Pall Corporation

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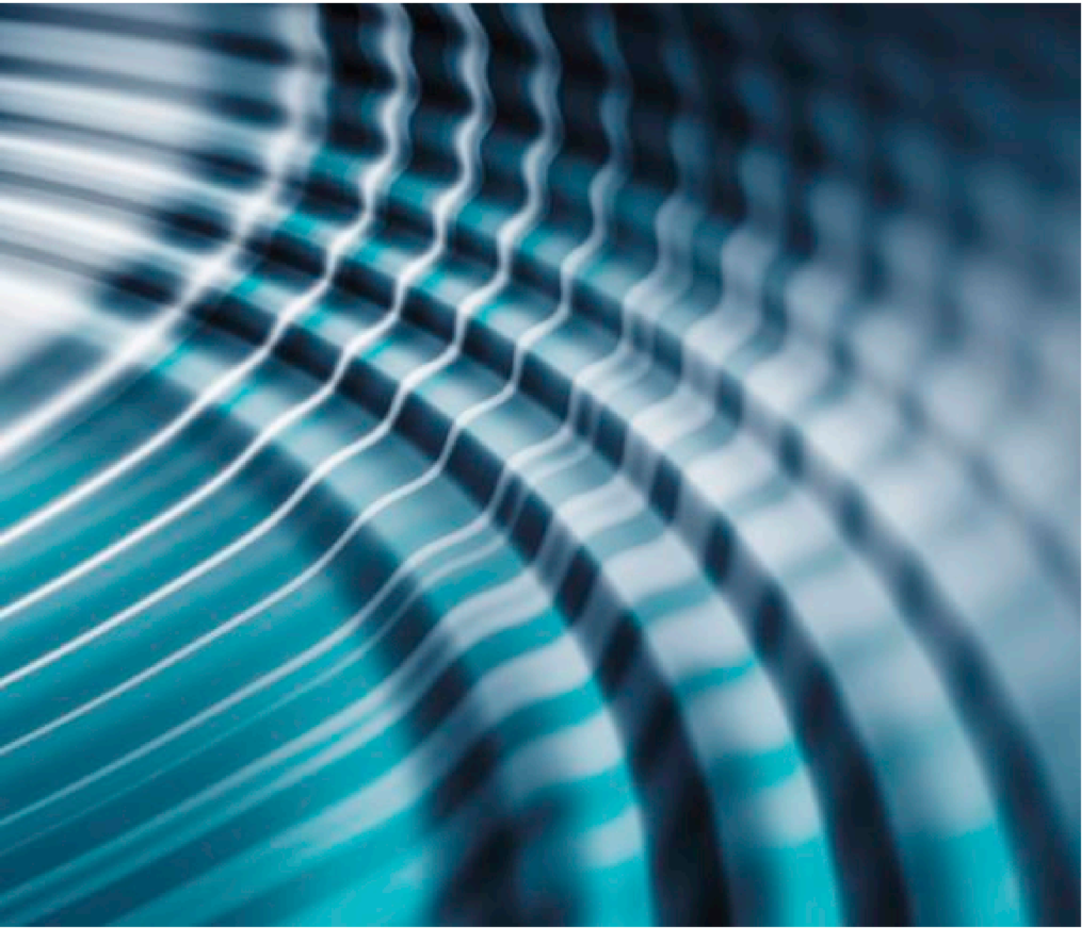


# Identifying Pd-Based Ternary Membranes for Carbon and Sulfur Applications

Amanda Lewis, Hongbin Zhao, & Scott Hopkins

**NETL $CO_2$ Capture Technology Meeting**

**Pittsburgh / July 29 – August 1, 2014**

# Outline

- ☐ Project overview
- ☐ Palladium membrane technology background
- ☐ Current project progress
- ☐ Future plans

# Project Overview

## Funding

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

## Performance Period

- October 1, 2009 to September 30, 2012 (three-year project as proposed)
- No cost extension(s) to September 30, 2014

## Participants

- Pall Corporation (project management, support fabrication, module construction, mixed-gas testing)
- Cornell University (composition spread fabrication on silicon wafer)
- Georgia Institute of Technology (surface characterization of exposed wafers)
- Colorado School of Mines (alloy membrane fabrication and annealing)

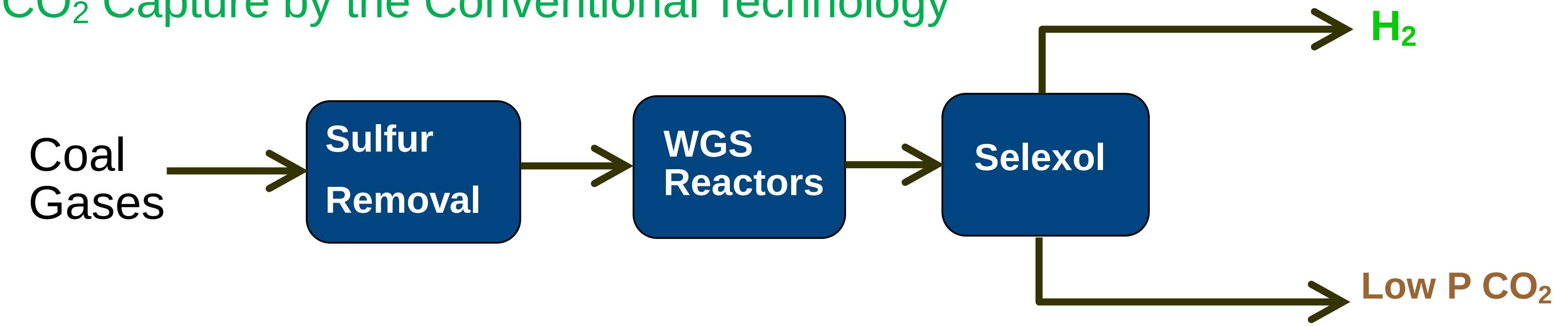
# Project Overview Continued

## Project Objectives

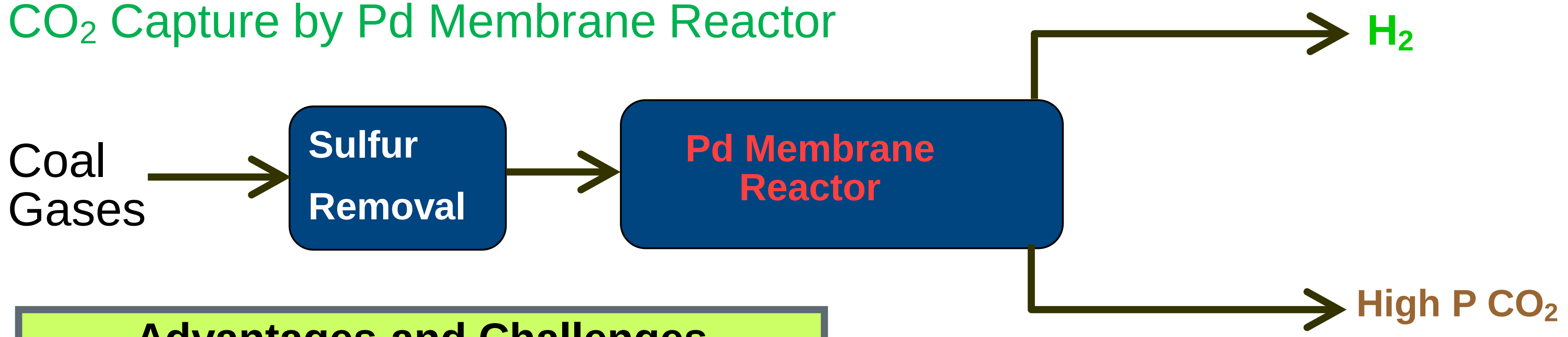
- ☐ Develop a high temperature and pressure membrane based system for $CO_2$ capture and hydrogen production that resists moderate levels of contaminants, typical in gasified coal.
- ☐ Identify chemically resistant palladium-based ternary alloy(s) using a high-throughput screening method.
- ☐ Demonstrate lab-scale fabrication and testing reproducibility.
- ☐ Understand long-term effects of carbon monoxide and hydrogen sulfide before scaling up.

# Current Technology

## $CO_2$ Capture by the Conventional Technology



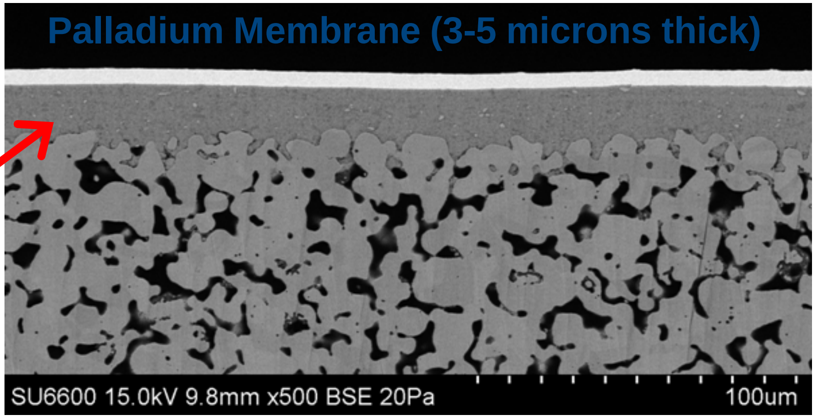
## $CO_2$ Capture by Pd Membrane Reactor

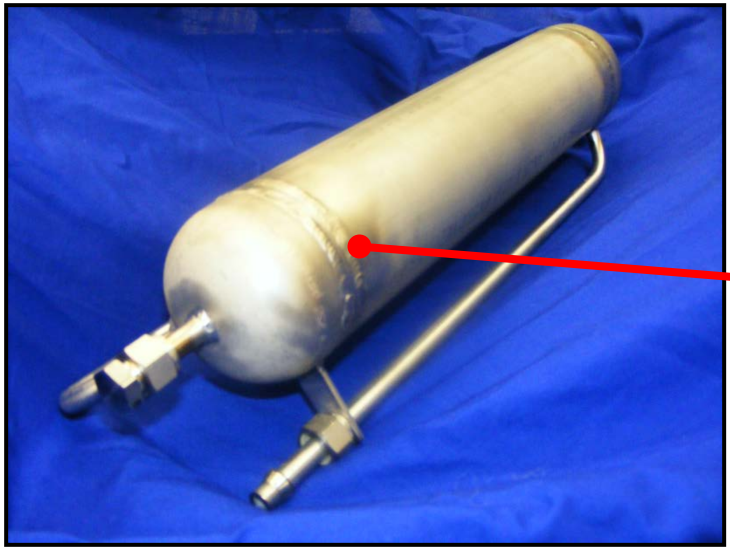


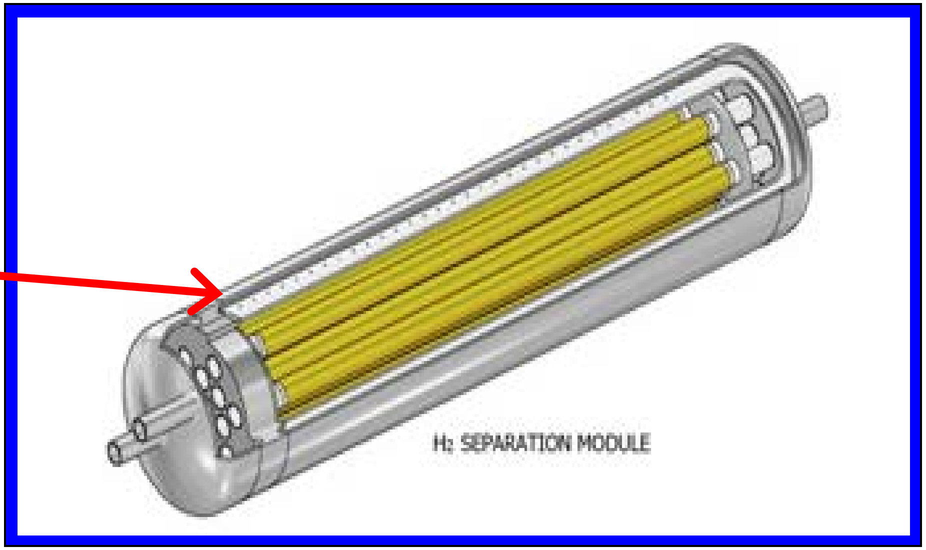
**Advantages and Challenges**

- ☐ Offer the potential for combined processes
- ☐ Reduce $CO_2$ compression costs
- ☐ Severe poisoning of membrane surface by sulfur and others

# Pall's Palladium Membrane Technology







# Why Palladium

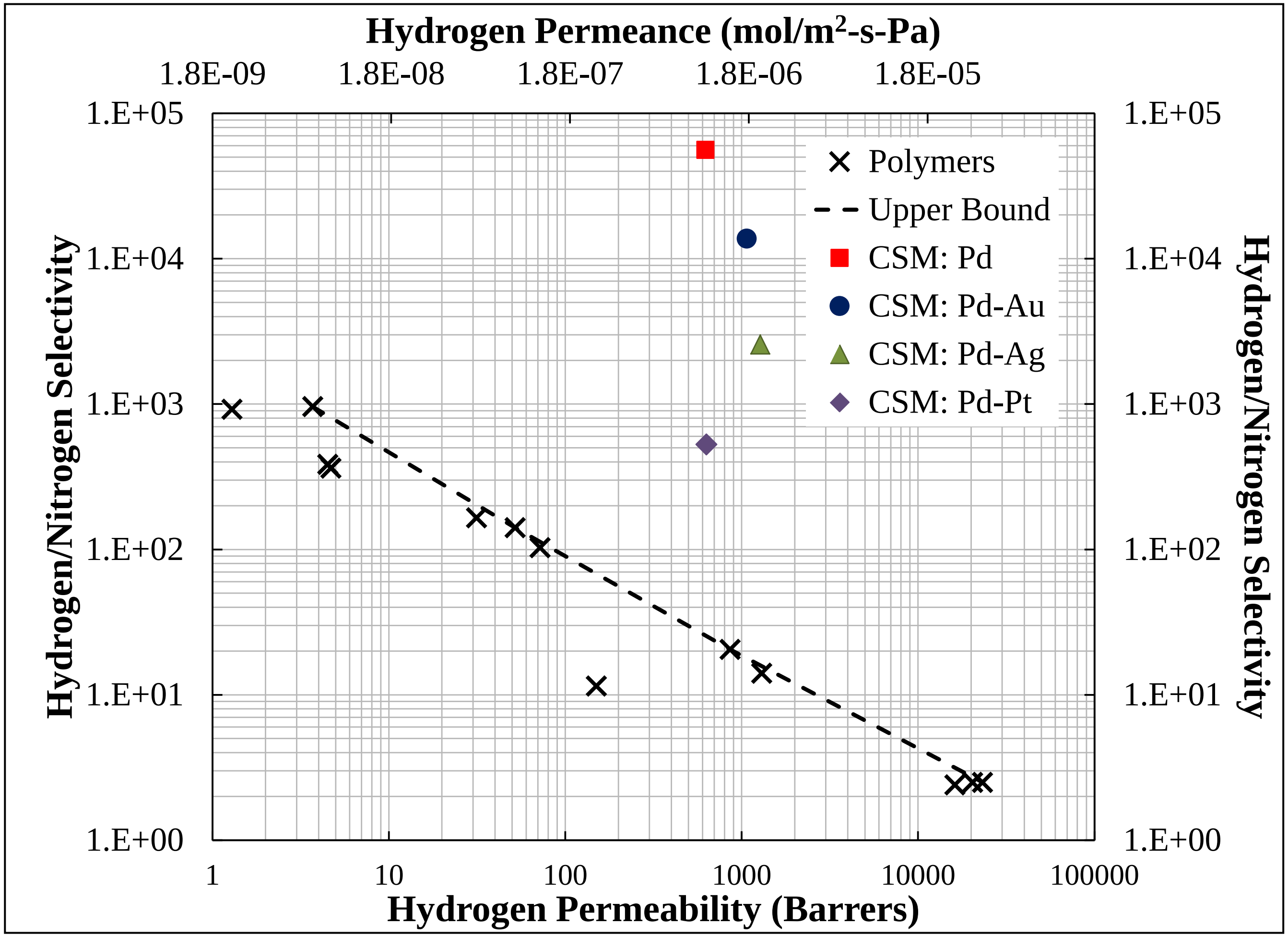


Figure adapted from:

1. Robeson, L.M. Journal of Membrane Science. **62**(2):(1991) p. 165-185.
2. Robeson, L.M. Journal of Membrane Science. **320**(1-2):(2008) p. 390-400.
3. Lewis, A. (2012) “How Contaminants and Alloying Metals Affect Hydrogen Permeation in Pd-Based Composite Membranes” (Ph.D. Thesis) – Colorado School of Mines.

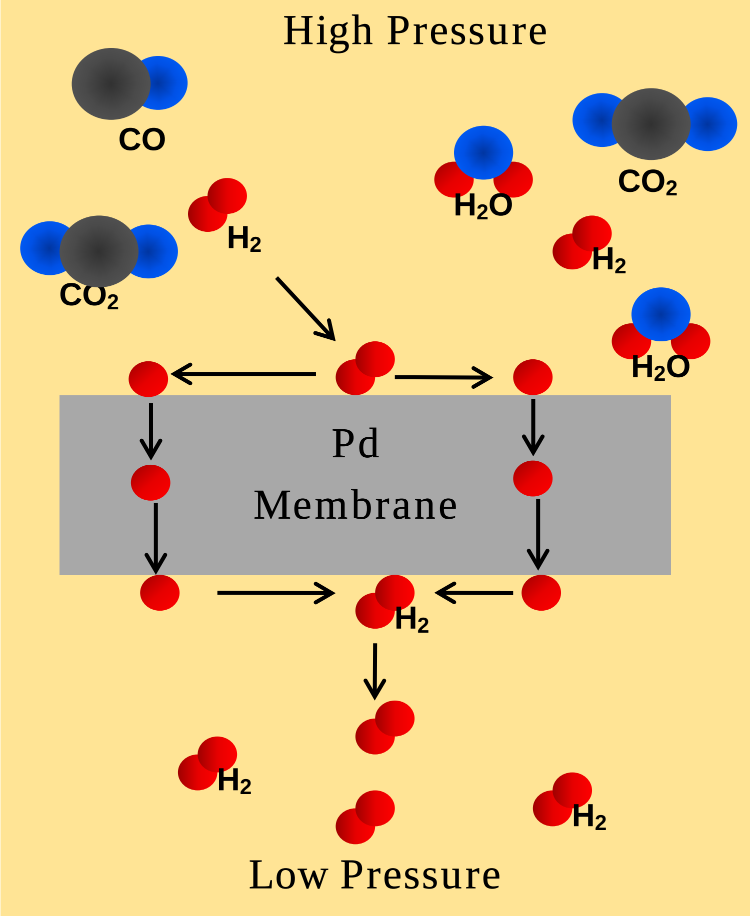
# How Palladium Membrane Works

Permeation

1. Dissociative Adsorption
2. Surface-to-bulk
3. Bulk Diffusion
4. Bulk-to-Surface
5. Recombinative Desorption

Disadvantages

1. Poor chemical resistance
2. Embrittlement



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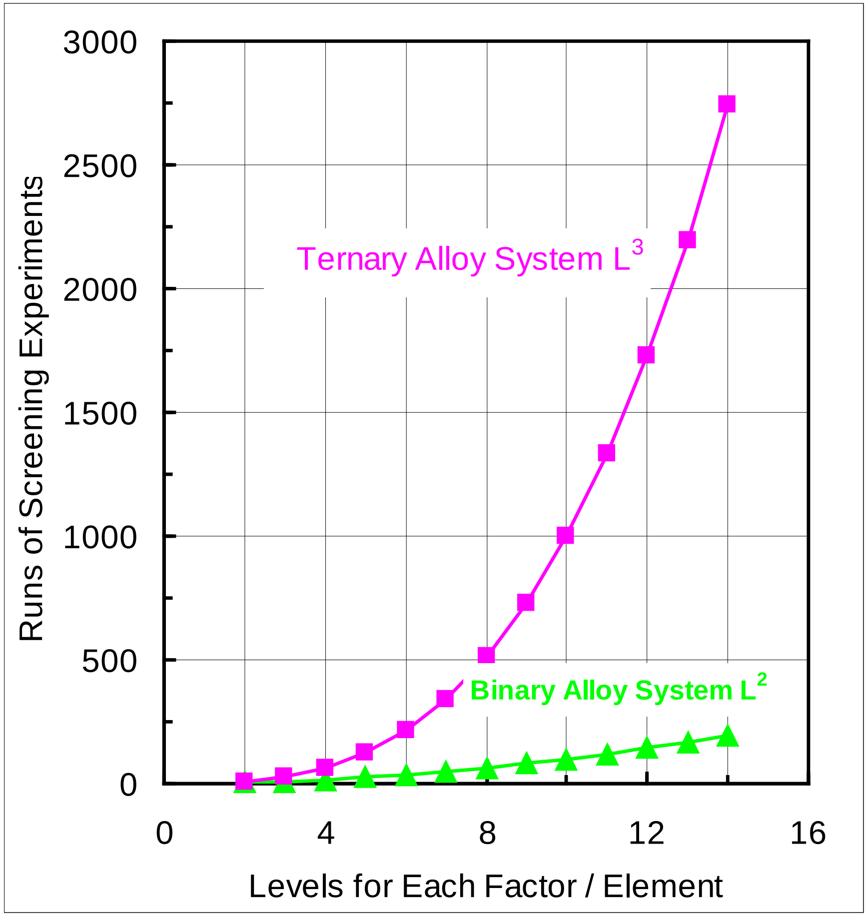
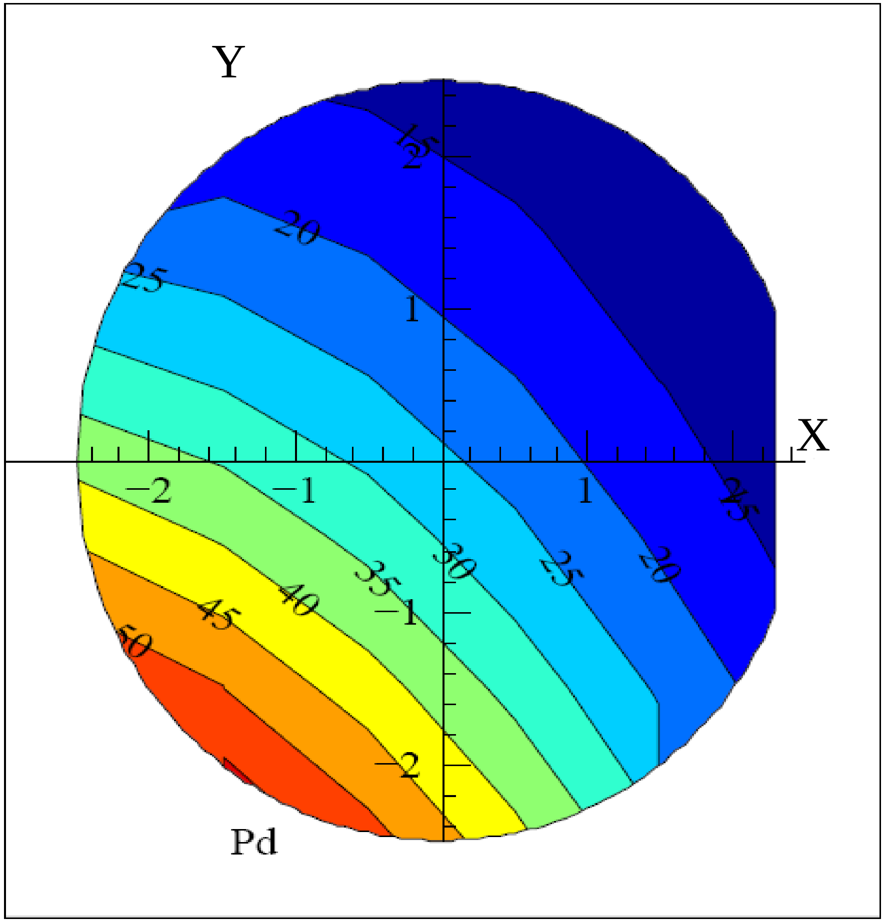
# High Throughput Alloy Screening

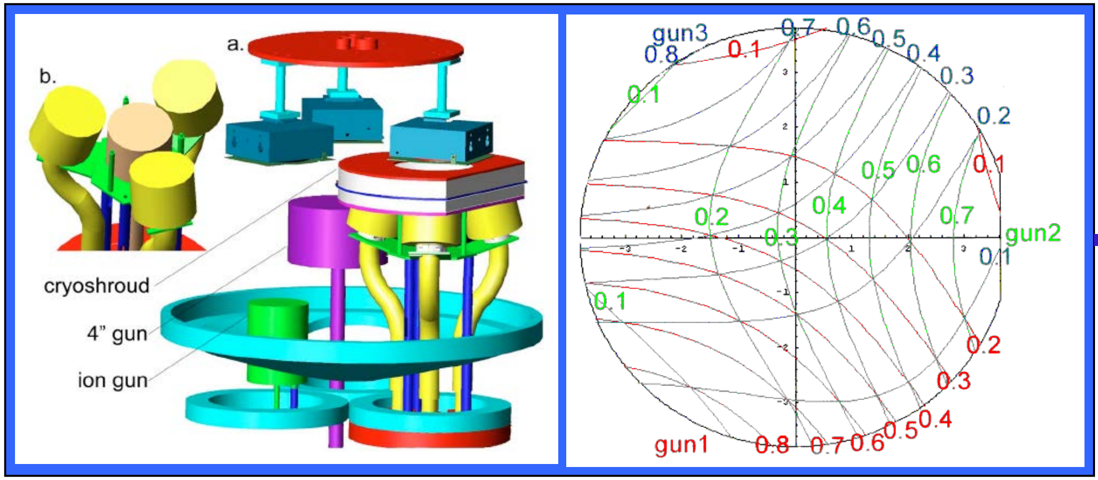
## Conventional: One at a Time vs. Combinatorial: Hundreds at a Time



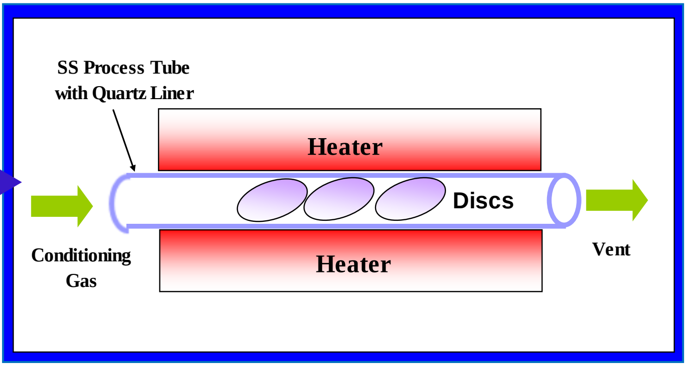


# Combinatorial Pd Alloy Development Workflow

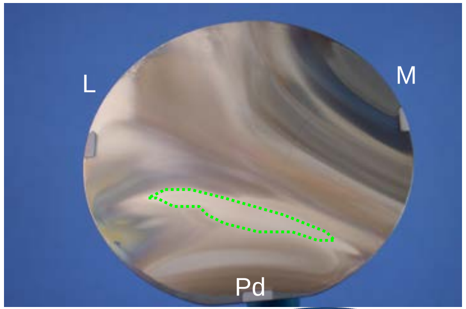
## Composition Spread Fabrication: 50 alloys
## Prof. Bruce van Dover (Cornell)



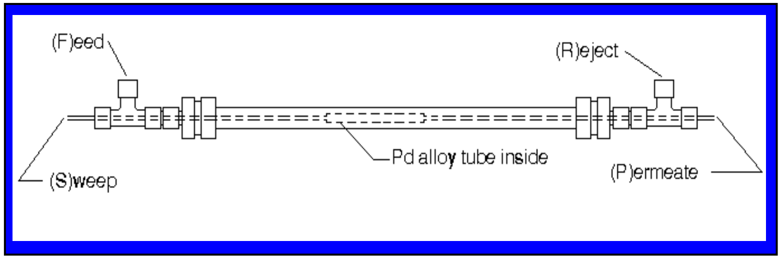
## Syngas Exposure:
## Pall Corporation



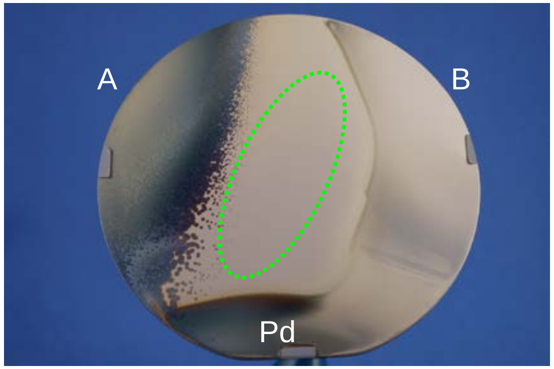
## Corrosion Assessment:
## Prof. Meilin Liu (Georgia Tech)

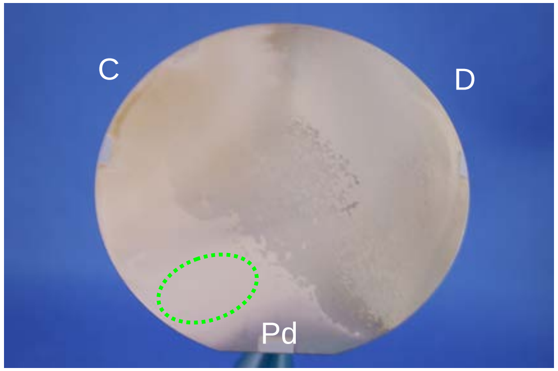


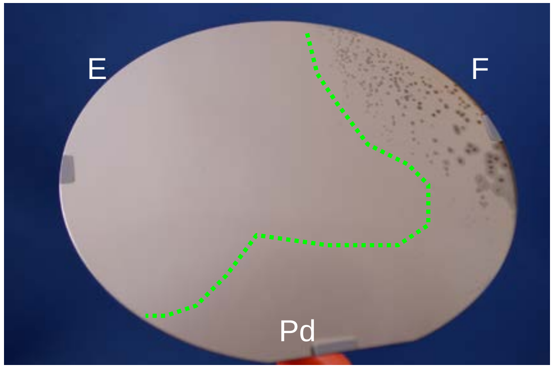
## Fabrication and Testing: 6 alloys
## Prof. Doug Way (CSM) and Pall

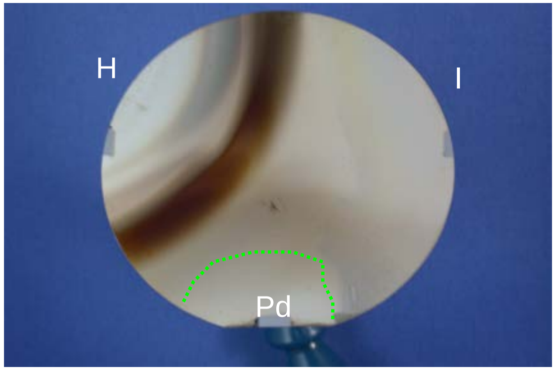


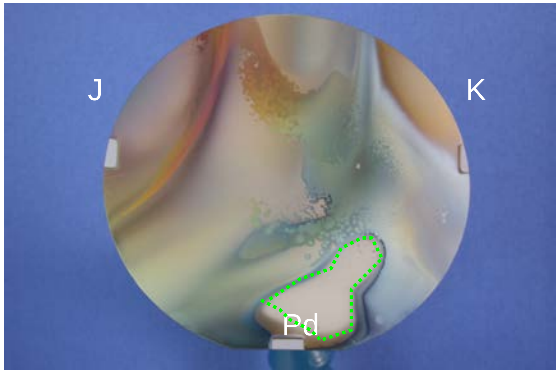
# Sputtered Wafers After Syngas Exposure

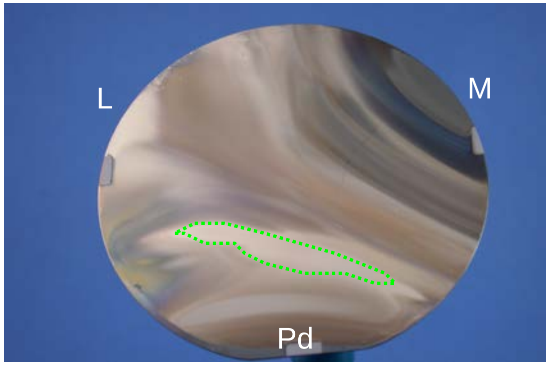


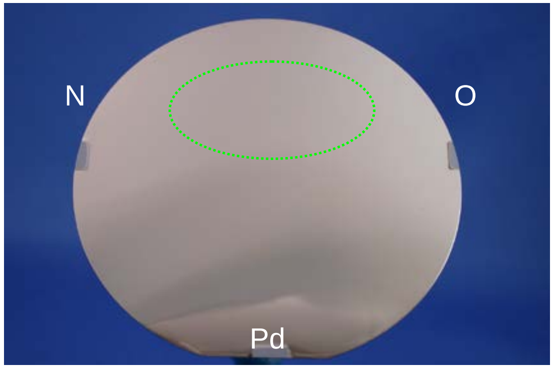


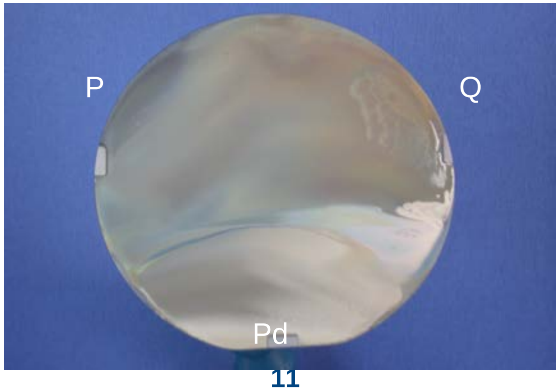


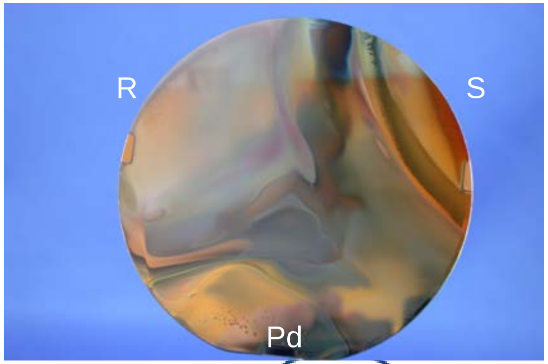




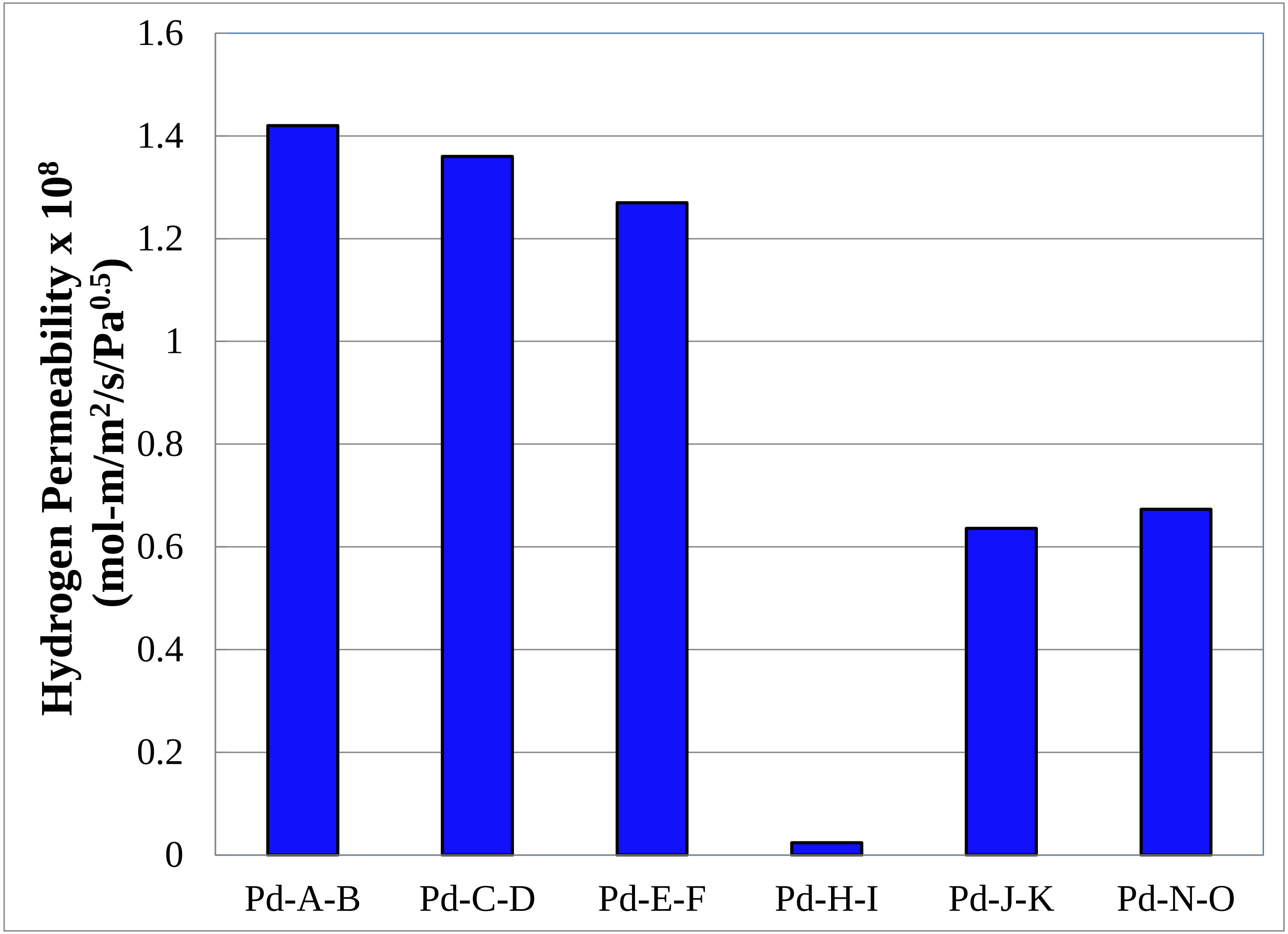








# Pure-gas Testing Summary at 500$^{o}$C



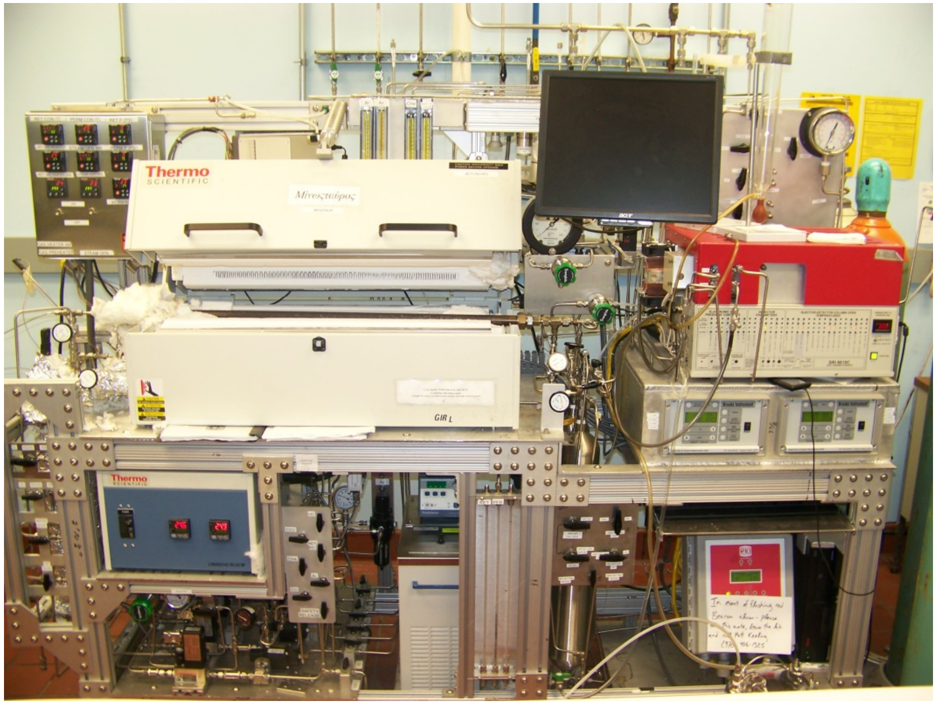
# Pd Alloy Simulated Syngas Testing

Testing Conditions

- Feed Pressure ~160 psig
- Temperature 400 / 500$^oC$

Testing Sequence

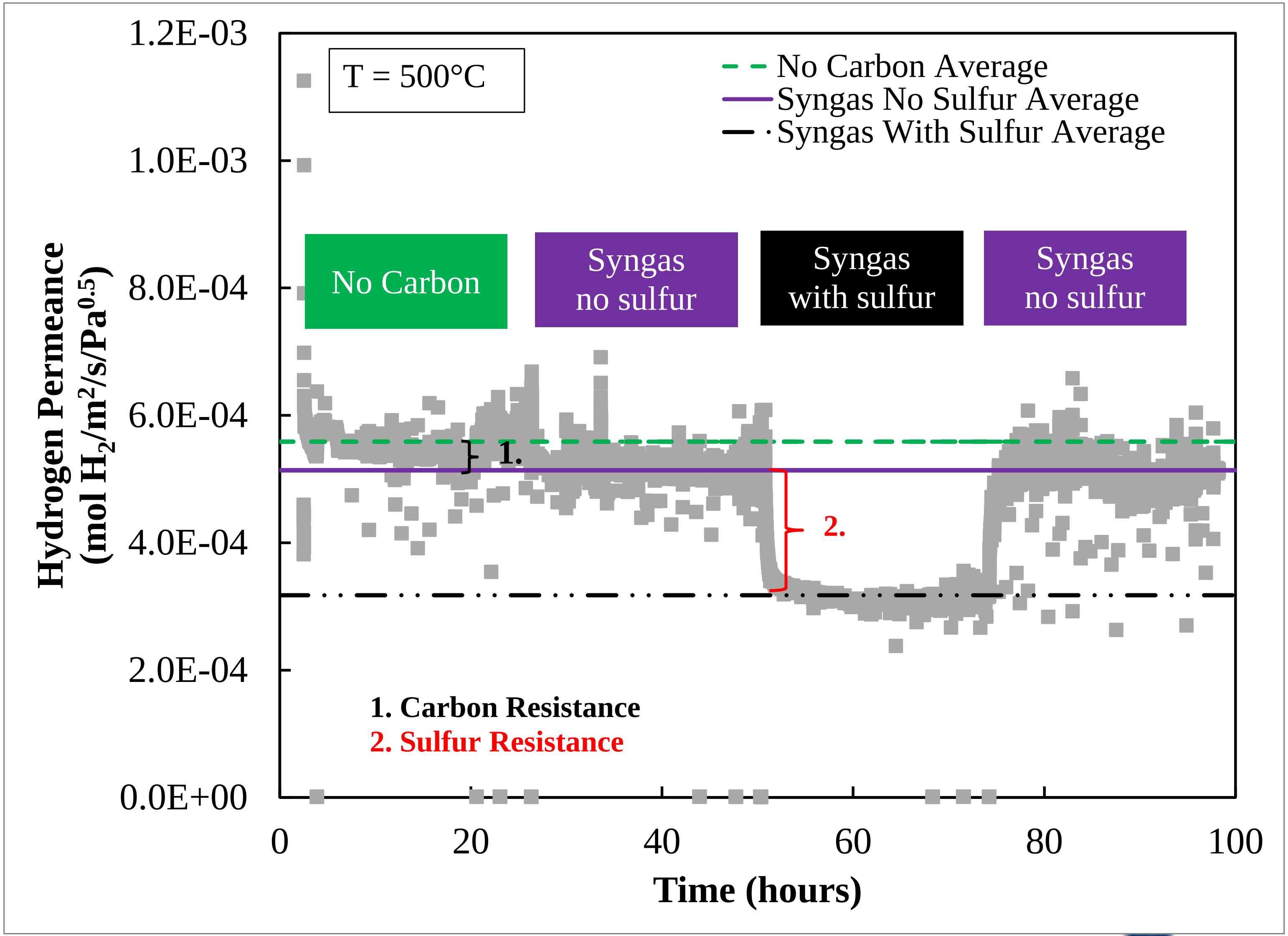
- 24 hours in 36 v% $H_2$, 3 v% $H_2O$, balance $N_2$
- 24 hours in syngas
- 24 hours in syngas + 20 ppm $H_2S$
- 24 hours in syngas



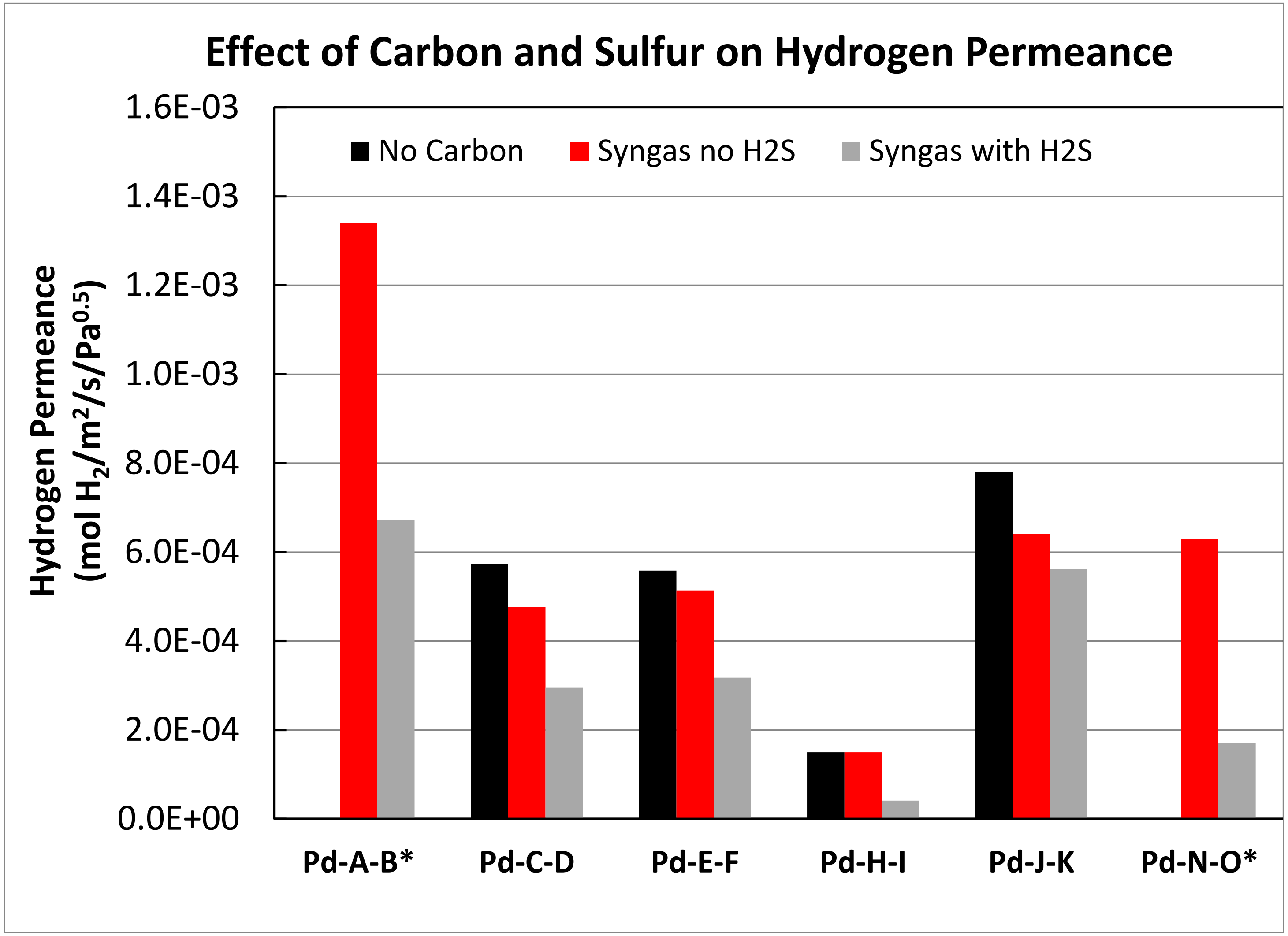
Syngas (air blown coal gasifier)

- $H_2$ = 36 v%
- $CO_2$ = 11 v%
- CO = 1.3 v%
- $H_2O$ = 3 v%
- $N_2$ = 49 v%

# Sample Test Sequence

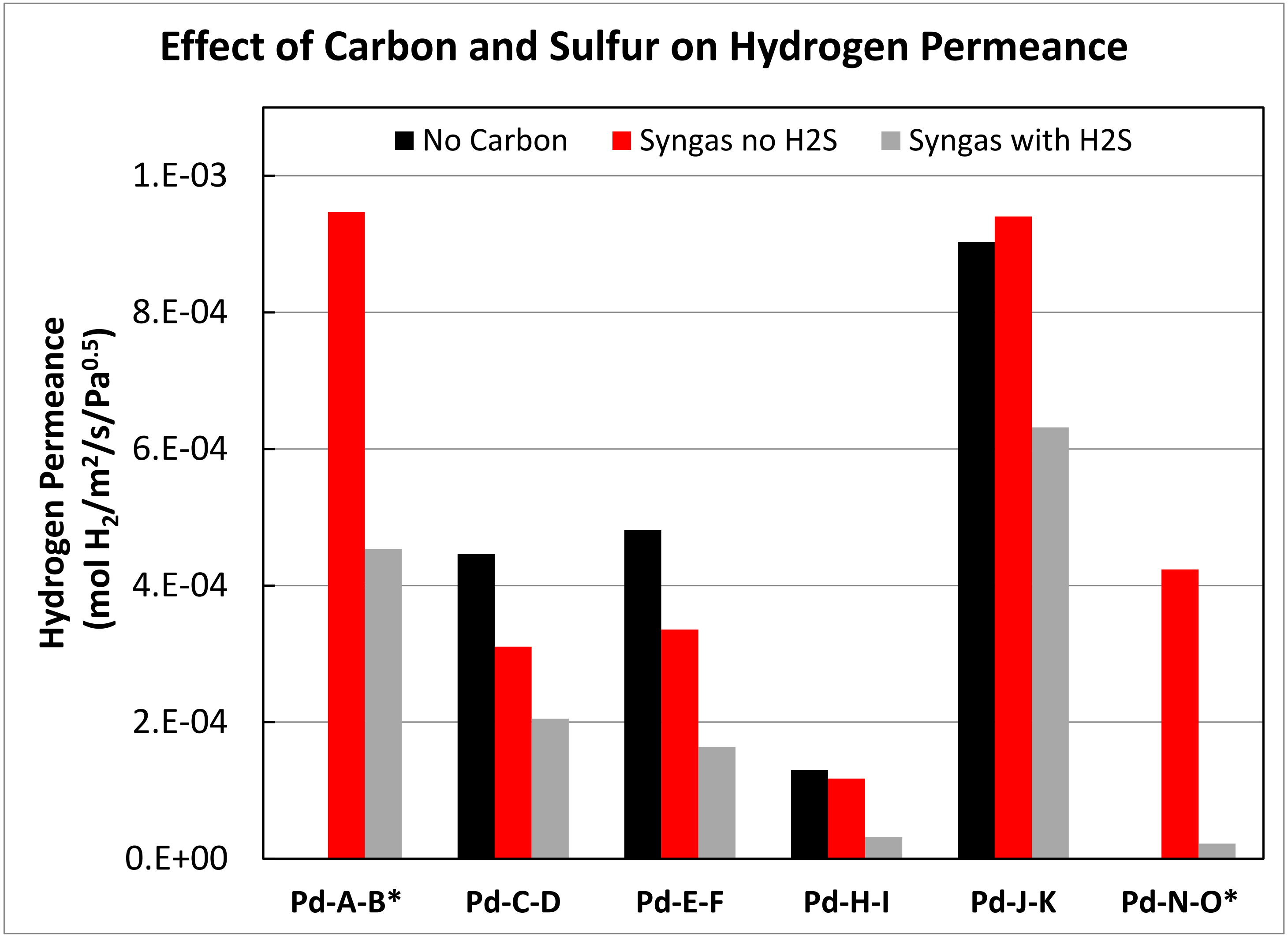


# Testing Results at 500ºC, $P_{feed}$ = 160 psig



*Note: membranes without the “no carbon” data were tested before the current testing plan was in place.

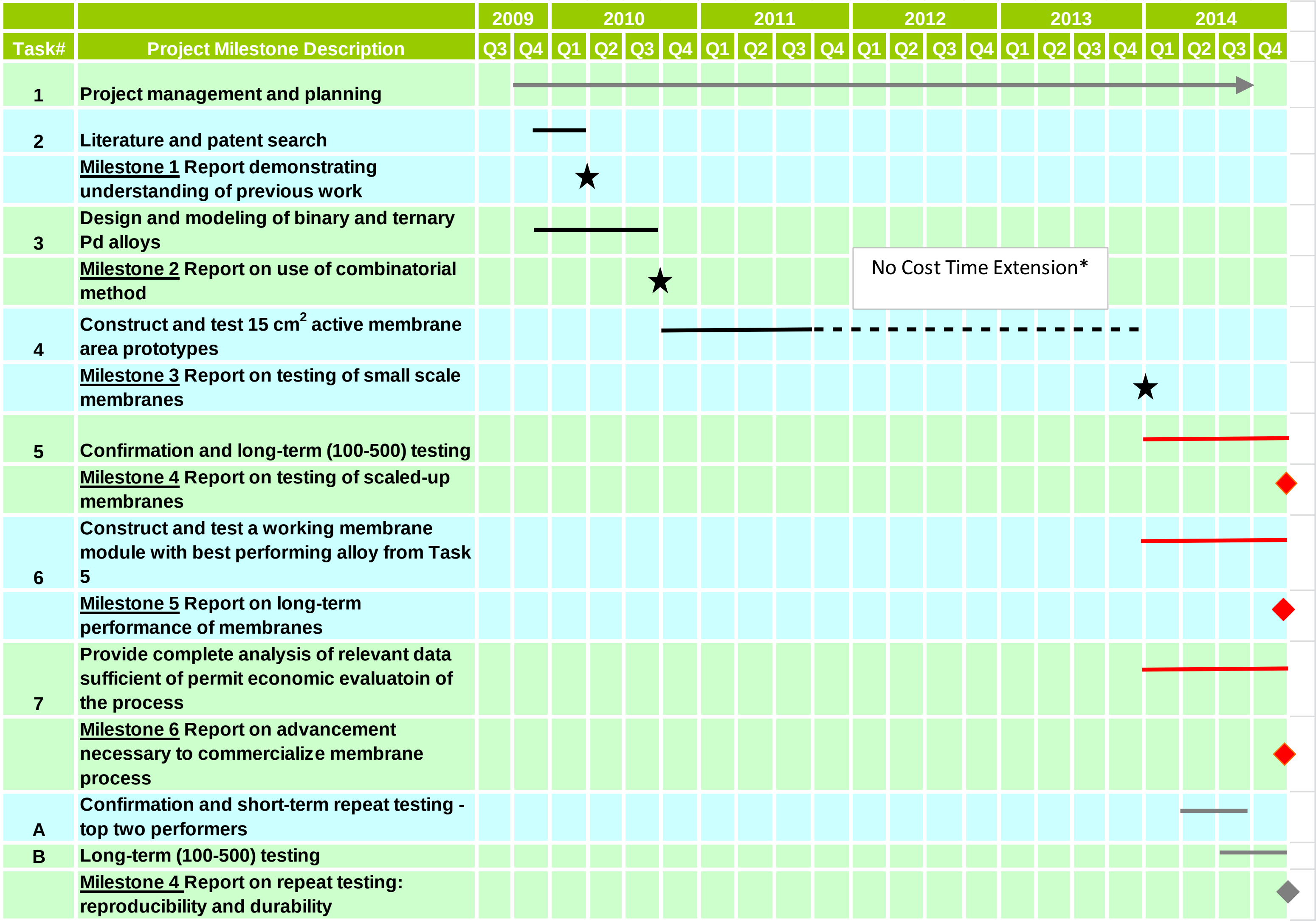
# Testing Results at 400ºC, $P_{feed}$ = 160 psig


Effect of Carbon and Sulfur on Hydrogen Permeance

*Note: membranes without the “no carbon” data were tested before the current testing plan was in place.

# Project Schedule & Milestones

**Completed** ▬ **Ongoing** ▬ **#Will not complete** ▬



| 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 | Confirmation and long-term (100-500) testing |
| | Milestone 4 Report on testing of scaled-up membranes |
| 6 | Construct and test a working membrane module with best performing alloy from Task 5 |
| | 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 |
| A | Confirmation and short-term repeat testing - top two performers |
| B | Long-term (100-500) testing |
| | Milestone 4 Report on repeat testing: reproducibility and durability |

***Task 4 was 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.**

**#Tasks 5, 6, and 7 were changed to A and B due to time constraints.**

# Progress and Current Status

## Task A

- ☐ Fabricate, anneal, and pure-gas test a minimum of three confirmation membranes of top two performing alloys.
- ☐ Completion: 100%

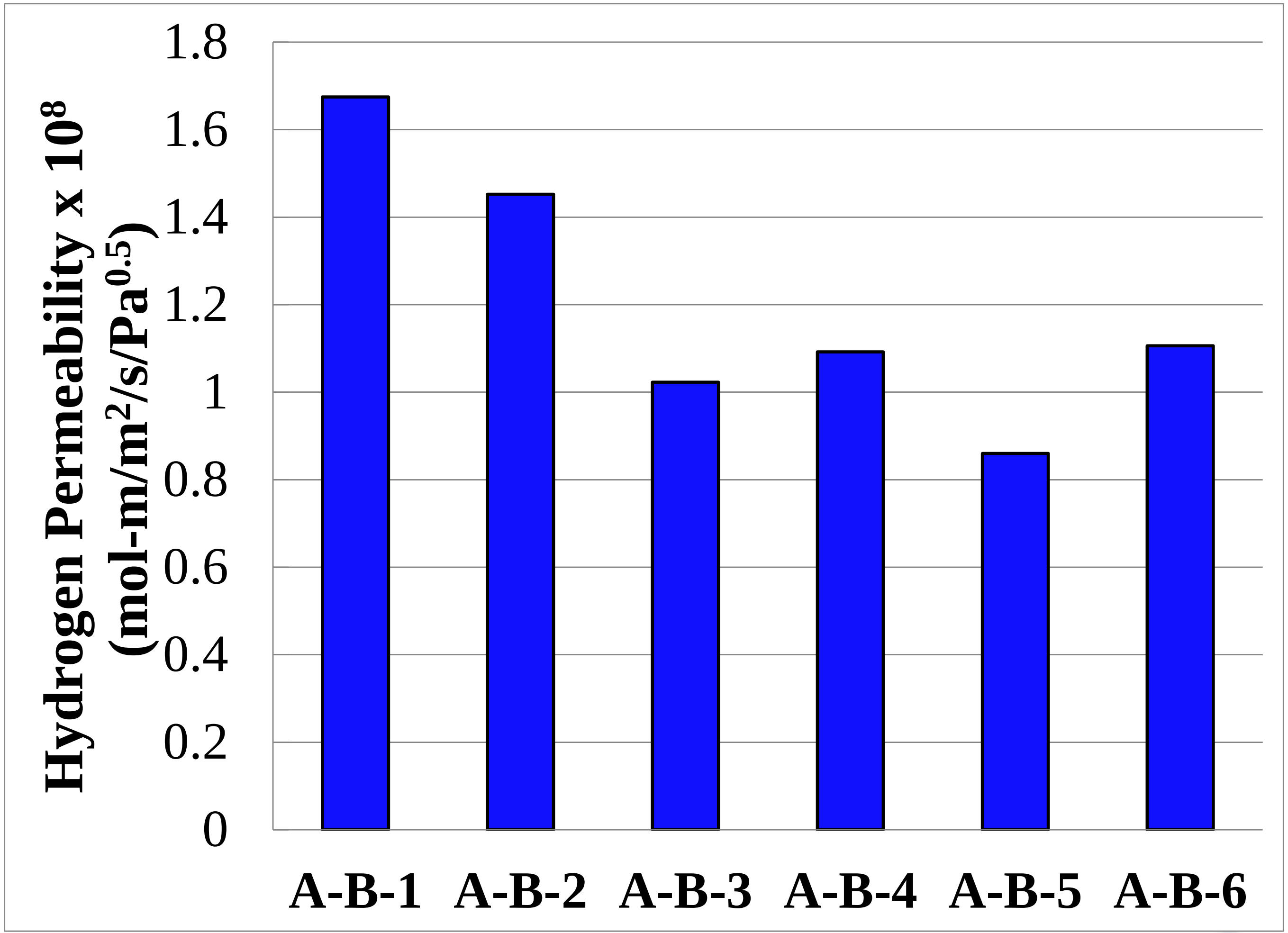
## Task B

- ☐ Repeat mixed-gas testing procedure to confirm initial testing results of at least three membranes.
  - ☐ Completion: 67% (two of each membrane have been mixed-gas tested, with one currently being tested)
- ☐ Understand long-term (100+ continuous hours in simulated syngas) effects of carbon monoxide and hydrogen sulfide before scaling up.
  - ☐ Completion: 0%

# Current Work: Repeat Testing of Pd-A-B

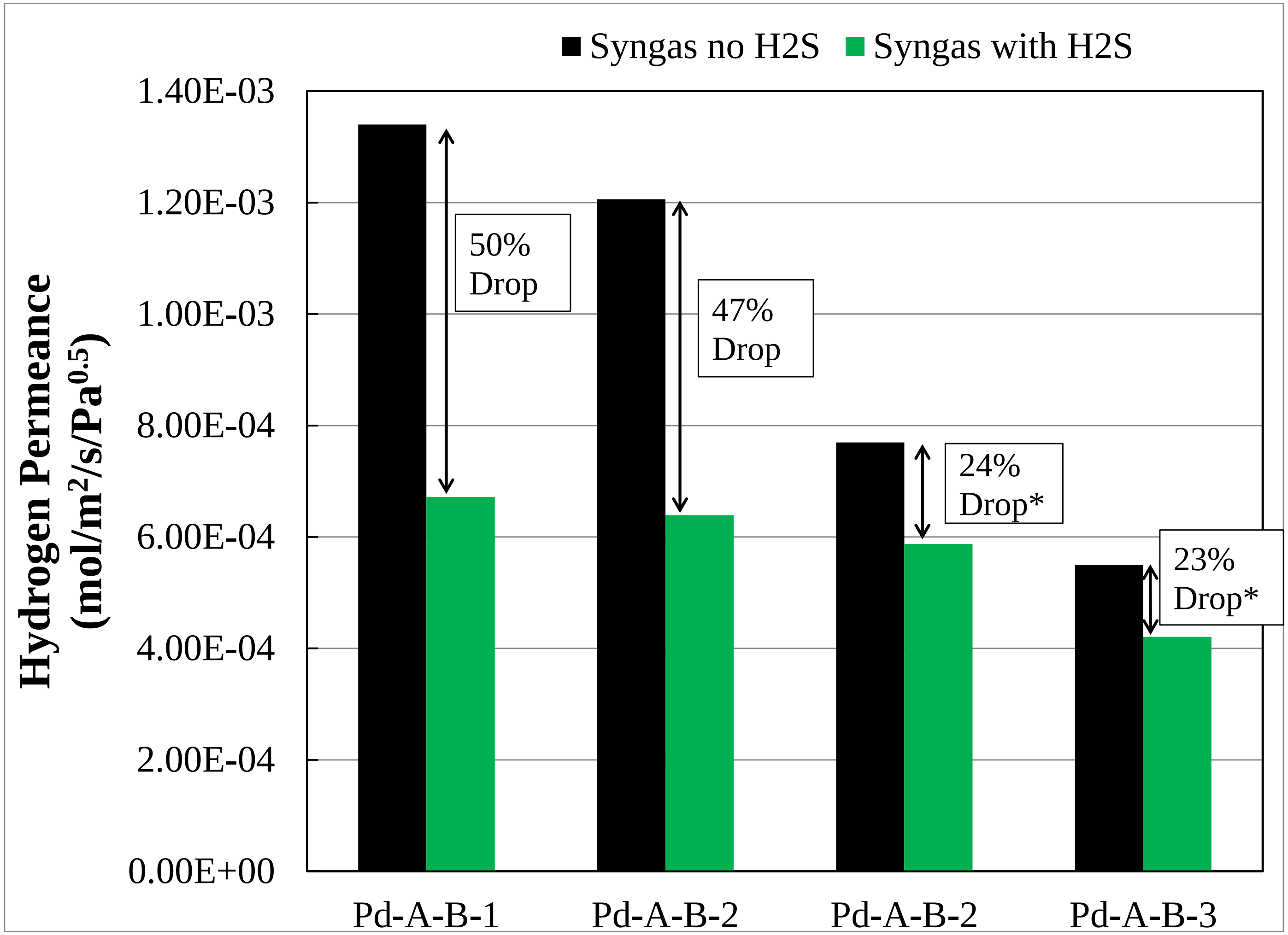
Demonstrates the sensitivity of permeability to composition

Permeability data taken at 500°C



# Current Work: Repeat Testing of Pd-A-B

Demonstrates the testing reproducibility (data is taken at 500°C)



Syngas (Test 2B)

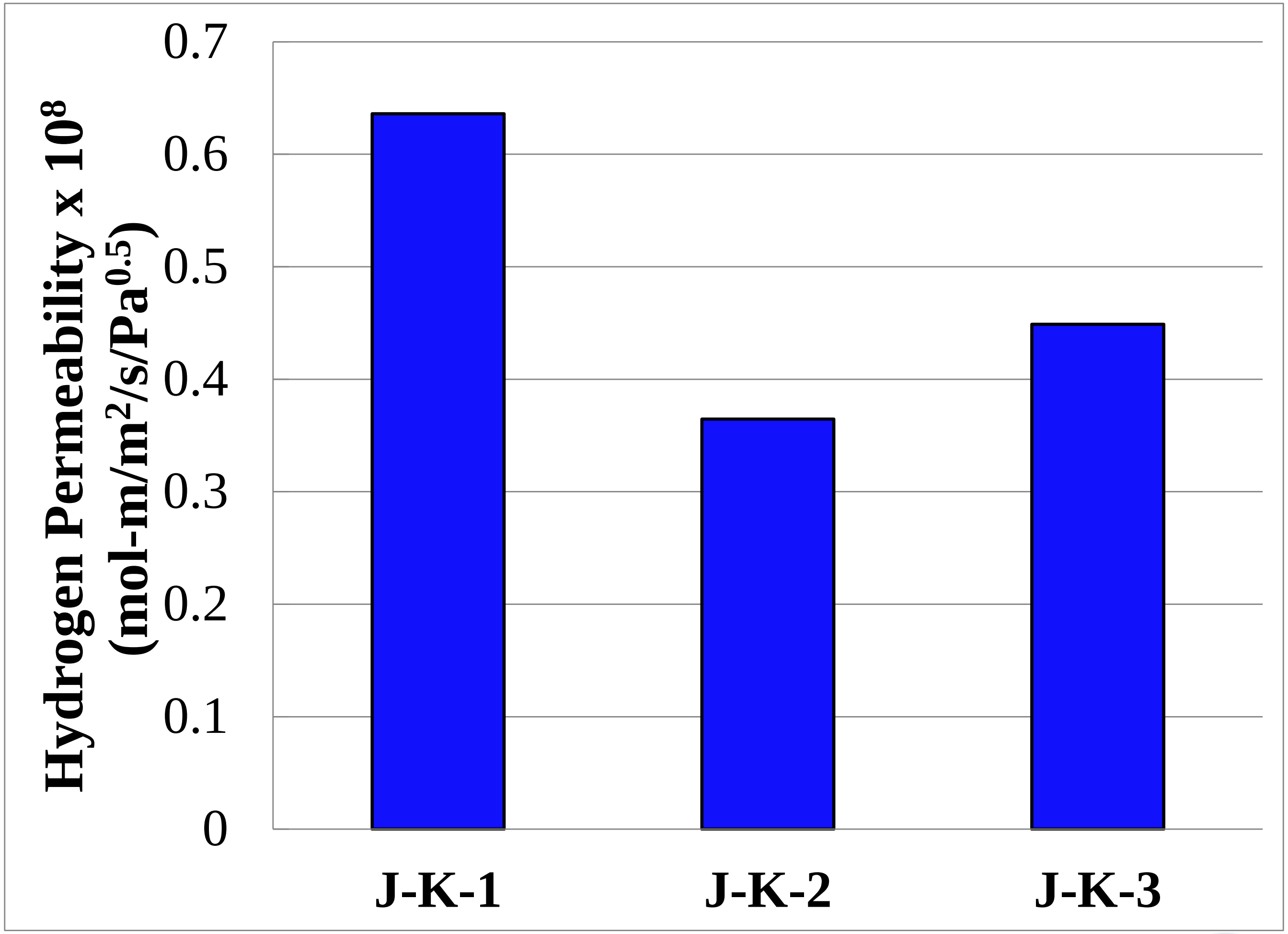
- ☐ $H_2$ 36% → 33%
- ☐ $CO_2$ 11% → 40%
- ☐ CO 1.3% = 1.3%
- ☐ $H_2O$ 3% → 25%
- ☐ $N_2$ 49% → 0%

*Changed feed gas composition to be DOE test protocol for H2 separating membranes (test condition 2B, but with 20 ppm $H_2S$ instead of 30)

# Current Work: Repeat Testing of Pd-J-K

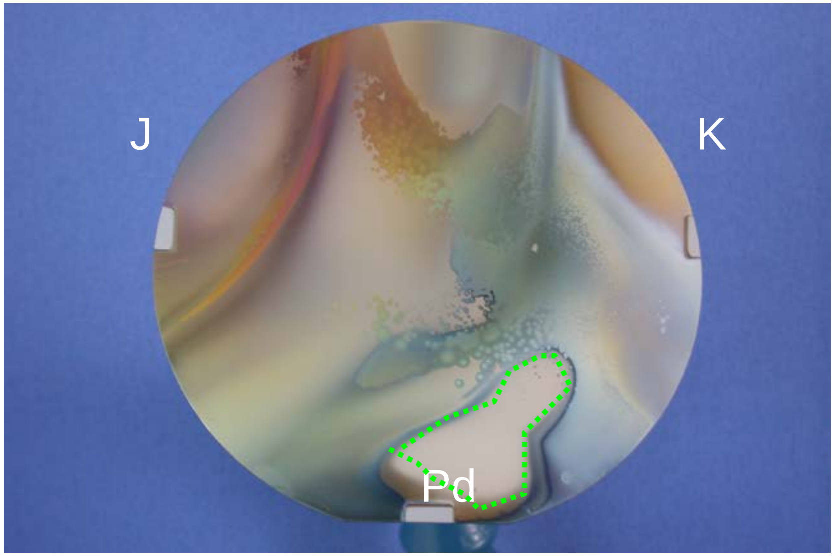
Demonstrates the sensitivity of permeability to composition

Permeability data taken at 500°C



# Current Work: Repeat Testing of Pd-J-K

- ❑ Two repeat membranes have been tested in mixed-gas
- ❑ Both failed upon the introduction of $H_2S$
- ❑ Current hypothesis is that the two repeat membranes are on the edge of what can resist carbon and sulfur species
  - ❑ ICP-MS analysis is being used to prove (or disprove) this hypothesis



# Plan for Completion

- Understand fabrication reproducibility
  - Have completed two repeat tests of each leading candidate with one remaining of Pd-J-K
  - Use analysis (ICP-MS) to help explain differences

- Conduct long-term (100+) hour performance test to gain insight to membrane durability of each composition

# Acknowledgements

- U.S. DOE National Energy Technology Laboratory
  - Jason Hissam
- Pall Corporation
  - Bill Hogan, Matthew Keeling
- Colorado School of Mines
  - Douglas Way, Colin Wolden, Dan Cooney