High-Pressure Operation of Dense Hydrogen Transport Membranes for Pure Hydrogen Production and Simultaneous CO$_2$ Capture

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Outline

♦ Introduction
♦ Project Goals
♦ Membrane Scale-Up Designs
  ↗ Planar
  ↗ Tubular
♦ High-Pressure Results
♦ Future Work
Project Goals

♦ Fabricate hydrogen separation membrane system which can retain CO$_2$ at coal gasifier pressures (450-1000 psi) for minimizing compression costs for CO$_2$ sequestration

♦ Fabricate membrane system for tolerance to water-gas shift reactor conditions (450-1000 psi; 360-400°C; 41% H$_2$ max; coal-derived impurities)

♦ Deliver pure hydrogen for use in fuel cells; hydrogen turbines; hydrocarbon fuel processing
Role of Hydrogen Separation Membranes in CO₂ Sequestration

- **Coal Slurry**
  - Coal Gasifier
    - >1040 °C
    - 1000 psi
    - Slag

- **Oxygen**
  - Air Separation Unit
  - Air

- **Synthesis Gas**
  - H₂ + CO
  - 1040 °C
  - 1000 psi
  - Water-Gas Shift Reactor
    - H₂ + CO
      - 320-440 °C
      - 1000 psi
      - Steam
      - H₂O
  - Catalyst Guard Beds
    - H₂ + CO
      - 320 °C
      - 1000 psi
  - Water-Gas Shift Reactor
    - 320-440 °C
    - 1000 psi
    - 40% H₂ + CO₂ + H₂O
      - 340-440 °C
      - 1000 psi
    - Condense H₂O
    - Compress CO₂ 2700 psi
    - CO₂ Pipelines

- **Electricity**
  - Hydrogen Turbine
    - Oxygen
    - Hydrogen Separation Unit
    - H₂
    - <400 psi
  - Fuel Cells
    - Steam
    - Turbine
    - Electricity

- **Petroleum Refining**
  - Synthetic Fuels
  - Compress H₂
    - 435 psi
  - Steam
  - 320° C
  - 1000 psi
  - H₂ + CO
    - 320° C
    - 1000 psi
  - Steam
  - 320° C
  - 1000 psi
  - H₂O

- **Oil + Gas Recovery**
  - Hydrogen Separation Unit
    - CO₂ Sequestration
      - Oil + Gas
      - Recovery
  - Condense H₂O
  - Compress CO₂ 2700 psi
  - CO₂ Pipelines
## Eltron Hydrogen Transport Membranes

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Operating Temperature Range (°C)</th>
<th>Permeation Rate (mL•min⁻¹•cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Phase Ceramic</td>
<td>700 to 950</td>
<td>~ 0.01</td>
</tr>
<tr>
<td>Ceramic / Ceramic</td>
<td>700 to 950</td>
<td>~ 0.1</td>
</tr>
<tr>
<td>Cermet</td>
<td>700 to 950</td>
<td>~ 1</td>
</tr>
<tr>
<td>Cermet with H₂ Permeable Metal</td>
<td>550 to 950</td>
<td>~ 4</td>
</tr>
<tr>
<td>Intermediate Temperature Layered Composite</td>
<td>320 to 440</td>
<td>20 - 420</td>
</tr>
</tbody>
</table>
Hydrogen Transport Across Eltron’s Membrane

- Hydrogen Dissociation
- Diffusion of Hydrogen in Dissociated Form
- Layers of Hydrogen Dissociation Catalyst
- Recombination and Desorption of H₂
Precedence for a 10 million cubic feet (25 tons) per day hydrogen plant using membranes (Pd-Ag) (Union Carbide, 1960s, Patent 3,336,730, Aug. 22, 1967)
Previous Scale-Up Design – Planar (Union Carbide)

Precedence for a 10 MMCFD (25 ton) Hydrogen Plant Using Membranes (Union Carbide, 1960s)

- Operated 10 MMCFD plant in 1960s in South Charleston, West Virginia
- Proved that large-scale hydrogen-membrane purification units are feasible
- Used dual guard beds to remove impurities
- Feed 500 psi (34.5 bar)
- Used Pd-Ag membranes (price of Pd now prohibitive, ~$200,000,000?)
Previous Scale-Up Design – Planar (SOFCo)

SOFCo Planar Design (DE-FC26-OINT41145)

- Wafer panel length 2 m (6.55 ft)
- 159 stacks
- 590 tons per day of hydrogen (234 MMSCFD)

FutureGen: Need to evaluate merits of tubular versus planar
Concepts For Membrane Scale-Up: Metal Tube Heat Exchangers

NORAM tubular membrane design based on tantalum-tube heat exchangers.
A. Concept for closed-one-ended ceramic tubes bundled for cermet membrane applications. B. Bundle of ceramic membrane tubes produced by CoorsTek for an earlier industrial separation application.
NORAM conceptual tubular design of a commercial membrane unit capable of separating 25 tons per day (~10 MMSCFD) of hydrogen. Sizing is based upon syngas at 1000 psig (68 barg), 450°C, 50 vol.% H₂ in feed.
High Pressure Reactor – Eltron Research

- Pressures up to 1000 psi
- Tests in Water-Gas Shift Mixture

Eltron has only facility in U.S. capable of testing hydrogen transport membranes under extreme pressure conditions.
Results: Hydrogen Flux Measurements at High Pressure and High Pressure Differential

Membrane: Group IVB-VB Material

- Sieverts’ Law followed very well.
- 100% Selectivity to $\text{H}_2$. No He leak.
- Permeability 440°C: $2.3 \times 10^{-7}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$.
- Flux: 423 mL min$^{-1}$ cm$^{-2}$ (STP).
- Disk withstood 33 bar differential pressure – minimum distortion.
High-Pressure Hydrogen Flux Data (380°C)

- Membrane ~500 microns thick.
- Feed Pressure: 66.5 bar (964 psi) absolute; 41% H₂
- Permeate Pressure: 7.4 bar (107 psi) absolute; pure H₂
High-Pressure Permeability Data (380°C)

- Permeability about ten times better than palladium
- Feed Pressure: 66.5 bar (964 psi) absolute; 41% H₂
- Permeate Pressure: 7.4 bar (107 psi) absolute; pure H₂
- Membrane ~500 microns thick.
High-Pressure Hydrogen Flux Data (380°C)

- Membrane ~500 microns thick.
- Hydrogen flux >70 mL min⁻¹ cm⁻² (STP) as feed pressure approaches 1000 psi (69 bar) with 41% H₂ M feed and low permeate pressure.
- Hydrogen flux drop with high hydrogen partial pressure in permeate in accord with Sieverts’ Law.
High-Pressure Hydrogen Flux Data – Water-Gas Shift Mixture (440°C)

- Hydrogen flux >50 mL min⁻¹ cm⁻² (STP) with 450 psi water-gas shift mixture: 41.0% H₂, 17.5% CO₂, 3.0% CO, 38.0% H₂O, balance He
- Pure hydrogen in permeate, 2.9 bar (42 psi) absolute
- Membrane ~500 microns thick.
High CO conversion of 96% and hydrogen productivity of 75% were achieved when an integrated membrane/shift reactor was operated at 120 psig on the feed side and ambient pressure on the permeate side without a sweep stream. The feed stream used 2000 h⁻¹ GHSV, and contained 47.8 mol% H₂, 6.2 mol% CO₂, 7.8 mol% CO, and 38.2 mol% steam.
High-Pressure Test Results – Summary

- Hydrogen flux $>50 \text{ mL min}^{-1} \text{ cm}^{-2} \ (\text{STP})$ under water-gas shift mixture at 450 psi at 440°C with 44 psi pure hydrogen in permeate (fuel cell use).

- Stable under tests up to 970 psi in feed and 500 psi pure hydrogen in permeate (under ideal hydrogen-helium).

- Permeate hydrogen pressure can equal partial pressure of hydrogen in feed.
Future Work

♦ Test under water-gas shift mixture to 1000 psi (69 bar)
♦ Identify economic routes to membrane scale-up
♦ Scale-up membrane modules
♦ Address issues of coal-derived impurities
  ➤ Improve membrane catalysts
  ➤ Incorporate warm-gas cleanup systems