One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

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Project ID PD30

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Overview

Timeline

- Start: 02/01/2007
- End: 06/30/2011
- Percent complete: 22%

Budget

- Total project funding: $3,396,186
  - DOE share: $2,716,949
  - Contractors share: $679,237
- Funding received in FY07: $676,403
- Funding for FY08: $544,152 planned $0 to date

Overview (con’t)

Barriers

- Hydrogen Production from Biomass Barriers
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technology I. Impurities N. Hydrogen Selectivity O. Operating Temperature P. Flux
- DOE Technical Targets
  - $2-3/kg H_2 from biomass delivered target
  - $1.60/kg H_2 from biomass without delivery

Partners

- Arizona State University
- National Energy Technology Laboratory
- Schott North America
- Wah Chang, an Allegheny Technology Company

Objectives

Long-term goal:

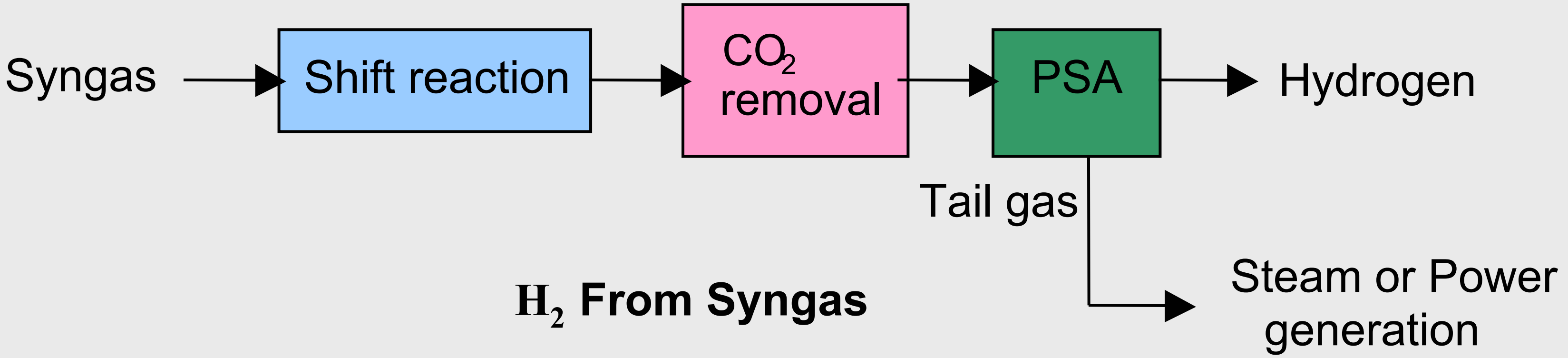
Determine the technical and economic feasibility of using the gasification membrane reactor to produce hydrogen from biomass

First-year goal:

Select an initial candidate membrane material that can be fabricated into a module for testing with the bench scale gasifier by evaluating ceramic, metallic, composite, and glass ceramic membranes

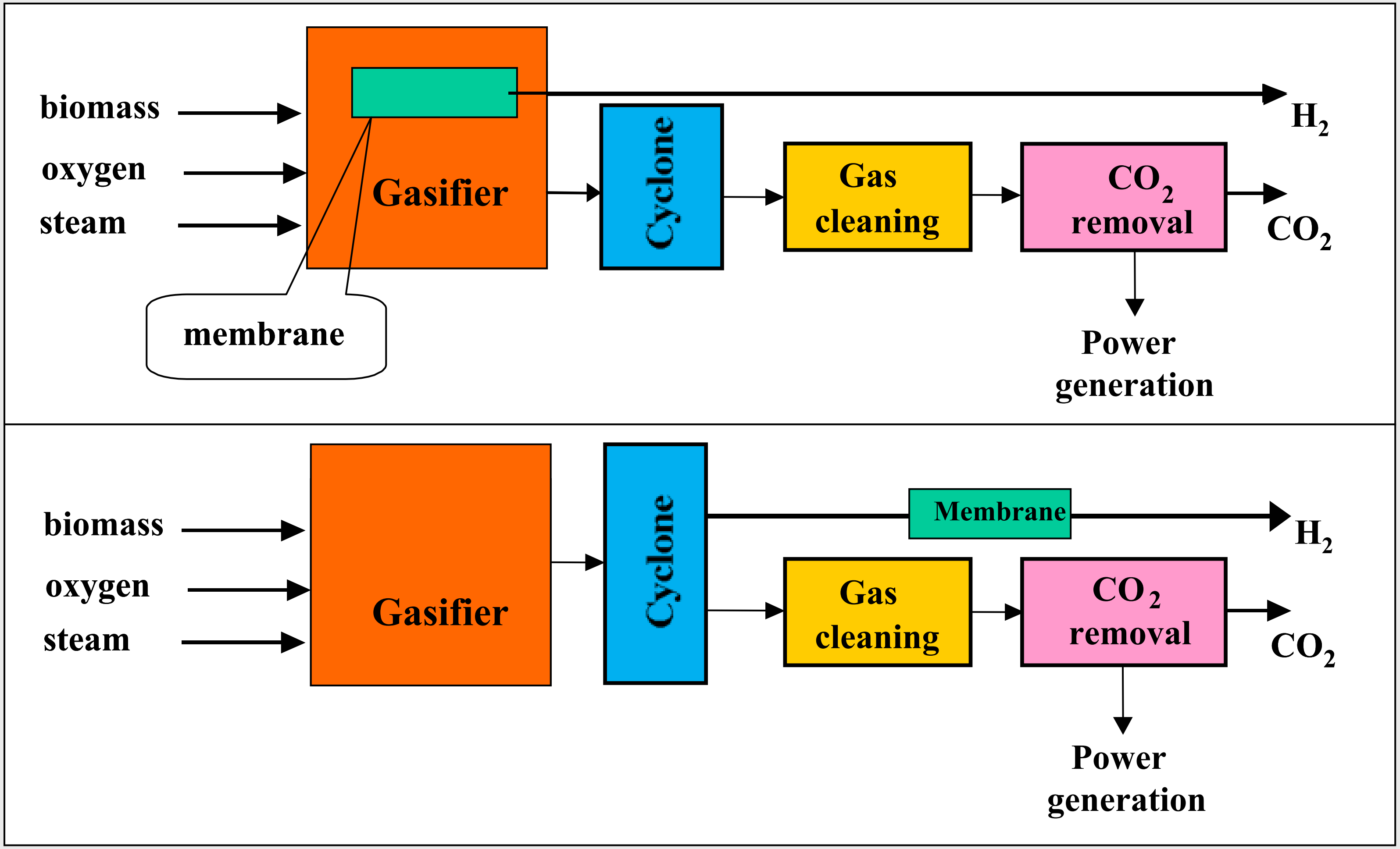
Hydrogen Production from Biomass Gasification Based On Conventional Technologies

Biomass Syngas Platform



H_2 From Syngas

Biomass Gasifier with Internal or Close-Coupled Membrane



Potential Benefits of Membrane Reactor for Hydrogen Production from Biomass

> **High H_2 production efficiency:**

– Thermodynamic analysis indicates potentially over 40% improvement in H_2 production efficiency over the current gasification technologies

Eliminate loss in PSA tail gas	
More CO shift	$H_2O+CO = CO_2+H_2$
Reform CH_4	$CH_4+H_2O = CO+3H_2$

> **Low cost:**

– reduce/eliminate downstream processing steps

> **Clean product:**

– no further conditioning needed, pure hydrogen

> **CO_2 sequestration ready**:

– simplify CO_2 capture process

> **Power co-generation**:

– utilization of non-permeable syngas

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Scope of Work

- Task 1. Membrane material development
  - 1.1 Ceramic material synthesis & testing ASU
  - 1.2 Metallic material synthesis & testing DOE-NETL
  - 1.3 Composite membrane synthesis & testing SCHOTT and GTI
  - 1.4 Optimization of selected candidate membranes
- Task 2. Gasification membrane reactor process development and economic analysis
- Task 3. Bench-scale biomass gasifier design and construction

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Scope of Work (con't)

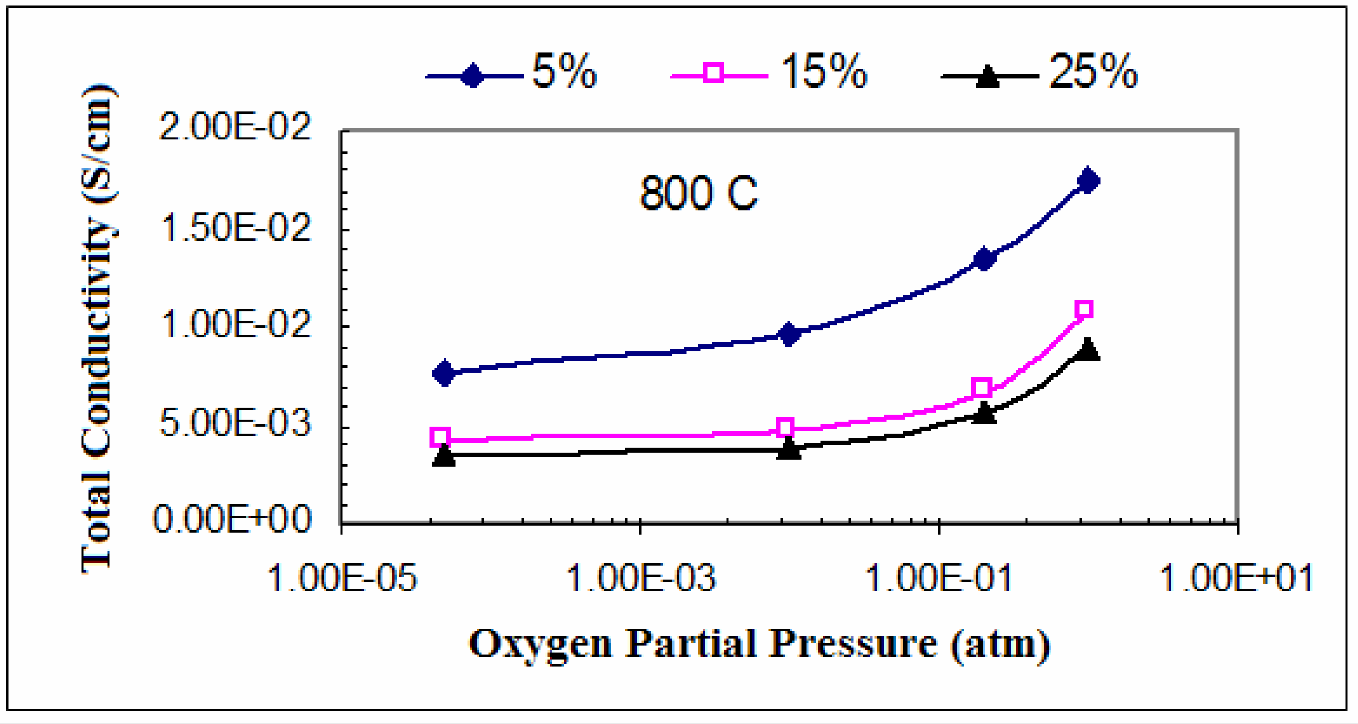
- Task 4. Integrated testing of initial membrane with gasifier
  - 4.1 Design of membrane module configuration Wah Chang assistance
  - 4.2 Membrane module fabrication Wah Chang
  - 4.3 Testing of bench-scale membrane reactor
- Task 5. Integrated testing of best candidate membrane with gasifier
- Task 6. Project Management and reporting

Milestones

Task		Revised/ Planned
1.3.2	Select Initial Candidate Membrane	5/29/08
3	Bench-Scale Biomass Gasifier Design And Preparation	7/31/09
4.3	Integrated Testing With Bench-Scale Gasifier	10/31/09

Results/Accomplishments ASU

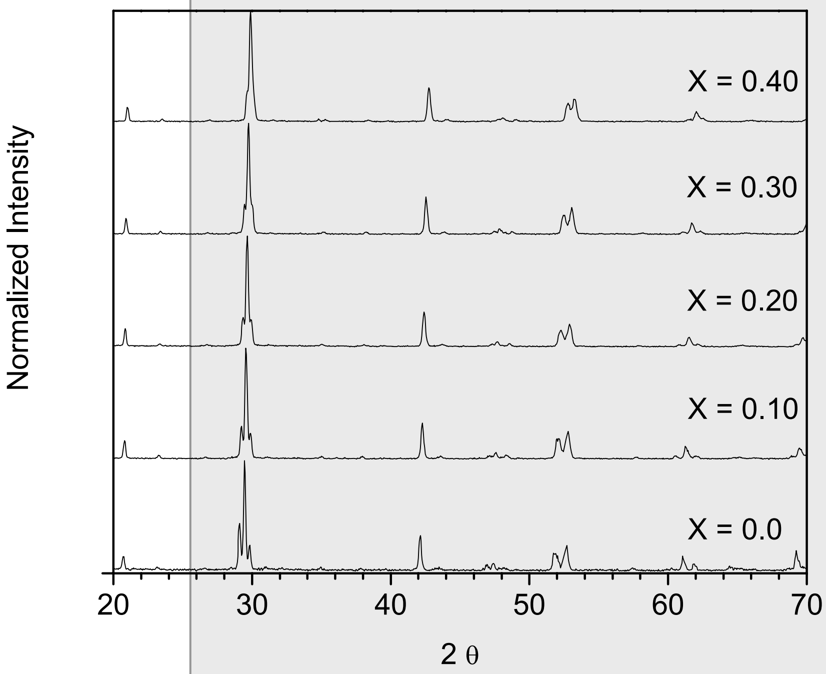
Total conductivity of $SrCe_{1-x}Tm_xO_{3-\delta}$ in N2/O2 Gas Mixtures



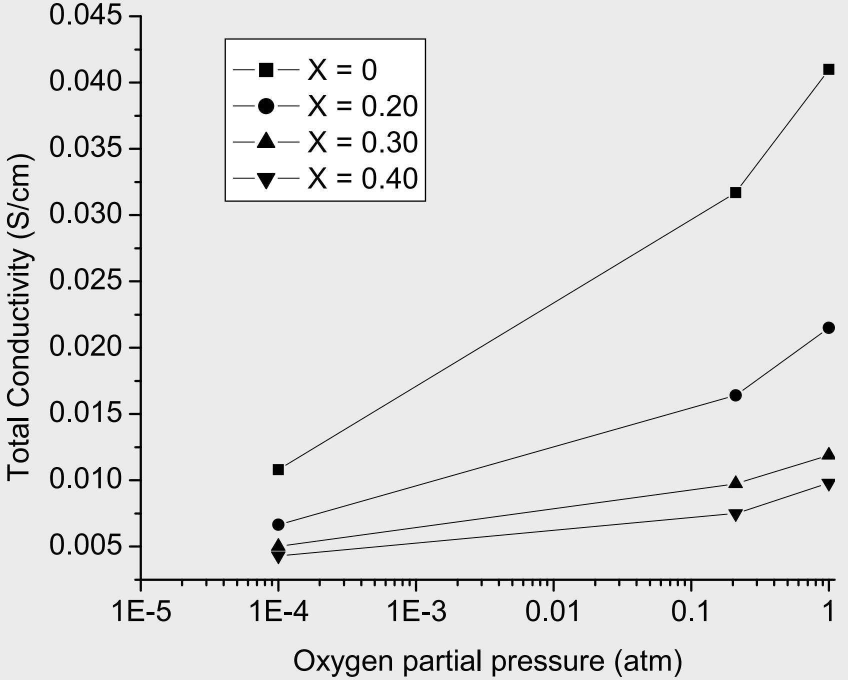
> Electronic conductivity decreases with increasing Tm doping due to additional phases beside perovskite present in $SrCe_{1-x}Tm_xO_{3-\delta}$ membranes at higher Tm doping levels

Results/Accomplishments ASU

•XRD patterns of $SrCe_{0.95-x}Zr_xTm_{0.05}O_{3-\delta}$



•Total conductivity of $SrCe_{0.95-x}Zr_xTm_{0.05}O_{3-\delta}$ at 900°C

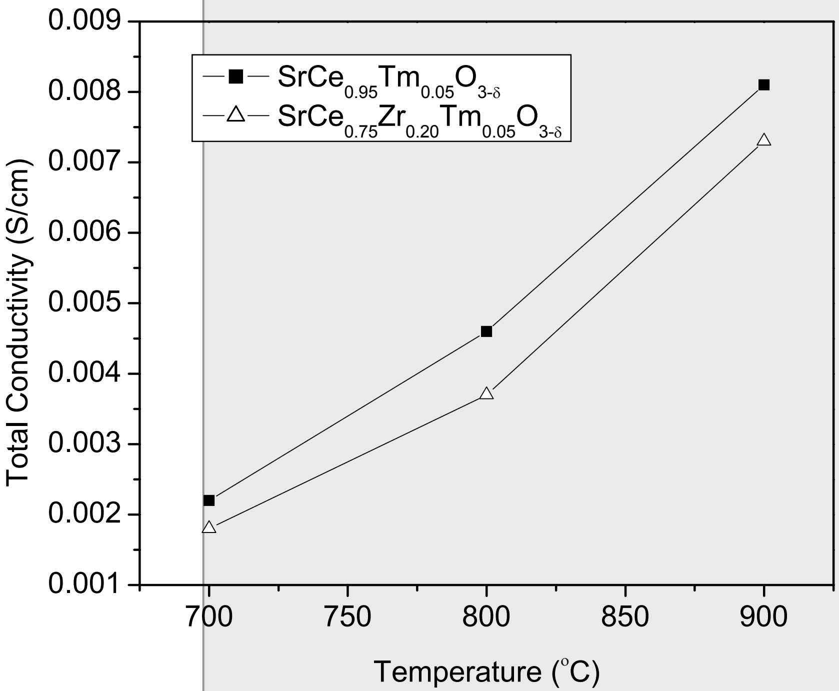


All membranes doped with Zr have single perovskite structure

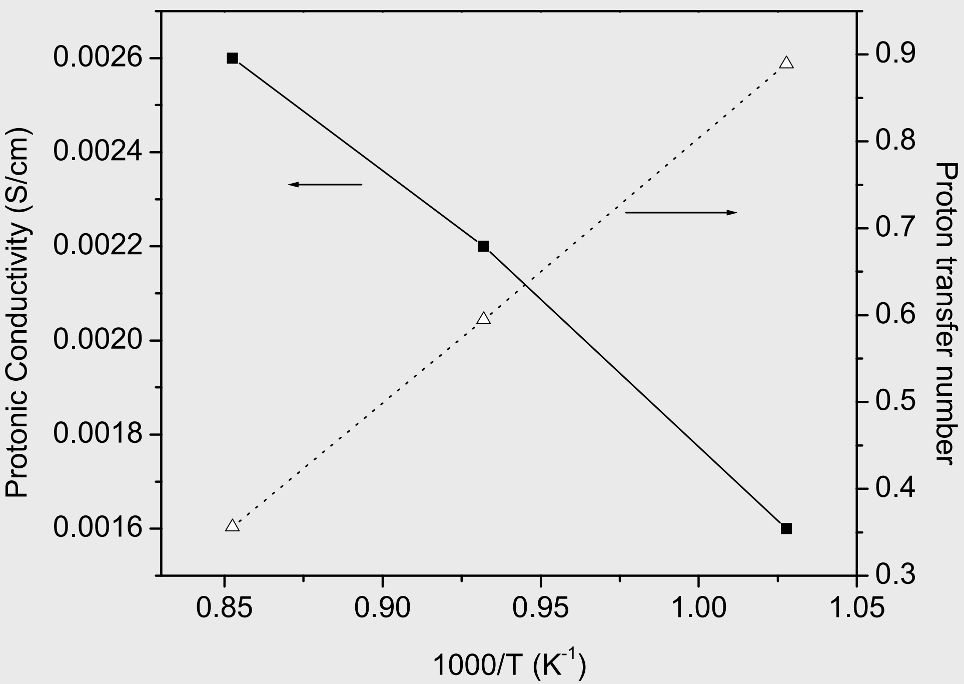
Total conductivity decreases with increasing Zr doping due to lower electronic conductivity of Zr

Results/Accomplishments ASU

- Total conductivity in 10% H_2/He environment



- Temperature dependence of protonic conductivity and proton transfer number of $SrCe_{0.75}Zr_{0.20}Tm_{0.05}O_{3-\delta}$



20% Zr doped membranes have comparable total conductivity values in H_2 environments

$SrCe_{0.75}Zr_{0.20}Tm_{0.05}O_{3-\delta}$ has appreciable protonic conductivity and protonic conductivity is dominant at lower temperatures

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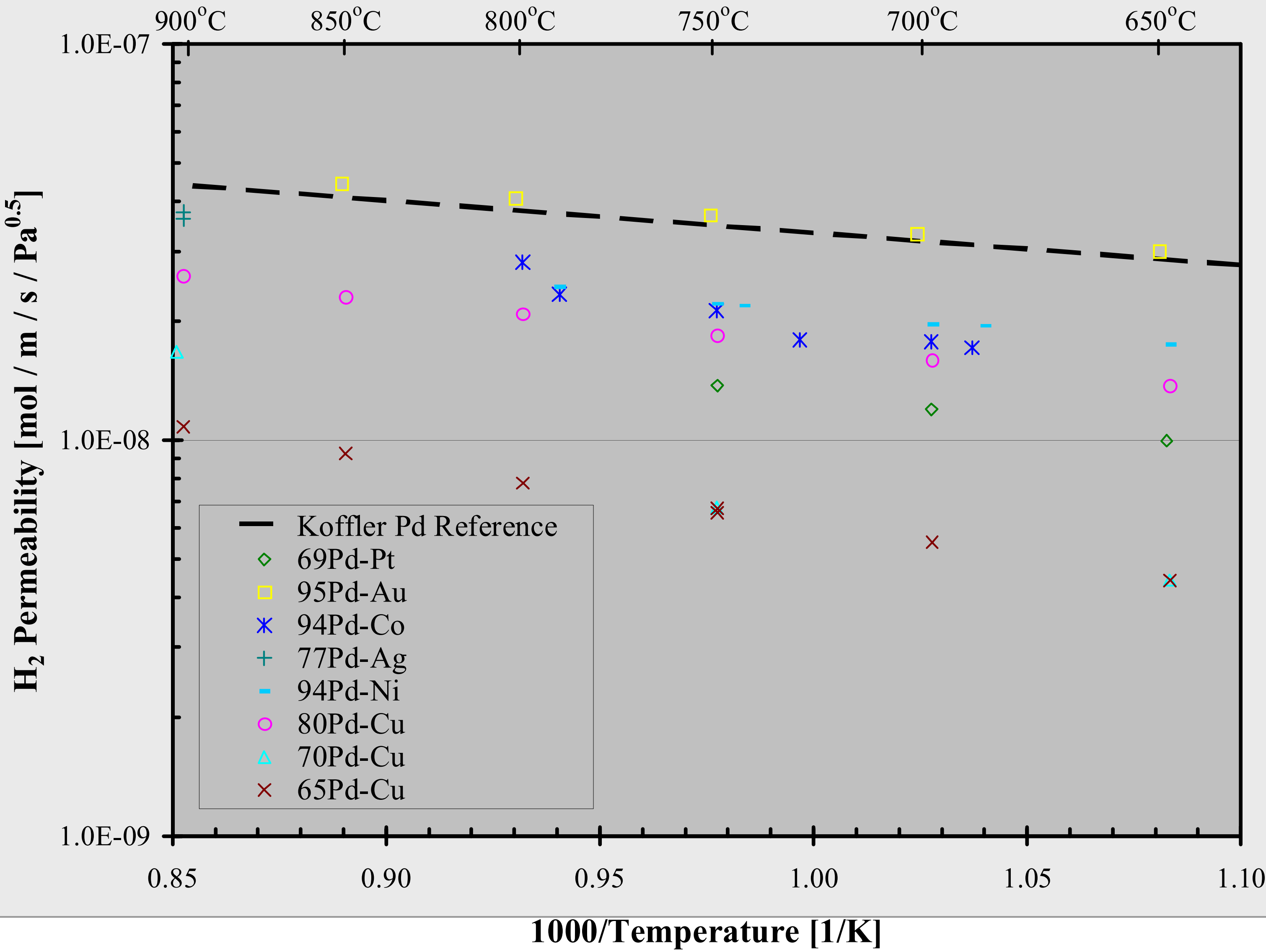
Results/Accomplishments DOE-NETL

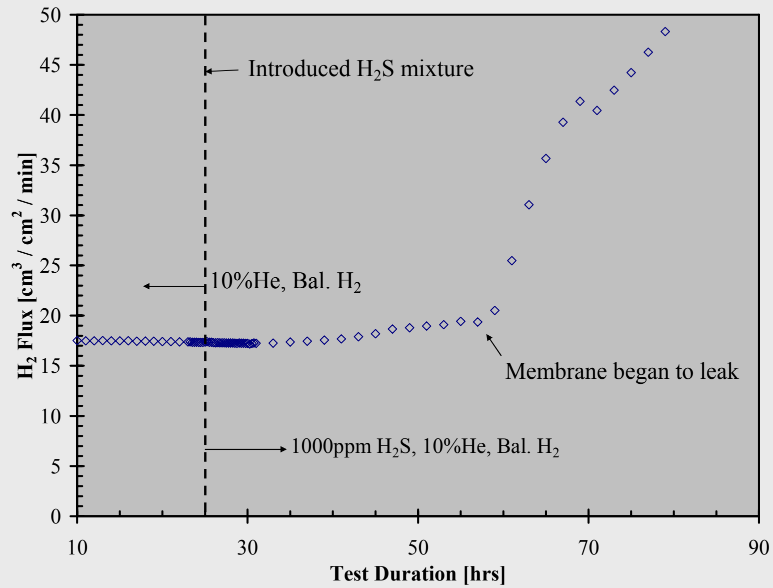
Membrane Performance in Clean H_2

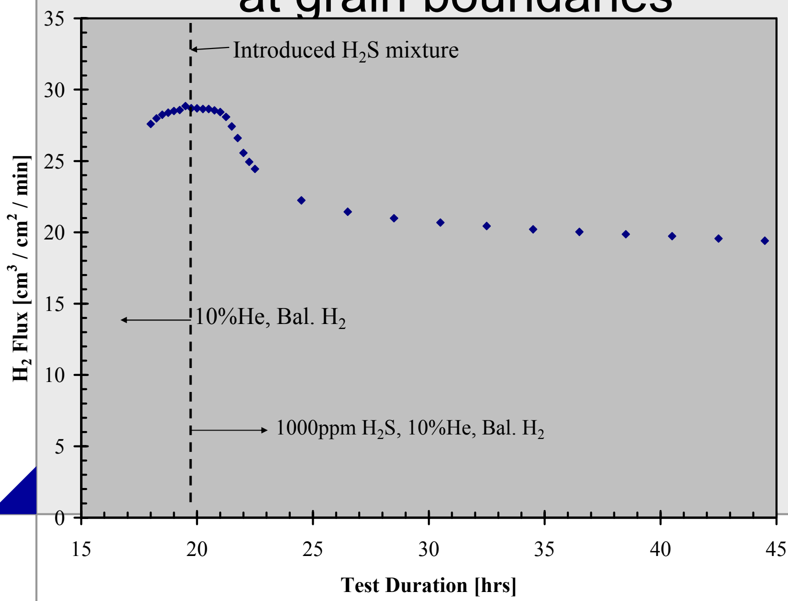


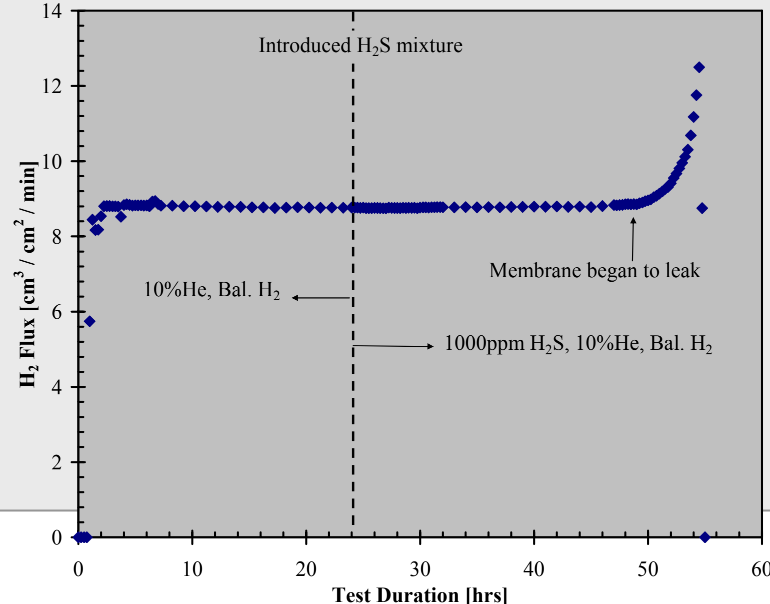
Results/Accomplishments DOE-NETL

Performance in Sour H_2

- At 700°C, all alloys tested showed negligible impact upon the introduction of a 0.1%-10%He-H_2 gas mixture.
  - All membrane samples formed leaks prior to test completion
    - Failure apparently occurs at grain boundaries





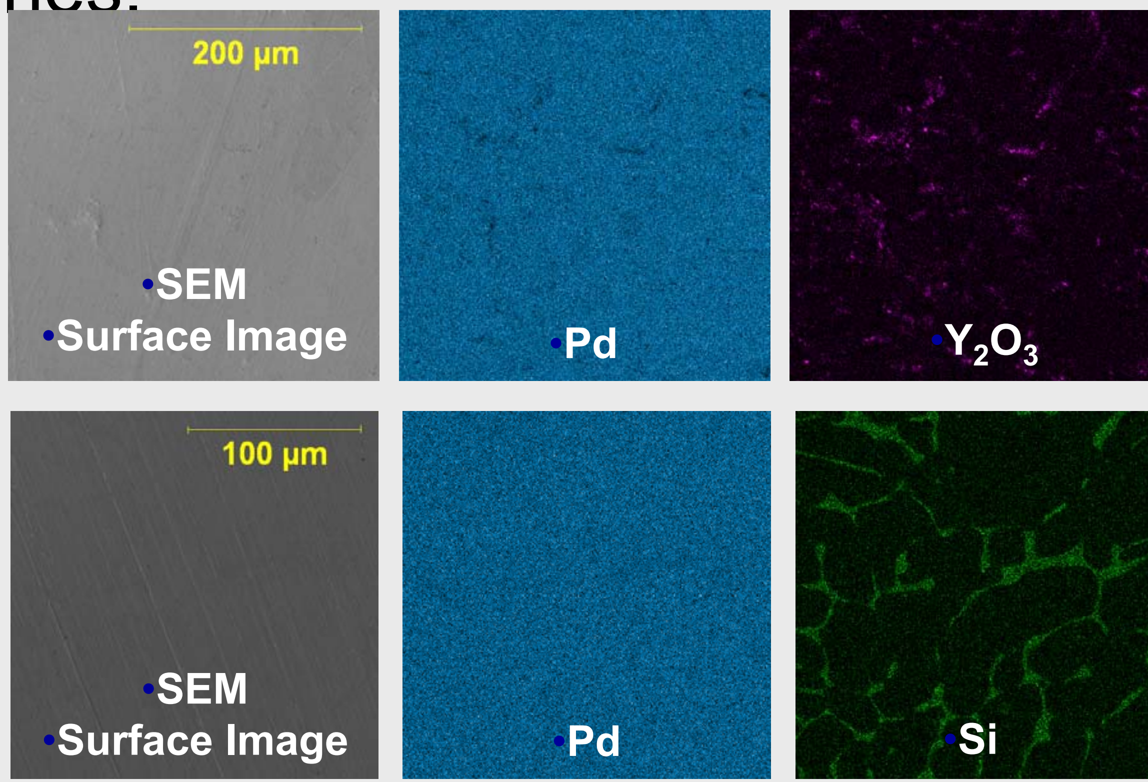


Results/Accomplishments DOE-NETL

Addition of Stabilizing Elements

> Select elements have shown promise in in enhancing corrosion resistance, mechanical strength and stabilization of grain boundaries.

- Ingots have been fabricated
- Working towards making a “testable” membrane



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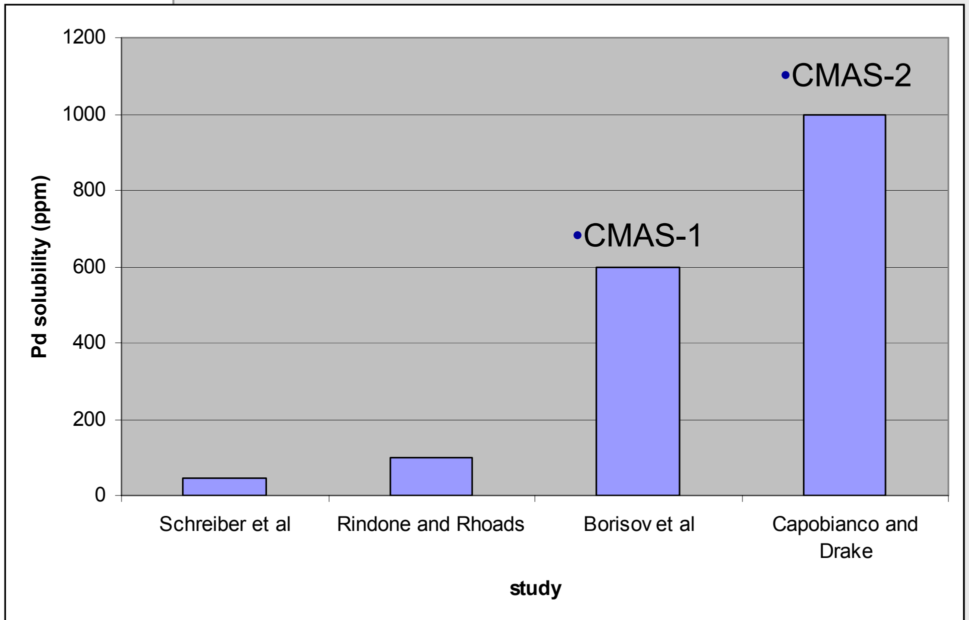
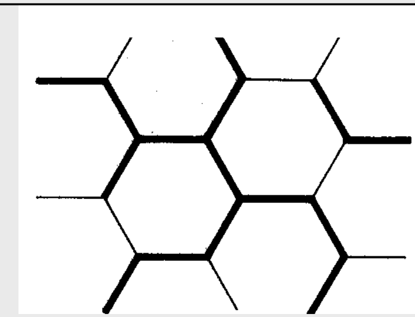
Accomplishments

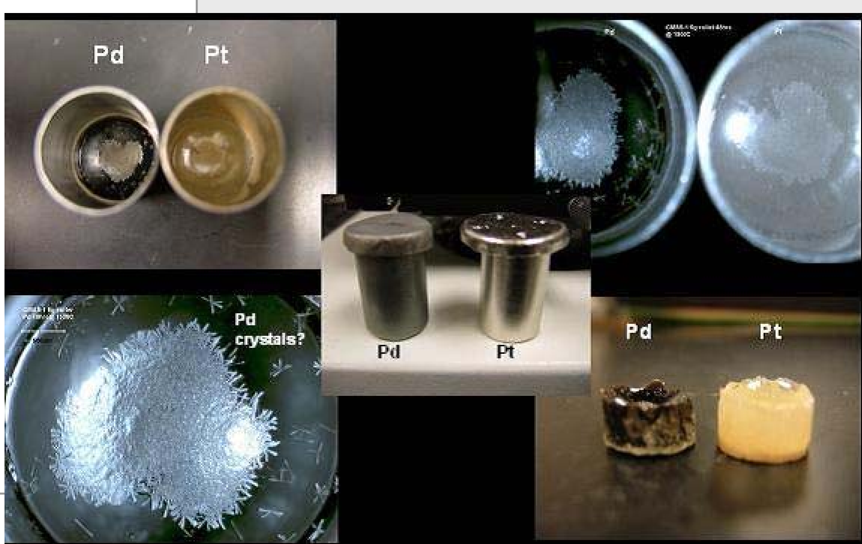
SCHOTT





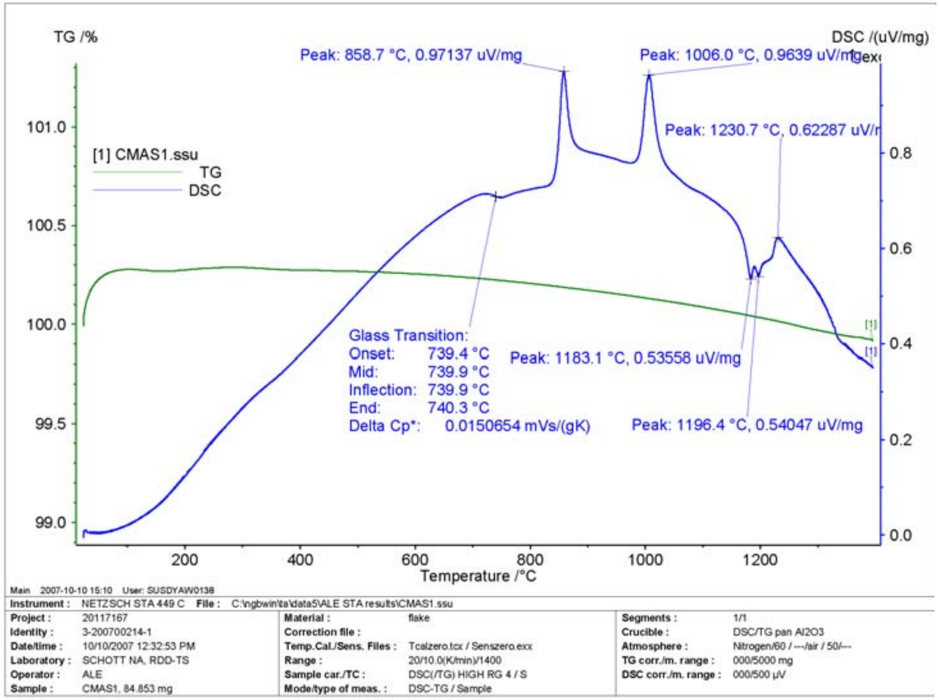
Desired microstructure

Sample	Pd (ppm)
CMAS-1 Pt pot remelt	< 5
CMAS-1 Pd pot remelt	592

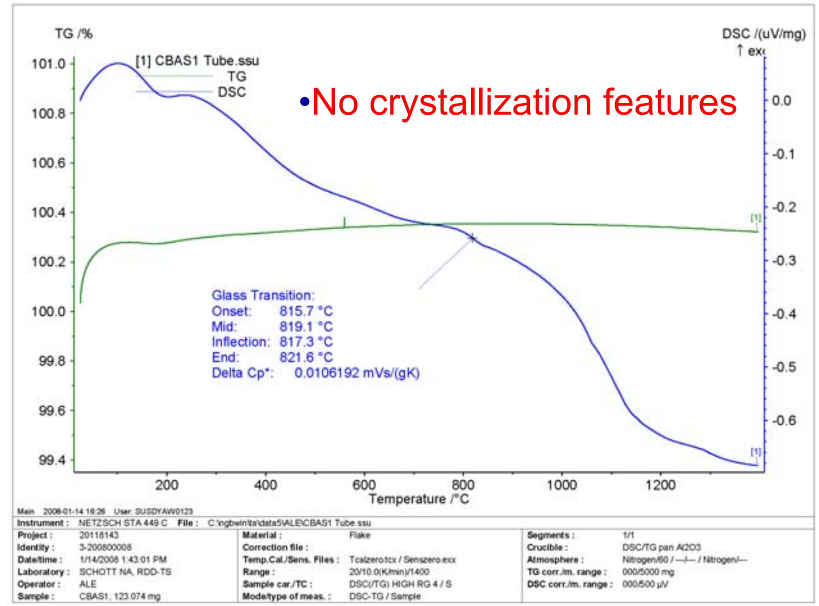


- ⇒ One composition identified and verified to have high Pd solubility

Accomplishments SCHOTT



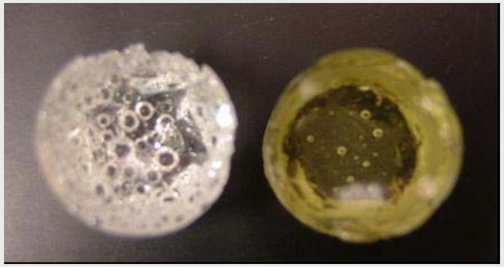
•CMAS-1



•No crystallization features

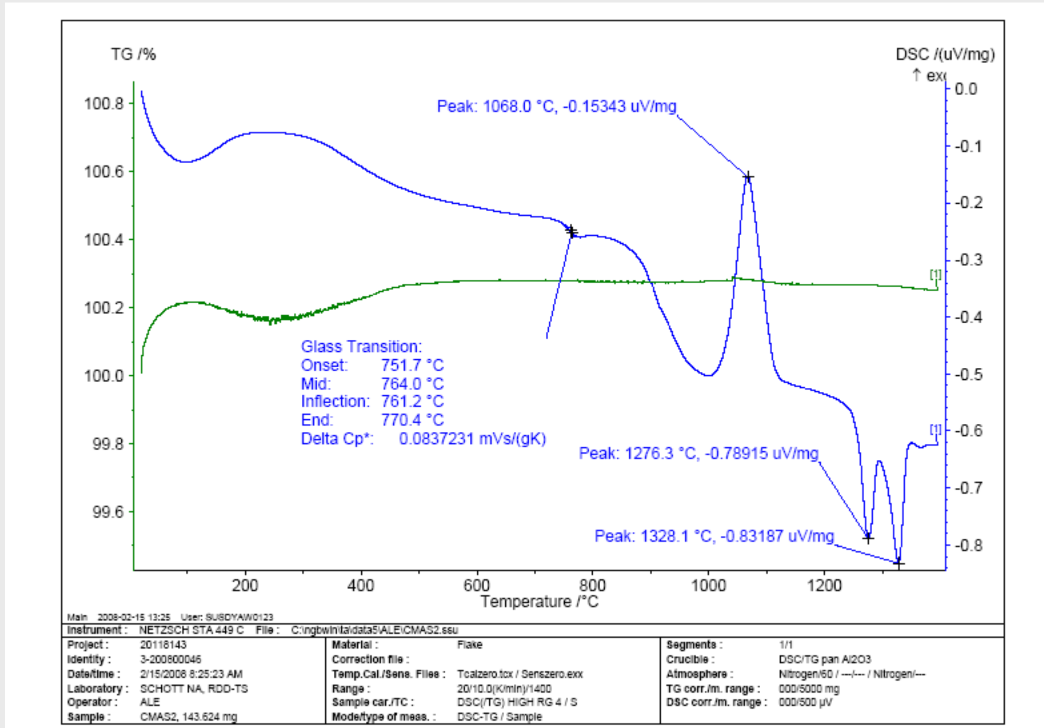
•CBAS-1

⇒ Thermal analysis further supports initial choice



•Pt •Pd

Accomplishments



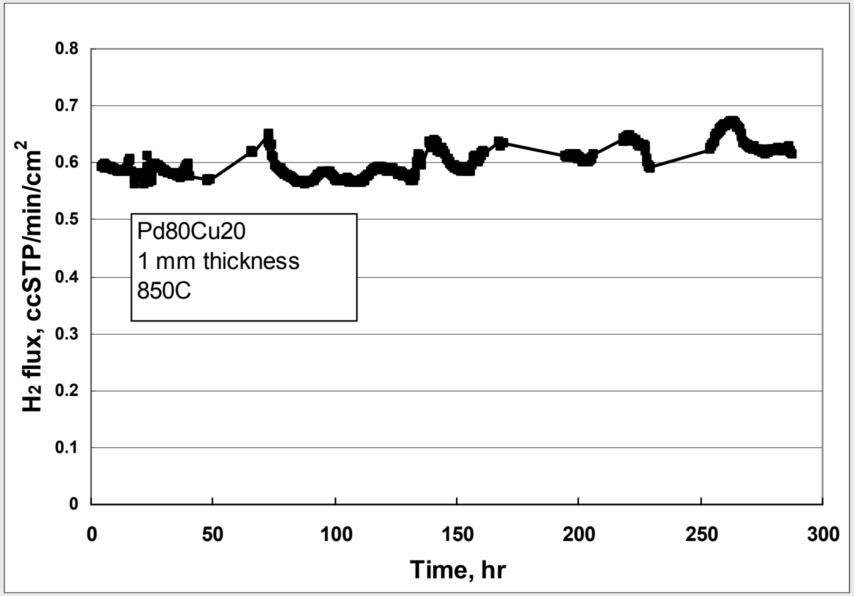
- CMAS-2

- Pd
- Pt

⇒ Solubility testing and thermal analysis reveals second possible composition

RESULTS

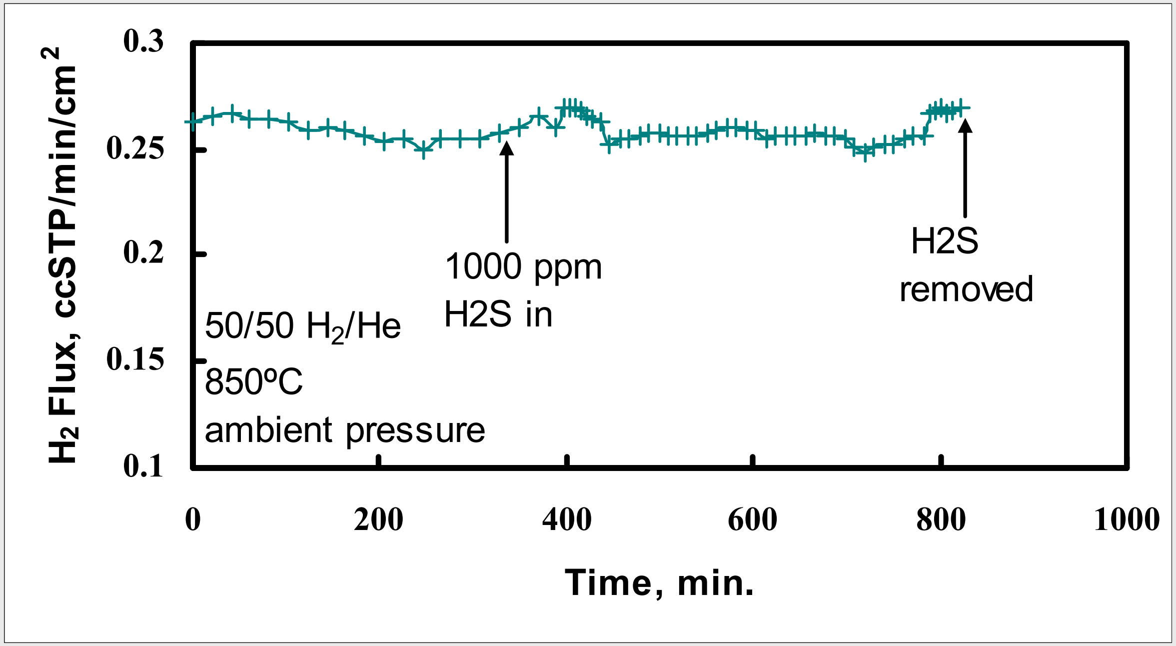
H_2/He Permeation Testing at 850°C and 1bar Pressure



- Thickness of membrane- 1mm
- Feed: 100% H_2
- Feed pressure-ambient
- Sweep gas-N_2
- Stable performance

RESULTS

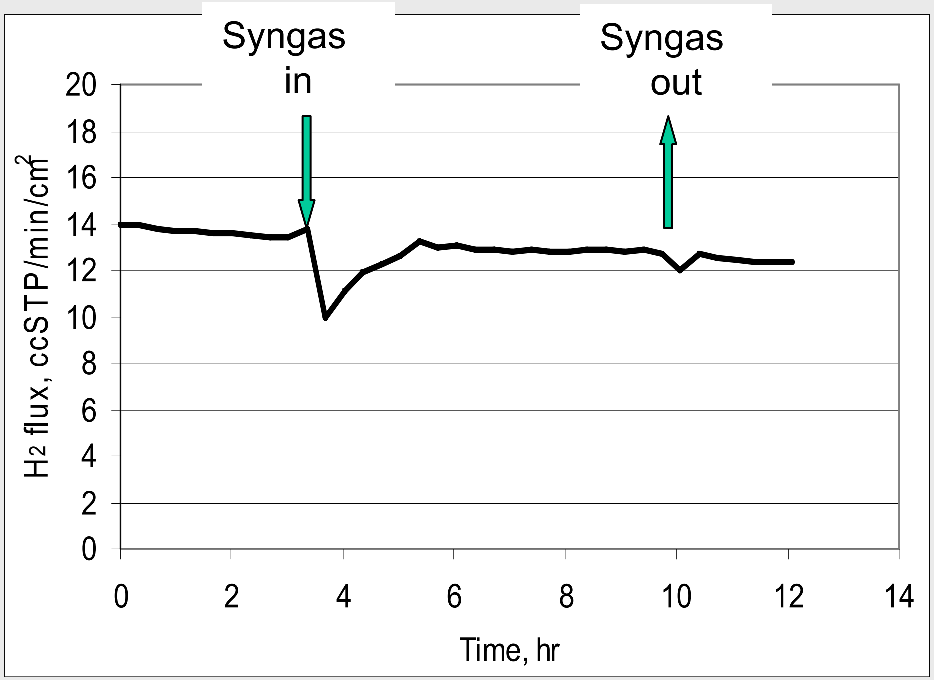
Effect of H_2S on $Pd_{80}Cu_{20}$ alloy membrane at 850°C



Sulfur tolerance at high temperature

RESULTS

Permeation testing with simulated biomass-derived syngas



Membrane Thickness-100 microns

Initial Feed Gas: 20%H_2/80%He

Syngas mixture: 20%H_2, 20% CO,10% CO_2, 10% H_2O with balance of Helium

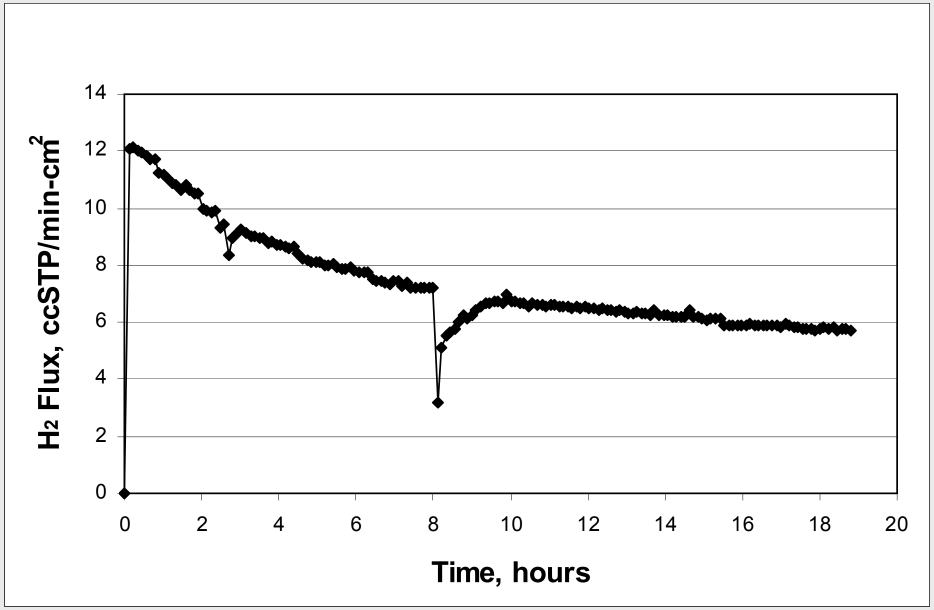
Feed pressure-30 atmospheres

Temperature – 850ºC

Sweep gas- N_2

RESULTS

Durability testing with simulated biomass-derived syngas at 850ºC



Thickness-100 microns

Feed : 20%H_2, 20% CO, 10% CO_2,

10% H_2O, balance of Helium

Feed pressure-30 atm

Temperature – 850ºC

Sweep gas- N_2

After 20 hours of testing membrane has

50% activity from initial value.

Future Work

- Study structural stability and H_2 permeance of different membrane compositions
- Synthesis of a thin-proton conducting ceramic membranes on a porous support
  - Synthesis method will be optimized so thin membranes up to 5μm thick will be developed
- Continue to identify metal additives to enhance the catalytic activity of Pd-based alloys in the presence of sour-H_2
- Continue to explore the feasibility of using “rare-earth” additives to enhance chemical and mechanical stability of highly-permeable Pd-based alloys

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Future Work

- Prepare Pd-containing glass melts in "significant" volume (liter-sized melts) and ceramize to make glass-ceramics
- Fabricate appropriate parts for H_2 permeation testing at GTI
- Use feedback from such testing to verify/deny current approach (potentially a go/no-go point)