UT-BATTELLE

2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies
Annual Program Review

# Ion Transport Membranes for Hydrogen Separation

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This presentation does not contain any proprietary or confidential information.

# Project Overview

- A number of oxide systems, including perovskites, pyrochlores, brownmillerites, and fluorites, have been investigated to identify an intermediate temperature proton conductor for hydrogen separation
- A new class of proton conductors stable at temperatures below 550°C has been discovered

# Project Objective

- To develop a practical high temperature proton transport membrane where high conductivity and stability are the primary requirements.

# Project Timeline

(Project initiated February 2004)

## Proton Transport Membrane Development

| 2004-2005 | 2005-06 | 2007 |
|---|---|---|
| **Phase I** | **Phase II** | **Phase III** |

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- Phase I: Proof-of-concept
  - 1 – Complete tests to determine viability of Pyrochlore/Perovskite materials (completed)
  - 2 – Complete tests to determine viability novel low-temperature material (completed)
  - 3 – Complete tests to determine viability of fluorite proton conductors (completed)
  - 4 – Down select to one structural family (completed)
- Development and Testing
  - 5 – Optimize flux, composition, and mechanical properties (in progress)
  - 6 – Asymmetric membrane development on metallic supports
  - 7 – Complete optimization of asymmetric membranes
- Phase II: Optimization, Scale up and Tech Transfer
  - 8 – Complete scale up and transition to industry

# Budget

Budget for FY2004 was $100k

Budget for FY2005 ($200k) was eliminated due to earmarks

# Technical Targets

- DOE Technical Barriers
  - A. Fuel Processor Capital Costs
  - B. Operation and Maintenance Costs
  - AB. Hydrogen Separation and Purification
- DOE Technical Targets for 2010
  - Purification: 90%at $0.03/kg Hydrogen

# Technical Approach

**Objective**

Develop a new proton conducting ceramic membrane capable of intermediate temperature (<600°C) operation

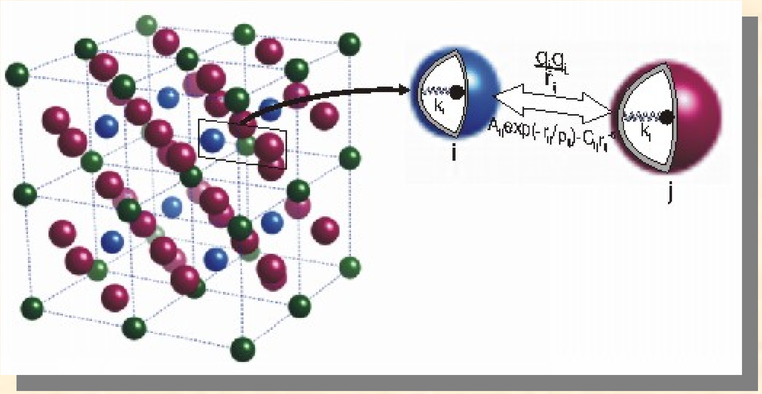
**Approach**

- Atomistic computer simulations to identify and evaluate potential new proton conducting ceramic systems
- Rapid high-purity materials synthesis using a modified "combustion synthesis" process
- Structure and properties characterization
- Long-term stability testing (e.g. in reformate and syngas)

# Technical Progress

- Potential proton transport materials have been identified in the pyrochlore, brownmillerite, fluorite, and related oxides
- Computer simulation with empirical potential models
  - model completed for several pyrochlore, perovskite, and brownmillerite end members. Solid solution models are in development.

- Crystal structure and phase identification studies completed for >100 samples prepared to date with more in progress
- High temperature conductivity measurements in air completed for >50 samples to date - studies in hydrogen are in progress
- Hydrogen permeance measurements initiated in summer 2004



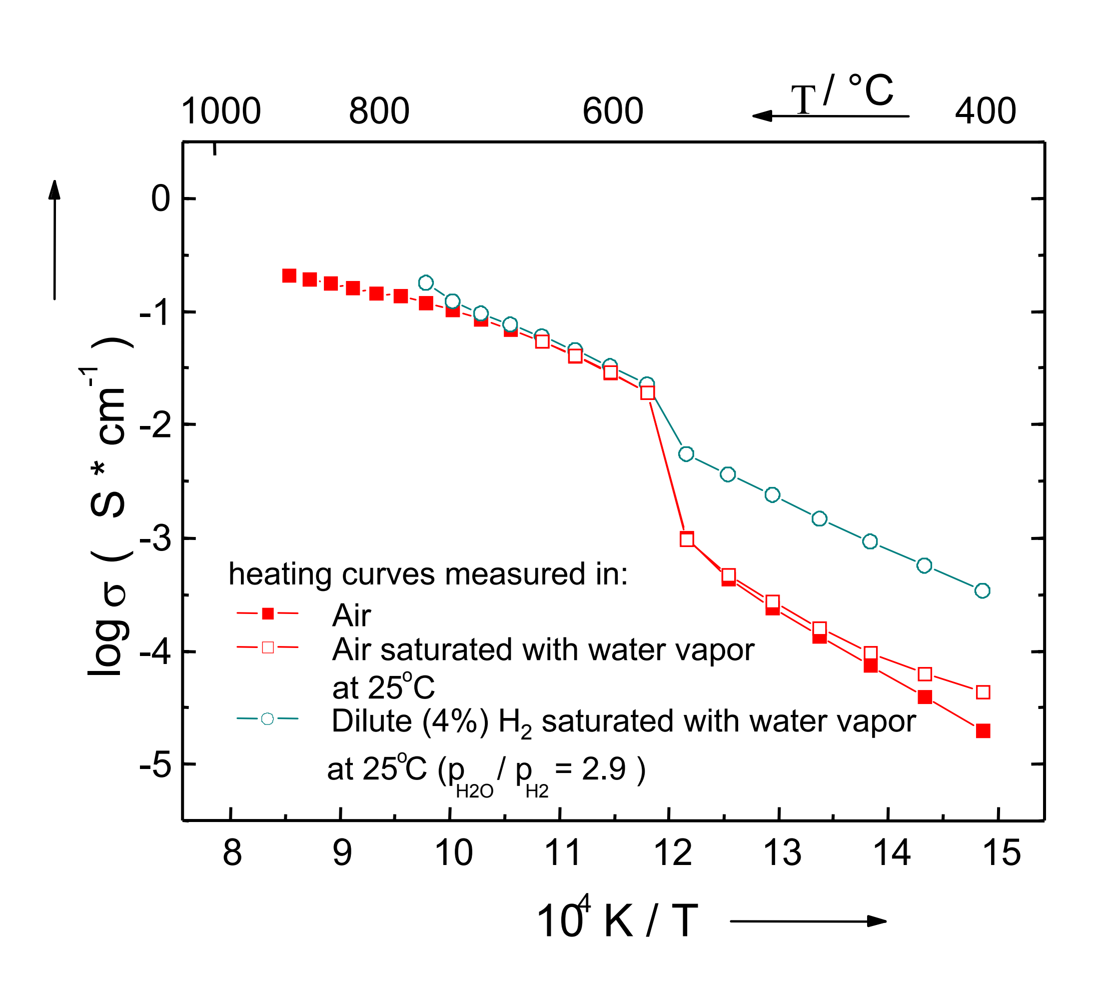
# Modeling Enables Stable Phases to be Predicted Based on Calculated Lattice Energies

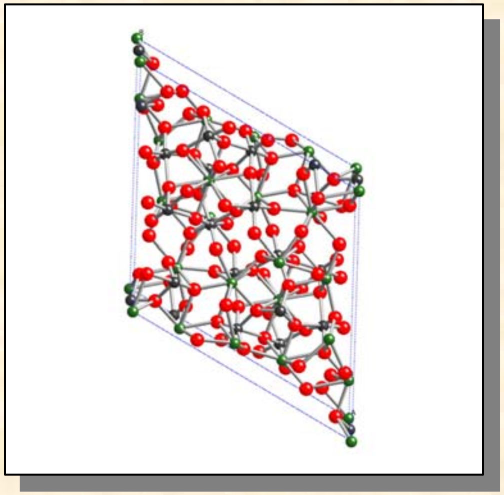
- Computational modeling has been utilized to predict potential proton conducting ceramic oxides in the perovskite and brownmillerite systems.
- New methodologies are being developed to evaluate a broader range of possible products to improve the accuracy of the models predictions.
- Modeling enables prediction of effects of chemical doping on structure and properties - the most promising candidates may be synthesized and tested.

# Numerous Candidate Systems have been Evaluated for Proton Conduction

- Perovskite, Pyrochlore, and Brownmillerite sytems yielded useful mixed conductors, but no practical proton conductor
- Fluorite system yielded useful oxygen and mixed conductors but no practical proton conductors
- New oxide system identified with high proton conductivity at temperatures below 550°C

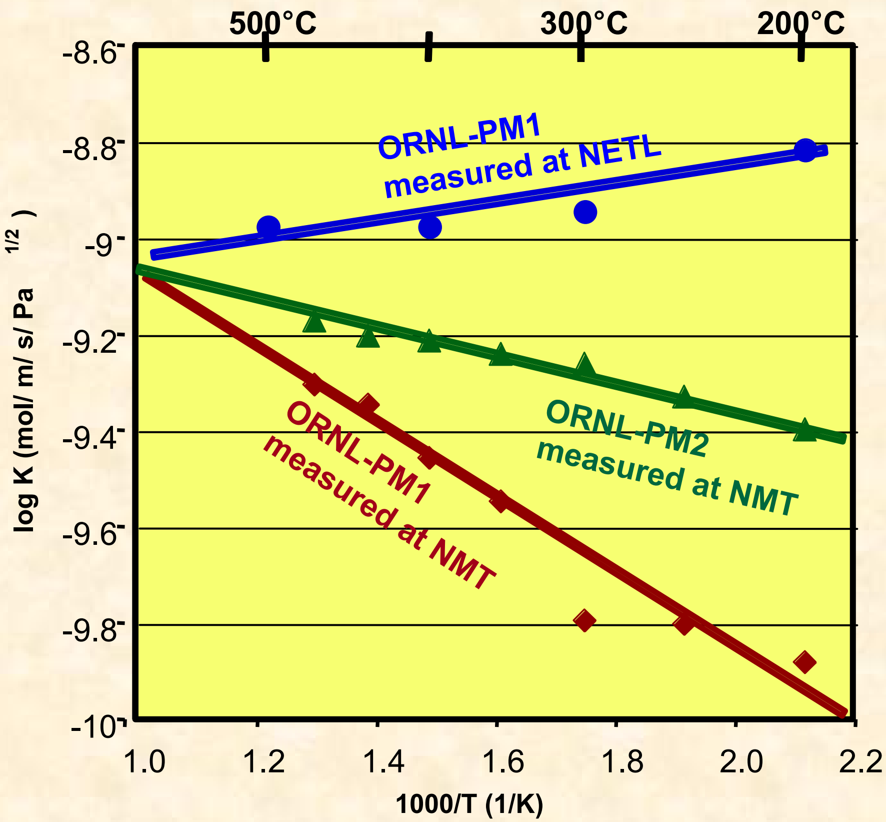
# New Low-Temperature Proton Conducting Oxide has Been Discovered



Invention disclosure has been filed

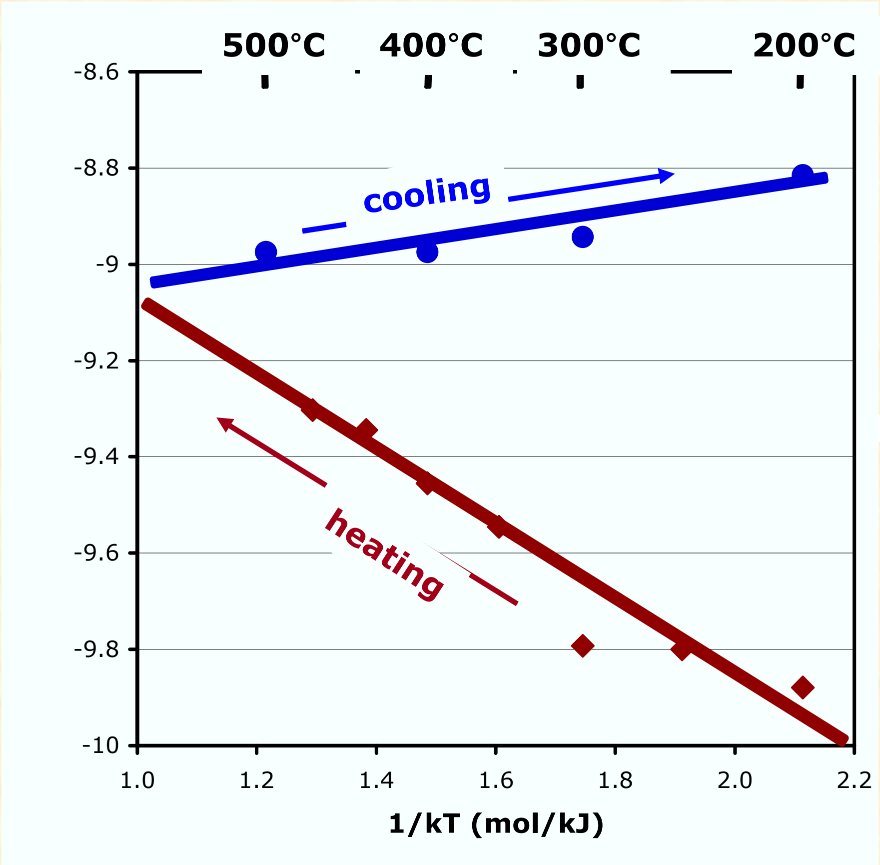
# Measurements Confirm Hydrogen Flux at <550°C



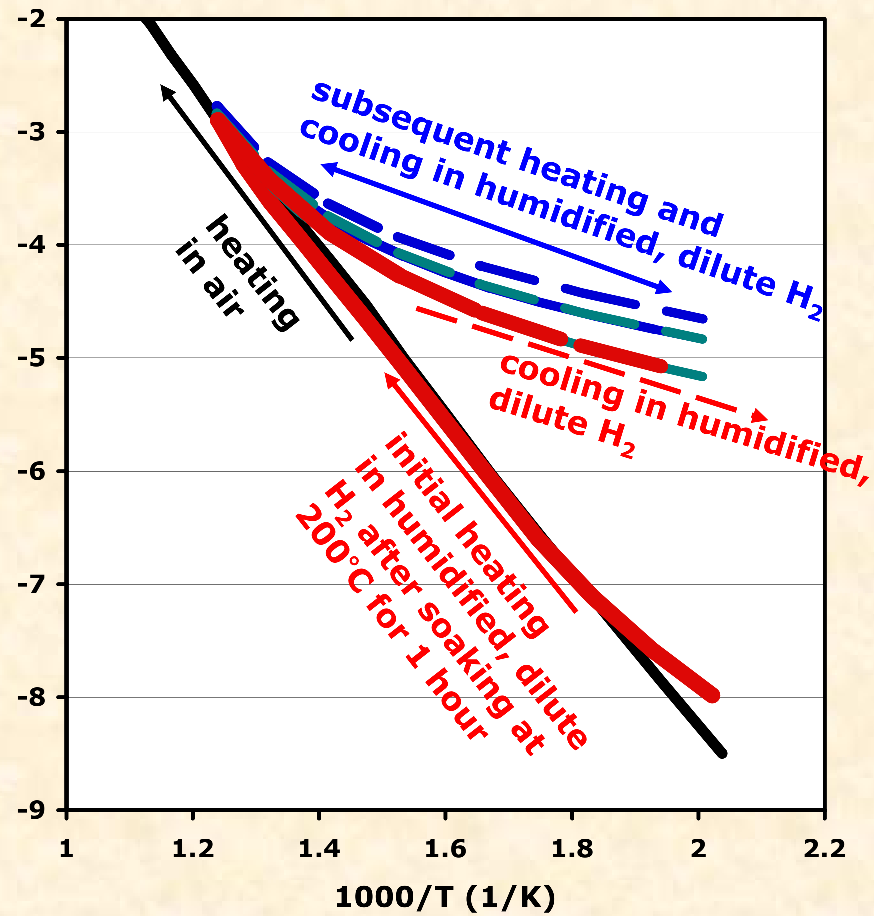

NETL data collected on cooling in 3 atm humidified $H_2$.
NMT data collected on heating in 1 atm humidified $H_2$.

- Conductivity data collected at ORNL indirectly demonstrated proton conduction
- Preliminary hydrogen permeation data collected at NETL and NMT definitively demonstrate hydrogen permeation
- ***Data collected on initial heating reflect hydrogen uptake - subsequent cycling follows the (higher flux) cooling data***

# Hydrogen Permeation Data Correlate Well With Total Conductivity Data



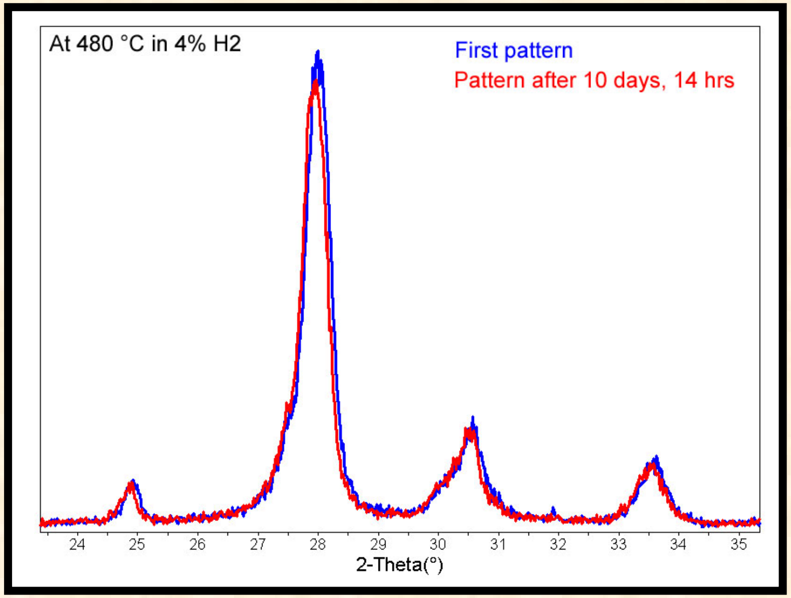

Hydrogen permeability measurements from NETL and NMT, made at 1 atm and 3 atm p($H_2$).

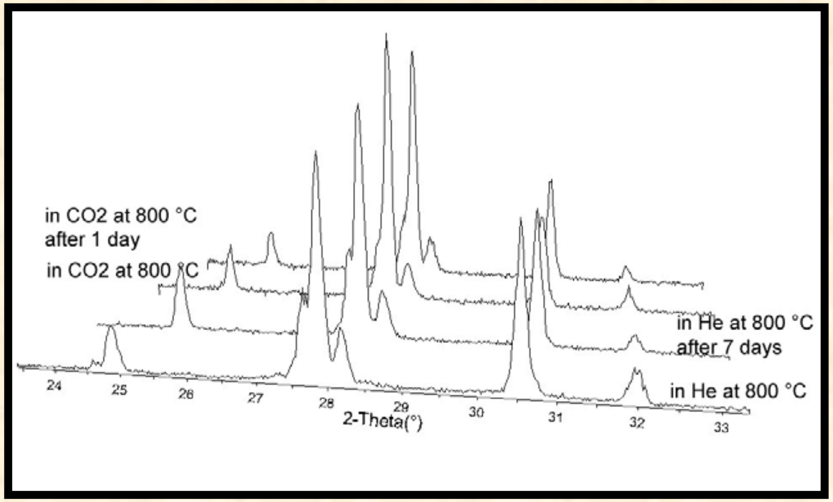



Van der Pauw dc conductivity measurement made in 4%$H_2$-Ar gas mixture at ORNL.

# New oxide is stable in $H_2$ and $CO_2$

- In-situ XRD demonstrated phase stability in $H_2$ and $CO_2$
  - Stable over 10 days in $H_2$ at 480°C
  - Stable over 2 days in $CO_2$ at 800°C
  - $H_2S$ stability yet to be determined



# Future Work

- Continue modeling and simulation effort to predict composition property relationships which can lead to optimized compositions
- Determine hydrogen flux as a function of temperature and pressure for candidate compositions
- Characterize long-term high-temperature stability under service conditions ($H_2S$, $CO_2$)
- Develop metallic supported asymmetric membranes using ORNL support tubes

# Interactions and Collaborations

- **Rutgers University:** technical collaboration on proton conducting materials
- **New Mexico Tech:** independent testing of hydrogen permeance
- **NETL:** independent testing of hydrogen permeance
- Discussions on implementation of technology are ongoing with
  - **ConocoPhillips, ChevronTexaco, Infinity Fuel Cells, Worldwide Energy and Praxair**

# Hydrogen Safety

- The most significant hazard associated with this project is handling of flammable hydrogen gas mixtures
- Our approach to deal with this hazard is Integrated Safety Management Pre-Planning and Work Control" (Research Hazard Analysis and Control)
  - Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers
  - The RSS is reviewed/revised yearly, or sooner if any change in the work results in a need for modification.
  - Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D
  - Periodic safety reviews of installed systems is required at ORNL