Ion Transport Membranes for Hydrogen Separation

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May 25, 2005, Philadelphia, PA

Project ID# PDP21

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


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 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 systems 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

heating curves measured in:
- Air
- Air saturated with water vapor at 25°C
- Dilute (4%) H₂ saturated with water vapor at 25°C ($p_{H_2O}/p_{H_2} = 2.9$)

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 H₂.
NMT data collected on heating in 1 atm humidified H₂.
Hydrogen Permeation Data Correlate Well With Total Conductivity Data

Hydrogen permeability measurements from NETL and NMT, made at 1 atm and 3 atm p(H₂).

Van der Pauw dc conductivity measurement made in 4%H₂-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$_2$S 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$_2$S, 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.