

## II.C.5 Ultra-Thin Proton Conduction Membranes for H<sub>2</sub> Stream Purification with Protective Getter Coatings

Margaret E. Welk (Primary Contact),  
Andrea Ambrosini and Robert K. Grubbs  
Sandia National Laboratories  
Org: 6338 MS: 0734  
P.O. Box 5800  
Albuquerque, NM 87185  
Phone: (505) 284-9630; Fax: (505) 844-7786  
E-mail: mewelk@sandia.gov

DOE Technology Development Manager:  
Rick Farmer  
Phone: (202) 586-1623; Fax: (202) 586-2373  
E-mail: Richard.Farmer@ee.doe.gov

Project Start Date: May 15, 2007  
Project End Date: September 30, 2009

### Objectives

- Increase proton conduction (and therefore hydrogen flux) via synthesis of ultra-thin dense ceramic membranes on microporous supports.
- Incorporate sulfur getter technology into microporous support layer to address impurities in the feedstock.
- Demonstrate the ability of these ultra-thin membranes to separate H<sub>2</sub> at a high flux rate that meets the DOE 2010 target of 250 scfh/ft<sup>2</sup>.

### 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:

- (K) Durability
- (L) Impurities
- (M) Membrane Defects
- (N) Hydrogen Selectivity
- (O) Operating Temperature
- (P) Flux
- (R) Cost

### Technical Targets

This project is studying the efficiency of ultra-thin dense ceramic membranes to separate H<sub>2</sub> at elevated temperatures. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation modules to meet the following DOE 2010 hydrogen separation targets:

- Flux: 250 scfh/ft<sup>2</sup>
  - Deposition of an ultra-thin film will enhance the flux rate per square foot by minimizing the time for protons to be conducted through the dense oxide.
- Hydrogen quality: 99.99% of total (dry) gas
  - The conduction mechanism of separation ensures high purity H<sub>2</sub> as only hydrogen is conducted through the gas-impermeable membrane.
- Operating capability: 400 psi
  - The use of a microporous support structure will enhance the ability of the membrane to withstand significant pressure drops.
- Durability: 26,280 hours between membrane replacement
  - Dense ceramics are resistant to steam. The development of a “getter support” on the feed side of the stream addresses other impurities, such as sulfur, and will support a lengthened membrane lifetime.

### Accomplishments

- Successfully deposited strontium oxide and titanium oxide separately using atomic layer deposition (ALD); optimization of the alternating deposition conditions of the two materials and subsequent sintering to make a gas tight strontium titanate membrane is underway.
- Successfully narrowed the pores of the support structure using ALD to deposit Al<sub>2</sub>O<sub>3</sub> onto the support.
- Confirmed that the entire mass of the 450 Å zinc oxide layer was able to sorb sulfur from H<sub>2</sub>S in a gas stream.
- Discovered that the zinc oxide layer was regenerable over many cycles, and due to the tortuosity of the support, no loss of zinc material from the internal surfaces of the support occurred.
- Calculated the sorbent lifetime of the ZnO layer to be 10 hours per square cm of support, or 70 days for a membrane module with 157 cm<sup>2</sup> of support.



## Introduction

Production costs for the high purity  $H_2$  necessary for fuel cells currently are estimated to be \$3.00 to \$5.00/kg – too high to be competitive with current fuels.  $H_2$  separation from the gas mixture that results from reforming of hydrocarbons or gasification is a major cost of production. The current method for large-scale separation proceeds via water-gas shift reactors followed by a pressure swing adsorption unit. Replacing this multi-step process with a membrane module can reduce hydrogen production costs and increase efficiency. This project addresses the separation of high purity  $H_2$  (>99%) from various feed streams using supported ultra-thin membranes of proton-conducting oxides, such as  $BaCeO_3$  and  $SrTiO_3$ . These dense oxide membranes exhibit 100% selectivity, resulting in extremely high purity  $H_2$ . Sulfur impurities that are typical of many feedstocks will be addressed through the deposition of a getter material, such as  $ZnO$ , onto the support structure.

We have demonstrated a low-pressure chemical vapor deposition process, ALD, which is capable of conformally coating very high-aspect ratio structures. Efficient vapor transport at low pressure, combined with selective surface chemistry and sequential introduction of reagents, ensures a highly conformal coating and precise thickness control of structures with aspect ratios  $>10^3$ . Both the getter and the proton conducting materials are deposited in this project using ALD and plasma-assisted ALD methodologies, which are capable of producing layers on the atomic scale in thickness. As thinner membranes generally have higher fluxes, this study is systematically synthesizing and testing membranes over a range of thicknesses. The sulfur getter material,  $ZnO$ , will be deposited in a conformal layer on the mesoporous support. This composite design, combining the best characteristics of dense membranes with those of microporous membranes, will exhibit high selectivity owing to gas separation via proton conduction and high flux owing to the thinness of the membrane.

## Approach

To reduce the cost of producing high purity hydrogen, we aim to design a multifunctional membrane module – it will both separate pure hydrogen at high flux rate, and eliminate sulfur contaminants. The module consists of a porous support internally coated with a sulfur getter and capped on one side with a thin proton conducting ceramic membrane. We are using a technique called plasma-assisted ALD. While this technique has not been previously used to fabricate membranes, the control of thickness and depth of penetration make it ideal for ultra-thin membrane

creation. The resulting ultra-thin membranes will have improved hydrogen flux over thicker membranes, and allow us to reach the DOE targets. ALD also is used to conformally coat the internal surfaces of the support with  $ZnO$ , a known sulfur getter with excellent capacity and reaction rates. By including contamination mitigation in the membrane module, the durability and lifetime of the membrane will be enhanced.

## Results

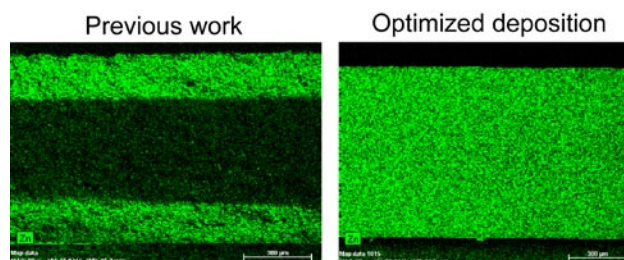
With the carryover funds from Fiscal Year 2008, we determined to focus on the sulfur sorbent portion of the research.

### Sulfur Uptake Measurements

Zinc oxide is known to react with  $H_2S$  impurities in gas stream to form  $ZnS$ . Additionally,  $ZnO$  can react in the same manner with other sulfur impurities, such as  $SO_2$ . The capacity, and hence lifetime, of the getter depends on the surface area, thickness, and reactivity of the getter film. Previously, we have demonstrated the ability of the ALD of  $ZnO$  reversibly sorb  $SO_2$  and  $H_2S$  forming  $ZnSO_4$  or  $ZnS$  respectively, regenerating  $ZnO$  under heating in air. Complete conversion of the  $ZnO$  layer was achieved, indicating that the entire mass of the deposited  $ZnO$  is available to act as a sulfur getter in this mesoporous structure. The ability to cycle without loss of material was confirmed last year. Seven cycles of sorption and regeneration did not cause decrepitude of the zinc coating; the tendency of this sorption material to agglomerate and then crumble apart appears to be mitigated by the tortuosity of the support.

We have perfected the deposition of  $ZnO$  throughout the porous support. The ALD process was modified to be quasi-static, with a 15-second dwell period of the diethyl zinc in the deposition chamber. Completely uniform coating was achieved when the supports were mounted vertically in the chamber (see Figure 1).

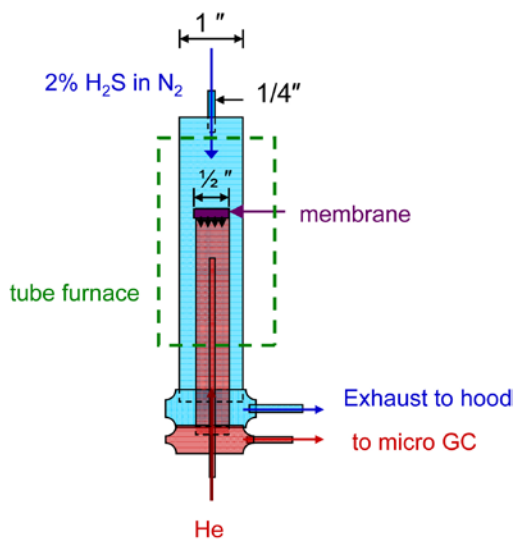
To determine the lifetimes of these sorbent materials, we determined the number of moles of  $ZnO$  per gram of coated support through thermogravimetric analysis



**FIGURE 1.** Cross Sections of  $ZnO$ -Coated Porous  $Al_2O_3$  Supports (Green indicates presence of Zn.)

(TGA) measurements. In these experiments, a coated support was completely converted to ZnS by flowing in 2% H<sub>2</sub>S for 3 hours at 500°C. The complete conversion has been verified using energy dispersive X-ray spectroscopy in past work. The sample was then placed in a TGA and heated under flowing air. The weight loss arising from the oxidation of ZnS to ZnO was recorded. Per square cm of porous support (1 mm thick), there are  $1.35 \times 10^{-4}$  moles of ZnO. In a gas stream with 100 ppm H<sub>2</sub>S present, flowing at 3 ml/min, at 700°C, each square cm of coated support would remove the sulfur from the gas stream for more than 10 hours. A tubular membrane and support module system with 2 cm diameter tubes 25 cm in length, or with 157 square cm of coated support would operate for more than 70 days before needing regeneration. A paper containing the results of this work is in progress.

Current work underway aims to confirm these results using breakthrough tests. A ZnO-coated support is sealed into the permeation unit (see Figure 2) using a



**FIGURE 2.** Permeation Unit 1" (outside diameter, outer tube) and 1/4" (outside diameter, inner tube), Alumina

pyrex O-ring that is melted at 950°C. A gas mixture of 2% H<sub>2</sub>S in N<sub>2</sub> flows to a mass flow controller where it can be diluted to 100 ppm H<sub>2</sub>S, then continues past the support on the feed side, and a helium sweep gas flows past the support on the permeate side, carrying any cross-over gas to the gas chromatograph for detection. Proper conditions (flow rate and H<sub>2</sub>S concentration) that will allow meaningful sulfur breakthrough curves are being investigated.

## Conclusions and Future Directions

No additional work is planned owing to lack of funding. Remaining issues that could be investigated include:

- Perfecting the deposition of a gas tight SrTiO<sub>3</sub> membrane with plasma-assisted ALD.
- Investigating the durability of the membrane and support assembly through many heating cycles.

## FY 2009 Publications/Presentations

1. M.E. Welk, R.K. Grubbs, A. Ambrosini "Sulfur sorption studies on ALD layers of ZnO enclosed in porous support." In progress, 2009.

## References

1. The Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (October 2007).
2. Alberti, G.; Casciola, M. Solid State Ionics 145 (2001)
3. Kreuer, K.D.; Schonherr, E.; Maier, J. Solid State Ionics, 70/71 (1994) 278.