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

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Overview

Timeline

- Project start date: June, 2007
- Project end date: Sept., 2010
- Percent complete: 60%

Budget

- Total project funding
  - DOE share: 100%
- Funding received in FY07: 200K
- Funding for FY08: 450K
- Funding for FY09: 0K
  - Carryover funds used to complete FY08 tasks.

Barriers

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

Partners

- Potential partners not pursued after FY08
  - *Eltron Research and Development for independent testing*
  - *Pall Corp. for additional support materials and end seal design assistance*

Relevance - Objectives

Overall:

- Provide a separation module containing high H_2 flux membranes on a support that is protective against corrosive impurities
  - Dense metallic membranes show up to 50% reduced proton flux after attack by corrosive species in the reformate gas stream. Ceramic membranes are also vulnerable. Our support will remove those species from the gas stream upstream of the membrane.
    - Addresses DOE target for Durability and target for Impurities
  - Synthesize an "ultra-thin" dense ceramic proton conducting membrane to increase H_2 flux with excellent purity over existing membranes
    - Addresses DOE target for H2 selectivity and target for Flux.

For FY08 (continued into FY09)

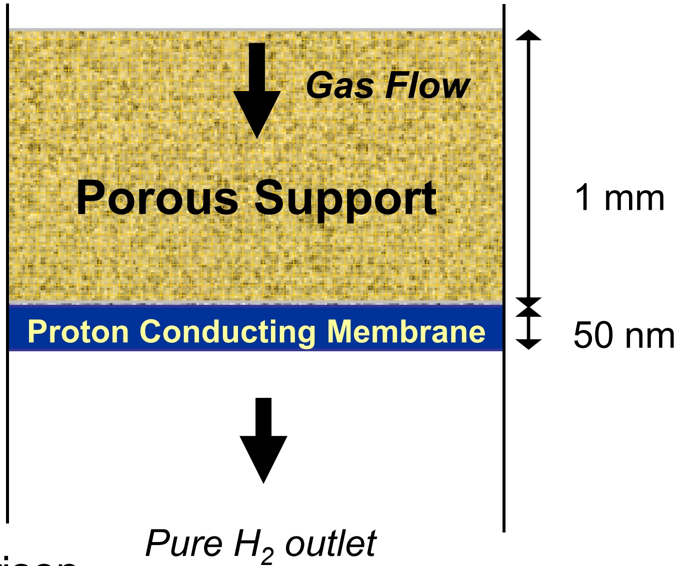
- Complete testing on ZnO coated membranes to demonstrate real world impact.
- Complete comparison testing on dense ceramic H_2 separation membranes to demonstrate effectiveness of ALD technique for membrane deposition.

Relevance - Impact

- Testing has revealed that the sulfur getter technology alone will impact costs:
  – In a gas stream with 100 ppm H_2S 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 cm^2 of coated support would operate for more than 70 days before needing regeneration.
  – Reduce the labor for replacement and disposal costs of typical sorbent materials.
  – As the sulfur getter operates at the same temperature as the reformation process, no additional heating or cooling is necessary, which also reduces cost.

Approach

- Use new technique for material deposition - plasma assisted Atomic Layer Deposition (ALD). 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.



- Optimize materials with known characteristics in a new form
  - Chose $SrTiO_3$ as proton conducting ceramic membrane
    - Known characteristics, good basis for comparison
  - Chose ZnO as sulfur getter
    - Excellent capacity and reaction rates.
    - Mitigate material degradation by 'enclosing' in porous support.

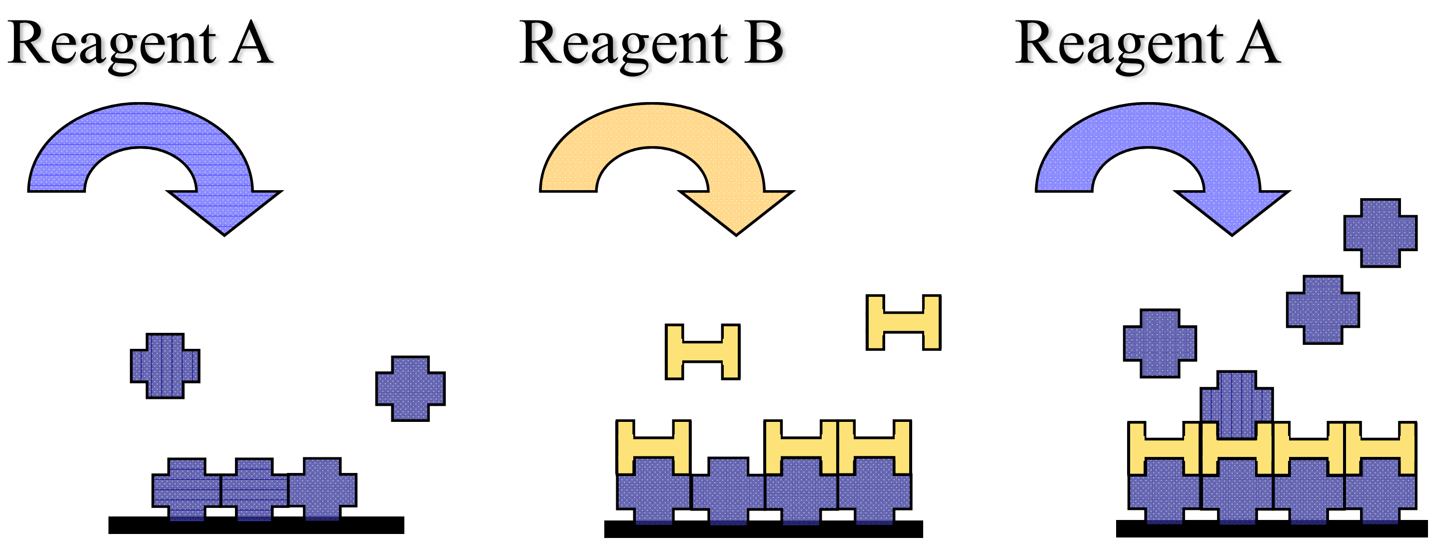
- Design membrane module to be multifunctional – provide chemical protection and support
  - Direct the gas flow through the support to the membrane surface
  - Coat support in getter material

Milestones

Milestone	Progress Notes	% Comp.
Develop ALD synthesis of proton conducting oxide	A change in Sr precursor has led to successful deposition of SrO. Conditions for growth of $SrTiO_3$ are under investigation.	60%
Reduce pore size of support at surface only	Deposition of Al_2O_3 via ALD to a depth of 20um into the support can tailor the pore size to any diameter.	100%
Demonstrate ability of getter coating to remove sulfur impurities	Capacity determination is complete. Rate of removal at temperature is under investigation.	90%
Determine the lifetime of the getter coating	Preliminary thermal cycling reveals coating is durable for more than 10 cycles. Tests continue in order to provide greater confidence in lifetime estimates.	90%
Demonstrate enhanced H_2 flux through membranes and compare to DOE targets	This task awaits successful deposition of the proton conducting membrane.	0%

Approach - ALD Process

- New approach to membrane fabrication
- 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

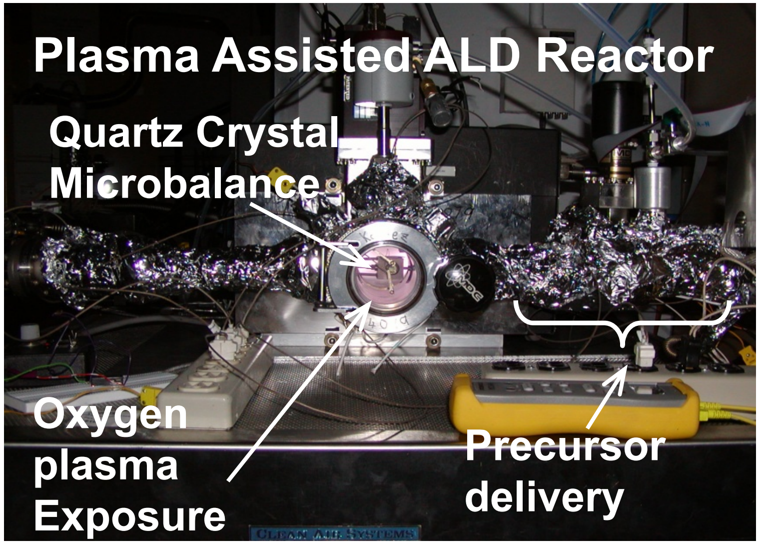


Previous Technical Progress

- Successful deposition of titania, and partial deposition of SrO.
  - The proton conducting membrane, $SrTiO_3$, will be formed by sintering alternating layers of SrO and TiO_2.
- Synthesis of microporous interlayer layer using sols.
- 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.

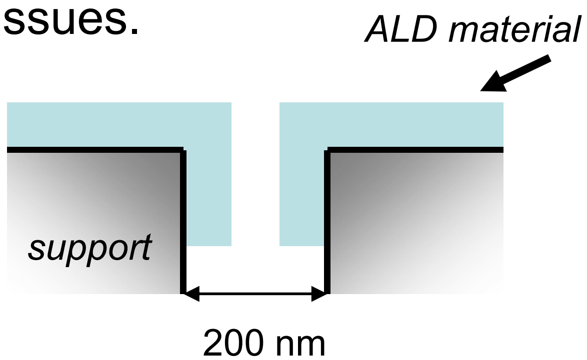
Technical Progress

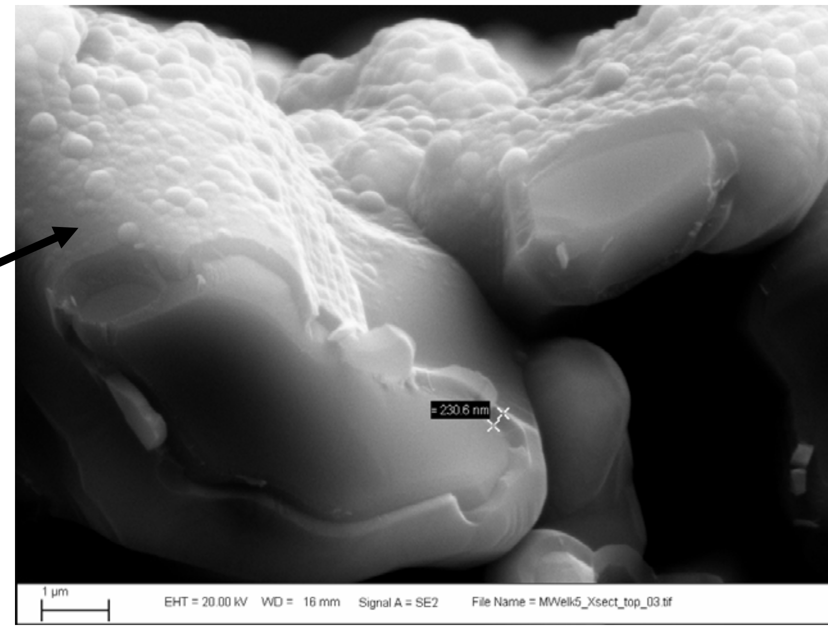
- New Sr precursor
  - Previous precursor, Sr(THD), proved incompatible with TiO_2 deposition. Water pulse partially removed deposited strontium. (verified using QCM).
  - Hyper Sr strontium precursor from Air Liquide has greatly improved vapor pressure and successfully deposits with TiO_2.
  - Optimization of layer thickness of both TiO_2 and SrO in order to produce ultra thin $SrTiO_3$ membrane is underway following recently published results.



Technical Progress

ALD deposited Al_2O_3 on porous Al_2O_3 support serves to neck down the pore size at the support surface. Material consistency eliminates thermal expansion issues.

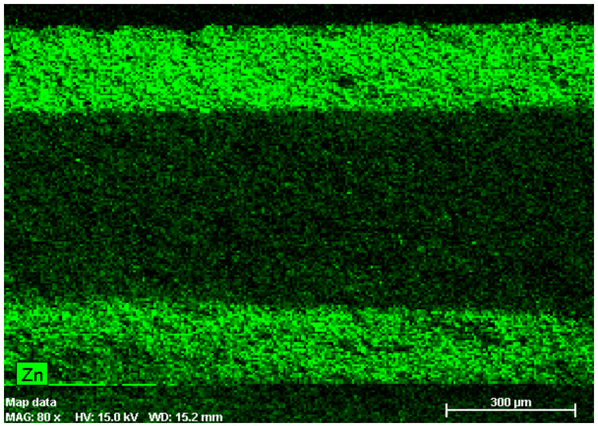




- Reduction of the pore diameter of the support only at the surface to be covered with thin membrane means that gas will flow unrestricted through the support to the membrane surface. (Eliminates dead zone.)

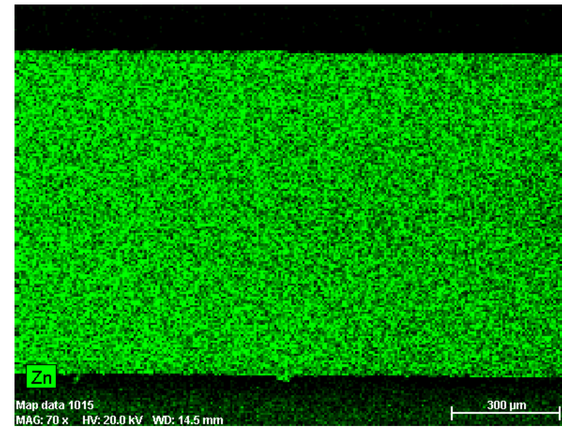
Technical Progress

Previous work



Cross sections of ZnO coated porous Al_2O_3 supports

Optimized deposition



Previous work led to incomplete ZnO deposition. (Green indicates presence of Zn). Uniform deposition throughout the porous support was accomplished using a quasi –static ALD process. This result means more sulfur getter per square inch of support = greater capacity = increased lifetime.

- Completed uniform deposition of ZnO (sulfur getter material) throughout the support increasing getter capacity.

Technical Progress

- To determine capacity, a coated support was reacted with a stream of H_2S gas until complete conversion was achieved. The sample was then placed in a Thermal Gravimetric Analyzer and heated under flowing air. The weight loss arising from the oxidation of ZnS to ZnO was recorded, and the moles of Zn per gram of coated material was calculated. Per square cm of porous support (1 mm thick), there are $1.35 * 10^{-4}$ moles of ZnO.

- A gas stream containing 100 ppm of H_2S (typical contaminant level in reformate streams), flowing at 3 mL/min over 1 cm^2 of coated support at >450°C would be purified for 10 hours. Scale that to a tubular membrane and support module system with 2 cm diameter tubes 25 cm in length, or with 157 cm^2 of coated support would operate for more than 70 days.

- Investigation on the rate of sulfur removal by the ‘enclosed’ ZnO sulfur getter is underway.

- A reformer design with two parallel streams could have one module removing sulfur, while regenerating the second to avoid shut down during regeneration. Each module would remove sulfur for more than 70 days continuous operation.

Collaborations

- Preliminary contacts with Eltron Research and Development and Pall Corporation were made in FY08 before H_2 production funding was zeroed.
  - Collaborations were not pursued.

Future Work

Remainder of FY09:

- Obtain correct stoichiometry for ALD deposited $SrTiO_3$ (6/09)
- Determine post processing conditions to obtain a dense film (7/09)
- Deposit $SrTiO_3$ films in 4 thicknesses and test H_2 permeation (9/09)
- Determine rate of sulfur uptake (7/09)

- **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 FY10, we will determine optimal membrane thicknesses, optimal amounts of getter material deposited, and optimal operating parameters. In addition, we will perform permeation tests under real-world conditions, capacity and lifetime experiments, and cost optimizations.

Summary

- Achieved uniform deposition of ZnO throughout high aspect ratio porous support
  - Maximizes mass of sulfur getter material thereby decreasing frequency of getter regeneration
- Tailor-able deposition of Al_2O_3 onto support
  - Control of both depth of penetration and thickness of deposited layer
    - Tailors support for ultrathin membrane while eliminating concerns about non-flowing gas, a “dead zone,” near membrane.
- Continued progress toward ALD deposition of proton conducting $SrTiO_3$ membrane with improved SrO precursor.