

## II.A.10 Novel Low-Temperature Proton Transport Membranes

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direction determined annually by DOE

### Objectives

- To develop a novel proton conductor based on  $\text{La}_2\text{Mo}_2\text{O}_9$  (LAMOXY) for use as a  $\text{H}_2$  separation membrane.
- To 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.
- To synthesize thin asymmetric membranes ( $<25 \mu\text{m}$  thick) from candidate materials with and without exchange catalysts for additional flux testing to determine the range of fluxes possible in these materials.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Fuel Processor Capital Costs
- (AB) Hydrogen Separation and Purification

### Approach

- Rapid high-purity materials synthesis using a modified combustion synthesis process.
- Structure and properties (particularly hydrogen flux) characterization.

- Long-term stability testing.
- Atomistic computer simulations to identify potential new proton conducting ceramics.

### Accomplishments

- 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 (XRD) 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.

### Future Directions

- Expand Analytical Interatomic Potential computer models.
- Refine models of hydrogen transport.
- Determine hydrogen flux as a function of temperature and pressure for candidate compositions.
- Characterize long-term stability of candidate materials under service conditions.
- Develop metal-supported asymmetric membranes using ORNL support tubes.



### Introduction

Current alkaline earth perovskite high-temperature proton conductors either have low conductivities or are highly susceptible to chemical attack by contaminants such as sulfur ( $\text{H}_2\text{S}$ ) and  $\text{CO}_2$ . The LAMOXY family of materials is a promising new class of proton conductors with potential as a hydrogen separation membrane.

In Fiscal Years 2004/2005 ORNL demonstrated that LAMOXY, specifically Nb- and W-doped  $\text{La}_2\text{Mo}_2\text{O}_9$ , are proton conductors at temperatures below  $550^\circ\text{C}$ . This was a new finding, as no oxide studied to that date had demonstrated significant proton conduction at temperatures less than  $500^\circ\text{C}$ . Proton conduction in

materials developed by ORNL was confirmed through independent measurements of hydrogen permeation at the New Mexico Institute of Mining and Technology (New Mexico Tech) and at the National Energy Technology Laboratory (NETL). The low-temperature conductivity was not as high as that of  $\text{BaCeO}_3$ ; however,  $\text{BaCeO}_3$  is unstable in all  $\text{CO}_2$  and  $\text{H}_2\text{S}$  containing environments and as a result has been largely abandoned for membrane applications.

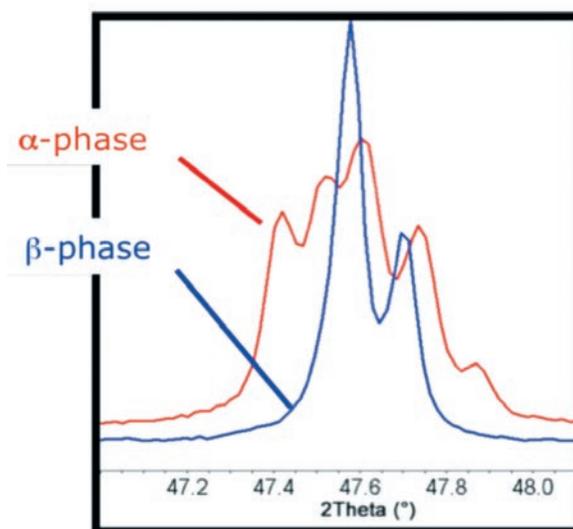
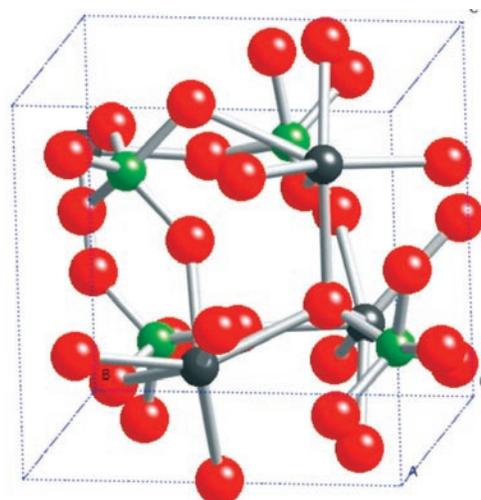
It appears that proton conduction is most pronounced in the  $\alpha$ -LAMOX phase, a complex polymorph of the fast oxygen-ion conducting cubic  $\beta$ -LAMOX phase (Figure 1). Additional experiments demonstrated that the low-temperature  $\alpha$ -phase of these LAMOX ceramics was much more stable than the high-temperature  $\beta$ -phase. LAMOX  $\alpha$ -phase ceramics did not decompose when exposed to reducing environments of  $\text{N}_2$ -4% $\text{H}_2$  at  $\sim 500^\circ\text{C}$  for over 10 days; in  $\text{CO}_2$  at  $800^\circ\text{C}$  for over 5 days; and in humidified  $\text{N}_2$ -4% $\text{H}_2$  at  $550^\circ\text{C}$  for over 3 days. These limited tests do not prove long-term stability of these materials, but are very encouraging.

Several characteristics of the LAMOX-based proton transport membrane are not well understood. For example, the LAMOX electrolyte must be heated to  $\sim 500^\circ\text{C}$  in humidified  $\text{H}_2$  before appreciable hydrogen flux can be measured; however, after the electrolyte is 'activated' at  $500^\circ\text{C}$ ,  $\text{H}_2$  conduction persists as the membrane is cooled to temperatures as low as  $200^\circ\text{C}$  and possibly even lower. Additionally, after 'activation' the  $\text{H}_2$  flux actually increases as the temperature is decreased. The mechanism by which protons migrate through the membrane is not currently understood, nor is the limit of hydrogen uptake. Furthermore, the mechanism of dissociation of the fuel at surface sites is not understood, nor is its impact on the overall flux - surface dissociation is often the rate-limiting step in proton conduction.

## Approach

For hydrogen separation applications, hydrogen flux is the single most important performance issue. Present literature suggests that hydrogen flux rates of between 5 and 50  $\text{mL}/\text{min}/\text{cm}^2$  will be required for commercial application of ceramic membranes.

Measurements of electrical conductivity on LAMOX samples revealed a significant increase in conductivity of the low-temperature alpha phase under reducing atmosphere. From these measurements alone the contributions from electrical, oxygen ion, and proton conductivity cannot be distinguished. In FY 2004 preliminary measurements (at New Mexico Tech and NETL) of hydrogen permeation were made on 3 mm thick samples of W-doped and Nb-doped  $\text{La}_2\text{Mo}_2\text{O}_9$ . These results were encouraging in that  $\text{H}_2$  permeation



**FIGURE 1.** In situ XRD data (right) from ORNL reveals that below  $550^\circ\text{C}$ ,  $\text{La}_2\text{Mo}_2\text{O}_9$  relaxes into the  $\alpha$ -phase in air, inert, or hydrogen atmosphere. The  $\alpha$ -phase (left) is a proton conductor with a complex oxygen sublattice ordering compared to the cubic  $\beta$ -phase.

was confirmed in both tests, however the magnitude was only about  $5 \times 10^{-5} \text{ mL}/\text{min}/\text{cm}^2$ .

In order to increase the hydrogen flux, four possible strategies were proposed, and tasks were assigned so that these could be done in parallel to speed development.

1. Reduce sample thickness – reduction from mm to  $\mu\text{m}$  dimensions will provide a 2-3 order of magnitude increase in flux based on the Nernst equation.
2. Increase  $\text{H}_2$  pressure differential – initial tests were done at a low Nernst potential: near 1 atm, with dilute  $\text{H}_2$  on the source side and inert sweep gas on the other. Such gain is logarithmic, so perhaps only an order of magnitude gain in flux might be realized,

and consequently this approach was not pursued as part of the FY 2008 work.

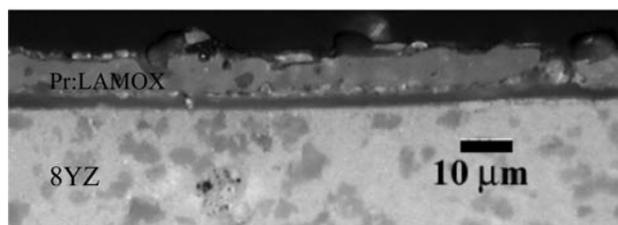
- Increase bulk proton conductivity – modifying the crystal chemistry with substitutional ion dopants could increase the mobility of protons within the structure, and/or alter the ratio of proton to electron conductivity. This approach in other solid oxide fuel cell systems had led to considerable success, but the magnitude of potential improvements are not yet predictable in the LAMOX system.
- Increase  $H_2$  to proton dissociation rate - use of surface catalysts has proven effective in the cerate systems and could provide 1-2 orders of magnitude increase in flux

Therefore, overall flux gains of 4-5 orders of magnitude appear to be realistically achievable in this system, which would make it comparable to established dense ceramic or cermet membranes, but with improved stability.

## Results

To address the primary task of reducing the sample thickness to increase the hydrogen flux, synthesis of thin LAMOX membranes on porous ceramic supports was initiated as thin plates of LAMOX are not mechanically robust. Thermal expansion data collected at ORNL suggested zirconia as a reasonably matched substrate material. Tungsten-doped lanthanum molybdate (W:LAMOX) was screen printed onto porous 8 mol% yttria stabilized zirconia (8YZ) pellets and sintered. The W:LAMOX material system was selected initially as a baseline for the supported asymmetric membrane task initially due to vast monolithic test data existing on this system. Although full density was not realized initially, thin (<20 μm), adherent, and conformal layers were achieved. This success was extended to praseodymium-doped lanthanum molybdate (Pr:LAMOX), which was also successfully screen printed onto porous 8YZ pellets and sintered (Figure 2). Note the decrease in membrane thickness (to ~10 μm) as well as the increase in the density of the Pr:LAMOX layer.

In order to increase the bulk proton conductivity and thereby increase the hydrogen flux, compositional development of LAMOX continued during FY 2008. Pr:LAMOX and niobium-doped lanthanum molybdate (Nb:LAMOX) were prepared. Pr:LAMOX was examined to determine if the greater free volume in this material (resulting from the larger ionic radius of Pr compared to La) might result in enhanced proton mobility. Test coupons made from  $(La_{1.5}Pr_{0.5})Mo_2O_9$  and  $(La_{1.2}Pr_{0.8})Mo_2O_9$  powders and sintered at 1050°C for 2 hours achieved greater than 95% theoretical density. Samples of LAMOX, W:LAMOX, Pr:LAMOX and Nb:LAMOX were prepared and shipped to University of Cincinnati (UC) for hydrogen permeation testing.



**FIGURE 2.** Scanning electron micrograph of a ~10 μm thick Pr:LAMOX membrane supported on a porous 8 mol% yttria stabilized zirconia substrate.

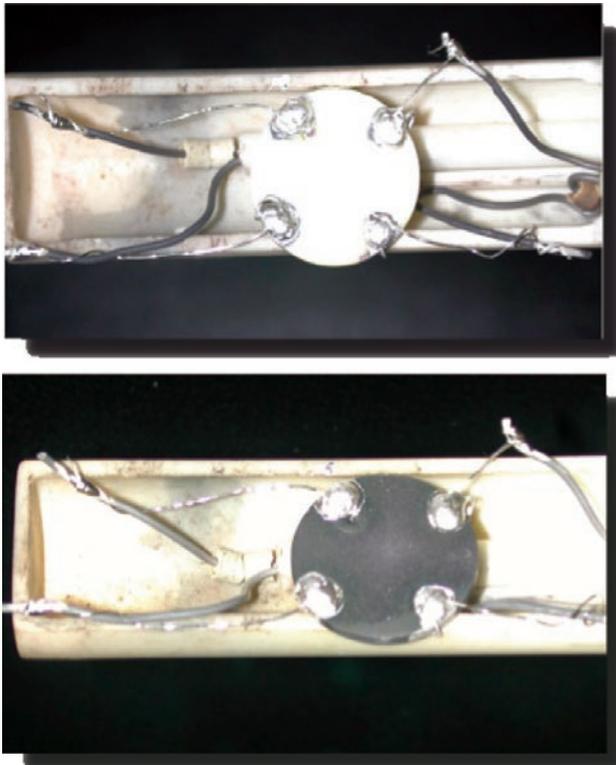
Nb:LAMOX was examined previously, however, concern over its long term stability and its tendency to form secondary phases resulted in it being dropped as a candidate material. Improved synthesis methods developed during FY 2008 prompted a re-evaluation of this material. It was found that significantly higher sintering temperatures (>1,250°C) were required to achieve greater than 95% theoretical densities in the  $La_2(Mo_{1.5}Nb_{0.5})O_9$  pellets. However, a secondary phase was again found in the Nb doped samples, even with lower Nb concentrations, so further work on this system was discontinued. In contrast, barium- and dysprosium-doped lanthanum molybdate (Ba:LAMOX, Dy:LAMOX) yielded excellent single-phase material, which allowed study of proton conduction as a function of dopant valence, substitutional site, and concentration.

Ceramic discs of LAMOX, strontium-doped lanthanum molybdate (Sr:LAMOX), Pr:LAMOX and W:LAMOX were prepared, and 4-wire electrical conductivity (consisting of electronic and ionic components) was characterized as a function of temperature in dry and wet air, as well as inert and hydrogen atmospheres. A typical set-up is shown in Figure 3, which also shows the reversible effect of reducing atmosphere on the sample appearance. Multiple samples were tested for each composition, with excellent reproducibility.

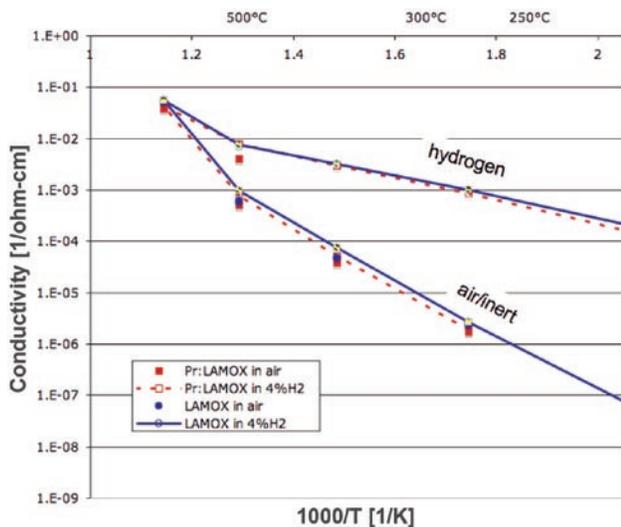
Pr:LAMOX was examined to determine if the larger ionic radius of Pr compared to La might result in enhanced proton mobility. As shown in Figure 4, the electrical conductivity was not significantly different compared to undoped LAMOX. These results indicate that lanthanum may be readily substituted by other lanthanide elements, but without much change in the conductivity.

LAMOX-based ceramics have excellent stability in  $H_2$  and  $CO/CO_2$  (Figure 5) compared to proton-conducting ceramics such as cerate-based perovskites, containing alkali earth elements (Ca, Sr, or Ba) that tend to decompose to more stable carbonates.

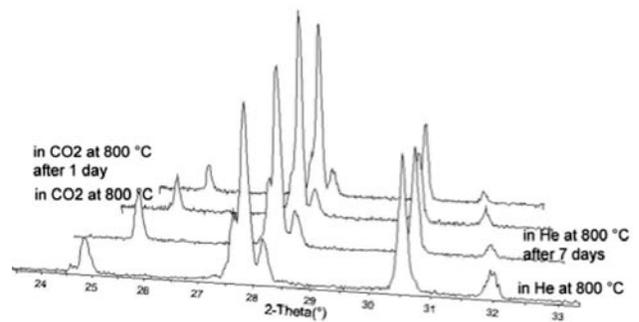
Tungsten was partially substituted for molybdenum primarily in a successful attempt to improve the sinterability of LAMOX, but these substitutions stabilized the  $\beta$ -phase to room temperature.



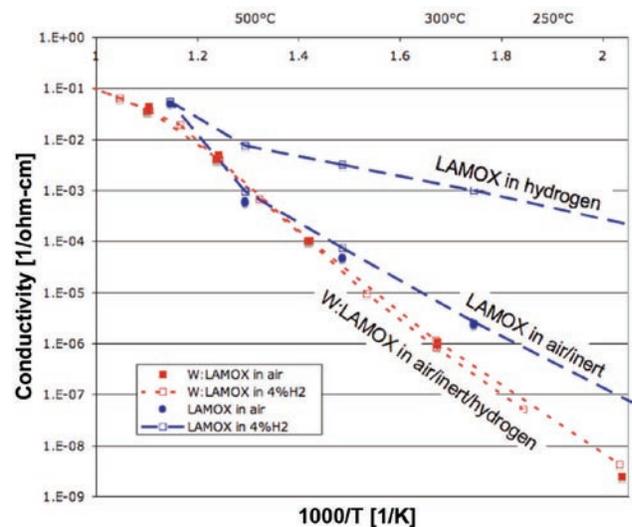
**FIGURE 3.** Ceramic disks with electrodes and platinum wires attached in an alumina holder for 4-wire conductivity tests, using the van der Pauw method. Note that undoped LAMOX samples at high temperatures reversibly turn black in hydrogen, and white in air, with no structural or mechanical degradation so long as the maximum temperature is kept below ~550°C.



**FIGURE 4.** Electrical conductivity of Pr-doped (Pr:LAMOX). The conductivity is not significantly different from that of undoped LAMOX, however both compositions show orders of magnitude enhanced conductivity in 4% H<sub>2</sub>.



**FIGURE 5.** In situ high-temperature XRD tests at ORNL demonstrate that La<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> is stable in pure CO<sub>2</sub> at 800°C, with no change in the XRD after 24 hours. The figure also shows stability in inert atmosphere (helium) after 7 days at 800°C.



**FIGURE 6.** Comparison of undoped (LAMOX) and tungsten-doped (W:LAMOX). Note lower conductivity of W:LAMOX, and no change under 4% H<sub>2</sub>, compared with undoped LAMOX.

Consequently, as confirmed by our conductivity results (Figure 6) hydrogen (i.e., proton) conductivity is a characteristic of the low-temperature  $\alpha$ -phase only, and no conductivity increase was observed in the W:LAMOX samples under H<sub>2</sub>.

**Flux Measurements:** A hydrogen permeation test rig at UC was used to make permeation measurements on candidate samples in collaboration with Prof. Junhang Dong. Thick (2-3 mm) ceramic samples were made from the latest materials to conform to the required dimensions of the UC measurement system (Figure 7). The UC tests gave results (Figure 8) comparable to the fluxes measured in 2004 but with improved accuracy.

The next phase of this study will be to test the hydrogen permeation of the new dense thin (10  $\mu$ m)

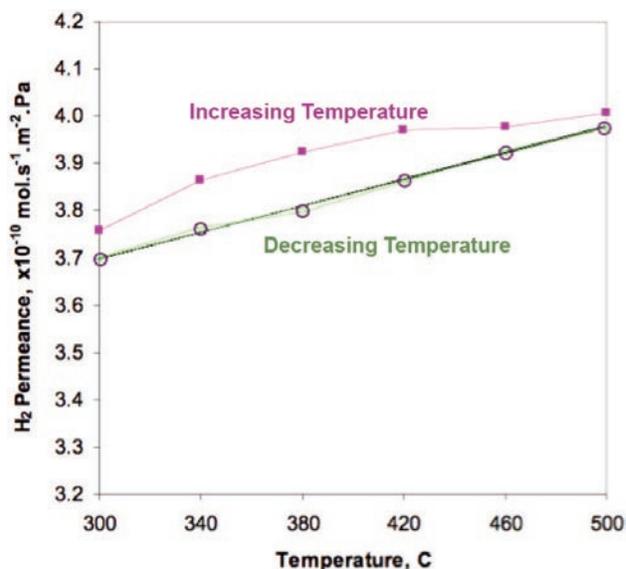


**FIGURE 7.** (top) UC hydrogen permeation cell with stainless steel components and graphite gasket for gas-tight seal; (bottom) 1-inch diameter fully-dense LAMOX ceramic with integrated gold seal around perimeter to minimize gas leakage.

supported ceramic membranes to see if the expected gains in permeation are realized.

### Review of Progress to Date

- FY 2007: phase-pure bulk made via combustion synthesis.
- FY 2007: thin samples made via tape casting, followed by lamination, pressing and firing.
- FY 2007/2008: inks developed for screen-printing ultra-thin membranes on porous supports.
- FY 2008: successful thin (<20  $\mu\text{m}$ ) membranes deposited on yttria stabilized zirconia (YSZ) support.
- FY 2007/2008 improvements in ceramic processing have allowed us to synthesize bulk quantities of powders, and establish correct sintering conditions to make dense single-phase membranes.
- FY 2007/2008 W improves sinterability but stabilizes  $\beta$ -phase; FY 2004 Nb found to generate problematic impurity phases.
- FY 2007 Ba appears good choice to increase oxygen vacancy concentration, but FY 2008 we find little change in conductivity; FY 2008 Sr doping found to be similar to Ba. FY 2007/2008 Pr appears good choice with larger lattice parameter and more free



**FIGURE 8.** Test Result from UC on Single-Phase 2 mm Thick Pr:LAMOX Ceramic

volume, but no change in conductivity is observed. Additional work is ongoing.

- FY 2008: no significant gains observed to date for humidified versus dry 4% H<sub>2</sub>.

### Conclusions

A new approach to development of proton-conducting ceramics, combining atomistic modeling and structure-properties characterization was developed at ORNL, through which the LAMOX series of ceramic oxides was identified as potential proton-conductor. Detailed characterization of these materials has been carried out using XRD (phase analysis, crystal structure), in situ high-temperature XRD (phase stability), and electrical conductivity in controlled temperature and gas environments. Hydrogen permeation tests were performed at UC.

Homogeneous powders are now routinely made by combustion synthesis from stock solutions. High quality samples are 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 improved powder processing methods developed in FY 2008 have enabled undoped samples to be sintered to near theoretical density without tungsten additions.

New undoped ( $\alpha$ -phase) samples confirmed previous conductivity results, and new W-doped ( $\beta$ -phase) material shows no proton conduction (as expected). New Pr-doped ( $\alpha$ -phase) material shows proton conduction similar to undoped LAMOX. New Ba-doped and Sr-doped ( $\alpha$ -phase) material shows

proton conduction similar to undoped LAMOX. YSZ was identified as a suitable material for porous supports, and 10-20  $\mu\text{m}$  thick membranes of LAMOX, Pr:LAMOX, and Sr:LAMOX on porous YSZ have been synthesized.

Further work in FY 2008 and into FY2009 will focus on characterization (in particular hydrogen permeation) of thin supported membranes, nuclear magnetic resonance studies are in progress to attempt to determine the quantity (and bonding) of hydrogen in LAMOX ceramics.

### **FY 2008 Publications/Presentations**

1. E.A. Payzant presented a project update to the Hydrogen Separations and Purification Working Group Meeting at Columbia, MD on November 7, 2007.