IONICALLY CONDUCTING MEMBRANES FOR HYDROGEN PRODUCTION AND SEPARATION

Presented by

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Arlington, Virginia

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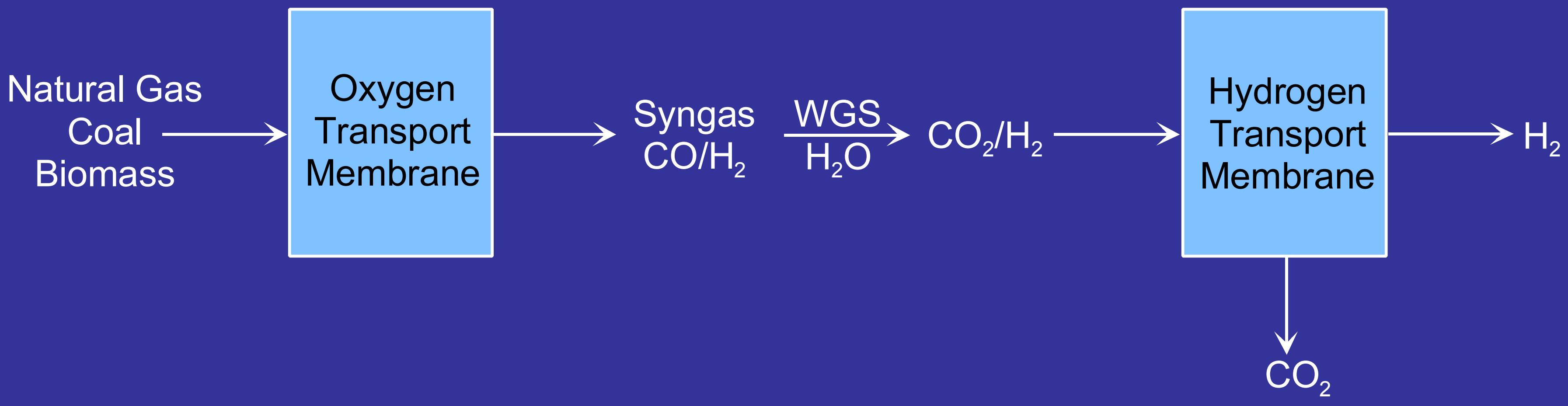
TO BE DISCUSSED

- **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



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INCENTIVES FOR OXYGEN TRANSPORT MEMBRANES FOR HYDROGEN PRODUCTION

- **Conventional Natural Gas Steam Reforming**

  $CH_4 + H_2O \rightarrow 3H_2 + CO$ **Endothermic (Energy Required)**

- **Membrane Driven Natural Gas Reforming**

  $CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO$ **Exothermic (Energy Produced)**

Energy Savings Greater than 30%.

OXYGEN TRANSPORT MEMBRANES FOR FEEDSTOCK PARTIAL OXIDATION TO SYNTHESIS GAS

Natural Gas

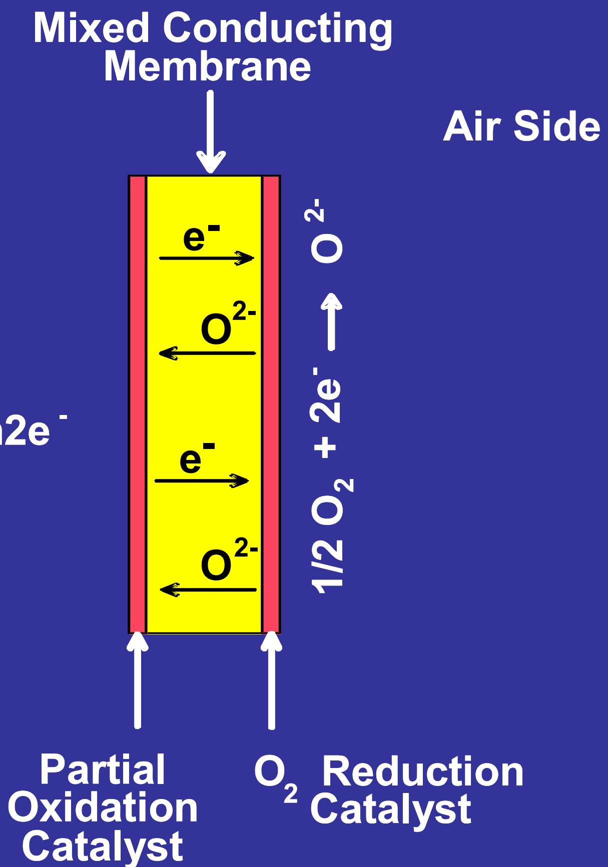
i) $CH_4 + O^{2-} \longrightarrow CO + 2H_2 + 2e^-$

Liquid Hydrocarbons

ii) $C_nH_{2n+2} + nO^{2-} \longrightarrow nCO + (n+1)H_2 + n2e^-$

Coal

iii) $2C + H_2O + O^{2-} \longrightarrow 2\,CO + H_2 + 2e^-$



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

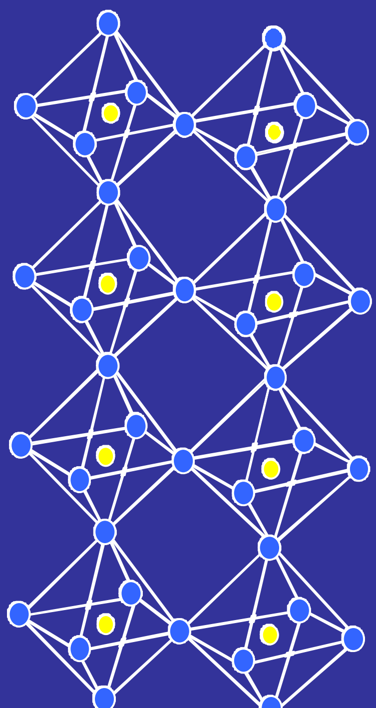
Neural Network Analysis $\longleftrightarrow$ Experiment

Crystallographic Thermodynamic and Mechanical Properties

Neural Network Analysis $\downarrow$ Trends Suggestions

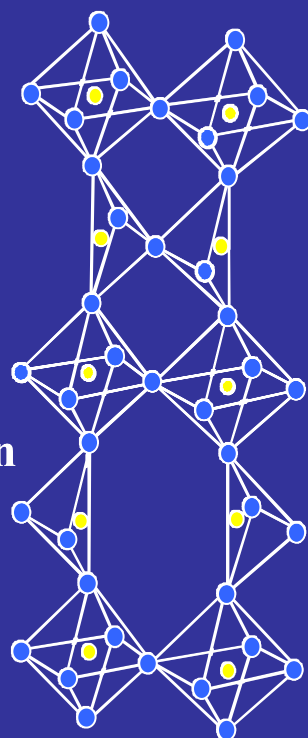
Experiment $\downarrow$ Emphasis

RATIONALLY SELECTED OXYGEN TRANSPORT MEMBRANE MATERIALS



Perovskite

- B, B′ Ions
- Oxygen Anion



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)

$$A_xA'_xA''_{2-(x+x')}B_yB'_{y'}B''_2\text{-}(y+y')O_{5+z}$$

HIGH PRESSURE OPERATION

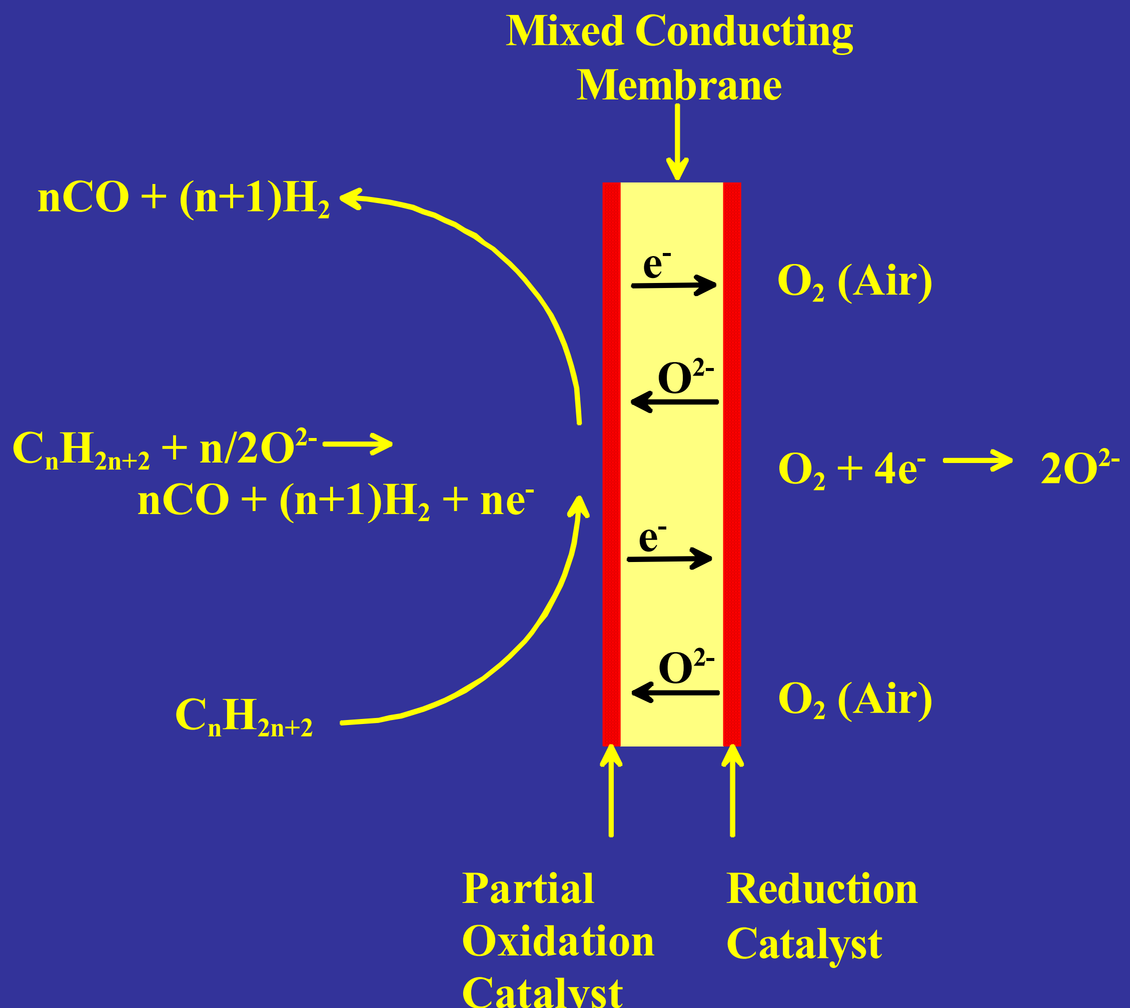
Eltron has successfully operated membrane reactors at high pressure (250 psi) on the natural gas surface and ambient pressure on the air (oxygen) surface at elevated temperatures. Over nine years operating experience.

SUMMARY OF ELTRON OXYGEN TRANSPORT MEMBRANE SYNGAS RESULTS

Syngas Reactor Studies
Tubular Reactors

- Syngas Production Rate – 60 mL/min cm^2 @ 900°C
- Equivalent O_2 Flux -10-12 mL/min-cm^2 (>1S cm^{-1}) @ 900°C
- H_2: CO Ratio - -1.9 - 2.0
- CO Selectivity - >96%
- Throughput Conversion - 90% CH_4, 70% O_2 (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



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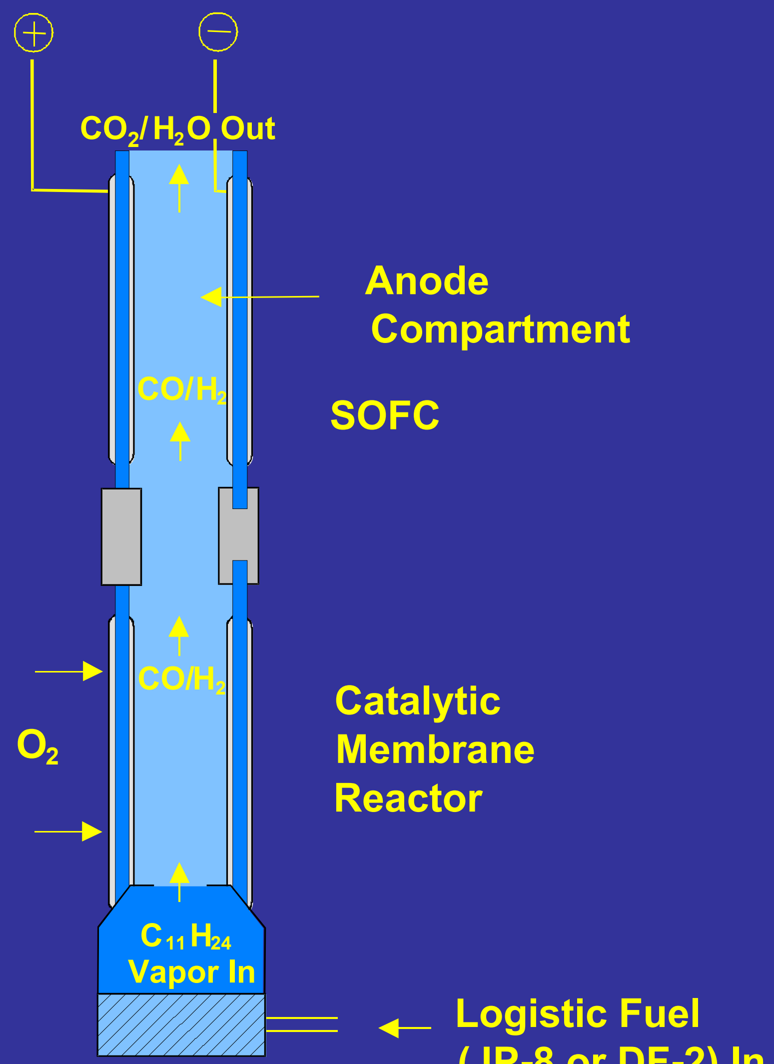
MEMBRANE LIQUID FUEL EFORMER INTEGRATED WITH SOFC



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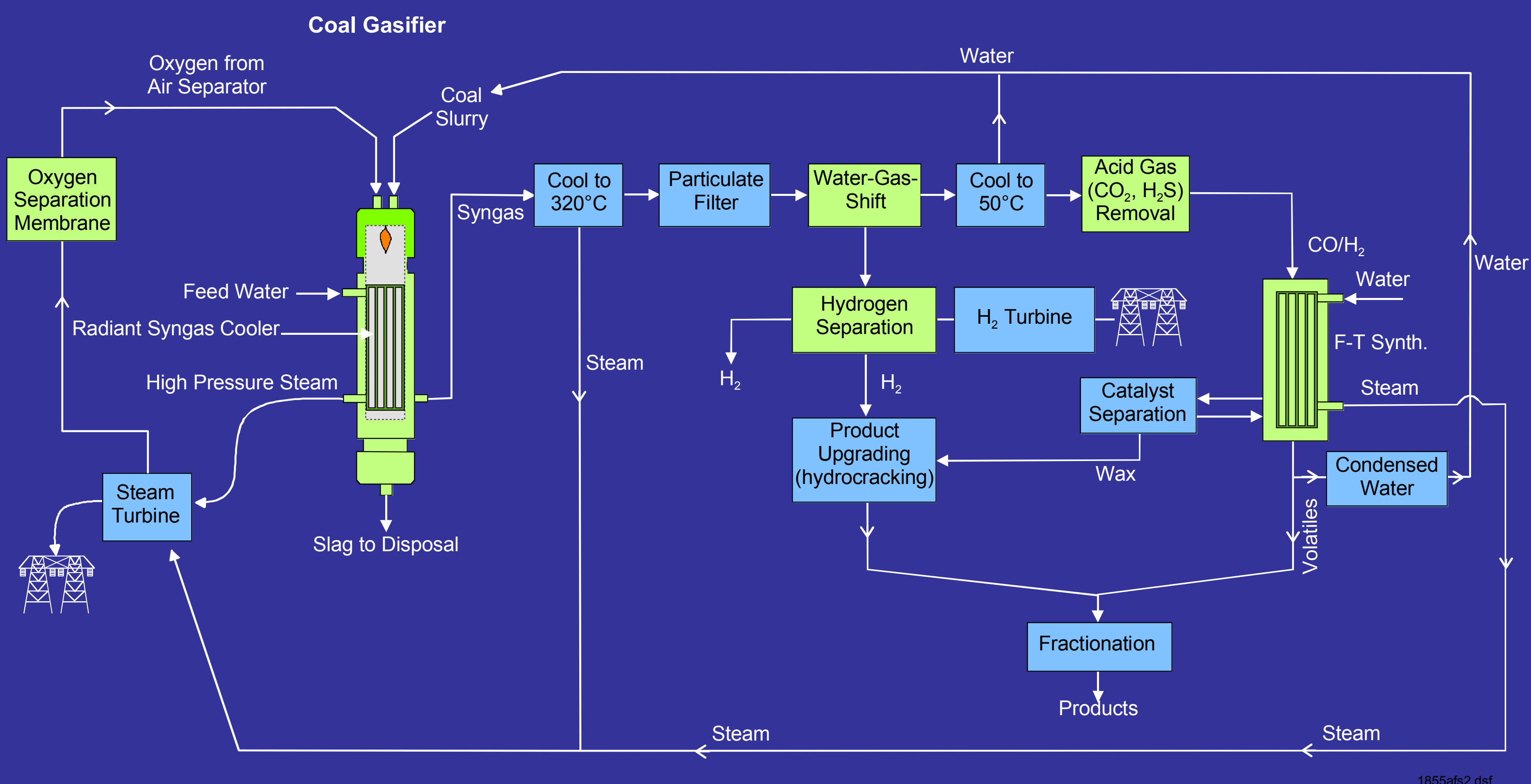
LIQUID FUEL REFORMING – CURRENT STATUS

- Synthesis gas production rates approaching 40 ml/min-cm^2 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-cm^2.
- 800 hours continuous operation on diesel fuel with no carbon deposition. Synthesis gas production rate >27 ml/min-cm^2 with 100% conversion.
- DF-2 reformed at 27 ml/min-cm^2 – corresponds to 3.9 A/cm^2 in a SOFC.
- Sulfur tolerant

COAL GASIFICATION PROCESS -

AREAS IN GREEN CORRESPOND TO NEW TECHNOLOGIES UNDER DEVELOPMENT AT ELTRON



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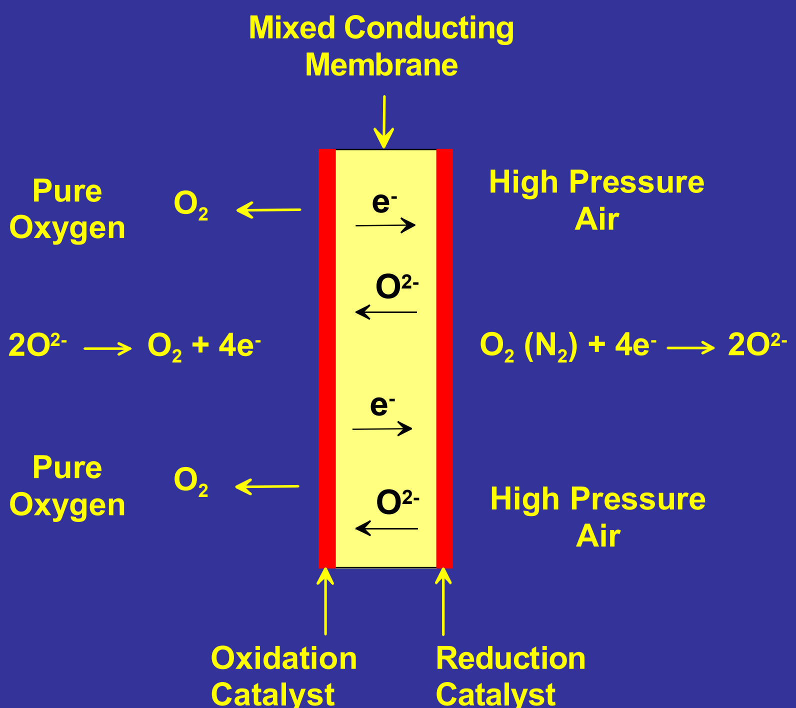
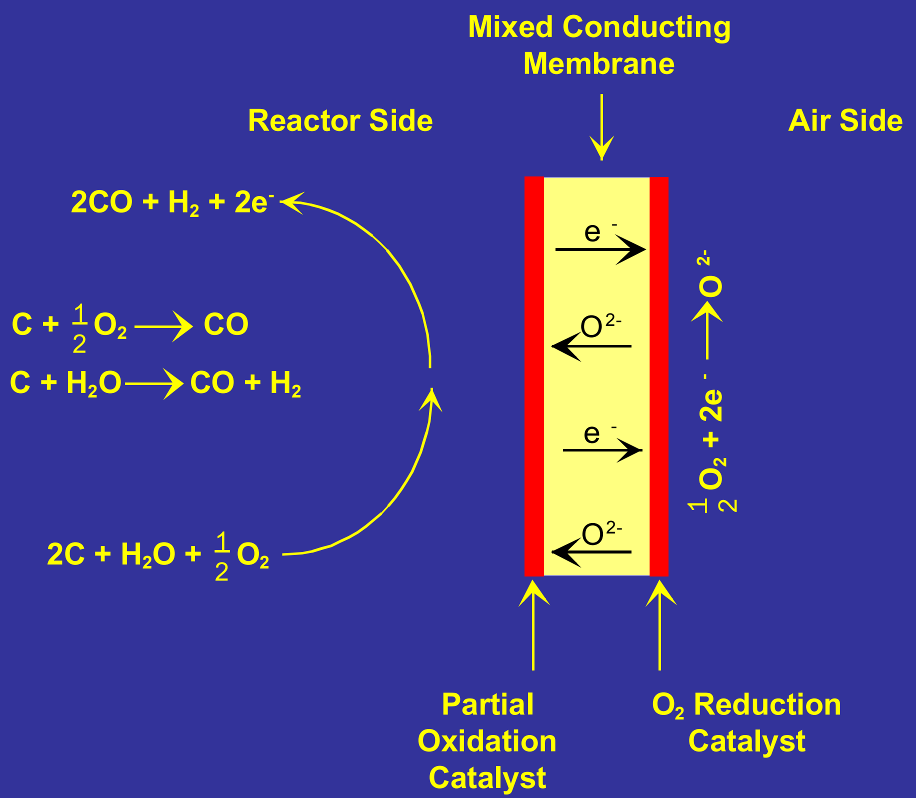
OXYGEN TRANSPORT MEMBRANES FOR INDIRECT AND DIRECT OXYGEN SUPPLY TO PROMOTE COAL GASIFICATION





6 ml/cm^2/min

20% $O_2 \rightarrow$ 2% O_2

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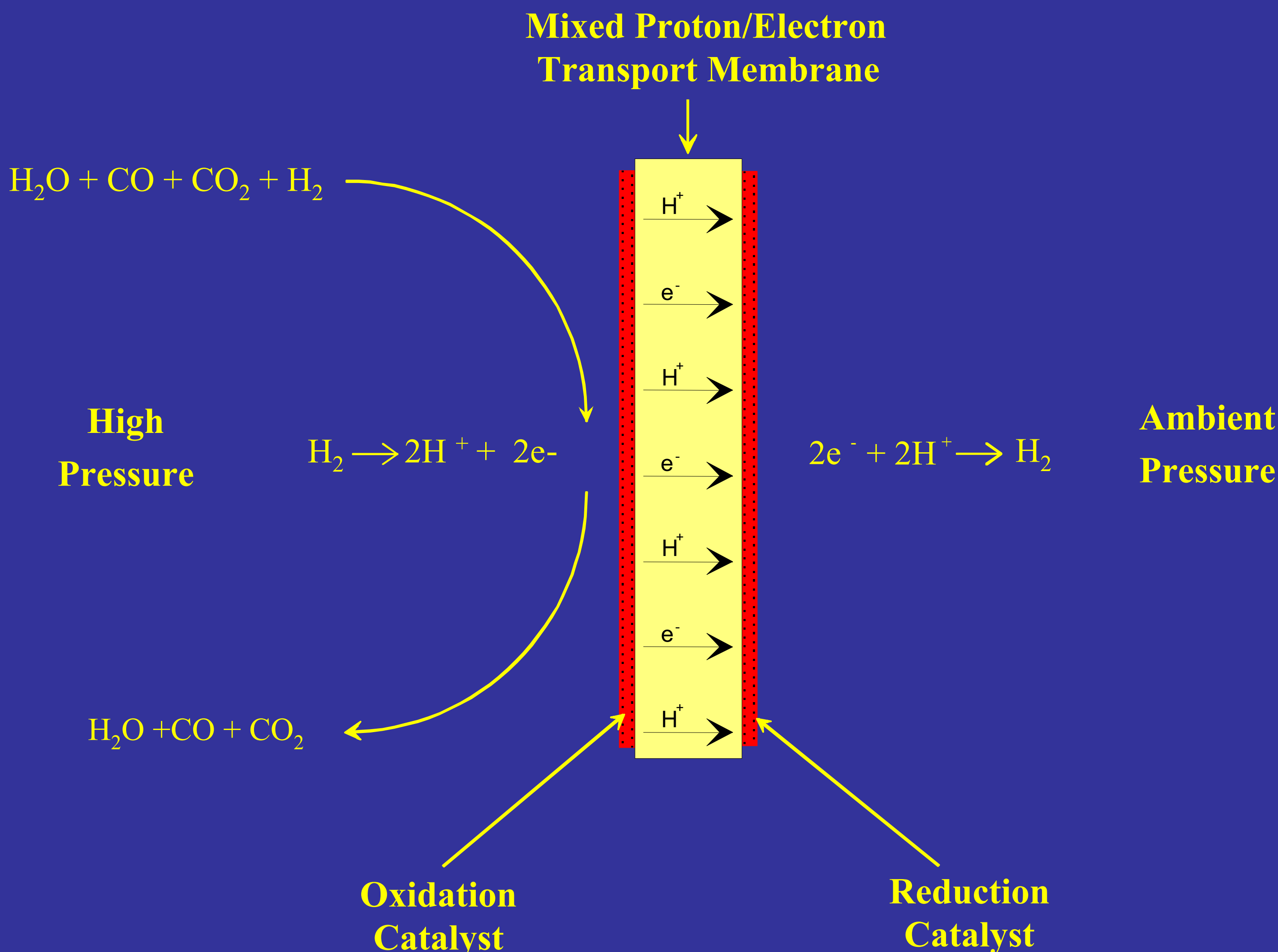
DIRECT COAL GASIFICATION FINDINGS

- 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 (H_2 + CO) flux rate = 17.8 ml/min/cm^2 (188 ml/min) with H_2:CO=2.2, CO selectivity=50%, and O_2 flux=3.5 ml/min/cm^2 at 70% O_2 depletion at 900^{o}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



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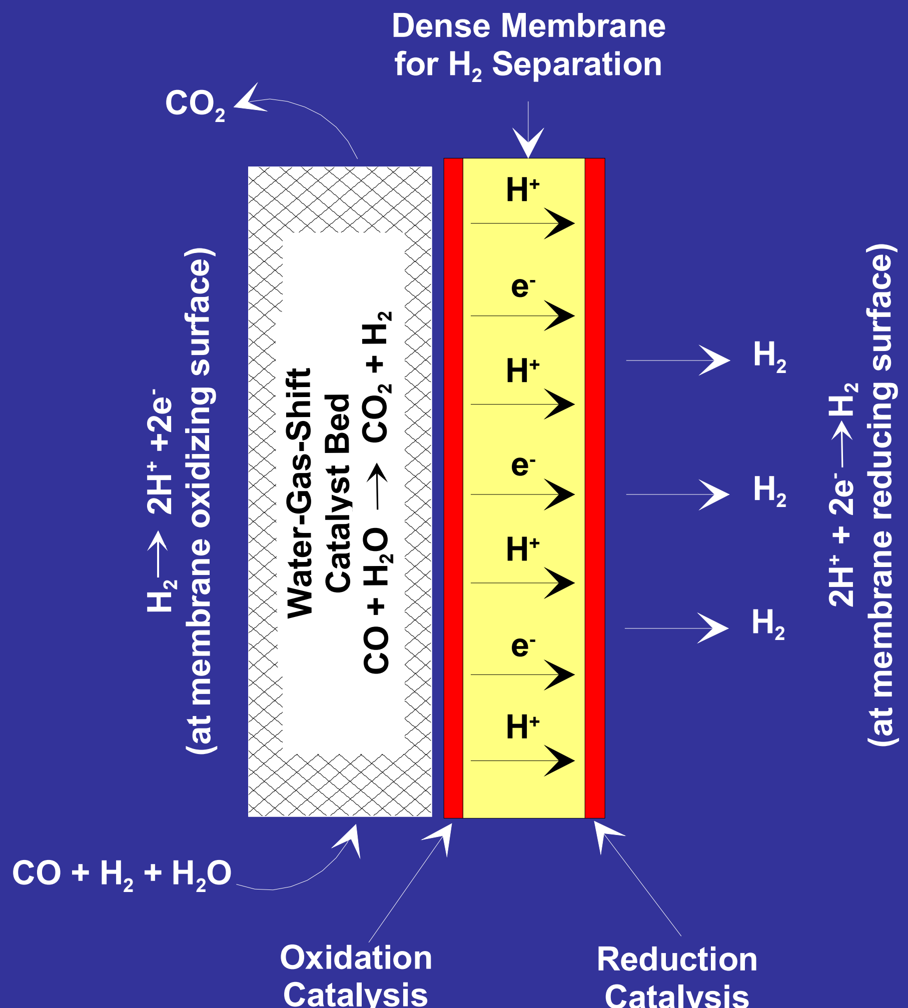
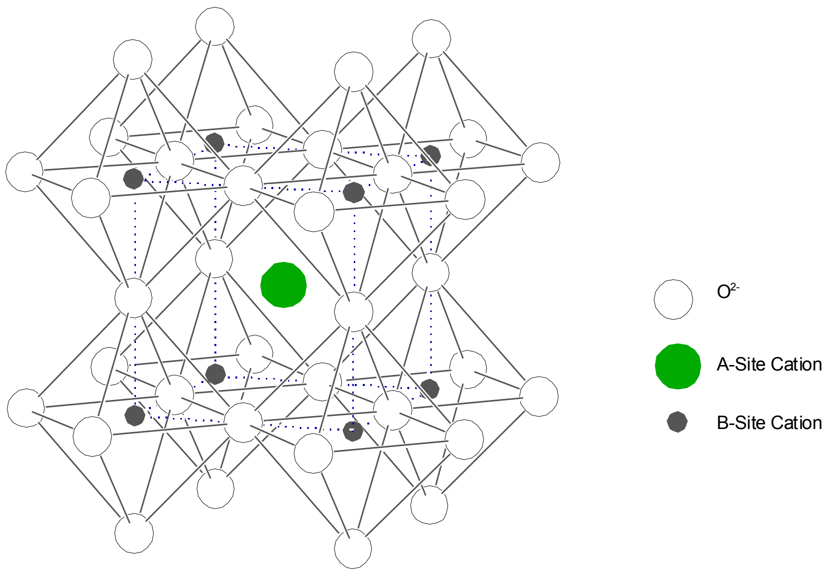
INTEGRATING WGS WITH HYDROGEN SEPARATION



PROTON-CONDUCTING PEROVSKITE

- Iwahara, early 1980s
- $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$
- 0.01 to 0.2 mol H^+/mol
- $SrCeO_3$ & $BaCeO_3$ doped with Y, Yb, Gd
- 10^{-2} S/cm at ~800°C



TRANSPORT MECHANISM

- **Introduction of charge carriers:**

$$H_2O + V_o^{\bullet\bullet} + O_o^{\times} \leftrightarrows 2OH_o^{\bullet}$$

$$\tfrac{1}{2} H_2 + O_o^{\times} \leftrightarrows OH_o^{\bullet} + e'$$

- **Driving force:**

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

- **Conducting species:**

  H^+ (< 850°C), OH^- (≥850°C)

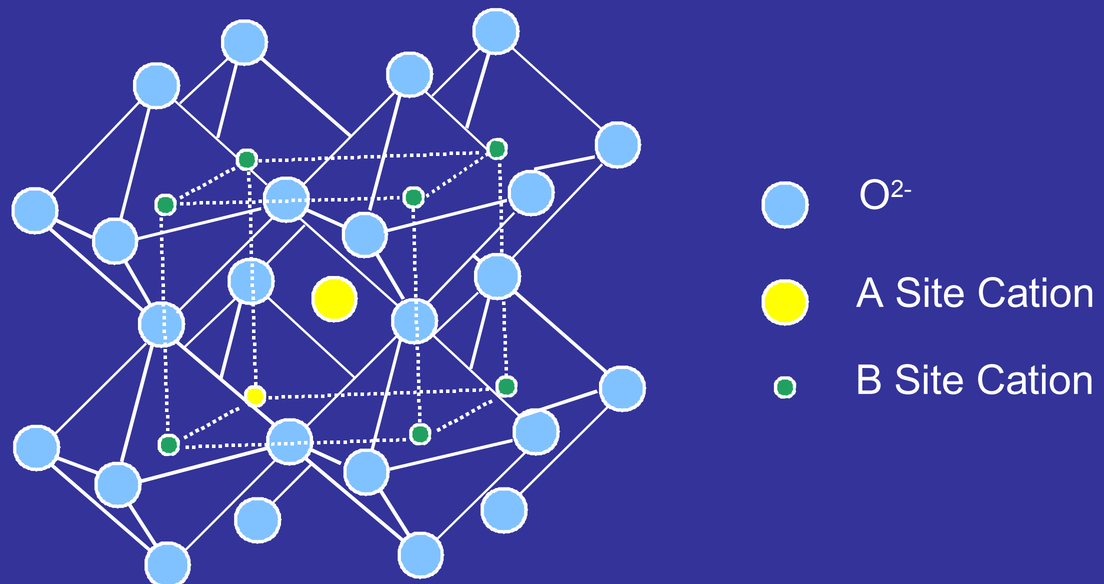
- **Proton conduction mechanism:**

  Proton "hopping" and reorientation

- **Electron conduction mechanism:**

$$B^{n+}\text{-}O^{2-}\text{-}B^{(n+1)+} \leftrightarrows B^{n+}\text{-}O^{-}\text{-}B^{n+} \leftrightarrows B^{(n+1)+}\text{-}O^{2-}\text{-}B^{n+}$$

INTRODUCING ELECTRONIC CONDUCTIVITY INTO PROTON CONDUCTING PEROVSKITES



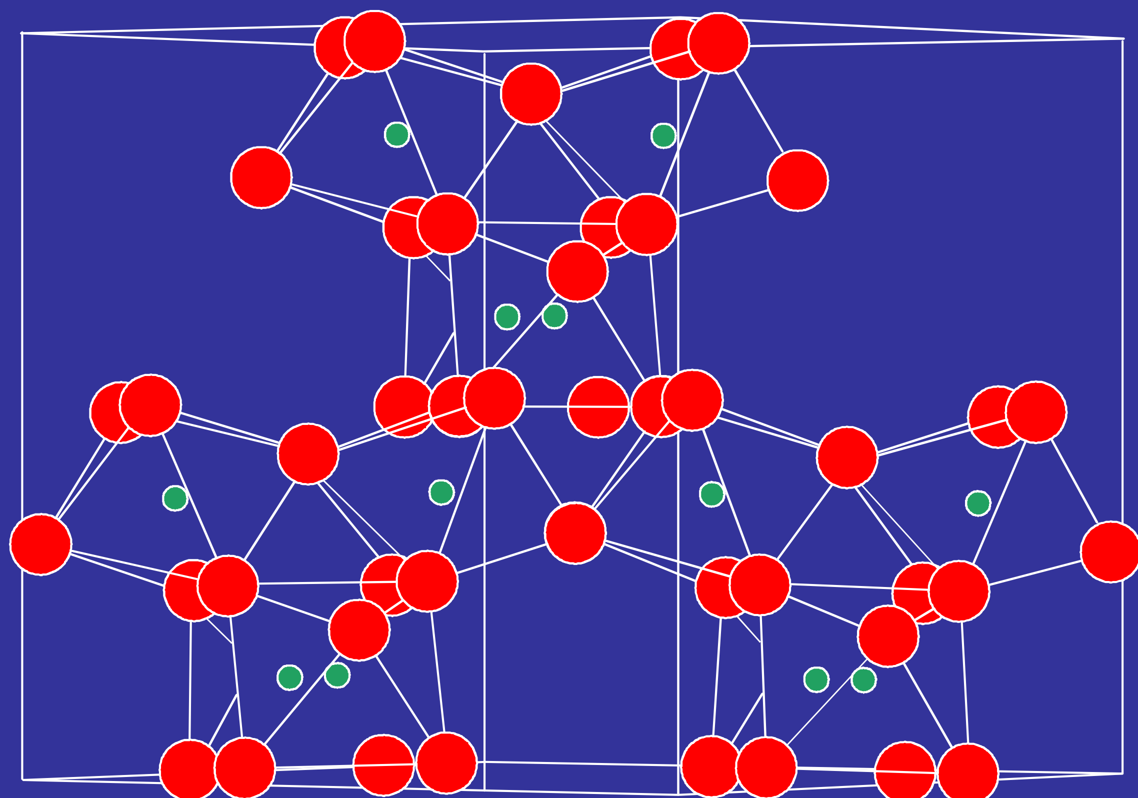
$A_{1-x}A_x'B_{1-y}B_y'O_{3-\delta}$, where x and y are the fractions of dopants in the A and B sites.

(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 CONDUCTION IN PYROCHLORES

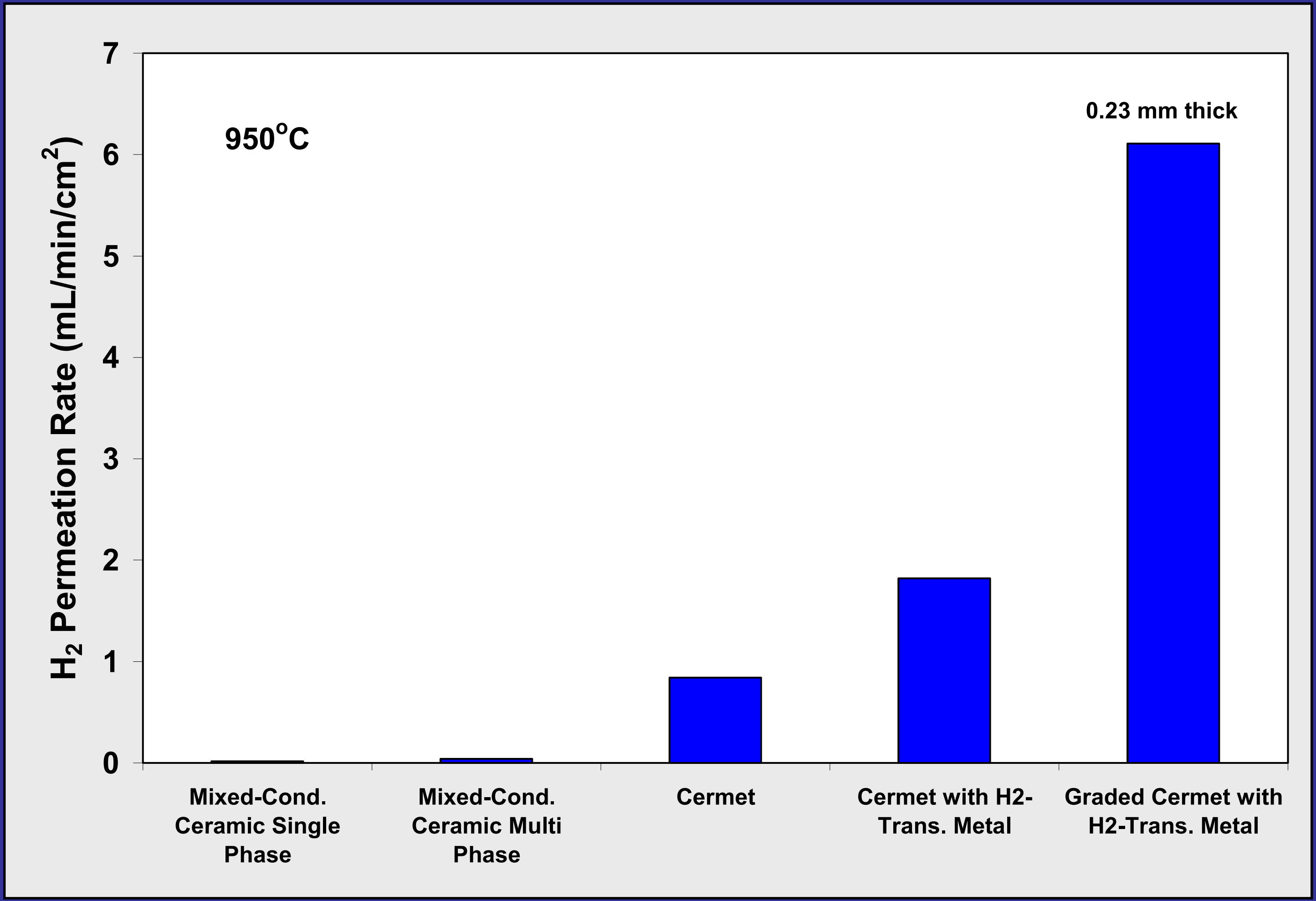


pyrochlore
$A_2B_2O_7$

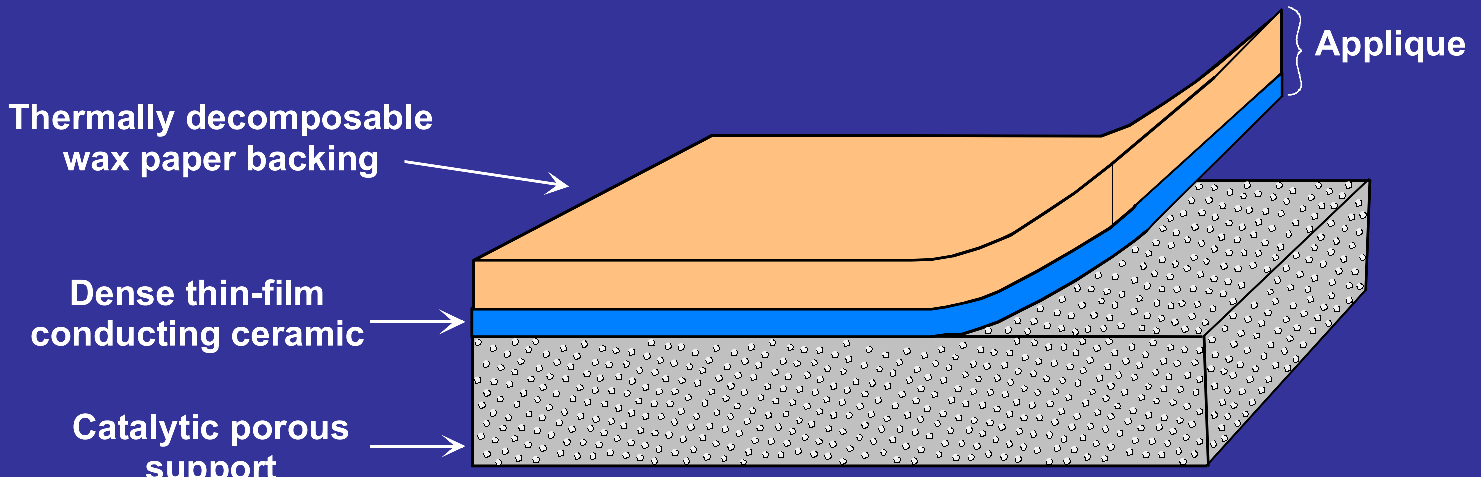
●	O^{2-}
●	B Site Cation
not shown	A Site Cation

Proton conductivities close to Perovskites have been reported (0.03 S/cm).

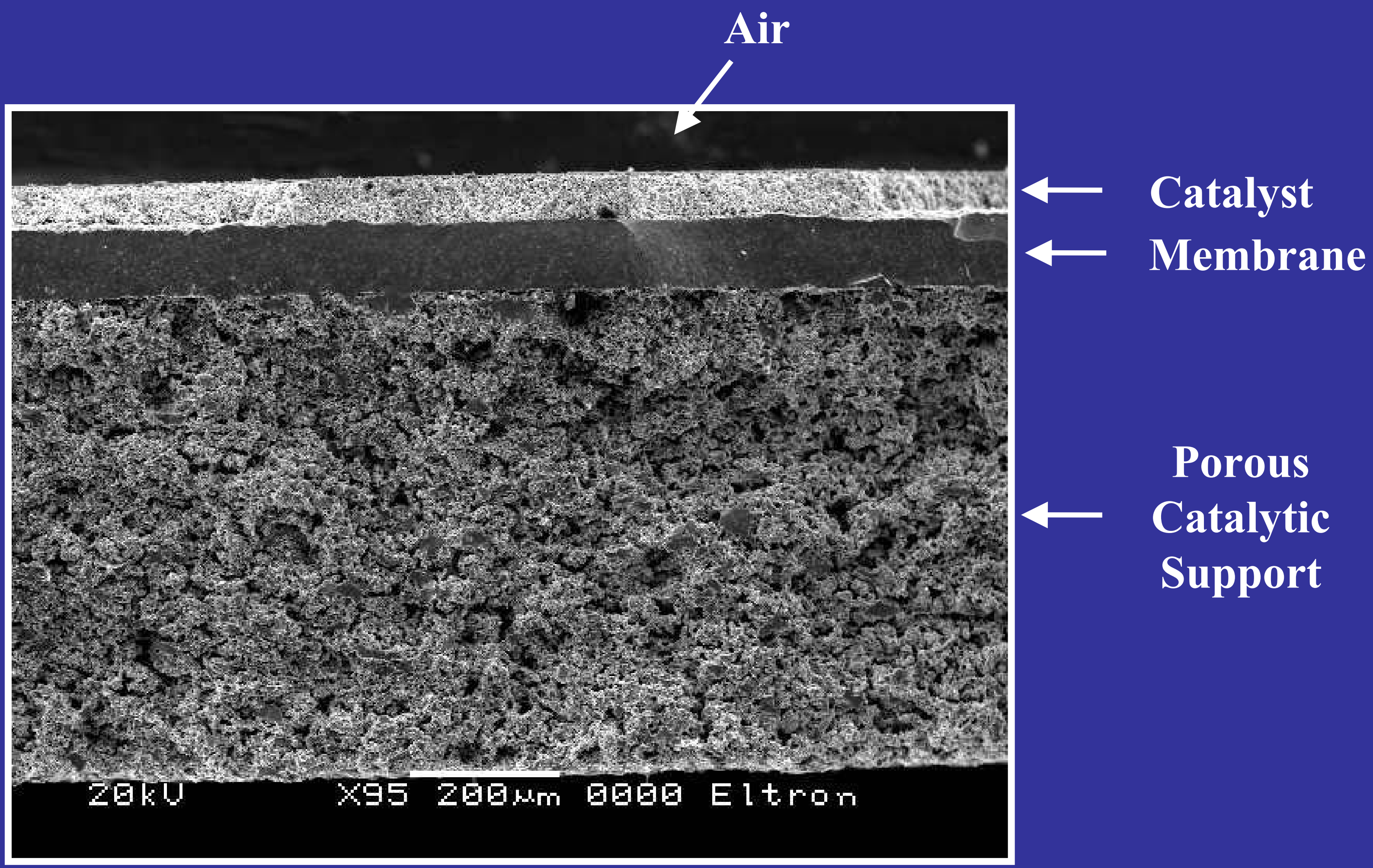
SUMMARY OF H_2 TRANSPORT MEMBRANES



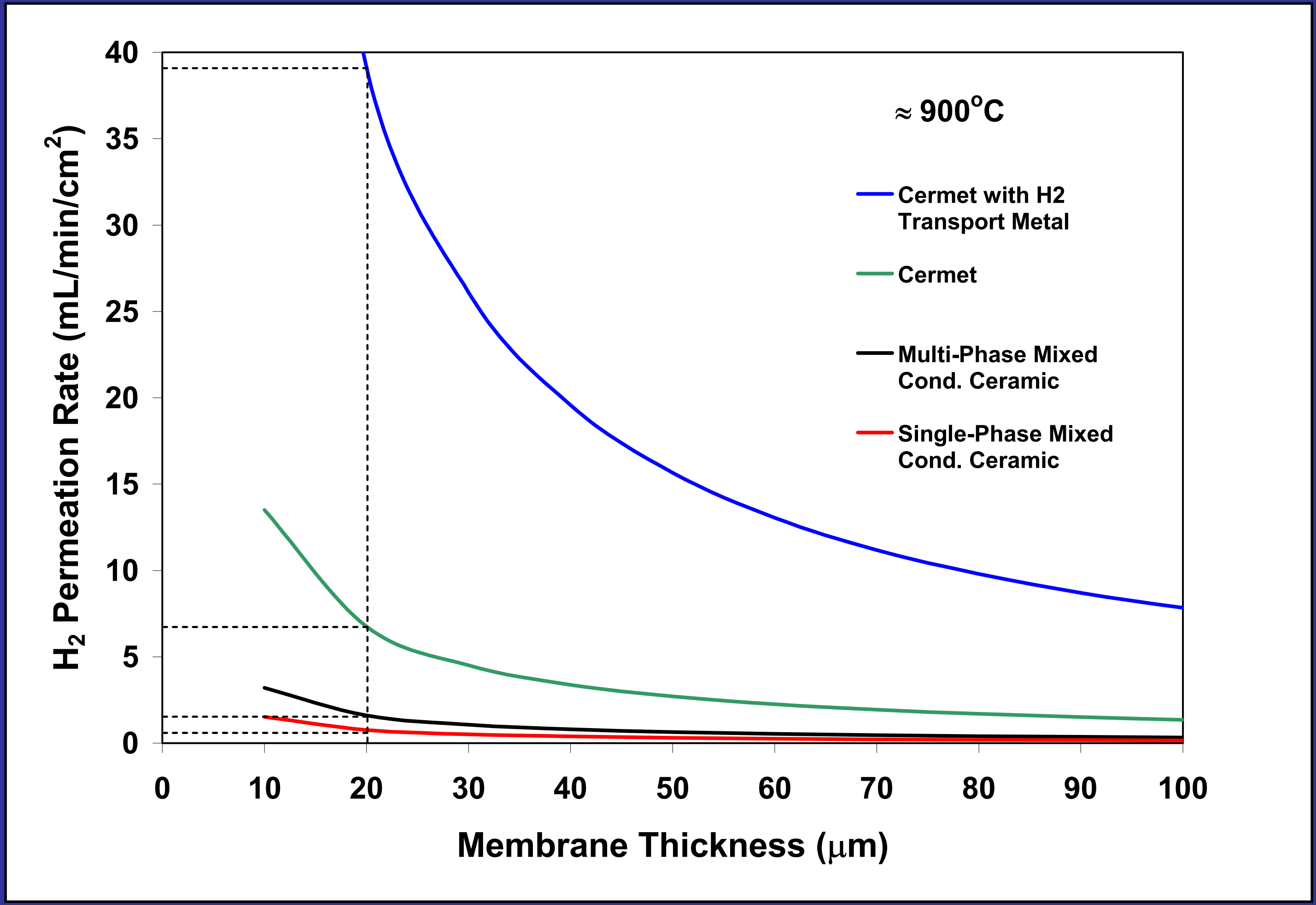
APPLICATION OF FLEXIBLE THIN-FILM IONICALLY CONDUCTING CERAMIC APPLIQUE TO A CATALYTIC POROUS SUPPORT FOLLOWED BY CO-SINTERING



SUPPORTED THIN FILM



HYDROGEN FLUX VERSUS MEMBRANE THICKNESS FOR HIGH TEMPERATURES



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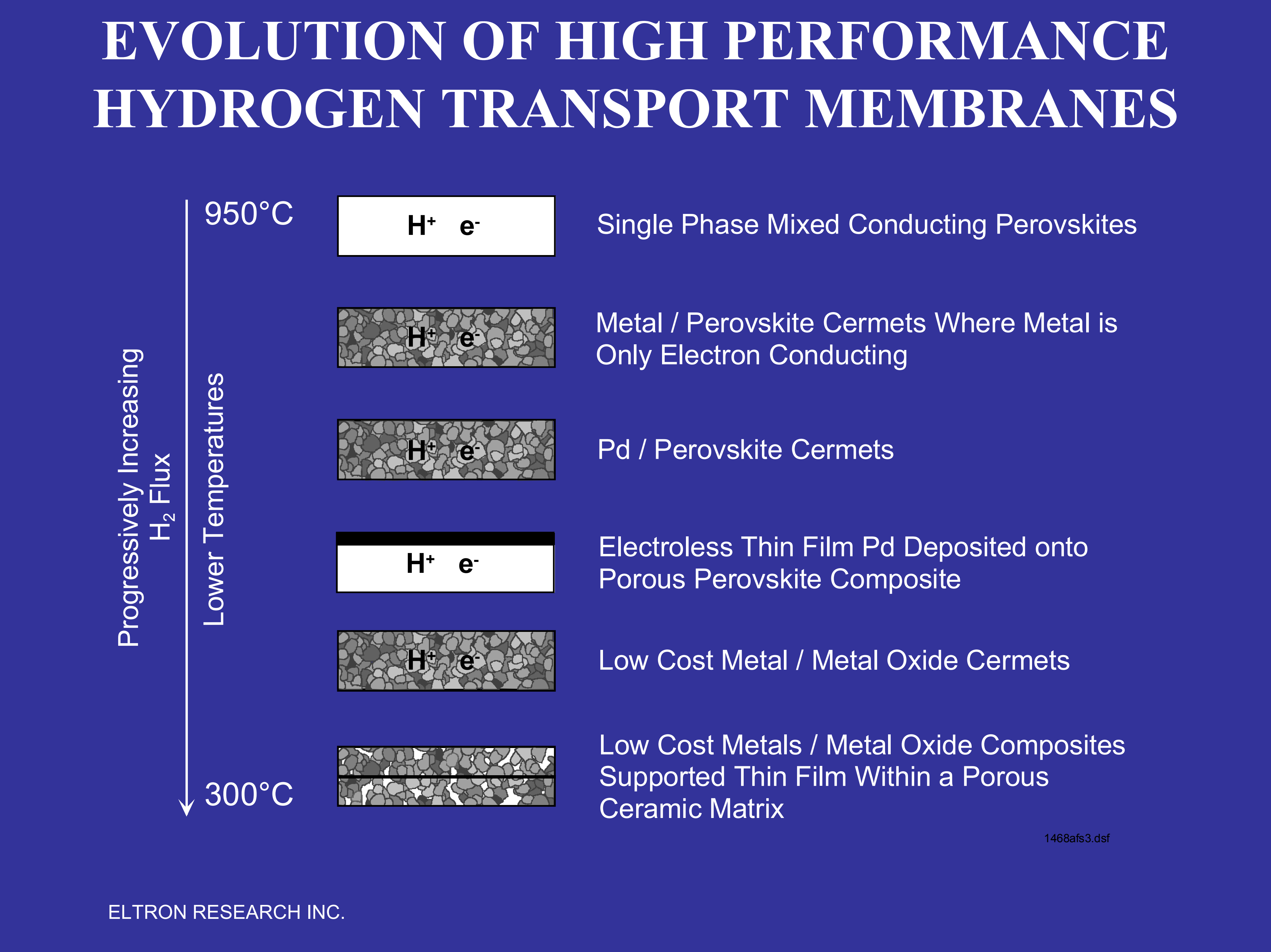
HYDROGEN SEPARATION MEMBRANE CHARACTERISTICS

Membrane Category	Temperature Range (°C)	Maximum Permeation Rate (mL min^{-1} cm^{-2})
Single Phase Ceramic	700 to 950	≈ 0.01
Ceramic/Ceramic	700 to 950	≈ 0.1
High-Temperature Cermet With Non H_2-Permeable Metal (Ni)	700 to 950	≈ 1
High-Temperature Cermet with H_2-Permeable Metal (Pd)	550 to 950	≈ 10
Thin Film Palladium on Porous Support	320 to 500	<50
Intermediate-Temperature Composite	340 to 440	>400


EVOLUTION OF HIGH PERFORMANCE HYDROGEN TRANSPORT MEMBRANES
950°C
300°C
Progressively Increasing H_2 Flux
Lower Temperatures
H^+ e^-
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
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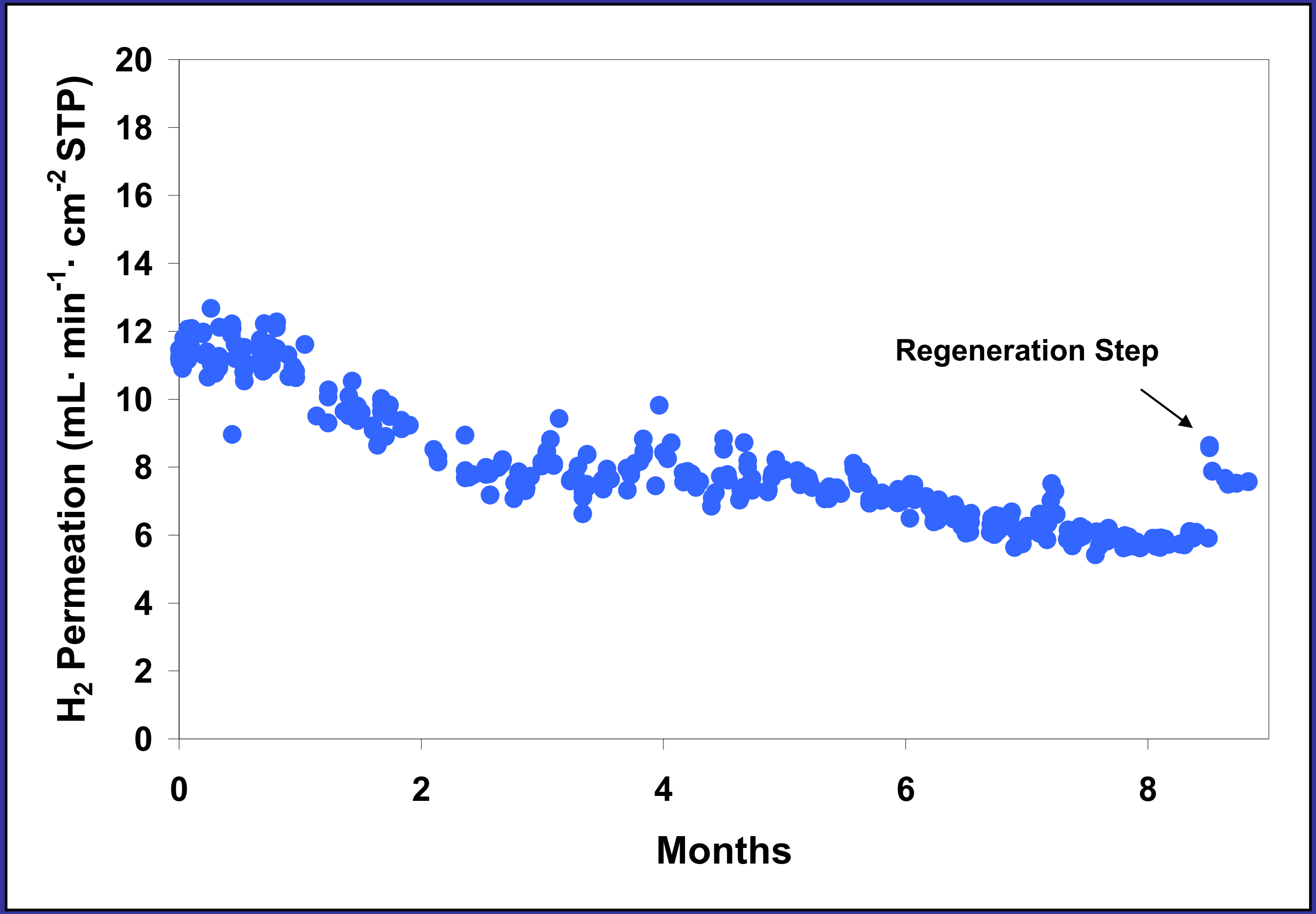
LONG-TERM AMBIENT PRESSURE PERFORMANCE

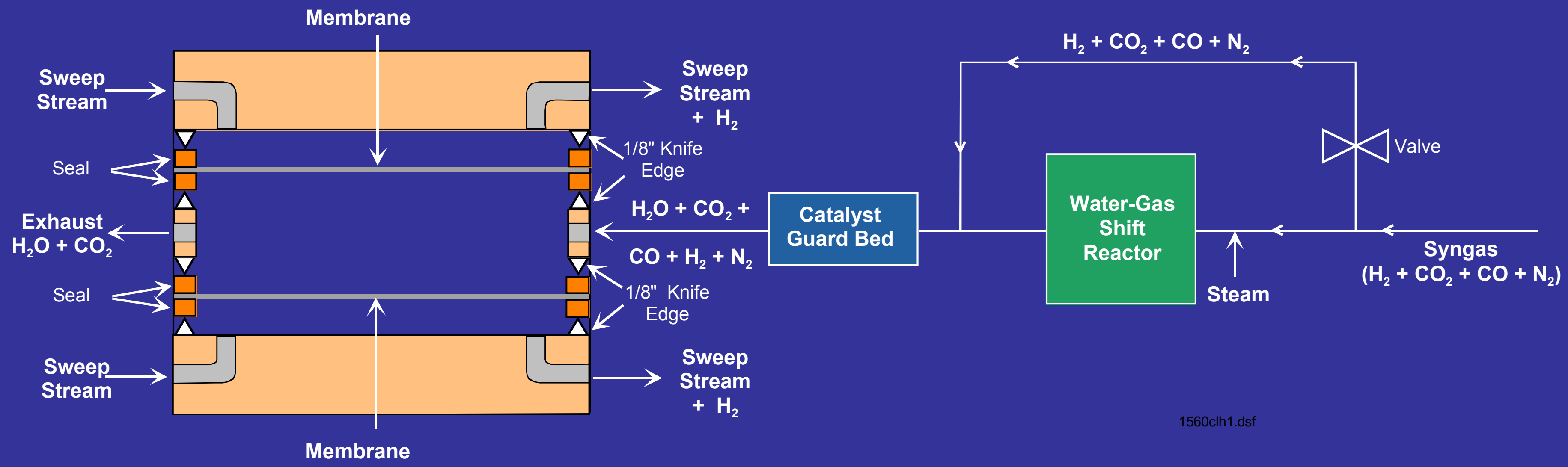
PERFORMANCE OF HYDROGEN TRANSPORT MEMBRANE

(80% H_2/20% He Feed at 320°C)



- No guard bed used to adsorb impurities.

CROSS–SECTIONAL SCHEMATIC OF STACKED HYDROGEN SEPARATION MEMBRANE UNIT



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Stacked Hydrogen Separation Membrane Unit

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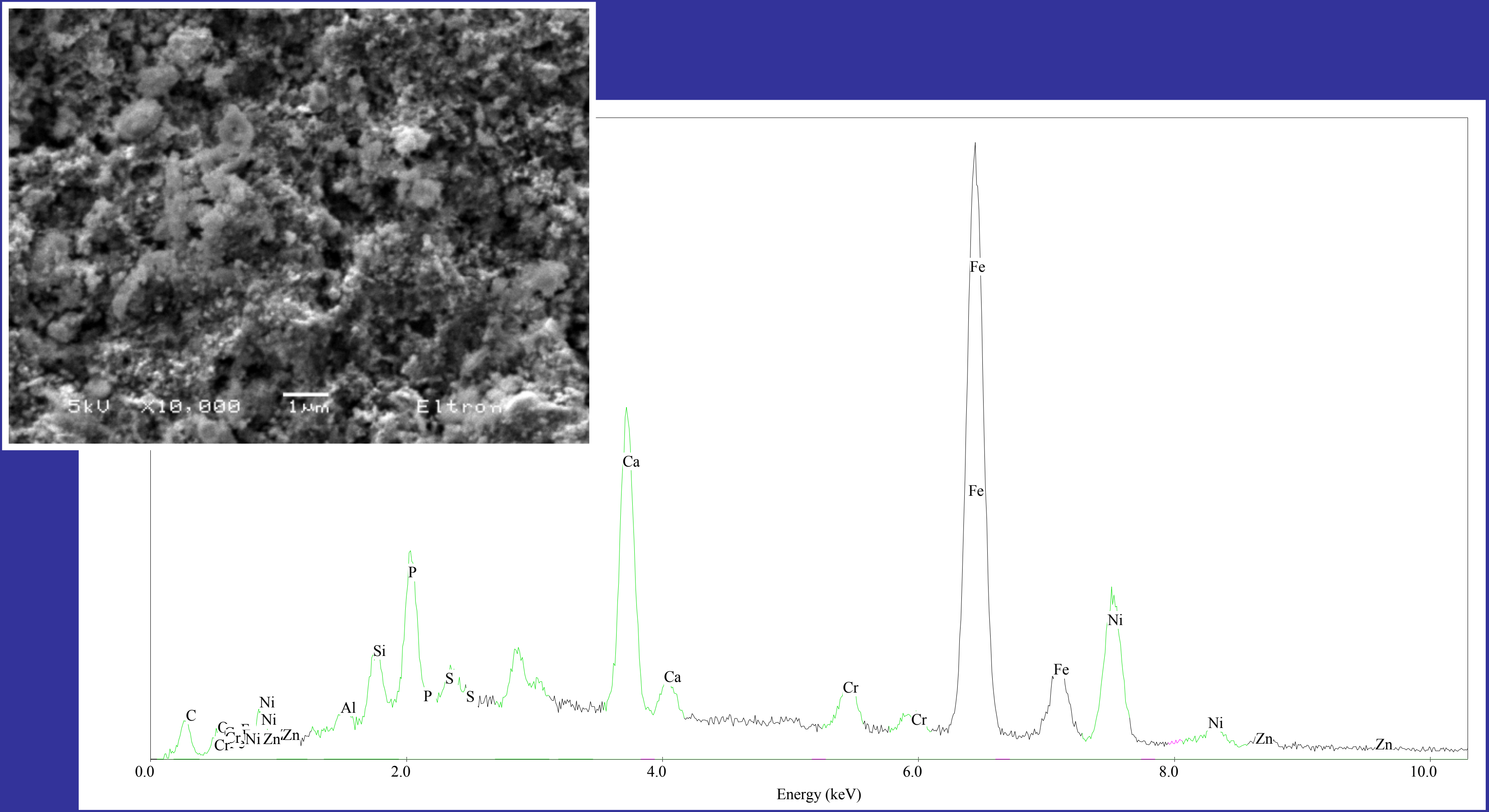
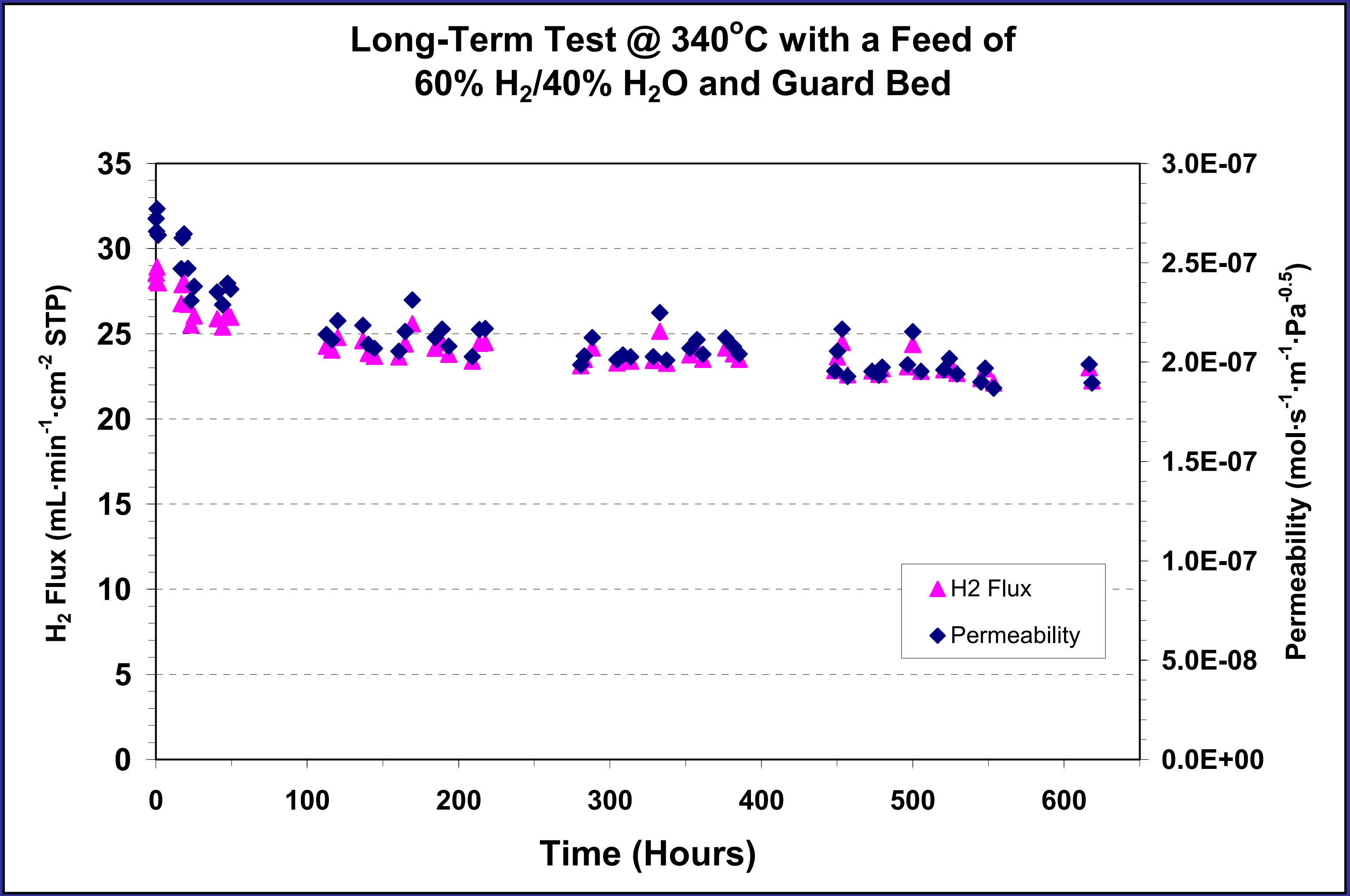
Membrane Area: 21.3 cm^2

Flange Diameter: 2 ¾ inch (70 mm)

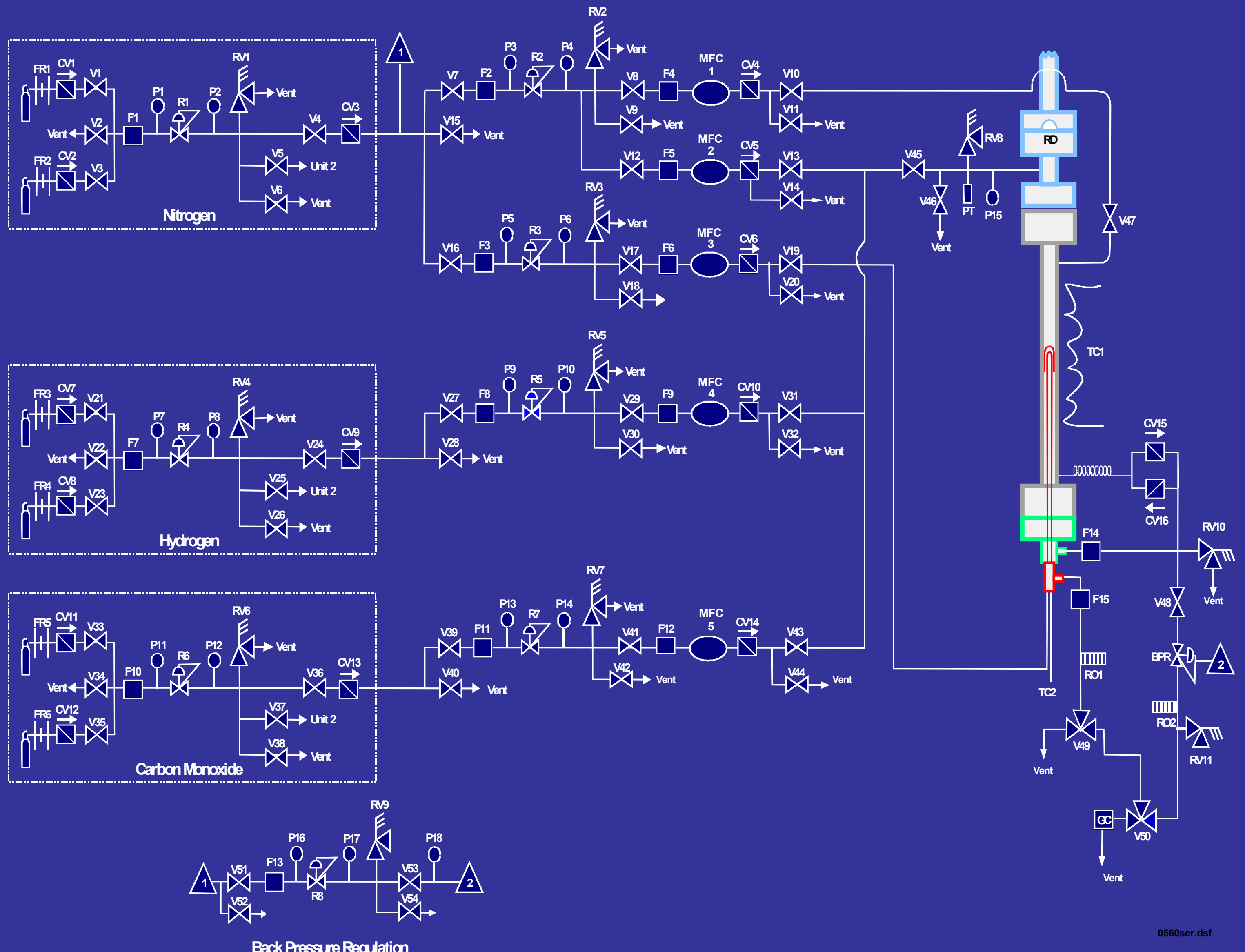
SURFACE OF HYDROGEN MEMBRANE FEED SIDE AFTER SYNGAS + STEAM – NO GUARD BED



AMBIENT PRESSURE MEMBRANE PERFORMANCE WITH STEAM AND IMPROVED GUARD BED



HIGH PRESSURE REACTOR CONFIGURATION FOR HYDROGEN SEPARATION MEMBRANE



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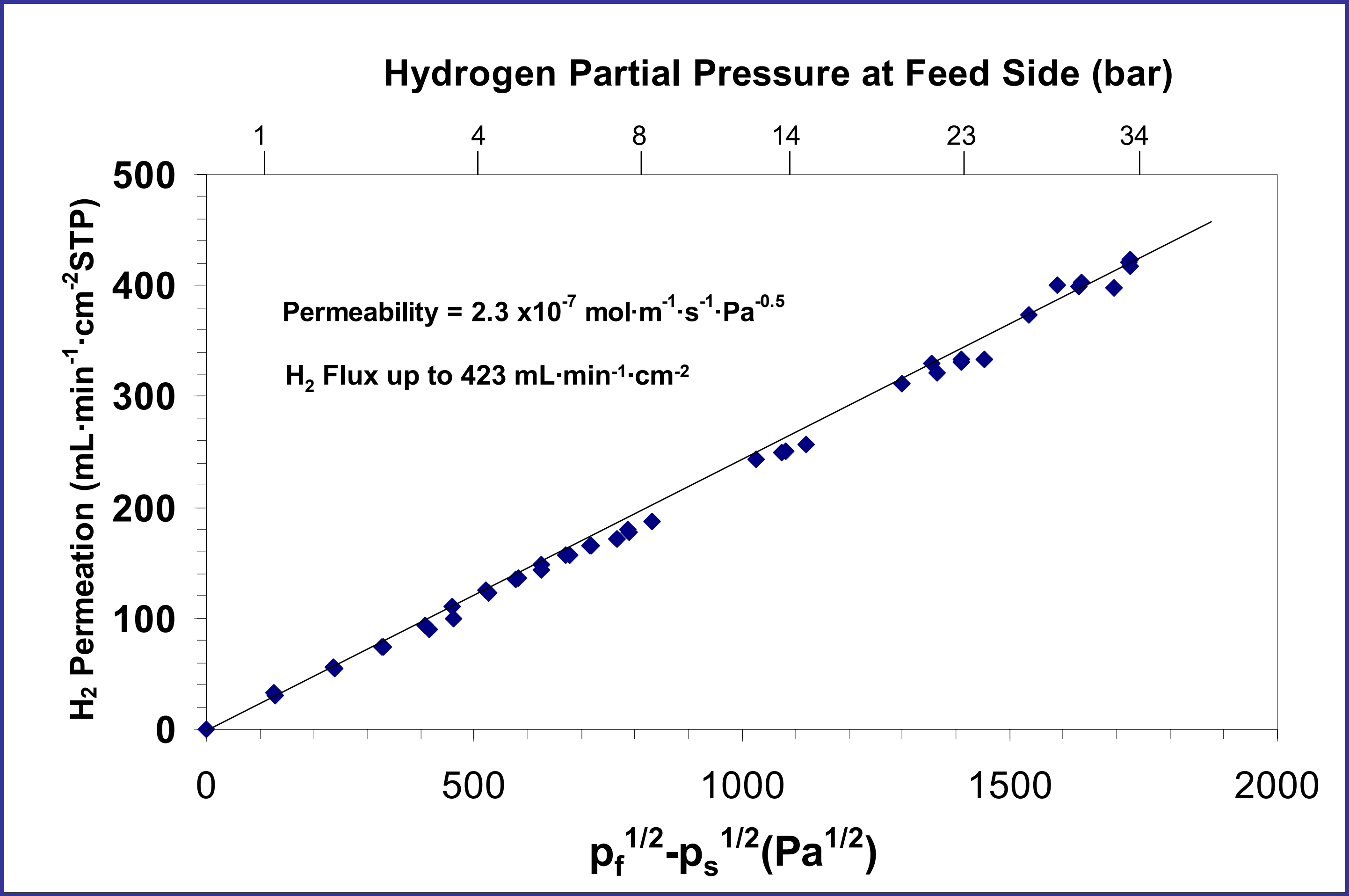
HYDROGEN FLUX AT HIGH PRESSURE DIFFERENTIAL



- Permeability of 2.3×10^{-7} mol m^{-1} s^{-1} $Pa^{-0.5}$ and hydrogen flux of 423 mL min^{-1} cm^{-2} (STP) achieved at 440^{o}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 H_2 Production Using Membrane Technologies

- **Natural gas reforming is ~63% of H_2 production cost.**

  (S. Lasher et al., Hydrogen Technical Analysis, *Proc. 2002 DOE Hydrogen Program Review*)

- **Reforming cost could be reduced by ~30% using Eltron O_2 separation membranes.**

- **H_2 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 H_2 separation membranes are ~200 times cheaper than analogous Pd membranes and permeate 10x faster.**

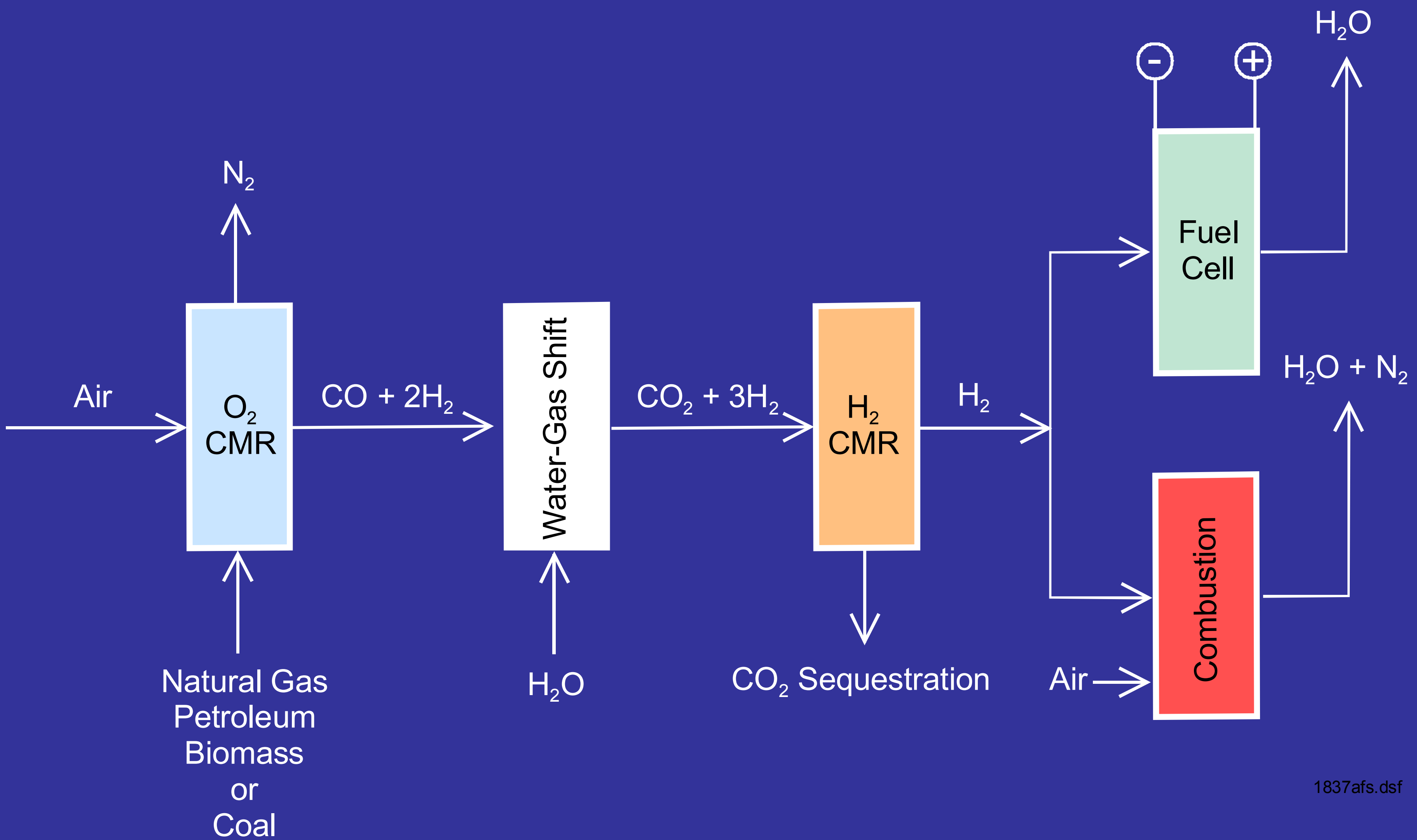
- **Estimated H_2 cost using combined oxygen and hydrogen transport membrane technologies is \$4/MMBtu or \$0.55/kg.**

  (Hydrogen Production Facilities: Plant Performance and Cost Comparison, Final Report for Contract No. DE-AM26-99FT40465, Parsons)

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



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