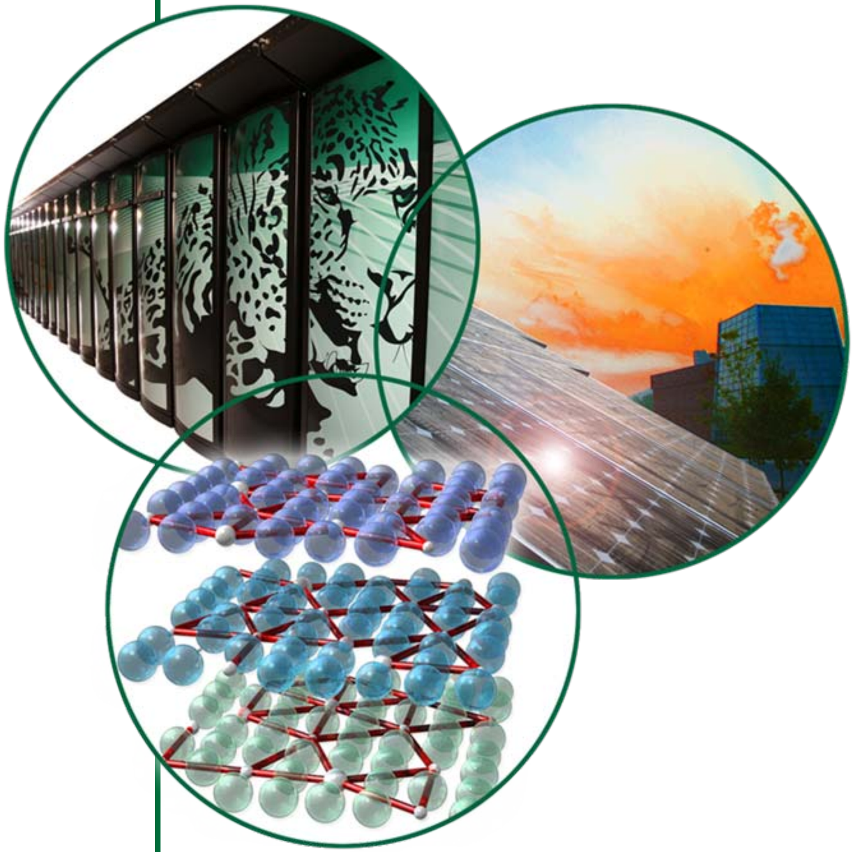
Project ID# PDP_13_Payzant

Novel Low-Temperature Proton Transport Membranes



U.S. DEPARTMENT OF ENERGY

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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

- **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)**
  - **FY08: $300k**
  - **FY09: $0k**

- **Barriers to be addressed**
  - Fuel Processor Capital Costs
  - Hydrogen Separation and Purification

- **Team members**
  - **Andrew Payzant**
  - **Tim Armstrong**
  - **Beth Armstrong**
  - **Junhang Dong, Cincinnati**

An alternative to perovskite ceramics

- Doped cerate proton conductors represent a well-established 20 year old technology, and further property improvements, though important, are likely to be modest
- $La_2Mo_2O_9$ was originally identified as a fast oxygen ion conductor by researchers in France in 1999/2000
- Focus was 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

Objectives

- Develop a novel proton conductor based on $La_2Mo_2O_9$ (LAMOX) for use as a H_2 separation membrane.
- Explore compositional development, characterization of the electrical properties, chemical stability, hydrogen flux, and thermomechanical properties; neutron analysis of selected materials to better understand the hydrogen transport properties, and evaluation of surface exchange catalysts.
- Synthesize thin asymmetric membranes (< 25 mm thick) from candidate materials with and without exchange catalysts for additional flux testing to determine the range of fluxes possible in these materials.

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, NETL, and U Cincinnati suggests similar to Y-doped $BaCeO_3$.
- **%H_2 recovery:**
  - to be determined
- **Hydrogen quality:**
  - As for all ion-transport systems, should be 100% H_2
- **Operating temperature, pressure:**
  - T<550°C, P yet to be determined (based on mechanical stability)
- **Durability:**
  - Needs to be stable at temperature in H_2O, CO, and CO_2. H_2S stability to be determined

Approach

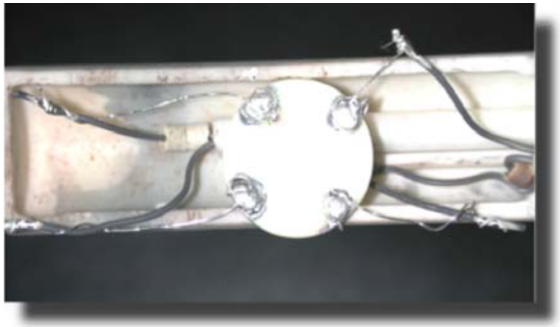
- Atomistic computer simulations to identify potential new proton conducting ceramics
- Rapid high-purity materials synthesis using a modified combustion synthesis process
- Structure and properties (particularly hydrogen flux) characterization
- Long-term stability testing
- Synthesis of thin ceramic membranes on porous ceramic or metal supports

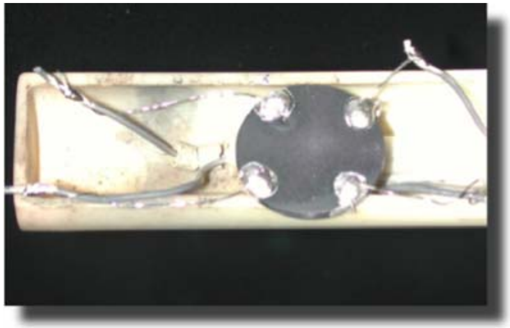
Accomplishments - overview

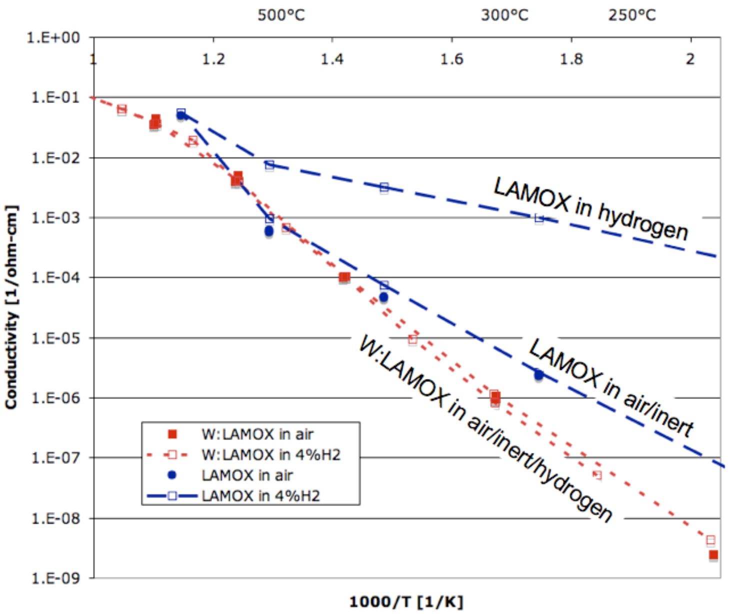
- Crystal structure and phase identification studies using x-ray and neutron diffraction completed for over 100 samples prepared to date
- High temperature conductivity measurements in air completed for over 40 samples to date – hydrogen testing is in progress
- High temperature structure and stability testing by x-ray diffraction completed for several systems in reducing atmospheres.
- Enhanced capabilities for in-situ conductivity measurements established with atmosphere control and capability for measuring High conductivity materials.
- Identified new proton-conducting ceramic oxide with strong potential to meet program requirements.

Accomplishments - Conductivity

- **High temperature conductivity measurements in air and dilute hydrogen completed at ORNL for over 40 samples to date**

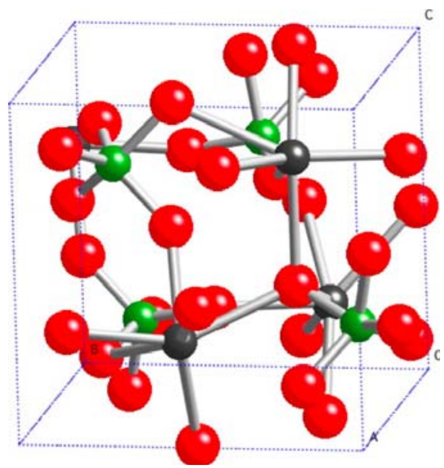


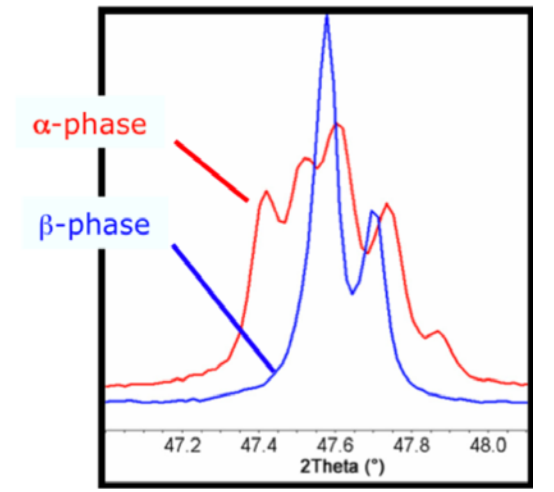




Accomplishments - Structure

- **XRD structure analyses completed at ORNL for doped and undoped samples under different atmospheres and pressures**

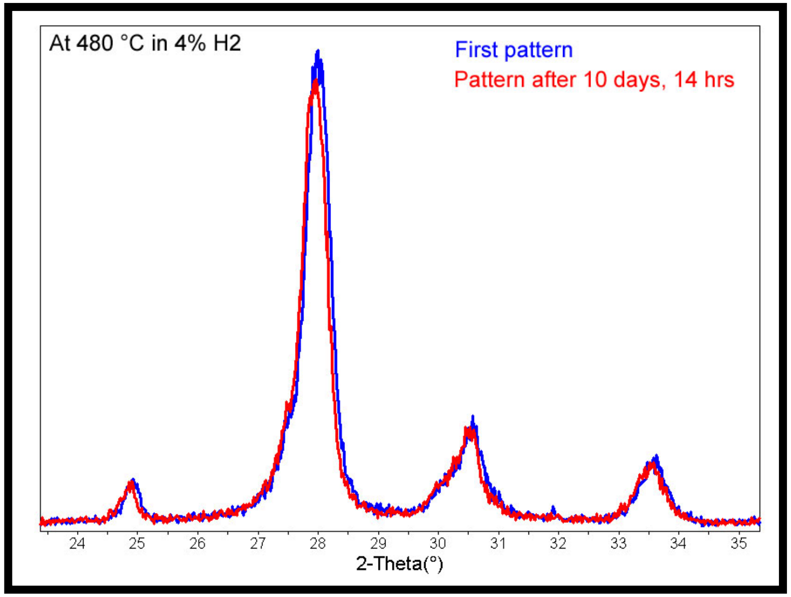


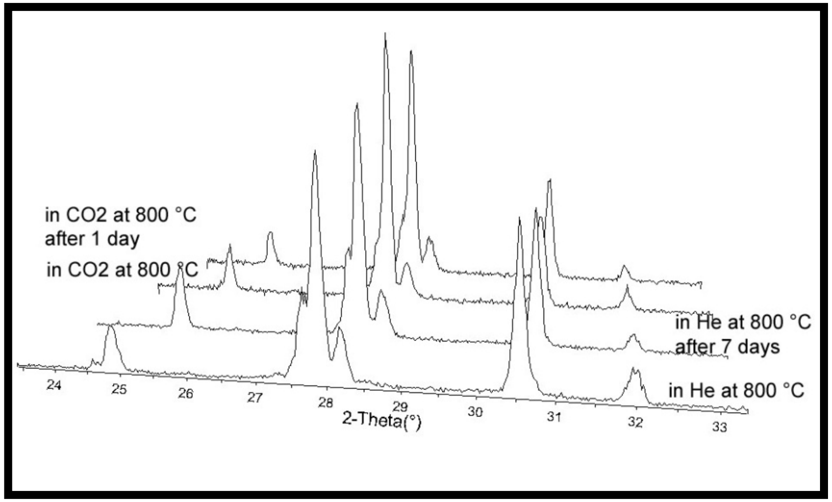


•In-situ XRD data (right) from ORNL reveals that below 550°C, $La_2Mo_2O_9$ relaxes into the α-phase in air, inert, or hydrogen atmosphere. The α-phase (left) is a proton conductor with a complex oxygen sublattice ordering compared to the otherwise similar cubic β-phase.

Accomplishments: stable in H_2 and CO_2

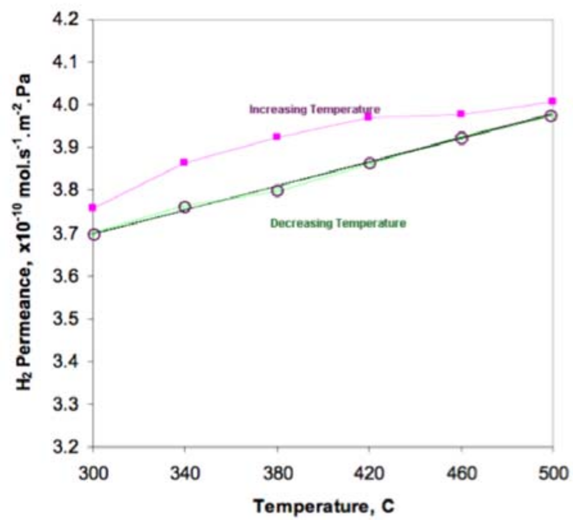
- In-situ HTXRD tests at ORNL demonstrate that $La_2Mo_2O_9$ is stable in H_2 and CO_2
  - Tested for 10+ days in H_2 at ~500°C
  - Tested for 2 days in CO_2 at 800°C - no decomposition





Accomplishments – Permeation Tests

- **Hydrogen permeation tested on bulk ceramic samples at University of Cincinnati (collaboration with Prof. Junhang Dong)**



(top left) University of Cincinnati hydrogen permeation cell with stainless steel components and graphite gasket for gas-tight seal; (bottom left) 1-inch diameter fully-dense LAMOX ceramic with integrated gold seal around perimeter to minimize gas leakage; (top right) Test result on single-phase 2mm thick Pr:LAMOX ceramic

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Hydrogen flux is the single most important performance issue

- **Present literature suggests that hydrogen flux rates of between 5 and 50 mL/min/cm^2 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 $La_2Mo_2O_9$**
- **Results were encouraging: H_2 flux was confirmed in both tests, but the magnitude was only 5 x 10^{-5} mL/min/cm^2**
- **So… how to increase this by 5 to 6 orders of magnitude?**

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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***

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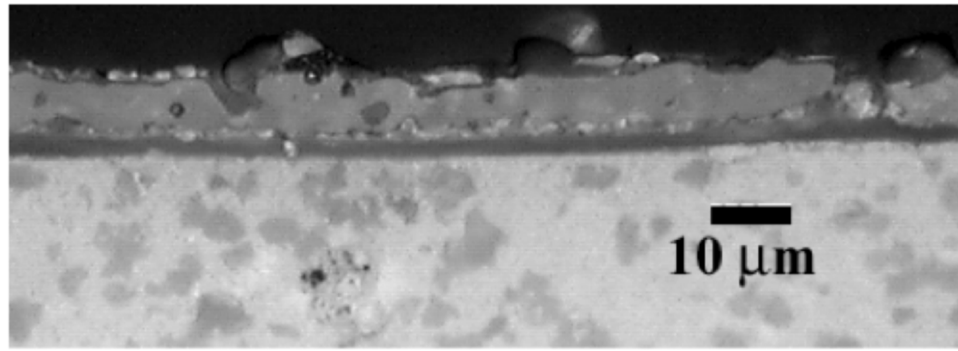
Accomplishments - Processing

- **Synthesized thin (~10μm) dense membranes on porous YSZ substrates.**

Pr-doped LAMOX

8mol%Y-stabilized zirconia



•Porous ceramic supports are required for mechanical strength
•Stabilized zirconia identified as a viable CTE-matched substrate material
•Doped lanthanum molybdates have been screen-printed onto porous 8 mol% yttria stabilized zirconia (8YZ) pellets and sintered
•Membrane thicknesses as low as10 μm have been achieved with good adherence and density.

Collaborations

- **Prof. Junhang Dong, University of Cincinnati**
  - Hydrogen permeation characterization
- **Prof. Stephen Skinner, Imperial College, London**
  - Impedence spectroscopy
- **Dr. Ed Hagaman, Oak Ridge National Laboratory**
  - Nuclear magnetic resonance (NMR) (to identify hydrogen bonding)

Summary

- The LAMOX series of ceramic oxides was identified as potential proton-conductor.
- Detailed characterization of these materials has been carried out
- Improved powder processing methods have enabled undoped samples to be sintered to near theoretical density without tungsten additions.
- 10-20 µm dense membranes of LAMOX, Pr:LAMOX, and Sr:LAMOX on porous YSZ substrates have been synthesized
- NMR studies are in progress to attempt to determine the quantity (and bonding) of hydrogen in LAMOX ceramics