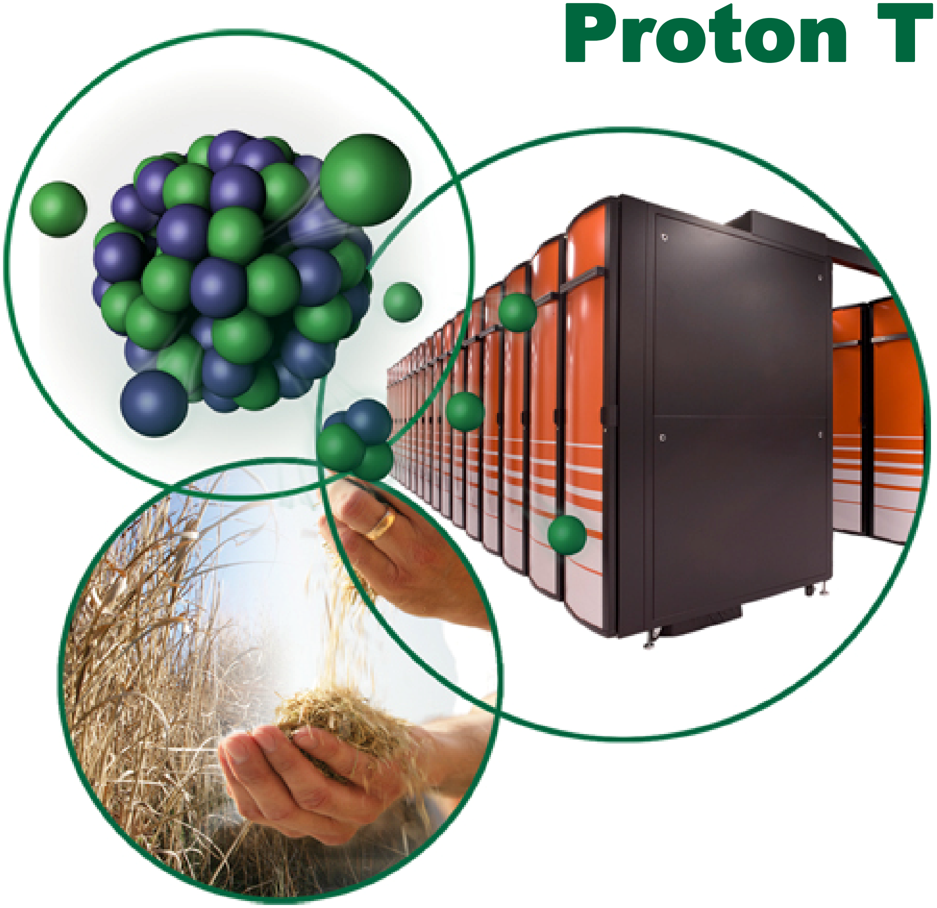
DOE Hydrogen Program

Novel Low-Temperature Proton Transport Membranes



Andrew Payzant

Oak Ridge National Laboratory

June 6, 2008

Project ID# PDP2

Overview

- Timeline
  - Started 02/2004
  - Stopped 12/2004
  - Restarted 04/2007
- Budget
  - FY04: $100k
  - FY05: $45k
  - FY06: $30k
  - FY07: $300k
  - FY08: $250k
- Barriers to be addressed
  - Low H_2 flux
  - Poor mechanical properties
  - Poisoning by CO_2 and H_2S
- Team members
  - Andrew Payzant
  - Beth Armstrong
  - Tim Armstrong
  - Junhang Dong, U. Cincinnati

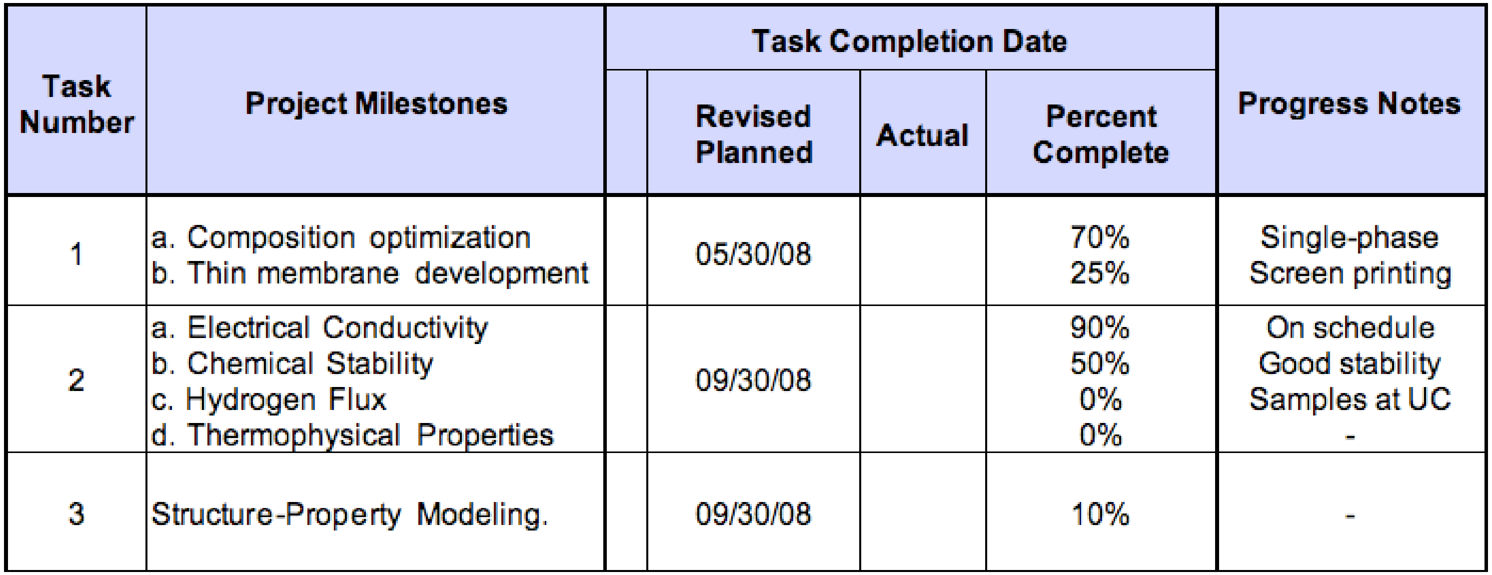
Objective

- The objective is to develop a novel ceramic proton conductor based on $La_2Mo_2O_9$ (LAMOX) for use as a H_2 separation membrane.
- The objective is achieved through:
  - compositional development;
  - characterization of the electrical properties, chemical stability, hydrogen flux, and thermo-mechanical properties;
  - Neutron diffraction analysis of selected materials to better understand the hydrogen transport properties; &
  - evaluation of surface exchange catalysts.
- The goal will be to synthesize thin asymmetric membranes (< 25 μm) 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 and NETL suggests fluxes similar to Y-doped BaCeO3, but at significantly lower temperatures.
- %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:
  - Stable at temperature in H_2O, CO, and CO_2. H_2S stability to be determined

Milestones



Task Number	Project Milestones	Task Completion Date				Progress Notes
			Revised Planned	Actual	Percent Complete	
1	a. Composition optimization b. Thin membrane development		05/30/08		70% 25%	Single-phase Screen printing
2	a. Electrical Conductivity b. Chemical Stability c. Hydrogen Flux d. Thermophysical Properties		09/30/08		90% 50% 0% 0%	On schedule Good stability Samples at UC -
3	Structure-Property Modeling.		09/30/08		10%	-

- **Status as of May 1, 2008: ready for Task 2c: hydrogen flux measurement, in collaboration with Prof. Junhang Dong at the University of Cincinnati**

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**
- **$La_2Mo_2O_9$ was identified as a fast oxygen ion conductor by researchers in France in 1999/2000**
- **Focus elsewhere is on oxygen ion conduction - efforts to stabilize high-temperature β-phase by anion and cation doping**
- **Low temperature α-phase first identified as a possible proton conductor at ORNL in 2003/2004**
  - **Conductivity measured at ORNL and Rutgers University**
  - **H_2 permeance measured at New Mexico Tech (NMT) and NETL**

T.R. Armstrong, E.A. Payzant, S.A. Speakman, M. Greenblatt, *Low Temperature Proton Conducting Oxide*, U.S. Patent Application # US 2006/0292416

Hydrogen flux is the single most important performance issue

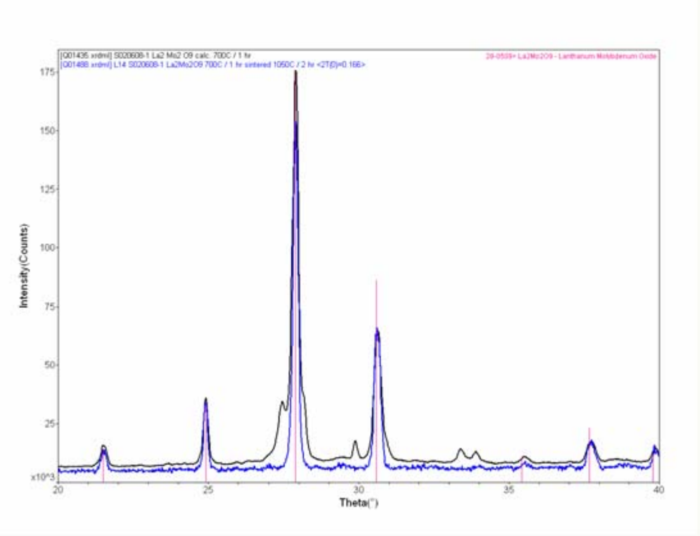
- Present literature suggests that hydrogen flux rates of between 5 and 50 mL/min/cm^2 will be required for commercial application of ceramic membranes
- In 2004 we made two preliminary measurements (at NMT and NETL) of hydrogen flux in 3mm thick samples of W-doped and Nb-doped $La_2Mo_2O_9$
- Results 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 flux by 5 to 6 orders of magnitude?

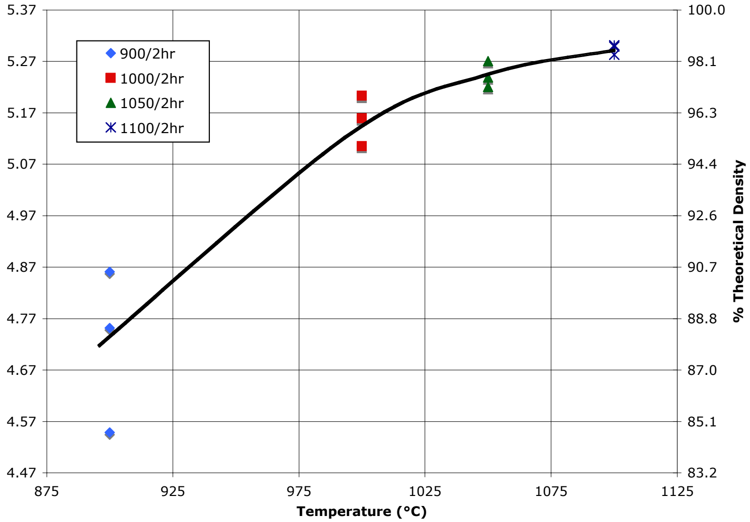
Strategies for increasing hydrogen flux

- **Task 1: Reduce sample thickness**
  - Reduction from mm to µm dimensions will provide a 2 order of magnitude increase in flux based on the Nerst equation
- **Task 2: Increase H_2 pressure differential**
  - Initial tests were done at a low Nernst potential: near 1 atm, with dilute H_2 on the source side and inert sweep gas on the other
  - Gain is logarithmic, so perhaps an order of magnitude gain in flux could be realized
- **Task 3: 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
  - Potential improvements are not predicable at this time
- **Task 4: 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

- ***Therefore, flux gains of 4-5 orders of magnitude are realistically achievable in this system, which would make it comparable to established dense ceramic or cermet membranes, <u>but with improved stability</u>***

Dense phase-pure ceramics are made from combustion synthesized powder

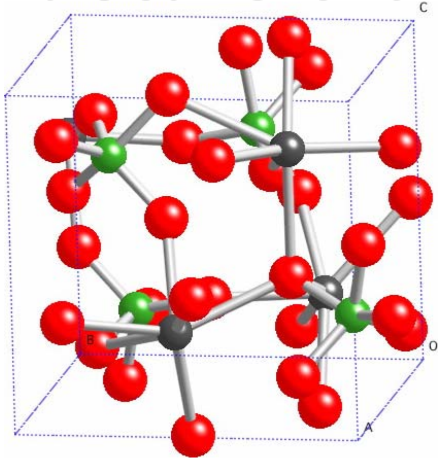




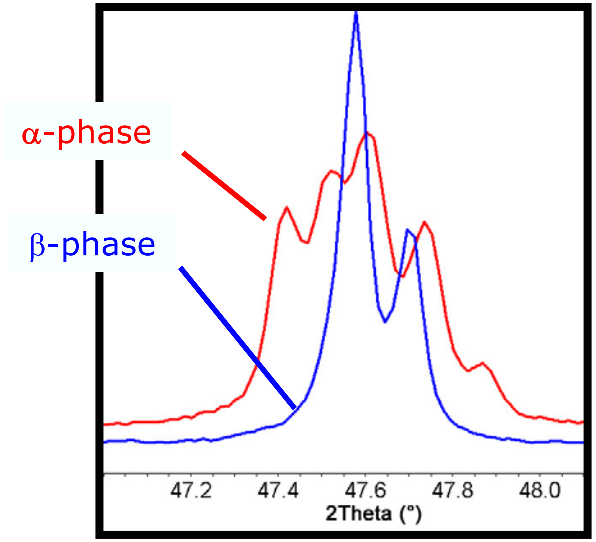
The XRD patterns contrast the as-prepared powder (gray) and the fully sintered ceramics (blue) - the latter are phase-pure LAMOX.

Undoped LAMOX powders sintered to >95% of theoretical density in 2 hours at temperatures above 1000°C.

α-phase $La_2Mo_2O_9$ has a more complex structure than perovskite or pyrochlore

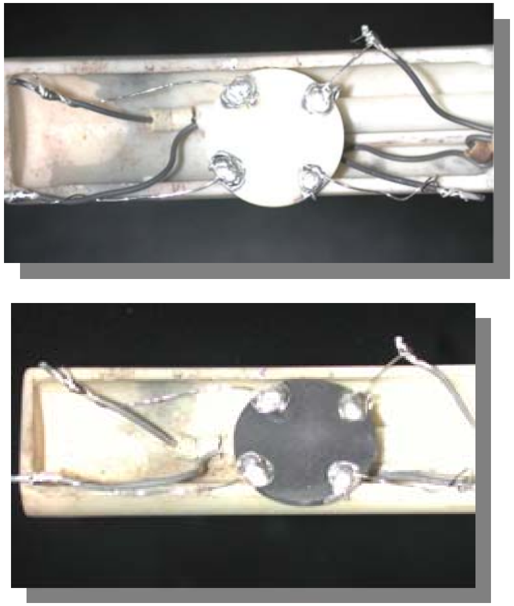


- The high-temperature β-phase $La_2Mo_2O_9$ is a fast oxygen-ion conductor while the α-phase is not.
  - W-doping stabilizes the β-phase at lower temperatures, and (at least in homogeneous phase-pure samples) suppresses the proton conduction

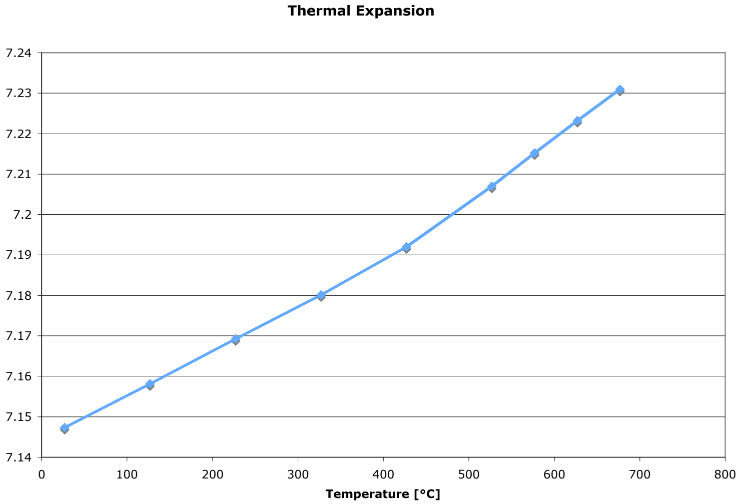


- In-situ XRD data from at ORNL reveals:
  - Below 550°C, $La_2Mo_2O_9$ relaxes into the α-phase in air, inert, or hydrogen atmosphere
  - The α-phase is a proton conductor with a complex oxygen sublattice ordering compared to the β-phase
  - Pr-doping dilates the $La_2Mo_2O_9$ lattice, but retains the α-phase structure, yielding slightly higher proton conductivity

The $La_2Mo_2O_9$ phase transformations are fully reversible

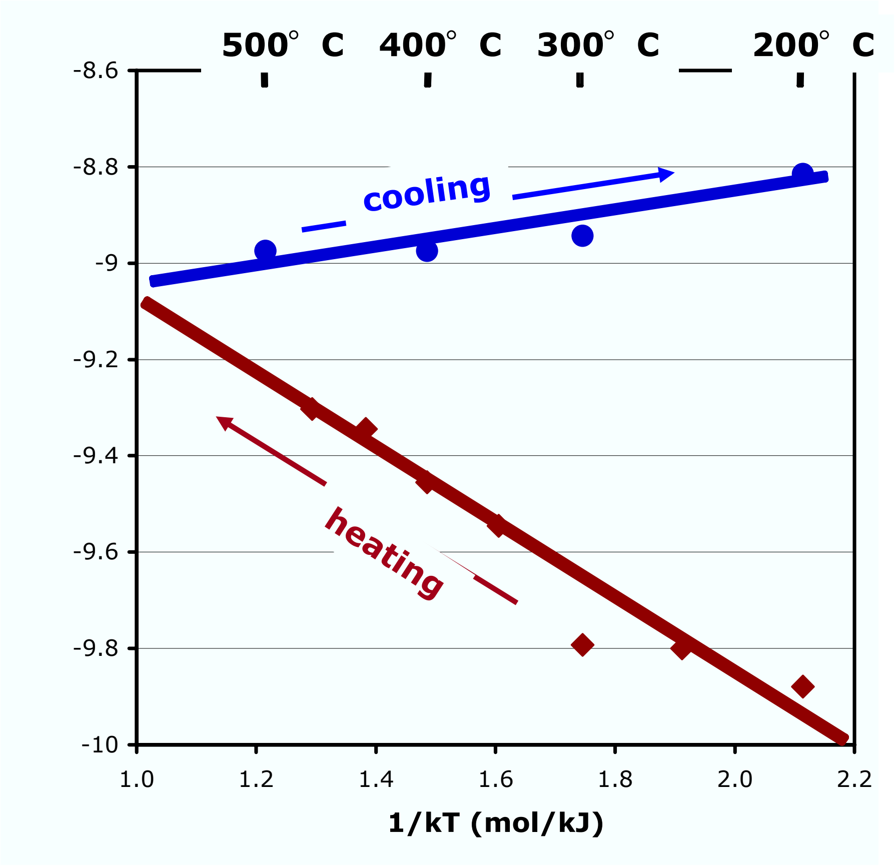


Undoped LAMOX samples reversibly turn black in hydrogen, white in air, with no structural degradation

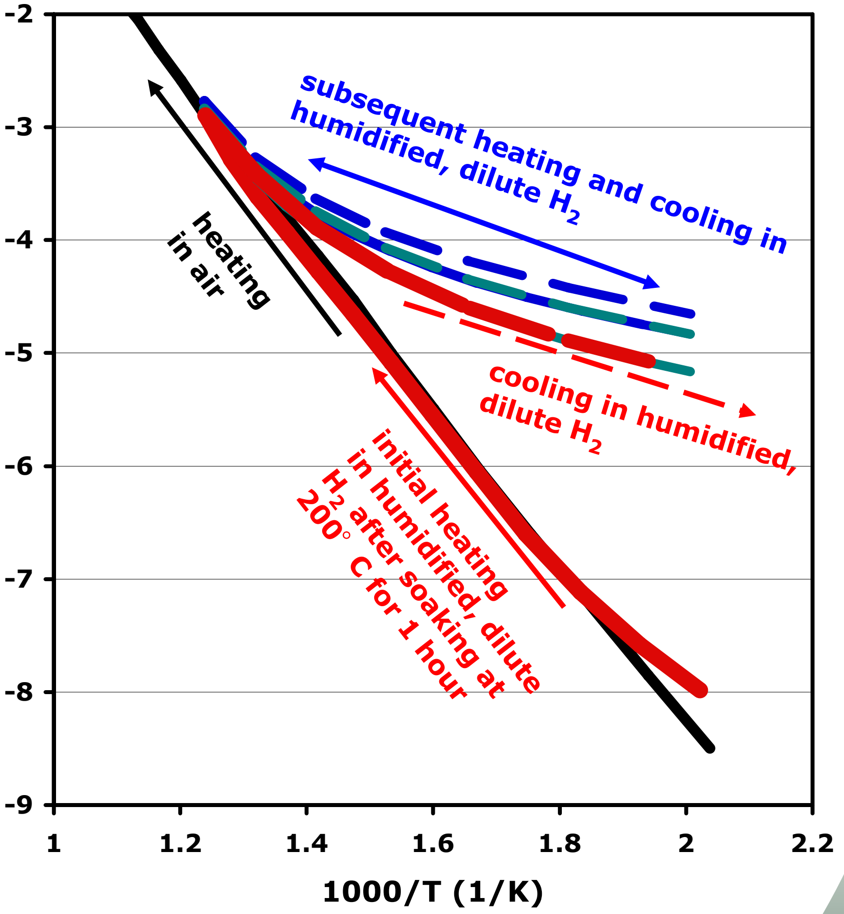


Because the phase transformation is related to ordering of oxygen vacancies, it should not result in large intergranular stresses and mechanical failure of the ceramic, nor to debonding from a support with reasonably matched thermal expansion

Lanthanum molybdates exhibit proton conductivity and hydrogen flux

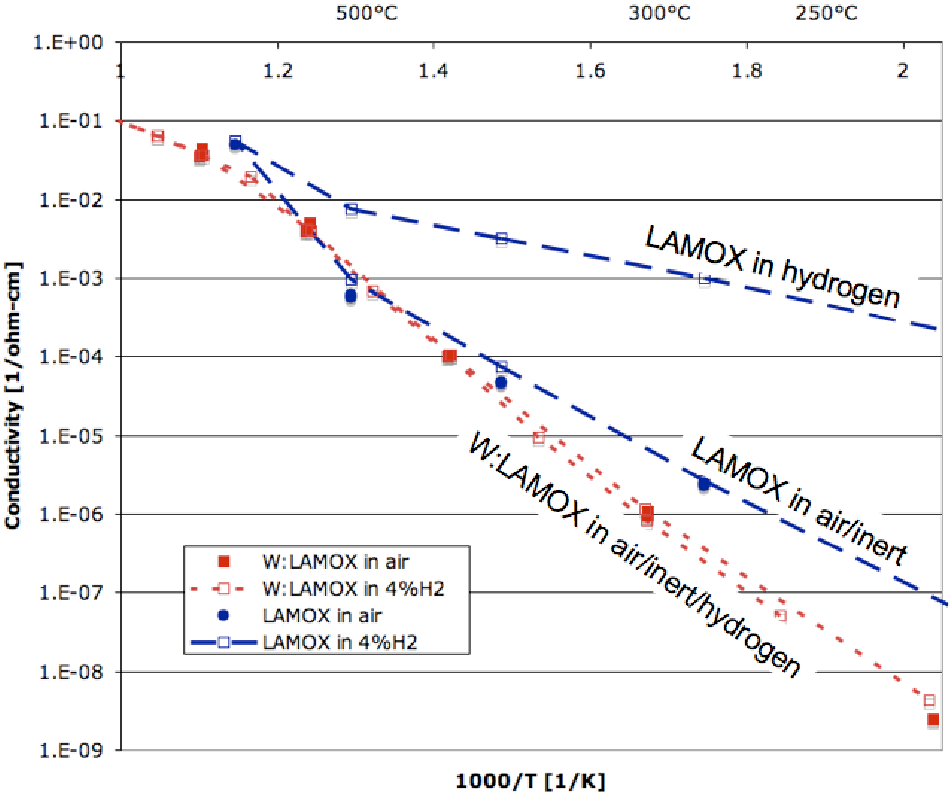


Hydrogen flux



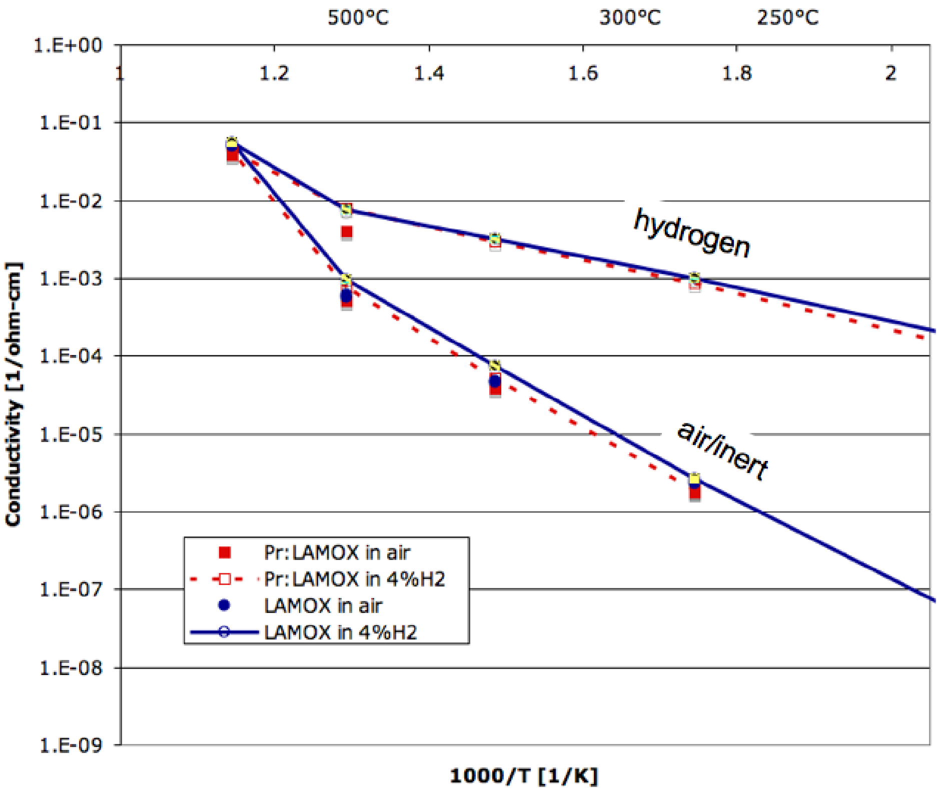
Conductivity

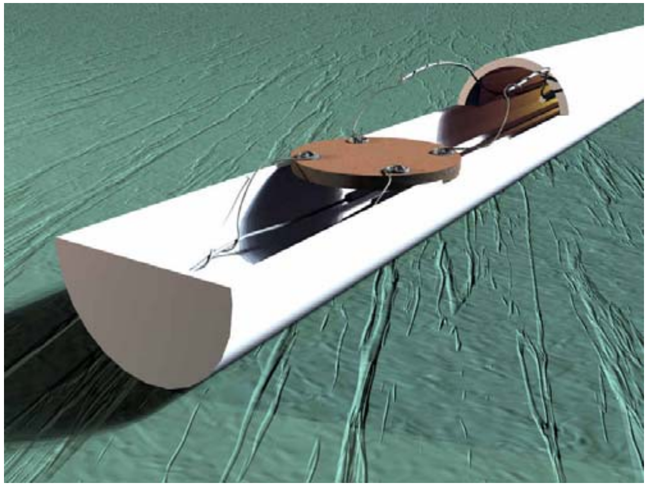
The α-phase structure is essential for the elevated conductivity in H_2



- W-doping can be used to stabilize the high-temperature β-phase LAMOX structure, but the conductivity of the stabilized phase is not sensitive to presence of H_2.
- Working to understand why the ordered defect structure is a proton conductor, whereas the disordered defect structure is a better oxygen ion conductor.

Conductivity of 10% Pr-doped LAMOX is similar to undoped LAMOX



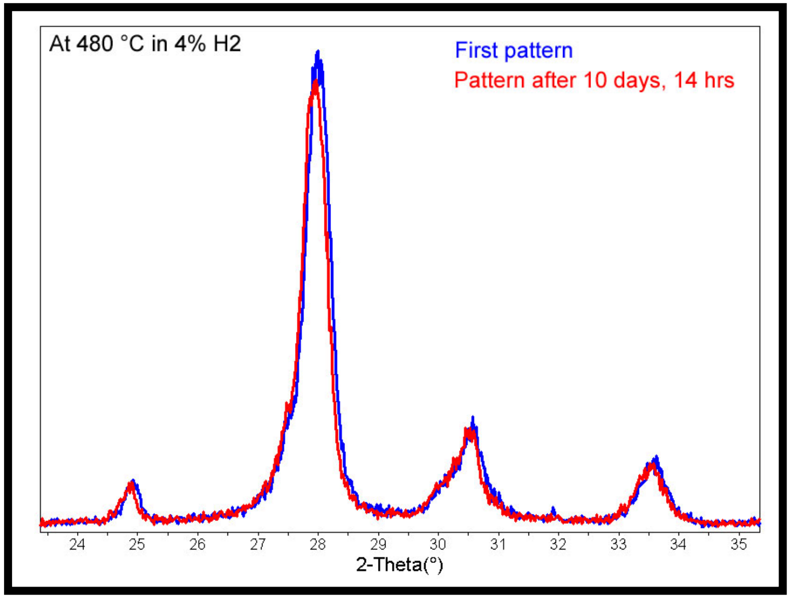


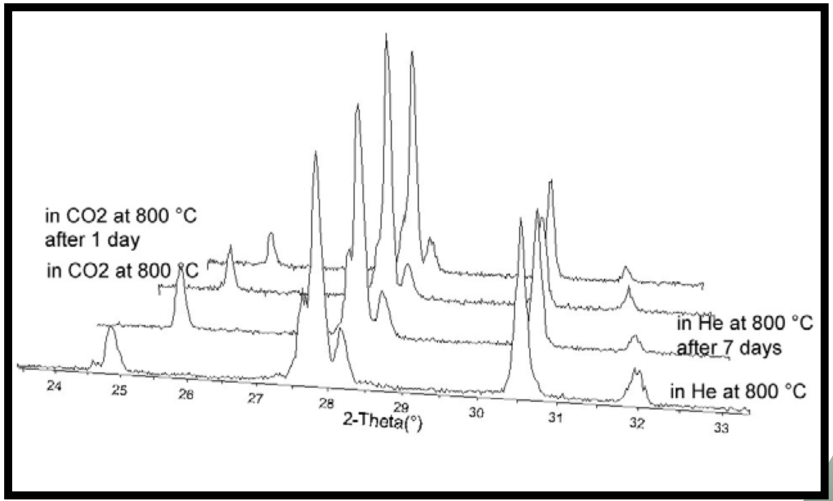
Sample mounted for 4-point conductivity measurement

- **Pr:LAMOX conductivity same as LAMOX, with same increased conductivity in H_2 atmosphere compared to air or inert**
- **No loss in conductivity from doping, but no gain from increased free volume**

$La_2Mo_2O_9$ is stable in H_2 and CO_2

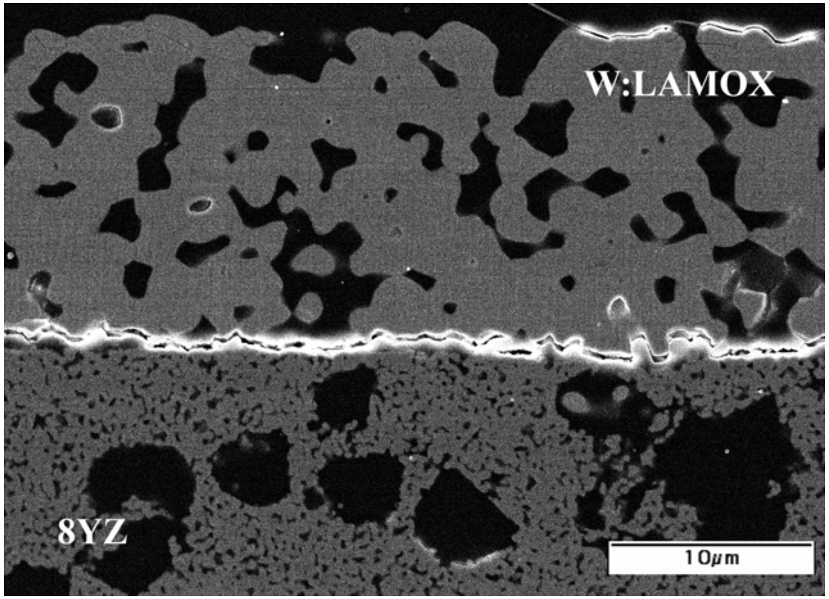
- **In-situ HTXRD tests at ORNL demonstrate that $La_2Mo_2O_9$ is stable in H_2 and CO_2**
  - **Tested for 10+ days in H_2 at ~500°C**
  - **Tested for 2 days in CO_2 at 800°C - no decomposition**





Thin supported membranes of $La_2Mo_2O_9$ have been fabricated

- W-doped lanthanum molybdate (W:LAMOX) was screen printed onto porous support.
- Although full density was not realized initially, thin (< 20 μm), adherent, and conformal layers were achieved.



SEM micrograph of a W:LAMOX membrane supported on a porous 8mol% Yttria Stabilized Zirconia (8YSZ) substrate.

Collection of hydrogen permeation data on $La_2Mo_2O_9$ is in progress

- Suitable 1-inch diameter dense ceramic membranes have been synthesized at ORNL, with gold seals to minimize gas leakage

Hydrogen permeation cell at the University of Cincinnati. Leakage tests have been completed as of 05/01/2008 and permeation tests are in progress

Progress and Future Work

- Task 1: reduce sample thickness
  - FY2007: phase-pure bulk powders via combustion synthesis
  - FY2007: thin samples via tape casting, followed by lamination, pressing and firing
  - FY2007: inks developed for screen printing ultra-thin membranes on porous supports
  - FY2008: successful thin (<20µm) membrane deposited on YSZ support
- Task 2: increase H_2 pressure differential
  - Porous supports are needed to provide adequate mechanical strength
  - FY2008 will establish suitable supports to avoid stresses and diffusion
- Task 3: increase proton conductivity
  - FY2007/08 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: FY2007/08 W improves sinterability but stabilizes β-phase; FY2004 Nb found to generate problematic impurity phases
  - A-site doping: FY2007 Ba appears good choice to increase oxygen vacancy concentration, but FY2008 we find little change in conductivity; FY2007/08 Pr appears good choice with larger lattice parameter and more free volume, but no change in conductivity
- Task 4: increase H_2 to proton dissociation rate
  - No significant gains observed to date for humidified versus dry 4%H_2
  - FY2008 will investigate effect of dispersed Ni or Pd catalysts

Project Summary

- Homogeneous powders 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 initially 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
- New Ba-doped (α-phase) material shows similar proton conduction to undoped material
- Porous supports being investigated - YSZ considered.

Acknowledgments

- This program presently includes significant technical support from John Henry, Jr. (ORNL), Robbie Peascoe (ORNL), Claire Chisholm (UTK), and Zhong Tang (UC).
- Past team members at ORNL included Scott Speakman, Robert Carneim, and Glen Kirby.