A Novel Membrane Reactor for Hydrogen Production from Coal

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Gas Technology Institute

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2005 DOE Hydrogen Program Review

Project ID PDP24

Overview

Timeline

- Start: 9/9/2003
- End: 9/8/2005
- Percent complete: 80%

Budget

- Total project funding: $602,816
  - DOE share: $482,247
  - ICCI share: $100,569
  - AEP share: $20,000
- Funding received in FY04: $352,700
- Funding for FY05: $250,116

Overview (con't)

Barriers

>High cost of coal to hydrogen

>Mature technologies employed for coal to hydrogen process – difficult to improve and reduce cost

Targets

>Reduce cost of hydrogen by 25% compared to current coal-based plants by 2015

(DOE Fossil Energy Hydrogen Program Plan, 6/2003)

Partners

>Dr. Jerry Lin of Arizona State University

>Dr. Eric Wachsman of University of Florida

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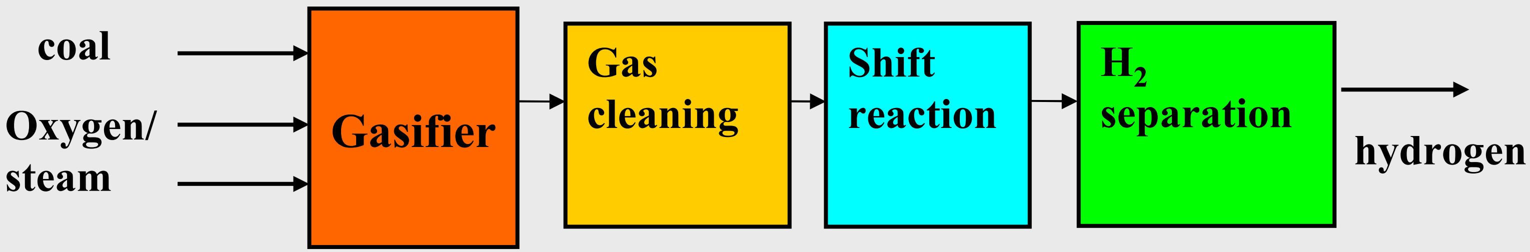
Project Objectives

> Determine the technical and economic feasibility of a membrane reactor coupled with a coal gasifier for clean, efficient, and low cost production of hydrogen from coal.
> Screen and test candidate membranes under high temperature and high pressure conditions of coal gasification

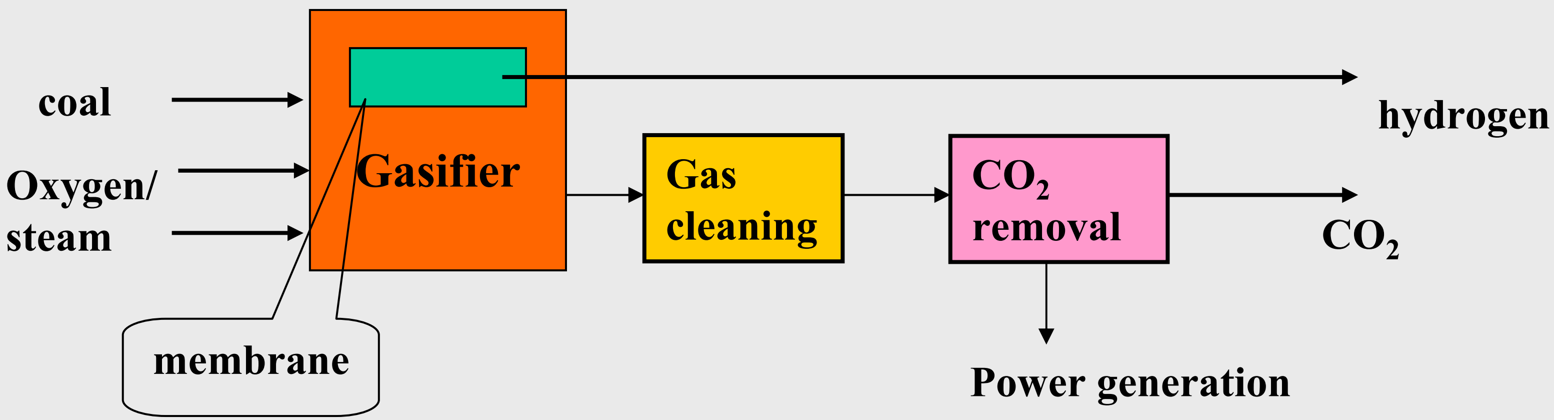
Technical Concept

Hydrogen from Coal via Gasification

Conventional gasifier



Membrane gasification reactor



Combine hydrogen separation, reforming, shift and gasification reactions in a close coupled way or within one reactor

Potential Benefits of Membrane Reactor for Hydrogen Production from Coal/Biomass

- **High H_2 production efficiency:**
  - Thermodynamic analysis and recent modeling work indicate over 40% improvement in H_2 production efficiency over the current gasification technologies
- **Low cost:**
  - reduce/eliminate downstream processing steps
- **Clean product:**
  - no further conditioning needed, pure hydrogen
- **CO_2 sequestration ready**:
  - simplify CO_2 capture process
- **Power co-generation**:
  - utilization of non-permeable syngas

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Approach

> Membrane Materials Screening and Testing
  – Design and construction of a membrane permeation apparatus
  – Testing candidate membranes at high temperatures and high pressures

> Conceptual Design of Membrane Reactor
  – Modeling
  – Membrane gasifier configuration

> Process Evaluation and Flow Sheet Development

> Economic Evaluation for Overall H_2 Production Process

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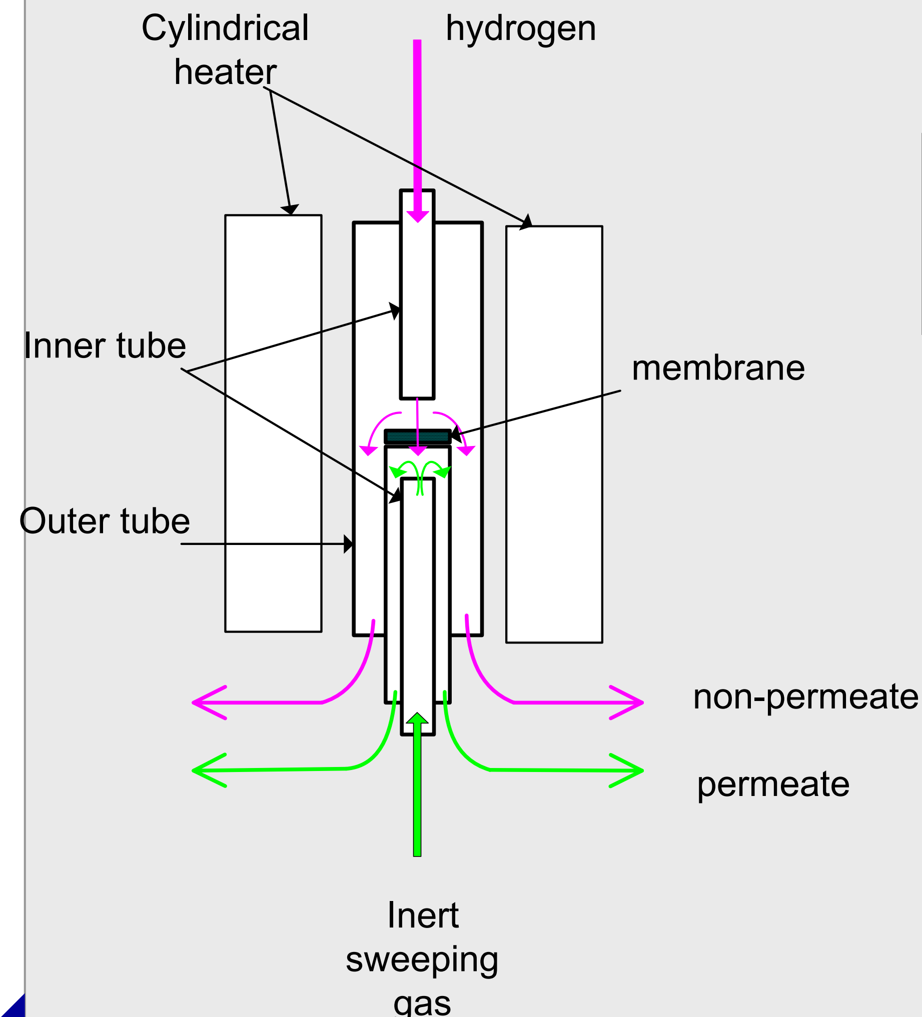
Accomplishments

- Constructed and commissioned a high temperature/high pressure (1100°C/1000 psi) membrane permeation unit.
- Developed fabrication techniques for making supported and unsupported ceramic membranes.
- Demonstrated high hydrogen flux for proton-conducting perovskite membranes in the high pressure membrane permeation unit.
- Developed membrane gasification reactor model and confirmed the improved hydrogen production efficiency (30-50%).
- Began evaluation of chemical stability issues for the perovskite materials.

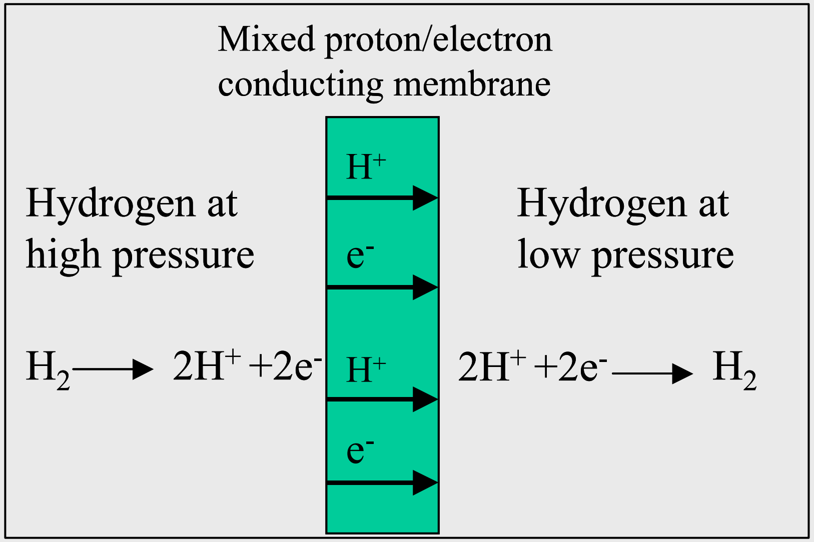
GTI High Temperature/High Pressure Permeation Unit



- Membrane diameter:1.25”
- Max Temp: 1100^{o}C
- Max Pressure:1000 psi

Perovskite Identified as Leading Candidate Membrane Material

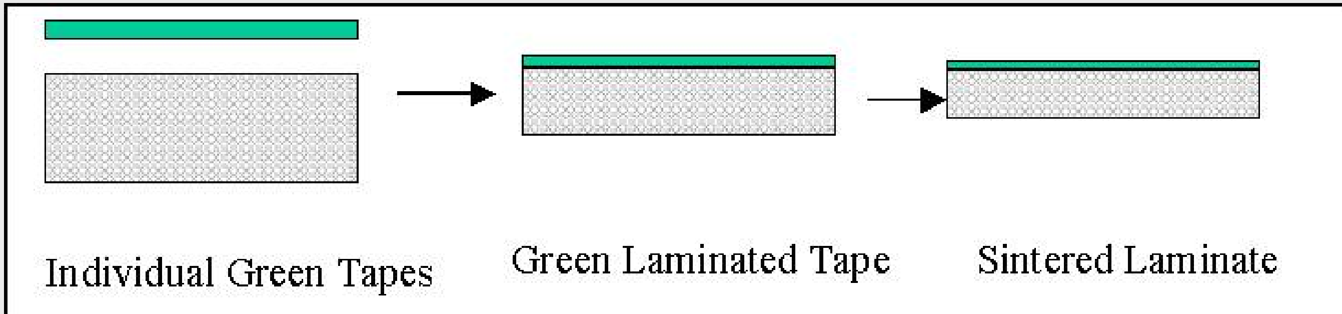
- Perovskite membranes evaluated:
  - $BaCe_{0.9}Nd_{0.1}O_{3-\alpha}$ (BCN) (supported or unsupported)
  - $BaCe_{0.8}Y_{0.2}O_{3-\alpha}$ (BCY)
  - $SrCe_{1-x}Eu_{x}O_{3-\alpha}$ (SCE)
  - $SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$ (SCTm)

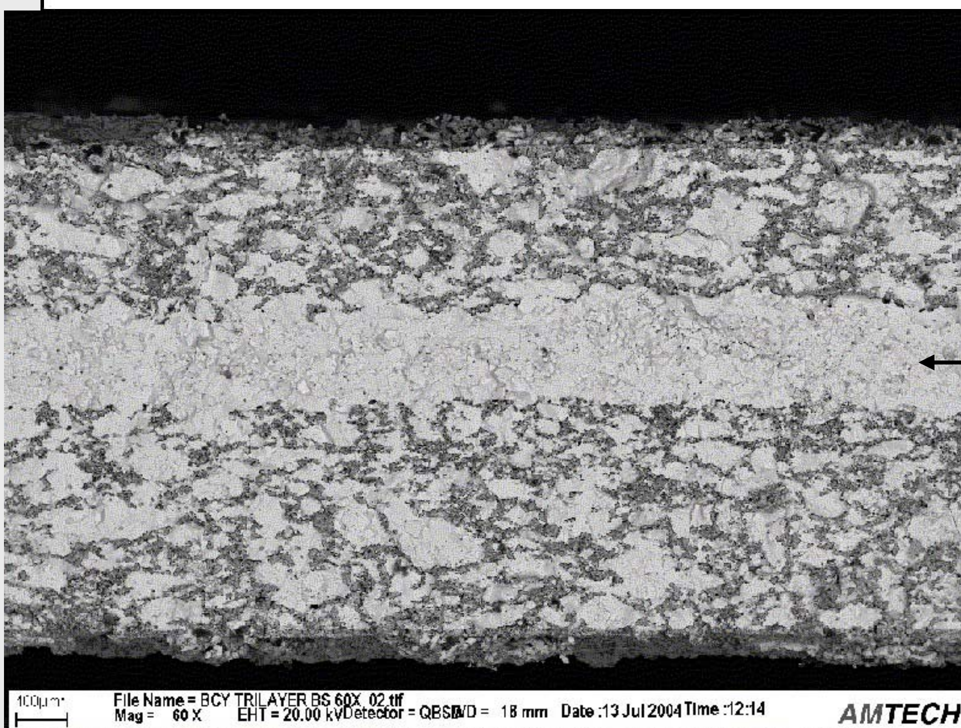


Membrane Fabrication

- Die pressing or tape casting for self supporting membranes
- Tape casting and lamination for supported thinner membranes

Developed Supported Ultra-Thin Membrane

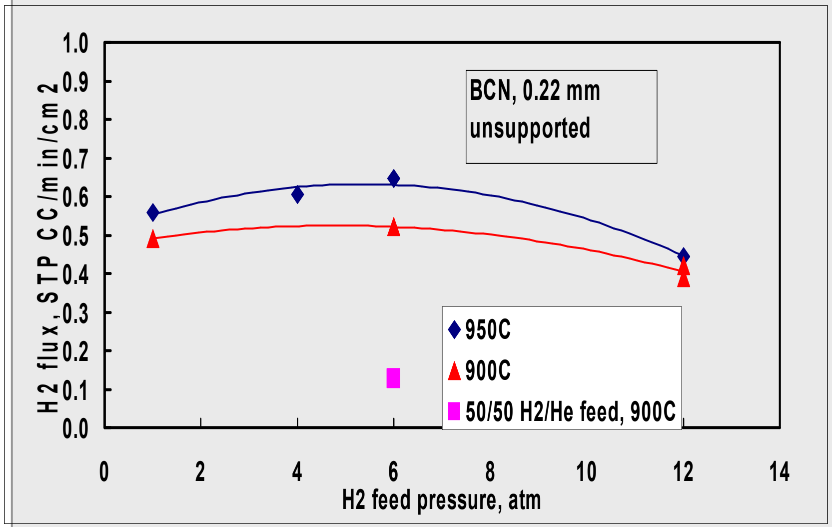


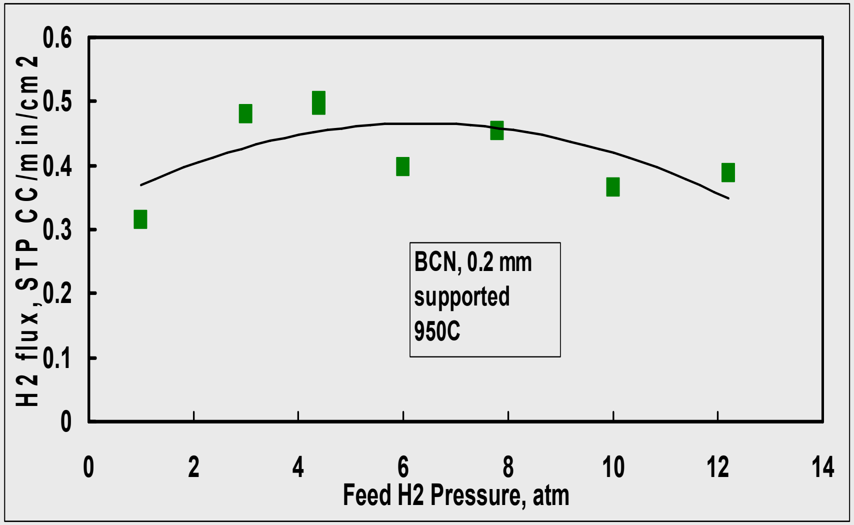


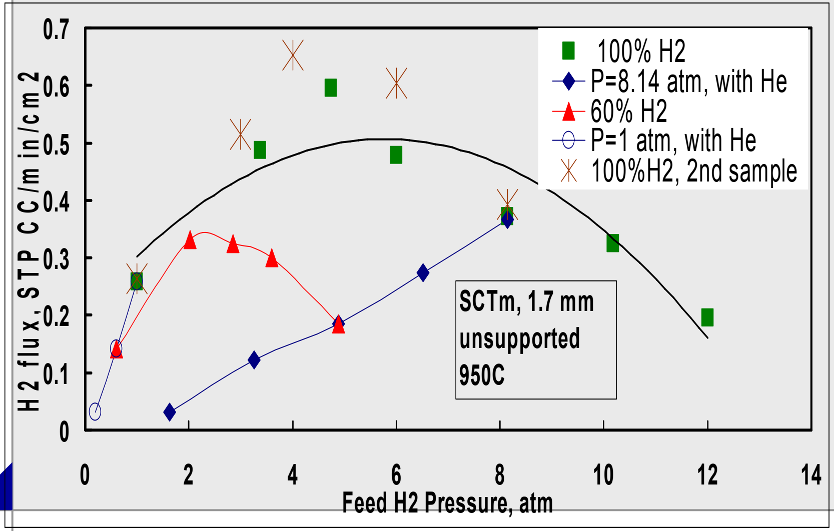
Membranes prepared by uniaxially pressing of disk

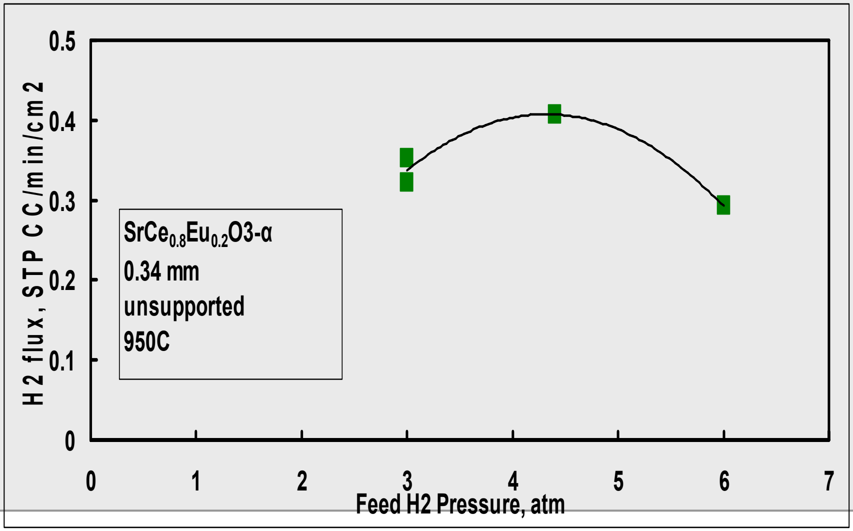
200 micron dense layer

Hydrogen Flux Measured from High Pressure Permeation Unit

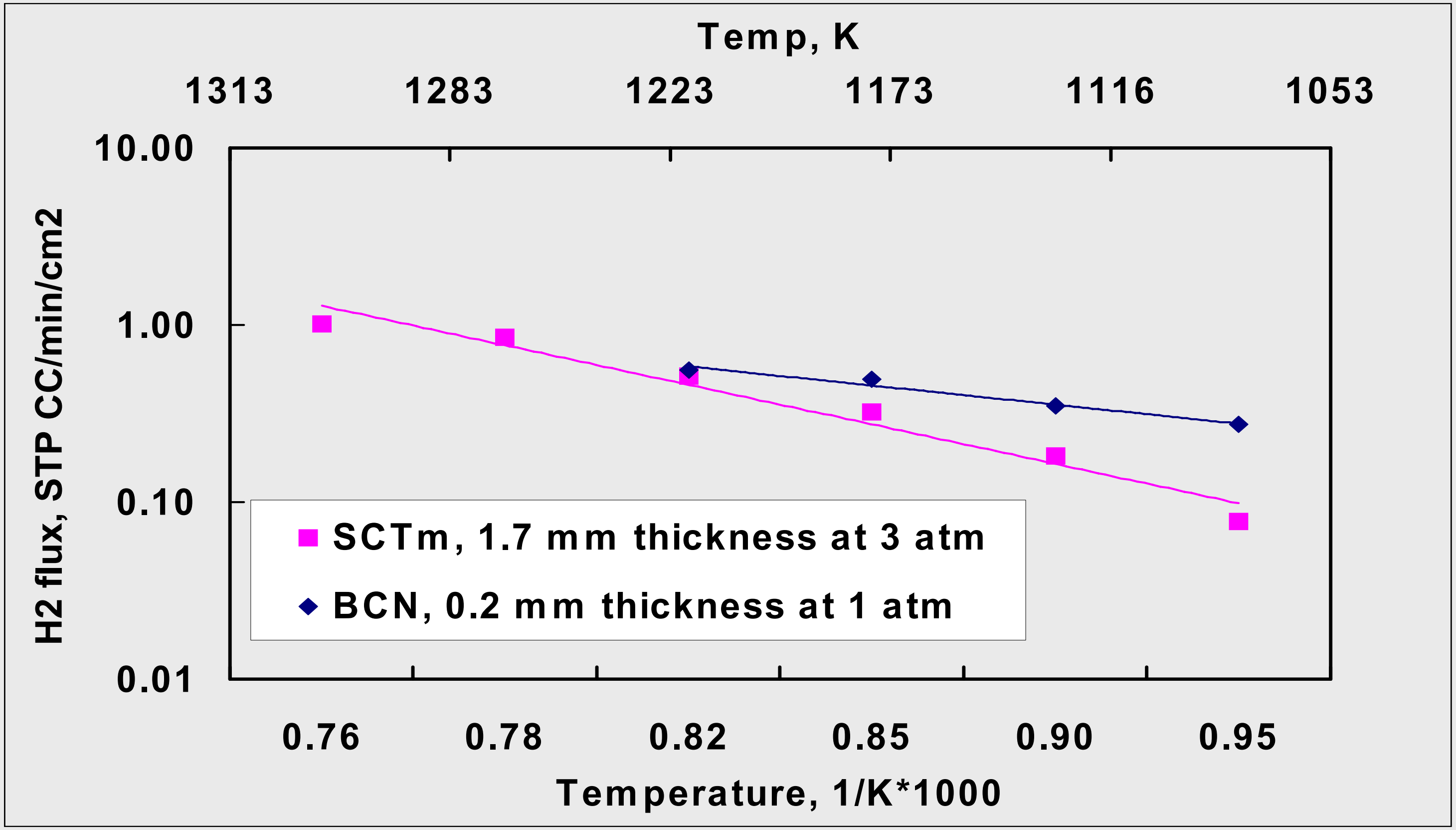








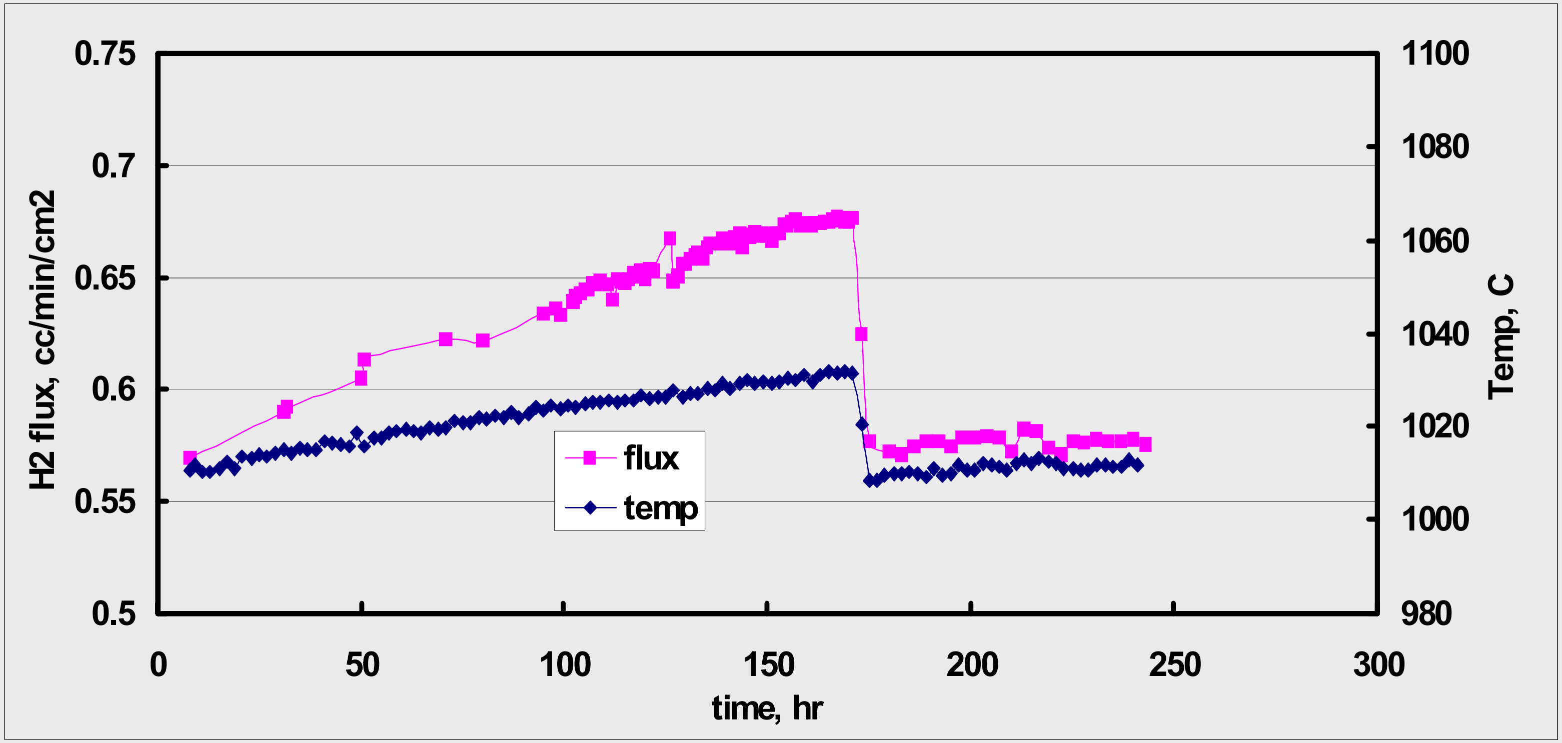
Temperature Dependency of Proton-Conducting Membranes



Activation energy 27 Kcal/mole for SCTm

12 Kcal/mole for BCN

Proton-Conducting Membrane Shows Good Long Term Stability Under Reducing Environment



SCTm membrane with pure hydrogen at feed and nitrogen as sweep gas at 1 atm

- Temperature drifted during the testing and was lowered to the original value at 170th hour.

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Key Conclusions from Membrane Permeation Testing

> Several barium/strontium cerate-based perovskite membranes show reasonable hydrogen flux at gasification temperatures

> Hydrogen flux increases with pressure (to about 4 bar) and temperature

> The perovskite membrane can operate more than 200 hours under a pure hydrogen feed condition at 1000C

> Proton conducting perovskite membranes are good candidate materials for gasification membrane reactor applications

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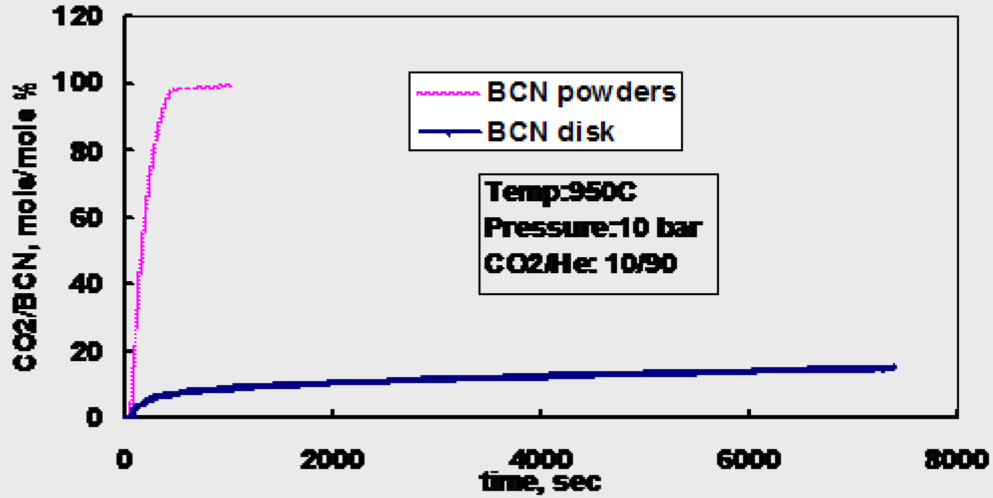
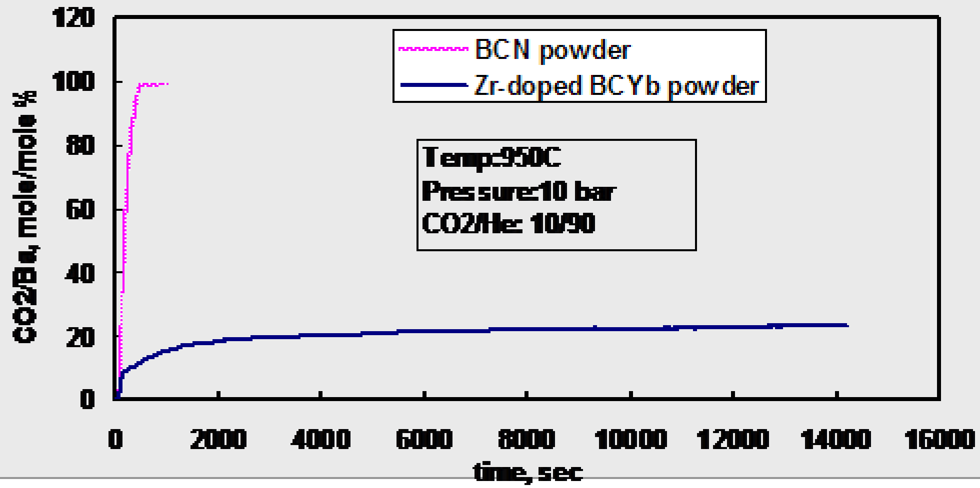
Evaluation of Chemical Stability for Perovskite Materials

- TGA (Thermo Gravimetric Analysis) Study

Dense membrane of BCN shows stronger resistance to CO_2 than powder form



Zr-doped barium-cerate perovskite shows stronger resistance to CO_2



Evaluation of Chemical Stability for Perovskite Materials

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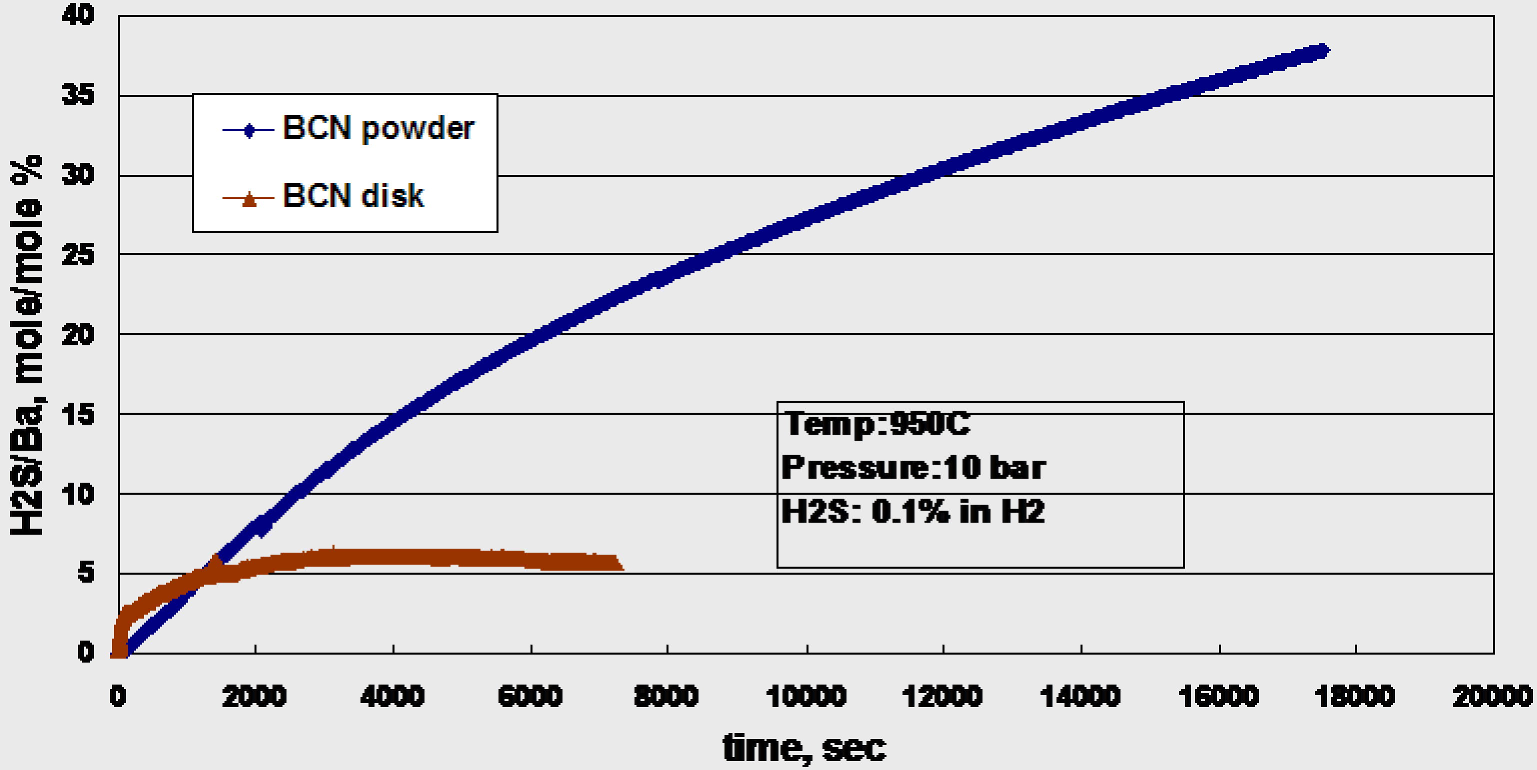

Dense membrane of BCN shows stronger resistance to H_2S than powder form

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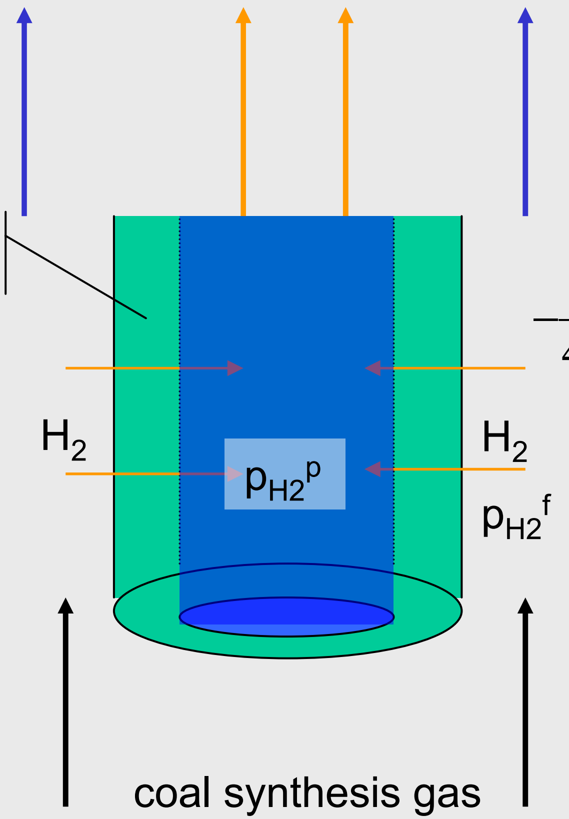
Membrane Gasification Reactor Modeling

- Matching reaction kinetics and hydrogen permeation rate



gas phase reaction

$H_2O+CO = CO_2+H_2$

$CH_4+H_2O = CO+3H_2$

$(CH_4+CO_2 = 2CO+2H_2)$

Reaction rates estimated from chemical kinetics:

14 species, 32 reaction steps

Karim & Metwally (1974)

$$J_{H_2} = -\frac{RT}{4F^2L}\frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+}+\sigma_{el}}\left(\ln(p^f_{H_2})-\ln(p^p_{H_2})\right)$$

F: Faraday constant

L: membrane thickness

σ_{H^+}: proton conductivity

σ_{el} : electronic conductivity

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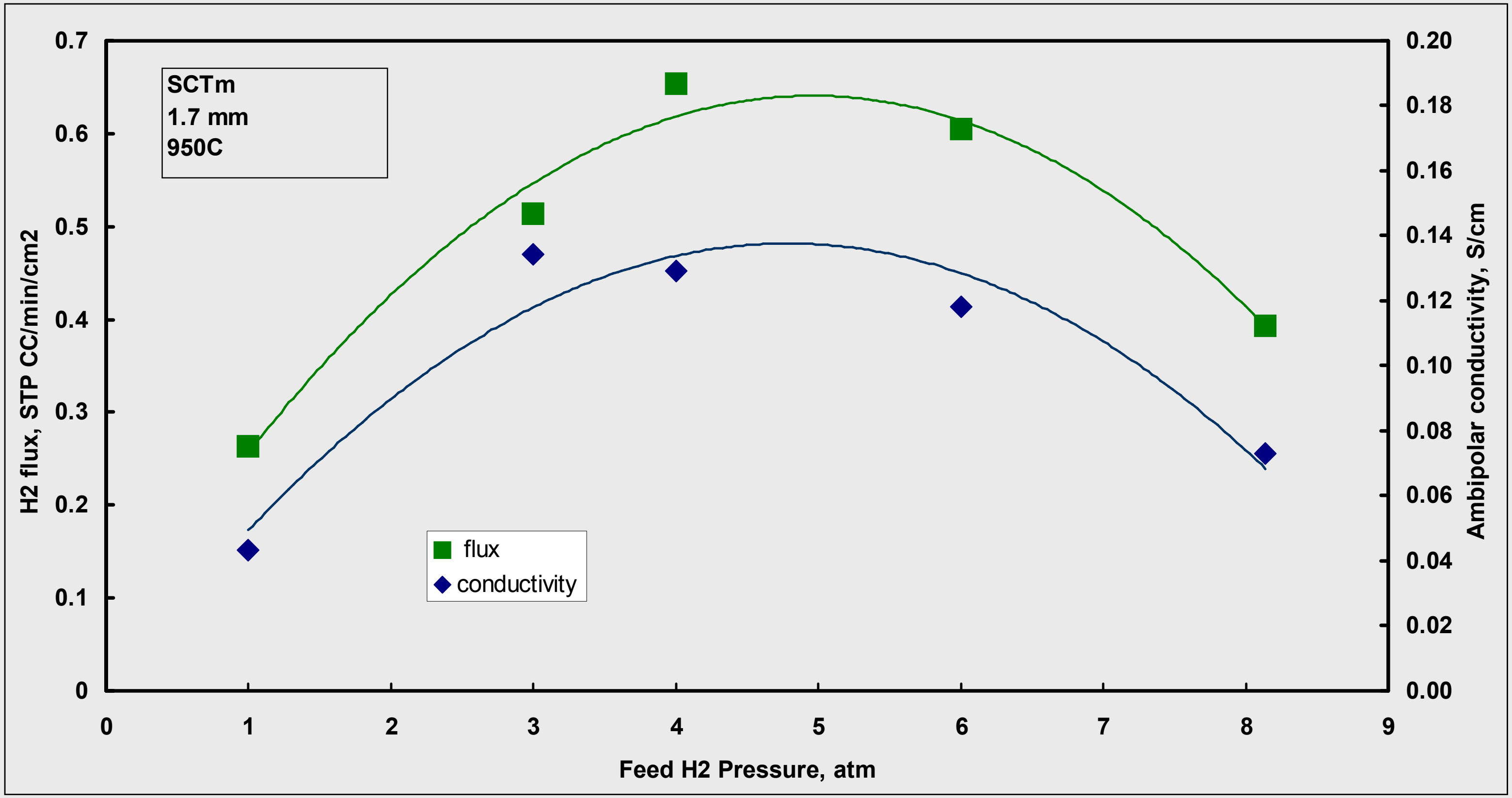
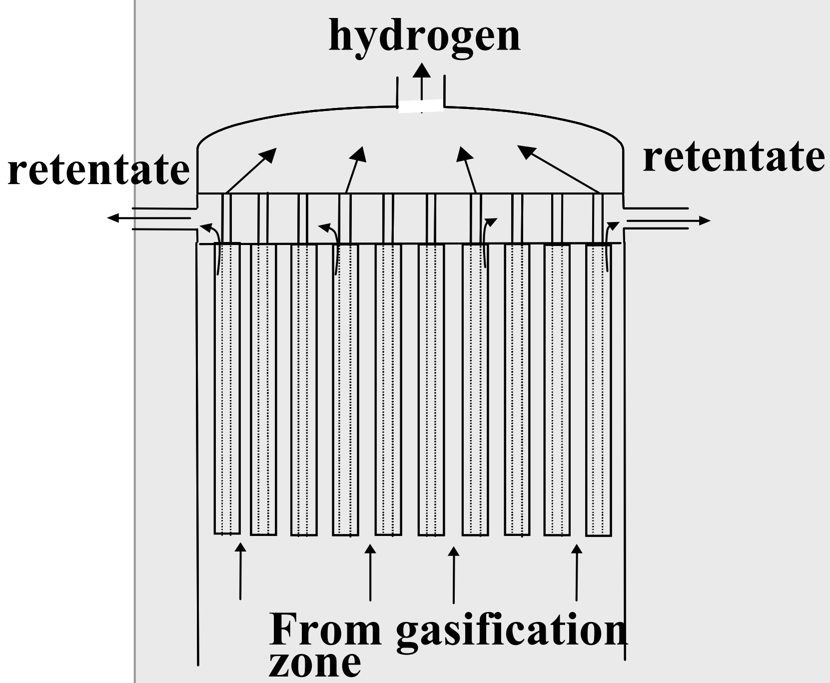
Ambipolar Conductivity Calculated From Measured Hydrogen Flux

$$\frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+}+\sigma_{el}} = -J_{H_2} / (\frac{RT}{4F^2L}\left(\ln(p^f_{H_2}) - \ln(p^p_{H_2})\right))$$



Membrane Gasifier Dimensions

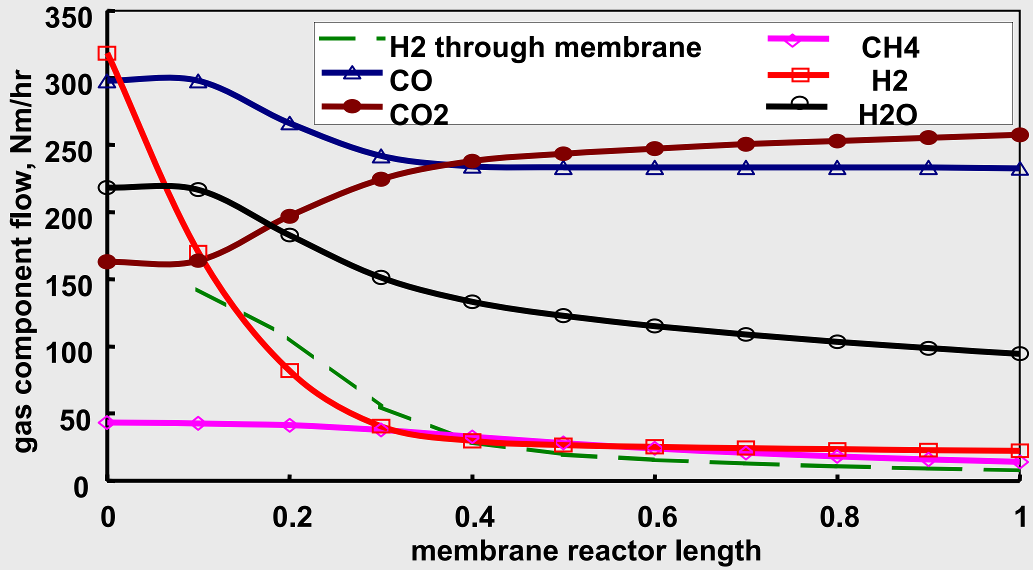
- a conceptual design example



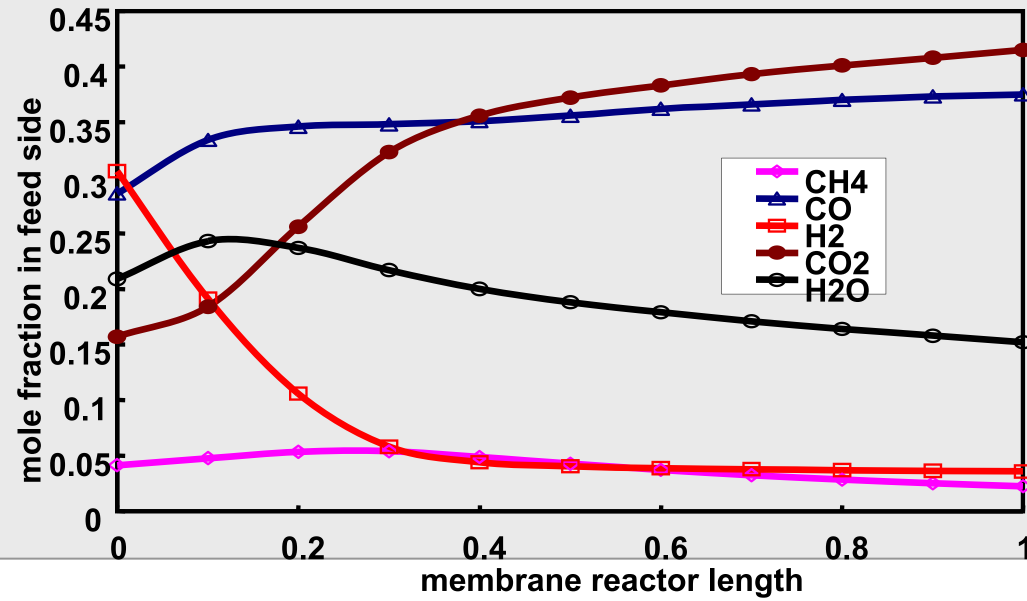
coal feed, TPD	1000
oxygen feed, TPD	600
steam feed to gasifer, TPD	595
steam feed to shift reactor,TPD	270
coal syngas flow rates, Nm/hr	97125
temperature, C	1100
pressure, atm	60
gasifier diameter, cm	330
membrane tube diameter, cm	1.250
membrane thickness, cm	0.0025
membrane tube length, cm	900
number of membrane tubes	21300
membrae area, m2	7550
ambipolar conductivity, S/cm	0.05
gas residence time of mem., sec	8

Modeling of Membrane Gasification Reactor

Gas component flow rates in the feed side of the membrane gasification reactor and hydrogen flow through the membrane



Gas compositions profiles in the feed side of the membrane gasification reactor



Feed: 30 atm,
permeate: 1 atm,
T:1000C

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Key Conclusions from Membrane Reactor Modeling

> Membrane gasification reactor can improve hydrogen production over the conventional coal gasification process by 30 ~ 50% for the same amount of coal feed.

> Membrane reactor performance determined by
  – Kinetics of reforming reaction
  – Equilibrium of shift reaction (high temperature)
  – Membrane hydrogen permeability

> Catalysts needed for reforming reaction

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Future Plans

Milestones for remainder of FY 2005

- Complete flowsheet simulation for hydrogen production based on membrane gasifier processes. Identify one concept for addressing chemical stability issues of perovskite membrane. (6/30/05)
- Complete technical and economical assessment of the membrane gasifier technology (9/30/05)

Future Work

- Continue improving hydrogen flux
  - Reduce thickness, 5- 15 micron
  - Dual-phase membranes
- Permeation testing with simulated syngas
- Membrane scale-up
- Bench scale testing

Publications and Presentations

- Shain J. Doong, Estela Ong, Francis Lau, Arun C. Bose, and Ron Carty, "**Direct Extraction of Hydrogen from Coal Using a Membrane Reactor Within a Gasifier"** paper presented at 21'st International Pittsburgh Coal Conference, Osaka, Japan, September 2004
- Shain J. Doong, Francis Lau, Mike Roberts, and Estela Ong, "**GTI's Solid Fuel Gasification to Hydrogen Program"** paper presented at the 3rd Natural Gas Technology Conference, Orlando, FL, February, 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen leakage
- Operation of high temperature and high pressure permeation unit

Hydrogen Safety

Our approach to deal with this hazard is:

> Hazard assessment
>
> – what-if/checklists, hazard and operability studies (HAZOP), failure mode and effects analyses (FMEA), fault tree analyses, and others.
>
> Risk management plan
>
> – identify approaches and actions required to mitigate and minimize exposure to identified risks
>
> Communication plan
>
> – failure reporting and corrective actions, periodic revision of all safety plans, training, emergency response plan development, and safety-related reporting to the sponsor

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