IONICALLY CONDUCTING MEMBRANES FOR HYDROGEN PRODUCTION AND SEPARATION

Presented by

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TO BE DISCUSSED

• Membranes for Hydrogen Production
  – Compositions
  – Feedstocks
  – Performance
  – Key Technical Hurdles

• Membranes for Hydrogen Separation
  – Compositions
  – *Ex Situ* vs. *In Situ* WGS
  – Performance
  – Key Technical Hurdles
OVERALL SCHEME FOR CONVERTING FEEDSTOCK TO HYDROGEN WITH SIMULTANEOUS CARBON DIOXIDE SEQUESTRATION

Natural Gas → Oxygen Transport Membrane → Syngas (CO/H₂) → WGS (H₂O) → CO₂/H₂ → Hydrogen Transport Membrane → H₂

Coal → Biomass
INCENTIVES FOR OXYGEN TRANSPORT MEMBRANES FOR HYDROGEN PRODUCTION

• Conventional Natural Gas Steam Reforming
  \[\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}\]  Endothermic (Energy Required)

• Membrane Driven Natural Gas Reforming
  \[\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO}\]  Exothermic (Energy Produced)

Energy Savings Greater than 30%.
OXYGEN TRANSPORT MEMBRANES FOR FEEDSTOCK PARTIAL OXIDATION TO SYNTHESIS GAS

Natural Gas
i) \( \text{CH}_4 + O^{2-} \rightarrow \text{CO} + 2\text{H}_2 + 2e^- \)

Liquid Hydrocarbons
ii) \( \text{C}_n\text{H}_{2n+2} + nO^{2-} \rightarrow n\text{CO} + (n+1)\text{H}_2 + n2e^- \)

Coal
iii) \( 2\text{C} + \text{H}_2\text{O} + O^{2-} \rightarrow 2\text{CO} + \text{H}_2 + 2e^- \)
MEMBRANE REQUIREMENTS FOR ACHIEVING HIGH IONIC CONDUCTIVITIES

• Small $E_a$ for Oxygen Anion Conduction

• High Population of Mobile Oxygen Anions
RATIONALLY SELECTED MEMBRANE MATERIALS
Thermodynamic and Crystallographic Parameters for Ionic and Electronic Conduction

- Metal-Oxygen Bond Energies
- Free Volume
- Ionic Radii of Lattice Substituents
- Valence of Lattice Substituents
- Lattice Polarizability
- Preferred Metal Ion Coordination Sphere
- Nonreducible Under Operating Conditions
TOWARDS CERAMIC MEMBRANE OPTIMIZATION

Neural Network Analysis

Crystallographic Thermodynamic and Mechanical Properties

Experiment

Trends Suggestions

Emphasis
RATIONALLY SELECTED OXYGEN TRANSPORT MEMBRANE MATERIALS

Perovskite

\[ A_xA'_x A''_x \text{B}_yB'_y B''_y \text{O}_{5+z} \]

Brownmillerite

(U.S. Patent No. 6,033,632, March 7, 2000)
(U.S. Patent No. 6,146,549, November 14, 2000)
(U.S. Patent No. 6,165,431, December 26, 2000)
(U.S. Patent No. 6,214,757, April 10, 2001)
(U.S. Patent No. 6,355,093, March 12, 2002)
(U.S. Patent No. 6,402,156, June 11, 2002)
(U.S. Patent No. 6,471,921, October 29, 2002)
(U.S. Patent No. 6,592,782, July 15, 2003)
(U.S. Patent No. 6,641,626, November 4, 2003)
HIGH PRESSURE OPERATION

Eltron has successfully operated membrane reactors at high pressure (250 psi) on the natural gas surface and ambient pressure on the air (oxygen) surface at elevated temperatures. Over nine years operating experience.
SUMMARY OF ELTRON OXYGEN TRANSPORT MEMBRANE SYNGAS RESULTS

Syngas Reactor Studies
Tubular Reactors

- Syngas Production Rate – 60 mL/min cm² @ 900°C
- Equivalent O₂ Flux -10-12 mL/min-cm² (>1S cm⁻¹) @ 900°C
- H₂: CO Ratio - -1.9 - 2.0
- CO Selectivity - >96%
- Throughput Conversion - 90% CH₄, 70% O₂ (From Air)
- Operated Continuously for Over One Year (1997)
- Over Nine Years Operational Experience Under High Pressure Differential
OXYGEN TRANSPORT MEMBRANES FOR LIQUID FUEL REFORMING

Mixed Conducting Membrane

\[ \text{nCO} + (\text{n+1})\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + \frac{n}{2}\text{O}_2^- \]

\[ \text{nCO} + (\text{n+1})\text{H}_2 + \text{ne}^- \rightarrow \text{C}_n\text{H}_{2n+2} \]

\[ \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}_2^- \]

Partial Oxidation Catalyst

Reduction Catalyst

O₂ (Air)

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MEMBRANE LIQUID FUEL EFORMER INTEGRATED WITH SOFC
LIQUID FUEL REFORMING – CURRENT STATUS

- Synthesis gas production rates approaching 40 ml/min-cm² have been achieved when converting dodecane as a simulant for diesel fuel. Throughput conversions were 99%. This corresponded to an oxygen flux rate across the membrane >6.3 ml/min-cm².

- 800 hours continuous operation on diesel fuel with no carbon deposition. Synthesis gas production rate >27 ml/min-cm² with 100% conversion.

- DF-2 reformed at 27 ml/min-cm² – corresponds to 3.9 A/cm² in a SOFC.

- Sulfur tolerant
COAL GASIFICATION PROCESS - AREAS IN GREEN CORRESPOND TO NEW TECHNOLOGIES UNDER DEVELOPMENT AT ELTRON

- Oxygen from Air Separator
- Coal Slurry
- Oxygen Separation Membrane
- Coal Gasifier
- Feed Water
- Radiant Syngas Cooler
- High Pressure Steam
- Syngas
- Cool to 320°C
- Particulate Filter
- Water-Gas-Shift
- Cool to 50°C
- Acid Gas (CO₂, H₂S) Removal
- CO/H₂
- Water
- F-T Synth.
- Steam
- H₂ Turbine
- Product Upgrading (hydrocracking)
- Catalyst Separation
- Condensed Water
- Wax
- Fractionation
- Volatiles
- Water
- Steam
- Steam
- Products
- Steam
- Steam
- H₂
OXYGEN TRANSPORT MEMBRANES FOR INDIRECT AND DIRECT OXYGEN SUPPLY TO PROMOTE COAL GASIFICATION

Mixed Conducting Membrane

High Pressure Air

Air Side

Mixed Conducting Membrane

Oxidation Catalyst

Reduction Catalyst

High Pressure Air

Reactor Side

Partial Oxidation Catalyst

O2 Reduction Catalyst

Pure Oxygen O2

2O2 → O2 + 4e-

O2 (N2) + 4e- → 2O2-

2C + H2O → CO + H2

2CO + H2 + 2e- → C + ½O2 + ½H2

C + ½O2 → CO

2C + H2O + ½O2 → CO + H2

6 ml/cm²/min

20% O2 → 2% O2

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DIRECT COAL GASIFICATION FINDINGS

• Complete gasification of coal fines occurs within the membrane partial oxidation compartment.

• Resulting coal ash remains as a powder and can be conveniently removed from the CMR.

• Because of the low CMR operating temperature, no slagging occurs.

• Coal gas (H₂ + CO) flux rate = 17.8 ml/min/cm² (188 ml/min) with H₂:CO=2.2, CO selectivity=50%, and O₂ flux=3.5 ml/min/cm² at 70% O₂ depletion at 900°C.

• Oxygen flux increases with a coal gas production rate.
KEY TECHNICAL HURDLES FOR HYDROGEN PRODUCTION USING OXYGEN TRANSPORT MEMBRANES

- Chemical Coefficient of Thermal Expansion
- Mechanical Creep Under a Pressure Differential
- Maintaining Stable Catalyst/Membrane Interface
- Tube vs. Planar Scale Up Configuration
- Catalysis Design for the Two Step Reforming Process
- Hot Seals Versus Cold
- Impurity Management Issues
- Improve Mechanical Properties While Maintaining High Oxygen Flux
- Non-Volatile Lattice Substituents
HYDROGEN SEPARATION FROM REFORMED FEEDSTOCKS

Mixed Proton/Electron Transport Membrane

H₂O + CO + CO₂ + H₂

High Pressure

H₂ → 2H⁺ + 2e⁻

Oxidation Catalyst

H₂O + CO + CO₂

Reduction Catalyst

2e⁻ + 2H⁺ → H₂

Ambient Pressure

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INTEGRATING WGS WITH HYDROGEN SEPARATION

Dense Membrane for H₂ Separation

CO₂

CO₂

H₂ → 2H⁺ + 2e⁻ (at membrane oxidizing surface)

Water-Gas-Shift Catalyst Bed
CO + H₂O → CO₂ + H₂

2H⁺ + 2e⁻ → H₂ (at membrane reducing surface)

Oxidation Catalysis

CO + H₂ + H₂O

Reduction Catalysis

H₂ → 2H⁺ + 2e⁻ (at membrane oxidizing surface)
PROTON-CONDUCTING PEROVSKITE

• Iwahara, early 1980s

• $A_{1-x} A'_{x} B_{1-y} B'_{y} O_{3-\delta}$

• 0.01 to 0.2 mol H$^+$/mol

• SrCeO$_3$ & BaCeO$_3$
  doped with Y, Yb, Gd

• $10^{-2}$ S/cm at $\sim 800^oC$
TRANSPORT MECHANISM

• Introduction of charge carriers:

\[ \text{H}_2\text{O} + \text{V}_0^- + \text{O}_0^x \rightleftharpoons 2\text{OH}_0^- \]
\[ \frac{1}{2} \text{H}_2 + \text{O}_0^x \rightleftharpoons \text{OH}_0^- + e^- \]

• Driving force:

\[ E = -\frac{RT}{nF} \ln \left( \frac{p_2}{p_1} \right) \]

• Conducting species:

\( \text{H}^+ (\lt 850^\circ\text{C}), \text{OH}^- (\geq 850^\circ\text{C}) \)

• Proton conduction mechanism:

Proton “hopping” and reorientation

• Electron conduction mechanism:

\[ \text{B}^{n+}\text{-O}^2-\text{-B}^{(n+1)+} \rightleftharpoons \text{B}^{n+}\text{-O}\text{-B}^{n+} \rightleftharpoons \text{B}^{(n+1)+}\text{-O}^2-\text{-B}^{n+} \]
INTRODUCING ELECTRONIC CONDUCTIVITY INTO PROTON CONDUCTING PEROVSKITES

$A_{1-x}A_x'B_{1-y}B_y'O_{3-\delta}$, where $x$ and $y$ are the fractions of dopants in the A and B sites.

(U.S. Patent 5,821,185, October 13, 1998)
(U.S. Patent 6,037,514, March 14, 2000)
(U.S. Patent 6,281,403, August 28, 2001)
Proton conductivities close to Perovskites have been reported (0.03 S/cm).
SUMMARY OF H₂ TRANSPORT MEMBRANES

950°C

H₂ Permeation Rate (mL/min/cm²) 950°C

0.23 mm thick
APPLICATION OF FLEXIBLE THIN-FILM IONICALLY CONDUCTING CERAMIC APPLIQUE TO A CATALYTIC POROUS SUPPORT FOLLOWED BY CO-SINTERING
SUPPORTED THIN FILM

- Air
- Catalyst
- Membrane
- Porous Catalytic Support
HYDROGEN FLUX VERSUS MEMBRANE THICKNESS FOR HIGH TEMPERATURES

![Graph showing the relationship between hydrogen permeation rate and membrane thickness for different materials at approximately 900°C.](image-url)
# Hydrogen Separation Membrane Characteristics

<table>
<thead>
<tr>
<th>Membrane Category</th>
<th>Temperature Range (°C)</th>
<th>Maximum Permeation Rate (mL min(^{-1}) cm(^{-2}))</th>
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</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>High-Temperature Cermet With Non H(_2)-Permeable Metal (Ni)</td>
<td>700 to 950</td>
<td>≈ 1</td>
</tr>
<tr>
<td>High-Temperature Cermet with H(_2)-Permeable Metal (Pd)</td>
<td>550 to 950</td>
<td>≈ 10</td>
</tr>
<tr>
<td>Thin Film Palladium on Porous Support</td>
<td>320 to 500</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Intermediate-Temperature Composite</td>
<td>340 to 440</td>
<td>&gt;400</td>
</tr>
</tbody>
</table>
EVOLUTION OF HIGH PERFORMANCE HYDROGEN TRANSPORT MEMBRANES

- Single Phase Mixed Conducting Perovskites
- Metal / Perovskite Cermets Where Metal is Only Electron Conducting
- Pd / Perovskite Cermets
- Electroless Thin Film Pd Deposited onto Porous Perovskite Composite
- Low Cost Metal / Metal Oxide Cermets
- Low Cost Metals / Metal Oxide Composites Supported Thin Film Within a Porous Ceramic Matrix
LONG-TERM AMBIENT PRESSURE PERFORMANCE

PERFORMANCE OF HYDROGEN TRANSPORT MEMBRANE

(80% H₂/20% He Feed at 320°C)

- No guard bed used to adsorb impurities.
CROSS-SECTIONAL SCHEMATIC OF STACKED HYDROGEN SEPARATION MEMBRANE UNIT

Membrane

Sweep Stream

Seal

Exhaust H₂O + CO₂

Seal

Sweep Stream

Membrane

Membrane

Sweep Stream + H₂

1/8" Knife Edge

H₂O + CO₂ + CO + H₂ + N₂

1/8" Knife Edge

Sweep Stream + H₂

Sweep Stream + H₂

Catalyst Guard Bed

Water-Gas Shift Reactor

H₂ + CO₂ + CO + N₂

Steam

Syngas (H₂ + CO₂ + CO + N₂)

Valve

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Stacked Hydrogen Separation Membrane Unit

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Membrane Area: 21.3 cm²
Flange Diameter: 2 ¾ inch (70 mm)
SURFACE OF HYDROGEN MEMBRANE
FEED SIDE AFTER SYNGAS + STEAM –
NO GUARD BED

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AMBIENT PRESSURE MEMBRANE PERFORMANCE WITH STEAM AND IMPROVED GUARD BED

Long-Term Test @ 340°C with a Feed of 60% H₂/40% H₂O and Guard Bed

- H₂ Flux (mL·min⁻¹·cm⁻² STP)
- Permeability (mol·s⁻¹·m⁻¹·Pa⁻0.5)

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HIGH PRESSURE REACTOR CONFIGURATION FOR HYDROGEN SEPARATION MEMBRANE
HYDROGEN FLUX AT HIGH PRESSURE DIFFERENTIAL

- Permeability of $2.3 \times 10^{-7} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ and hydrogen flux of 423 mL min$^{-1}$ cm$^{-2}$ (STP) achieved at 440°C (713K) under ideal hydrogen-helium mixture up to 33 bar (476 psi) differential pressure and partial pressure of hydrogen of 34 bar (488 psi).

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Relative Costs of H₂ Production Using Membrane Technologies

- Natural gas reforming is ~63% of H₂ production cost.  
  (S. Lasher et al., Hydrogen Technical Analysis, Proc. 2002 DOE Hydrogen Program Review)

- Reforming cost could be reduced by ~30% using Eltron O₂ separation membranes.

- H₂ separation membranes could reduce purification cost by ~30% relative to PSA.  
  (S. Lasher et al., Hydrogen Technical Analysis, Proc. 2002 DOE Hydrogen Program Review)

- Eltron H₂ separation membranes are ~200 times cheaper than analogous Pd membranes and permeate 10x faster.

- Estimated H₂ cost using combined oxygen and hydrogen transport membrane technologies is $4/MMBtu or $0.55/kg.  
KEY TECHNICAL HURDLES FOR HYDROGEN SEPARATION MEMBRANE

• Long Term Stability of Catalyst/Membrane Interface
• Low Cost Catalyst Deposition
• Long Term Sulfur Tolerance
• Planar vs. Tubular Configurations
• Seal Strategy
• Approach to Integrating WGS with Membrane – Mass Transfer Issues
• Low Cost Manufacture
MEMBRANES FOR HYDROGEN SUPPLY

Air → CO₂ Sequestration → H₂ → Fuel Cell

Air → CO₂ Sequestration → H₂ → Combustion

Natural Gas, Petroleum, Biomass, or Coal

Water-Gas Shift

H₂O

Air → CO₂ Sequestration → H₂ → Combustion

H₂O + N₂