SAND2008-3682P

Ultra-thin Proton Conduction Membranes for H_2 Stream Purification with Protective Getter Coatings

Progress Report

Dr. Margaret E. Welk
Senior Member of the Technical Staff
Sandia National Laboratories

4/16/2006 9:00 AM

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

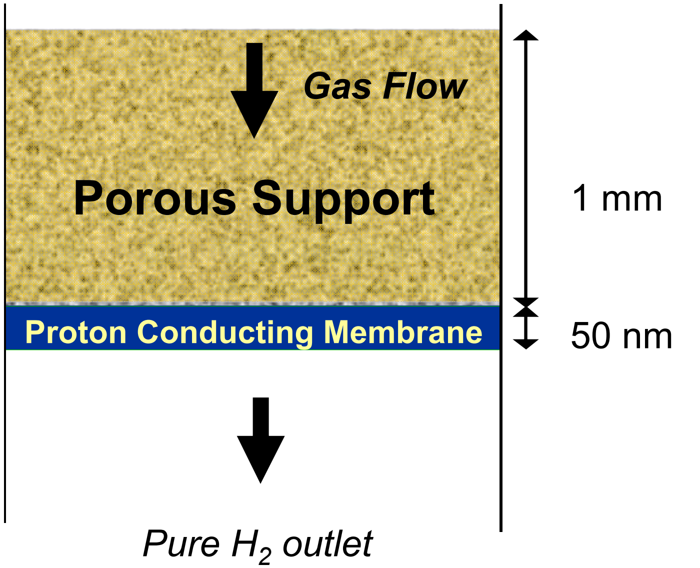
Project Objectives

- Provide a functional support that will protect membranes from corrosive species in reformate 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 H_2 flux over existing membranes

Rationale / Innovation

- **Make all aspects of the membrane platform work toward the goal of pure hydrogen**
- **Use new technique for material deposition - plasma assisted Atomic Layer Deposition (ALD) – control thickness, depth of penetration, stoichiometry**
- **Use materials with known characteristics and optimize in new forms and constructs**
- **Direct the gas flow through the support to the membrane surface**



Goals

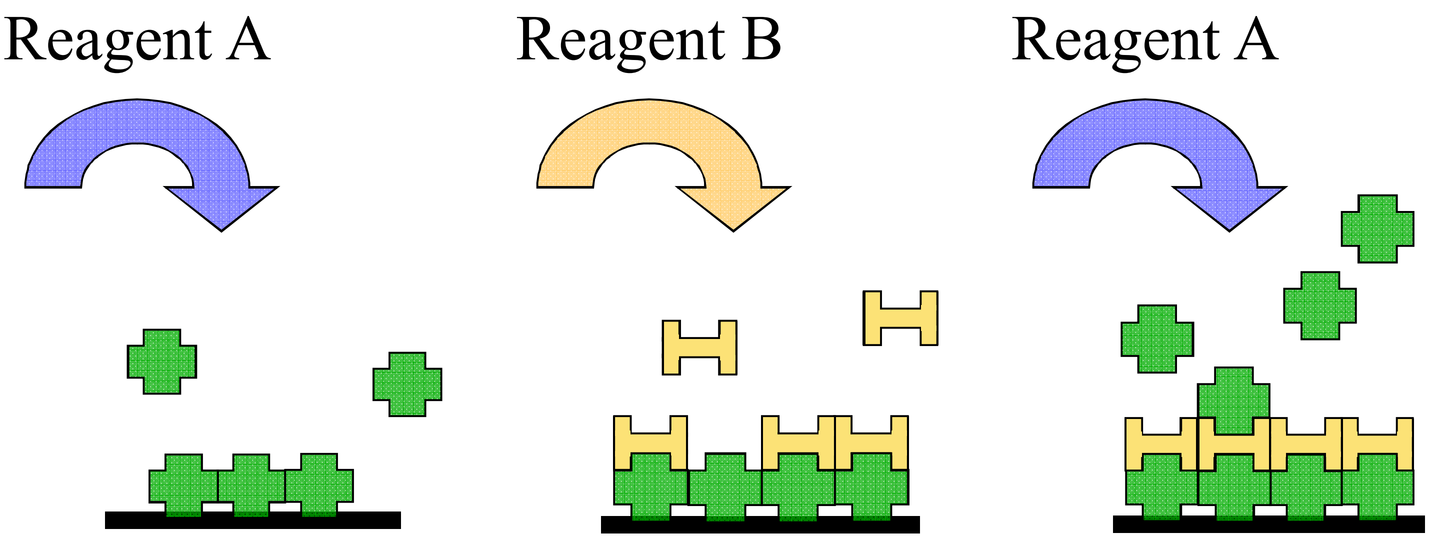
- **Milestone table for FY08**

Task 2: Ultra-thin Proton Conducting Membranes for H_2 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	1/08
Deposit proton conducting films in 4 different thicknesses	6/08
Subtask 2.2 - Synthesis of Microporous Silicate Support materials	
Synthesize support films with four different pore sizes	01/08
Complete studies on effect of pore size and thickness of support layer on membrane thickness.	06/08
Subtask 2.3 - H_2 permeation	
Test the H_2 permeance of all synthesized membranes	Ongoing
Study effect of H_2 conducting film thickness on permeation	09/08
Subtask 2.4 - Sulfur uptake measurements	
Complete sulfur uptake studies on ZnO	09/08

Sandia National Laboratories

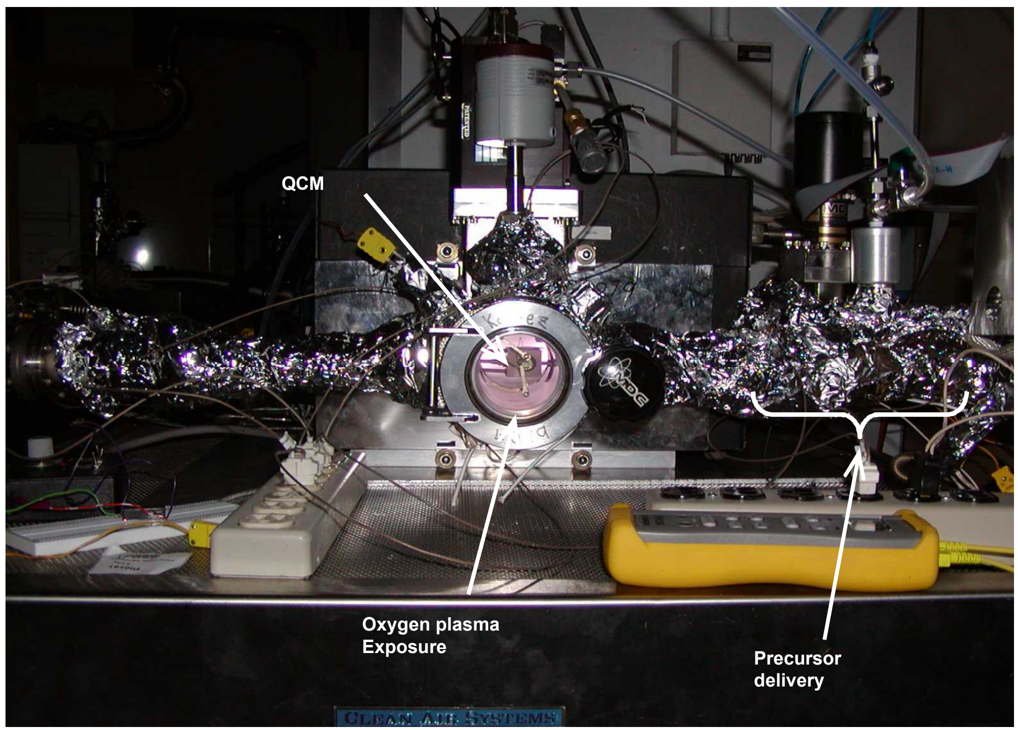
ALD Process

- 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



ALD Reactor

Plasma – Assisted Atomic Layer Deposition reactor. QCM stands for Quartz Crystal Microbalance.

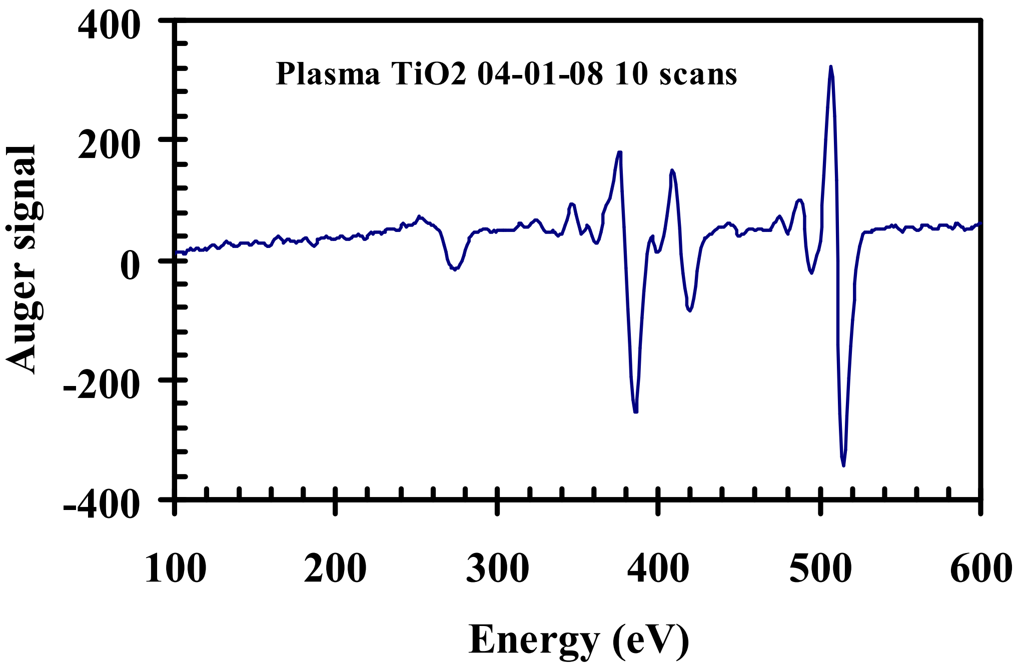


ALD Progress, Cont.

- In order to deposit a ternary oxide such as $SrTiO_3$, we will need 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.

ALD Titania Precursor

- **The titanium precursor, Ti(isopropoxide)$_2$(THD)$_2$ was deposited at 200C in the presence of the oxygen plasma:**



Ti(iso)$_2$(THD)$_2$ reaction:

-Ti(OCH(CH$_3$)$_2$)$_4$ + 35O* $\rightarrow$

-TiO + 12CO$_2$ + 14H$_2$O

Progress vs. Milestones

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

Develop ALD synthesis of selected H_2 conducting oxide	1/08
Deposit proton conducting films in 4 different thicknesses	6/08

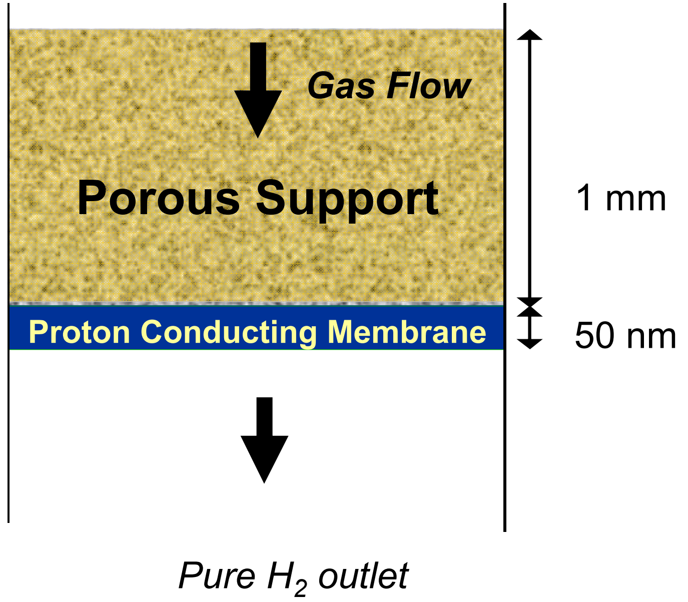
For this subtask to be on track, we will:

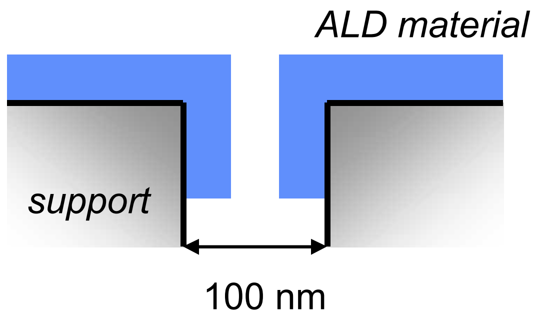
• Obtain correct stoichiometry for $SrTiO_3$	5/31/08
• Determine whether a sintering step will be necessary	5/31/08
• Deposit films in 4 thicknesses	6/30/08

Sandia National Laboratories

Microporous Layer

- Desire pore openings approximately 50 nm after silica layer formation.
- Two potential routes
  - Apply microporous silicate layer
  - Use ALD deposition of sulfur getter or alumina to narrow the effective pore diameter





Sandia National Laboratories

Microporous Layer, Cont.

- A silicate forming sol is synthesized by adding nitric acid to a mixture of TEOS (tetraethyl orthosilicate) and 2-propanol.
- A thixotropic agent constituted from modified urea (BYK-420 from BYK Chemie) is added in an amount between 6 to 10% of the final sol volume.
- The surface of the Al_2O_3 disk is brought into contact with the sol, then laid flat until set.
- The disk is then placed in a drying oven at 50°C for a minimum of 3 hours. Calcination at 500°C for 3 hours removed the templating agent.
- The resulting film is approximately 1 um thick, with pores that may be tuned in average diameter from 2 to 10 nm by increasing the amount of the thixotropic agent. [1]

- 1] Boffa, v., ten Elshof J. E., Blank, D. H. A. Microp. Mesop. Mat. 100, (2007) 173.

Sandia National Laboratories

Progress vs. Milestones

Subtask 2.2 - Synthesis of Microporous Silicate Support materials

Synthesize support films with four different pore sizes	01/08
Complete studies on effect of pore size and thickness of support layer on membrane thickness.	06/08

For this subtask to be on track, we will:

- Form a silicate microporous film in one additional pore diameter — 5/31/08
- Compare deposited films on the 4 coated supports — 6/30/08

Protective Coating

To form the ZnO layer, we cycled between Diethyl Zinc $[Zn(C_2H_5)_2]$ and water at 200 °C.

DEZ half-reaction:

$Zn(C_2H_5)_2 + -OH^* \rightarrow -OZn(C_2H_5)^* + C_2H_6$

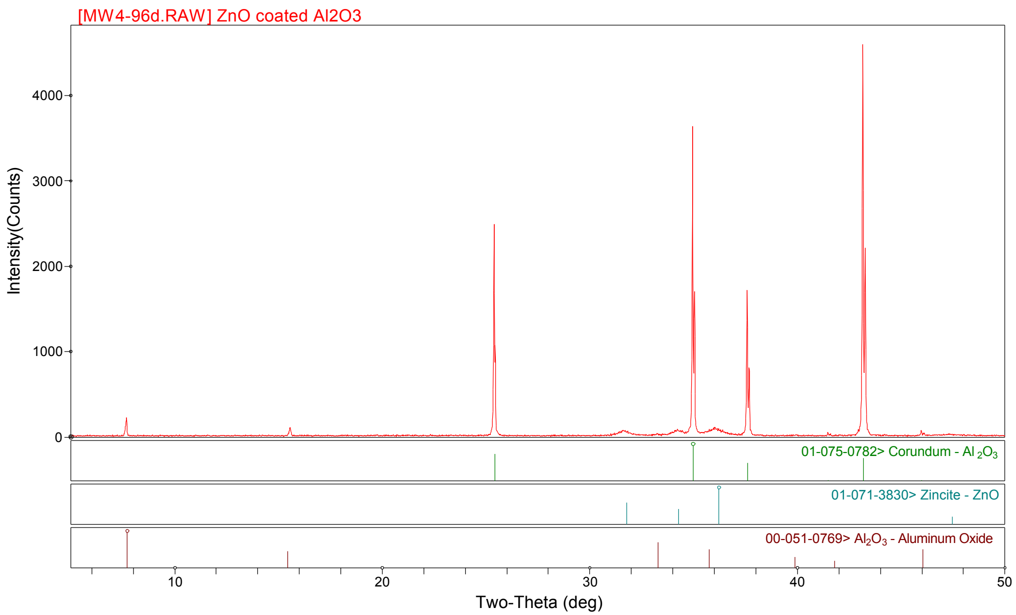
H_2O half-reaction:

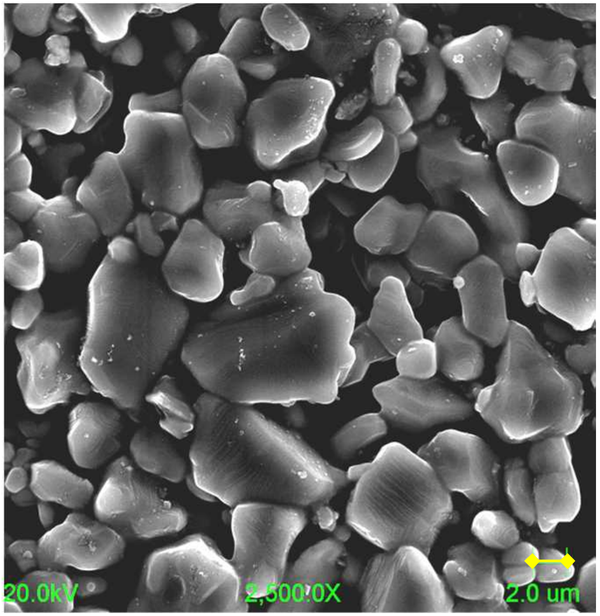
$H_2O + -Zn(C_2H_5)^* \rightarrow -Zn(OH)^* + C_2H_6$

(* - surface species)

Protective Coating

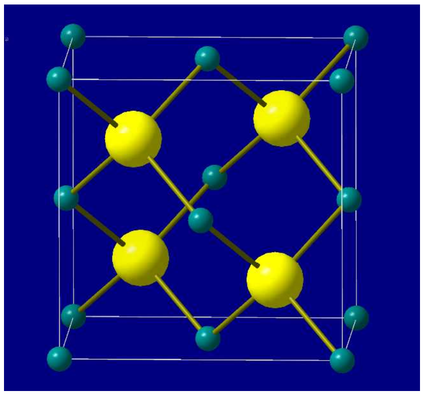
- We deposited 450 Å of ZnO on a γ-Al_2O_3 mesoporous disk support (effective pore diameter is 1.8 μm).
- The coated support has a surface area of 1.19 ± 0.03 m^2/g, whereas the uncoated support has a surface area of 1.65 ± 0.04 m^2/g.



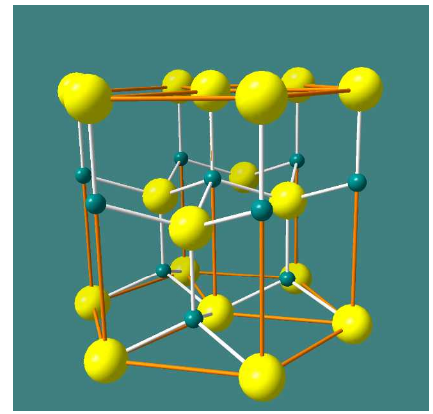


Sandia National Laboratories

Sulfur Sorption Process



ZnO,
Cubic,
a = 5.41 Å

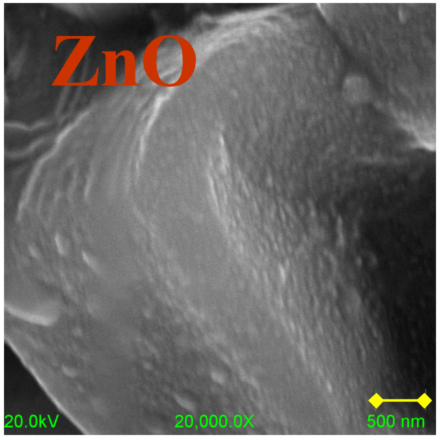


ZnS,
Hexagonal,
a = 5.41 Å

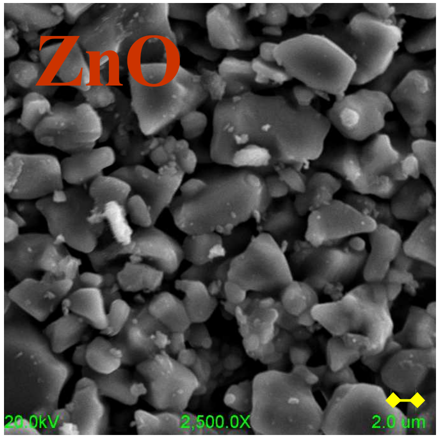
- While ZnO scavenges sulfur readily, the phase change and corresponding lattice parameter change between ZnO and ZnS leads to decrepitude in solid pellets. To investigate the effect of cycling on the thin ZnO coating, several ZnO coated supports were placed in a furnace and heated to 500°C at a ramp rate of 1 degree per minute. The supports were exposed to 2% H_2S in N_2 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

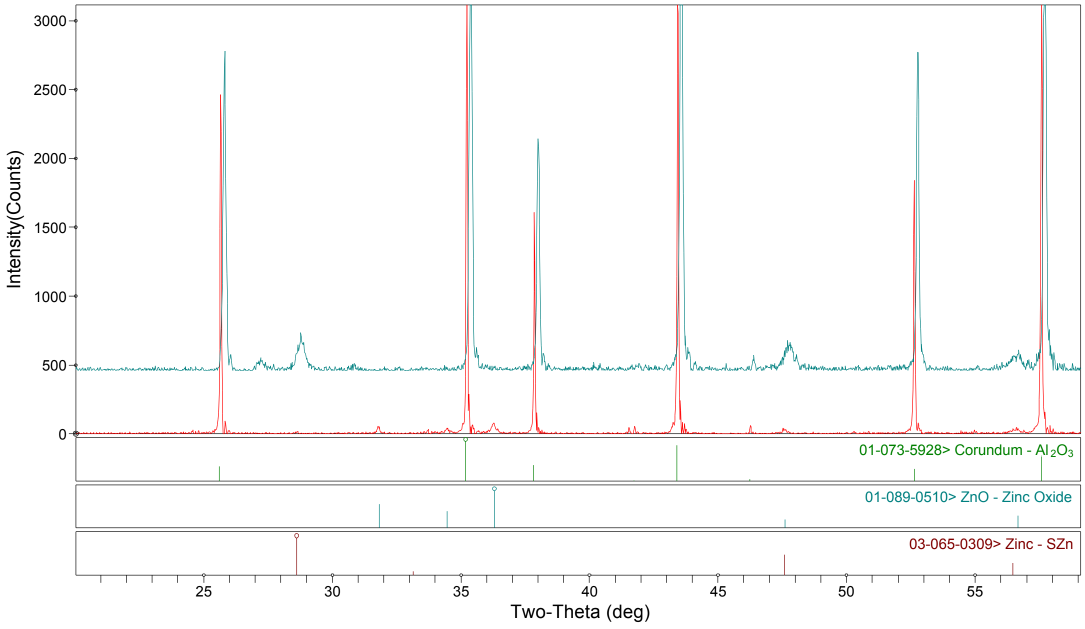
- **After converting the coating to ZnS and then back to ZnO, the coating surface is noticeably rougher as seen in the SEM.**



500 nm

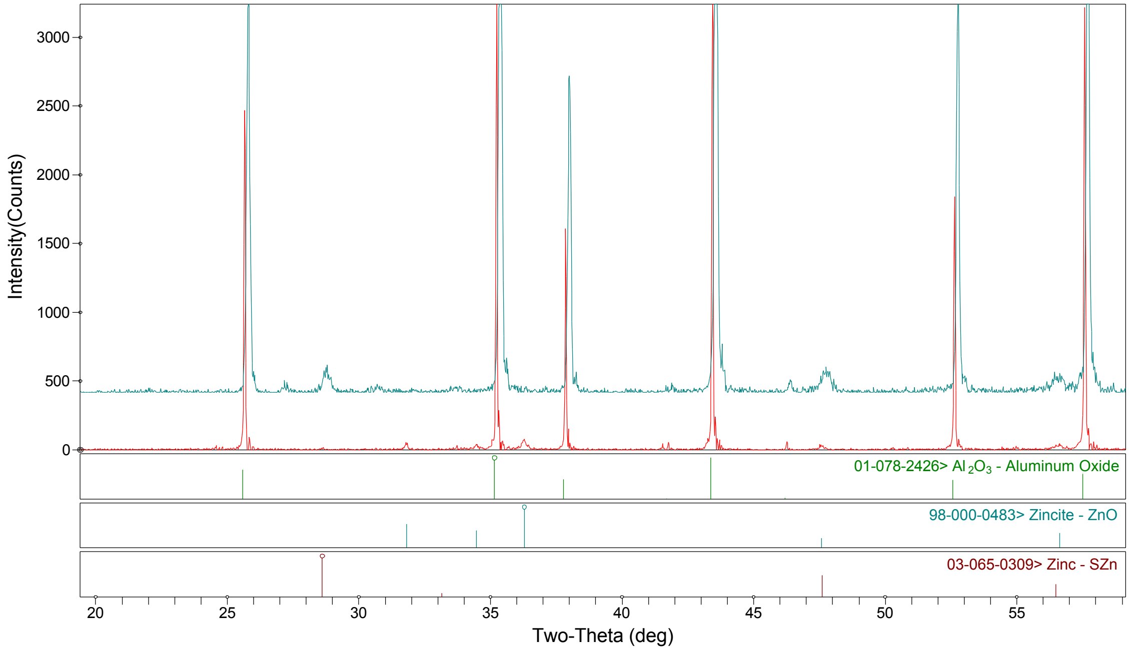


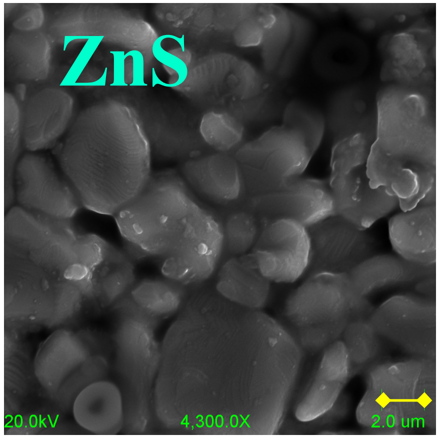
2.0 μm



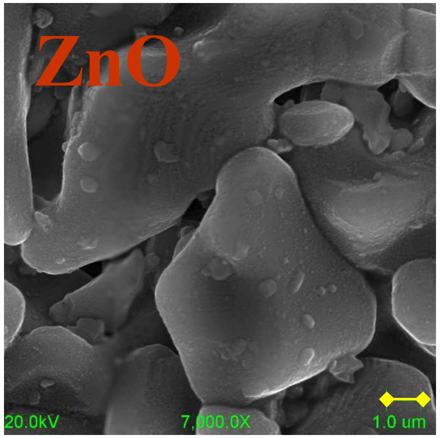
After 3 cycles

- **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

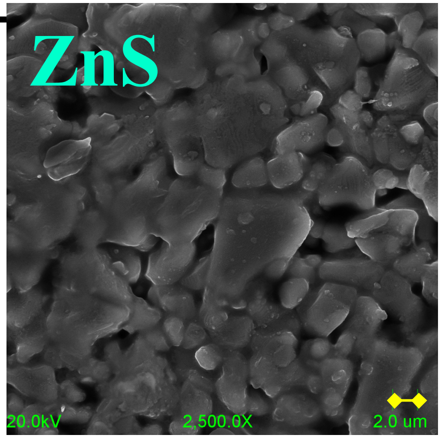


1.0 μm

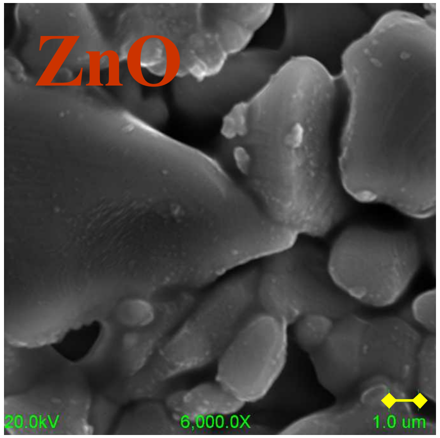
Sandia National Laboratories

After 7 cycles

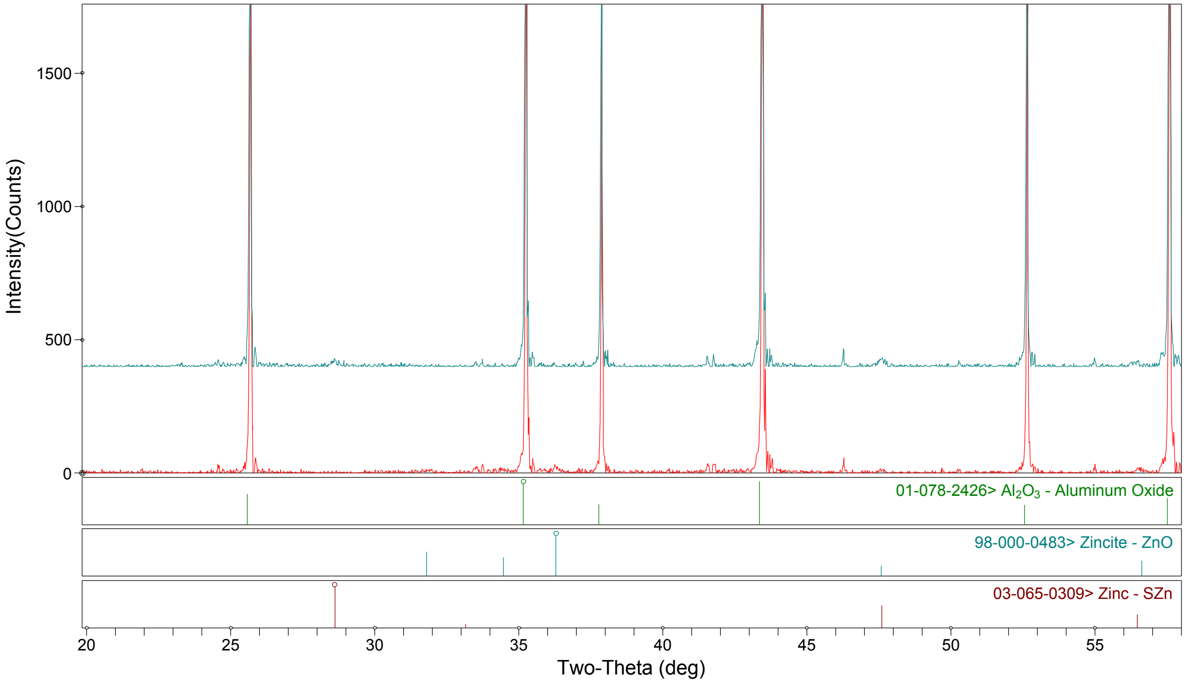
- After seven cycles, peak intensity is much reduced. A few islands remain visible in SEM images.



2.0 μm



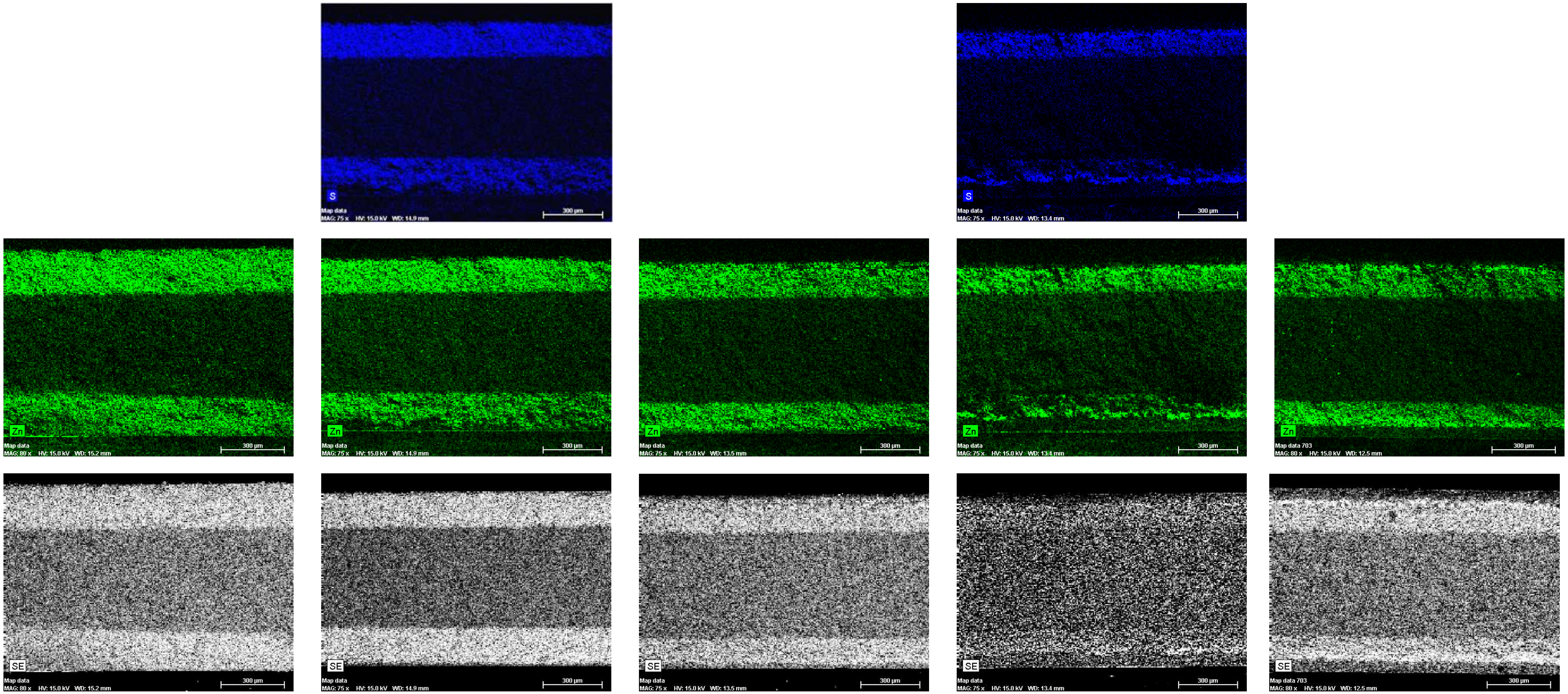
1.0 μm



Sandia National Laboratories

Comparative SEM/EDS results

Blue – sulfur, Green – zinc



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

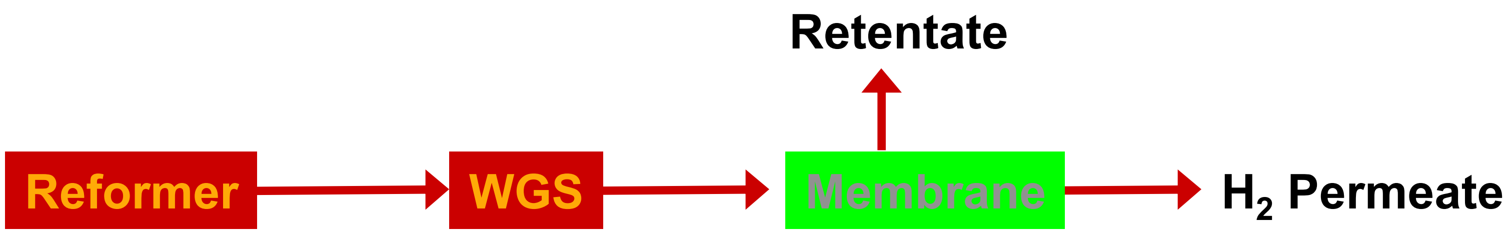
Progress vs. Milestones

Subtask 2.2 - Synthesis of Microporous Silicate Support materials
Complete sulfur uptake studies on ZnO 09/08

We will complete this subtask ahead of schedule:

- Determine capacity of getter coating 5/31/08
- Determine rate of sulfur uptake 7/30/08

Conceptual systems



- Ideally will replace part or all of the PSA systems (follow the WGS in a system installation)
  - Potential for application within the WGS unit
- Membrane module will use natural gas feedstocks, and potentially reformed bio-derived feedstocks
- Other energy usage: use co-generated heat and supplement

DOE Targets

Rough Estimates using data from bulk membranes:

- **Cost per square foot of membrane:** Estimated $1000 [a]
- **Module cost:** Estimated $2000 [a]
- **Flux rate:** Current bulk ceramic proton conductors = 25 scfh/ft^2 (not thin membranes) [b, c, d]
- **% H_2 recovery:** estimated 50% [b, c, d]
- **Hydrogen quality:** Conduction mechanism produces pure, >99.9% H_2. Experiments will bear this out. [b, c, d]
- **Operating temperature:** Anticipate 650 to 900°C [b, d]
- **Operating pressure:** Anticipate up to 400 psi. [b, c, d]
- **Durability:** Unknown. Module has the potential for long service life. Dependant on interaction of getter with proton conducting membrane.

References:

- Based on unoptimized precursors and deposition parameters.
- Matsumoto, H.; Hamajima, S.; Iwahara, H. Solid State Ionics 145 (2001) 25.
- Shimura, T.; Tokiwa, Y.; Iwahara, H. Solid State Ionics 154 (2002) 653.
- Kokkofitis, C.; Ouzounidou, M.; Skodra, A.; Stoukides, M. Solid State Ionics 178 (2007) 507.

Sandia National Laboratories

Additional Opportunities

- Sulfur removal
  - Water purification – such as produced water
  - Almost all mined gas streams
- Thin proton conducting membranes
  - Any steam reforming process
  - Thermo-chemical cycles
- Other:
  - Conformal coating of ternary oxides could be important in electro ceramics (ferroelectrics, SHG materials, piezoelectrics)

Sandia National Laboratories

Summary

- Successful deposition of titania, and recently SrO
- Synthesis of microporous layer using sols and ALD
- Successful deposition of ZnO. Studied the conversion of coating to ZnS, and the effects of multiple regenerations

Acknowledgments

- Robert K. Grubbs
- Andrea Ambrosini