Ceramic Membranes of Mixed Ionic-Electronic Conductors for Hydrogen Separation

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Research Goals & Objectives

- Develop high temperature dense ceramic oxide membranes with mixed ionic-electronic conductors for hydrogen separation.
- Achieve appreciable hydrogen permeation flux using both disk-type (1-3 mm thick) & thin film-type (1-3 μ thick) strontium cerate oxide membranes doped with terbium.
- Enhance the limited hydrogen permeability data base & asses the viability of perovskite materials as hydrogen-permeable membranes.

Relevance to Current State-of-the-Art

- Clean product (100% pure hydrogen) & does not require external electrical power.
- Low-cost compared with Pd membranes.
- Simple & flexible compared to pressure swing adsorption (PSA).
- Reduce down stream processing & eliminate hydrogen loss in PSA, CO shift, & reformer.
- Membranes can be interfaced easily with various industrial unit operations.

Relevance to NASA

- On site hydrogen separation & production for NASA-KSC using inexpensive & light weight materials.
- Membranes materials can be used for Mars exploration, fuel cells, & other relevant space programs.

Budget, Schedule, & Deliverables

- **Budget: $190,000**

- **Schedule:**

  1st quarter: Development of hydrogen permeation set up.
  2nd quarter: Fabrication of disk & thin film geometry membranes.
  3rd quarter: membrane characterizations & development of gas-tight seal between membrane & processing unit.
  4th quarter: Generation of hydrogen flux data.

- **Deliverables:**

  1 – Hydrogen flux as a function of temperature, water vapor, & hydrogen partial pressure.
  2 – Preliminary results on effect of nickel deposition on enhancing hydrogen flux.
  3 – Spin coating of dense thin membrane films.
  4 – Development of porous substrates for thin film deposition.

Anticipated Technology End Use

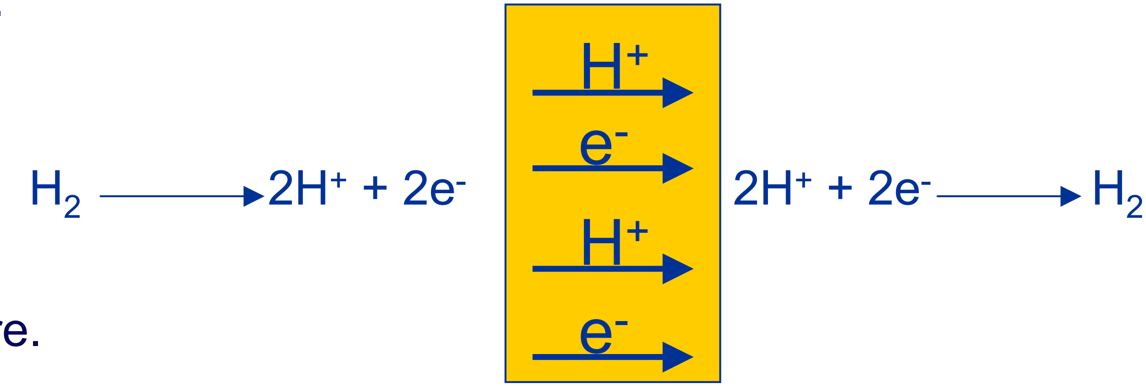
- Local hydrogen separation & production units for the NASA-KSC.
- Support the growth of the hydrogen economy.
- Ion transport membranes could enhance the widespread use of hydrogen.
- Ion transport membranes can eliminate the costly, conventional hydrogen-manufacturing facilities.
- Direct applications in Fuel cells, sensors, & Mars mission.
- Existing permeation set up can be used for oxygen separation.

Ion Transport in Perovskite Structures

Kinetics

- ❑ Gas-solid interfacial rxn.
- ❑ Ion migration through solid lattice.
- ❑ Solid-gas interfacial rxn.

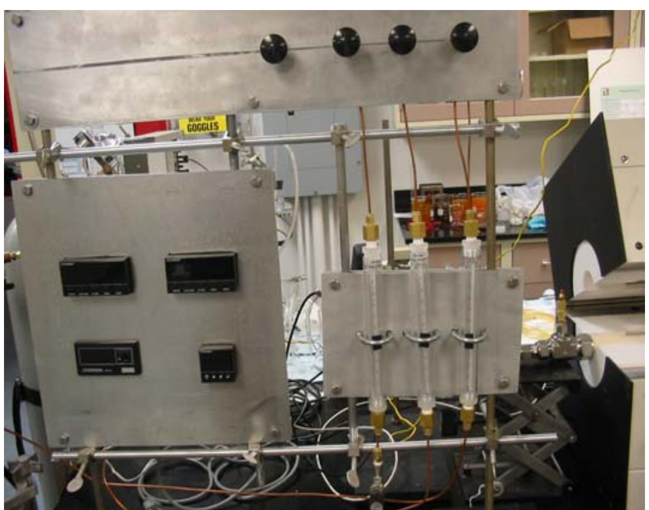
Hydrogen Flux

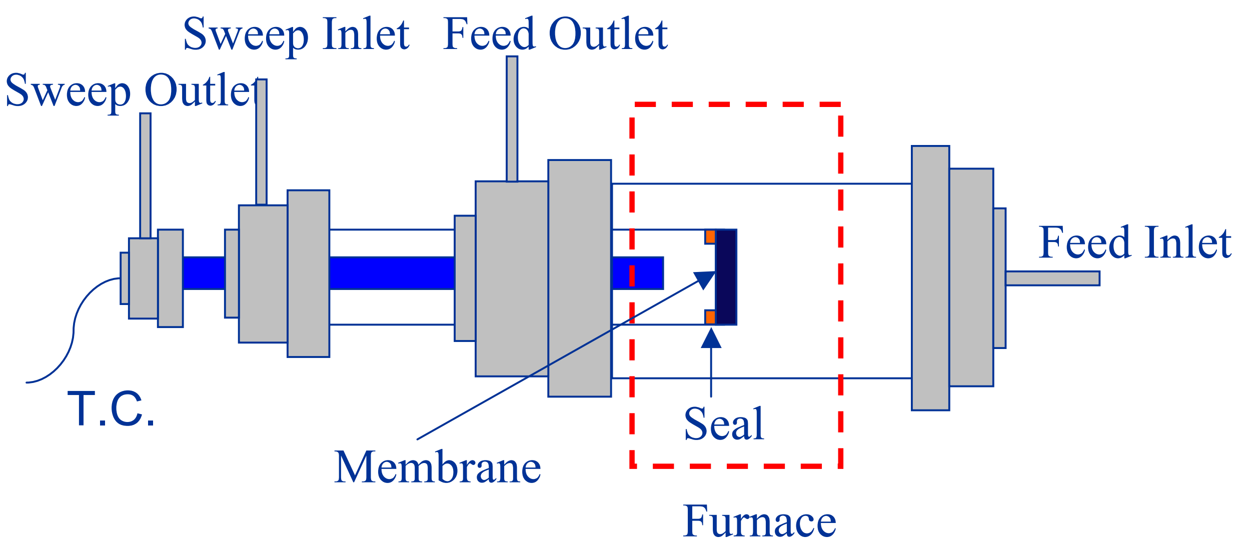


- ❑ Temperature.
- ❑ Hydrogen partial pressure.
- ❑ Water vapor.
- ❑ Membrane thickness & surface area.
- ❑ Doping type & percentage

Hydrogen Permeation Set Up

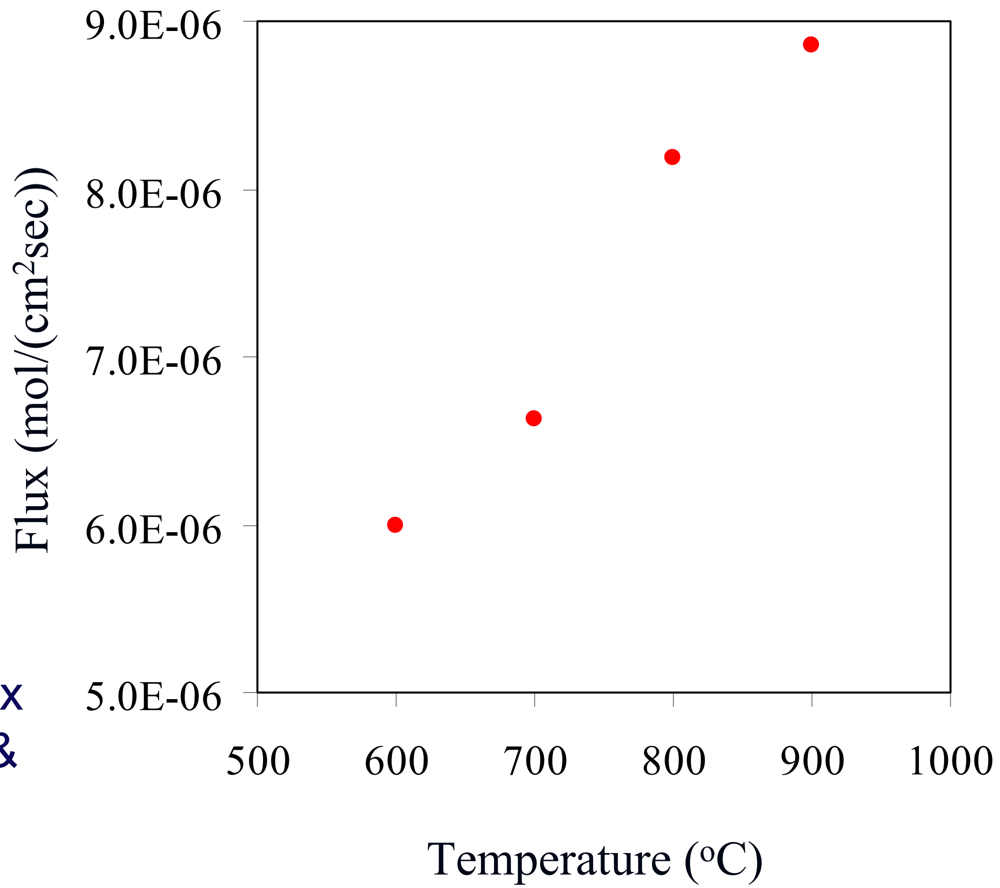
- Up to 1200^{o}C & atmospheric pressure.
- Disk-type & thin film-type membranes.
- Membrane surface area scale up to 1.5 in^{2}.
- Hydrogen & oxygen flux data.





Results: Temperature Dependence of Hydrogen Permeation Flux of $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$

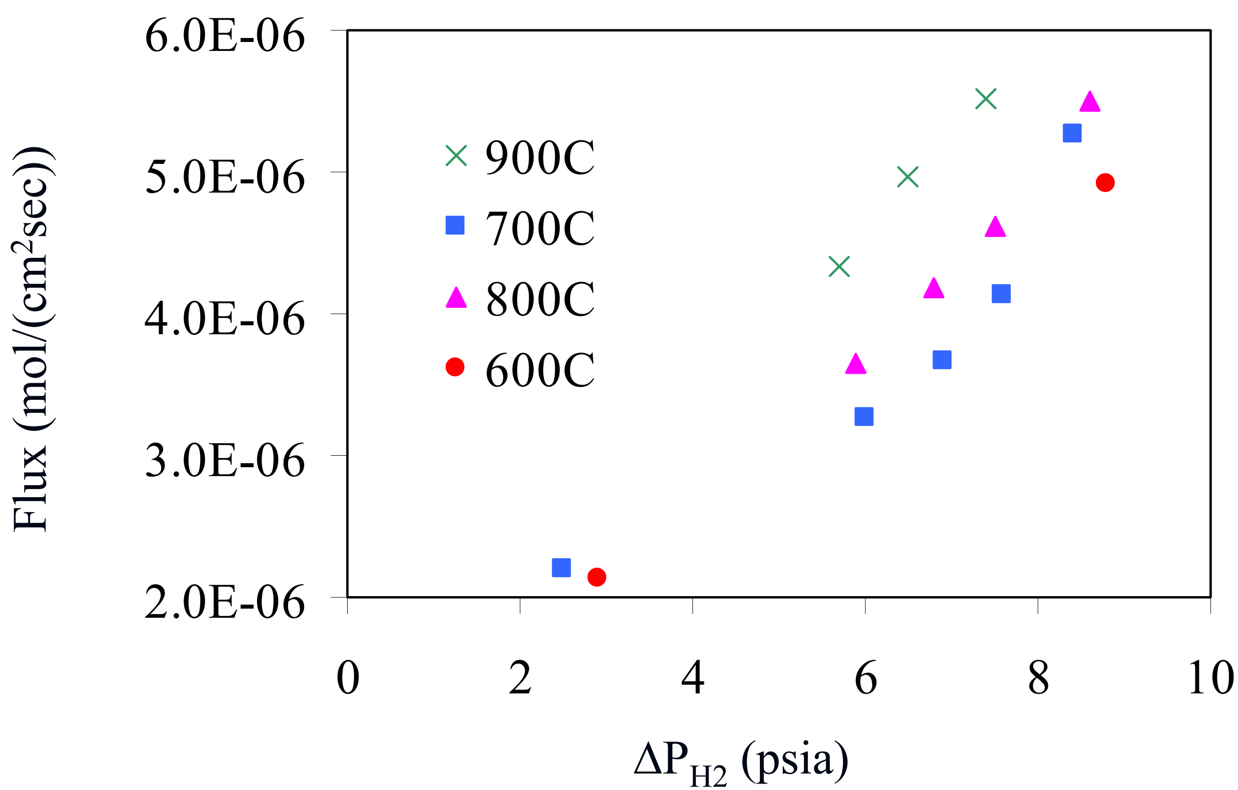
- Hydrogen flux increases linearly with temperature.
- Operating temperature above 600°C.
- Sealing limits upper temperature to 900°C.



Synthesis of Polymeric Precursor

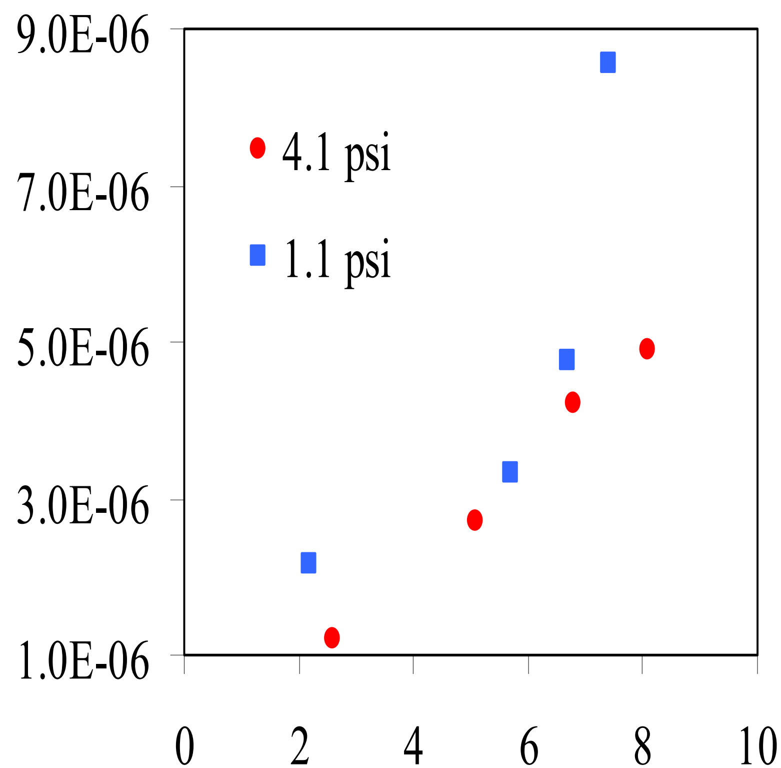
- Metal nitrates dissolved in citric acid based solution.
- Polymerization process forms complex chelating mixture between citric acid & metal cations.
- Sequence of heating & drying steps.

Results – Influence of ΔPH_2 at Different Temperatures Under Dry Conditions on Hydrogen Flux of $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$



Results – Influence of Water Vapor Pressure & Ni Deposition on Hydrogen Flux of $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$

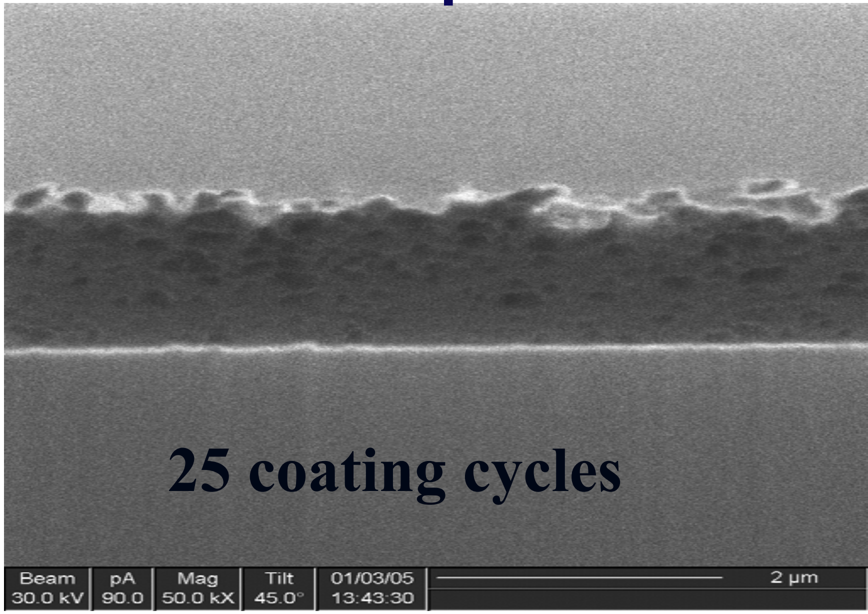
- Hydrogen permeability decreases with increasing water vapor pressure due to increase in P_{O2}.
- Ni enhances hydrogen permeability by enhancing catalytic activity at solid-gas interface..

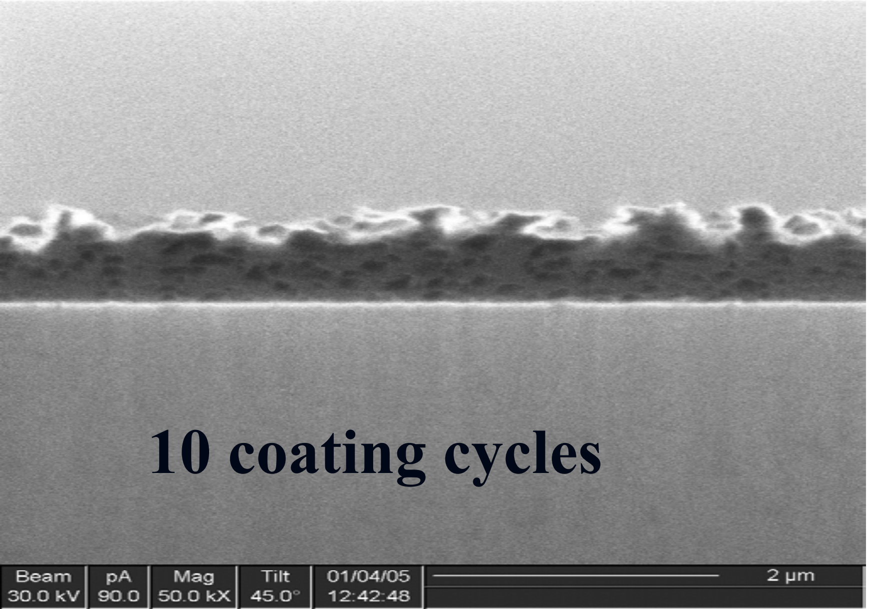


membrane	H_2 flux mol/(cm^{2}sec)	thickness mm
$SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ + Ni	1.12×10^{-5}	2.3
$SrCe_{0.95}Tb_{0.05}O_{3-\delta}$	8.18×10^{-6}	1.5

Results – SEM Surface Morphology of Dense $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ Thin film Spin-coated at 3000 rpm for 20 s

- Ethylene glycol-based polymeric precursor.
- Non-porous silicon-based substrate.
- Precursor spin-coated on substrate & converted to dense polycrystalline metal oxide films.





- Low sintering temperature (400°C).
- 0.2-2 µm film thickness can be produced by controlling the number of spin-coating cycles.

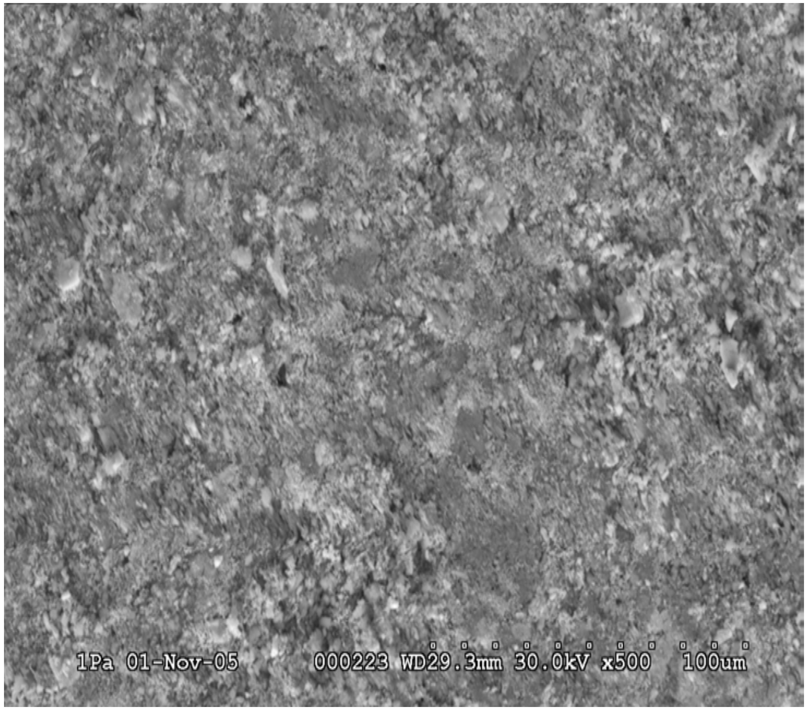
Results – SEM Surface Morphology of 2mm Thick Porous Substrate Suitable for Spin Coating Thin Membrane Film $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ + 10 wt% Carbon Black

Synthesis of Porous Substrate

- Ultrasonically mixing $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ with carbon black.
- Porosity created as carbon black is combusted at 600^{o}C & 2 ^{o}C.min^{-1} for 2 h.

Parameters to be Optimized

- Carbon black content.
- Sintering temperature.
- Heat treatment time.



Future Plans

- Continue generate hydrogen permeability data for disk-type & thin film-type membranes.
- Optimize parameters influencing porous substrates.
- Develop hydrogen reactors for hydrogen permeability using tube-geometry membranes.
- Finish up the impedance spectroscopy set up for conductivity measurements.
- Generate hydrogen permeability data with Ni impregnation technique.
- Support FSEC-DOE project on H_2 purification & production by thermochemical water-splitting cycles (FSEC, U. Turabo, SAI).

Proposals & Publications

Proposals:

"Development of Mixed Ionic-Electronic Conducting Thin Membrane Films (1-5 μ thick) for Hydrogen Separation", NSF-SGER - Pending

Publications:

- M. Elbaccouch, S. Shukla, N. Mohajeri, S. Seal, and A. T-Raissi, "Microstructural Analysis of Doped-Strontium Cerate Thin Film Membranes Fabricated via Polymer Precursor Technique," *Langmuir, Submitted.*
- M. Elbaccouch, S. Shukla, S. Seal, and A. T-Raissi Ali, "Hydrogen Permeability Data of Ceramic Oxide Membranes," The 30th International Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, USA, January 22-27, 2006.
- S. Shukla, M. Elbaccouch, S. Seal, and A. T-Raissi, "Polymer Precursor Route to Perovskite-Type Tb-Substituted $SrCeO_3$ Thin Membrane Films and Effects of Microstructural Evolution," The 30th International Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, USA, January 22-27, 2006.

Acknowledgments

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Thank you