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

Working Group Meeting Presentation

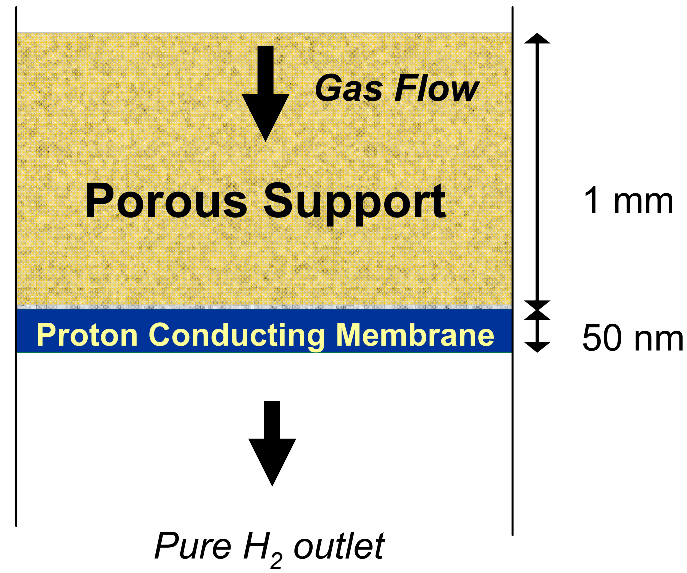
11/07/07

Margaret Welk
Sandia National Laboratories
Team: Robert Grubbs, Andrea Ambrosini

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.

Overview

- **Project Objective**
  - **Synthesize a proton conducting ceramic (e.g. perovskite) membrane using atomic layer deposition (ALD) techniques**
    - **Membrane will be thin – 10 to 100 nm**
    - **Membrane support will be coated with a sulfur getter to deal with contaminants**
      - **Sulfur getter (e.g. ZnO) will be deposited on the mesoporous alumina support via ALD to conformally coat all surfaces**



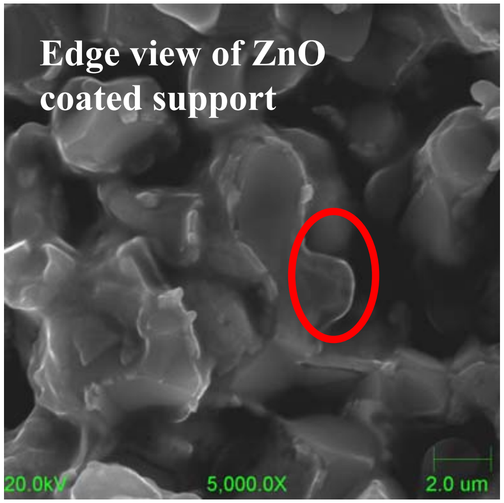
Work to Date

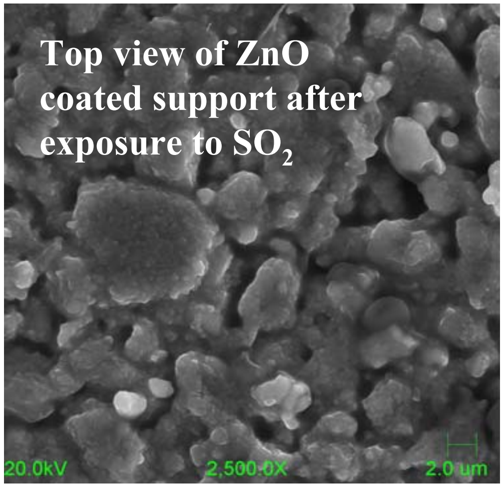
Preparatory Work

- Designed permeation unit
- Identified promising ceramic systems – $SrTiO_2$ and $SrCeO_3$
- Installed oxygen plasma unit for plasma assisted ALD

Experimental Work

- Deposited ZnO conformally on alumina support
- Confirmed phase of deposited material, measured retained porosity of ZnO coated support
- Studied the results of the conversion of ZnO to $ZnSO_4$ after exposure to SO_2





Innovation

- Couple thin proton conducting membrane with protective "getter" support
  - Provide contaminant resistant membrane module
- Use ALD and plasma assisted ALD to obtain desired film and coating characteristics
  - Excellent control with ALD technique
  - Ultra-thin membrane
    - Increase flux
    - Reduce temperature requirements
    - Reduce cost
  - Support conformally coated with getter

Key Performance Metrics

Estimates:

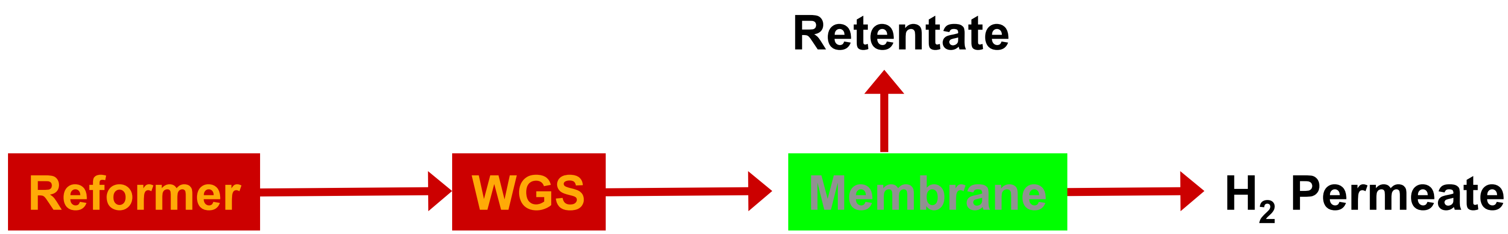
- **Cost per square foot of membrane:** Estimated $1000 [a]
- **Module cost:** Estimated $2000 [a]
- **Flux rate:** Current bulk ceramic proton conductors = 25 scfh/ft^2 (not thin membranes) [b, c, d]
- **% H_2 recovery:** estimated 50% [b, c, d]
- **Hydrogen quality:** Conduction mechanism produces 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

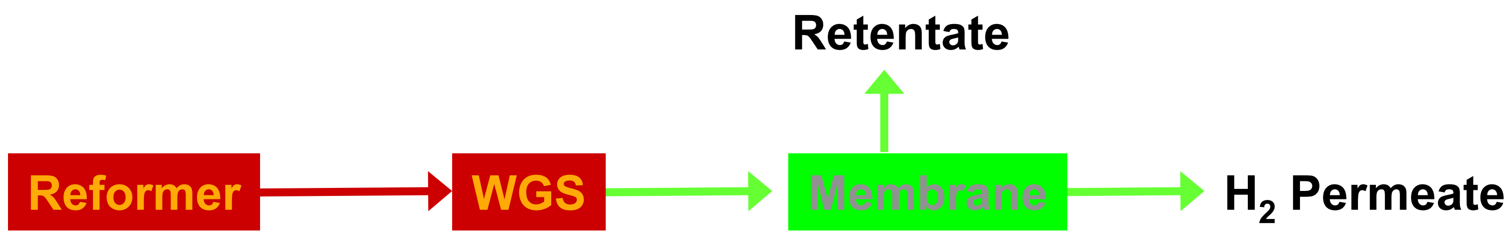
Summarize Unique H2A Inputs



- Ideally will replace part or all of the PSA systems (follow the WGS in a system installation)
- Membrane module will use natural gas feedstocks, and potentially reformed bio-derived feedstocks
- Other energy usage: use co-generated heat and supplement
- Total yearly operating costs: Unknown at this time

Sandia National Laboratories

System Definition



- Will define our system as only the Membrane Module
  - Includes support, membrane and integration structure

  Back of the envelop calculations for bulk membranes:
  - Capacity: estimated per module 0.15 kg H_2/day
  - Inputs: reformed natural gas (steam + NG)
  - Outputs: H_2, retentate consisting of H_2O, CO, CO_2, CH_4, H_2, periodic regeneration of getter material releases SO_2.
  - Anticipated size: Targeting desired flux of H_2 size would currently be approximately 20x20x50 cm

Feed and Energy

- Energy input and output of a membrane module
  - Characteristics of primary feed:
    - LHV of natural gas = 930 Btu/ft^3, or 34.6 MJ/m^3
      - Reformed NG?
  - Energy Utilities with usage rate
    - Unknown
- Other inputs:
  - For membrane module, none.

Other Material Input and Output

- Other materials needed
  - Filter for particulates (part of reforming unit)
  - Purge gas (Air) for getter regeneration
  - Scrubber for sulfur gasses released from regenerated sulfur getter
- Other outputs:
  - Retentate will contain CO, CO_2, H_2O, H_2, CH_4.
  - Regeneration of getter will release SO_2.

Sandia National Laboratories

Assessment of Status

- Uncertainties in the above information
  - All numbers are based on literature values for pressed pellets (~ 1-2 mm thick) of ceramic proton conductors. Until we make and test our first thin membranes (10-50 nm thick) all of these numbers are extremely speculative.
  - Operating temperature, flux, operating pressure, and cost estimates may all change significantly. Our first membrane will be tested early next year.