

II.D.6 Novel Low-Temperature Proton Transport Membranes

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Project Start Date: March, 2007 (restarted
after 2-year funding hiatus)
Project End Date: Project continuation and
direction determined annually by DOE

- Flux: 200 scfh/ft²
- Cost: <\$100/ft² of membrane
- Durability: >5 years
- Differential Pressure: 400-1,000 psi
- Hydrogen Recovery: 100%
- Hydrogen Purity: 99.99%

Accomplishments

- Coefficients of thermal expansion have been determined on several different lanthanum molybdenum oxide (LAMOx) compositions of proton conductor.
- Hydrogen flux measurements have been made on thick ceramic pellets.
- Thin membranes have been successfully formed via tape casting of homogeneous powders prepared by combustion synthesis.
- Tests have been carried out to determine that LaMOx is stable in CO₂ and sulfur containing environments.



Objectives

- Identify optimal composition
- Development of thin electrolyte membranes
- Characterization of the electrical properties (ion transport) and chemical stability
- Evaluation of the thermomechanical properties
- Modeling and simulation of structure-property relationships
- Demonstrate laboratory-scale hydrogen separations with ability to scale-up

Technical Barriers

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

- (A) Fuel Processor Capital Costs
- (G) Efficiency of Gasification, Pyrolysis, and Reforming Technology
- (AB) Hydrogen Separation and Purification

Technical Targets

This project is conducting fundamental studies on new ceramic oxide proton (hydrogen) transport membranes. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation materials that meet the following DOE hydrogen separations targets:

Introduction

Dense ion transport membranes provide a practical means of ensuring 100% selectivity, but to date the known materials are unable to achieve DOE requirements in terms of temperature stability, ion flux, durability and cost. This project began as a search for more robust ceramic oxides for proton conductors; it was determined that the recently discovered lanthanum molybdates, which are oxygen ion conductors at high temperature, also facilitated a significant hydrogen flux at moderate temperatures. The objective of this project is to establish whether these materials would be suitable as proton conducting ceramic membranes for hydrogen gas separation or membrane reactor applications.

Approach

To test the suitability of lanthanum molybdate based ceramics for hydrogen separation the following approach was used. First a high-temperature four-probe conductivity test compared dilute hydrogen to air to identify optimal compositions and temperature range. *In situ* X-ray diffraction (XRD) was used to verify the phase stability in environments including dilute hydrogen. A processing study was undertaken to determine the optimal conditions for synthesis of fully dense ceramic membranes via tape casting. A high-

temperature single-ended fuel cell test station was constructed to measure the hydrogen flux as a function of gas partial pressure differential.

Results

Undoped lanthanum molybdate proved difficult to sinter to acceptable density, but this could be improved by doping with Nb or W on the Mo site. Even though the hydrogen fluxes recorded for W-doping at New Mexico Tech (NMT) and the National Energy Technology Laboratory (NETL) were lower than for Nb-doping, in the previous year we had determined that Nb-doping often led to undesired second phases, whereas W-doping did not. New powders with carefully controlled compositions at a 10% W-doping level were made using a modified combustion synthesis process. These powders were calcined, ball-milled, tape cast, punched, laminated, and sintered to form thin 1-inch diameter disks, suitable for sintering studies (Figure 1) and hydrogen conductivity testing.

The coefficient of thermal expansion (CTE) of the lanthanum molybdenum tungsten oxide (LMWO) calculated using high-temperature X-ray diffraction

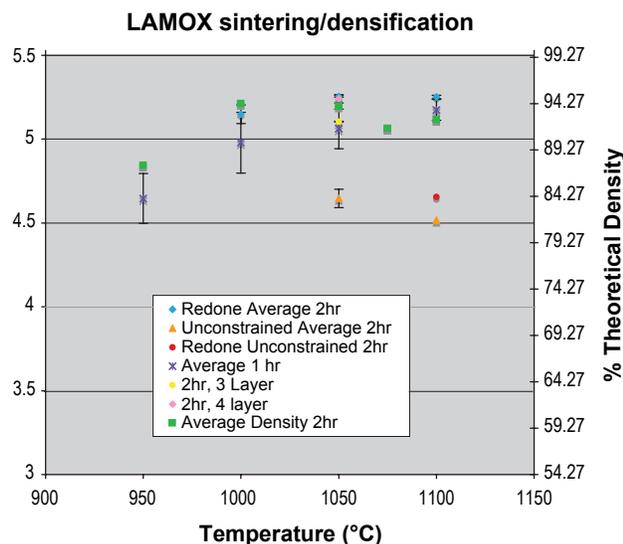


FIGURE 1. Densification data for 10% W-doped LAMOX, or LMWO, *i.e.*, $\text{La}_2\text{Mo}_{1.8}\text{W}_{0.2}\text{O}_9$, indicating $T > 1,000^\circ\text{C}$, $t > 1$ hr, and use of sintering constraints yielded densities greater than 90% of theoretical, suitable for separation membranes and fuel cell electrolytes.

XRD thermal expansion

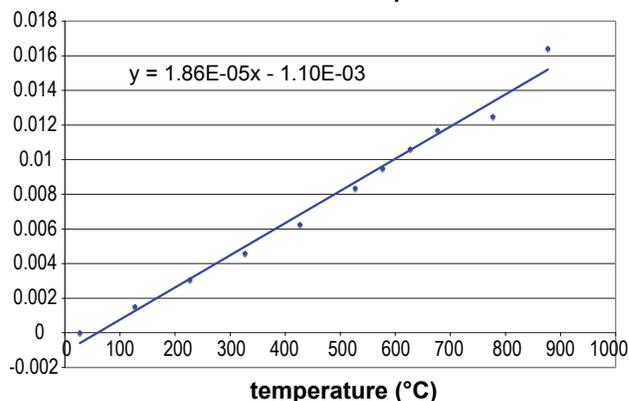


FIGURE 2. Lattice parameters (corrected for instrumental errors) determined from 25–900°C indicate a thermal expansion coefficient of 18.6×10^{-6} .

(HTXD) refined lattice parameters (Figure 2) showed that the CTE of LMWO is very large compared to a typical ceramic oxide (approximately 19×10^{-6}). Though the uncertainties in the lattice parameter calculations were high, a CTE value higher than reported in the literature was calculated which, if correct, would suggest the leading cause for the cracking of the pellet during testing is a CTE mismatch between the LMWO and the current testing set-up/materials. Validation of the CTE value using another technique (dilatometry) is planned in the next quarter.

Conclusions and Future Directions

LMWO provides an entirely new class (*i.e.*, non-perovskite) of proton-conducting ceramic oxides for hydrogen separations. Initial hydrogen flux measurements conducted at NETL and NMT indicate that for practical application, the ceramic membrane needs to be very thin. Measured fluxes at 500°C correspond well with hydrogen fluxes measured in barium cerate at 800°C.

Special Recognitions & Awards/Patents Issued

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