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

Ion Transport Membranes for Hydrogen Separation

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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**
1 2, 3, 4	**5 6 7**	**8**

- 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 <u>eliminated</u> 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

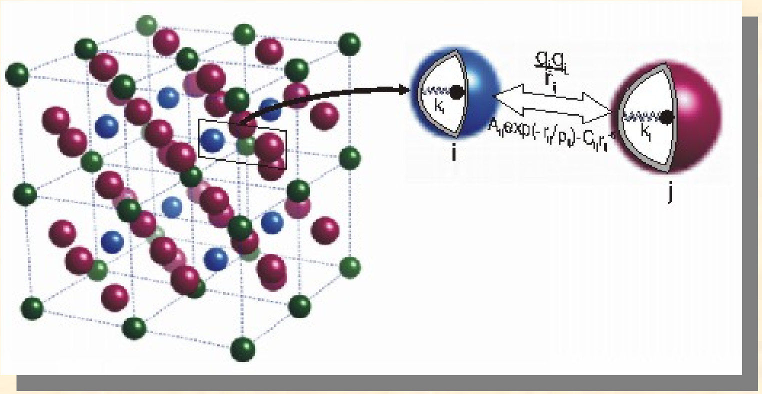
Approach

- 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



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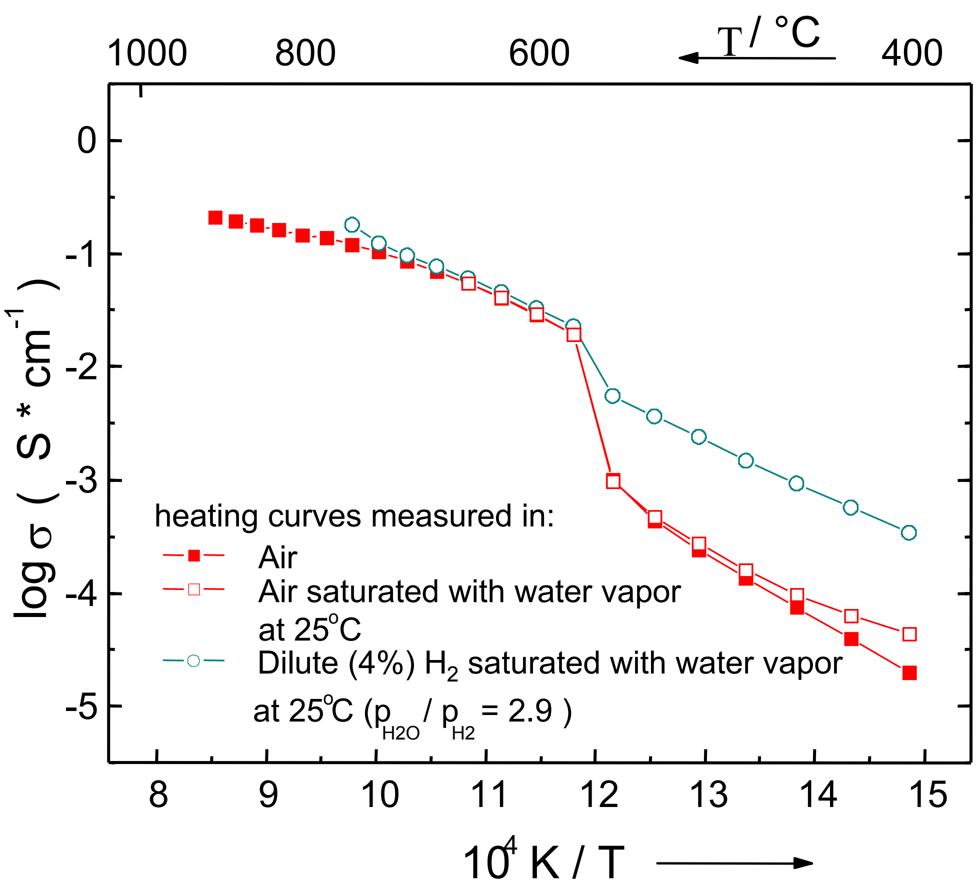
Modeling Enables Stable Phases to be Predicted Based on Calculated Lattice Energies

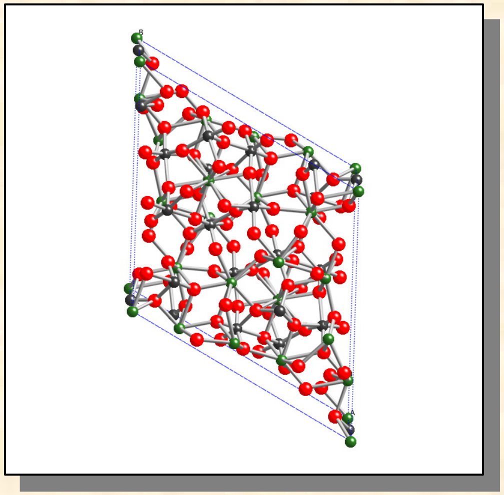
- Computational modeling has been utilized to predict potential proton conducting ceramic oxides in the perovskite and brownmillerite systems.
- New methodologies are being developed to evaluate a broader range of possible products to improve the accuracy of the models predictions.
- Modeling enables 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

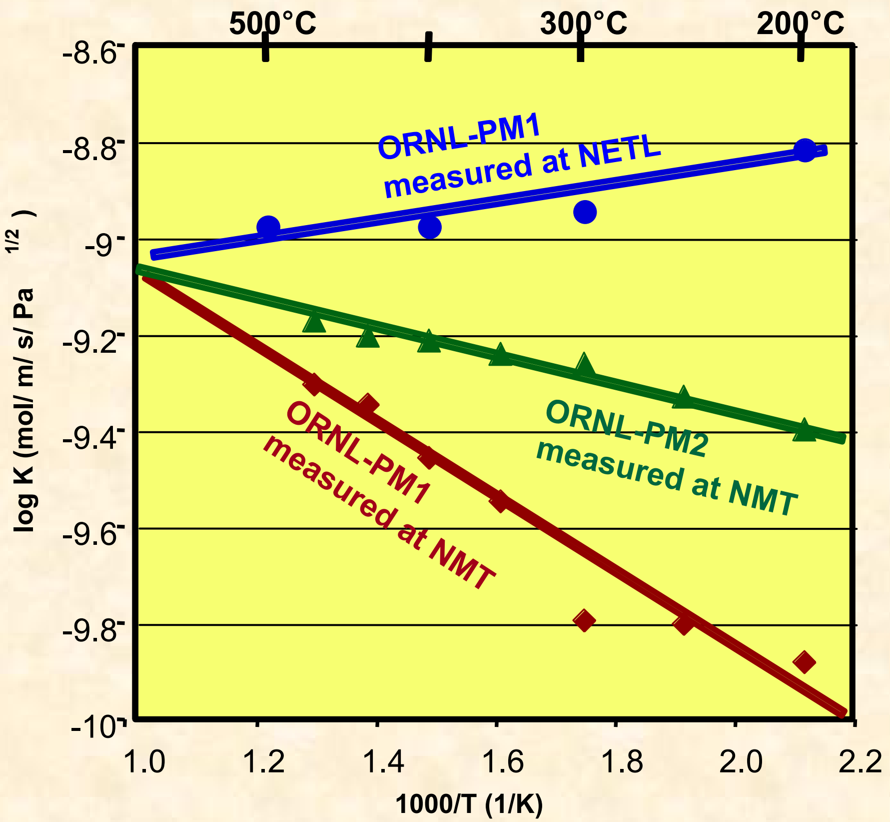
New Low-Temperature Proton Conducting Oxide has Been Discovered





Invention disclosure has been filed

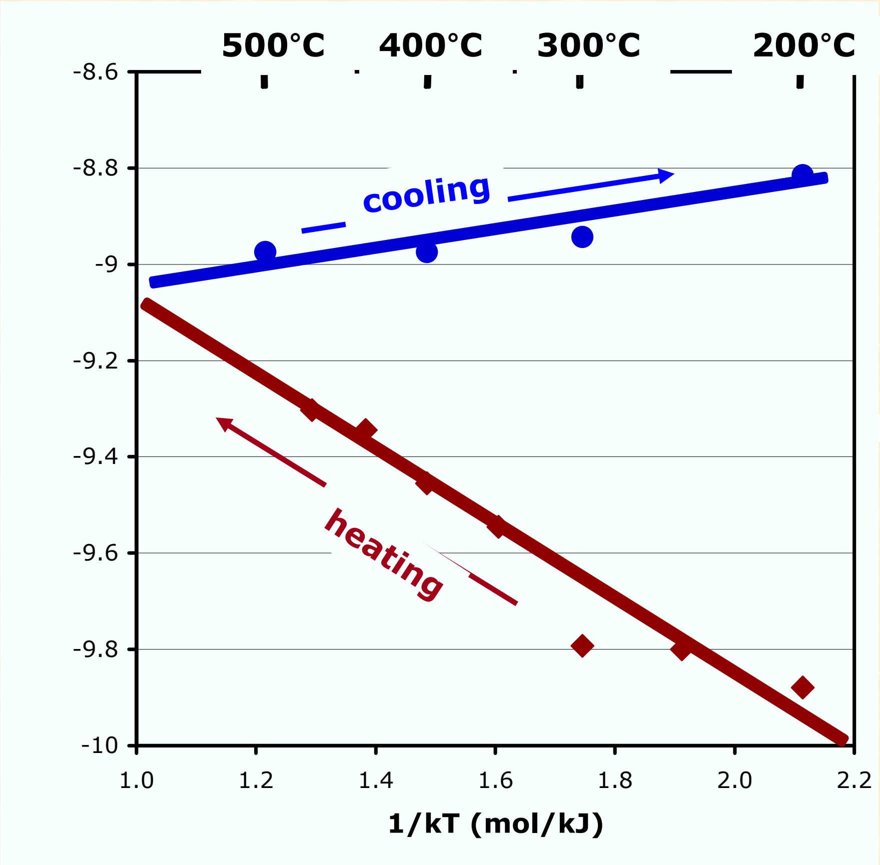
Measurements Confirm Hydrogen Flux at <550°C



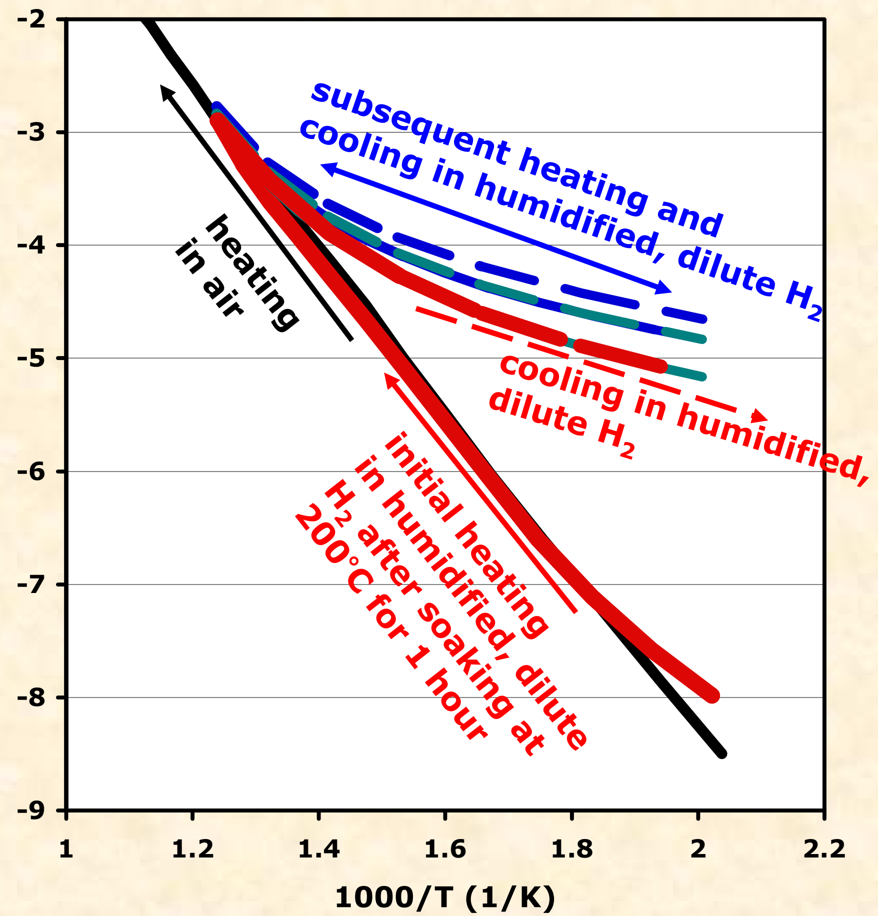
- **Conductivity data collected at ORNL indirectly demonstrated proton conduction**
- **Preliminary hydrogen permeation data collected at NETL and NMT definitively demonstrate hydrogen permeation**
- ***Data collected on initial heating reflect hydrogen uptake - subsequent cycling follows the (higher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

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

Hydrogen Permeation Data Correlate Well With Total Conductivity Data



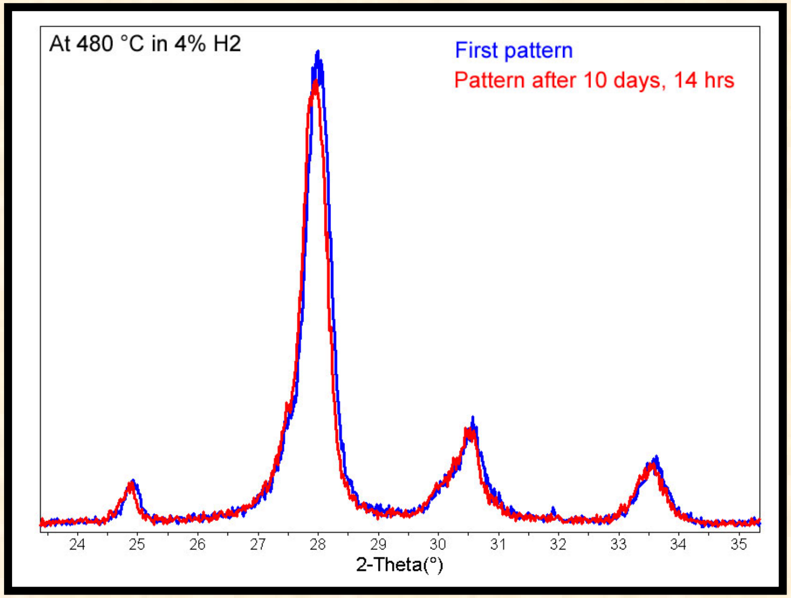
Hydrogen permeability measurements from NETL and NMT, made at 1 atm and 3 atm $p(H_2)$.

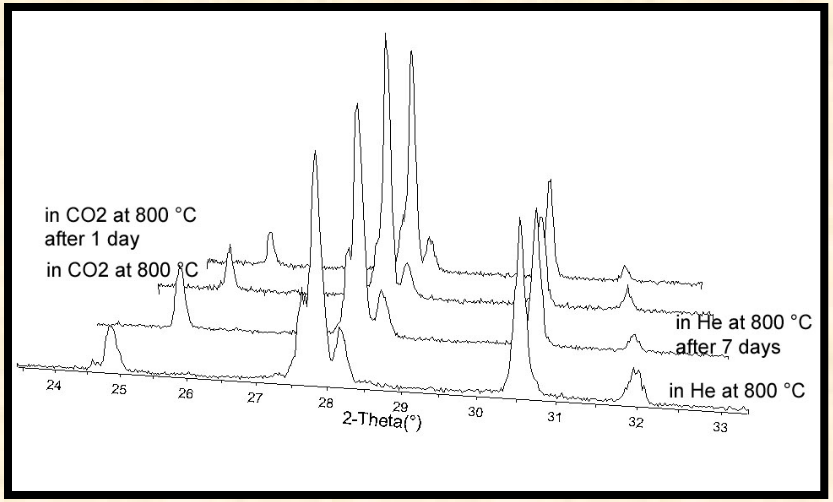


Van der Pauw dc conductivity measurement made in 4%H_2-Ar gas mixture at ORNL.

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