

II.C.4 Novel Low-Temperature Proton Transport Membranes

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Objectives

- To develop a novel proton conductor based on $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX) for use as a 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 microns 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:

- (A) Reformer Capital Costs
- (N) Hydrogen Selectivity

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 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 (H_2S) and CO_2 . The LAMOX family of materials is a promising new class of proton conductors with potential as a hydrogen separation membrane.

In Fiscal Year 2004/2005 ORNL demonstrated that LAMOX, specifically Nb- and W-doped $\text{La}_2\text{Mo}_2\text{O}_9$, are proton conductors at temperatures below 550°C . ***This was a new finding, as no oxide studied to that date had demonstrated significant proton conduction at temperatures less than 500°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 and at the National Energy Technology Laboratory. The low-temperature conductivity was not as high as that of BaCeO_3 ; however, BaCeO_3 is unstable in all CO_2 and H_2S 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. Additional experiments demonstrated that the low-temperature α -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 N_2 -4% H_2 at $\sim 500^\circ\text{C}$ for over 10 days; in CO_2 at 800°C for over five days; and in humidified N_2 -4% H_2 at 550°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 H_2 before appreciable hydrogen flux can be measured; however, after the electrolyte is 'activated' at 500°C , H_2 conduction persists as the membrane is cooled to temperatures as low as 200°C and possibly even lower. Additionally, after 'activation' the 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 the National Energy Technology Laboratory) 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 H_2 permeation 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 μm dimensions will provide a 2-3 order of magnitude increase in flux based on the Nernst equation.
- (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. 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.
- (3) 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 (SOFC) systems had led to considerable success, but the magnitude of potential improvements are not yet predictable in the LAMOX system.
- (4) 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 (8YSZ) 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 ($<20 \mu\text{m}$), 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 8YSZ pellets and sintered (Figure 1). Note the decrease in

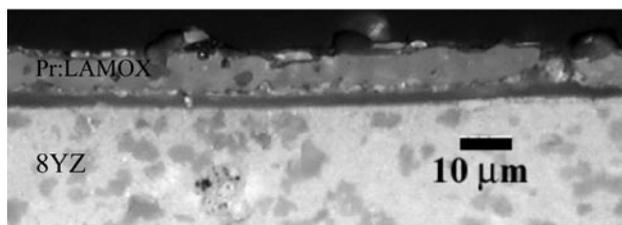


FIGURE 1. Scanning electron micrograph of a $\sim 10 \mu\text{m}$ thick Pr:LAMOX membrane supported on a porous 8 mol% yttria stabilized zirconia substrate.

membrane thickness (to $\sim 10 \mu\text{m}$) as well as the increase in the density of the Pr:LAMOX layer.

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 ($>1,250^\circ\text{C}$) were required to achieve greater than 95% theoretical densities in the $\text{La}_2(\text{Mo}_{1.5}\text{Nb}_{0.5})\text{O}_9$ 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 undoped 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 setup is shown in Figure 2, 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. The electrical conductivity was not significantly different compared to undoped LAMOX, indicating that lanthanum may be readily substituted by other lanthanide elements, but without much change in the conductivity. 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. Consequently, as confirmed by our conductivity results (Figure 3) hydrogen (i.e., proton) conductivity is a characteristic of the low-temperature α -phase only, and no conductivity increase was observed in the W:LAMOX samples under H_2 .

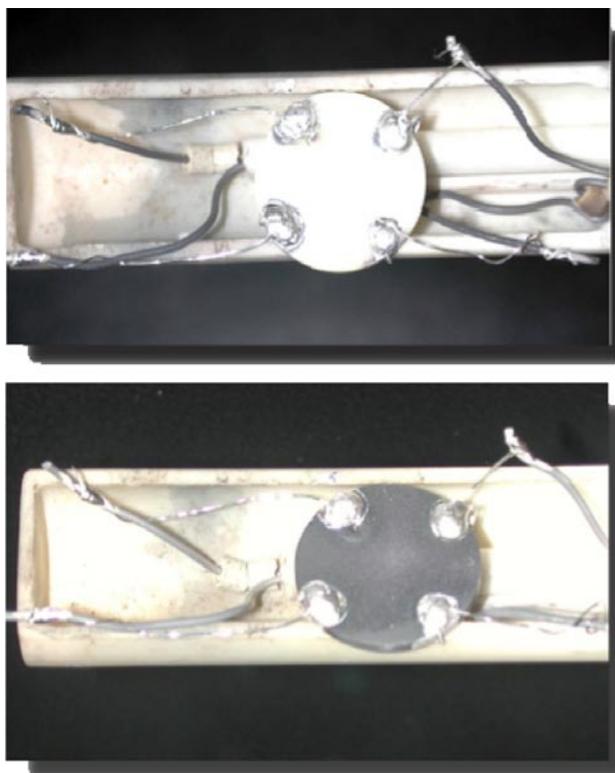


FIGURE 2. Ceramic disks with electrodes and platinum wires attached in an alumina holder for 4-wire conductivity tests, using the van der Pauw method. Note that undoped LAMOX samples at high temperatures reversibly turn black in hydrogen, and white in air, with no structural or mechanical degradation so long as the maximum temperature is kept below $\sim 550^\circ\text{C}$.

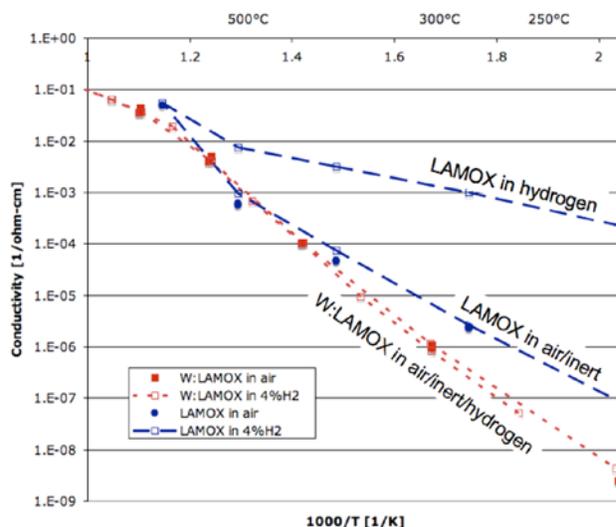


FIGURE 3. Comparison of undoped (LAMOX) and tungsten-doped (W:LAMOX). Note lower conductivity of W:LAMOX, and no change under 4% H_2 , compared with undoped LAMOX.

Flux Measurements: A hydrogen permeation test rig at the University of Cincinnati (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. The UC tests gave results (Figure 4) comparable to the fluxes measured in 2004 but with improved accuracy.

SOFC Measurements: For hydrogen gas permeation applications, it is important that the electronic conductivity of the electrolyte be high enough to prevent electrons from forming a charge layer at the electrolyte surface that repels diffusion of protons. Conversely, a low electronic conductivity is essential for a fuel cell electrolyte, as the surface electrons generate the voltage across the cell necessary to provide useable power. While our focus is on the separation membrane application, a fuel cell application is still of significant interest to the DOE Hydrogen Program. Though the initial interest in the beta-phase materials was on oxygen-ion transport for fuel cell applications, to our knowledge there are still no published reports showing working fuel cells from this material. Further, the fuel cell characteristics of these materials will provide valuable insight into the relationship between oxygen-ion, hydrogen-ion (proton), and electron conductivity in this system. A single-cell fuel cell test rig was built at ORNL to enable characterization of electrolytes in a cell with air on one side and dilute (4%) hydrogen on the other, at temperatures up to 1,200°C.

Thin ceramic membranes were synthesized by screen printing multiple coatings of LAMOX inks on

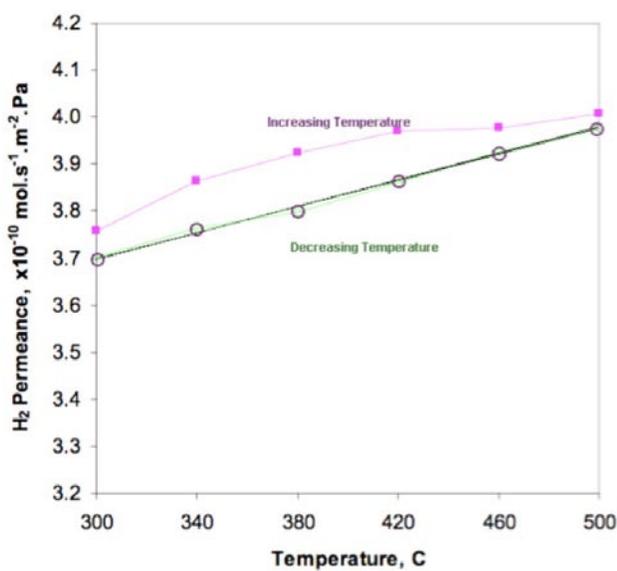


FIGURE 4. Test result from UC on single-phase 2-mm thick Pr:LAMOX ceramic.

NiO/8YSZ 30% pore pre-fired disk substrates, followed by firing at 1,050 degrees Celsius. Platinum paste was applied to both sides to attach platinum mesh electrodes, as shown in Figure 5.

The alpha-phase Pr:LAMOX sample cracked, and new tests are in progress. The beta-phase W:LAMOX sample had small cracks in the ceramic seal, compromising the hydrogen seal and leading to a reduced open circuit voltage, but the sample itself remained intact over a week of testing and enabled the first measurements of fuel cell power in the system (Figure 6).

Future Work: The next phase of this study will be to test the hydrogen permeation of the new dense thin (10 μm) supported ceramic membranes to see if the expected gains in permeation are realized. Further fuel cell testing, nuclear magnetic resonance, and permeation testing is in progress.

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.

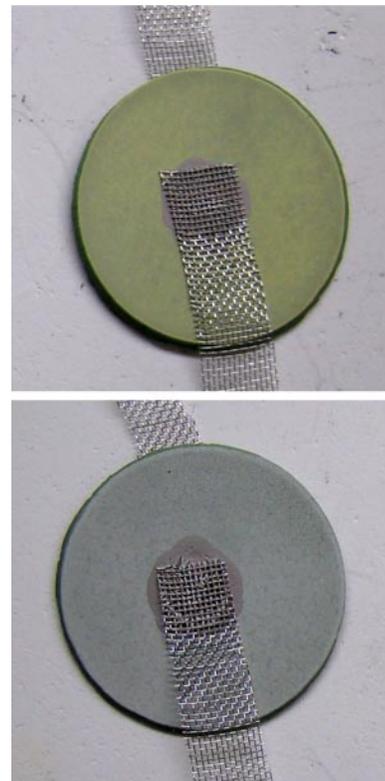


FIGURE 5. (top) Pr:LAMOX and (bottom) W:LAMOX samples prepared for fuel cell testing with Pt contact and Pt gauze electrodes attached. Disks are ~1 inch diameter.

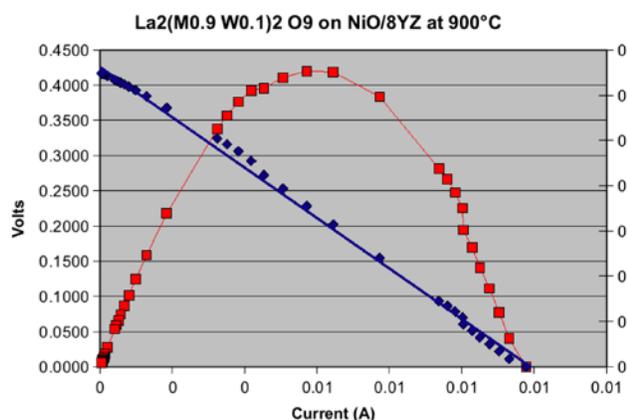


FIGURE 6. Fuel cell performance of W:LAMOX membrane. The red curve (and right y-axis scale) are Power, and the values range from 0 to 1.4 milliwatt in intervals of 0.2 mW. The blue curve and left y-axis scale is the output voltage as the load is varied.

- FY 2007/2008: inks developed for screen-printing ultra-thin membranes on porous supports.
- FY 2008: successful thin (<20 μm) membranes deposited on 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 in 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 volume, but no change in conductivity is observed. Additional work is ongoing.
- FY 2009: Successful thin (<20 μm) membranes deposited on porous Ni/NiO support.
- FY 2009: First successful test results for W-doped (beta-phase) LAMOX in fuel cell application at temperatures between 450 and 900°C.
- FY 2009: Preliminary nuclear magnetic resonance testing is inconclusive.
- FY 2009: First successful test results for W-doped LAMOX in fuel cell application.
- FY 2009: No significant differences observed to date for humidified versus dry 4% H_2 .

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 a potential proton-conductor. Detailed characterization of these materials has been carried out using X-ray diffraction (phase analysis, crystal structure), in situ high-temperature X-ray diffraction (phase stability), and electrical conductivity in controlled temperature and gas environments. Hydrogen permeation tests were performed at the University of Cincinnati.

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 progress in FY 2009 has enabled thin membranes to be reliably synthesized on porous supports.

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 show proton conduction similar to undoped LAMOX. Ytria-stabilized zirconia was identified as a suitable material for porous supports, and 10-20 μm thick membranes of LAMOX, Pr:LAMOX, and Sr:LAMOX on porous YSZ have been synthesized.