On-Board Vehicle, Cost Effective Hydrogen Enhancement Technology for Transportation PEM Fuel Cells
DE-FC04-02AL67628

Merit Review and Peer Evaluation
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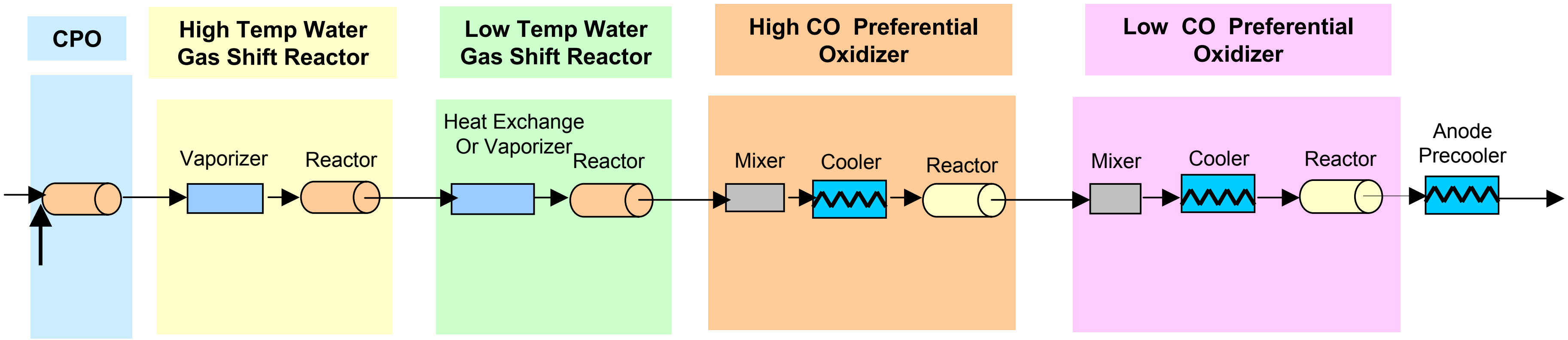
United Technologies Research Center

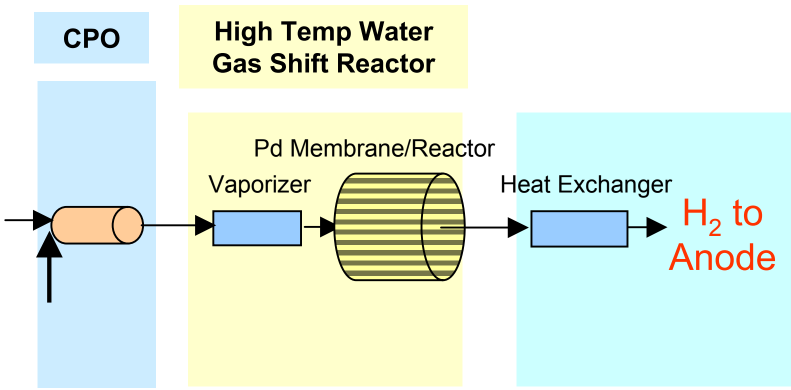
Integrated Pd Membrane Water Gas Shift Reactor

System simplification for size and cost reduction

Non Pd membrane FPS

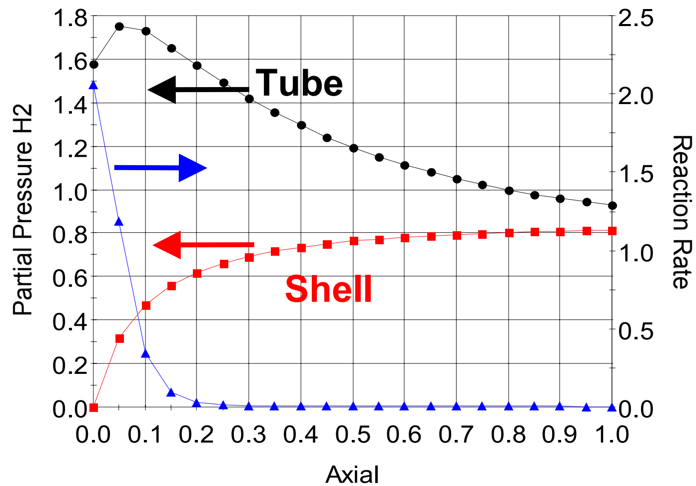


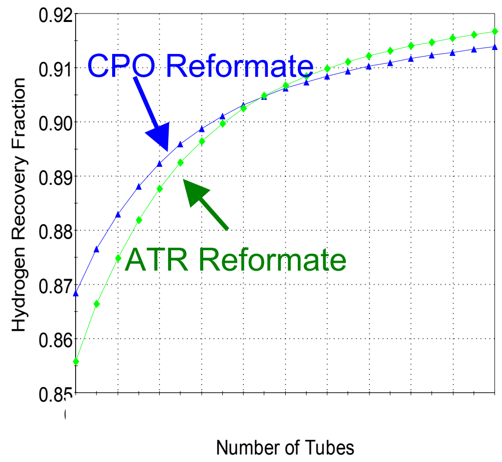
Simplified system

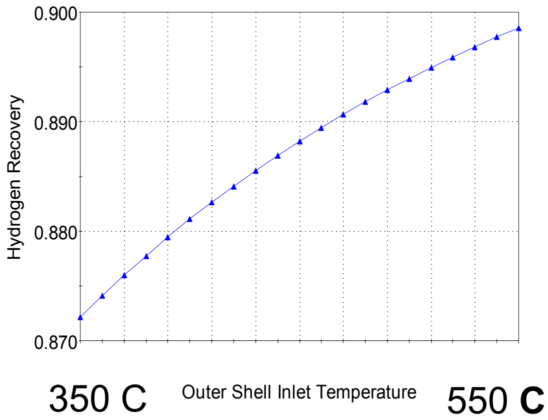


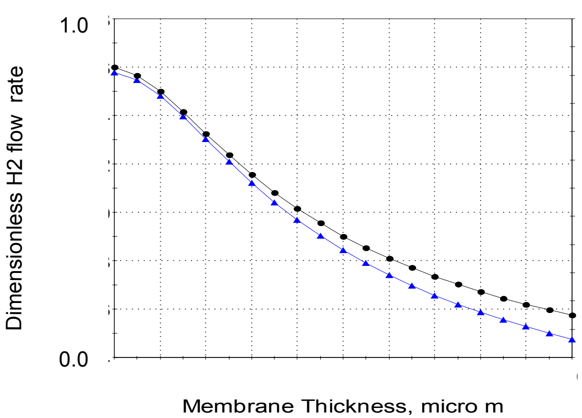
FPS and Membrane Reactor Modeling & Analysis

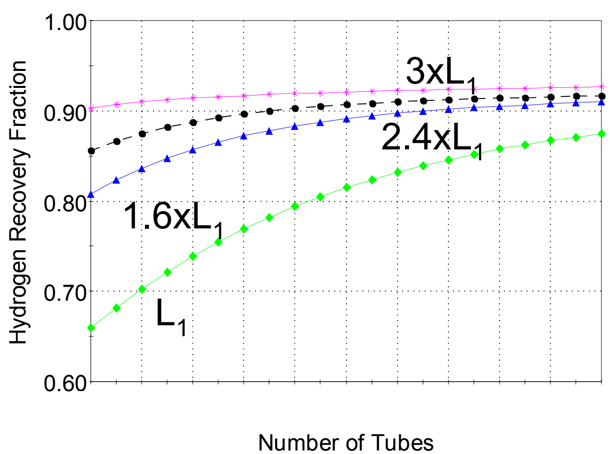
Reactor volume & efficiency is a trade off between differential pressure, membrane area (number of tubes, length) and permeance (Pd thickness)

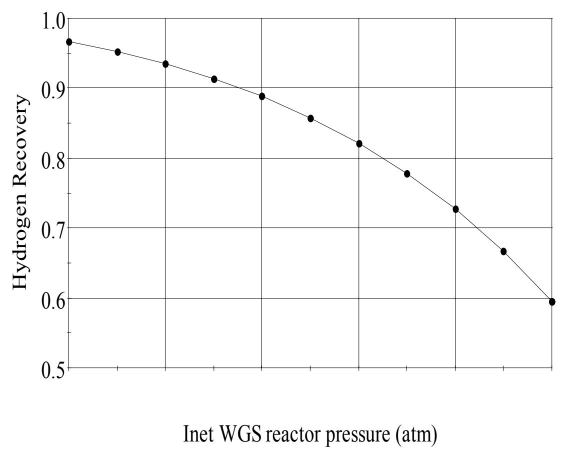






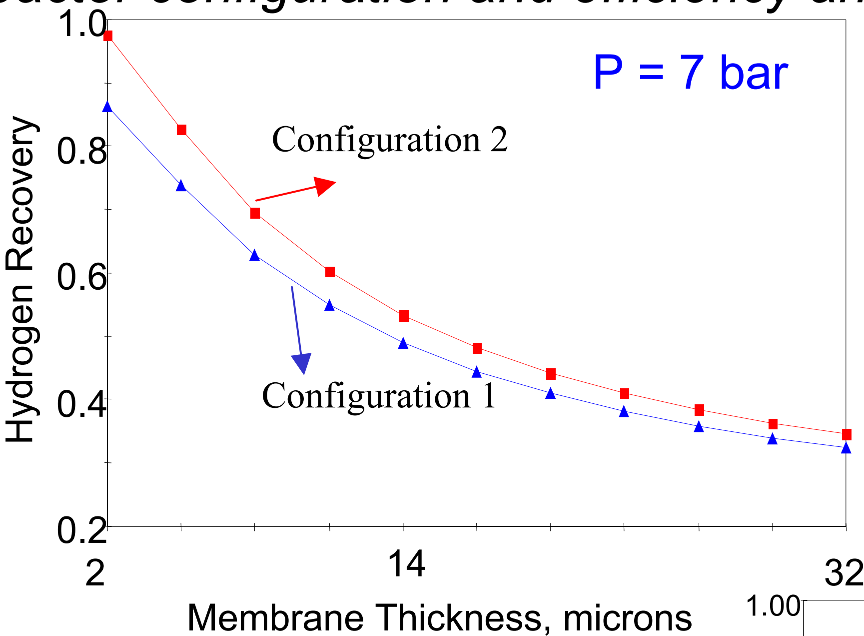




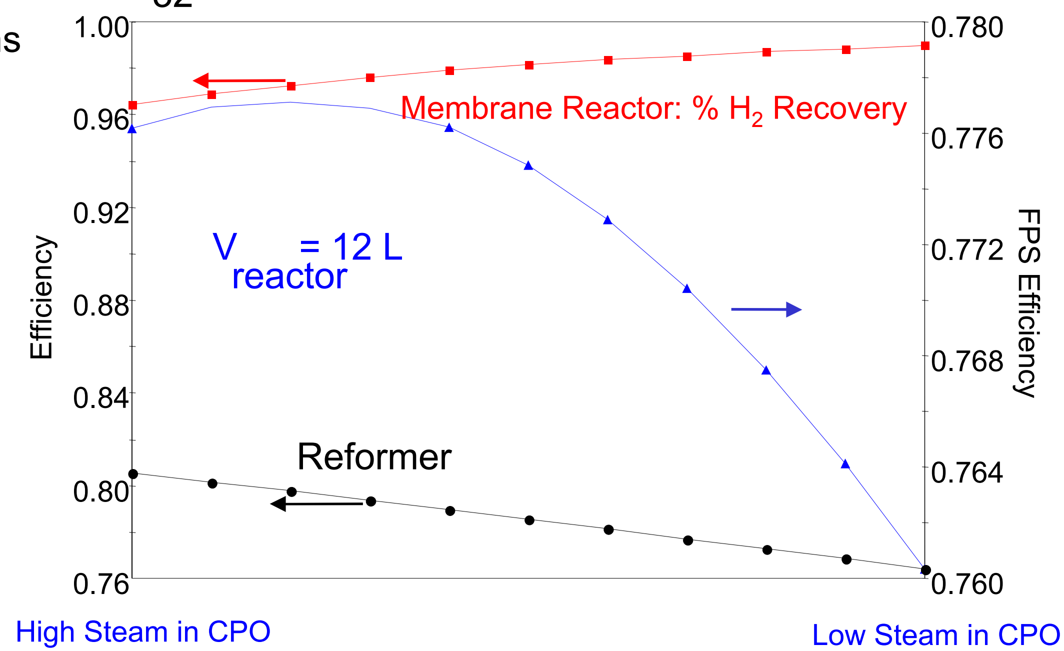


FPS and Membrane Reactor Modeling & Analysis

Reactor configuration and efficiency and FPS efficiency optimized



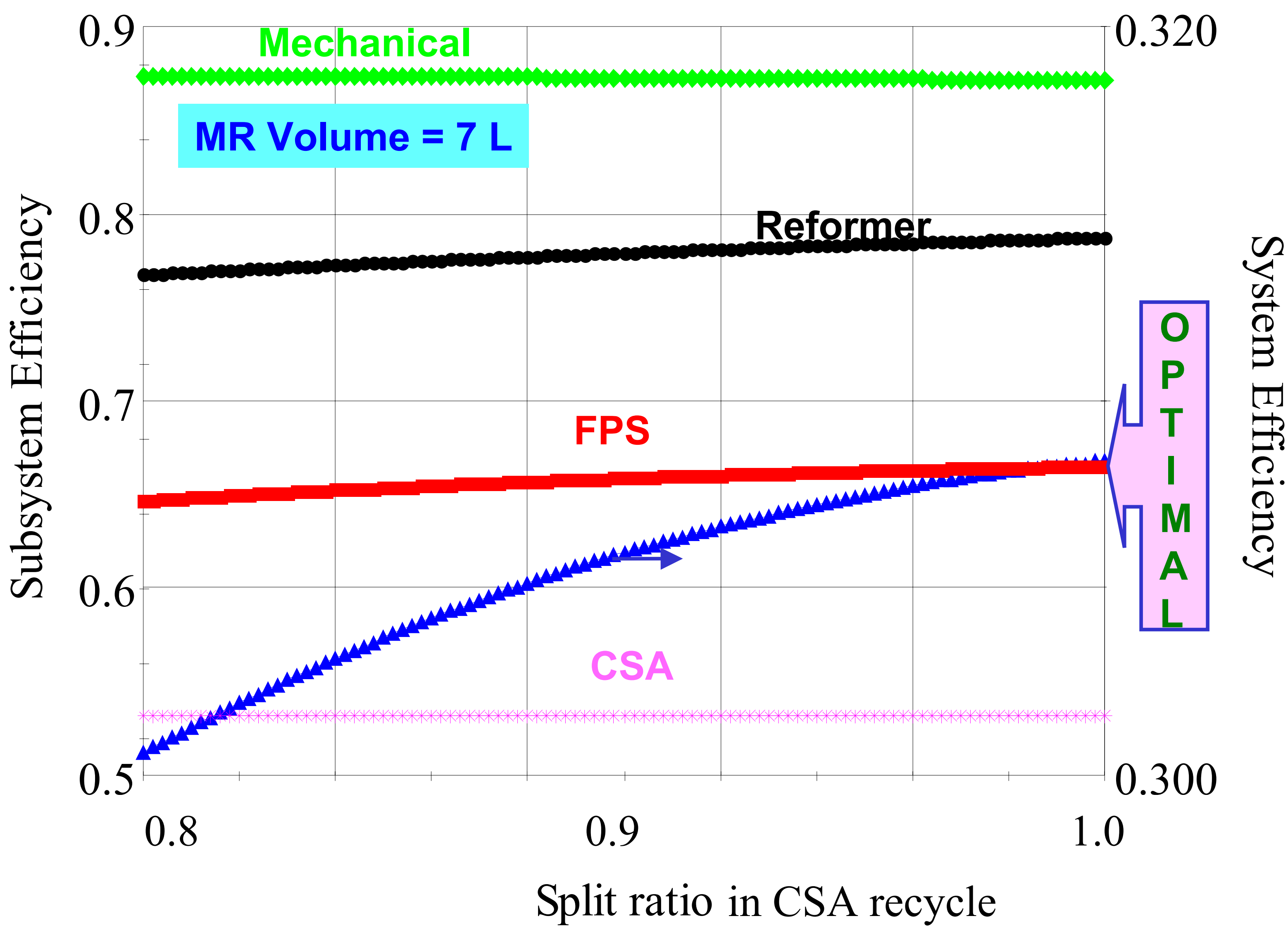
Configuration 2 provides better hydrogen recovery over configuration 1 for similar operating conditions and membrane thickness



For specified reactor volume, maximum reformer efficiency does not translate to optimal FPS efficiency

FPS and Membrane Reactor Modeling & Analysis

Optimum fuel cell system efficiency of 30.8% with ~68% FPS efficiency



FPS and Membrane Reactor Modeling & Analysis

Key Findings

- Adding an expander to the exit of the retentate gas stream from the membrane reactor to drive the air compressor improves mechanical efficiency dramatically (increases by 15 %)

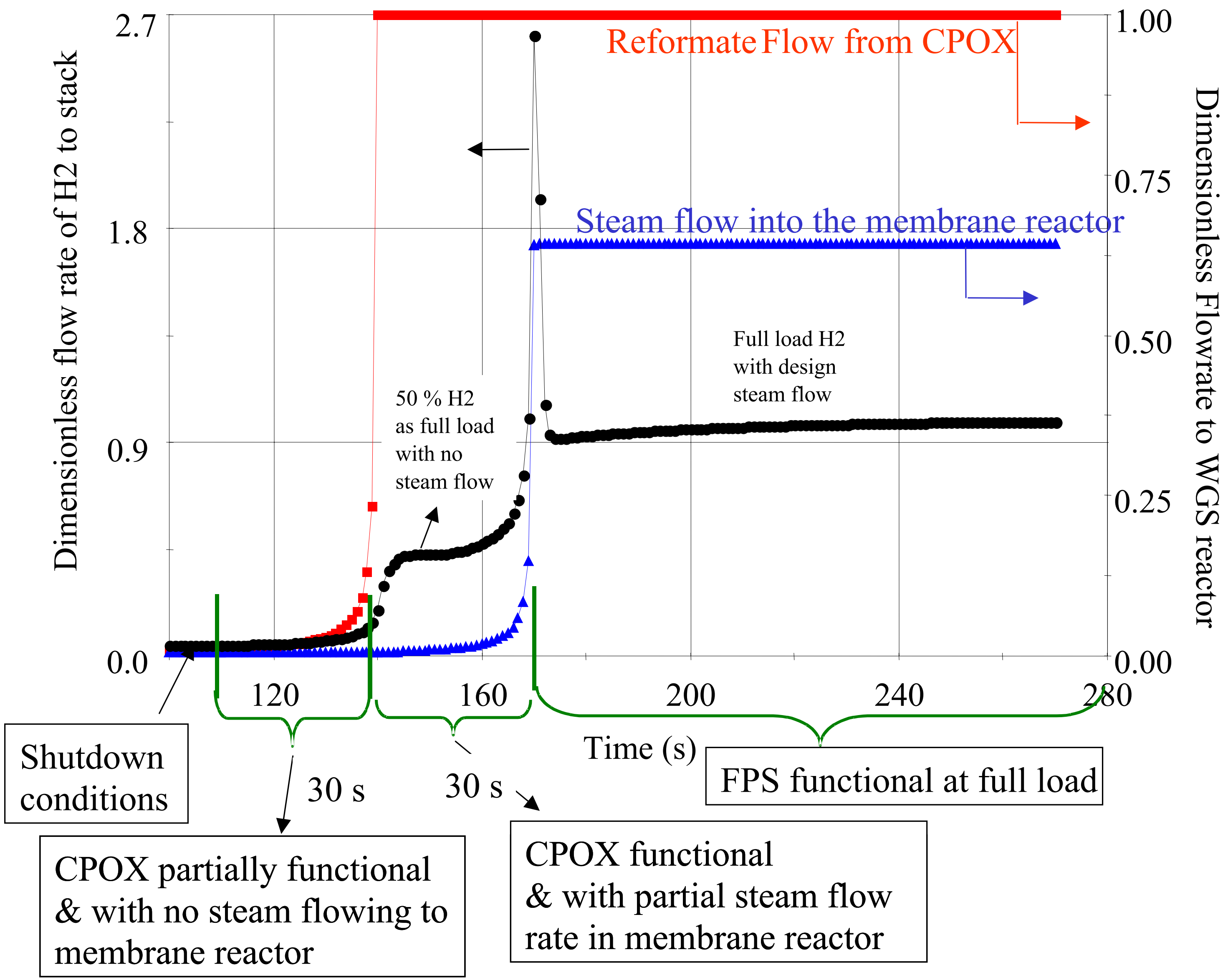
- Optimizing the membrane reactor configuration provides considerable membrane reactor volume reduction (to 7 L) in the system level model when operated “near optimal efficiency” (~30.8%). In order to sustain the power plant, the membrane reactor is forced to operate at lower efficiency (85 %)

- Maximum FPS efficiency does not necessarily imply maximum FC efficiency

- The overall FC system efficiency rather than FPS efficiency should be maximized

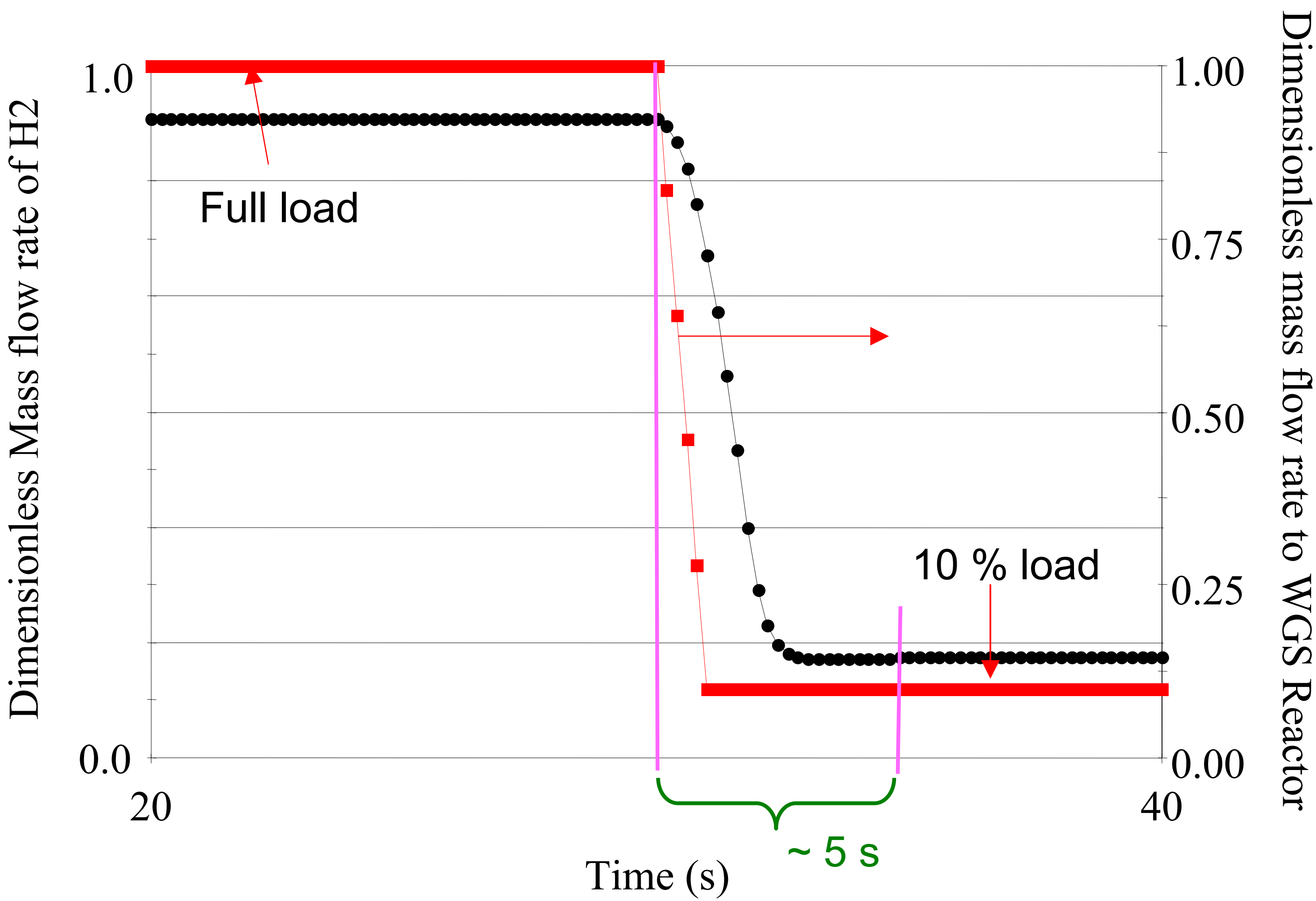
FPS and Membrane Reactor Modeling & Analysis

Startup time of less than 1 min for 50 % of FPS full power



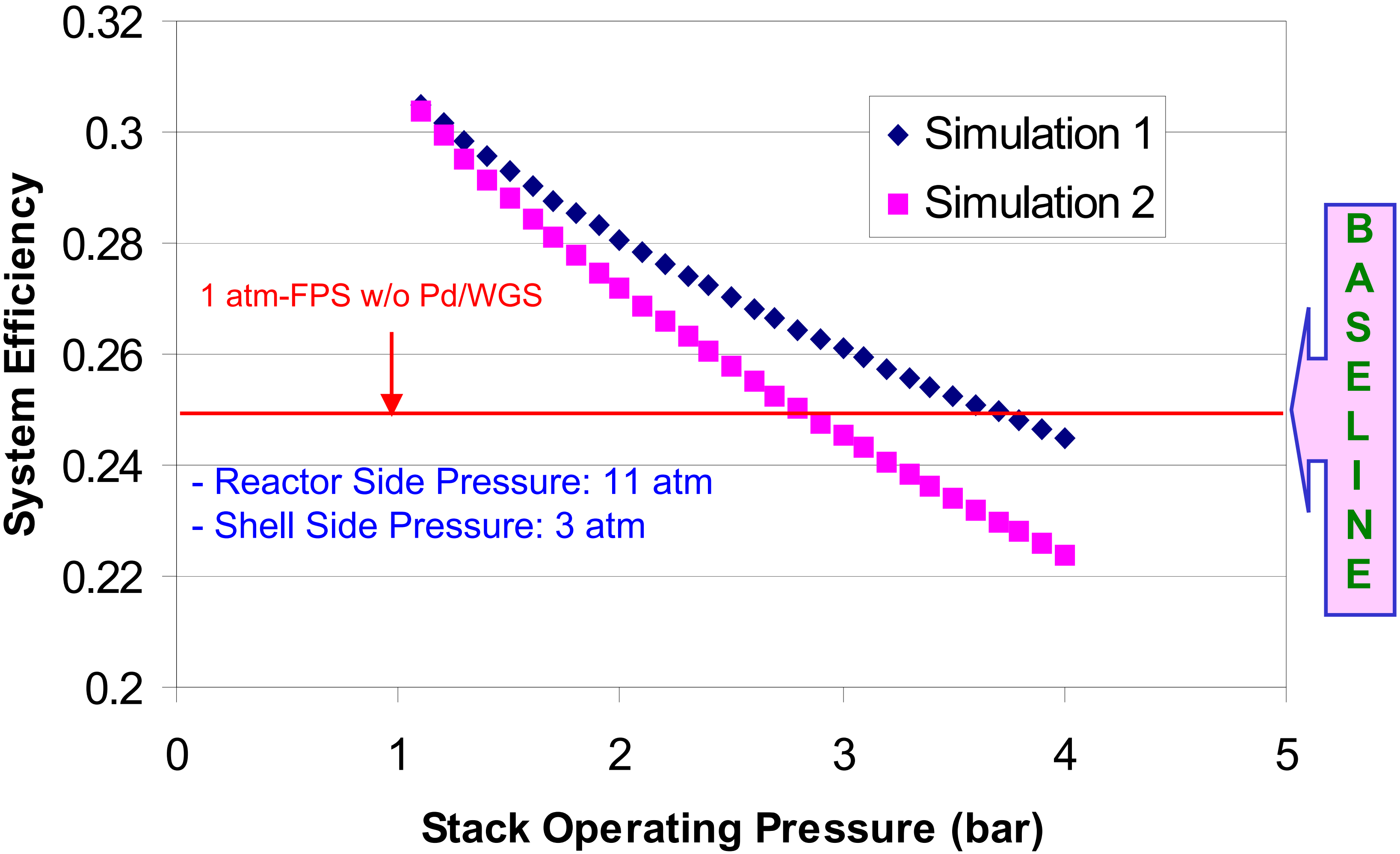
FPS and Membrane Reactor Modeling & Analysis

< 5 sec 90% to 10% down transient for the membrane reactor



FPS and Membrane Reactor Modeling & Analysis

Fuel cell system efficiency is reduced at 3 atm of operating pressure

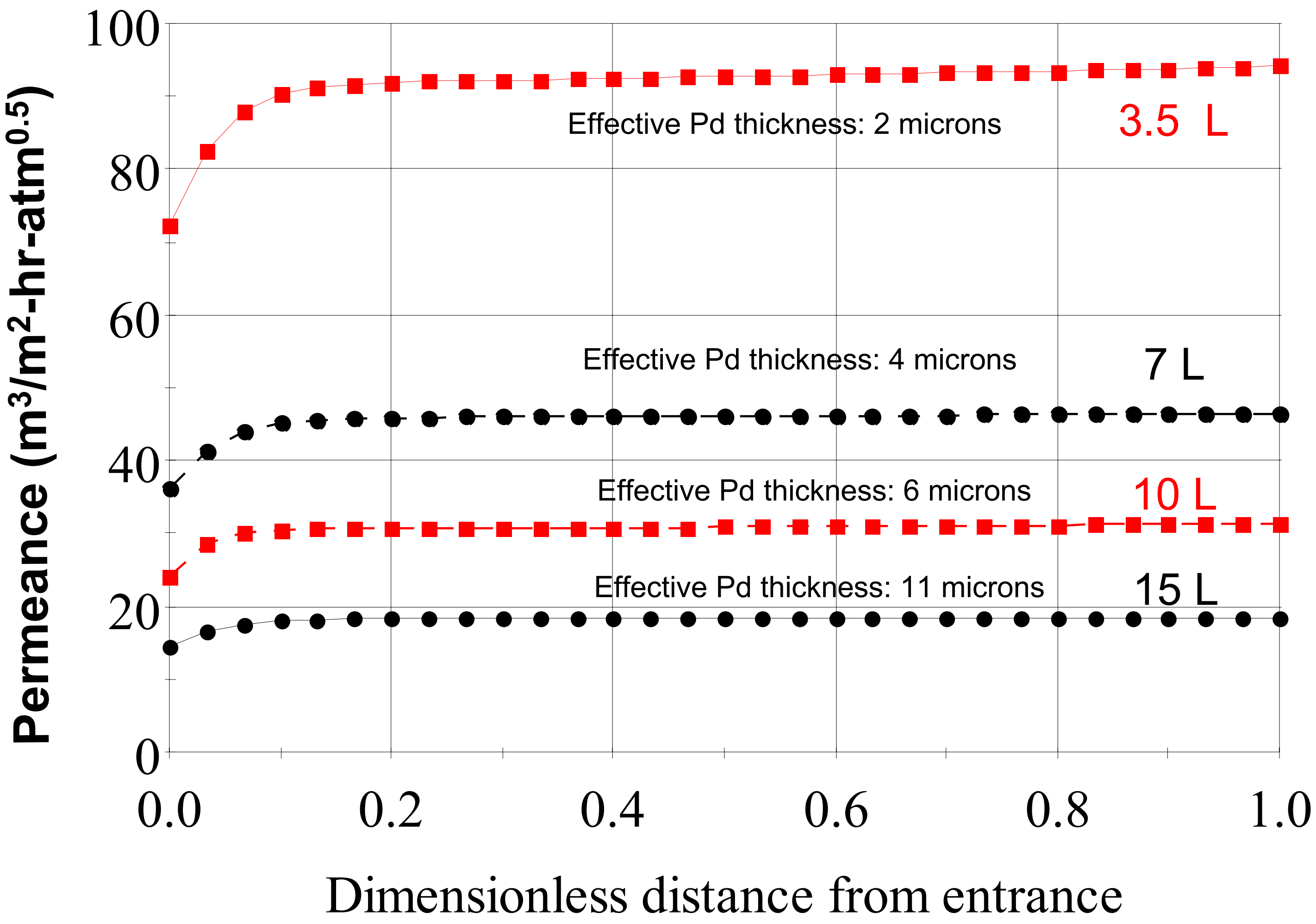


Simulation 1: Very Good compressor/Expander efficiency (0.8)

Simulation 2: Reasonable compressor/Expander efficiency (0.7)

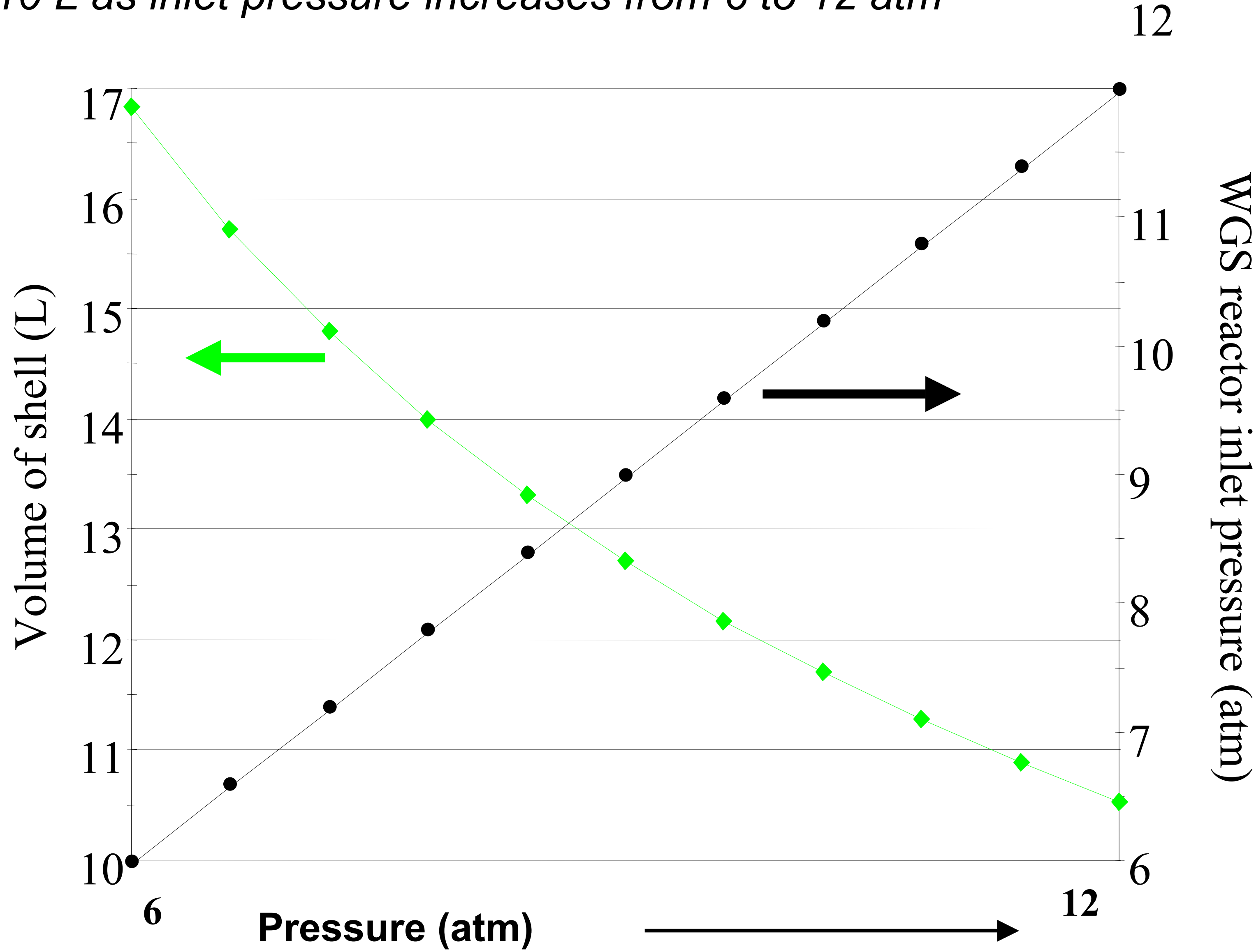
FPS and Membrane Reactor Modeling & Analysis

< 10 L reactor volume with $\eta_{FC\ power\ plant}$=30.8%, η_{FPS}=68% for 6 atm inlet pressure and < 6 microns Pd thickness (> 30 m^3/m^2-hr-$atm^{0.5}$ permeance)



FPS and Membrane Reactor Modeling & Analysis

For permeance of 20 m^3/m^2-hr-$atm^{0.5}$, the reactor volume decreases from 17 L to 10 L as inlet pressure increases from 6 to 12 atm



FPS and Membrane Reactor Modeling & Analysis

Excellent progress made towards DOE system targets

Metric	DOE Target	Non Membrane FPS	Status (04/03)
FPS Efficiency	78%	67%	77.7%
FPS Power Density (with insulation)	> 700 W/L	570 W/L	1100 W/L
H_2 Recovered in Pd WGS Reactor	-	N/A	96%
FPS Cost ($/KW)	25	C	0.4xC + $16/KW
FPS Start Up Time	< 1 min for 33% Full Power (FP)	~ 3 min for < 50% FP (non optimized)	< 1min (~30 sec for Pd/ WGS) for 50% of FP
FPS 10%-90% Transient Response Time	≤ 5 sec	-	< 5 sec for Pd WGS Reactor
PEM Fuel Cell System Efficiency (ambient P)	-	24.7%	30.8%

Based on FPS subsystem (yellow)

Based on power plant system (blue)

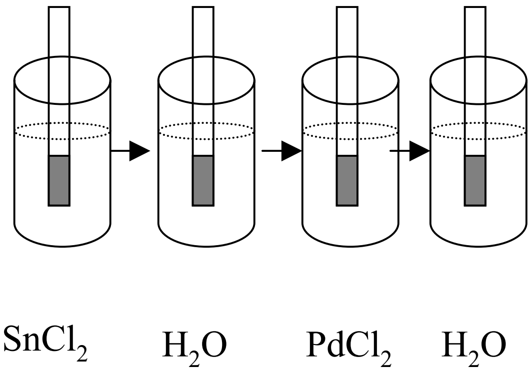
Pd Membranes Synthesis

Electroless plating process (current state of the art)

Activation of the support

Surface of the support seeded with Pd nuclei

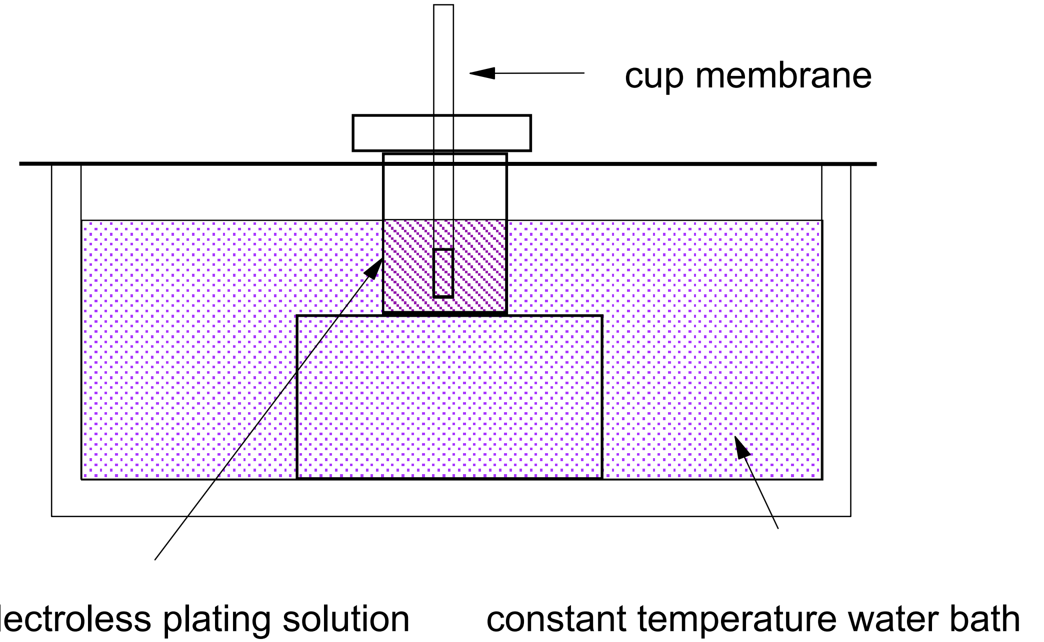
$$Pd^{2+} + Sn^{2+} = Pd^0 + Sn^{4+}$$



Electroless plating

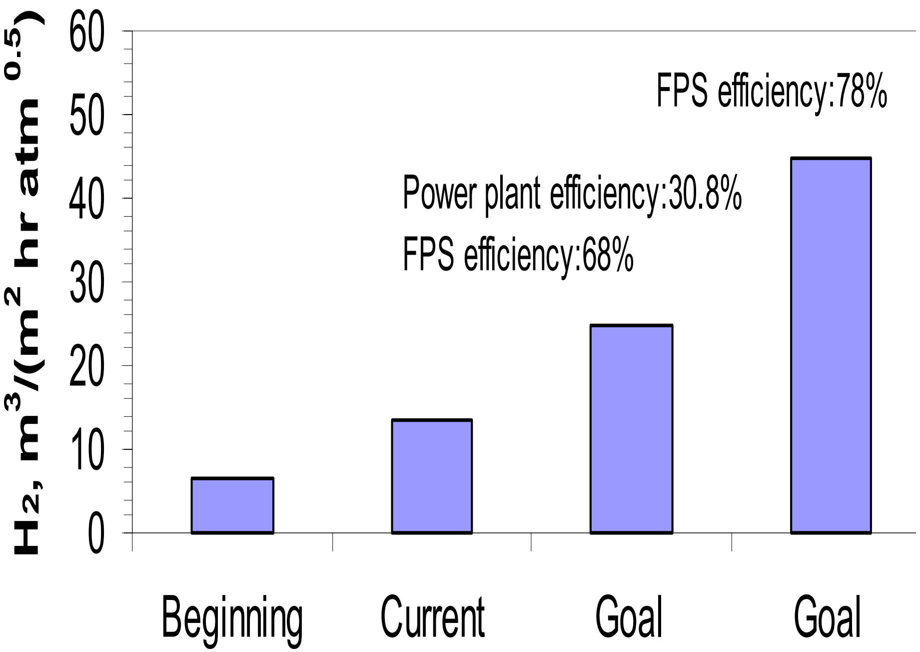
Autocatalyzed reduction of complex on target surface

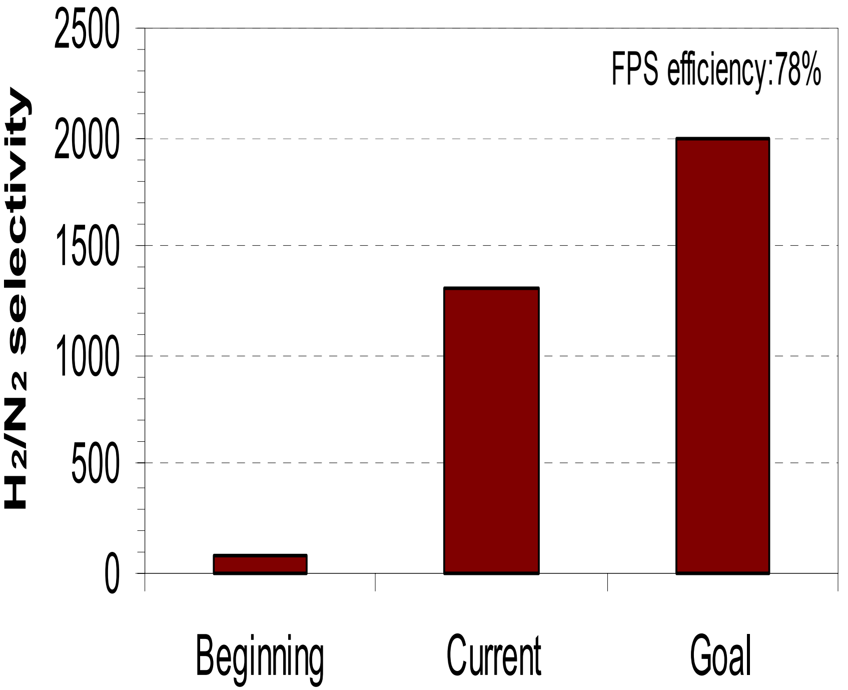
$$2Pd^{2+} + H_2NNH_2 + 4OH^- = 2Pd^0 + N_2 + 4H_2O$$



Pd Membranes Synthesis

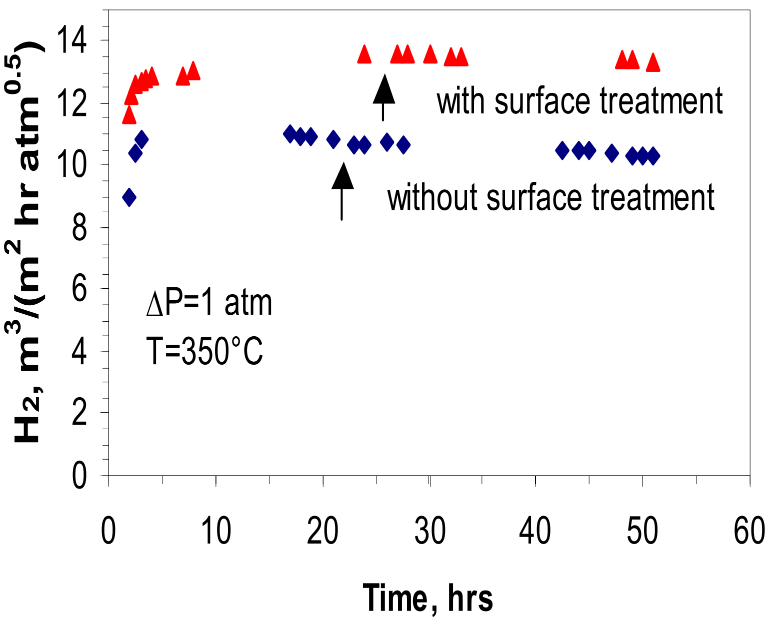
Significant progress made on both permeance and selectivity. On trajectory to achieve project goals

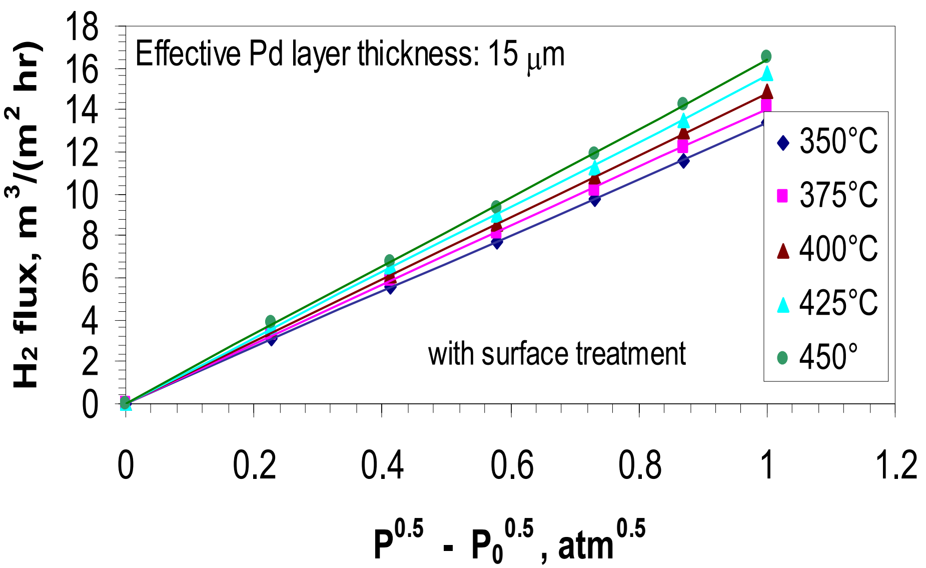




Pd Membranes Synthesis

Surface treatment enhances Pd membrane H_2 permeance. Process not optimized



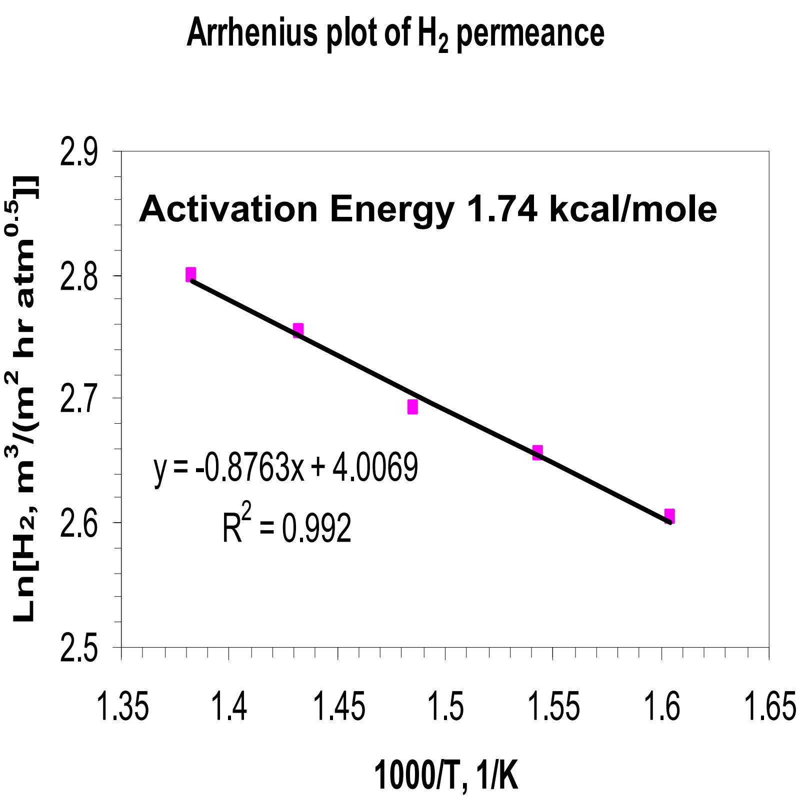


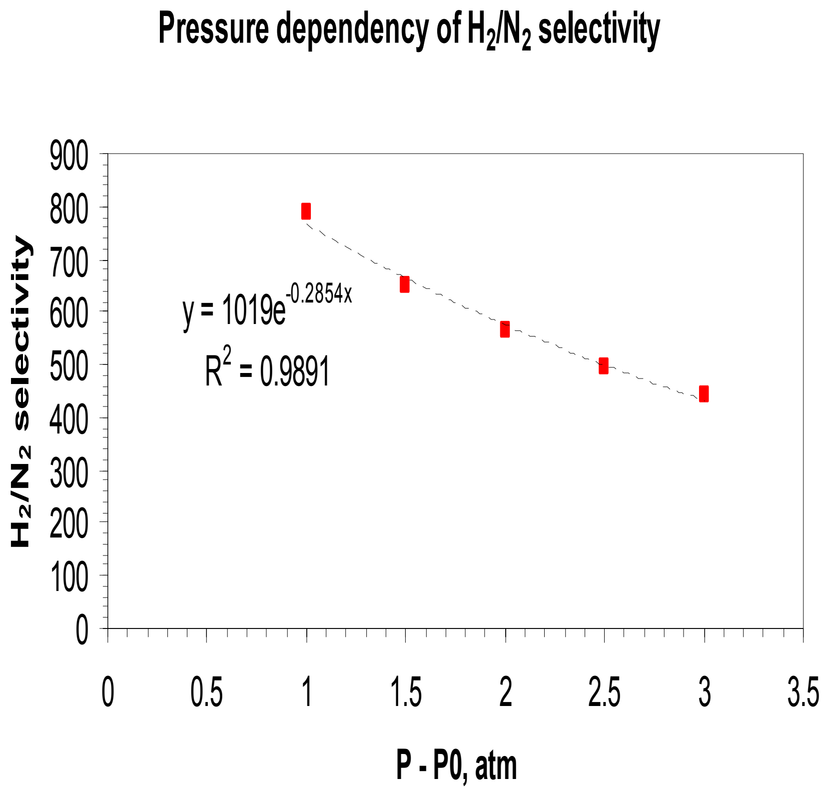
<u>H_2/N_2 selectivity:</u>

- 1100 without surface treatment
- 800 with surface treatment

Pd Membranes Synthesis

Temperature has a weak effect on permeance but pressure has an adverse effect on selectivity





Summary of Accomplishments

- Pd membrane WGS reactor optimized for H_2 recovery efficiencies between 85-96%

- Optimum FPS (77.7%) and PEM fuel cell power plant system efficiency (30.8%) identified

- Excellent progress made towards DOE FPS volume, start up, transient response and cost targets

    - Simulated Pd Membrane/WGS FPS: 1100 W/L, < 1 min for 50% full power, 5 sec 10%-90% transient response and \$16/kW +0.4x(Cost of FPS w/o Pd) projected cost

- Optimum FPS efficiency does not correspond to optimum PEM FC power plant efficiency

- Significant progress made on synthesis of Pd membranes on both H_2 permeance and Selectivity

    - Current Status: 13.5 m^3/m^2-hr-$atm^{0.5}$ H2 permeance @ 350 ^oC & 800 selectivity at 1 atm of differential operating pressure

- On track to achieve the aggressive project goals with a Pd alloy: 2x-3x increase in permeance, 2,000 selectivity at 1 atm of differential operating pressure

Future Work

Targeted to increase membrane H_2 permeance by 2x-3x and selectivity by > 2x on a Pd alloy membrane

- Synthesize Pd membranes on internal surface of PSS substrate
- Synthesize Pd membranes on smoother external surface of PSS substrate.
- Seek PSS substrates with narrow pore size distribution
- Seek a PSS substrate tube coated on the internal surface with a ceramic-coated layer of 0.02 – 0.1μm pore size
- Alternative intra-pore Pd deposition process development

  - ❑ Decision point: Select best approach (10/30/03)

- Synthesize Pd alloy membranes (Start: 05/15/03)

2003 Milestones

Stated milestones represent significant stretch

Requirement	Project Goals	Calendar Year 2003 Goals (12/20/03)	Current Status
H_2 Permeance at 350 ^oC (in m^3/m^2-hr-$atm^{0.5}$) with a Pd Alloy	25-45	25	13.5 with pure Pd
Maximum Equivalent Pd Phase Thickness	< 5 microns	< 8 microns	15 microns
H_2/N_2 Selectivity at 350 ^oC and differential operating pressure of: - 1 atm - 6 atm	 2,000 500	 1,000 250	~200 (Projected from Data between 1-3 atm) ~ 800 ~ 180 (Projected from Data between 1-3 atm)
Membrane Module Life Testing under HT WGS Conditions	5% Performance loss for 400 hrs & 100 Start Up/Shut Down cycles	10% Performance loss for 150 hrs & 10 Start Up/Shut Down cycles	

Key Technical Barriers

Significant technical barriers must be overcome to demonstrate (critical risk reduction) and commercialize this technology

- Achieving a pin hole -“free”, thin (< 5 microns) Pd alloy, metal-supported membrane that will withstand up to 1,000 start up/shut down cycles for 4,000 hrs with < 25% performance deterioration in a reformate (high CO) gas environment

- Identification of a cost-effective route to commercialize Pd alloy metal supported membranes for mass production