Scale-up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

Presented by

Doug S. Jack

Eltron Research & Development Inc.

June 13, 2008

Project PD-39

Overview

Timeline

➢ Phase I Start	1 Oct 2005
➢ Phase II Start	1 Apr 2009
➢ Phase II End	30 Jun 2013

Budget ($000)

➢ Phase I Funding	$ 5,415
✓ DOE share:	$ 4,330
✓ Contractor share:	$ 1,085
➢ Funding for FY08	$ 2,000
➢ Phase II Funding	$40,000
✓ DOE Share	$31,000
✓ Contractor share	$ 9,000

Barriers Addressed

- Reducing hydrogen cost
- Hydrogen production from diverse pathways
- Hydrogen of sufficient purity for fuel cells

Technical Targets

- Low-cost system to produce H_2 from coal-derived synthesis gas and enable cost effective capture of CO_2 for sequestration
- Obtain engineering scale-up data in 220 lb H_2 /day unit
- Design, build and operate 4 ton/day unit
- Tolerant to syn gas contaminants

Partners (prior to October 1, 2007)

- NORAM Engineering
- CoorsTek
- Praxair

DOE Project Manager – Arun Bose

DOE Contract DE-FC26-05NT42469

Program Objectives

- Develop H_2/CO_2 Separation System, which
  - ✓ Retains CO_2 at coal gasifier pressures
  - ✓ Operates near water-gas shift conditions
  - ✓ Tolerates reasonably achievable levels of coal-derived impurities
  - ✓ Delivers pure H_2 for use in fuel cells, gas turbines, and hydrocarbon processing
  - ✓ Is cost effective compared to alternative technologies for carbon capture

Milestones

- **FY07**
  - ✓ **1Q** – Establish optimum operating conditions for metal membranes to achieve DOE 2010 flux, selectivity, and cost targets and select candidate membranes for scale-up and tests in the sub-scale engineering prototype.
  - ✓ **2Q** - Complete fabrication of new alloy materials and select metal materials for further scale-up and tests in the sub-scale engineering prototype.
  - ✓ **3Q** - Complete the design and cost estimate of the Impurity Management System upstream of the hydrogen membrane separation module unit to achieve the designed membrane operating life and engineering performance.
  - ✓ Select candidate catalyst composition and deposition technique to be scaled up for tests in the sub-scale engineering prototype.
  - ✓ **4Q** - Complete the economic analysis of hydrogen separation membrane modules and balance of plant.
  - ✓ Deliver capital and operating cost estimates for large-scale membrane structures and identify a cost-effective means to manufacture large-scale membranes required for the SEP.
- **FY08**
  - ✓ **1Q** – Complete commissioning activities on high pressure lifetime skid units
  - ✓ **2Q** – Begin operations of high pressure lifetime skid units
  - ✓ **3Q** – Select feed catalyst composition for impurity testing
  - ✓ **4Q** – Update process flow sheets and demonstrate improved economics utilizing HTM in IGCC plants

Stage Gate Prior to Phase 2

- Clearly establish the economic advantages of our system applied to an IGCC flow sheet;
- Understand the manufacturability and costs for a scaled-up membrane system;
- Demonstrate the performance of the membranes in long term use - with and without sulfur impurities; and,
- Develop a design basis for the PDU.

Plan and Approach

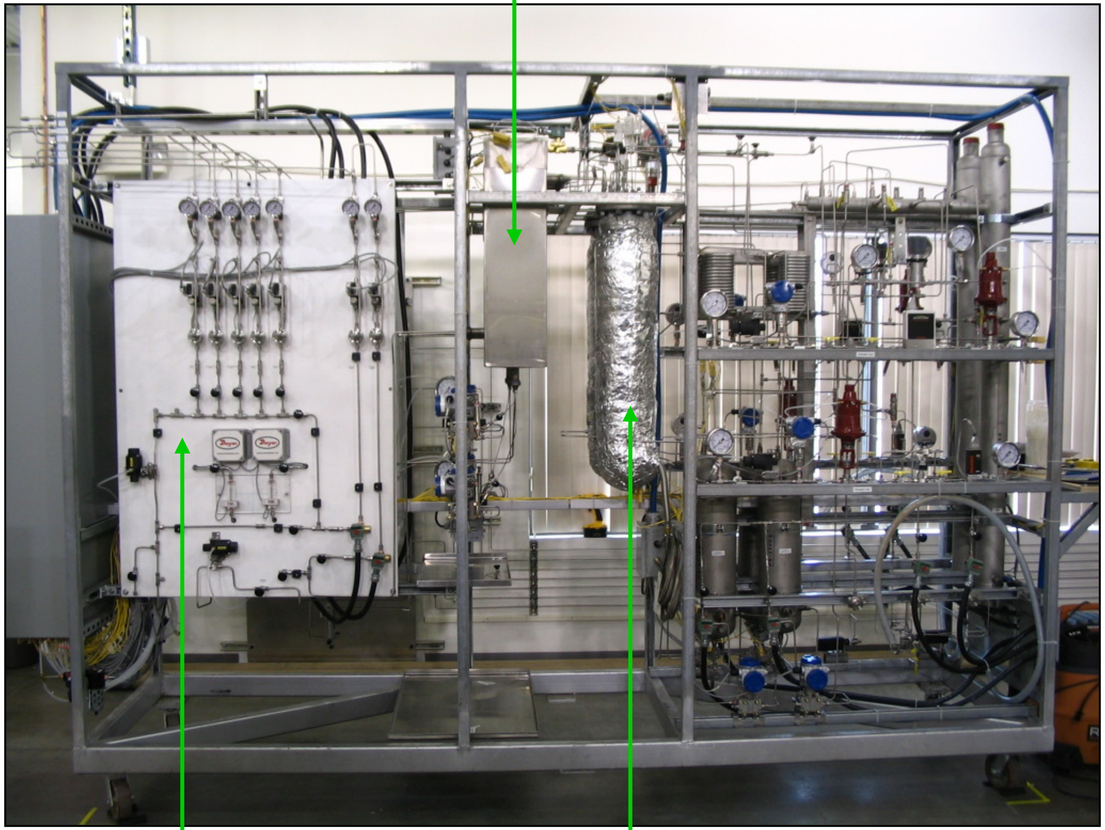
- Materials Development
  - ✓ Examine membrane and catalyst compositions
  - ✓ Develop preparation techniques
  - ✓ Develop improved analytical characterization
- Performance Screening
  - ✓ Evaluate flux, life, impurities effects using WGS composition
  - ✓ Establish range of operating conditions
- Mechanical Design
  - ✓ Assess strength of materials, embrittlement, welding techniques, et al
  - ✓ Address manufacturing costs and maintenance issues
- Process Design and Economics
  - ✓ Integrate into IGCC flow sheets – with and without co-production of H2 & power
  - ✓ Determine methods for impurity management
  - ✓ Develop models for membrane performance and design
  - ✓ Compare process economics versus other technologies
- Scale-up steps
  - ✓ 1.5 lbs/day H2 production – lab scale using simulated gas compositions
  - ✓ 220 lbs/day H2 production – using coal-based SG slipstream
  - ✓ 4 tons/day H2 production – complete engineering data package
  - ✓ Commercial module expected to be ~ 35 TPD H2 Production (4-8 required for 275 MW FutureGen plant)

Accomplishments Summary

- Designed, constructed and began operations on high pressure lifetime skids
- Improved characterization of membranes leading to better understanding of preparation and performance
- Developed alloys for membranes and catalysts leading to improved performance and manufacturability
- Demonstrated more stable membrane performance at lower temperature
- Developed modeling tools to characterize and design membranes/systems
- Improved membrane-based IGCC flow sheets showing:
  - ✓ Carbon capture over 95%
  - ✓ HHV efficiency ~6% better than conventional technology
  - ✓ Cost of electricity ~10% better than conventional technology

Lifetime High Pressure Reactors

Steam Generation / Pre-Heat



Flow Control

Membrane Modules

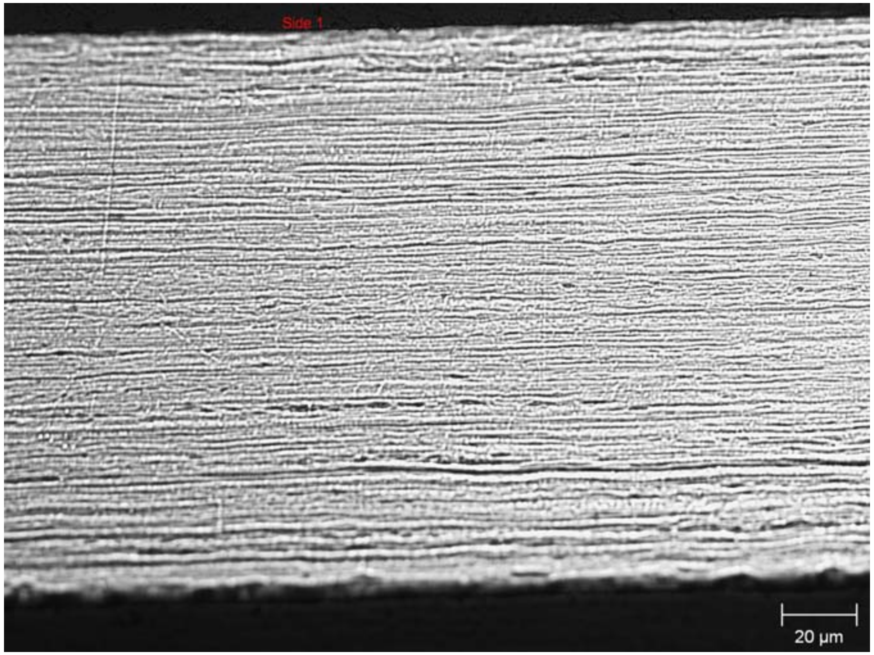
HTM System Capabilities

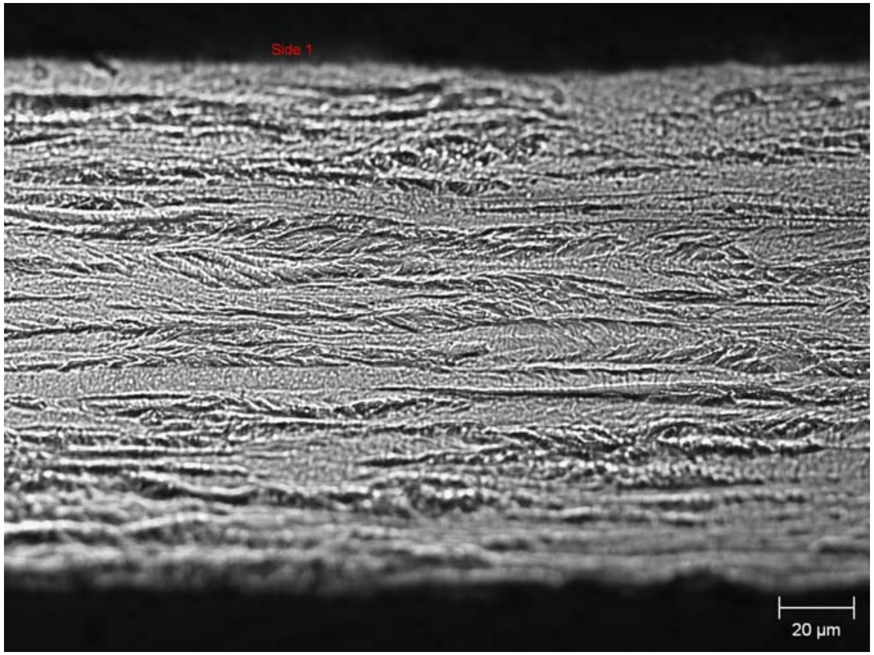
- Ambient Reactors (2)
  - ✓ Used for materials/parameter screening
  - ✓ Flow rates <500 ml/min
- Lab Reactors (2)
  - ✓ High pressure screening; not WGS-capable
  - ✓ Flow rates 3-5 L/min
- High Pressure Lifetime Test Units (2)
  - ✓ Full WGS capability
  - ✓ Fully automated for unattended operation
  - ✓ Flow Rates 1-2 L/min
- Scale-up Unit (1-4 reactors)
  - ✓ Full WGS capability
  - ✓ Flow rates >30 L/min

Membrane Characterization

Analytical Technique	Membrane Feature Characterized
X-ray Diffraction	• Phase(s) • Crystallite size • Orientation
XPS / Auger Depth Profiling	• Element Analysis • Contaminants
SEM • High Resolution • EDX	• Morphology • Contaminants • Grain Structure
TEM	• Catalyst Thickness • Element Analysis • Catalyst / Membrane Interface

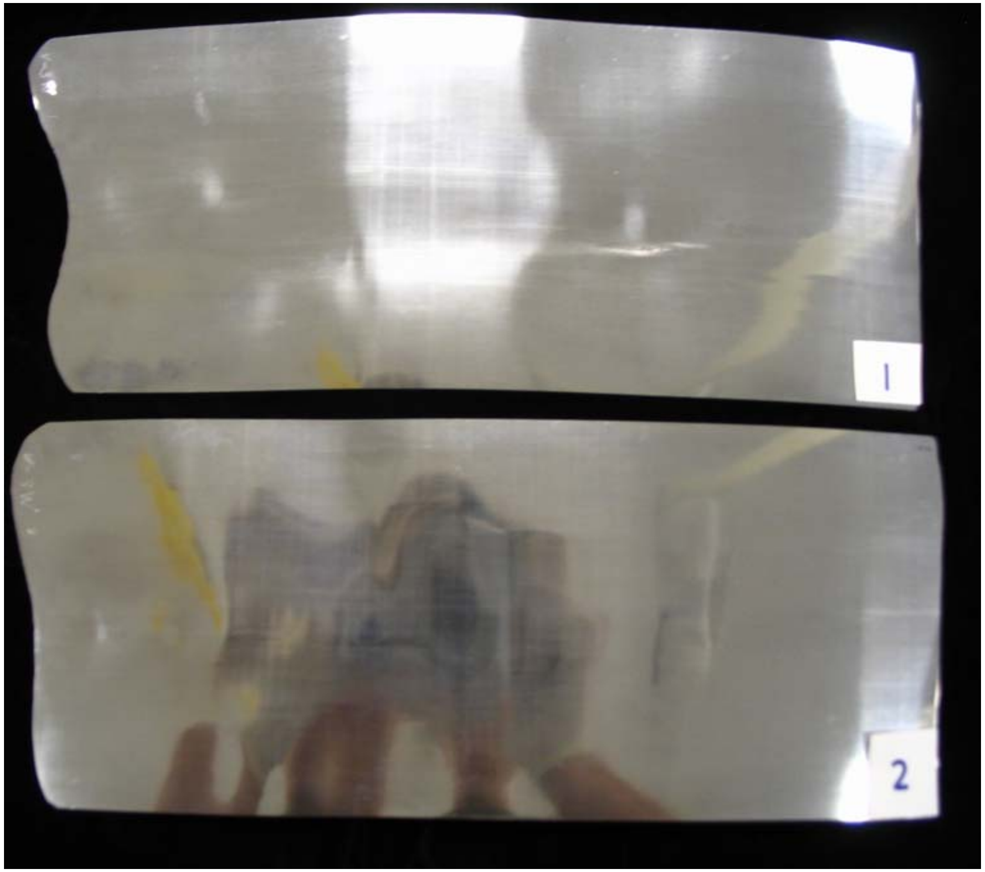
Membrane Microstructure
Cold-rolled vs. Deep Drawn





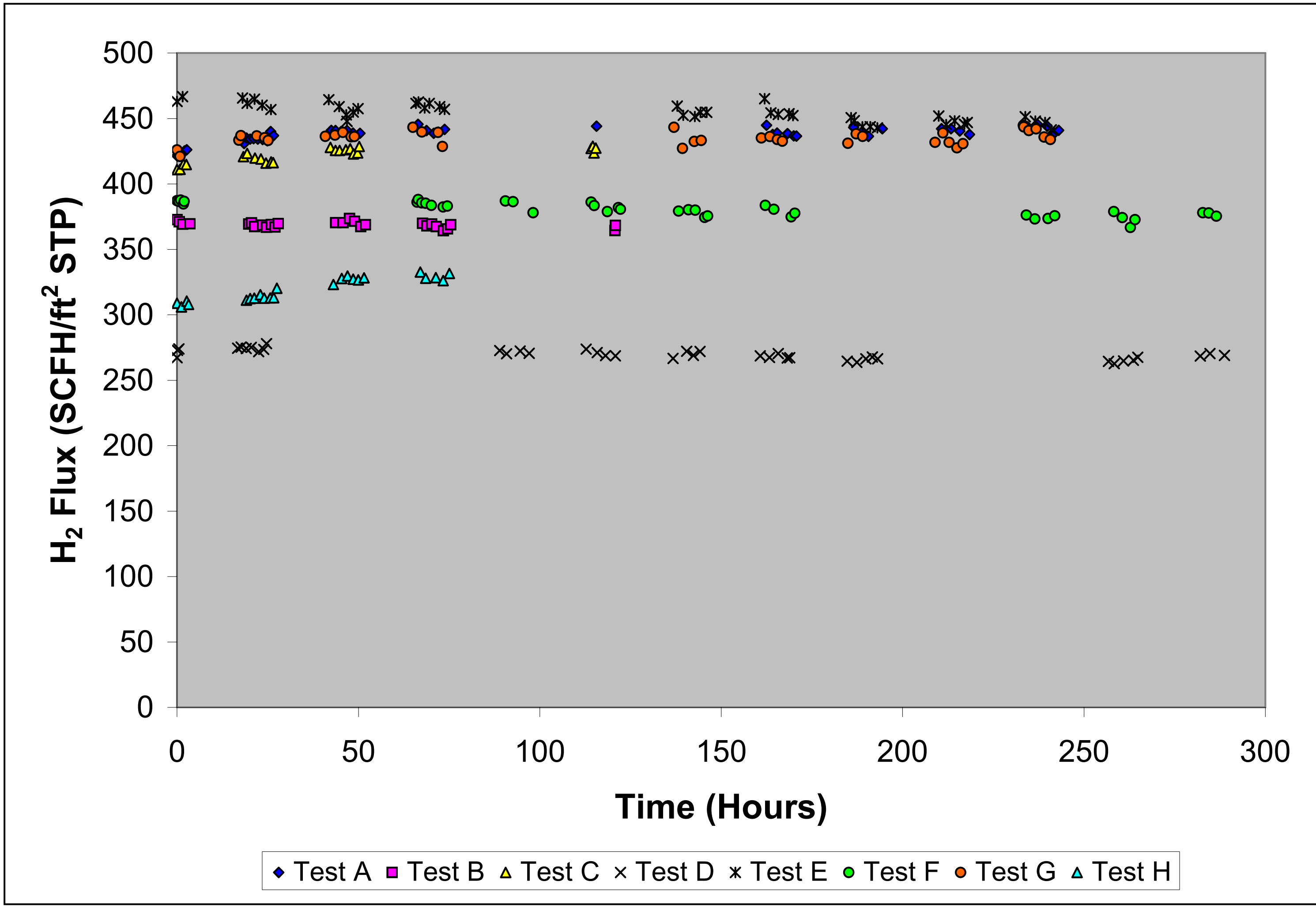
Alloy Sheets Prepared by Commercial Manufacturer

- 5” x 10”
- 225 μm thick
- Prepared by commercial method – low C,O,N impurities
- 4 alloys tested
- 6 additional alloys ordered



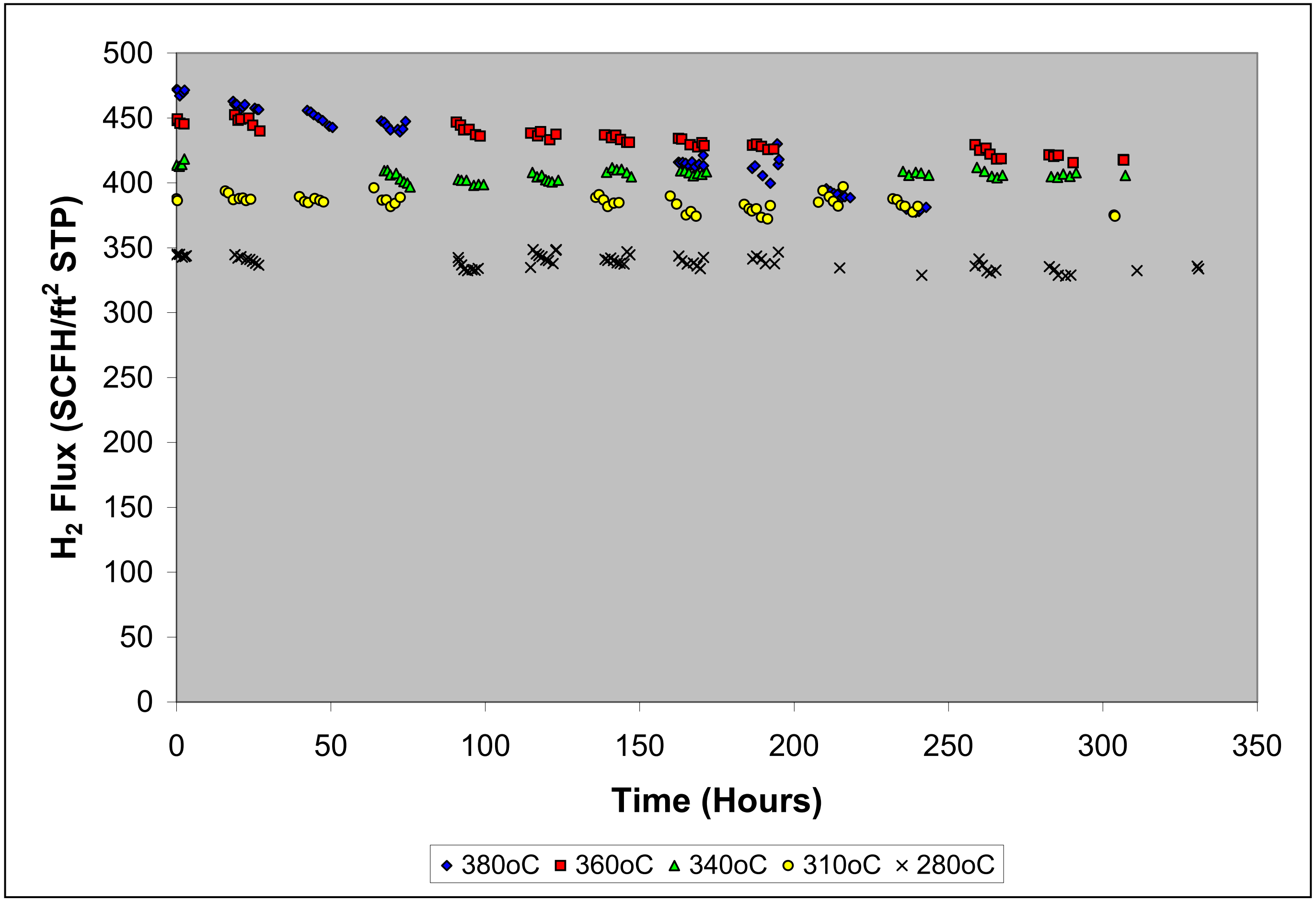
Membrane Alloy & Catalyst Alloy Permeation Data

- 340°C



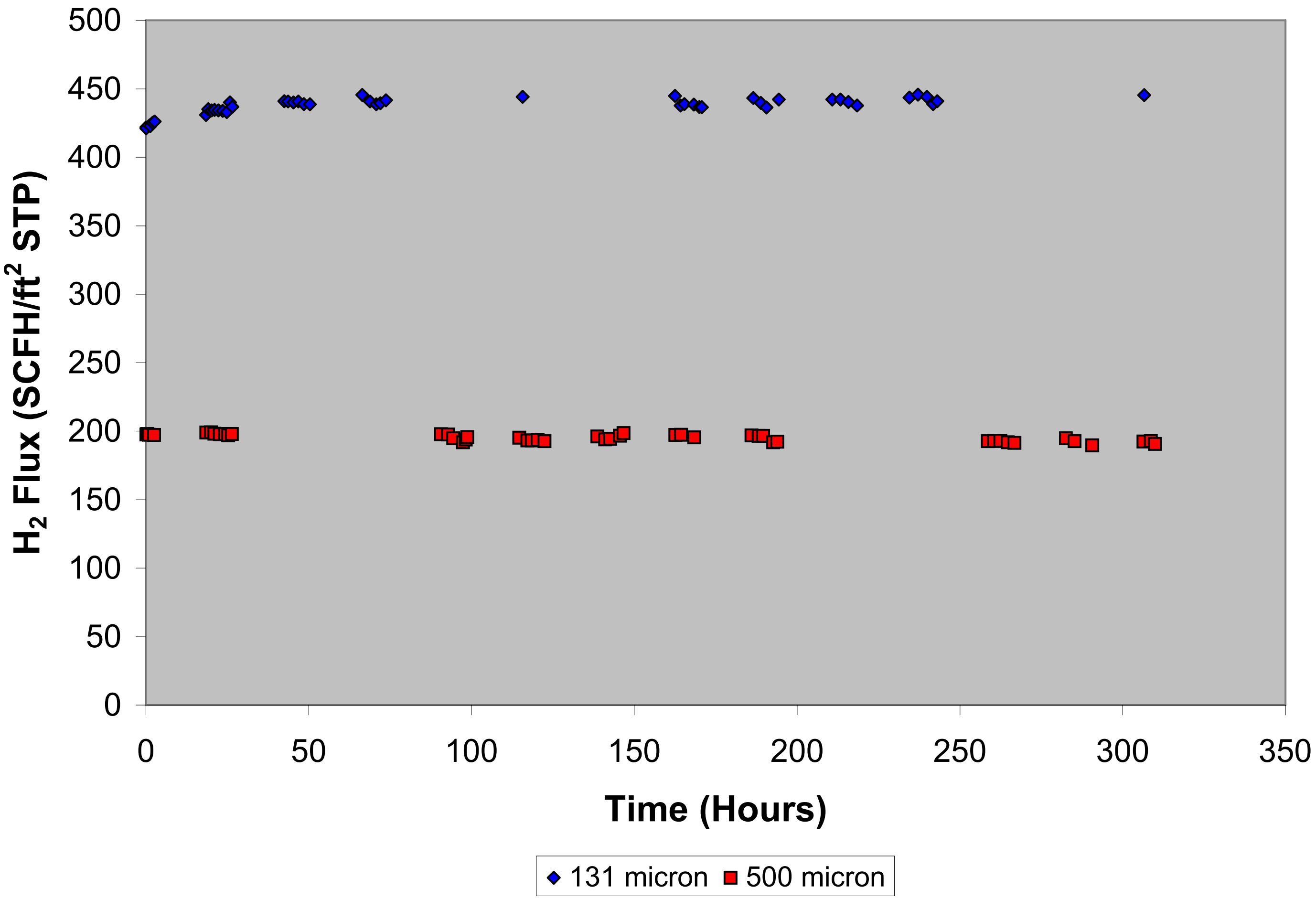
Effect of Temperature on Membrane Stability

- 150 µm
- Feed
  - ✓ 40% H_2
  - ✓ 60% He
  - ✓ 450 psig
- Sweep
  - ✓ Ar
  - ✓ 50 psig



Membrane Thickness

- 340°C



Model Development

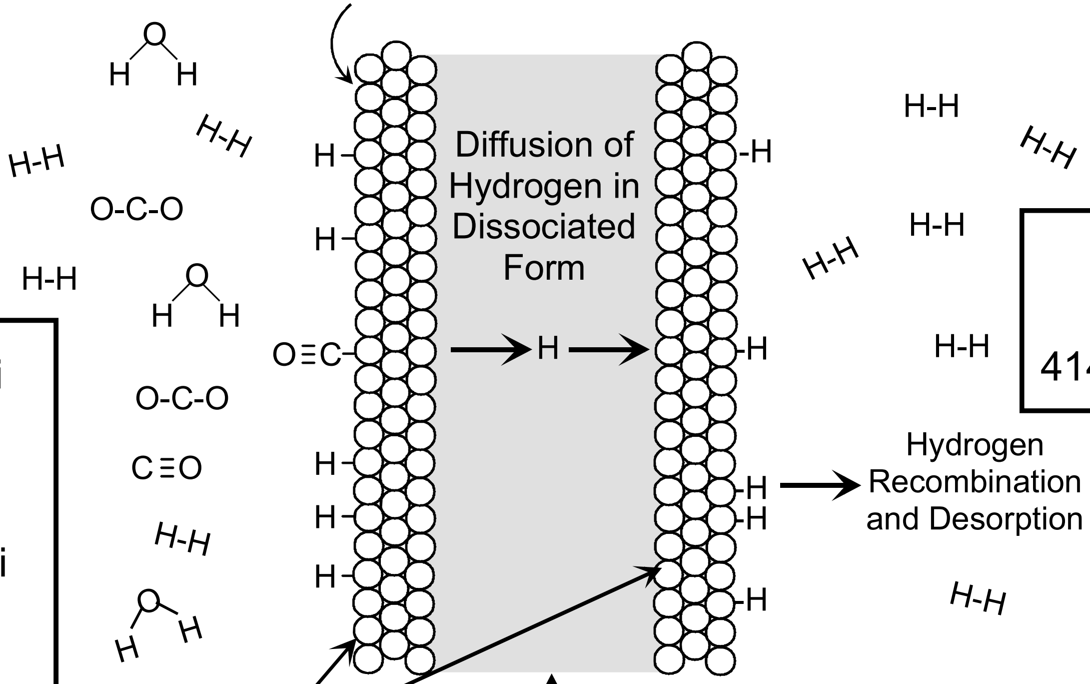
- Transport resistance model
- Process model
- Integration into IGCC flow sheet
- Process Economics

Goal is to improve carbon capture, decrease cost of electricity, improve thermal efficiency, and ensure membrane performance and lifetime.

Membrane Fundamentals

Retentate
(Water-Gas Shift Mixture)

Permeate
(Pure Hydrogen)



Hydrogen Adsorption and Dissociation

Diffusion of Hydrogen in Dissociated Form

Hydrogen Recombination and Desorption

Layers of Hydrogen Dissociation Catalyst

Hydrogen Transport Membrane Materials

H_2 - 414 psi

CO_2 - 178 psi

H_2O - 373 psi

CO - 33 psi

Pure H_2

414 psi maximum

2285mvm.dsf

Hydrogen Transport Resistance Model

- Mass transport from feed gas to feed side catalyst surface
- Dissociation of hydrogen on feed side catalyst surface
- Hydrogen transport through feed side catalyst layer
- Resistance at feed side catalyst-membrane interface
- Hydrogen transport through membrane
- Resistance at permeate side catalyst-membrane interface
- Hydrogen transport through permeate side catalyst
- Recombination/desorption of hydrogen on permeate side
- Mass transport of hydrogen into permeate stream

Experiments being performed to furnish data to validate model for improving membrane design and performance

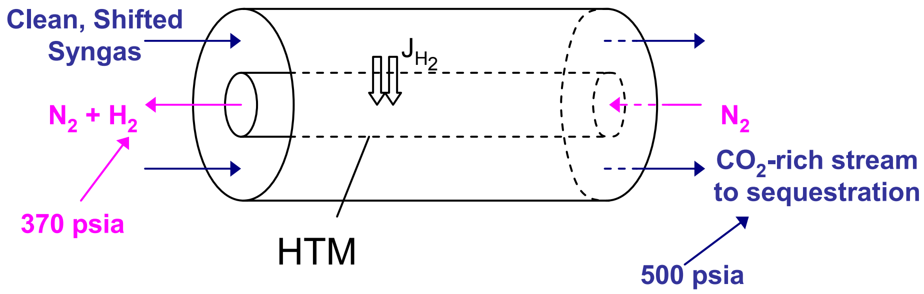
HTM Model

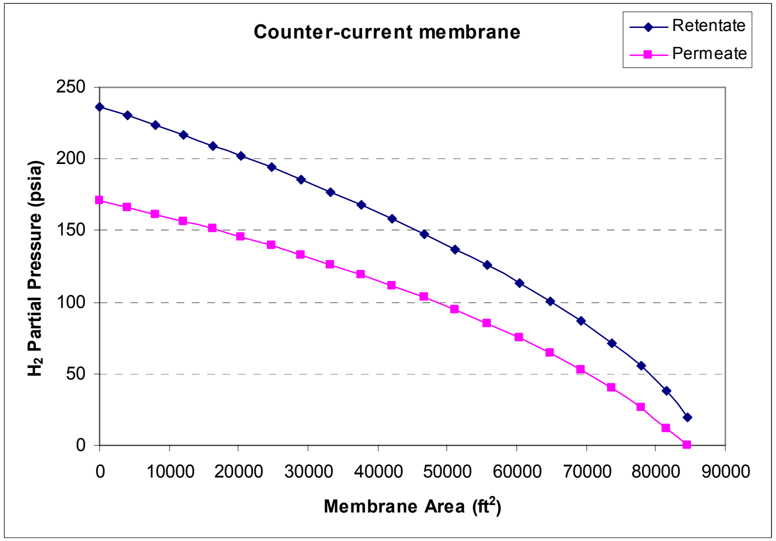
- Modeled as a subflowsheet of unit operations in Hysys

$$Flow_{H_2} = J_{H_2} A_{HTM}$$

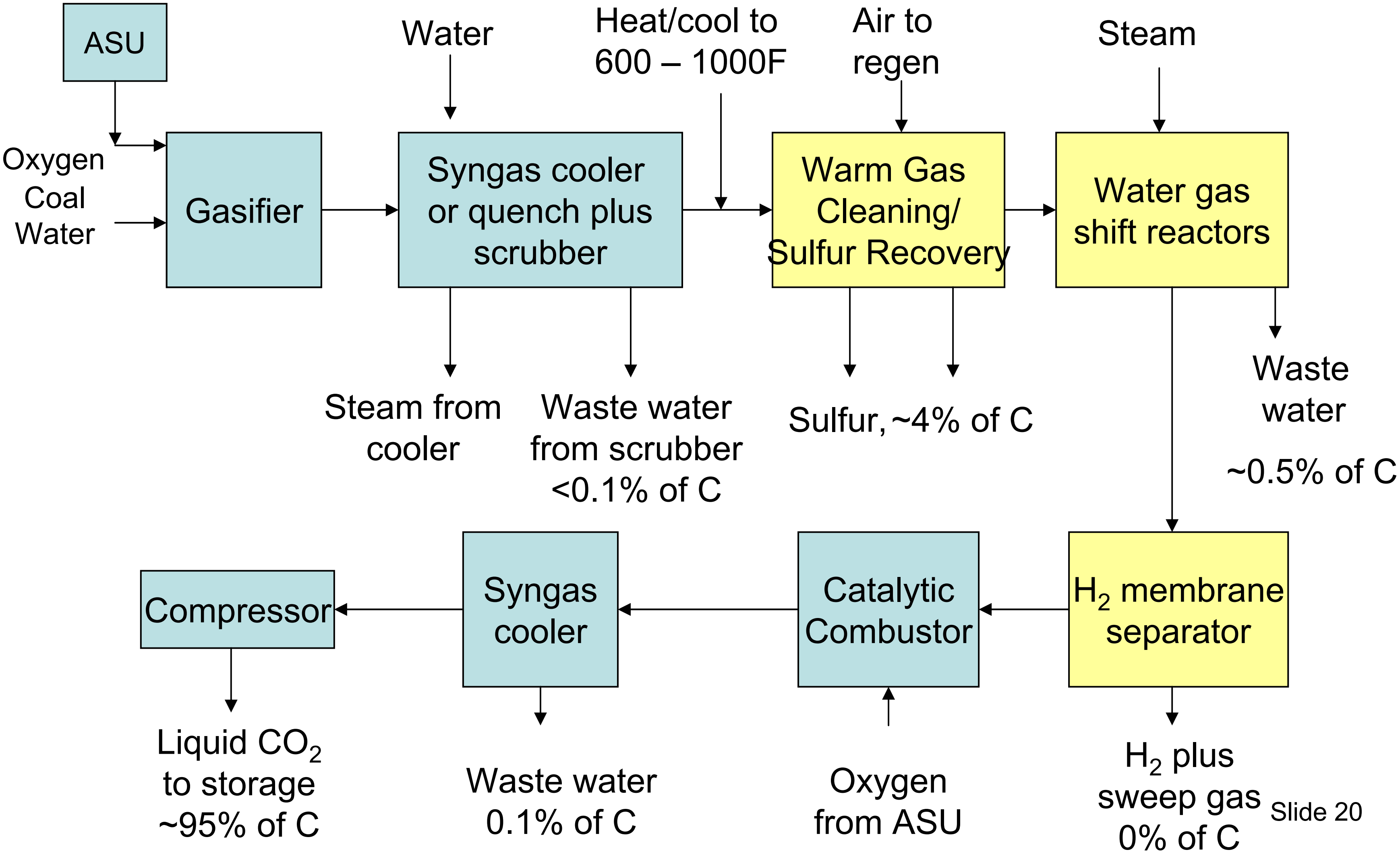
$$J_{H_2} = \frac{P_0}{l} \exp\left(\frac{-E_A}{RT}\right)\left(P_{H_2,\mathrm{Ret}}{}^{1/2} - P_{H_2,Perm}{}^{1/2}\right)$$

- Model parameters derived from Eltron membrane data





Pre-combustion CO_2 capture with membrane technology and warm gas cleaning



ASU

Oxygen
Coal
Water

Gasifier

Water

Syngas cooler or quench plus scrubber

Steam from cooler

Waste water from scrubber
<0.1% of C

Heat/cool to
600 – 1000F

Air to regen

Warm Gas Cleaning/ Sulfur Recovery

Sulfur, ~4% of C

Steam

Water gas shift reactors

Waste water

~0.5% of C

H_2 membrane separator

H_2 plus sweep gas
0% of C

Catalytic Combustor

Oxygen from ASU

Syngas cooler

Waste water
0.1% of C

Compressor

Liquid CO_2 to storage
~95% of C

Economic Results Summary

CO_2 Capture Method	None[1]	Pre-combustion Selexol	Eltron WGCU & Membrane	∆ Selexol vs. Eltron WGCU & Membrane
Coal Feed (tpd)	5,876	3,258	3,526	268
Net Power (MW)	640	239	318	79
HHV Efficiency	38.2%	27.4%	33.6%	6.2%
% CO_2 Captured	0%	91.3%	95.3%	4.0%
Cost of Electricity ($/MWh)	78.0	115.5	106	77.3[2]
Plant Cost ($/kW)	1,813	2,434	2,292	1,863[2]

[1] NETL Report, “Cost and Performance Baseline for Fossil Energy Plants,” May 2007

[2] Cost applicable only to the incremental net power produced

Future Work

- Develop design basis for scale-up to 220 lb/day Process Development Unit (PDU)
  - ✓ Discussions initiated with host facilities
- Continue to work with commercial suppliers on manufacturing of full-size alloy membranes
    - ❖ Catalyst deposition
    - ❖ Testing/Evaluation
- Life testing
- Understand impacts of contaminants
  - ✓ Experimentally
  - ✓ Process design
- Improve techno-economic models
  - ✓ Process optimization
  - ✓ Guide research/scale-up studies

Summary

- ➢ Eltron is currently bringing together all aspects of membrane technology
  - ✓ Ability to test long term under expected operating conditions
  - ✓ Substrate alloys / manufacturing
  - ✓ Catalyst alloys / deposition
  - ✓ Tubular membrane geometry
  - ✓ Demonstration of economic performance
- ➢ Results obtained to date show that this system is on track to meet DOE targets for 2010/2015

Progress Towards DOE FutureGen Targets

Performance Criteria	*2007*	*2010 Target*	*2015 Target*	*Current Eltron Membrane*
Flux, SCFH/ ft^2	320	200	300	450
Operating Temperature, ^{o}C	380-440	300-600	250-500	250-440
Sulfur Tolerance (ppmv)	20 (prelim.)	2	20	20 (prelim.)
System Cost (\$/ft^2)	<200	500	<250	<200
ΔP Operating Capability (psi)	1,000	400	800-1000	1,000
Carbon monoxide tolerance	Yes	Yes	Yes	Yes
Hydrogen Purity (%)	>99.99	99.5	99.99	>99.99
Stability/Durability (years)	0.9	3	>5	0.9
Permeate Pressure (psi)	270	N/A	N/A	400