

II.A.11 Ultra-Thin Proton Conduction Membranes for H₂ Stream Purification with Protective Getter Coatings

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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 H₂ at a high flux rate that meets the DOE 2010 target of 250 scfh/ft².

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 thin dense ceramic membranes to separate H₂ 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/ft²
 - 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 H₂ 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 strontium titanate is underway.
- Successfully narrowed the pores of the support structure using ALD to deposit Al₂O₃ onto the support.
- Confirmed that the entire mass of the 450 Å zinc oxide layer was able to sorb sulfur from H₂S 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 or decrepitude of zinc material from the internal surfaces of the support occurred.



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 [1]. 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 $SrTiO_3$ [2,3]. 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 are designing 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

Deposition of the Proton Conducting Membrane

Previous work in Fiscal Year 2007 led us to focus on the plasma assisted ALD of strontium titanate, $SrTiO_3$, as our proton conducting oxide material. An oxygen plasma assisted ALD reactor was constructed in Q1 FY 2008 for the deposition of complex perovskites. The reactor is a hybrid of a solid precursor delivery system and an oxygen plasma source. Several specialized precursors were obtained for the deposition of $SrTiO_3$: the titanium precursor, 2,2,6,6-tetramethyl-3,5 heptanedionato titanium isopropoxide $Ti(isopropoxide)_2(THD)_2$, and the solid phase strontium precursor, 2,2,6,6-tetramethyl-3,5 heptanedionato strontium [aka, $Sr(THD)$]. Plasma assisted ALD, in comparison with ALD, allows us to control the deposition penetration depth of the proton conducting membrane into the support. While a small amount of penetration is necessary for adequate adhesion, we also want to keep the proton conducting membrane thin to maximize the flux.

Work this year has resulted in the successful deposition of 450 Å of TiO_2 on an Al_2O_3 support. Each cycle of $Ti(THD)$ in the presence of the oxygen plasma delivers 1.5 Å of TiO_2 on the support surface; repeated 150 times, this results in 450 Å of TiO_2 . The delivery of the titanium precursor was monitored with a witness wafer on the quartz crystal microbalance. Post deposition tests using Auger spectroscopy confirmed the presence of titanium. Deposition of strontium oxide (SrO) has also been achieved after optimizing reactor temperature and distance to sample wafer. Each cycle of $Sr(THD)$ deposits 0.5 Å of SrO on the support surface.

The effective pore size of the Al_2O_3 support has been reduced near the surface by depositing 300 nm of Al_2O_3 using plasma assisted ALD (see Figure 1). This step is important in order to make a membrane less than 100 nm thick. The effective pore size of the support must be less than 200 nm for the membrane deposition method to form a continuous film. The plasma within the ALD reactor causes the decomposition of the aluminum precursor at the surface of the support, so the additional alumina only penetrates into the support 10 μm . The layer thickness of the alumina is greatest at the top surface of support, and decreases rapidly over the 10 μm .

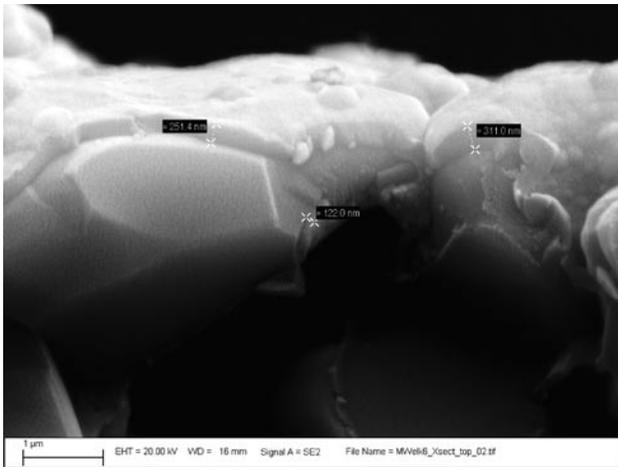


FIGURE 1. SEM Image of Al₂O₃ Deposition on Al₂O₃ Support

Sulfur Uptake Measurements

Zinc oxide reacts with H₂S impurities in a gas stream to form ZnS. Additionally, ZnO can react with other sulfur impurities, such as SO₂. The removal of sulfur impurities is of prime importance for both dense metallic and dense ceramic membranes, as these membrane materials react with sulfur and the efficiency of hydrogen separation is reduced up to 50%. The capacity, and hence lifetime, of the getter depends on the surface area, thickness, and reactivity of the getter film. We have successfully deposited ZnO via ALD in a layer that is 450 Å thick. This year we have demonstrated the ability of the ALD-deposited ZnO to reversibly sorb SO₂ and H₂S forming ZnSO₄ or ZnS, respectively, and to regenerate back to ZnO by 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.

This year we began testing the continued reversibility of the ZnO-ZnS reaction. A ZnO-coated Al₂O₃ disk was placed in a furnace, and ramped to 500°C at a ramp rate of 1°C/min. At a flow rate of 1 to 5 ml/min, 2% H₂S in N₂ was passed over the disk for 4 hours, then cooled to room temperature at a rate of 1°C per min. After analysis, the sample was replaced and heated under air for 14 hours and analyzed again. This cycle has been repeated seven times to date. In each instance under H₂S flow, the ZnO layer was completely converted to ZnS, as determined by X-ray diffraction (XRD). Complete conversion back to ZnO was achieved each time when heated under air.

Note in the X-ray diffraction patterns (Figures 2 and 3) the diminution of peak intensity for the desired phase (ZnO or ZnS), which caused concern about degradation in the sulfur getter layer (cracking and/or coarsening) resulting in material loss. We performed scanning electron microscopy (SEM) with energy

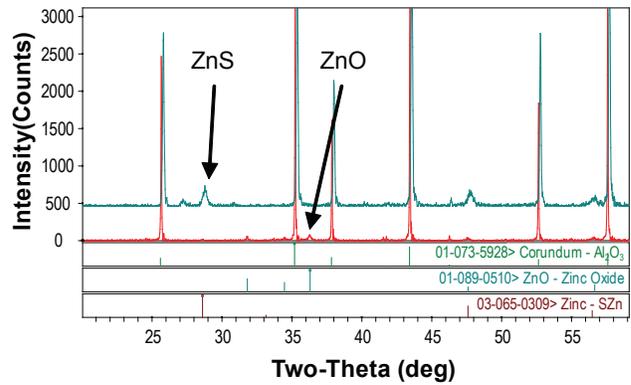


FIGURE 2. XRD Pattern after one H₂S exposure (blue pattern – ZnS). Red pattern was taken after sample was regenerated by heating in air (ZnO). Intense peaks are from Al₂O₃ support.

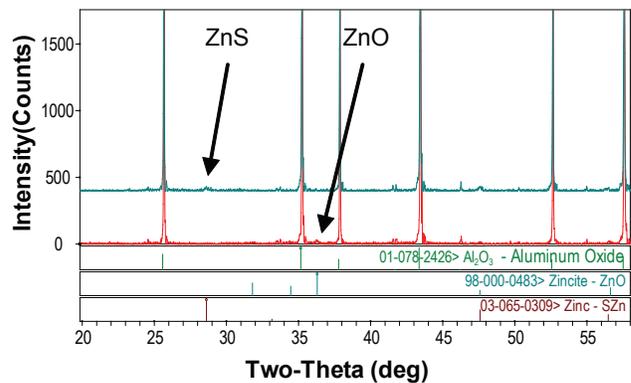


FIGURE 3. XRD patterns after seven cycles: blue pattern shows ZnS, red pattern shows ZnO. Intense peaks are from Al₂O₃ support. Note reduced peak size of ZnO and ZnS over cycle 1 patterns.

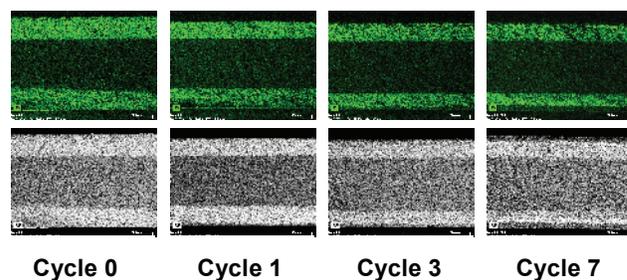


FIGURE 4. SEM (bottom row of images) and EDS (top row of images) cross sectional scans of four coated supports during cycling of sulfur sorption and regeneration. In the EDS images, the bright areas indicate the presence of zinc.

dispersive X-ray spectroscopy (EDS) to determine whether surface depletion of the zinc phases extended to the interior surfaces of the support (Figure 4). The EDS reveals that the zinc phases persist after the cycling with no indication of diminution. The distinct band structure

visible in these cross section images shows that the ZnO coating on the interior surfaces is incomplete; ZnO is only present to a depth of approximately 200 microns from the top and bottom of the support. The purge and dwell cycles during the deposition of ZnO are being modified to correct this issue.

Conclusions and Future Directions

In FY 2008, we successfully deposited titanium dioxide and strontium oxide using ALD. Alternating the deposition of these two materials will result in a proton conducting membrane of SrTiO₃. This work is underway; for the remainder of 2008 we will deposit a SrTiO₃ membrane, optimize the depth of penetration, develop post processing conditions and vary the thickness of the deposited membrane. The pore size of the support has been reduced only near the surface through the deposition of Al₂O₃ to allow for the formation of the thin membrane. Further work in 2008 will compare the proton conduction through ALD membrane to the conduction through bulk sol gel membranes. The H₂ flux through the ALD membrane will be compared with the DOE target for dense membranes.

ALD of ZnO on the internal surface of the support allowed the study of the conversion of ZnO coating to ZnS. Complete conversion of the 450 Å layer was accomplished for each cycle over seven cycles. Multiple regeneration cycles resulted in the coarsening of the ZnO layer, but the internal surfaces exhibited no material attrition as seen in the cross sectional images. For the remainder of FY 2008, we plan to complete fabrication of the proton conducting membranes, and test their proton conduction. Further, we plan to determine the capacity and rate of uptake of the ZnO sulfur getter coating.

Out-year Plans: Research in subsequent years will focus on combining the support layer, getter material, and proton conducting oxide membrane into a module optimized for cost per unit of H₂ flux. Geometry, support materials, and attachments to steam reformation units will all be considered. Collaborating with an industry partner will be essential in engineering an appropriate design. Eltron Research and Pall Corporation will be contacted for their expertise. In FY 2009, we will determine optimal membrane thicknesses, optimal amounts of deposited getter material, and optimal operating parameters. In FY 2010, we will perform permeation tests under real-world conditions, capacity and lifetime experiments, and cost optimizations.

FY 2008 Publications/Presentations

1. M.E. Welk, R.K. Grubbs, A. Ambrosini “Thin Protective Coating of ZnO Using Atomic Layer Deposition” Zing Solid State Chemistry Conference, March 10-13th, 2008.
2. R.K. Grubbs*, M.E. Welk, A. Ambrosini “Hydrogen Stream Purification Using ALD Nanostructure” 8th International Conference on Atomic Layer Deposition, June 29th – July 2nd, 2008.
3. M.E. Welk*, R.K. Grubbs, A. Ambrosini “Ultra thin proton conducting membranes with protective getter coatings” H2 workshop, Sandia National Laboratories, May 8–9th, 2008.

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.