Photopolymerization/Pyrolysis
Route to Microstructured Membrane Development

Kathryn A. Berchtold
Jennifer S. Young
Los Alamos National Laboratory
Materials Science & Technology Division
26 May, 2004

This presentation does not contain any proprietary or confidential information
Objectives

Provide a rational approach to the design of synthesis processes for robust ceramic membranes with high gas permselectivity.
Budget

Funding in FY04 : 200K

Subtask 1a: Establishment of the membrane fabrication and testing capability and a coarse grained approach to understanding the interrelationship between polymer microstructure and composition and the separation characteristics of the ceramic membrane product.
Technical Barriers and Targets

DOE Technical Barriers for Hydrogen Production:

- Distributed Hydrogen Production from Natural Gas or Liquid Fuels Barriers
  - A. Fuel Processor Capital Costs
  - D. Carbon Dioxide Emissions
- General (Cross Cutting) Hydrogen Production Barriers
  - AB. Hydrogen Separation and Purification

DOE Technical Target for Separation Membranes for Hydrogen Production for 2010

- Flux Rate 200 scfh/ft²
- Cost <$100/ft²
- Operating Temperature 300-600 °C
**Approach**

 Formation of defect-free, robust, ceramic membranes that will maintain gas productivity and selectivity to temperatures in excess of 1000°C

 Fabrication of these membranes via economically viable and established polymer processing techniques.
Thin Film of Liquid Phase Precursors $\xrightarrow{hv}$ Polymeric Membrane $\xrightarrow{\Delta}$ Amorphous / Crystalline Ceramic Membrane

**Spin Coat / Cast**
- (spin cycle conditions, acceleration, velocity, & duration of each step in the cycle)

**UV/Vis Exposure**
- (wavelength, environment, intensity, initiation mechanism & rate, temperature)

**Pyrolysis**
- (environment, pyrolysis rate, ultimate temperature)
Impact

- First commercially viable production of ceramic membranes
- Enabling technology for fuel reforming
- Reduction of parasitic losses in carbon sequestration processes
Challenges

- Forming defect free membranes
- Optimizing membrane fixturing
- Optimizing processing conditions to achieve meaningful selectivity and permeability
Project Safety

Integrated Work Management

- All processes are compliant with the LANL Integrated Work Management process. All processes have had the required management walk-downs. All of the associated Integrated Work Documents / Hazard Control Plans have had all required reviews and all required approvals have been obtained.
Project Timeline

Phase I – Feasibility/Capability Development
A. Design coarse grained experimental program
B. Select Initial Material Chemistries/Functionalities to Evaluate
C. Establish membrane synthesis capability through the proposed processing route.
   - This capability includes all processing steps and experimental protocols necessary to produce, characterize, and test a ceramic membrane as it is produced from inorganic/organic photoactive precursors. Extend our high temperature testing capabilities.

Phase II – Pre-Ceramic Polymer and Ceramic Thin Film Development & Testing
D. Perform initial evaluations on a limited set of preceramic polymer precursors with dramatically different microstructures.
   - Report results on polymer thin film material properties as a function of comonomer composition and polymerization conditions
E. Perform initial evaluations on amorphous ceramic thin film material properties as a function of pre-ceramic polymer properties and pyrolysis conditions
   - Report results from initial ceramic material evaluations

Phase III – Amorphous Ceramic Membrane Testing
F. Membrane production and testing
   - Report results from initial evaluations on amorphous ceramic membrane permselectivity as a function of pre-ceramic polymer properties, pyrolysis conditions, and operating temperature
Technical Accomplishments/Progress

- Established membrane synthesis capability through the proposed processing route with selected materials.
  - Established Experimental Design
  - Selected Chemistries/Materials for Initial Evaluation
  - Integrated Work Management
    - All processes are compliant with the LANL Integrated Work Management process. All processes have had the required management walk-downs. All of the associated Integrated Work Documents / Hazard Control Plans have had all required reviews and all required approvals have been obtained.
  - With a Single Formulation:
    - Initial film casting procedures were established
    - Cast films were photopolymerized under controlled conditions
    - Polymerization kinetics monitoring and evaluation protocols were established and tested
    - Controlled Pyrolysis Capability was Established
      - Multiple atmospheres including reactive environments can be used
      - Temperature range: ambient to 1700 °C
      - Control of temperature ramps, soaks, and gas switching during pyrolysis
    - Protocols and equipment are in place for TGA, MS, and FTIR evaluation of the pyrolysis process
Technical Accomplishments/Progress

- Established membrane synthesis capability through the proposed processing route with selected materials.
  - A membrane fixture for high temperature (ambient – 800 °C) permeation testing of ceramic membrane films has been designed and constructed.
  - Single gas and multi-gas permeation test rigs are in place for membrane permselectivity evaluation.
  - A membrane fixture for high temperature above 800 °C has been designed and is being fabricated.
Experimental - FTIR

- Monitor the decay in reactive functionalities and appearance of new functionalities via the change in the appropriate absorbance peaks over time.

- Temporal resolution: 30 ms

- Obtain complete monomer → polymer → ceramic spectra with time.

**The spectra presented above are NOT representative of the materials utilized in this work.**
Sample Stage/ Sample Holder (incorporating temperature (-40 to 250°C transmission and ambient to 1400°C gas phase during pyrolysis) and atmosphere control)

- Horizontal Orientation
- Increased Control
- Repeatability
Large Scale Photopolymerization for Membrane Fabrication

1000W Arc Lamp
Optical Train

Controlled Atmosphere Chamber
Future Work

Remainder of FY 2004

- Continue initial evaluations of pre-ceramic polymer thin film properties as a function of comonomer concentration on a limited set of precursors.
- Perform initial evaluations on amorphous ceramic thin film material properties as a function of pre-ceramic polymer properties and pyrolysis conditions.
- Amorphous Ceramic Membrane Production & Testing

Remainder of FY 2004 - FY05 (Funding Dependant)

- Subtask 1b: Implementation of a full factorial experimental design to elucidate the factors that most significantly impact the permselectivity of the final membrane product.
Funding

Department of Energy
DOE / EERE Hydrogen Production & Delivery
Los Alamos National Laboratory

Los Alamos National Laboratory is operated by the University of California for the United States DOE under Contract W-7405-ENG-36. This document has been designated LA-UR-04-2805.