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

Presented by
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Eltron Research & Development Inc.
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Project PD-39

This presentation does not contain any proprietary or confidential information.
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

Technical Targets
- Low-cost system to produce H₂ from coal-derived synthesis gas and enable cost effective capture of CO₂ for sequestration
- Obtain engineering scale-up data in 220 lb H₂/day unit
- Design, build and operate 4 ton/day unit
- Tolerant to syn gas contaminants

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

Partners (prior to October 1, 2007)
- NORAM Engineering
- CoorsTek
- Praxair

DOE Project Manager – Arun Bose
DOE Contract DE-FC26-05NT42469
Program Objectives

- Develop $\text{H}_2/\text{CO}_2$ 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

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

- Test A
- Test B
- Test C
- Test D
- Test E
- Test F
- Test G
- Test H

Temperature: 340°C

H₂ Flux (SCFH/ft² STP) vs Time (Hours)
Effect of Temperature on Membrane Stability

- **150 μm**
- **Feed**
  - 40% H₂
  - 60% He
  - 450 psig
- **Sweep**
  - Ar
  - 50 psig
Membrane Thickness

340°C

![Graph showing H₂ Flux (SCFH/ft² STP) vs Time (Hours) for 131 micron and 500 micron thicknesses at 340°C.](slide15.png)
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)

Hydrogen Adsorption and Dissociation

Hydrogen Transport
Membrane Materials

Permeate
(Pure Hydrogen)

Diffusion of
Hydrogen in
Dissociated Form

Layers of
Hydrogen Dissociation Catalyst

H₂ - 414 psi
CO₂ - 178 psi
H₂O - 373 psi
CO - 33 psi

Pure H₂
414 psi maximum

Hydrogen Recombination and Desorption
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

\[
\text{Flow}_{H_2} = J_{H_2} A_{HTM}
\]

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

- 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
  - Heat/cool to 600 – 1000F
  - Air to regen
  - Steam from cooler

- **Syngas cooler or quench plus scrubber**
  - Waste water from scrubber <0.1% of C

- **Warm Gas Cleaning/Sulfur Recovery**
  - Sulfur, ~4% of C

- **Water gas shift reactors**
  - Waste water ~0.5% of C

- **Compressor**
  - Liquid CO$_2$ to storage ~95% of C

- **Syngas cooler**
  - Waste water 0.1% of C

- **Catalytic Combustor**
  - Oxygen from ASU

- **H$_2$ membrane separator**
  - H$_2$ plus sweep gas 0% of C
# Economic Results Summary

<table>
<thead>
<tr>
<th>CO₂ Capture Method</th>
<th>None¹</th>
<th>Pre-combustion Selexol</th>
<th>Eltron WGCU &amp; Membrane</th>
<th>Δ Selexol vs. Eltron WGCU &amp; Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Feed (tpd)</td>
<td>5,876</td>
<td>3,258</td>
<td>3,526</td>
<td>268</td>
</tr>
<tr>
<td>Net Power (MW)</td>
<td>640</td>
<td>239</td>
<td>318</td>
<td>79</td>
</tr>
<tr>
<td>HHV Efficiency</td>
<td>38.2%</td>
<td>27.4%</td>
<td>33.6%</td>
<td>6.2%</td>
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<tr>
<td>% CO₂ Captured</td>
<td>0%</td>
<td>91.3%</td>
<td>95.3%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Cost of Electricity ($/MWh)</td>
<td>78.0</td>
<td>115.5</td>
<td>106</td>
<td>77.3²</td>
</tr>
<tr>
<td>Plant Cost ($/kW)</td>
<td>1,813</td>
<td>2,434</td>
<td>2,292</td>
<td>1,863²</td>
</tr>
</tbody>
</table>


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

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>2007</th>
<th>2010 Target</th>
<th>2015 Target</th>
<th>Current Eltron Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux, SCFH/ ft²</td>
<td>320</td>
<td>200</td>
<td>300</td>
<td>450</td>
</tr>
<tr>
<td>Operating Temperature, °C</td>
<td>380-440</td>
<td>300-600</td>
<td>250-500</td>
<td>250-440</td>
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<tr>
<td>Sulfur Tolerance (ppmv)</td>
<td>20 (prelim.)</td>
<td>2</td>
<td>20</td>
<td>20 (prelim.)</td>
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<tr>
<td>System Cost ($/ft²)</td>
<td>&lt;200</td>
<td>500</td>
<td>&lt;250</td>
<td>&lt;200</td>
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<tr>
<td>ΔP Operating Capability (psi)</td>
<td>1,000</td>
<td>400</td>
<td>800-1000</td>
<td>1,000</td>
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<tr>
<td>Carbon monoxide tolerance</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>Stability/Durability (years)</td>
<td>0.9</td>
<td>3</td>
<td>&gt;5</td>
<td>0.9</td>
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<tr>
<td>Permeate Pressure (psi)</td>
<td>270</td>
<td>N/A</td>
<td>N/A</td>
<td>400</td>
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