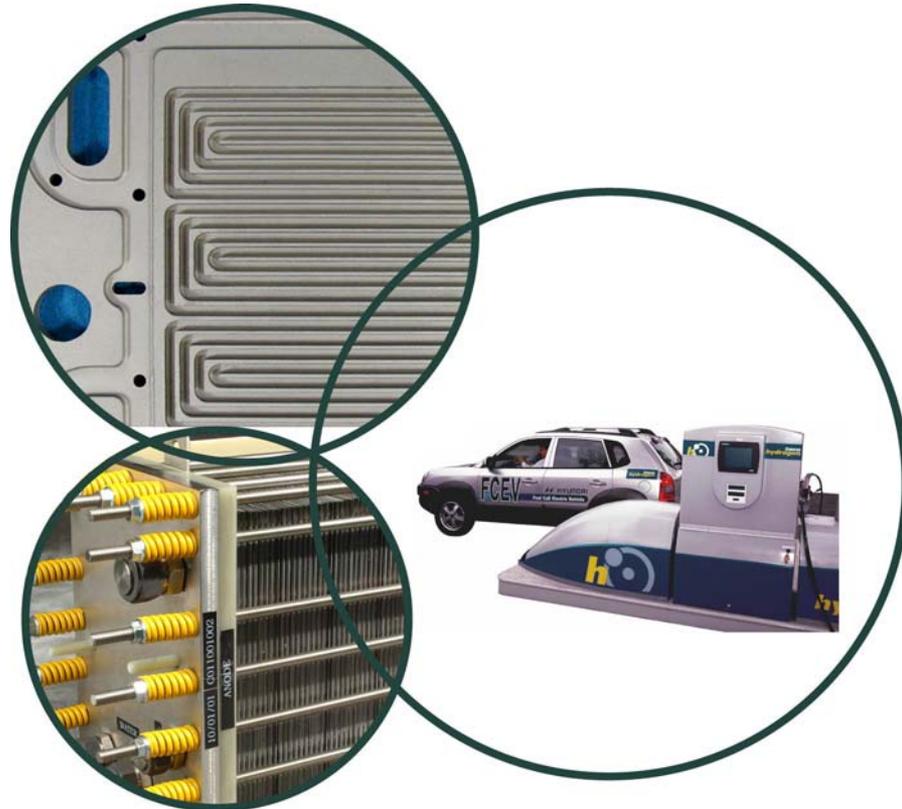


Novel Low-Temperature Proton Transport Membranes



**Hydrogen Separations and
Purification**

Working Group Meeting

Nov. 7, 2007

Ion transport membranes provide unique H₂ separation characteristics

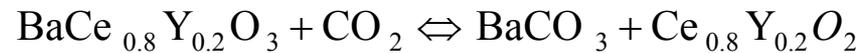
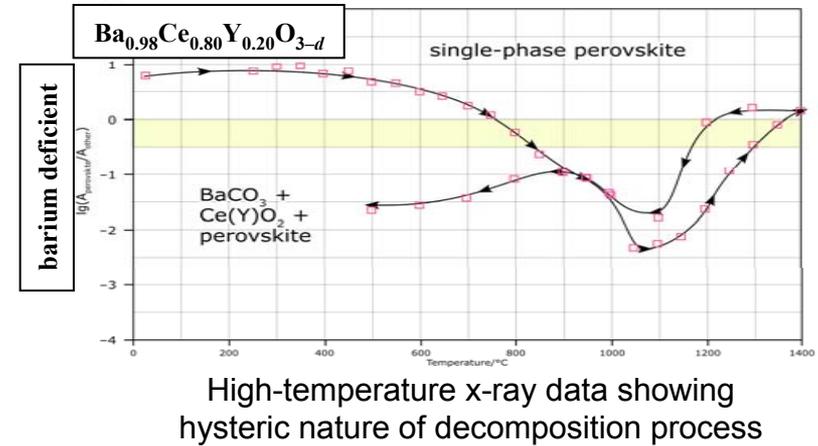
- Gas separation accomplished by surface ionization, transport of H⁺ ions (protons) through the membrane, followed by recombination to form H₂
- This process is 100% selective, but fluxes tend to be low
- In the early 1980's, Iwahara identified proton conductivity in SeCeO₃ and BaCeO₃ perovskites doped with Y, Yb, or Gd
- Perovskite proton conductors all have stability issues (chemical and mechanical) that impact their application for hydrogen separation

Mechanical and chemical stability: an nagging issue for ceramic membranes

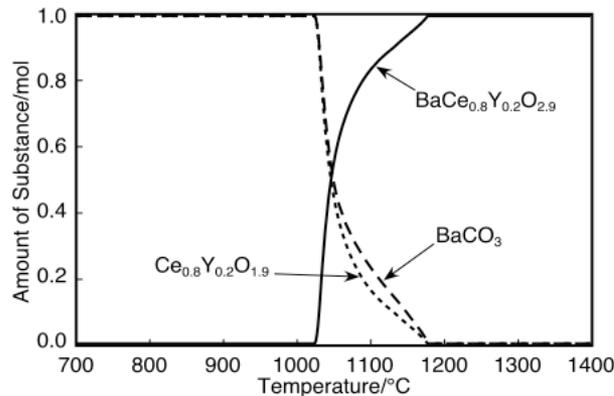
- **Thin barium cerate membranes are required to obtain high H₂ throughput, but are mechanically weak**
 - **Solution is to use a porous metal or ceramic support to provide mechanical strength with only a small flux and weight penalty**
- **Barium cerate (doped or undoped) is unstable in H₂ gas streams containing CO₂**
 - **Need to either regenerate perovskite and drive off carbonates, or add additional infrastructure to eliminate CO₂ from gas stream - no simple solution for this problem**

Stability of Cerates in CO₂

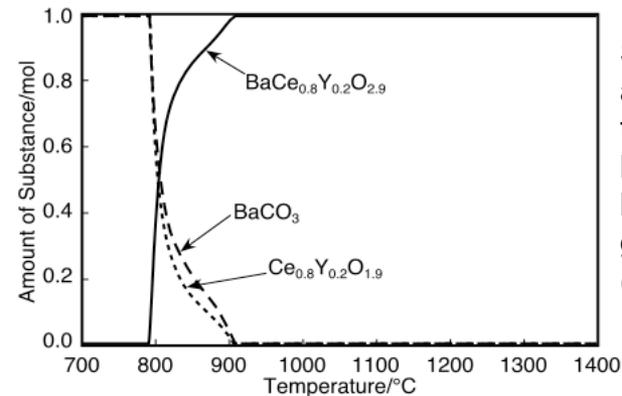
- Demonstrated through experimentation that yttrium-doped barium cerate is unstable in **all** CO₂ laden H₂ streams at temperature
- Thermodynamic modeling verified that yttrium-doped barium cerate is unstable in **all** CO₂ laden H₂ streams at temperature
Decomposition reaction proceeds:
- Showed that replacement of Ce with Zr slightly improves stability at the expense of electrical and protonic conductivity



Stability diagram as a function of temperature for barium Cerate in high CO₂ containing gas streams (PO₂≈10⁻⁸ atm)



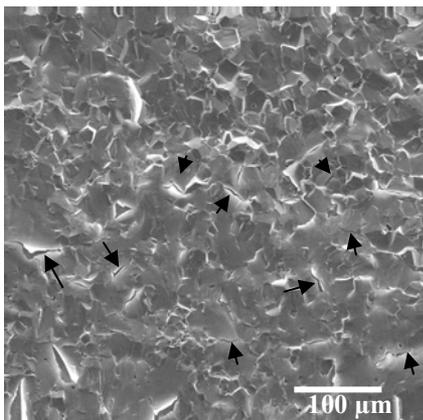
Stability diagram as a function of temperature for barium Cerate in low CO₂ containing gas streams (PO₂≈10⁻¹⁷ atm)



Research funded at ORNL by Office of Fossil Energy

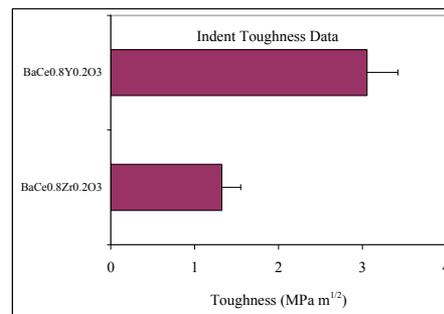
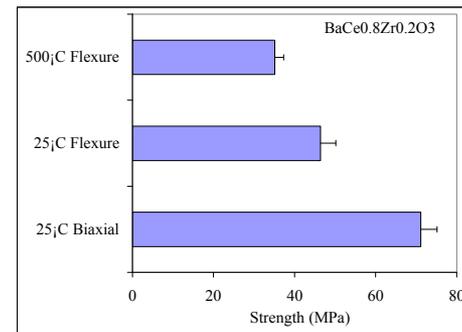
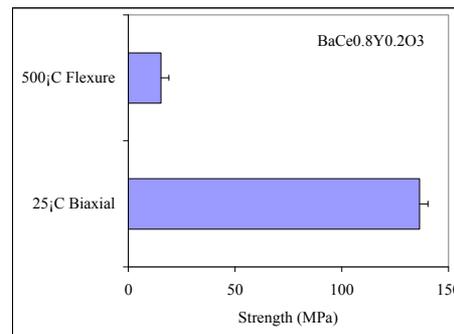
Mechanical Properties of Barium Cerates

- Failure is due to volume defects (pores, voids) and the strength decreases with sample thickness.
- **Replacement of Ce with Zr increases high-temperature strength and microstructural uniformity, while decreasing fracture toughness**
- **Barium cerate internally microcracks under small loading rates similar to those seen in candle filter flanges**
- Due to its poor strength, barium cerate is a poor choice as a monolithic separator material



Microcracks resulting from low loading rate (0.0001 mm/sec) in BaCe_{0.8}Y_{0.2}O₃.

Matt Ferber, Robert Carneim, and Timothy Armstrong, "Mechanical Properties of Ceramic Membranes for Hydrogen Separation," submitted J. Mat. Sci..

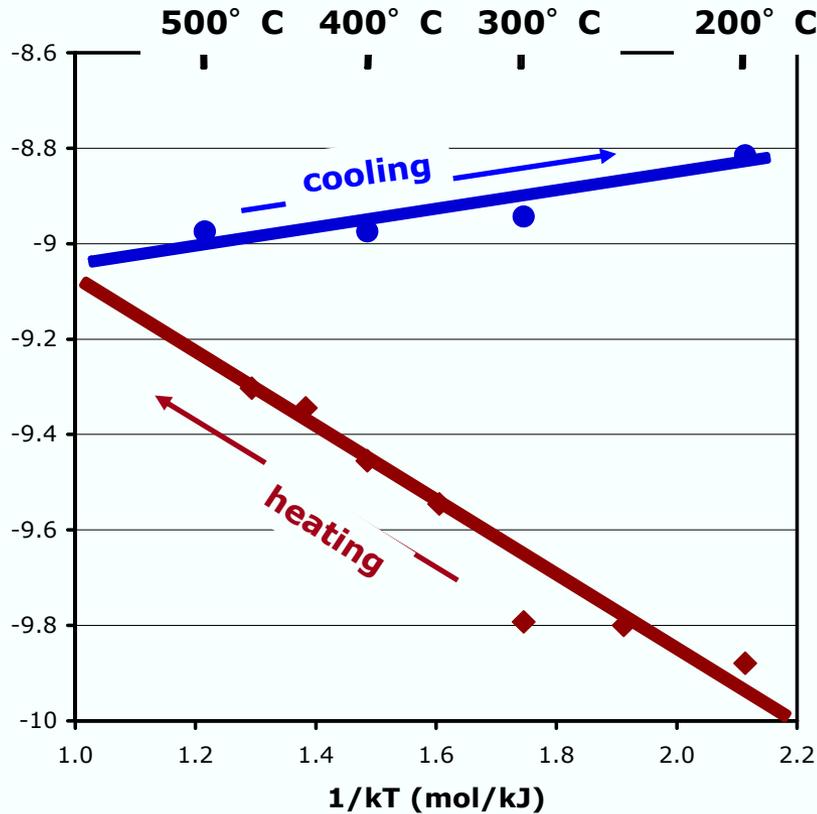


Research funded at ORNL by Office of Fossil Energy

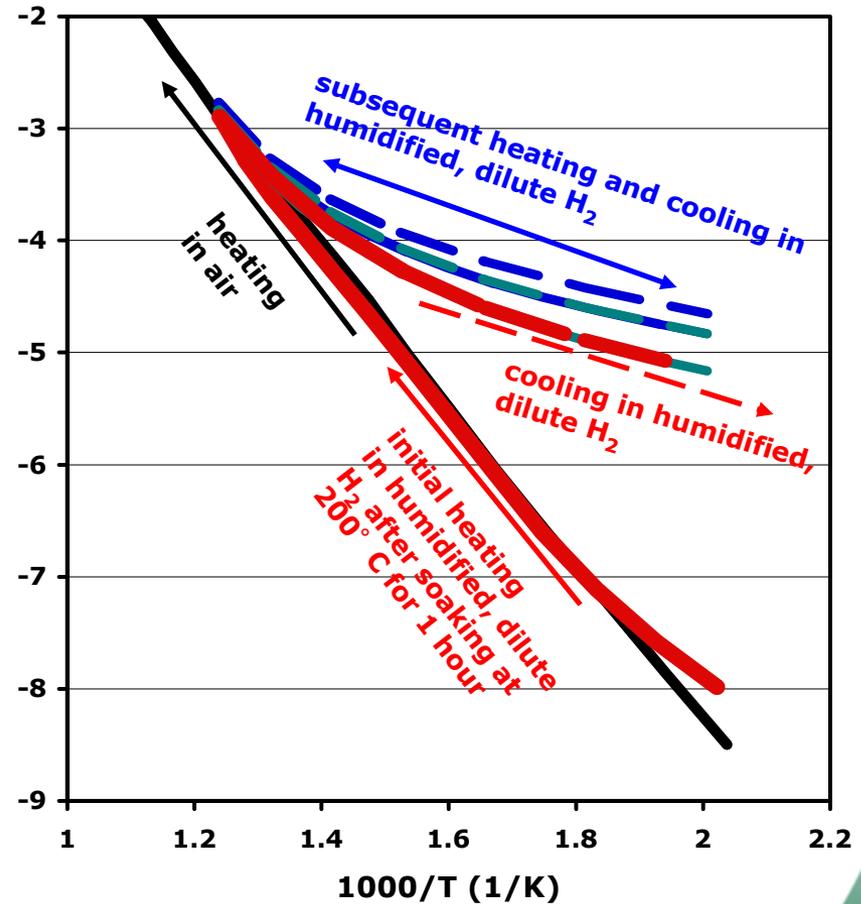
Lanthanum molybdates: a potential alternative to perovskite ceramics

- Doped cerate proton conductors represent a well-established 20 year old technology, and further property improvements are likely to be modest
- $\text{La}_2\text{Mo}_2\text{O}_9$ was originally identified as a fast oxygen ion conductor by researchers in France in 1999/2000
- Focus on oxygen conduction - much effort to stabilize high-temperature β -phase by anion and cation doping
- Low temperature α -phase first identified as a proton conductor at ORNL in 2003/2004
 - Conductivity measured at ORNL and Rutgers
 - H_2 permeance measured at NMT and NETL
 - Research interrupted from Dec/2004 to Apr/2007

Lanthanum molybdates have proton conductivity and hydrogen flux



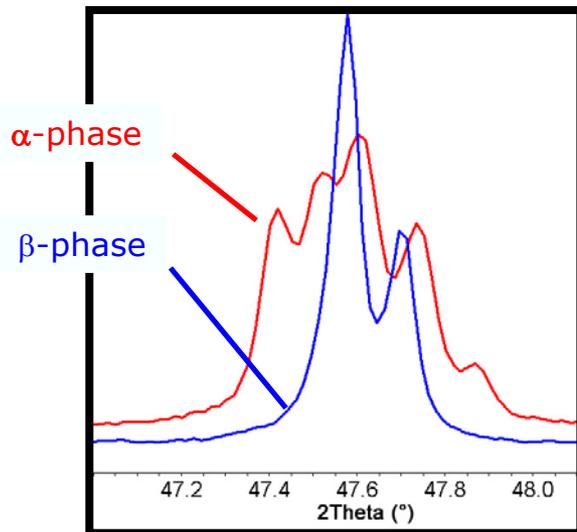
- Hydrogen flux



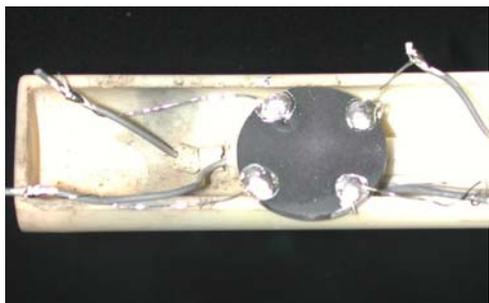
- Conductivity

α -phase $\text{La}_2\text{Mo}_2\text{O}_9$ has a more complex structure than perovskite or pyrochlore

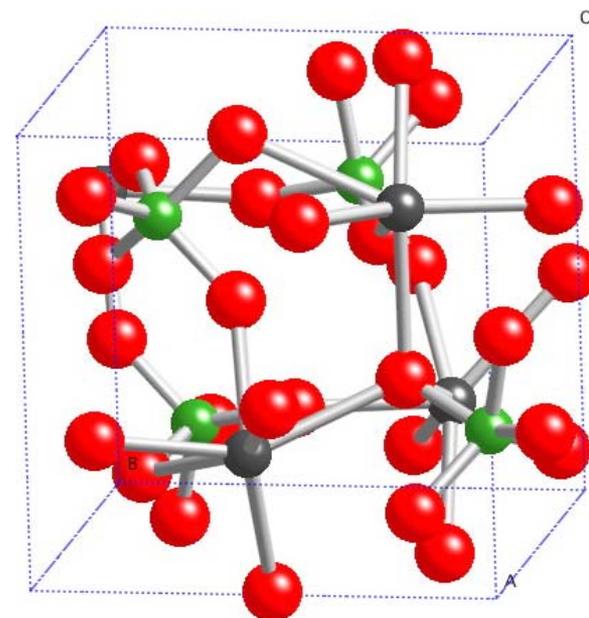
- $\text{La}_2\text{Mo}_2\text{O}_9$ the high-temperature β -phase is a fast oxygen-ion conductor while the α -phase is not.
 - W-doping stabilizes the β -phase at lower temperatures, and (at least in homogeneous phase-pure samples) suppresses the proton conduction
- In-situ XRD data from at ORNL reveals:
 - Below 550°C , $\text{La}_2\text{Mo}_2\text{O}_9$ relaxes into the α -phase in H_2
 - The α -phase is a proton conductor with a complex oxygen sublattice ordering compared to the β -phase
 - Pr-doping dilates the $\text{La}_2\text{Mo}_2\text{O}_9$ lattice, but retains the α -phase structure, yielding slightly higher proton conductivity



The $\text{La}_2\text{Mo}_2\text{O}_9$ phase transformations are fully reversible



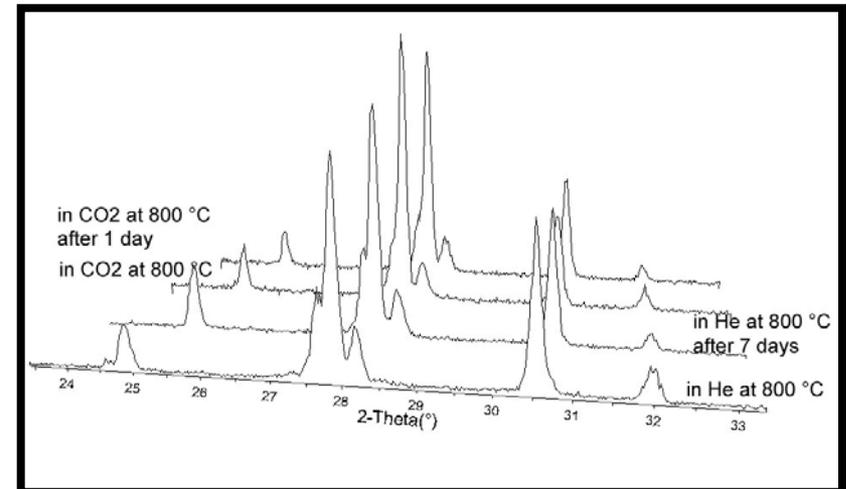
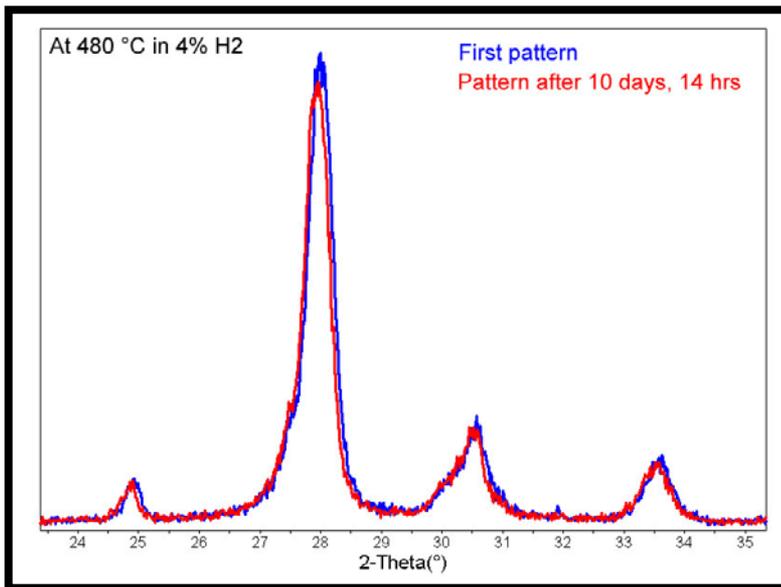
- Undoped samples turn black in hydrogen, white in oxygen



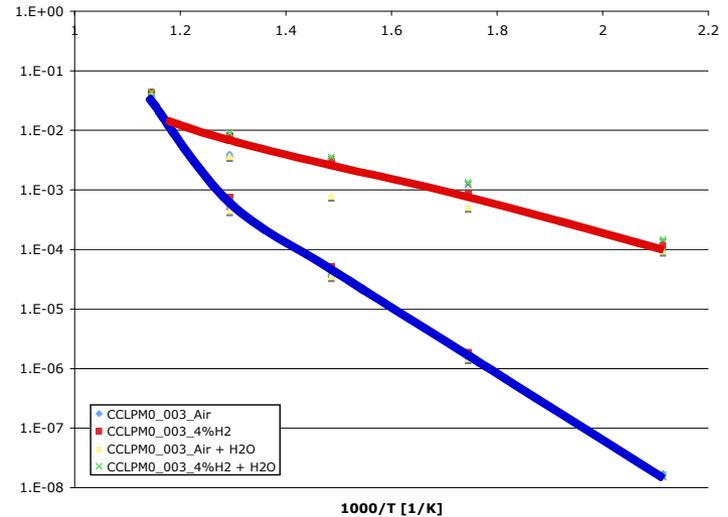
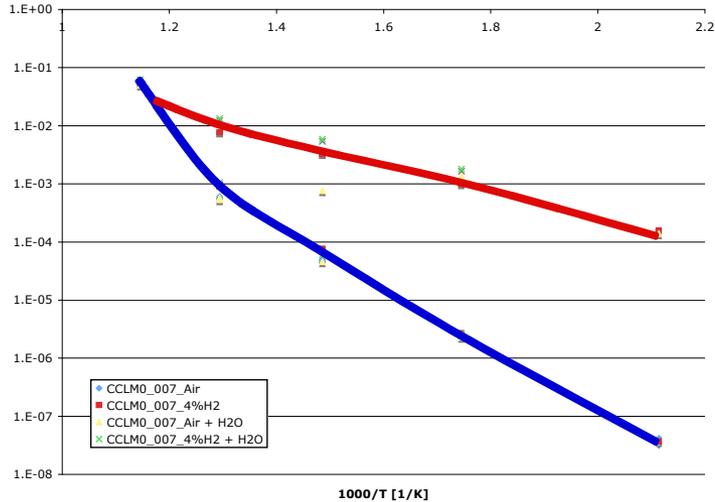
- The high temperature structure is cubic with disordered oxygen vacancies
- The low temperature structure is monoclinic because of the ordered oxygen superlattice

La₂Mo₂O₉ is stable in H₂ and CO₂

- In-situ HTXRD tests at ORNL demonstrate that La₂Mo₂O₉ is stable in H₂ and CO₂
 - Tested for 10+ days in H₂ at ~500°C
 - Tested for 2 days in CO₂ at 800°C - no decomposition



10% Pr-doped conductivity is very similar to undoped



- XRD revealed α -phase with slightly increased lattice parameter (expected due to larger Pr ion radius)
- Conductivity similar to undoped (no loss from doping)

Optimization of the material(s) key to achieving a high permeation rate

- Hydrogen flux is a function of several variables which allows several paths for optimization
 - $J = \sigma/2FL(E-\eta)$
- For charge balance, electrons need to flow to balance the protons:
 - σ = ambipolar part of the total current (H^+ and e^-)
- The Nernst equation:
 - $E = -(RT/2F)\ln(P_2/P_1)$
 - The diffusion rate may be impacted by changing the temperature or partial pressure difference
- The energy barrier for dissociation, η , (H_2 to $2H^+$) at the surface limits the number of protons
 - Use of a surface catalyst may be necessary to provide protons at surface
- Flux is inversely proportional to the thickness, L
 - Use of a porous support may be necessary to provide mechanical strength for ultra-thin membranes

Review of performance metrics

- **Cost per sq foot material:**
 - unknown but likely closely similar to other ceramic membranes
- **Module cost:**
 - unknown but likely closely similar to other ceramic membranes
- **Flux rate:**
 - very limited permeation data collected to date at NMT and NETL suggests similar to Y-doped BaCeO₃. Additional measurements at U Cinn on improved compositions are planned for this quarter
- **%H₂ recovery:**
 - to be determined
- **Hydrogen quality:**
 - As for all ion-transport systems, should be 100% H₂
- **Operating temperature, pressure:**
 - T<550°C, P yet to be determined (based on mechanical stability)
- **Durability:**
 - stable at temperature in H₂O, CO, and CO₂. H₂S stability to be determined

Hydrogen flux is the single most important performance issue

- Present literature suggests that hydrogen flux rates of between 5 and 50 mL/min/cm² will be required for commercial application
- In 2004 we made two preliminary measurements (at NMT and NETL) of hydrogen flux in 3mm thick samples of W-doped and Nb-doped La₂Mo₂O₉
- Results were encouraging: H₂ flux was confirmed in both tests, but the magnitude was only 5×10^{-5} mL/min/cm²
- So... how to increase this by 5 to 6 orders of magnitude?

Strategies for increasing hydrogen flux

- **Reduce sample thickness**
 - Reduction from mm to μm dimensions could provide a 2 order of magnitude increase in flux
- **Increase H_2 pressure differential**
 - Initial tests were done at near 1 atm, with dilute H_2 on the source side and inert sweep gas on the other, so a low Nernst potential
 - Gain is logarithmic, so perhaps a 1 order of magnitude gain in flux
- **Increase proton conductivity**
 - Alter crystal chemistry with dopants to increase mobility of protons within the structure, and to alter the ratio of proton to electron conductivity, gains may be possible but are not predicable at this time
- **Increase H_2 to proton dissociation rate**
 - Use of surface catalysts has proven effective in the cerate systems and could provide 1-2 order of magnitude increase in flux
- *It would appear that gains of 4-5 orders of magnitude are realistically achievable in this system, which would make it comparable to established dense ceramic membrane systems, and still higher gains may be possible*

Experimental plans continuing through FY2008 for increasing hydrogen flux

- **Reduce sample thickness**
 - FY2004: high quality bulk powders via combustion synthesis
 - FY2007: thin samples via tape casting, followed by lamination, pressing and firing
 - FY2007: inks for screen printing ultra-thin membranes on porous supports
- **Increase H₂ pressure differential**
 - Porous supports are needed to provide adequate mechanical strength
 - FY2008 will establish suitable supports to avoid stresses and diffusion
- **Increase proton conductivity**
 - FY2007 improvements in ceramic processing have allowed us to synthesize bulk quantities of powders, and establish correct sintering conditions to make dense single-phase membranes
 - B-site doping: FY2004 Nb found to generate problematic impurity phases
 - A-site doping: FY2004/07 W stabilizes β -phase and improves sinterability, FY2007 Pr appears good choice with larger lattice parameter and more free volume
- **Increase H₂ to proton dissociation rate**
 - No significant gains observed to date for humidified versus dry 4%H₂
 - FY2008 will investigate effect of dispersed Ni or Pd catalysts

Assessment of status

- **Homogeneous powder routinely made by combustion synthesis from stock solutions**
- **High quality samples synthesized by dry pressing of powders, or by tape casting slurries made from these powders, followed by lamination and sintering.**
- **Tungsten was previously added to improve sinterability, but new undoped samples can be sintered to near theoretical density without tungsten (due to improved processing)**
- **Phase analysis by XRD, phase stability by in-situ HTXRD**
- **Conductivity analysis by 4-point van der Pauw method in controlled temperature and gas environment**
- **New undoped (α -phase) samples confirmed previous conductivity results, but new W-doped (β -phase) material shows no proton conduction (as expected)**
- **New Pr-doped (α -phase) material shows similar proton conduction to undoped material**
- **Porous supports being investigated - YSZ considered.**

Lanthanum molybdate may be a viable dense ceramic oxide membrane option

- **Pros:**

- Superior stability in H_2O , CO_2 , CO
- H_2 conductivity at moderate temperatures ($<550^\circ\text{C}$), even measurable flux at 200°C

- **Cons:**

- New material, so properties not well established
- H_2 permeance is low (common to all ceramic oxides, presently looking to enhance by multiple strategies)
- Difficult to sinter to full density (originally solved by W-doping, now solved by improved processing techniques)
- Mechanical strength is low (presently working on porous ceramic supported membrane)

- **Unknowns:**

- Compatibility with support and catalysts not yet determined
- Stability in H_2S not yet tested (should be good considering other La-based perovskite oxides)

Summary

- **Timeline**

- Started 02/2004
- Stopped 12/2004
- Restarted 04/2007

- **Budget**

- FY04: \$100k
- FY05: \$45k (zeroed 12/2004)
- FY06: \$30k (zeroed 12/2005)
- FY07: \$200k (04/2007 start)

- **Barriers to be addressed**

- Low H₂ flux
- Poor mechanical properties
- Poisoning by CO₂ and H₂S

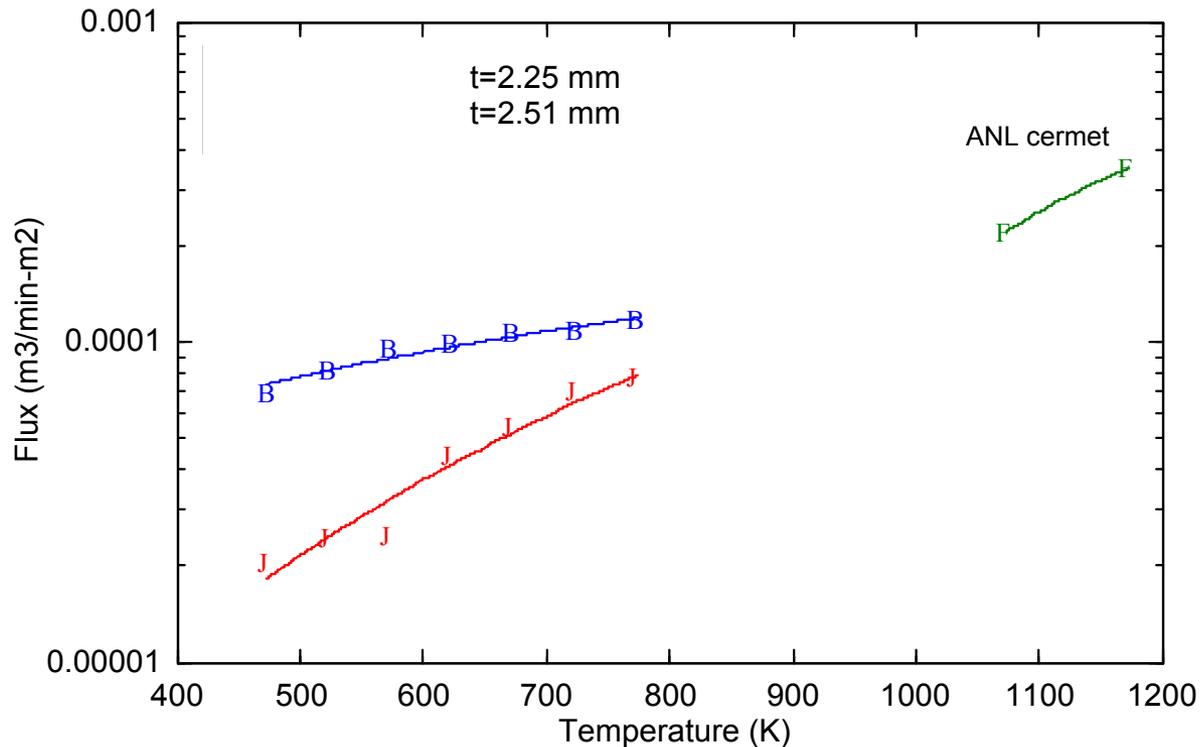
- **Team members**

- Andrew Payzant
- Tim Armstrong
- Beth Armstrong
- Junhang Dong, Cincinatti

Q&A

- **Last merit review was 2004, so no questions from 2007 review to be addressed**
- **New questions and comments are welcome**

Low-temperature flux comparable high temperature perovskites



- Advantages

- Not reactive with CO₂
- Probably not reactive with H₂S
- Operating temperature less than 600°C
- Proton transport measured down to 200°C