Development Activities at the Oak Ridge National Laboratory in Support of a Hydrogen Economy

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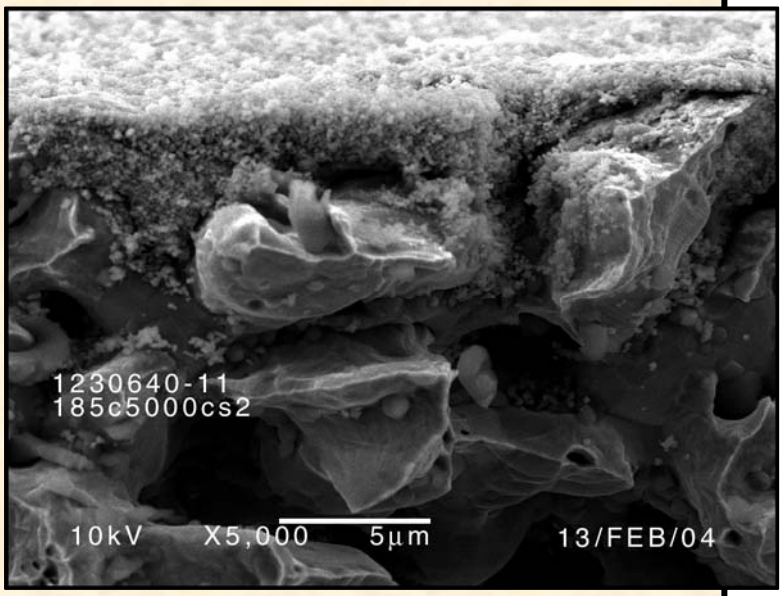
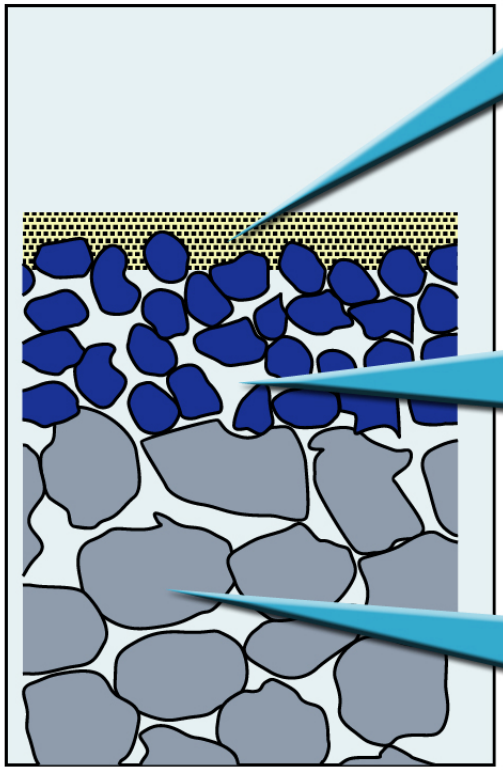
ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

- Pore diameters of 0.5 nm – 20,000 nm; for H_2, pore diameters of <1 nm are preferred
- Tubular support structure and layer made of variety of metals and ceramics
- Excellent mechanical, thermal, and chemical stability
- Membrane layer(s) applied to inside of support tube
- Membrane layer thickness of 2 μm or less yields high gas flows at low pressure drop; small pores result in high selectivity
- Proven scalability

A Thin Separation Layer Allows High Flow of Gases Through Small Pore Membranes





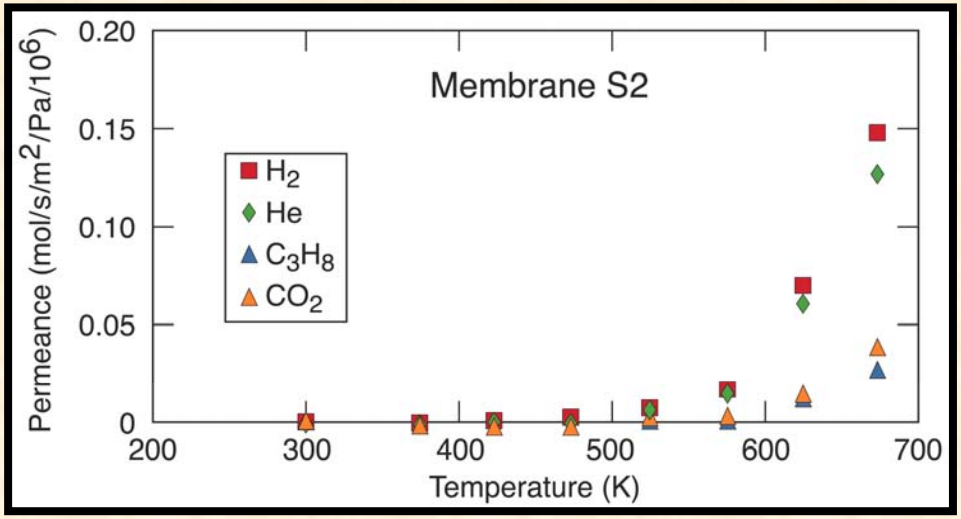
Critical Membrane Layer
Pore Size: 0.4-5 nm
Thickness: 0.01-0.5 µm

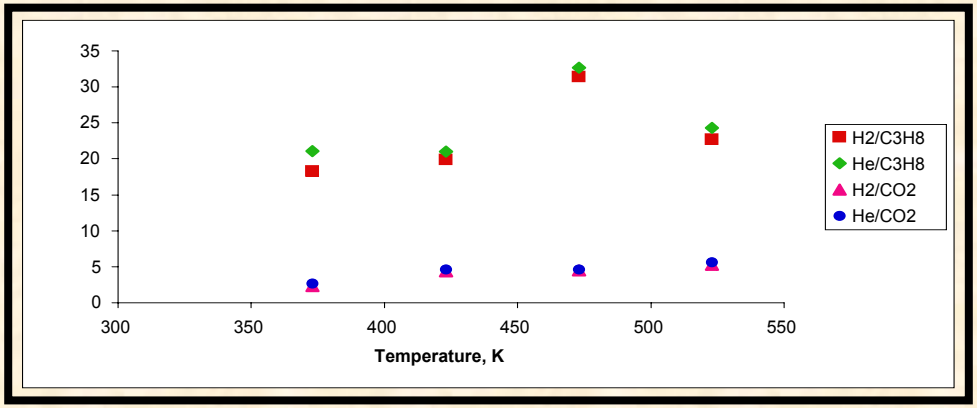
Primary Layer
Pore Size: 0.005-0.5 µm
Thickness: 1-20 µm

Porous Support
Pore Size: 0.5-50 µm
Thickness: >400 µm

High Operating Temperatures Result in Both Higher Permeances and Higher Separation Factors

- As the temperature is increased, the permeance of hydrogen and helium increase faster than CO_2 and propane.
- This phenomenon results in larger separation factors as temperatures are increased.

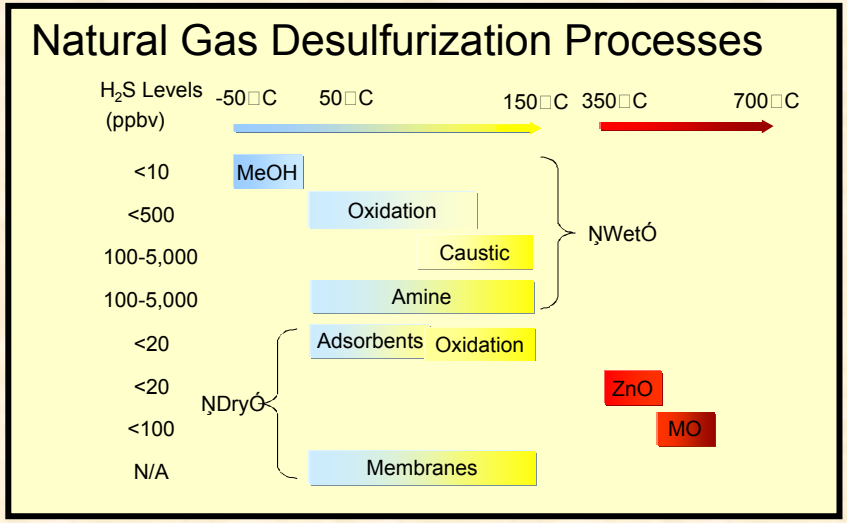




Desulfurization of H_2 Feedstocks

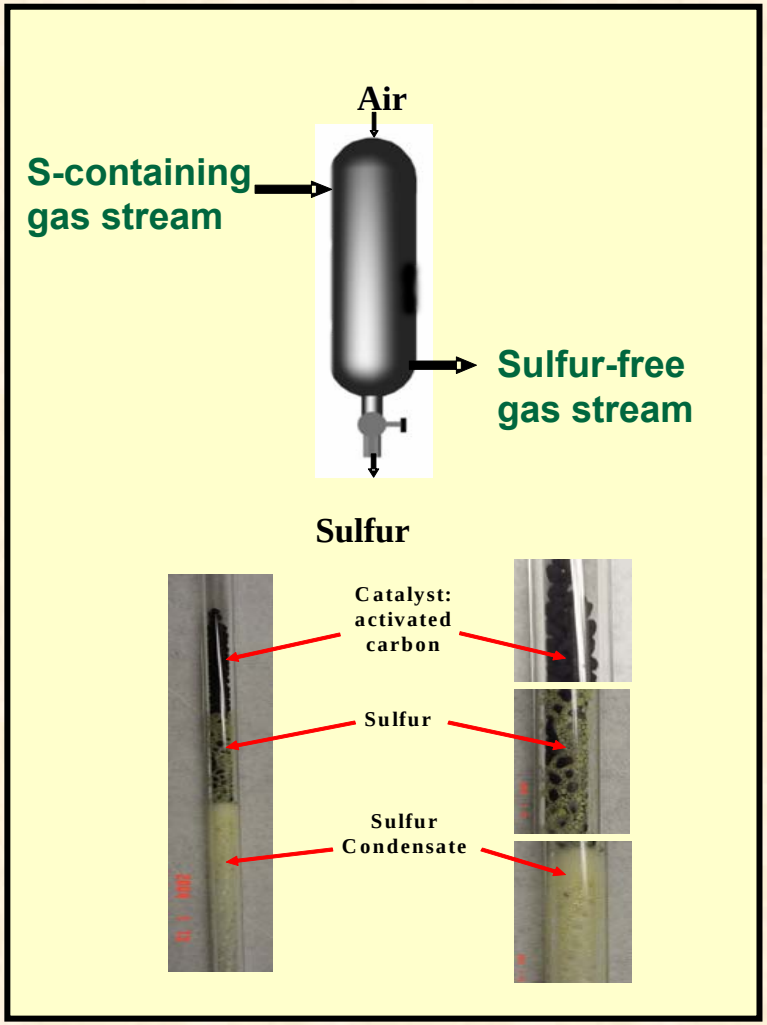
Challenge: All fossil fuels have persistent S contamination. Production of H_2 in the next several decades will be derived from fossil fuels (NG, coal, petroleum). Desulfurized H_2 is a necessity to facilitate fossil fuel reforming, H_2 storage, & fuel cell use.

Objective: Develop an emissionless process to reduce S levels to ppb range.

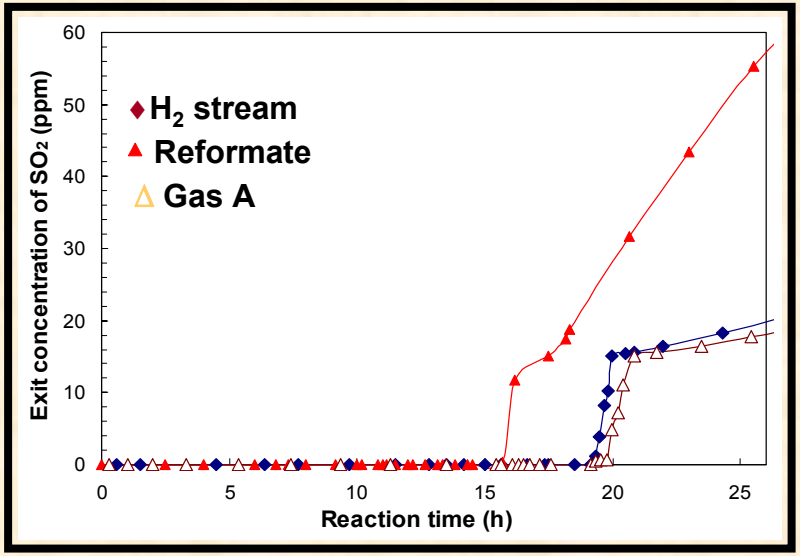


- Adsorption processes remove organic sulfides and require high pressure H_2 to regenerate
- High temperature MO catalysts have very short lifetimes and show rapid decrease in activity
- High-temperature processes, while needed generate SO_2

ORNL Catalyst Works Well Under Severe Conditions 1000 ppm H_2S



$$H_2S + 1/2O_2 \rightarrow S + H_2O$$



New Materials for Hydrogen Pipelines

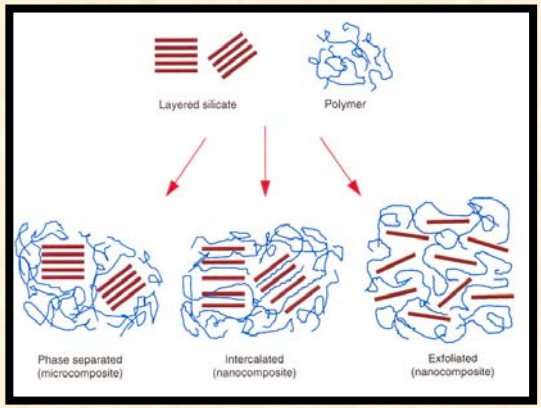
- **Fiber-reinforced polymer (FRP) pipeline for H2 Delivery**
  - Identify performance targets for H_2 pipelines as they relate to FRP technology.
  - Identity potential manufacturing options and joining/repair techniques.
  - Determine what is required to make the technology economically feasible?

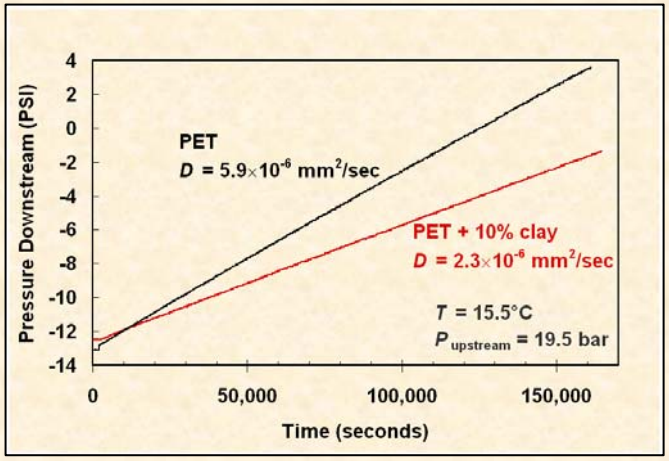
Picture provided courtesy of FiberSpar.

Picture provided courtesy of Ameron International.

Nanostructured Plastic With Reduced H_2 Permeance

- Synthesize nanocomposites in polyethylene terephthalate (PET) using layered organo-modified nanostructured montmorillonite (clay).
- Evaluate hydrogen permeability and mechanical properties of sample coupons of modified PET.
- Optimize permeance of modified PET by adjusting organo-modifier, montmorillonite loading, and extrusion conditions.





FRP Piping Feasibility Assessment

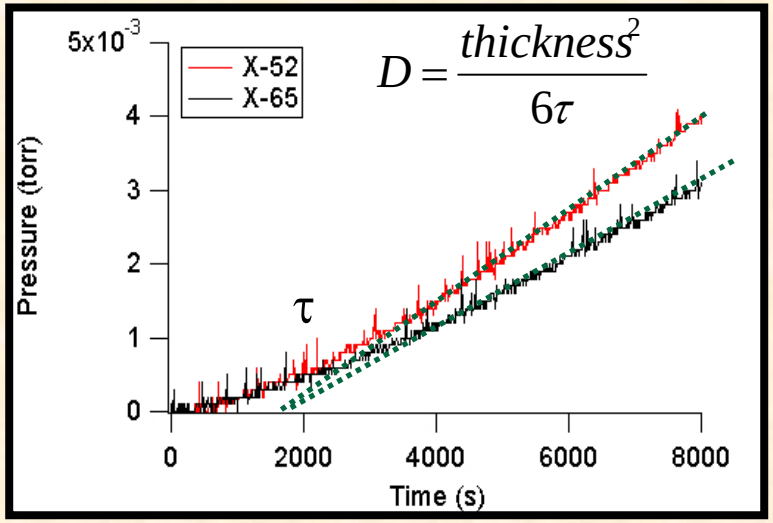
- Current capital cost (materials and installation) for 4-inch ID, 1000 PSI-rated fiber-reinforced polymer piping is approximately $53K to $106K per mile.
- Transmitting H_2 to a population of 100,000 would require five 4-inch ID pipelines, at an approximate capital cost of $250K to $500K per mile.
- This estimate is well below the DOE 2015 target for hydrogen delivery ($800K per mile).
- However, current fiber-reinforced piping needs liner with acceptably low hydrogen permeation and needs qualification for high-pressure H_2 service.

Hydrogen Permeability and Integrity of Hydrogen Delivery Pipelines

- High-pressure H_2 permeation and mechanical tests using ORNL's unique internally heated pressure vessel (IHPV)
  - Hydrogen permeation (solubility and diffusivity) and embrittlement behavior as function of pressure and temperature
  - Effects of steel composition and microstructure, and surface condition (including coating)
  - Effects of welding: weld microstructure, residual stress, and geometrical discontinuities
  - A database for common pipeline steels
- A risk assessment based approach to ensure the integrity and safety of H_2 pipelines
  - Hydrogen management
  - Microstructure management
  - Stress management
- Application of modern, hydrogen-cracking resistance, high-strength pipeline steels for hydrogen delivery and storage

X65 Steel Shows Lower H_2 Permeability than X52 Steel

- **API Grade X52 steel - 1950 production**
  - **20 inch dia - 0.312 inch thick**
  - **Fe-0.3C-1.16Mn (wt.%)**
- **API Grade X65 steel - 1990 production**
  - **16 inch dia - 0.500 inch thick**
  - **Fe-0.18C-1.36Mn (wt.%)**
- **Weld metal**
  - **Self-Shielded Flux Cored Arc Weld**
  - **Fe-0.22C-0.53Mn-1.77Al (wt.%)**



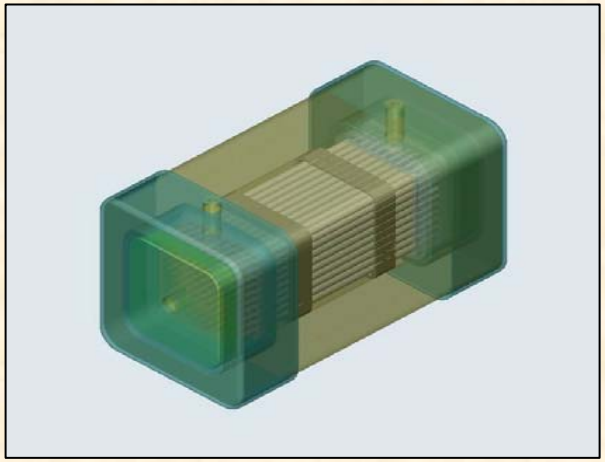
X65 steel shows lower permeability than X52 steel

Fuel Cell Breakthrough

ORNL has Developed Metallic Supported SOFC

Derived from the inorganic membrane technology

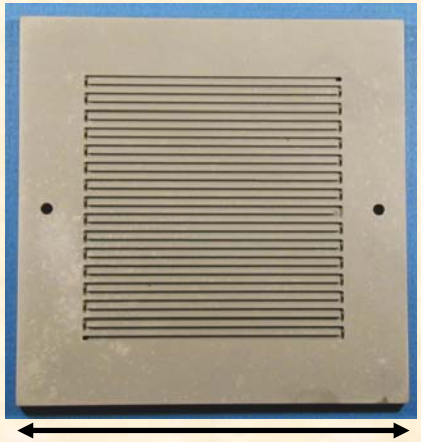
Advantages include:



- Metallic support:
  - allows for simple braze sealing
  - provides high rigid high strength support
  - on fuel side
  - acts as current collector
- Design eliminates need for individual interconnect
- Membranes co-fired onto metallic support
  - No vapor phase deposition of any kind required
- Fuel cell membrane on inside of tube - in compression- stronger configuration
- Stack costs projections at <$100/kW

ORNL's PEM Program Focuses on Component Development

- **Metallic and carbon bipolar plate development**
- **Carbon based heat exchangers**
- **Fiber optic temperature sensors**
- **Sulfur mitigation/catalysts**
- **MEA Characterization**
- **Spatial Resolved Mass Spectrometry**



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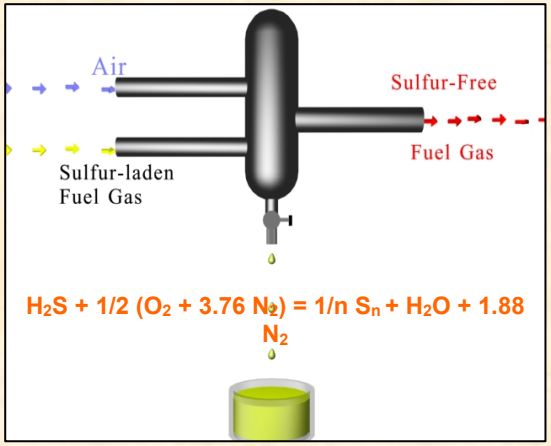
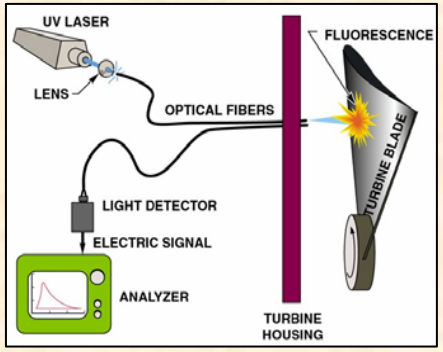
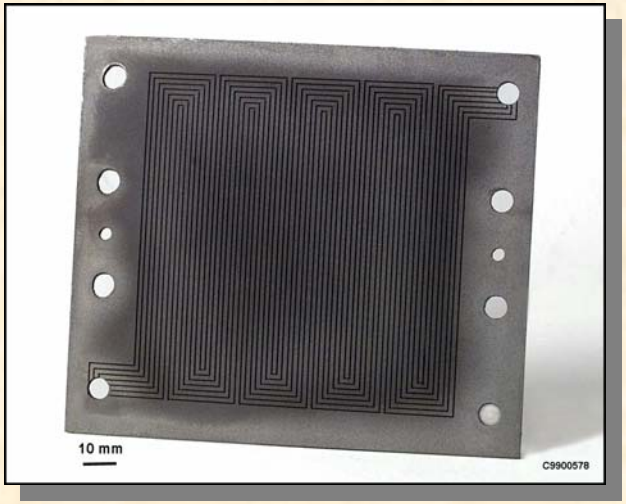
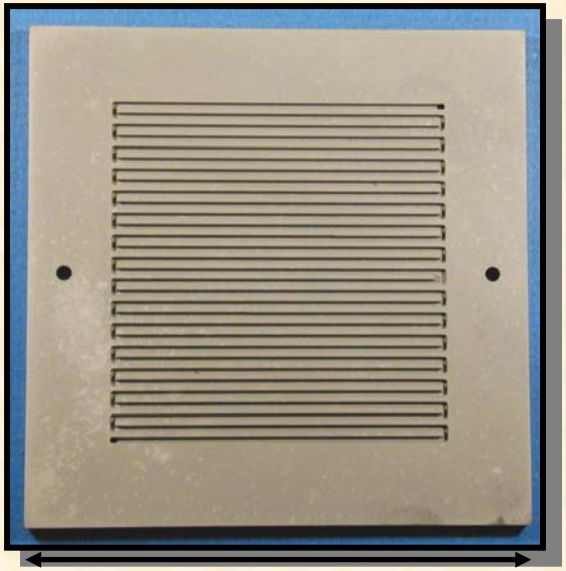




Hydrogen Fuel Cell Successes

- **FY04 top 10 accomplishments**
  - **MEA Characterization**
  - **Sulfur Mitigation Project**
- **Carbon Composite Bipolar Plate**
  - **DOE Tech Transfer Award**
  - **Top 10 fuel cell accomplishment FY 2003**
  - **Licensed to Porvair**
- **Metallic Bipolar Plate**
  - **Top 10 fuel cell accomplishment FY 2003**
- **Carbon Foam Heat exchangers**
  - **Part of FASTER project - top 10 fuel cell accomplishment FY 2003**





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Summary

- ORNL is working in all areas important to a hydrogen economy and is leading efforts in hydrogen distribution

- Breakthroughs are being made in:
  - Hydrogen separation - microporous (7A) membrane
  - Solid oxide fuel cells - low-cost metallic supported cells

- Other notable contributions
  - Renewable hydrogen production from algae
  - “HyTrans” - a model describing the transition to a hydrogen economy
  - Hydrogen storage utilizing metal hydrides and carbon
  - Numerous contributions to PEM fuel cells