



Ultra-thin Proton Conduction Membranes for H₂ Stream Purification with Protective Getter Coatings

Dr. Margaret E. Welk

Senior Member of the Technical Staff

Team: Dr. Robert Grubbs, Dr. Andrea Ambrosini

Sandia National Laboratories

4/16/2006

Project ID #
PDP3_Welk

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Overview

Timeline

- Project start date: June, 2007
- Project end date: Sept., 2010
- Percent complete: 25%

Budget

- Total project funding
 - DOE share: 100%
- Funding received in FY07: 200K
- Funding for FY08:
 - 250K at start of FY08
 - Reduced scope of work on microporous interlayer
 - Reduced work on bulk dense ceramic proton conductors
 - Additional 200K granted in May 2008

Barriers

- Barriers addressed
 - K. Durability
 - L. Impurities
 - N. Hydrogen Selectivity
 - P. Flux

Partners

- Currently considering appropriate potential partners
 - *Eltron Research and Development for independent testing*
 - *Pall Corp. for additional support materials and end seal design assistance*



Project Objectives

- **Provide a functional support that will protect membranes from corrosive species in reformat gas stream**
 - **Dense membranes, whether metallic or ceramic especially are vulnerable to sulfur attack**
- **Synthesize an “ultra-thin” dense ceramic proton conducting membrane to increase H₂ flux over existing membranes**



Goals

- **Milestone table for FY08**

Task 2: Ultra-thin Proton Conducting Membranes for H₂ Purification with Protective Getter Coatings	
Subtask 2.1 - Synthesis of an Ultra Thin Proton Conducting Membrane through ALD	
Develop ALD synthesis of selected H ₂ conducting oxide	6/08
Deposit proton conducting films in 4 different thicknesses: 20, 35, 50, and 75 nm	7/08
Subtask 2.2 - Synthesis of Microporous Support Interlayer	
Synthesize support films with four different pore sizes: 40, 70, 100 and 150 nm	07/08
Determine pore size best suited to improved flux.	09/08
Subtask 2.3 - H₂ permeation	
Demonstrate enhanced flux through membranes compared to bulk systems, Compare to DOE targets (2010 target – 200 scfh/ft ²)	09/08
Study effect of H ₂ conducting film thickness on permeation	09/08
Subtask 2.4 – Complete Sulfur uptake measurements	
Demonstrate ability of getter coating to remove sulfur impurities. Determine lifetime.	09/08



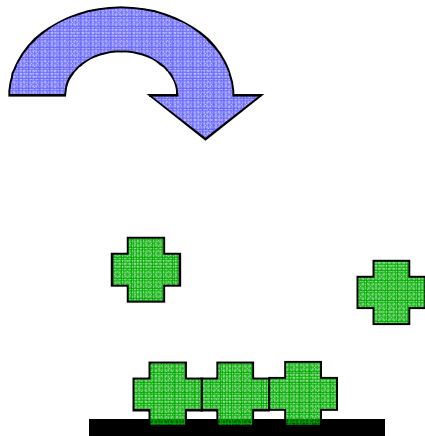
Approach

- **Use new technique for material deposition - plasma assisted Atomic Layer Deposition (ALD) – fine control thickness, depth of penetration, stoichiometry. Allows:**
 - Formation of ultra thin membranes (atomic scale) which will improve flux.
 - Conformal coating of supports with getter materials.
 - Tailoring of support through deposition of additional material.
- **Use materials with known characteristics and optimize in new forms and constructs.**
 - Chose SrTiO_3 as proton conducting ceramic membrane in FY2007
 - Known characteristics, good basis for comparison
 - Amenable to ALD chemistry
 - Chose ZnO as sulfur getter
 - Excellent capacity and reaction rates.
 - Mitigate material degradation by enclosing in support.
- **Design membrane module to be multifunctional**
 - Direct the gas flow through the support to the membrane surface
 - Coat support in getter material

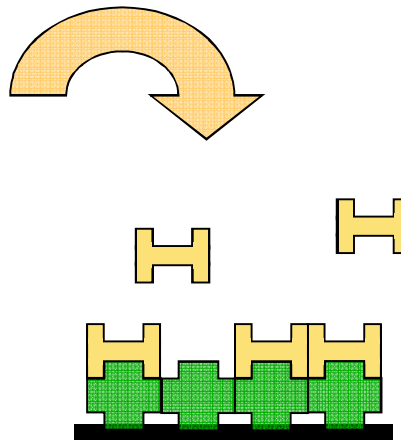
Technical Progress - ALD Process

- Sequential exposure to reagents
- Each reagent chemisorbs to surface but not to itself to create a monolayer
- Fine control over layer thickness to atomic scale
- Excellent at conformally coating high aspect ratio structures

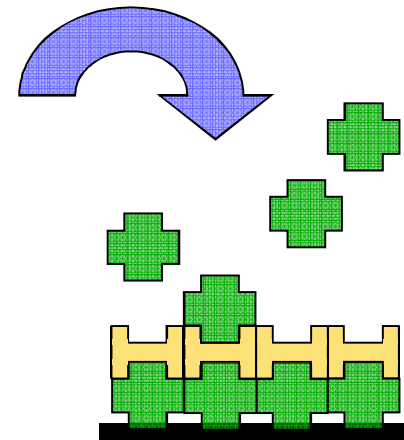
Reagent A



Reagent B



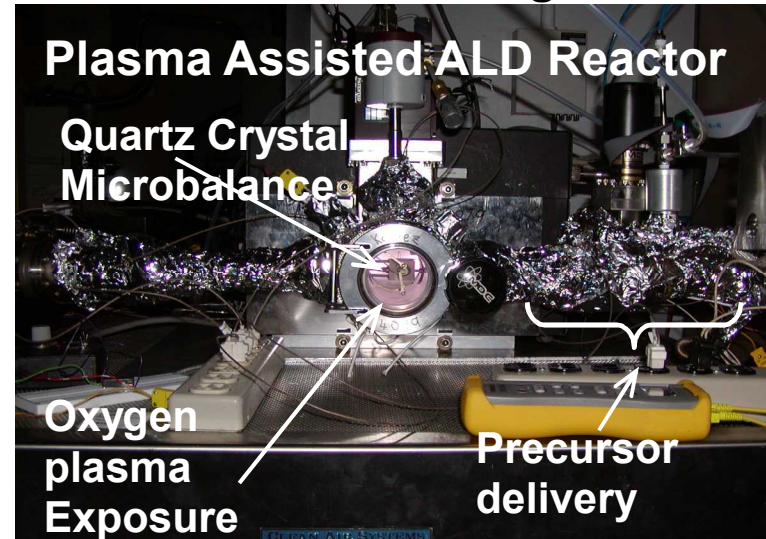
Reagent A



Technical Progress

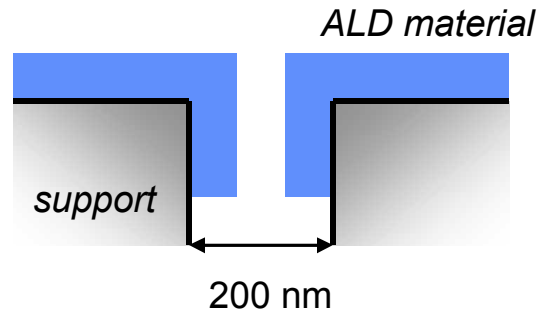
Subtask 2.1 - Synthesis of an Ultra Thin Proton Conducting Membrane through ALD

- To deposit SrTiO_3 , we needed to optimize the deposition of two precursors – one for SrO and one for TiO_2 .
 - Strontium precursor, 2,2,6,6-tetramethyl-3,5 heptanedionato strontium [aka, Sr(THD)].
 - Deposition of the solid precursor has required reorientation of the plasma system, increased delivery gas to carry more precursor to substrate, optimized precursor chamber temperature, and reorientation of the sample perpendicular to the precursor stream. We are still working to optimize the SrO deposition
 - We have successfully deposited TiO_2 . The titanium precursor, $\text{Ti}(\text{isopropoxide})_2(\text{THD})_2$ was used to deposit TiO_2 at 200°C in the presence of an oxygen plasma.



Technical Progress, cont.

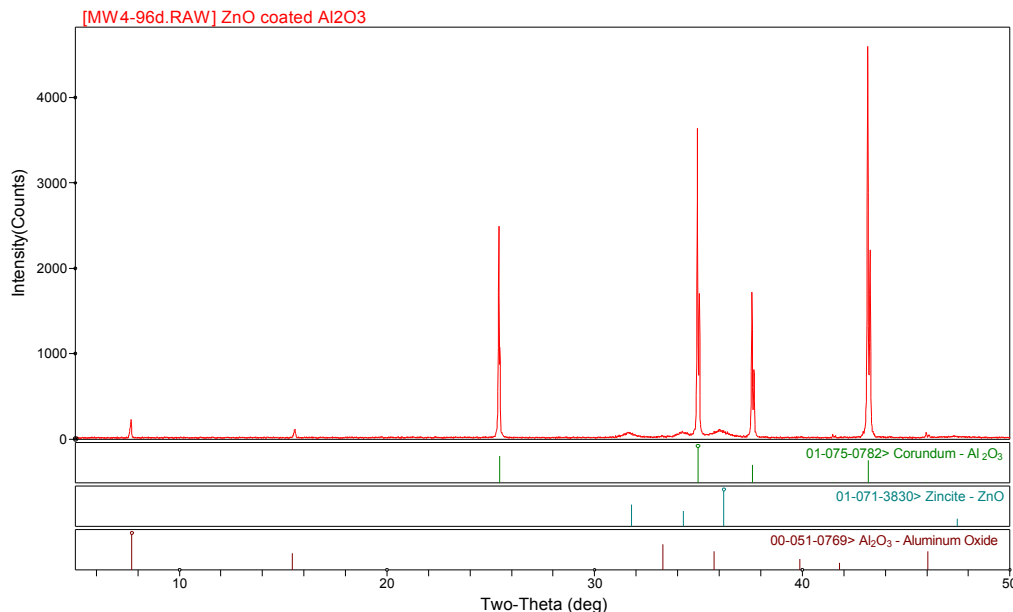
Subtask 2.2 – Deposit a microporous support interlayer



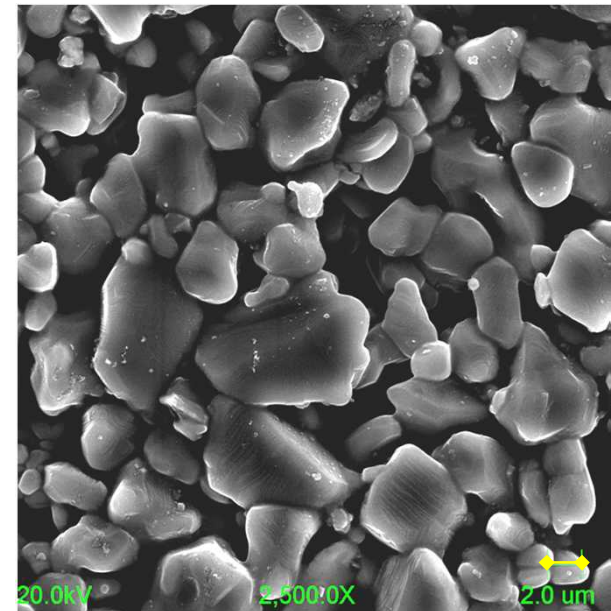
- To support an ultra thin membrane, the support must have a fine pore structure. To narrow the pore structure to 40 to 100 nm in diameter:
 - We have successfully synthesized a silicate interlayer on the porous supports using a sol with pores on the order of 10-20 nm. Many pore sizes are available with different sized pore formers in the sol.
 - To minimize materials compatibility issues and complexity, we have decided to use ALD instead to deposit Al_2O_3 onto the top 100 nm of the Al_2O_3 support.

Technical Progress: Getter Coating

- We deposited 450 Å of ZnO on a γ - Al_2O_3 mesoporous disk support (effective pore diameter is 1.8 μm). ZnO scavenges sulfur from gas streams.
- The coating caused minimal loss in surface area and did not block the support pore structure. The coated support has a surface area of $1.19 \pm 0.03 \text{ m}^2/\text{g}$, whereas the uncoated support has a surface area of $1.65 \pm 0.04 \text{ m}^2/\text{g}$.

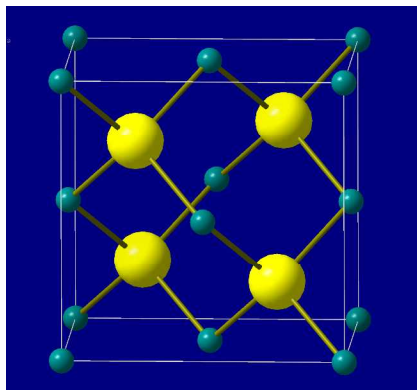


XRD showing Al_2O_3 with small ZnO peaks



SEM image – coating is smooth and even.

Sulfur Sorption Process

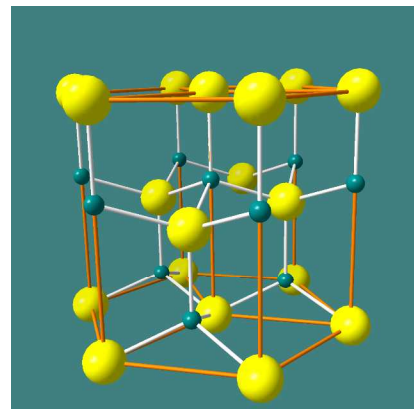


ZnO,

$a, b = 5.41 \text{ \AA}$

$c = 5.210 \text{ \AA}$

Density = 5.658 g/cm³



ZnS,

$a, b = 5.812 \text{ \AA}$

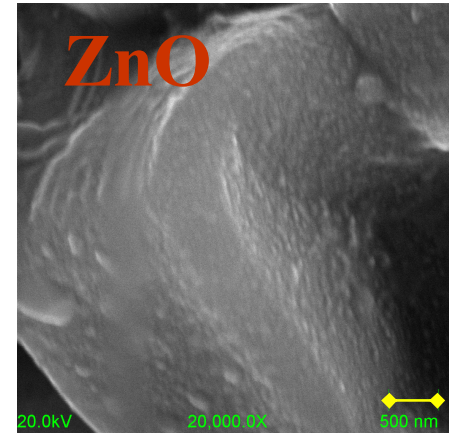
$c = 18.69 \text{ \AA}$

Density = 4.128 g/cm³

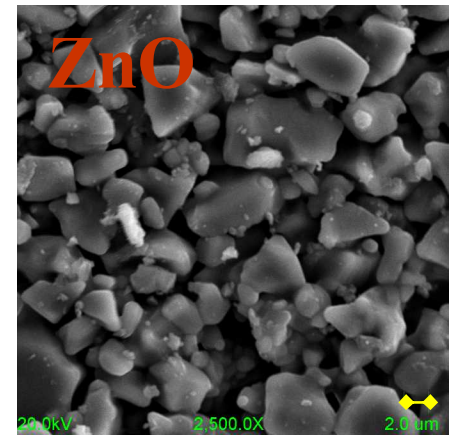
- While ZnO scavenges sulfur readily, the phase change and corresponding large density change between ZnO and ZnS leads to decrepitude in solid pellets.
- To investigate the effect of cycling on the thin ZnO coating, several ZnO coated supports were placed in a furnace and heated to 500°C at a ramp rate of 1 degree per minute.
 - The supports were exposed to 2% H₂S in N₂ flowing at a rate of 1 to 5 mL/min for 4 hours, then the gas was switched to air for 15 hours.
 - This cycle was repeated 7 times. Samples were taken for analysis after one cycle, three cycles, and seven cycles.

After 1 cycle

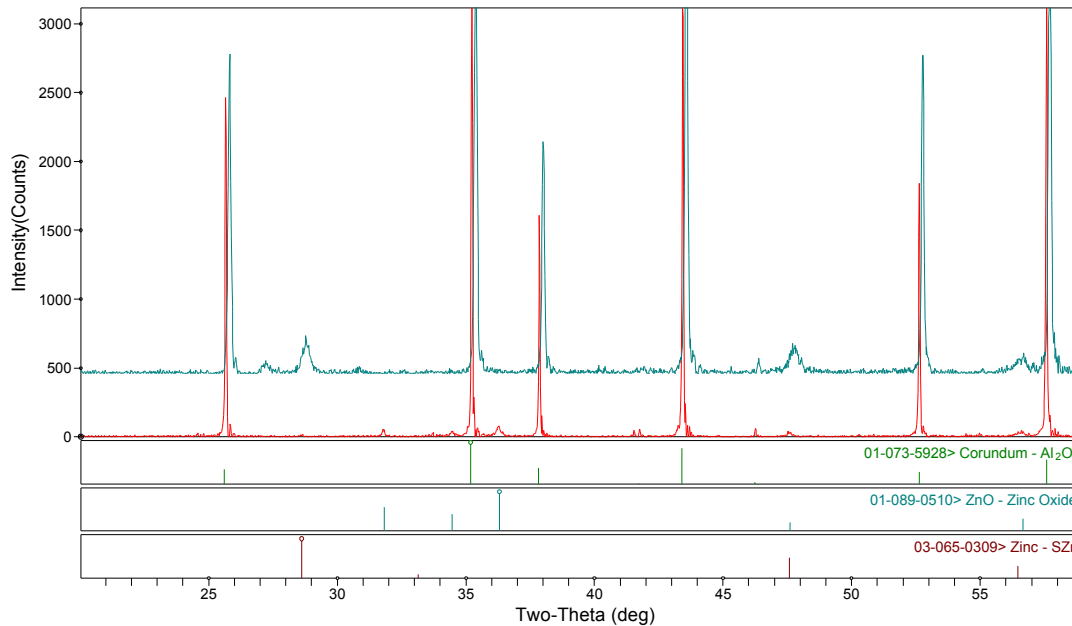
- After converting the coating to ZnS and then back to ZnO, the coating surface is noticeably rougher as seen in the SEM.



500 nm

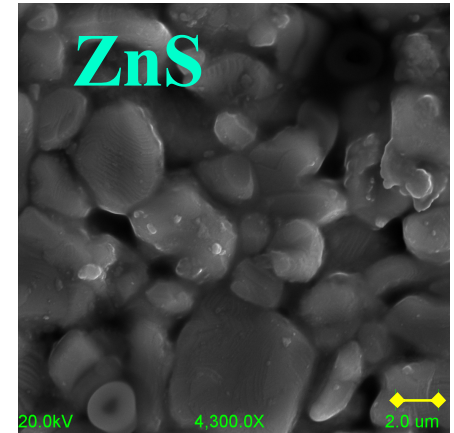
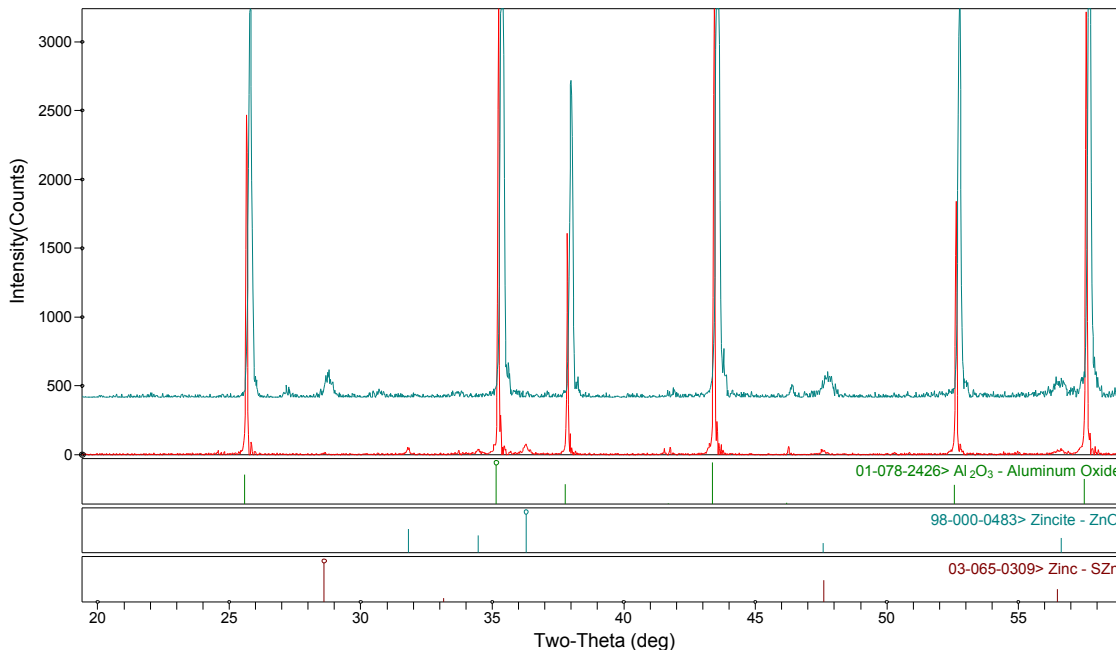


2.0 μm

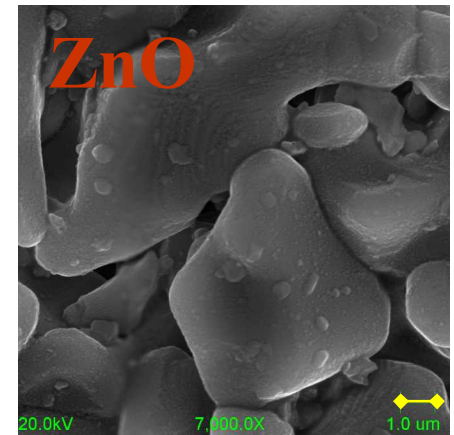


After 3 cycles

- After 3 cycles, visible “islanding” has occurred, and reduction in XRD peak intensity may be a result of material loss on the surface.



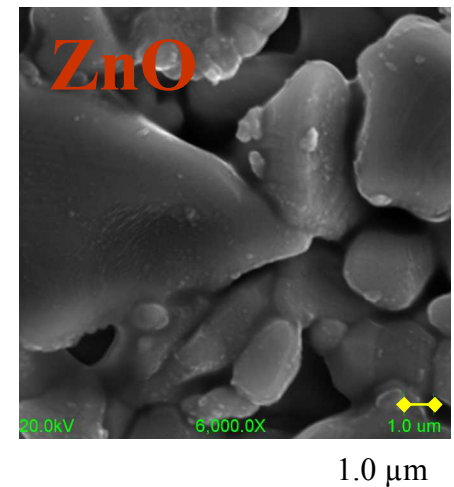
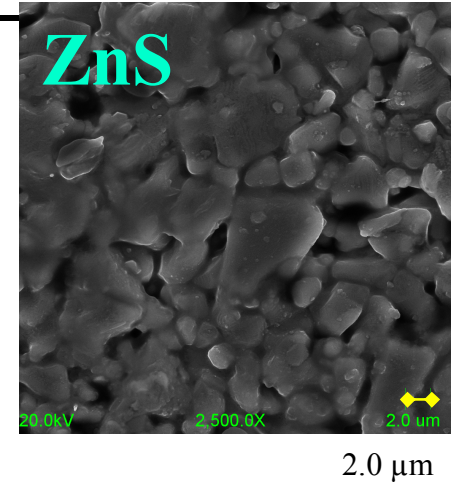
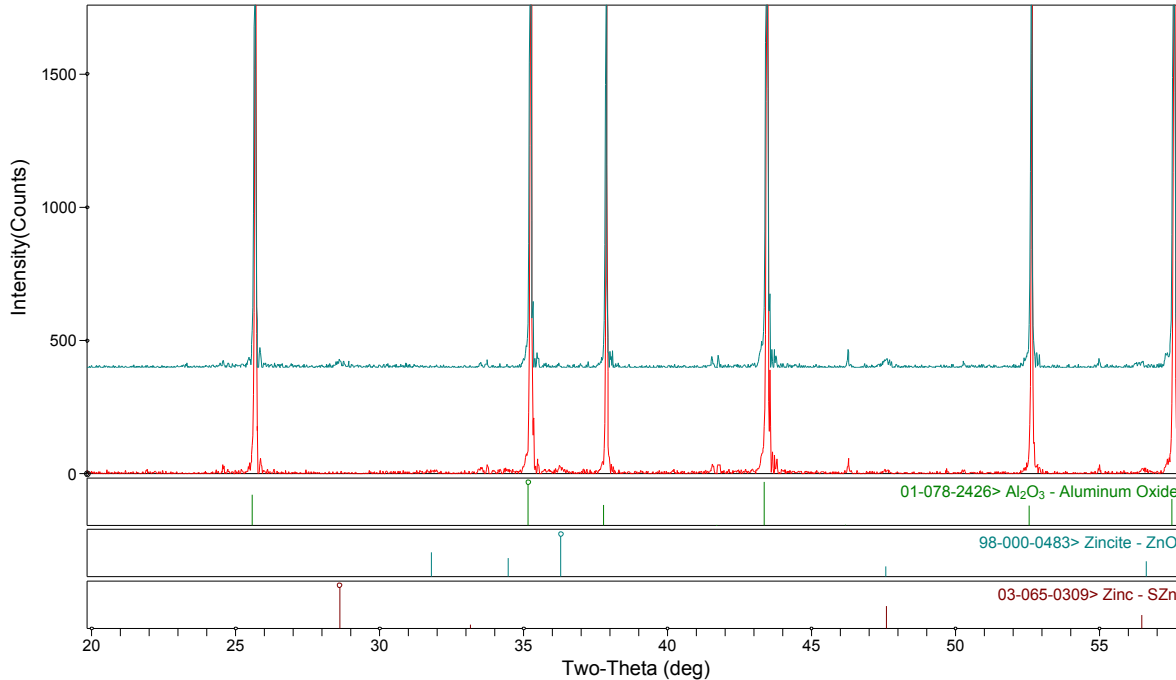
2.0 μm



1.0 μm

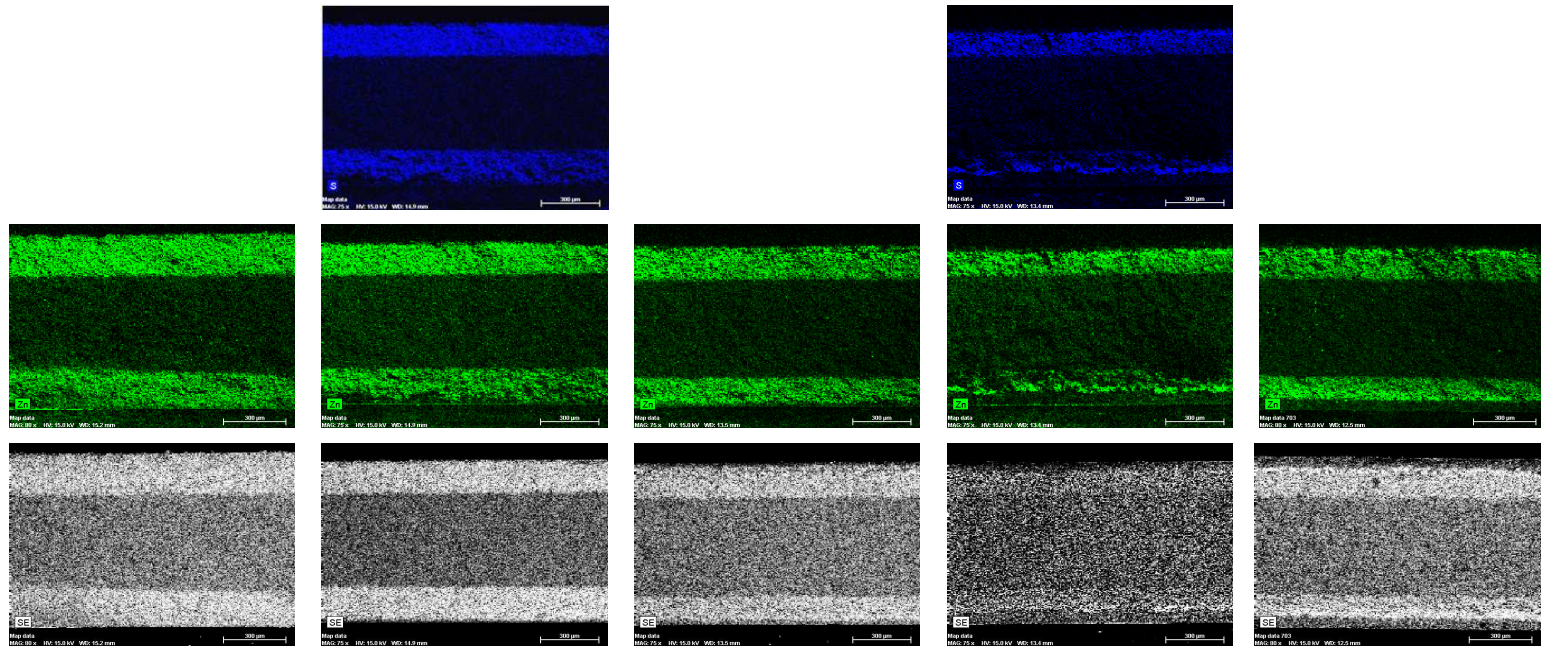
After 7 cycles

- After seven cycles, peak intensity is much reduced. A few islands remain visible in SEM images.



Comparative SEM/EDS cross section results

Gray = backscatter image, Blue = sulfur, Green = zinc



Cycle 0 – ZnO Cycle 1 – ZnS Cycle 3 – ZnO Cycle 7 – ZnS Cycle 7 – ZnO

- On these cross-sectional images, the amount of zinc and of sulfur (the intensity of the green and the blue colors) does not seem to decrease over the seven cycles. This indicates that ZnO or ZnS is not being lost from the interior of the porous support. Close examination of the images reveals that the top and bottom of the coated support have little to no ZnO or ZnS remaining after 7 cycles.
- While material is being lost at the surface, the tortuosity of the support prevents the loss of zinc from the interior of the support.**



Future Work

Remainder of FY08:

- Obtain correct stoichiometry for ALD deposited SrTiO_3
- Determine post processing conditions to obtain a dense film
- Deposit SrTiO_3 films in 4 thicknesses
- Deposit Al_2O_3 to narrow pores in support structure. Create an interlayer with pores of 40, 70, 100 and 150 nm in diameter
- Determine capacity of getter coating
- Determine rate of sulfur uptake
- **Out-year Plans:** Research in subsequent years will focus on combining the support layer, getter material, and proton conducting oxide membrane into a optimized structure. In FY09, we will determine optimal membrane thicknesses, optimal amounts of getter material deposited, and optimal operating parameters. In FY10, we will perform permeation tests under real-world conditions, capacity and lifetime experiments, and cost optimizations.



Summary

- **Successful deposition of titania, and recently SrO.**
- **Synthesis of microporous interlayer layer using sols and ALD.**
 - **Future interlayers will be formed of Al_2O_3 to avoid materials compatibility issues.**
- **Successful deposition of ZnO.**
 - **Studied the conversion of ZnO coating to ZnS.**
 - **Complete conversion of the 450 Å layer was accomplished for each cycle over 7 cycles.**
 - **Studied the effects of multiple regenerations on the getter coating.**
 - **Some material attrition was evident on the surface of the support.**
 - **Cross-sectional studies revealed that the ZnO coating on the interior had coarsened, but the amount of material on the interior remained constant over the seven cycles.**
 - **Complete conversion on the interior coating still occurred after seven cycles.**



Additional Slides



Responses to Previous Year Reviewer Comments

- **Early stage in this research; Need to better identify targets and dates for achievement**
 - **Our primary targets are Durability, Impurities, Hydrogen Selectivity, and Flux. We will have data points for each of these targets by the end of the year.**
- **Thermal expansion will be an issue with multiple materials**
 - **We have eliminated the silicate interlayer material to reduce complexity. In FY09, we will investigate the effect of thermal cycling on the entire membrane module.**
- **Need to highlight possible benefits from**
 - **Membrane cost may be reduced compared to metallic membranes (discounting capital cost). Membrane durability in steam, CO₂, and in the presence of small amounts of sulfur is expected to be superior to metallic membranes. Selectivity for hydrogen will be comparable to metallic membranes.**



Publications or Presentations

- **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.**
- **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.**
- **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.**



Critical Assumptions and Issues

- **Deposition of SrO is difficult due to the solid phase of the precursor.**
 - We are prepared with a back up plan to use a sol gel casting procedure readily available at SNL.
- **Materials incompatibilities in thermal expansion may be an issue.**
 - The getter coated support structure may be separated from the membrane if necessary. Engineering of the plant and membrane module could minimize thermal cycling.
- **Increasing the flux by reducing the membrane thickness may reach a plateau and not match DOE targets.**
 - By comparing several thicknesses of membrane with bulk values, we can quantify the gains that can be made with regards to thickness only. This provides a “go/no go” metric.