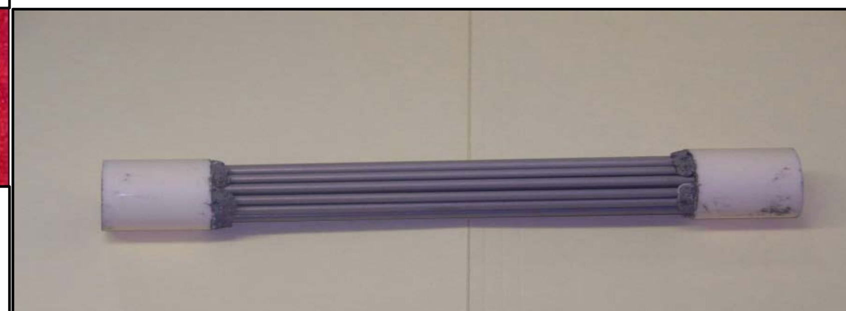
MEMBRANE BUNDLE AND HOUSING PREPARATION as 2nd Generation Module for Phase II Field Test

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^{o}C
- Pressure cycling tested at 0 to 1000 psig



<u>Unique Features</u>

- low cost
- existing engineering/materials know-how

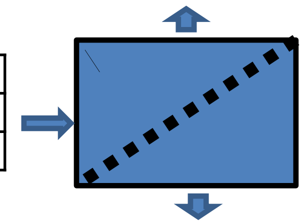
<u>Our Accomplishments</u>

- successfully thermal/pressure cyclic tested

Performance and Thermal Cycling Stability of The 2nd Generation Module: Pd Membrane Bundle

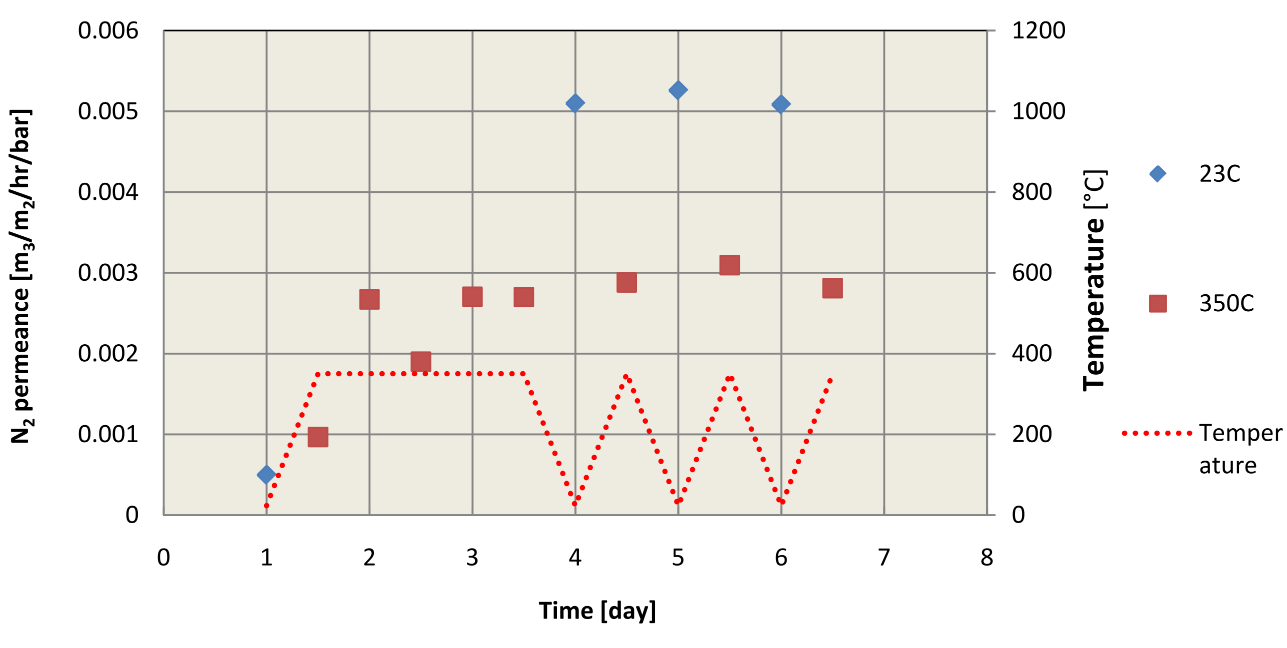
Pilot Test at M&P with Synthetic Mixture

350°C, 14 psig, 4.5 liter/min	
H_2 [vol%]	80
CO_2	20



Reject [liter/min]	2.0
H_2 [vol%]	68
CO_2	32

Permeate [liter/min]	2.5
H_2 [vol%]	99.9
CO_2	0.1

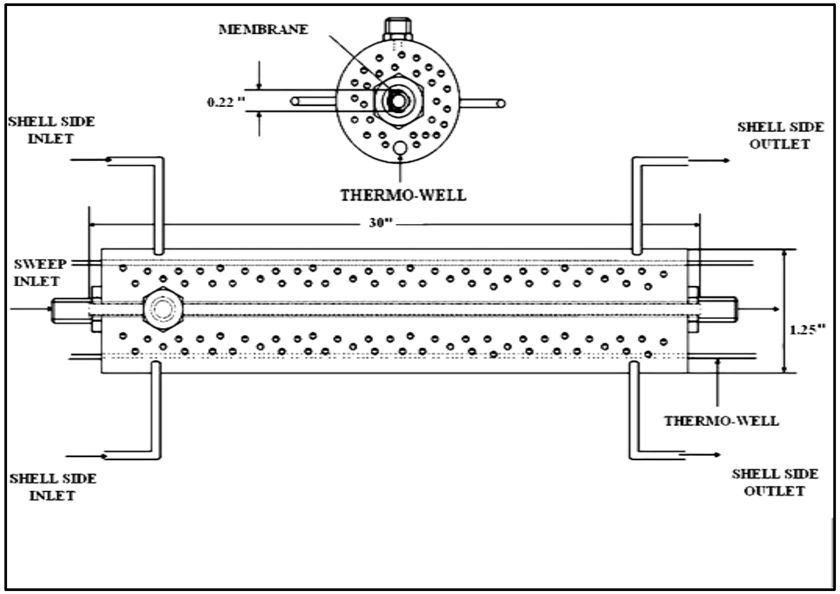


- Temperature Range: 25 to 350 C
- At 350 C, membrane was exposed to hydrogen
- At <350 C, membrane was exposed to nitrogen

- Bundle leaking is acceptable and stable through the multiple thermal cycling test.
- Pd bundle configuration for the 2nd 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 <u>full-scale</u> H_2 selective membrane to demonstrate high CO conversion and high purity hydrogen product at a high hydrogen recovery ratio



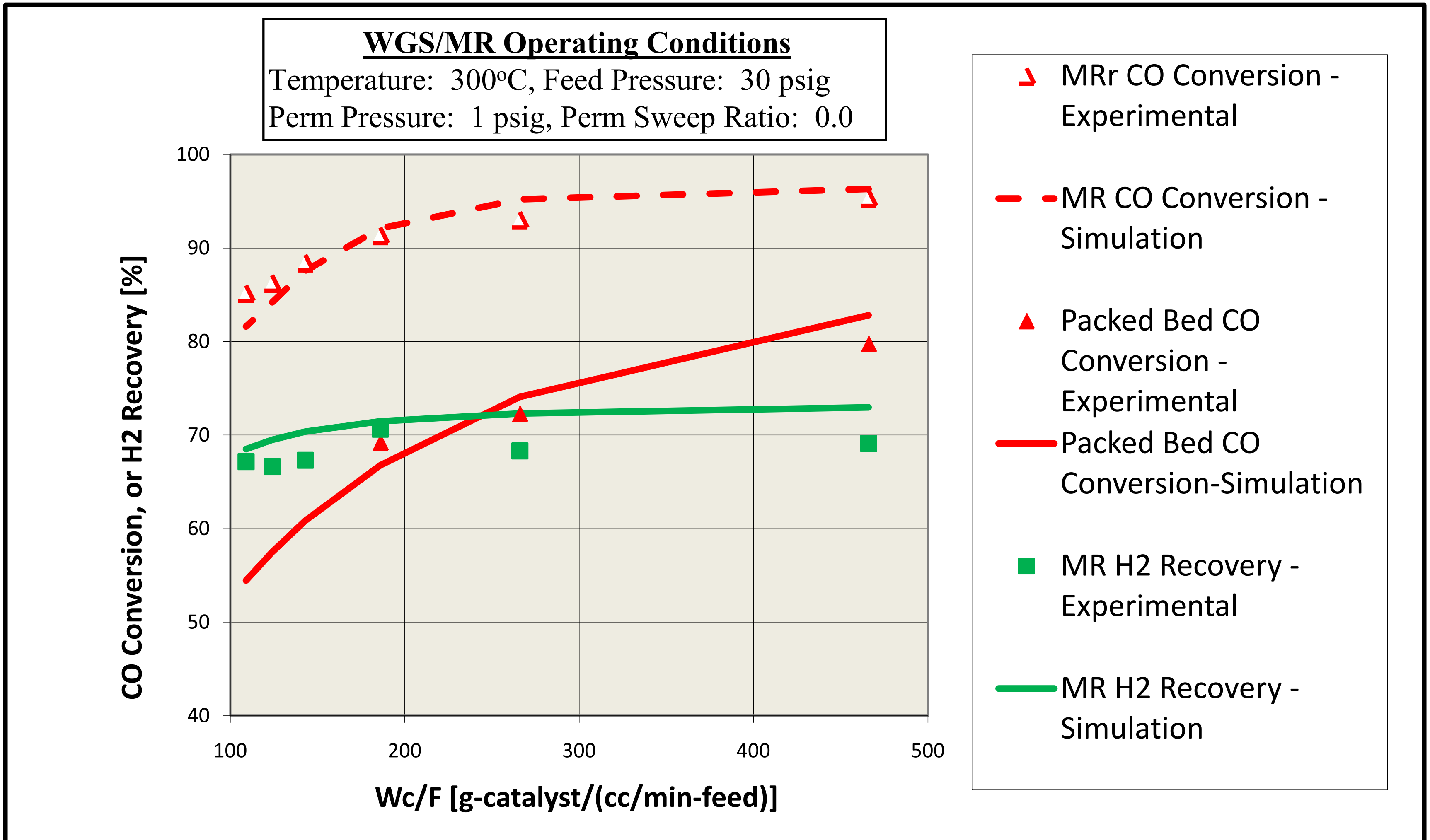
Physical Characteristics and Operating Parameters	
Pd Membrane:	30"L, 0.57cm OD
Temperature:	300°C
Catalyst:	30g of Cu/ZnO
Feed:	
H_2:CO:CO_2:CH_4:H_2O	5.22:1:0.48:0.22:2.8
Pressure:	30 to 50 psig
Sweep Ratio:	0 to 0.3

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

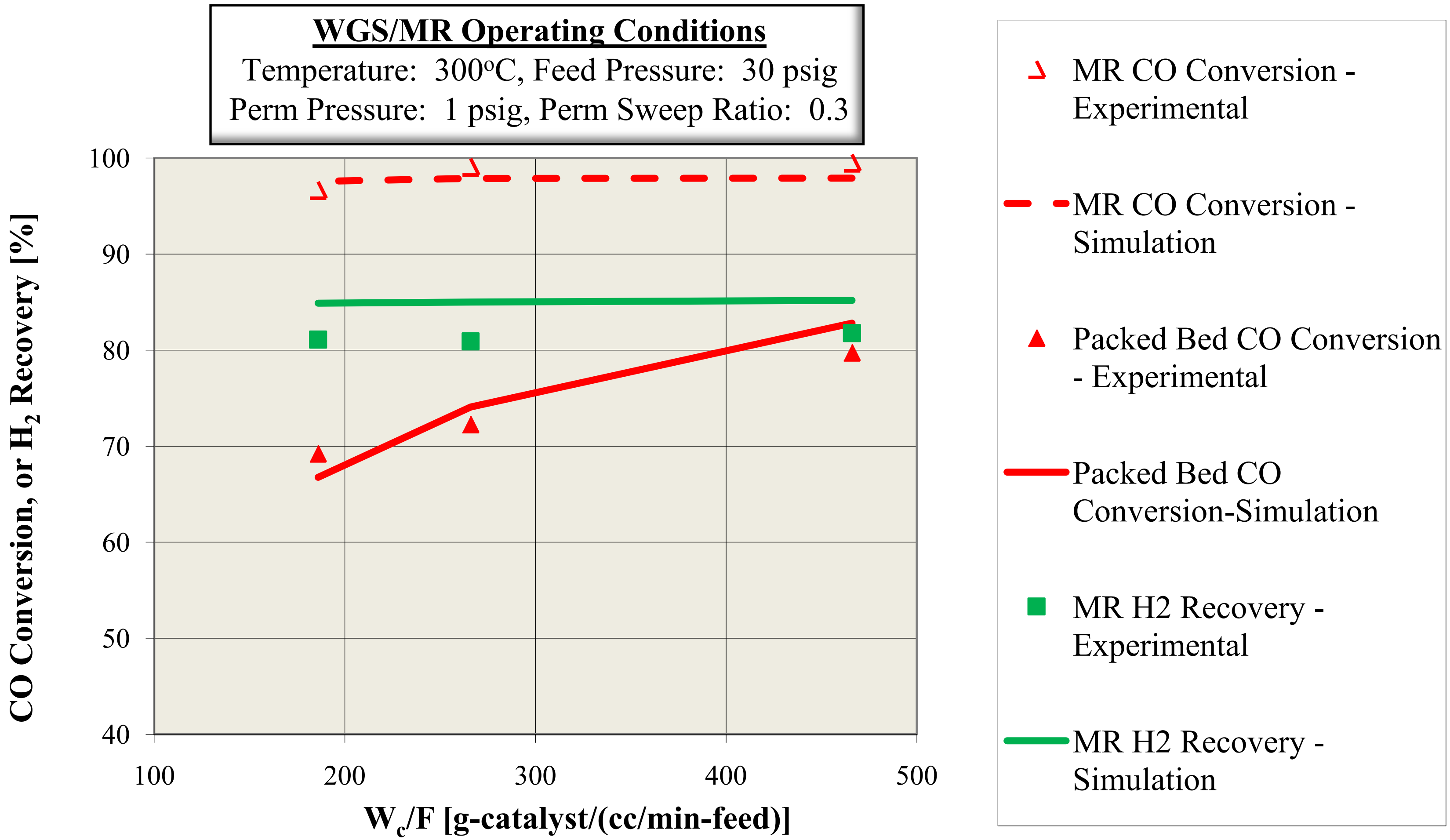
Experimental Results from operation *at 30 psig and with no sweep*



CO concentration of <50 ppm and H_2 Purity >99.9% were obtained experimentally.

WGS-LTS Membrane Reactor Activities in FY09-10

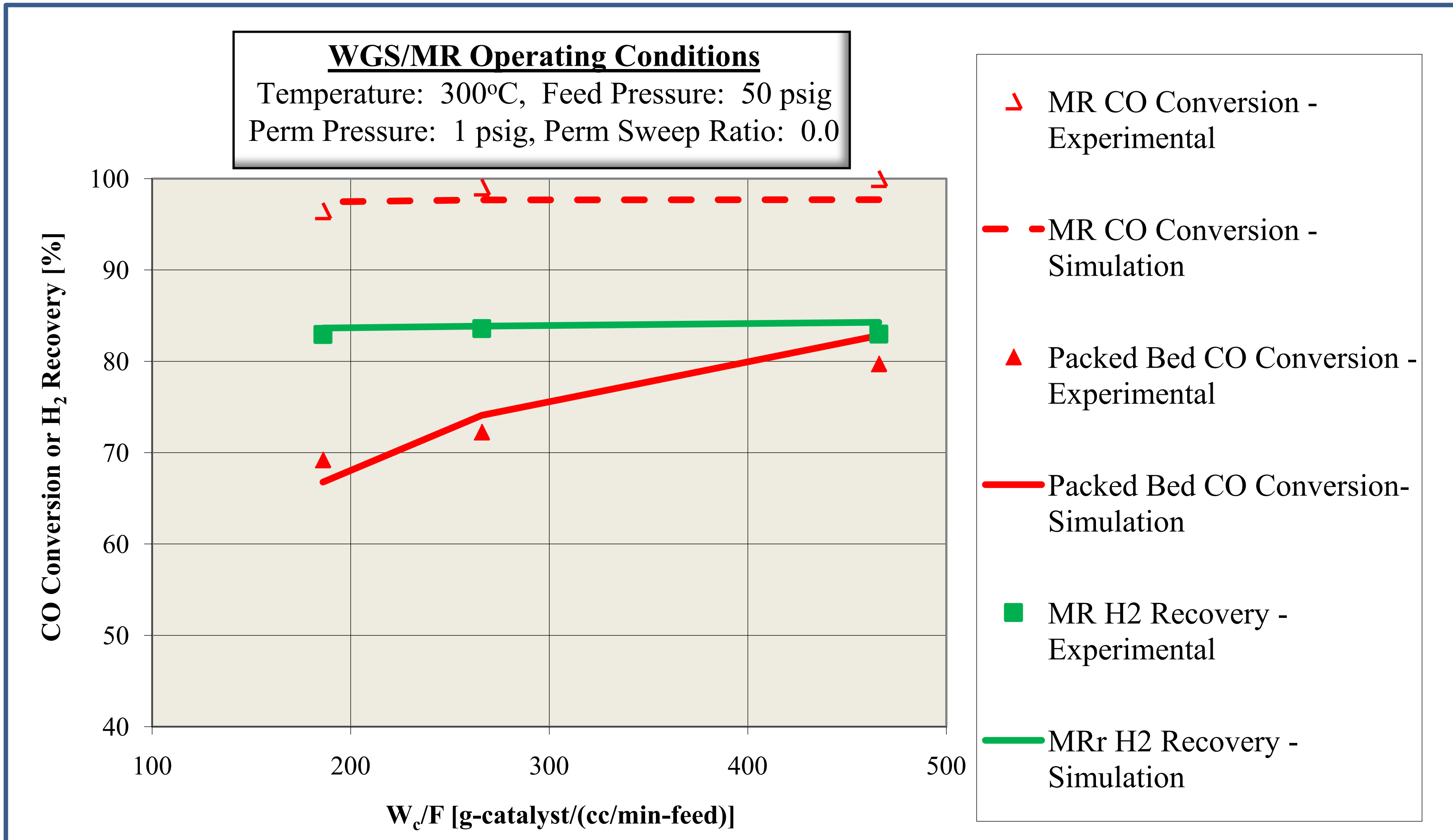
Experimental Results from the operation *at 30 psig and sweep ratio = 0.3*



>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_2 recovery ratio at >99.9% H_2 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 1st 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 2nd 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^{nd} generation module, which will be the focus of our Phase II project.

Phase II: Field Test Activities

1. Prepare 2^{nd} 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.