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Commercialization of Pd Alloy Composite Membranes for Small Scale Hydrogen Generation

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This presentation does not contain any proprietary or confidential information

Presentation Outline

- Brief overview of Pall
  - Core technologies relevant to Pd membranes
- Drivers for hydrogen generation
- Small scale hydrogen generation application
  - Market segments and opportunity
  - Requirements
  - Challenges
- Pd-alloy composite membrane and module development
  - Porous substrate and Pd-alloy membrane development
  - Membrane parametric testing and results
- Future activities and Summary

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Pall – A global company

- 78 Locations in 34 Countries, Approximately 10,000 Employees
- Annual sales ~ $ 2.7 Billion
- Core business
  - Filtration and Separation

Pall Industrial

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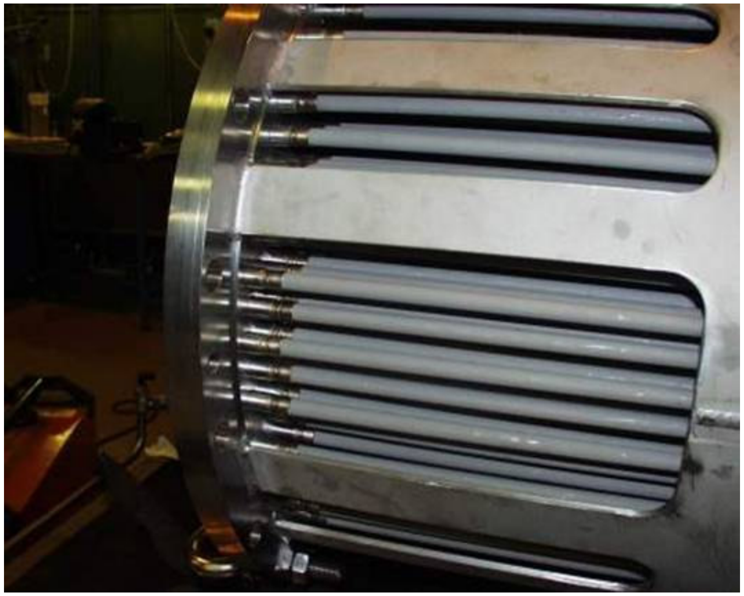
Pall's Core Technologies

- Unique Porous/Nonporous Materials
  - Sintered Porous Metals
  - Ceramic Structures and Processing
  - Inorganic Metal (Pd-alloy) Membranes
- Manufacturing of Membranes and Modules
  - Scale-up of substrates and membranes
  - Welding of porous tubes to non-porous tubes
  - Fabrication of multi-tubular modules for High Temperature and High Pressure Application
- Application Engineering/Technical Support
  - Modification of membranes and modules for specific applications



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Hydrogen Economy and Production

Two major drivers for hydrogen production

- Hydrogen as energy carrier – Transportation, Power generation and heat generation
- Conversion of fossil/biomass fuels to Hydrogen with pre-combustion CO_2 capture to reduce GHG emissions

Hydrogen Production

- Can be produced from multiple pathways – natural gas, logistic fuels e.g. methanol, coal, and biomass
- Near term large scale production from Natural Gas
- Longer term large scale hydrogen production from Coal and renewable sources (biomass, solar, wind)
- Small scale production from logistic fuels and NG

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Scale of Hydrogen Production

- Central hydrogen production – Very large scale
  - Million Kg/day – NG, coal, biomass feedstocks
- Distributed hydrogen production (fueling stations)
  - Up to 1500 Kg/day (~ 1 MW equivalent H_2) – NG, BILI
- On-site industrial hydrogen production
  - Up to 500 Kg/day – NG, oil/naphtha
- Small stationary power sources
  - Up to 15 Kg/day (~ 10 kW equivalent H_2) – logistic fuels
  - Back-up power, Remote power – (UPS)
  - Combined heat and power - (CHP) – Residential
- Hydrogen purification membranes could be used at all of these scales

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Small scale hydrogen generation
Market and Opportunity

- Back-up power, Remote power – (UPS)
  - Telecom towers for mobile phones in developing countries
  - About 1 million towers in operation just in India + China
  - Typically need 5 kW power either on-grid or off-grid
  - Even on-grid systems need up to 5 hours/day backup power
  - PEM fuel cell based telecom power systems exhibit greater reliability, quieter operation, less pollution/noise
  - Attractive alternative to diesel generators in niche areas
- Combined heat and power (CHP) – Residential (1-10 kW)
  - Strong programs in Japan, Korea, and Europe
- 2010 sales of small stationary power systems
  - ~7500 units for CHP (85%) and backup/remote power
  - Projected to increase rapidly over the next few years.

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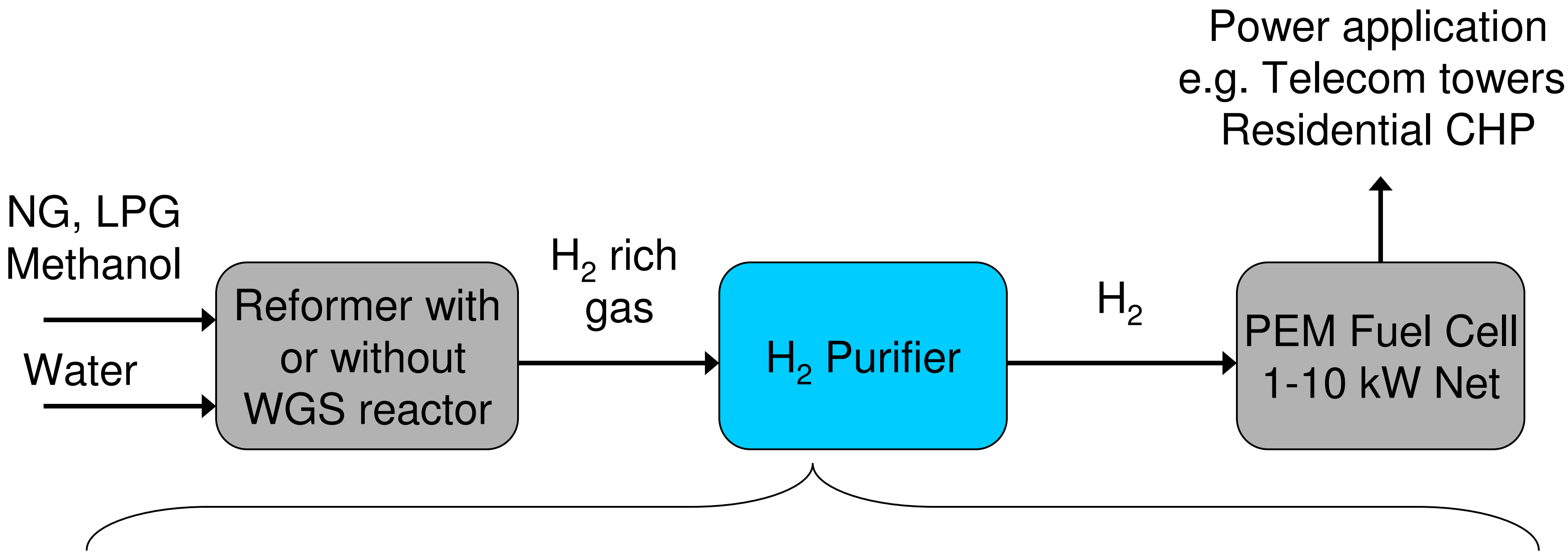
Small Stationary Power System



Options: Pd-alloy foils or tubes (current) - Expensive

Pall's solution – lower cost

Pd-alloy composite membrane module

Single membrane tube trials
Design/fabrication/testing of multi-tube modules
Durability and operation/thermal cycling tests
Field test trials

Hydrogen purifier requirements

- Currently working with methanol reformers
- Hydrogen output needed ~ 12 SLPM/kW
- Hydrogen purity needed > 99.95% over 1,000 hours
- Typical reformate conditions
  - 150 to 250 psig pressure
  - 300 to 400 C temperature
  - 5 to 10 % CO depending on WGS reactor use
  - 55 to 65% H_2
  - Up to 1% un-reacted fuel
- Reformer/purifier cycling with load demand
  - Run, standby, and shutoff conditions
- Customer trials and testing at customer conditions

Hydrogen purifier - Challenges

- Physical integration of purifier with the reformer
- Thermal integration to heat purifier (~400 ^{o}C) and to minimize overall heat requirement
- Reformer/purifier operation modes
  - Run – load following reformer operation
  - Standby – reformer off, pressure/flow bleed system maintained at T_{min}, possible air infiltration
  - Shutdown – complete thermal cycle
- Frequent changes in membrane feed gas conditions
  - Composition, pressure, temperature
  - Unsteady-state operation
- Need time responsiveness – low thermal mass
- Acceptable hydrogen purifier cost

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Pd-alloy membrane development

Existing technology – Pd-alloy tubes and foils

- Need sufficient thickness for structural strength
  - Tubes ~ 50-60 µm, Foils ~ 25 µm
- Expensive, Niche applications – small H_2 purifiers

Pall's Technology – Thin Composite Membranes

- Thin films on porous metal substrates
- Substrate provides structural integrity and strength
- Fine pore size substrate allows for thin, defect-free Pd-alloy films by various techniques ~ 1 – 5 µm
- Membrane tubes welded in to housing - Better seals for High T – High P applications
- Lower cost – thin Pd layer and less membrane area

Components of a Composite Membrane

1) Porous stainless steel (AccuSep®)

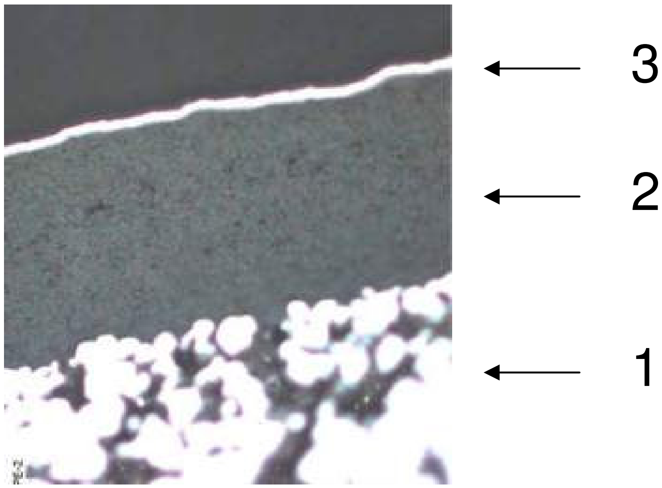
- Provides mechanical support that can withstand the operating conditions of the process
- Critical features: permeability, weld configuration, mechanical, thermal and chemical compatibility

2) Diffusion barrier (ceramic)

- Enables formation of functional layer
- Critical features: surface properties, material, gas permeability, number of defects

3) Pd alloy membrane

- Functional layer provides for gas separation
- Critical features: thickness, alloy composition, durability and number of defects



Excellent adhesion to zirconia layer, uniform thickness, and surface contour following of Pd-alloy metal film

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Pd-alloy Membranes

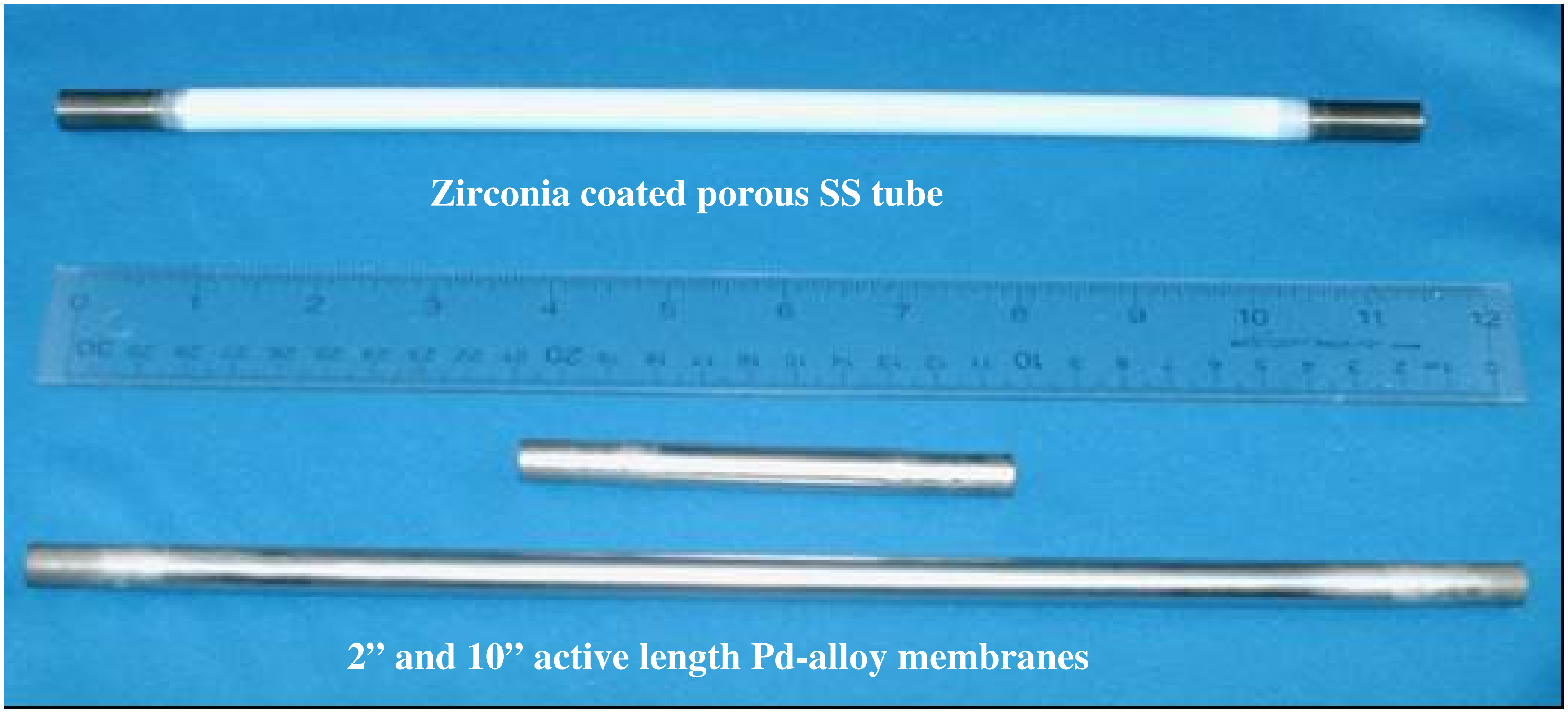
Typical Performance Data

Average for >100 membranes

- **H_2 flux 150 SCFH/ft^2, H_2/Ar SF ~ 10,000**

Under test conditions

- **Pure gas permeation @ 400 C, Feed 20 PSIG**
- **Permeate atmospheric**



Zirconia coated porous SS tube

2” and 10” active length Pd-alloy membranes

Pd-alloy Membrane Modules

12-tube module with
12” elements
~ 5 kW equivalent H_2 Production
~ 60 slpm with methanol reformate

Customer process integration and testing ongoing with 2.5 kW and 5 kW equivalent Hydrogen Generation systems

Relevant Membrane Testing

- Hydrocarbon reformer based hydrogen generation conditions – methanol and NG –
  - Membrane used as hydrogen separator
  - Membrane durability in reformate environment
  - Membrane thermal cycling stability
  - Steam to CO ratio needed to prevent coking
  - Minimization of concentration polarization
- Customer trials and testing at actual customer site conditions ongoing

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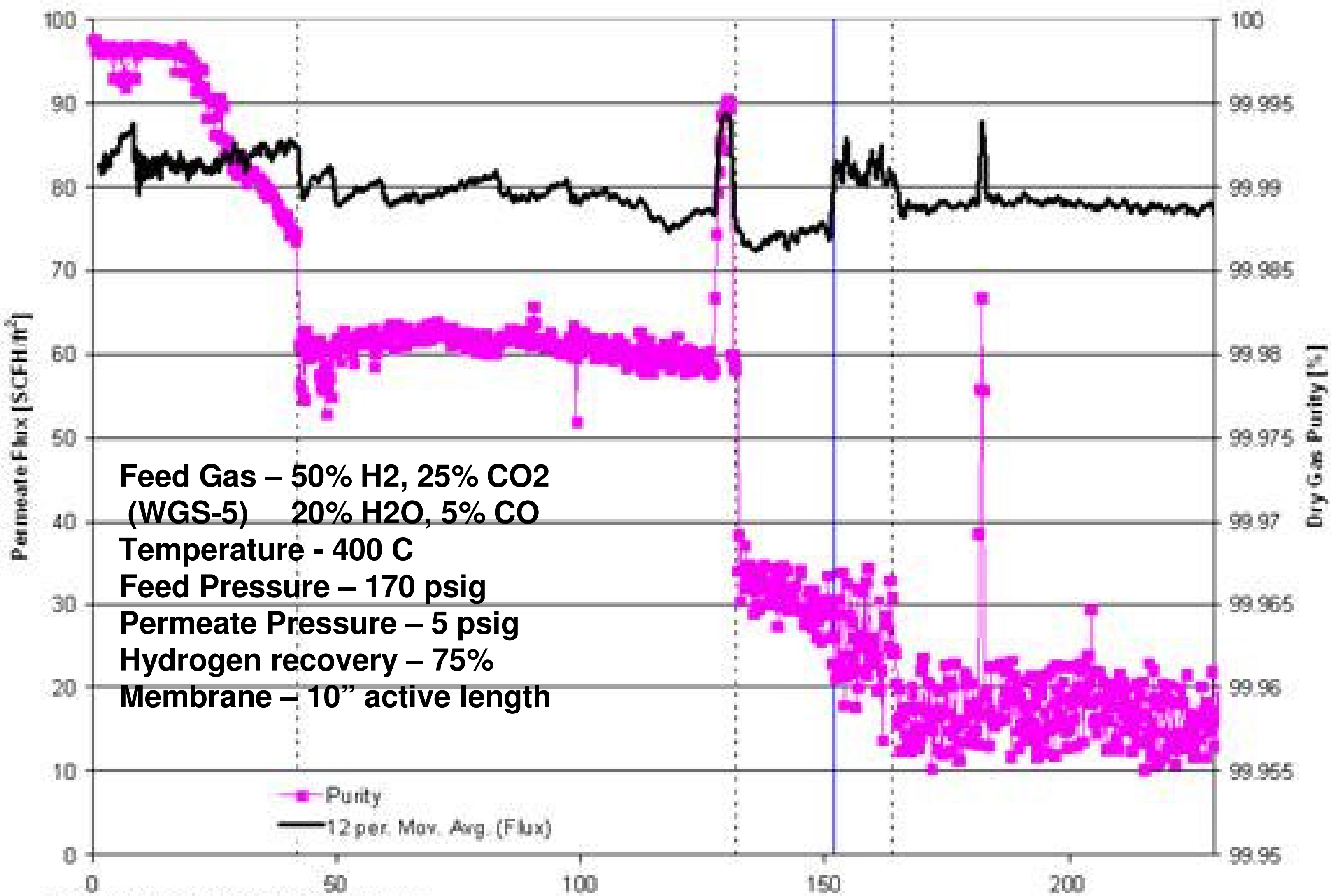
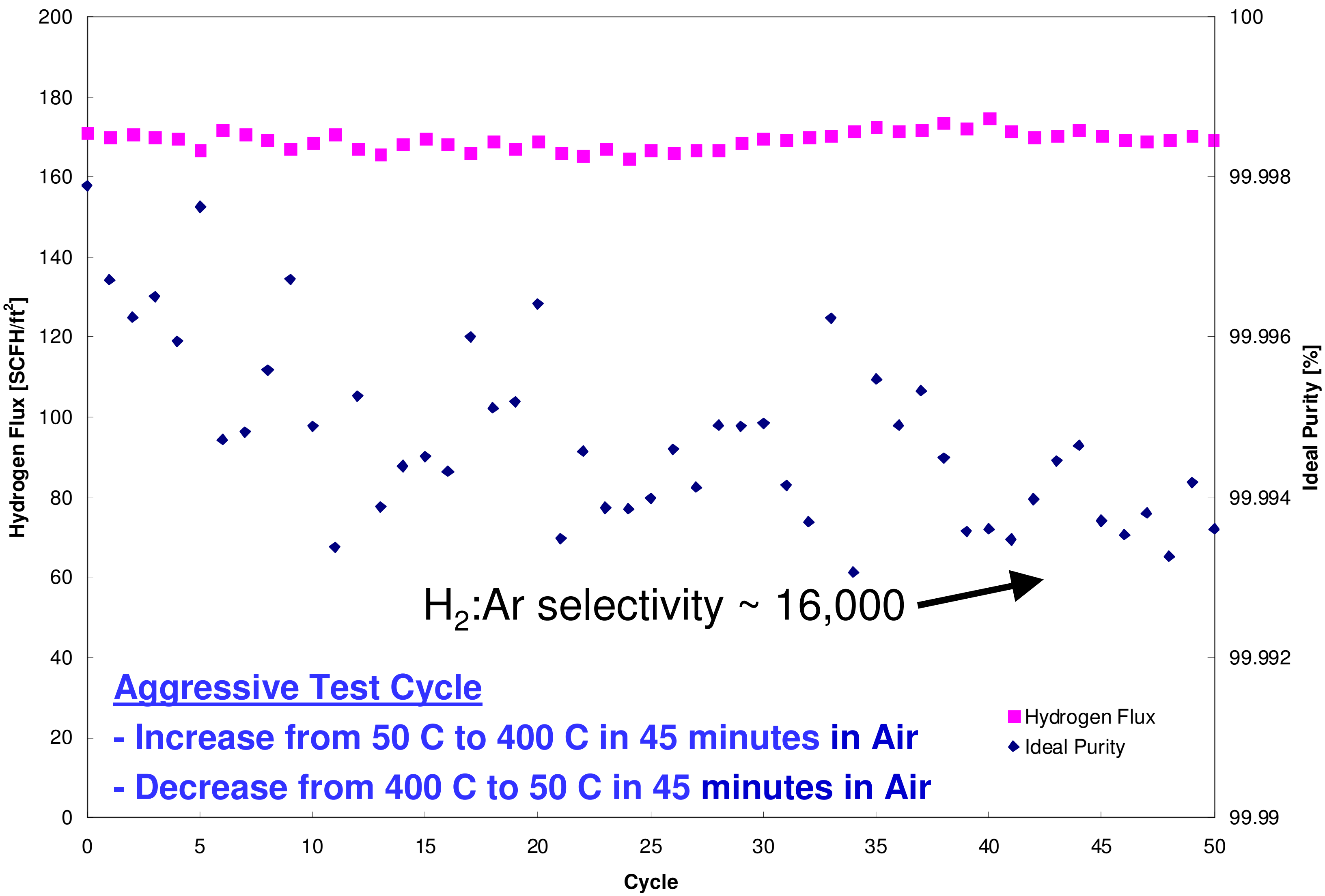
Pd-alloy Membrane test in WGS Environment



Dashed lines correspond to shut downs
Blue line corresponds to change in feed stream

Membrane Thermal Cycling Durability



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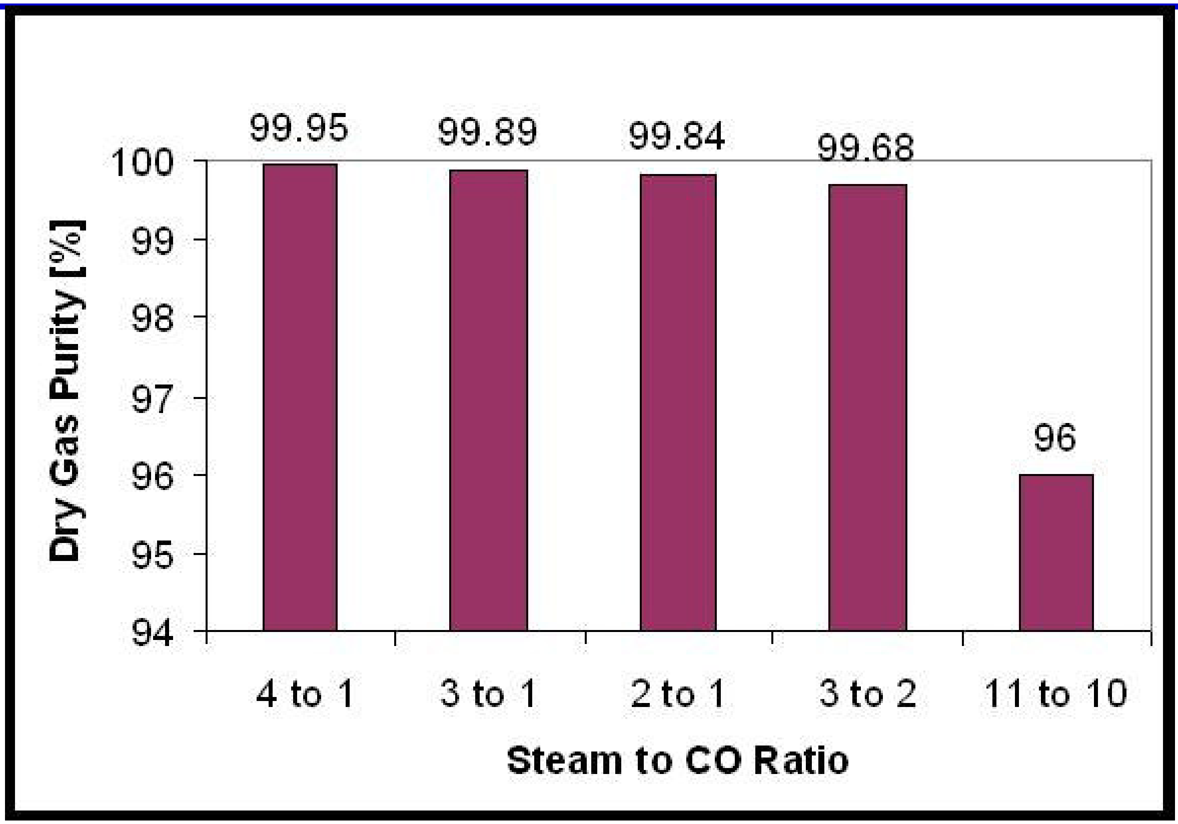
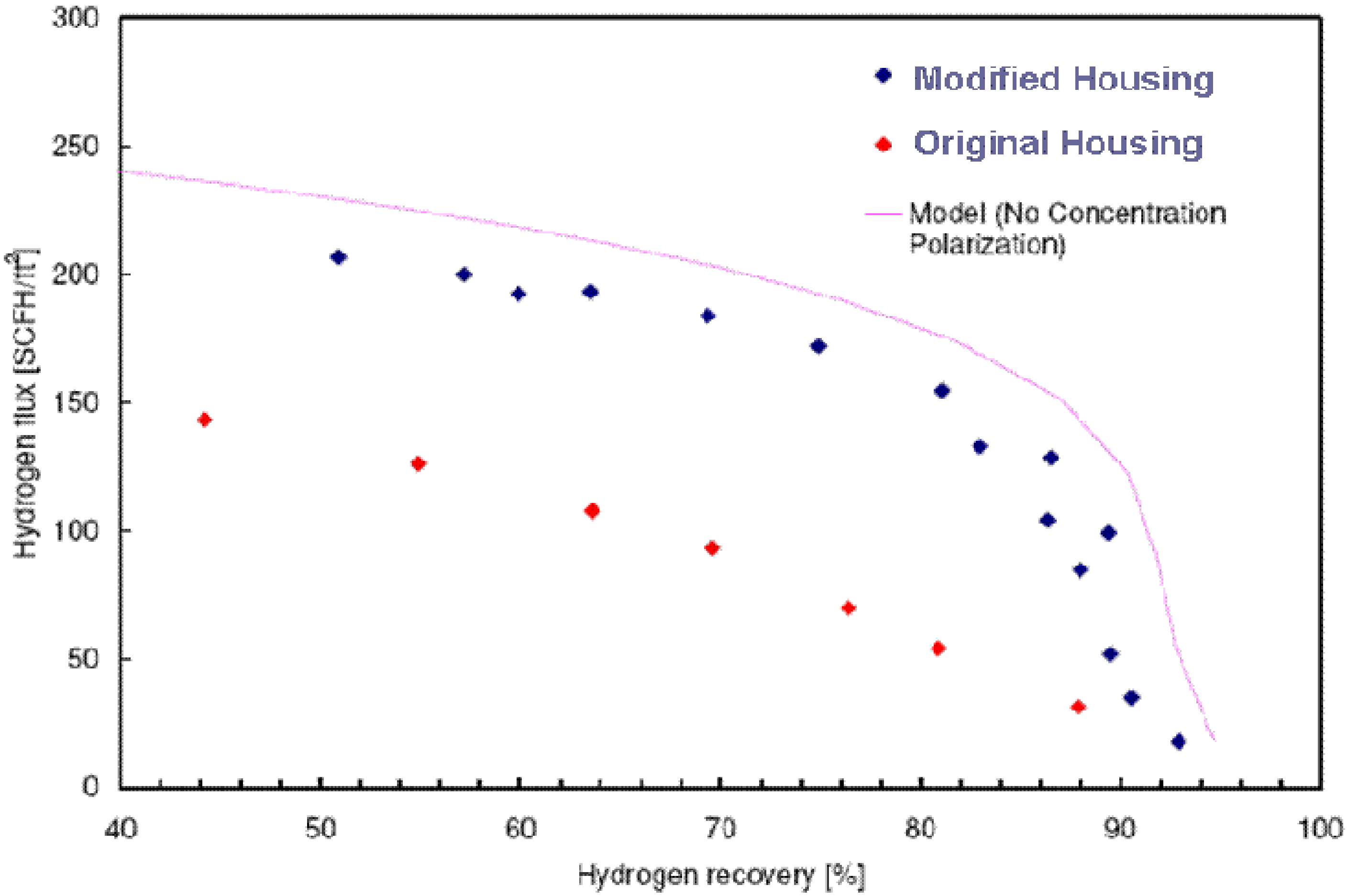
Effect of Steam/CO ratio in the feed gas



- WGS composition; 50% H_2, 5% CO, CO_2 and H_2O as appropriate
- Feed rate 2 LPM, Feed pressure 80 psig, Permeate pressure 5 psig, Temperature 400^{o}C
- H_2 flux stable with varying steam to CO ratios with the H_2 concentration in the feed gas being kept constant.
- Steam to CO ratio >1.5 is recommended

Membrane module design to reduce concentration polarization



- 70% H_2, 30% Ar, 75 psig, 400℃
- H_2 flux 160 SCFH/ft² , H_2 purity 99.995% , H_2 recovery 82%
- Modified housing substantially reduced concentration polarization

Customer Integration and Testing

- Integration of Hydrogen Purifier with Reformer
  - Physical integration – plumbing and connections
  - Thermal integration to provide heat to purifier
  - Control of temperature, pressure, and flow rate
- Testing of integrated system
  - Reformer/purifier operation in response to load demand
  - Startup mode – heating of the system in air, starting fuel feed and stabilization of process conditions
  - Run Mode – Hydrogen output as needed for load
  - Standby Mode – reformer off, pressure/flow bleed, system maintained at T_{min}, possible air infiltration
  - Shutdown – Fuel feed off, cooling in air
- Time responsiveness for startup – low thermal mass

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Research → Development → Manufacturing

- Research
  - Discovery and feasibility
- Development ←
  - Viability and practicality

Status - 12" membranes and membrane modules

↓ **Customer interactions, Understanding requirements, Product development at an acceptable cost and price**

- Manufacturing
  - Material cost, labor costs, resource utilization, overheads & yield
  - **Cost reduction by automation**

Future Activities

- Continue developing products for different power scales for methanol and natural gas-based Hydrogen Generators for small stationary power application
- Expand applications to other liquid logistics fuels – diesel, JP-8. Will use Sulfur and Carbon tolerant membranes currently under development
- Scale up the size of membrane modules offered by two orders of magnitude for on-site hydrogen production and distributed hydrogen production markets

Acknowledgment

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Questions ?

Thank You !