Pall Corporation

Centre for Applied Materials Science

High Throughput Design of Ternary Pd Alloys for Optimum Sulfur / Carbon Resistance in Hydrogen Separation & Carbon Capture Membrane Systems

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NETL CO_2 Capture Technology Meeting
Pittsburgh / July 8 – 11, 2013

Palladium Membrane Technology: Problem and Opportunity

Pending development to address sulfur and carbon poisoning problem

1988 — The State Nitrogen Industry, Russia
1.7 million ft^3/day H_2 Diffusion Plant, Capillary

1965 — D L McKinley @ Union Carbide Corp.
9 million ft^3/day H_2 Diffusion Plant, Plates

1962 — J Bishop & Co
115,000ft^3/day H_2 Diffusion Plant

1960 — J B Hunter et al
Large Scale Diffusion Cell, Tubes

1956 — J B Hunter @ Bishop
Pd-Ag Alloy

1923 — L W McKeehan
α & β-Phase Pd Hydrides

1866 — Thomas Graham @ Royal Mint
H_2 Permeation Pd

Industrial hydrogen purification application by Johnson Matthey

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Outline

- Project overview
- Palladium membrane technology background
- Project progress as of 06/30/2013
- Future plans

Project Overview – (1)

Funding

- $1,517,000 Total
- $1,207,000 U.S. Department of Energy
- $310,000 Cost Share

Performance Period

- Oct 1, 2009 to Sept 31, 2012 (three-year project as proposed)
- No cost extension to July 2014

Participants

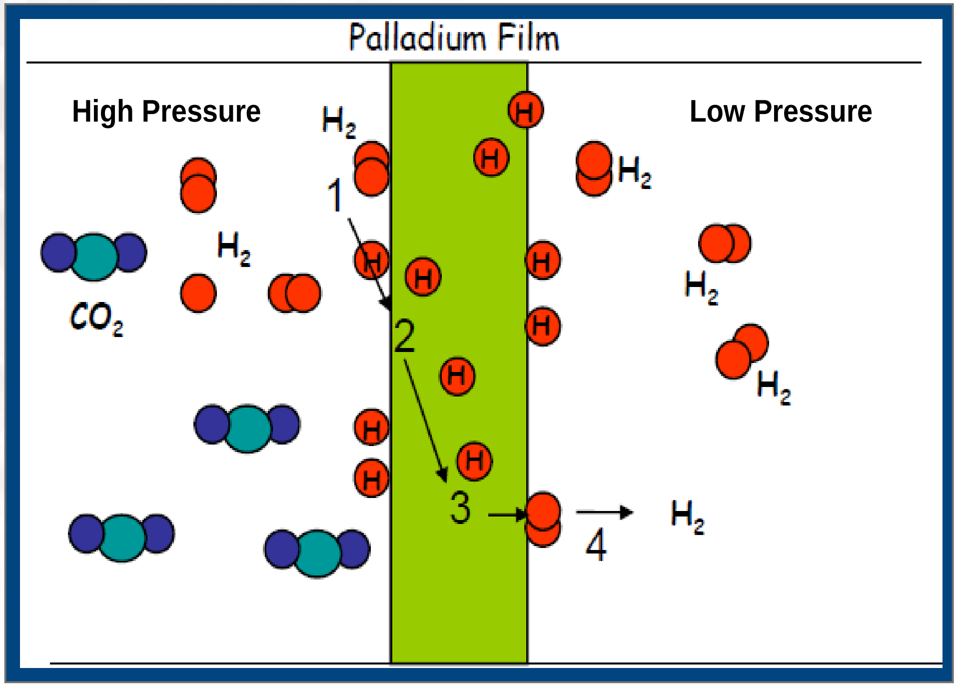
- Pall Corporation (project management, membrane fabrication, membrane scale-up, module construction, slipstream test)
- Georgia Institute of Technology (Surface characterization of alloys)
- Cornell University (composition spread fabrication on silicon wafer)
- Colorado School of Mines (Alloy membrane fabrication on practical support)
- Oak Ridge National Laboratory (in-situ XRD of alloy phases)
- Southern Company / U.S. DOE – NCCC (slipstream test)

Project Overview – (2)

Project Objectives

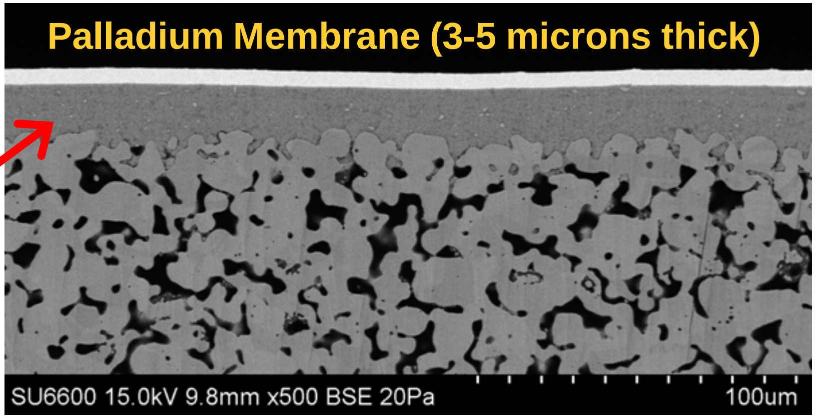
- Develop an economic, high temperature and pressure, hydrogen separation membrane system for CO_2 capture that resists moderate levels of contaminants, typical in gasified coal.
- Create an advanced palladium alloy for optimum hydrogen separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability by long term testing of a pilot membrane module at a commercial coal gasification facility.
- Understand long term effects of the coal gasifier environment on the metallurgy of the membrane components.

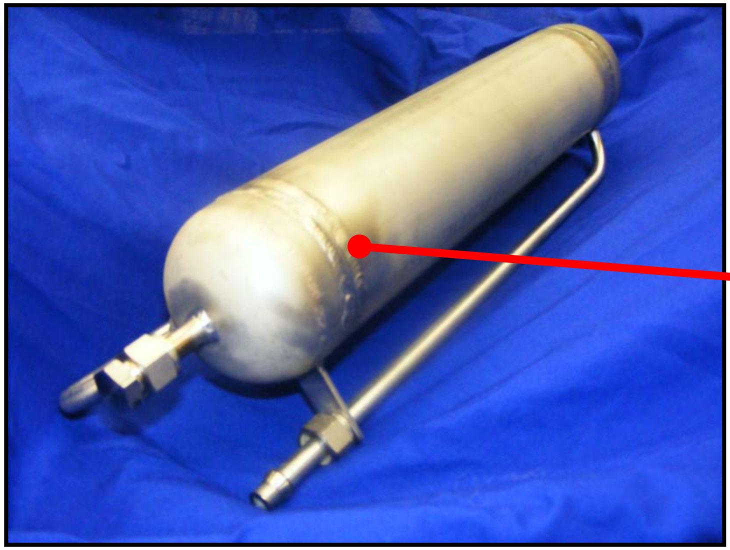
How Palladium Membrane Works

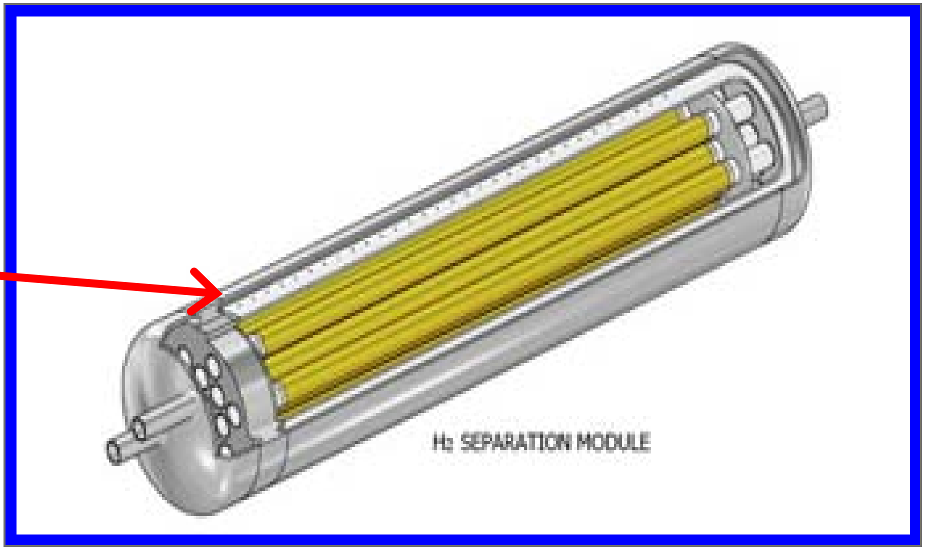


- H_2 dissociation on metal
- H dissolves into metal
- H diffuses through metal
- Recombination to form H_2
- High H_2 selectivity
- High H_2 flux

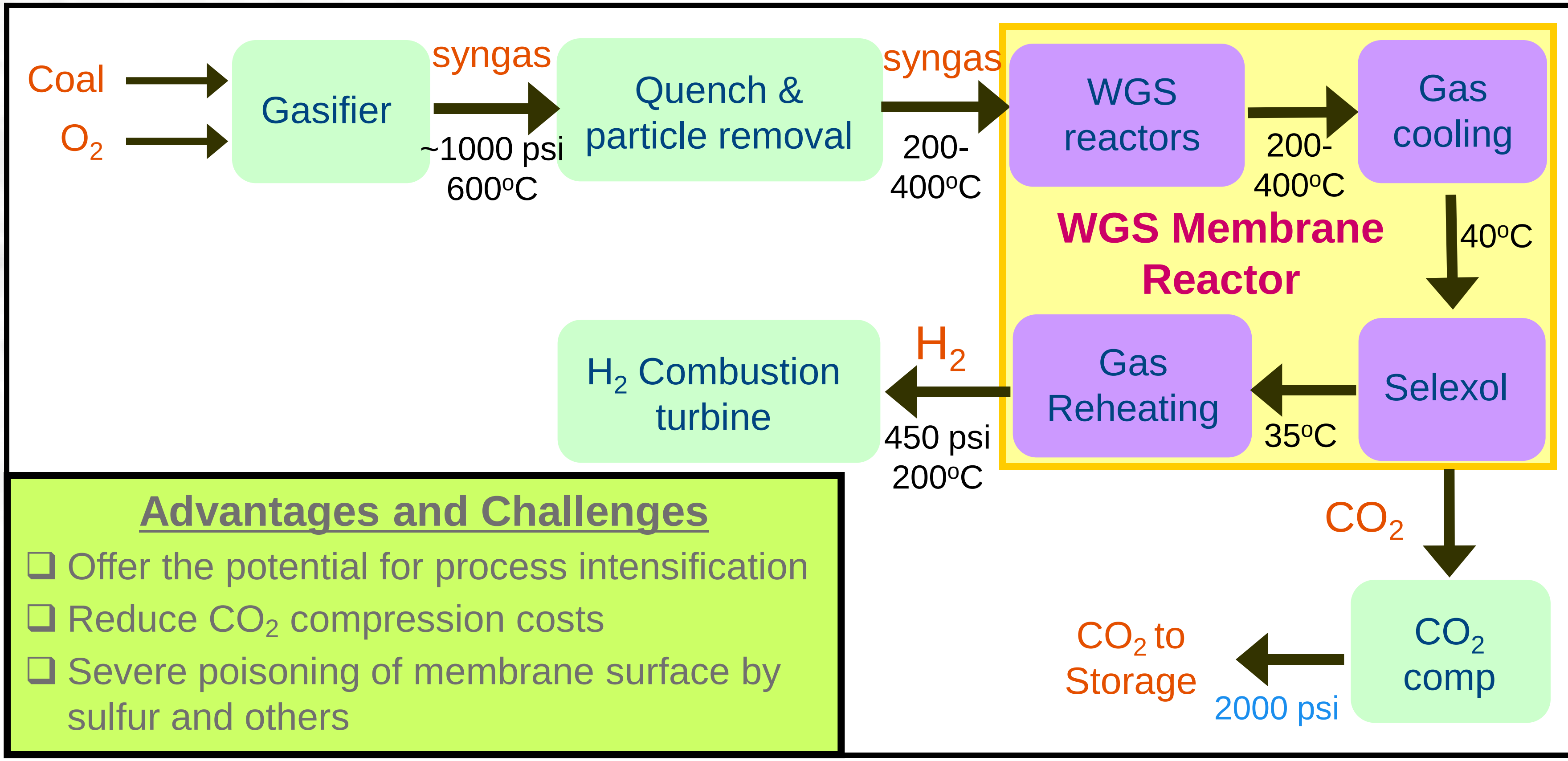
Pall's Palladium Membrane Technology







H_2/CO_2 Separation at IGCC Power Plant: Pd Membrane vs. Scrubbing



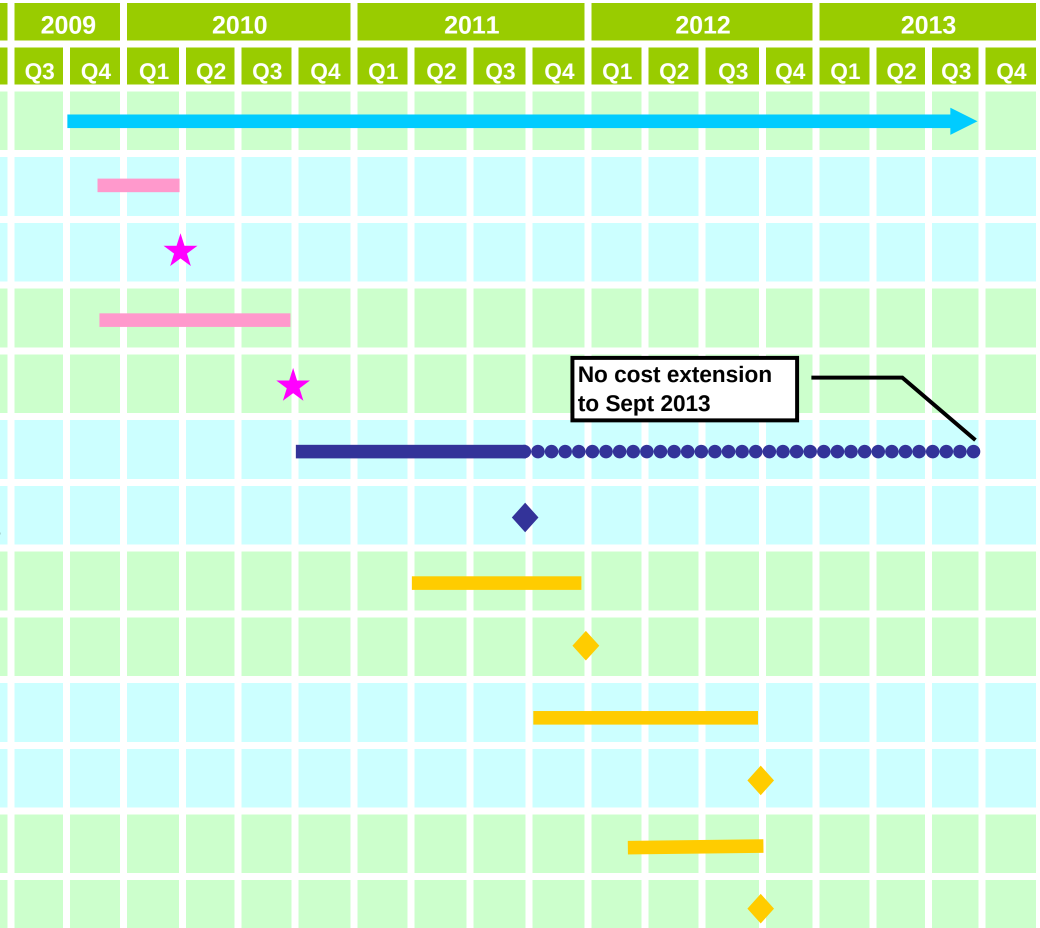
Advantages and Challenges

- ❑ Offer the potential for process intensification
- ❑ Reduce CO_2 compression costs
- ❑ Severe poisoning of membrane surface by sulfur and others

Project Schedule & Milestones

Completed — Ongoing — To be completed

Task#	Project Milestone Description
1	Project management and planning
2	Literature and patent search
	Milestone 1 Report demonstrating understanding of previous work
3	Design and modeling of binary and ternary Pd alloys
	Milestone 2 Report on use of combinatorial method
4	Construct and test 15 cm^2 active membrane area prototypes
	Milestone 3 Report on testing of small scale membranes
5	Scale up active membrane area from 15 to 75 cm^2
	Milestone 4 Report on testing of scaled-up membranes
6	Construct and test a working membrane module
	Milestone 5 Report on long-term performance of membranes
7	Provide complete analysis of relevant data sufficient of permit economic evaluatoin of the process
	Milestone 6 Report on advancement necessary to commercialize membrane process



*Task 4 is delayed, due to 1) negotiation of subcontract with Cornell University, 2) change of subcontractor from Cornell University to Colorado School of Mines to acquire technical capability of alloy membrane deposition on tubular substrate.

Progress and Current Status

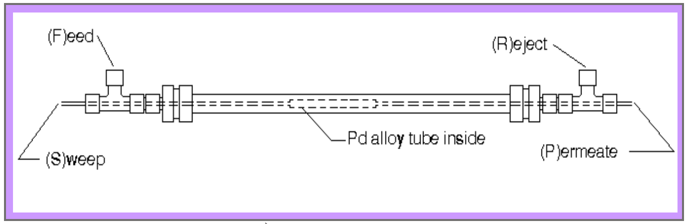
Task	Timeline	Completion
Task 4 Construct and test 15 cm^2 active surface area prototypes of novel Pd alloy membranes for use as high temperature, high pressure gas separation membranes under coal gasifier conditions	Oct 2010 to Sept 2011 (no cost extension to Sept 2013)	
❑ Optimize process for making zirconia substrates suitable for each candidate Pd alloy		completed
❑ Fabricate best candidate palladium alloys into thin film membrane prototypes with 15-cm^2 active surface area over optimized zirconia substrate		40%
❑ Test hydrogen separation performance of each best candidate alloy under coal gas conditions with trace amounts of impurities, including sulfur, for extended period		40%

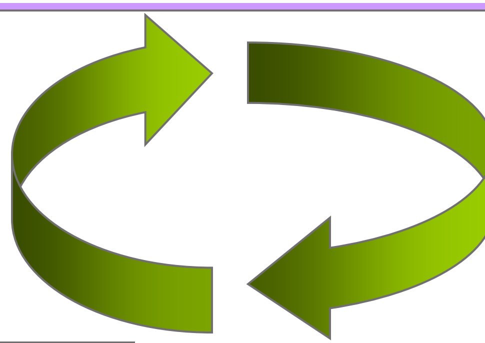
Combinatorial Pd Alloy Development Workflow

Alloy Screening*

- ❑ Make alloy Membrane
- ❑ Run H_2 Permeation Test
- ❑ Post-test characterizations

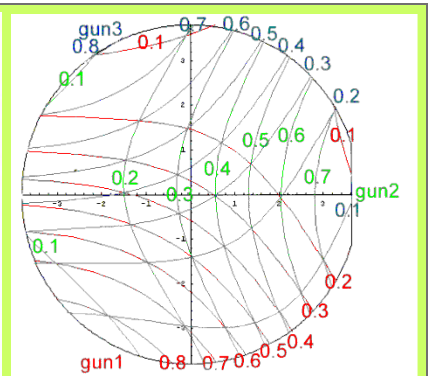
*Combinatorial method for direct measurements of hydrogen permeability, S.De Man et al, Journal of Membrane Science 444 (2013) 70





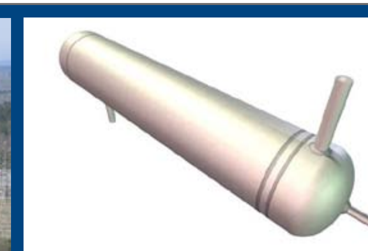
Combinatorial Discovery

- ❑ Make composition spread
- ❑ Run corrosion test
- ❑ Raman surface chemical mapping



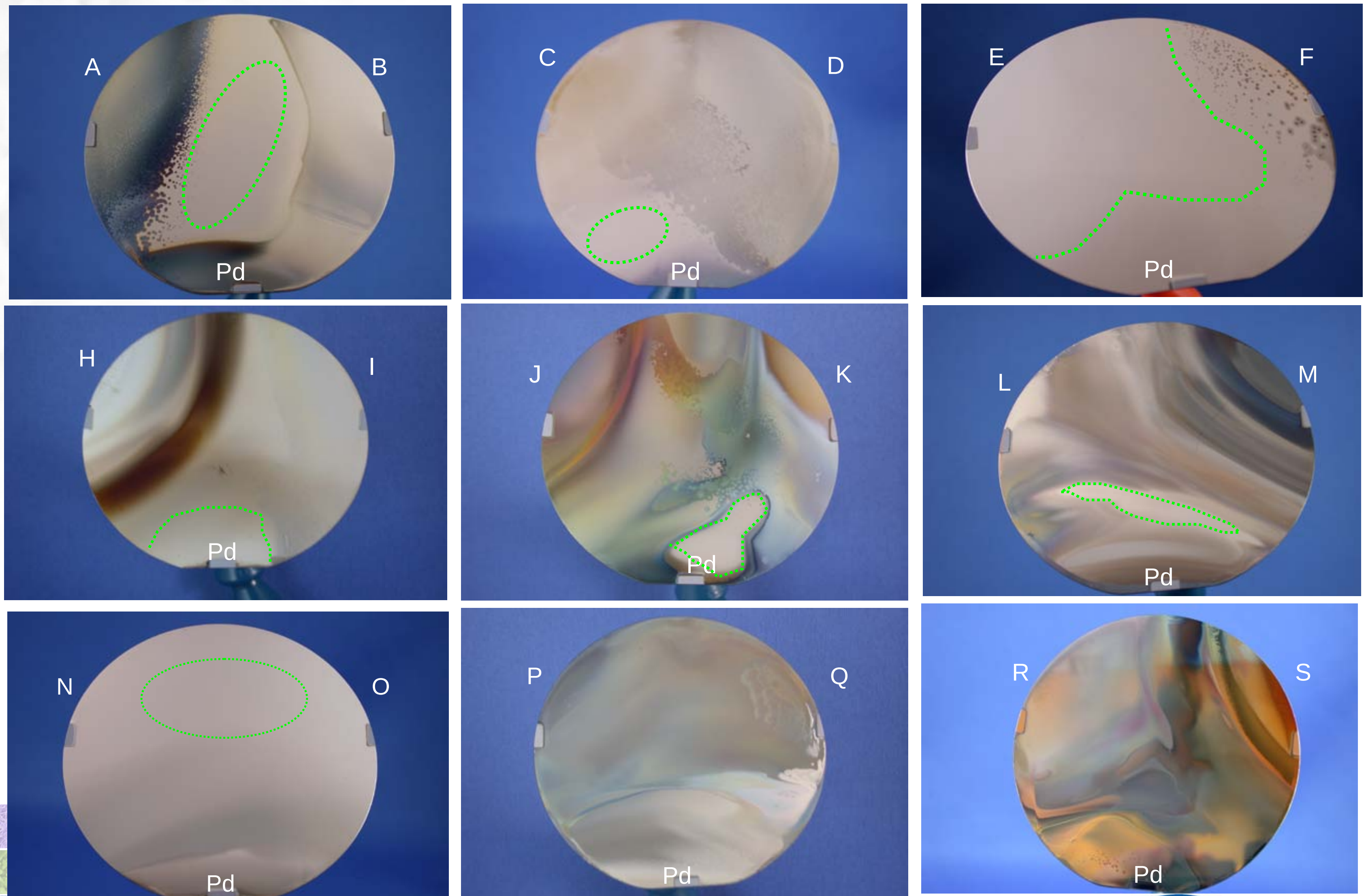
Performance Testing

- ❑ Scale up membrane element
- ❑ Develop membrane module
- ❑ Run slipstream test at NCCC



Combinatorial Discoveries Through Task #3

Ternary composition spreads were tested for corrosion resistance



Coal Gas Corrosion-Resistant Alloys

- Pd-A-B (tested)
- Pd-N-O (tested)
- Pd-E-F
- Pd-C-D
- Pd-J-K
- Pd-H-I

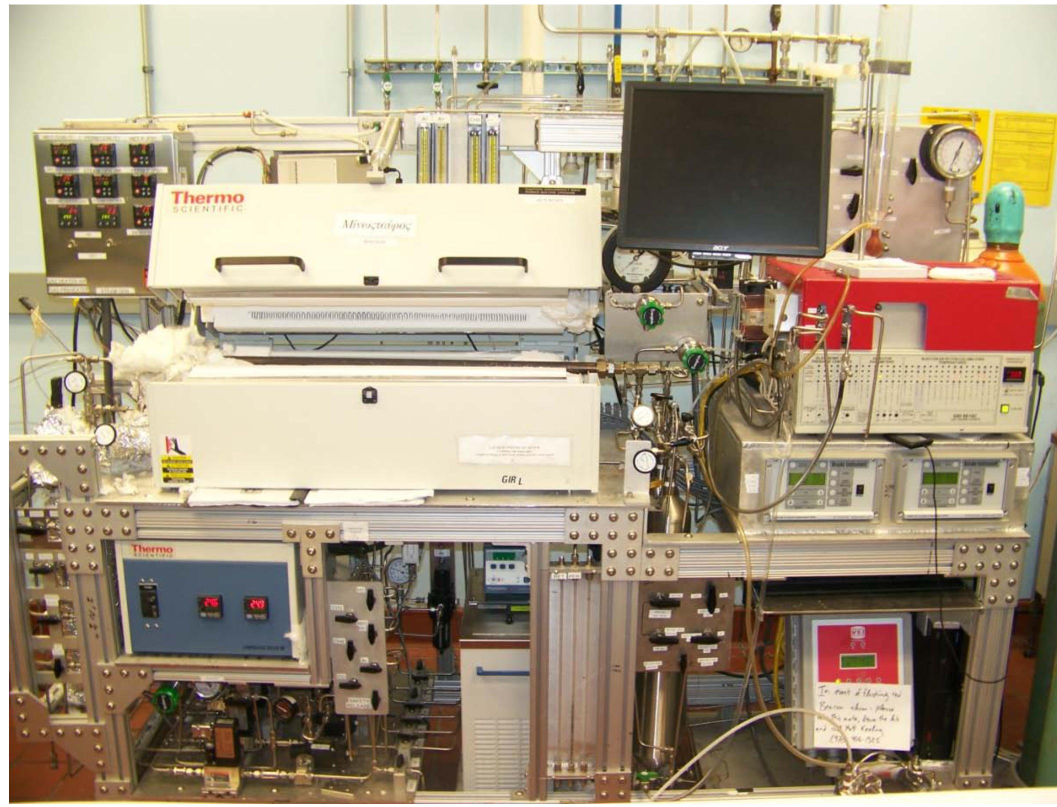
Best Sulfur/Carbon Resistant Pd Alloys in Literature

- Pd-Au-Pt (tested)
- Pd-Au (tested)
- Pd-Pt

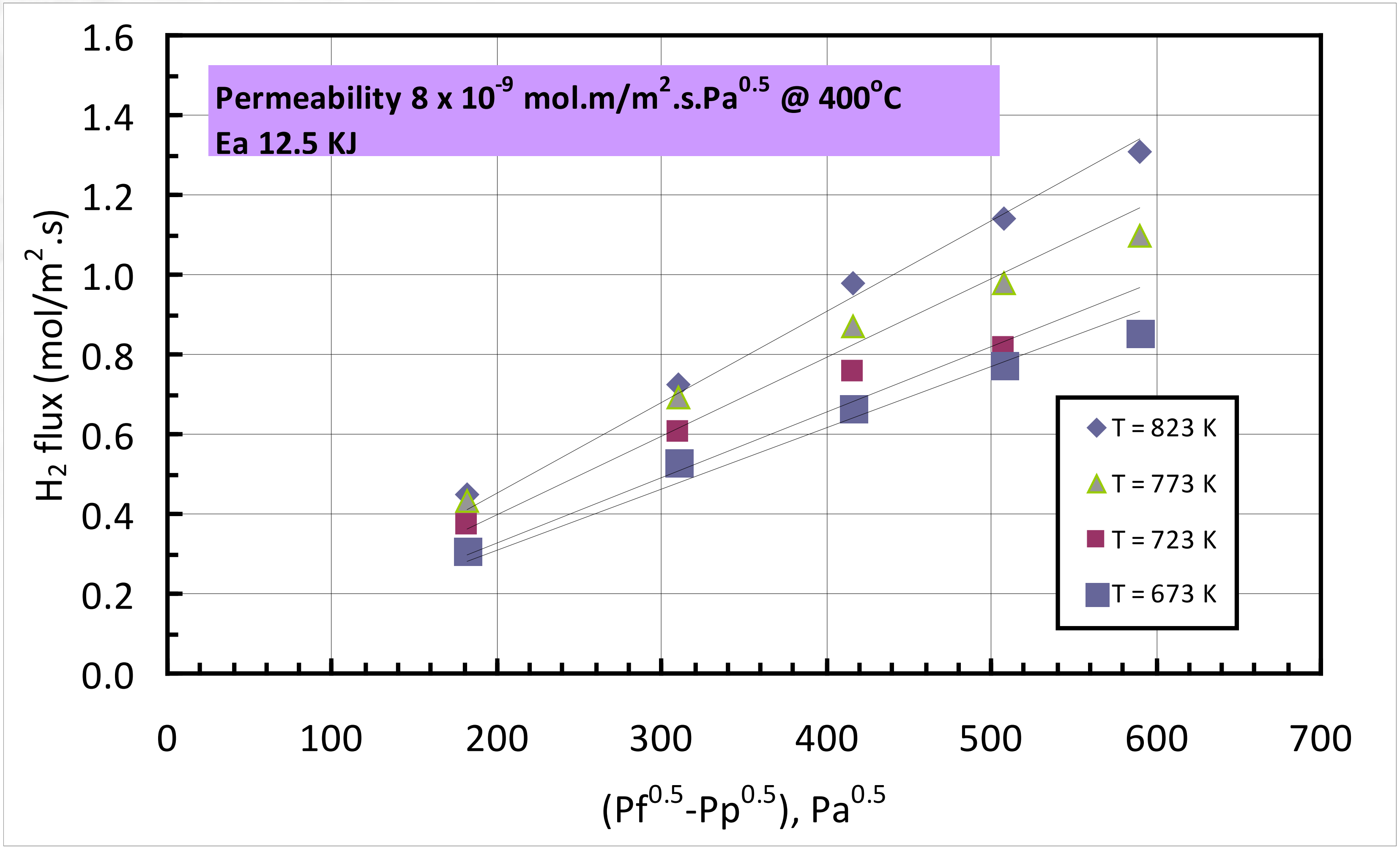
Pd Alloy Screening Test

Impact of carbon / sulfur upon hydrogen permeation

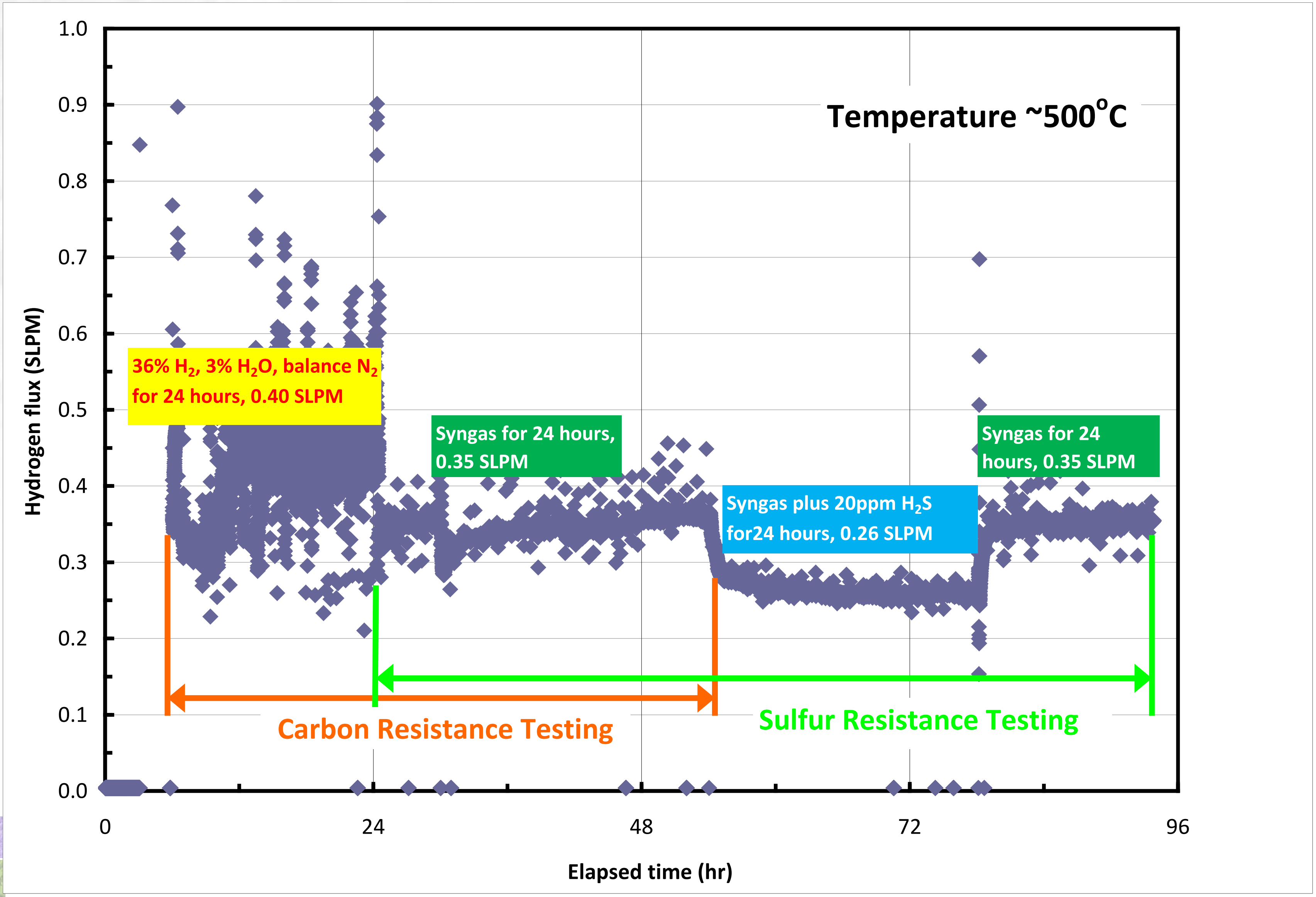
- ❑ Gas composition (air blown coal gasifier)
  - ✓ H_2 = 36 v%
  - ✓ CO_2 = 11 v%
  - ✓ CO = 1.3 v%
  - ✓ H_2O = 3 v%
  - ✓ N_2 = 49 v%
  - ✓ H_2S = 20 ppmv
- ❑ Pressure ~160 psig
- ❑ Temperature 400 / 500^{o}C



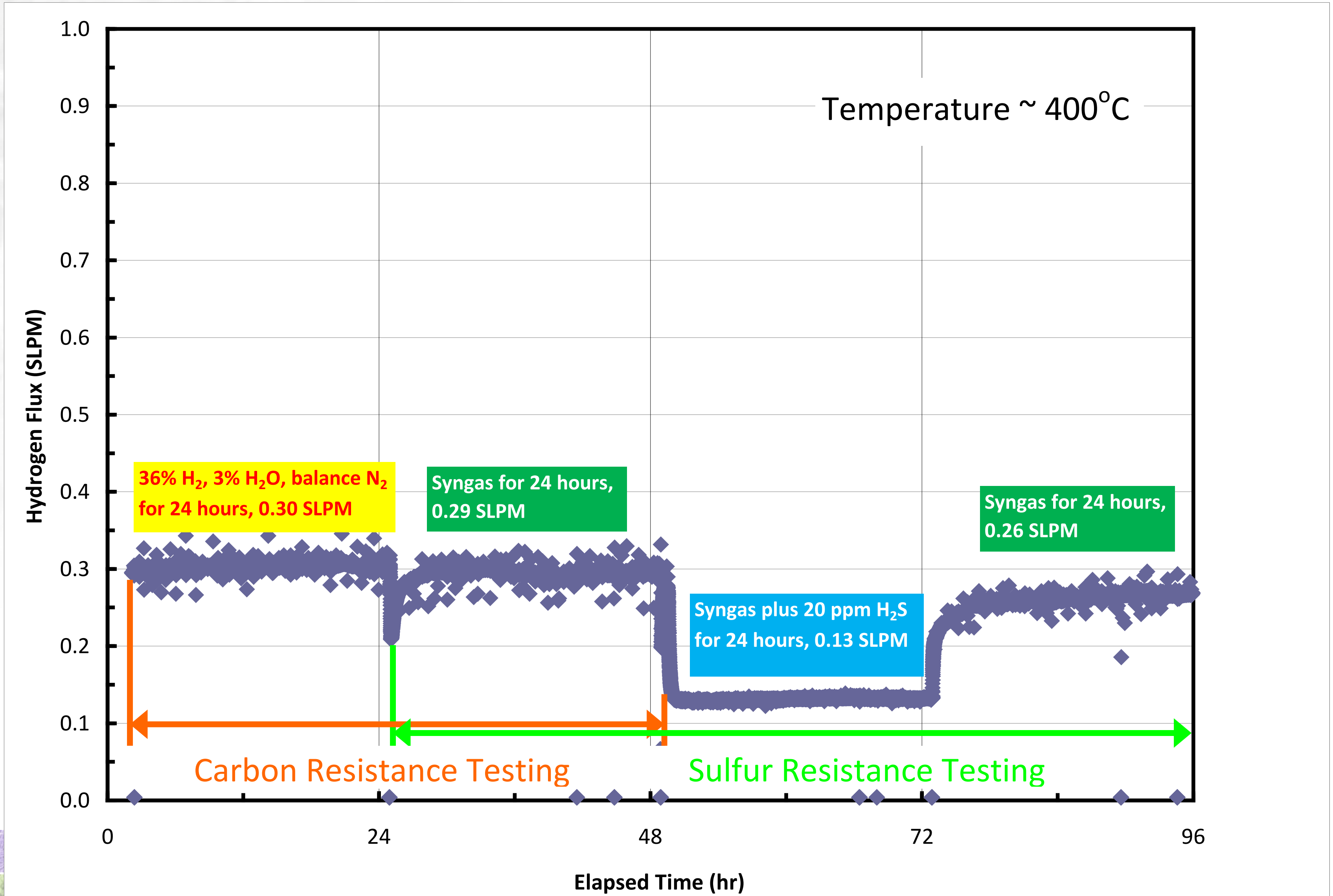
Pure H_2 Permeation Test on Pd-Au-Pt Alloy Membrane



Sulfur / Carbon Resistance Test on Pd-Au-Pt Alloy Membrane



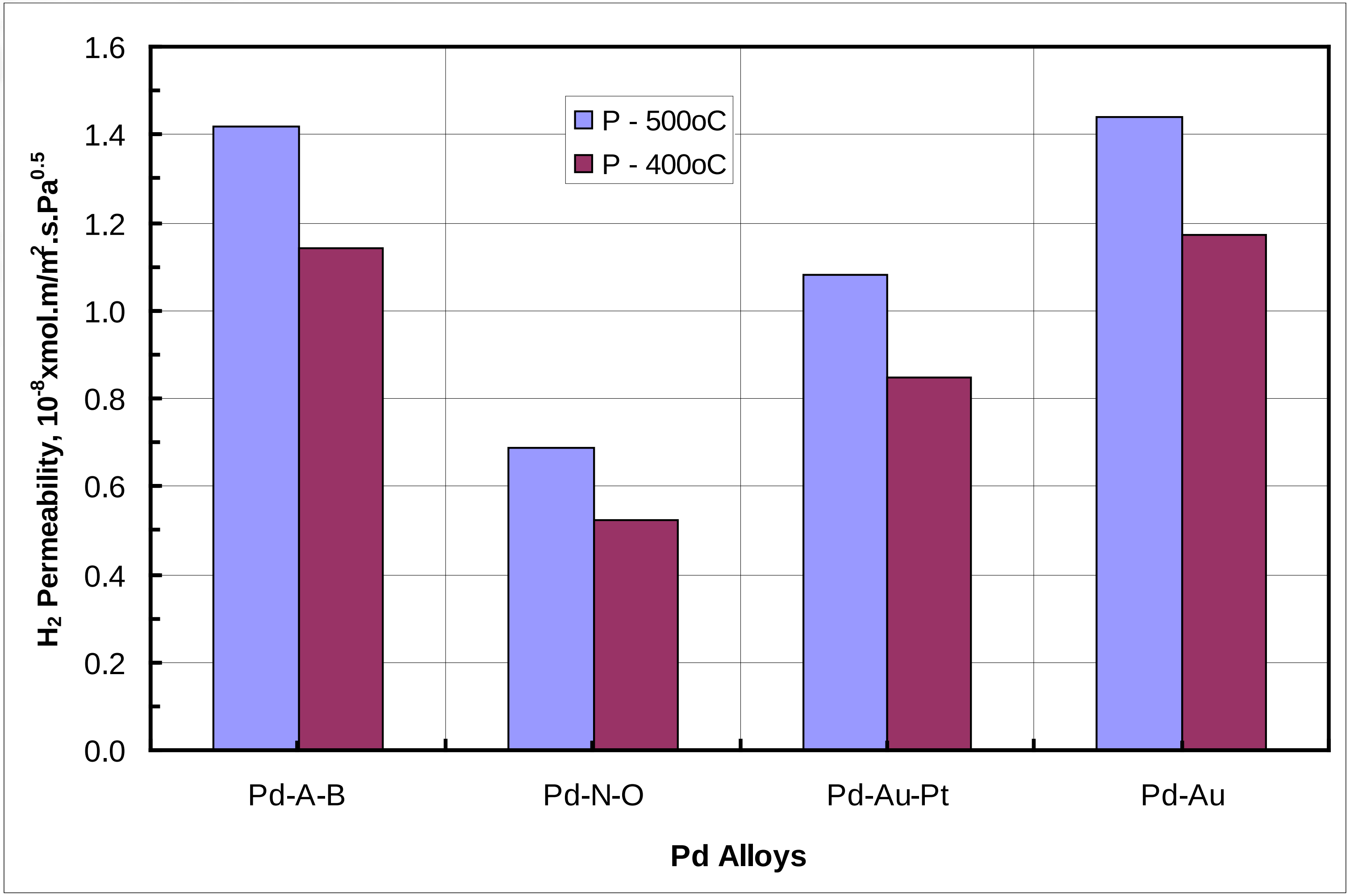
Sulfur / Carbon Resistance Test on Pd-Au-Pt Alloy Membrane



Pure H_2 Permeability of Several Pd Alloys

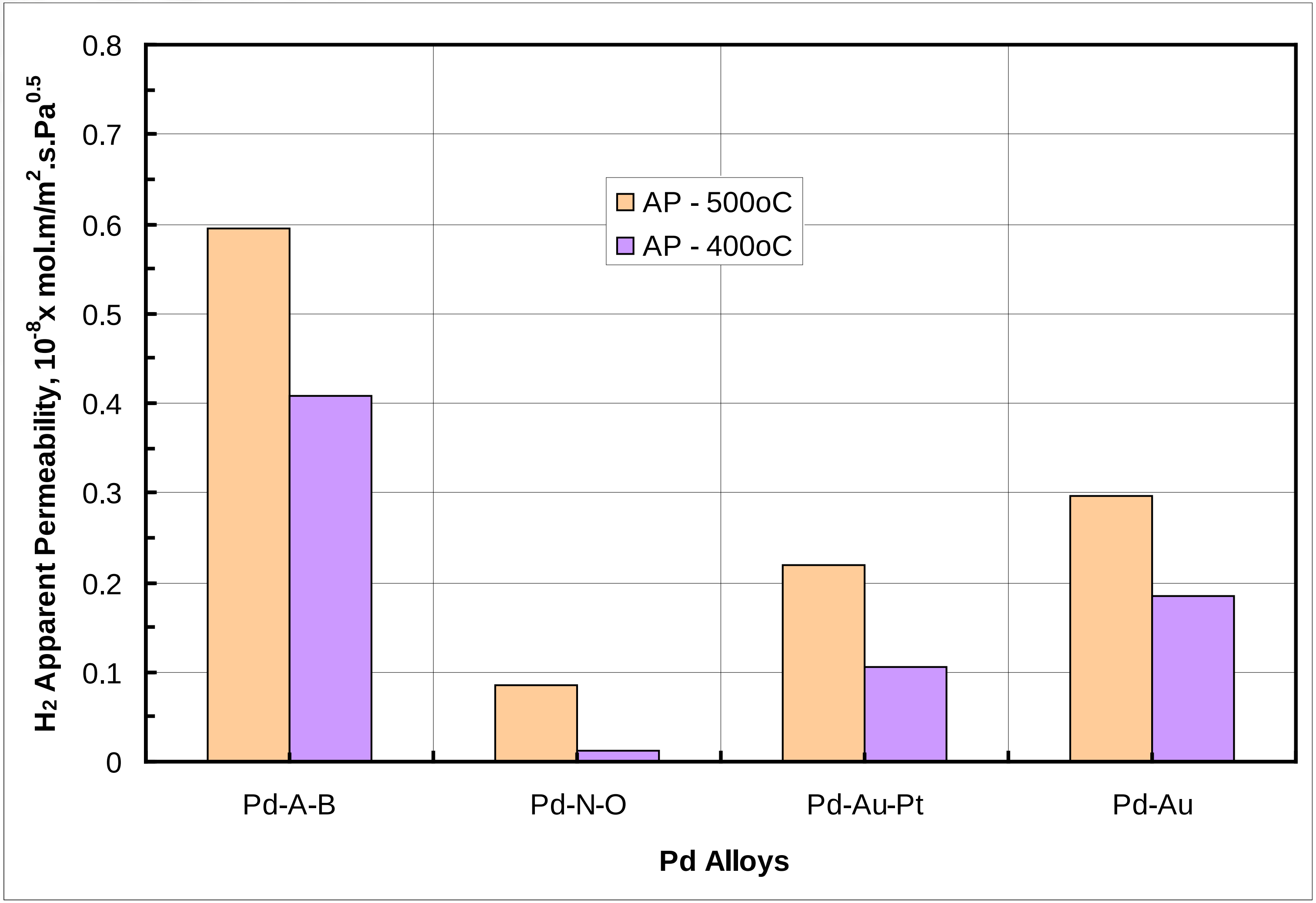
*Pd-A-B ≈ Pd-Au > Pd-Au-Pt > Pd-N-O

(*Room temperature H_2 embrittlement resistance)



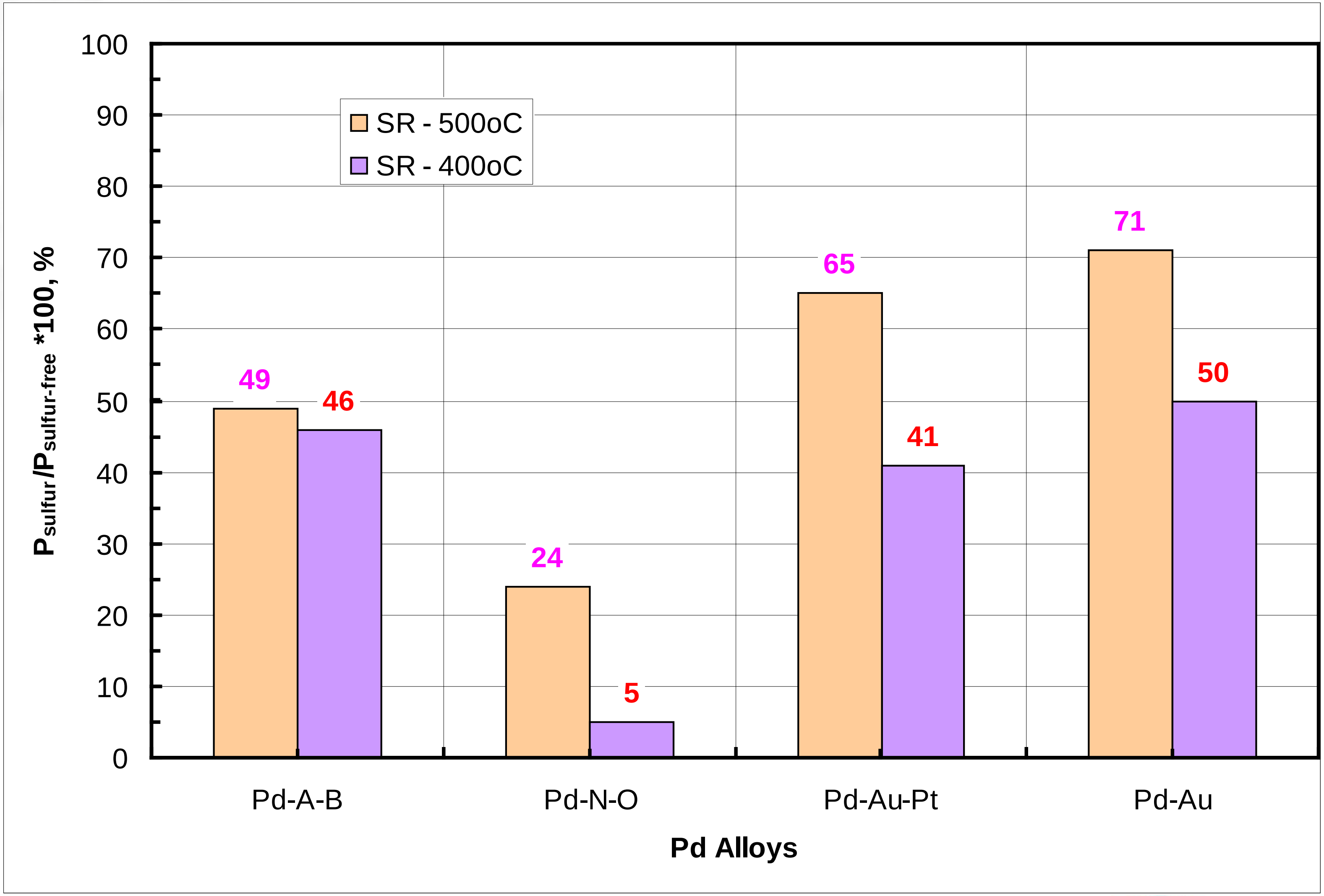
H_2 Apparent Permeability of Several Pd Alloys in Presence of 20 ppm H_2S

Pd-A-B > Pd-Au > Pd-Au-Pt > Pd-N-O



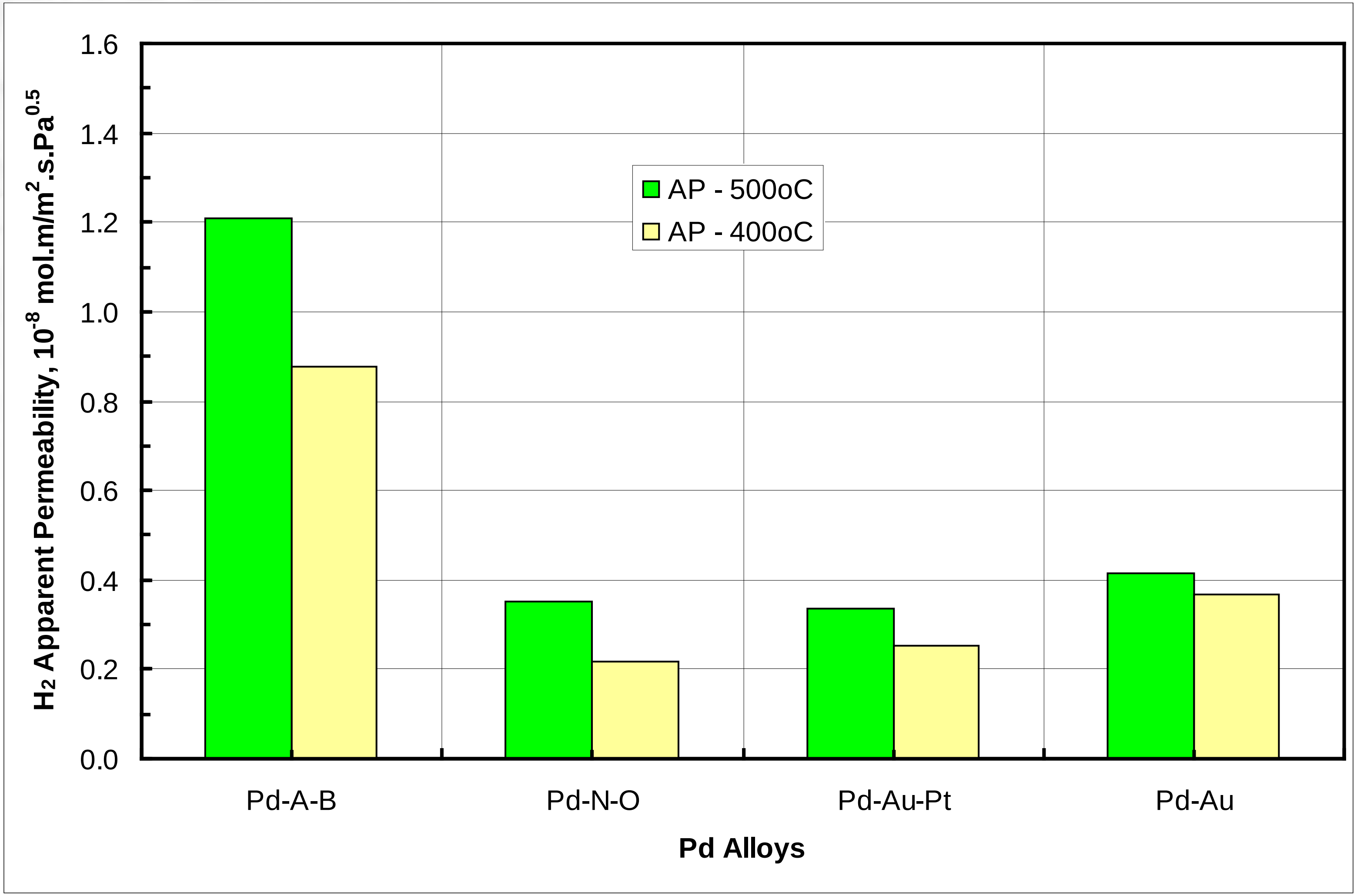
Sulfur Resistance of Several Pd Alloys

Pd-Au > Pd-Au-Pt > Pd-A-B >> Pd-N-O @ 500^{o}C



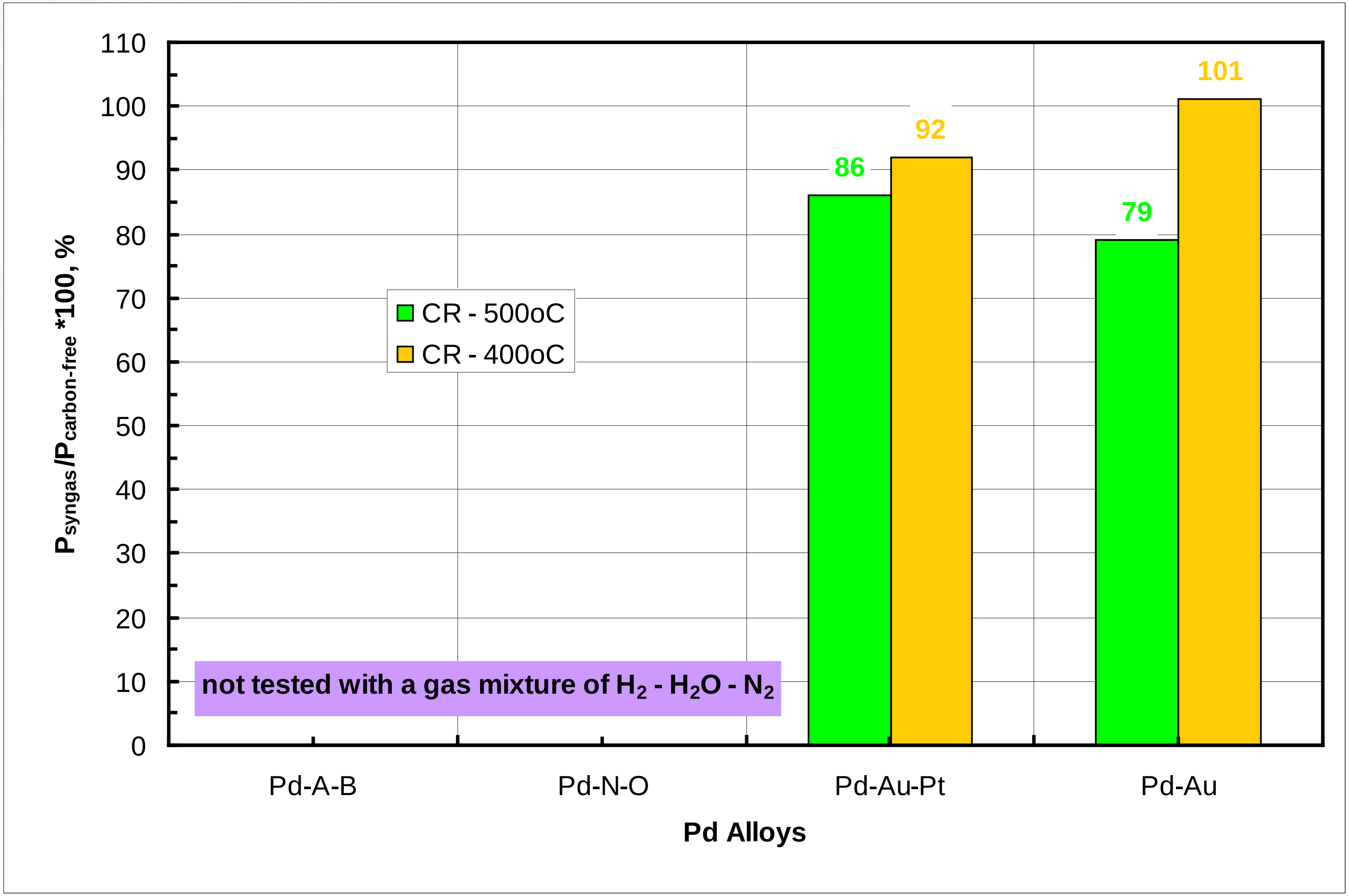
H_2 Apparent Permeability of Several Pd Alloys in Sulfur-Free Syngas

Pd-A-B >> Pd-Au ≈ Pd-Au-Pt ≈ Pd-N-O



Carbon Resistance of Several Pd Alloys

Pd-Au versus Pd-Au-Pt



Our Current Leading Candidate: Pd-A-B Alloy

- Sulfur resistance: H_2 permeation rate 4.08 mol.m/m^2.s.Pa$^{0.5}$ (2.2 times as much as Pd-Au alloy)
- Carbon resistance to be determined.
- Pure H_2 permeability 1.14 mol.m/m^2.s.Pa$^{0.5}$ (close to Pd-Au alloy)
- Coal gas corrosion resistance (better than Pd-Au alloy)
- Room temperature hydrogen embrittlement resistance

Plans to Complete Project

- Continue palladium alloy screening out of candidates discovered through the task #3.
- Select top two alloys and make full-scale membrane elements with active surface area 75 cm^2.
- Conduct 100-500 hour performance test on these 75-cm^2 membranes with simulated coal gas and practical operating conditions.
- Construct a working membrane module capable of extended service as a hydrogen separation system.
- Conduct 500 hour field test with gasifier slipstream at U.S. DOE / NCCC.
- Develop detailed application process and perform its economic analysis of developing palladium alloy membrane technology.

Acknowledgements

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  - Patricia Rawls,
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