Photopolymerization/Pyrolysis Route to Microstructured Membrane Development

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Objectives

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

Budget

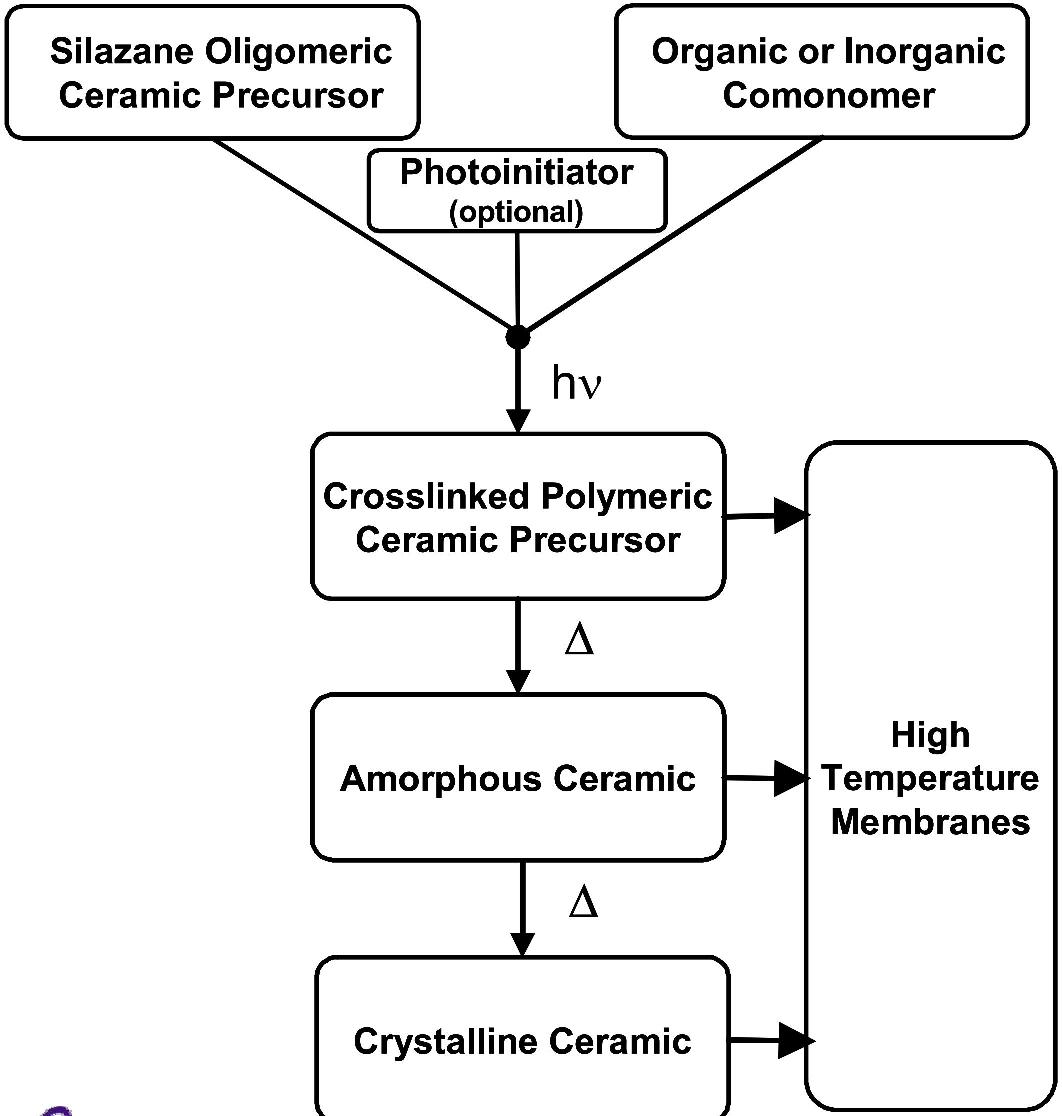
- Funding in FY04 : 200K

  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

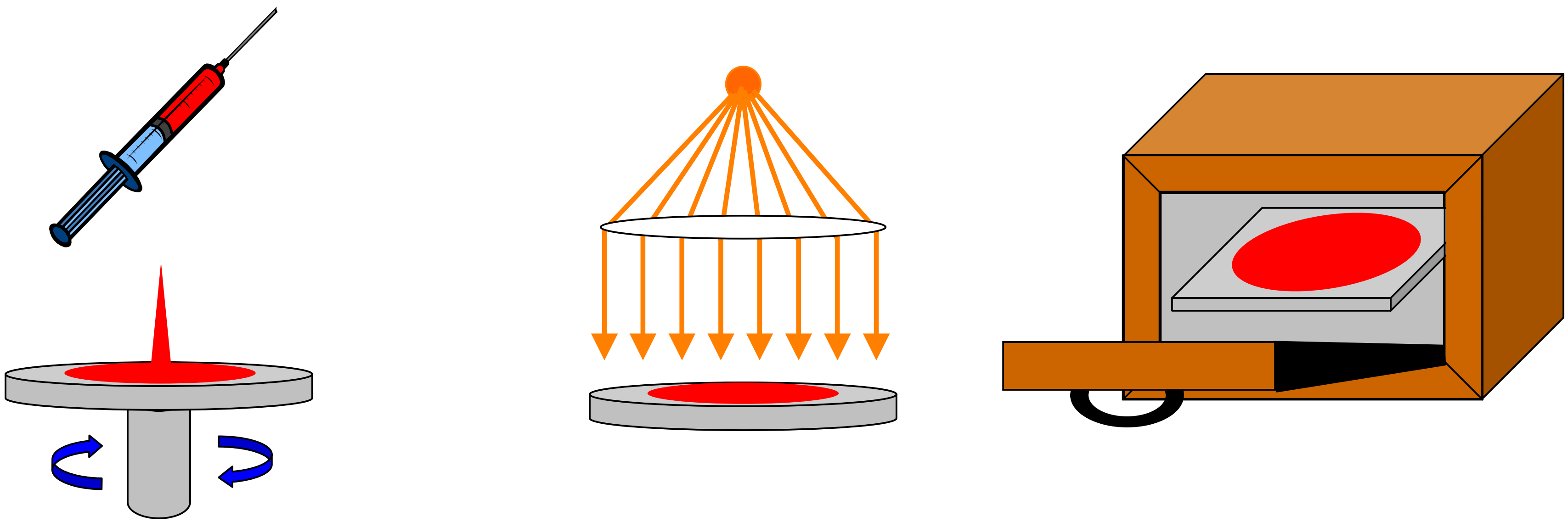
- DOE Technical Barriers for Hydrogen Production:
  - Distributed Hydrogen Production from Natural Gas or Liquid Fuels Barriers
    - A. Fuel Processor Capital Costs
    - D. Carbon Dioxide Emissions
  - General (Cross Cutting) Hydrogen Production Barriers
    - AB. Hydrogen Separation and Purification
- DOE Technical Target for Separation Membranes for Hydrogen Production for 2010
  - Flux Rate 200 $scfh/ft^2$
  - 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 → (hν) → Polymeric Membrane → (Δ) → Amorphous / Crystalline Ceramic Membrane



Spin Coat / Cast

(spin cycle conditions, acceleration, velocity, & duration of each step in the cycle)

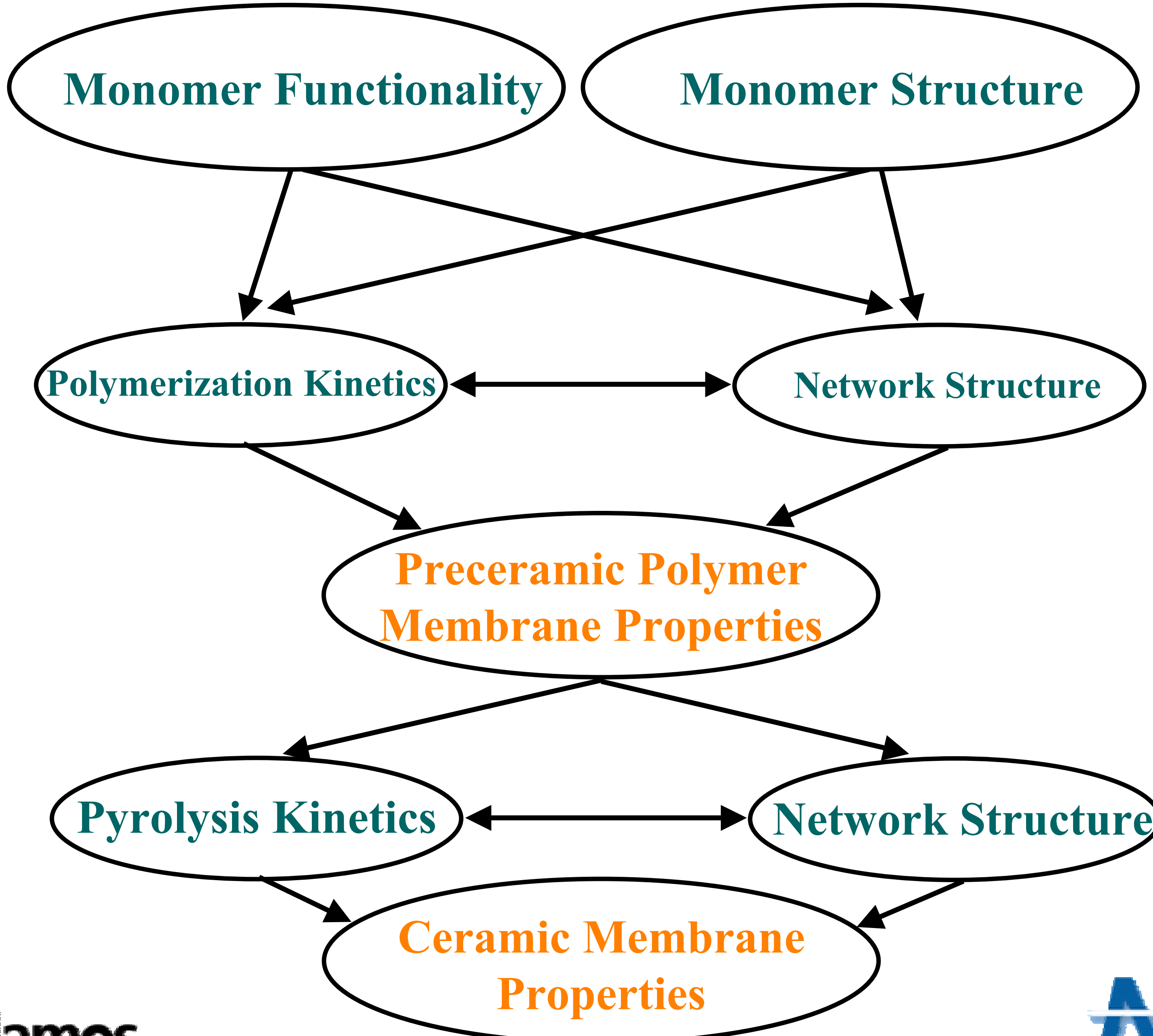
UV/Vis Exposure

(wavelength, environment, intensity, initiation mechanism & rate, temperature)

Pyrolysis

(environment, pyrolysis rate, ultimate temperature)

Membrane Property Manipulation



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Impact

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

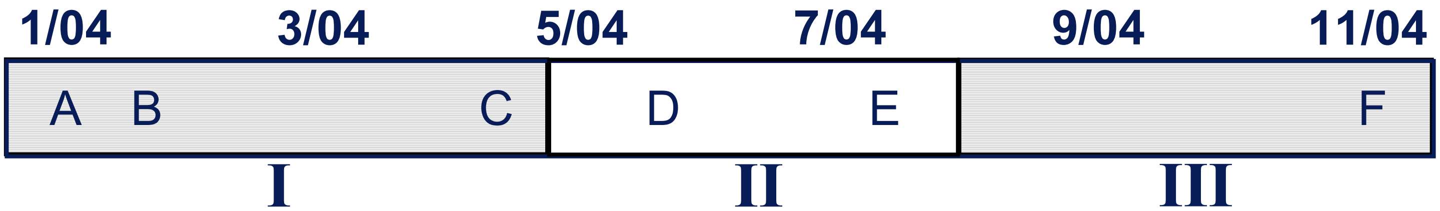
Challenges

- 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

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Technical Accomplishments/Progress

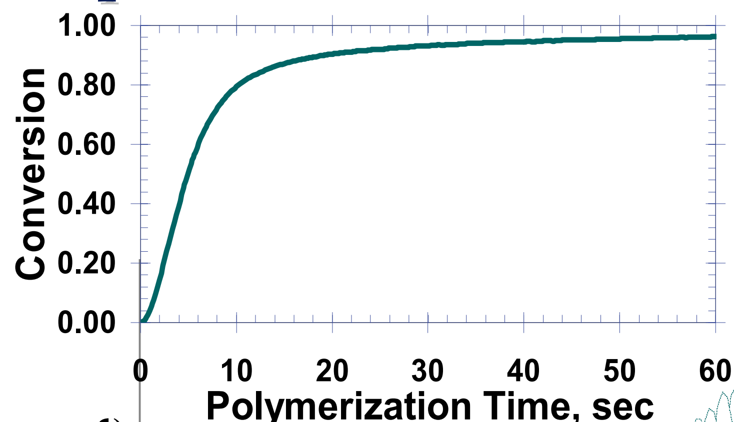
- Established membrane synthesis capability through the proposed processing route with selected materials.
  - Established Experimental Design
  - Selected Chemistries/Materials for Initial Evaluation
  - Integrated Work Management
    - All processes are compliant with the LANL Integrated Work Management 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

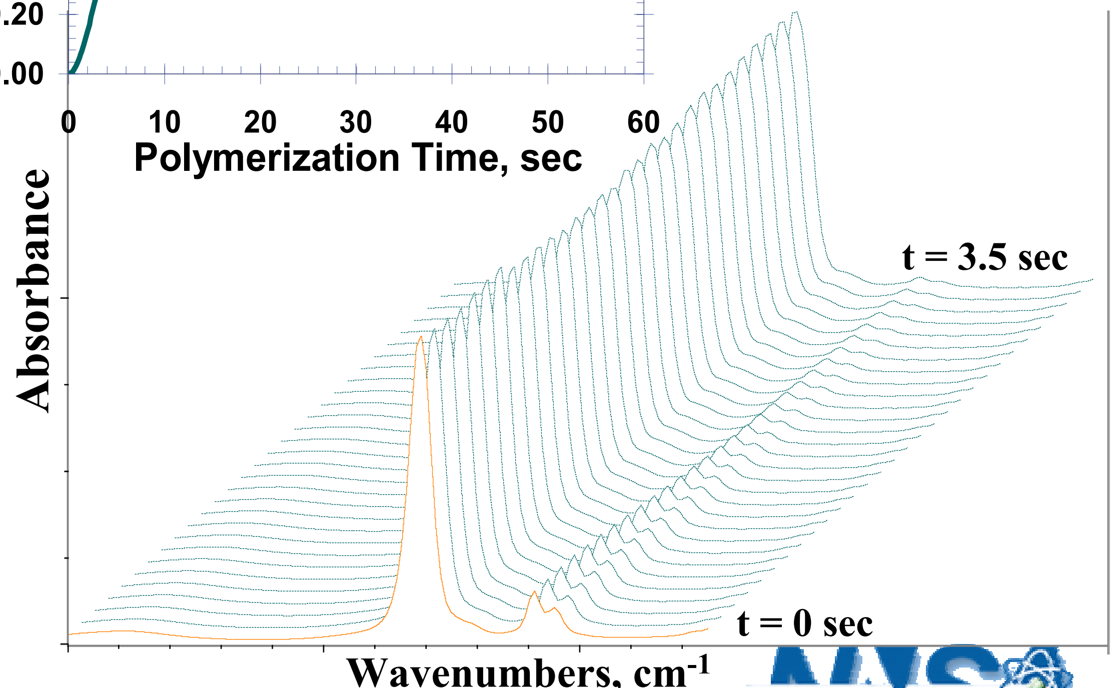
Technical Accomplishments/Progress

- 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

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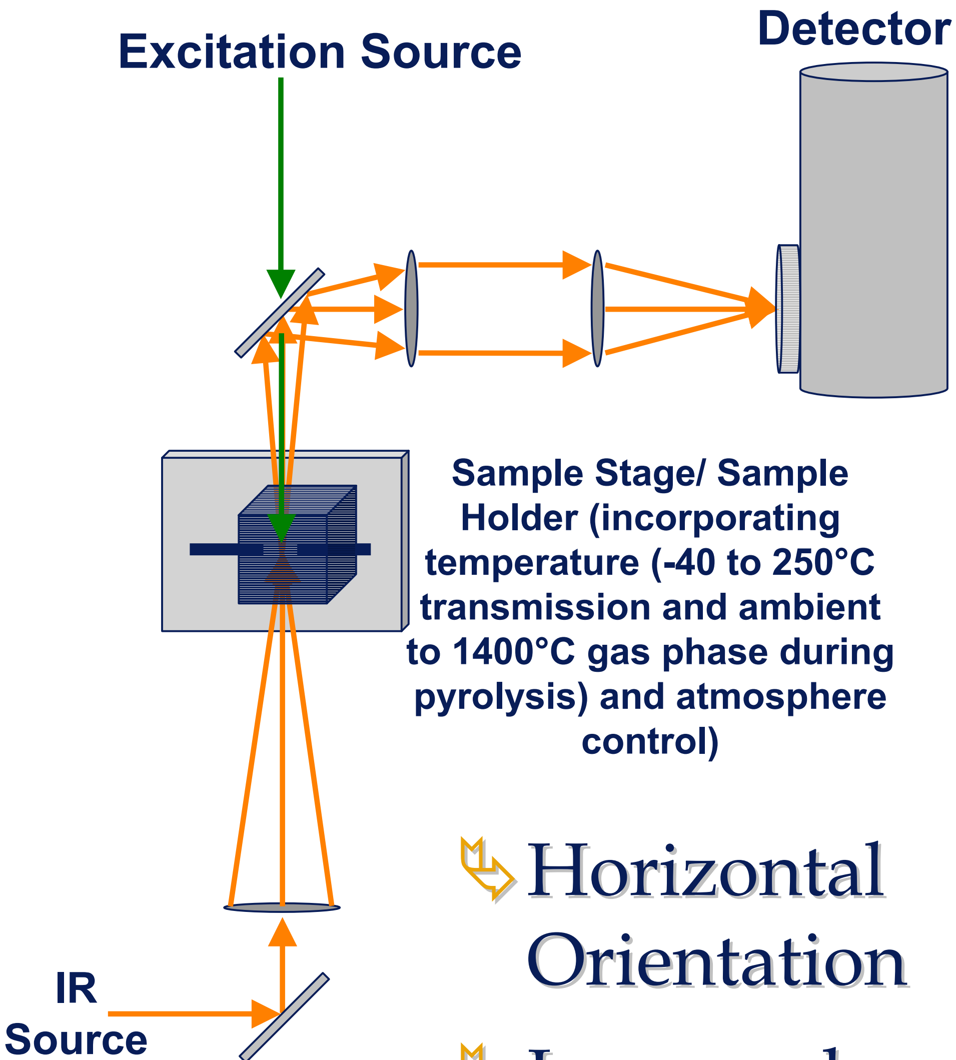

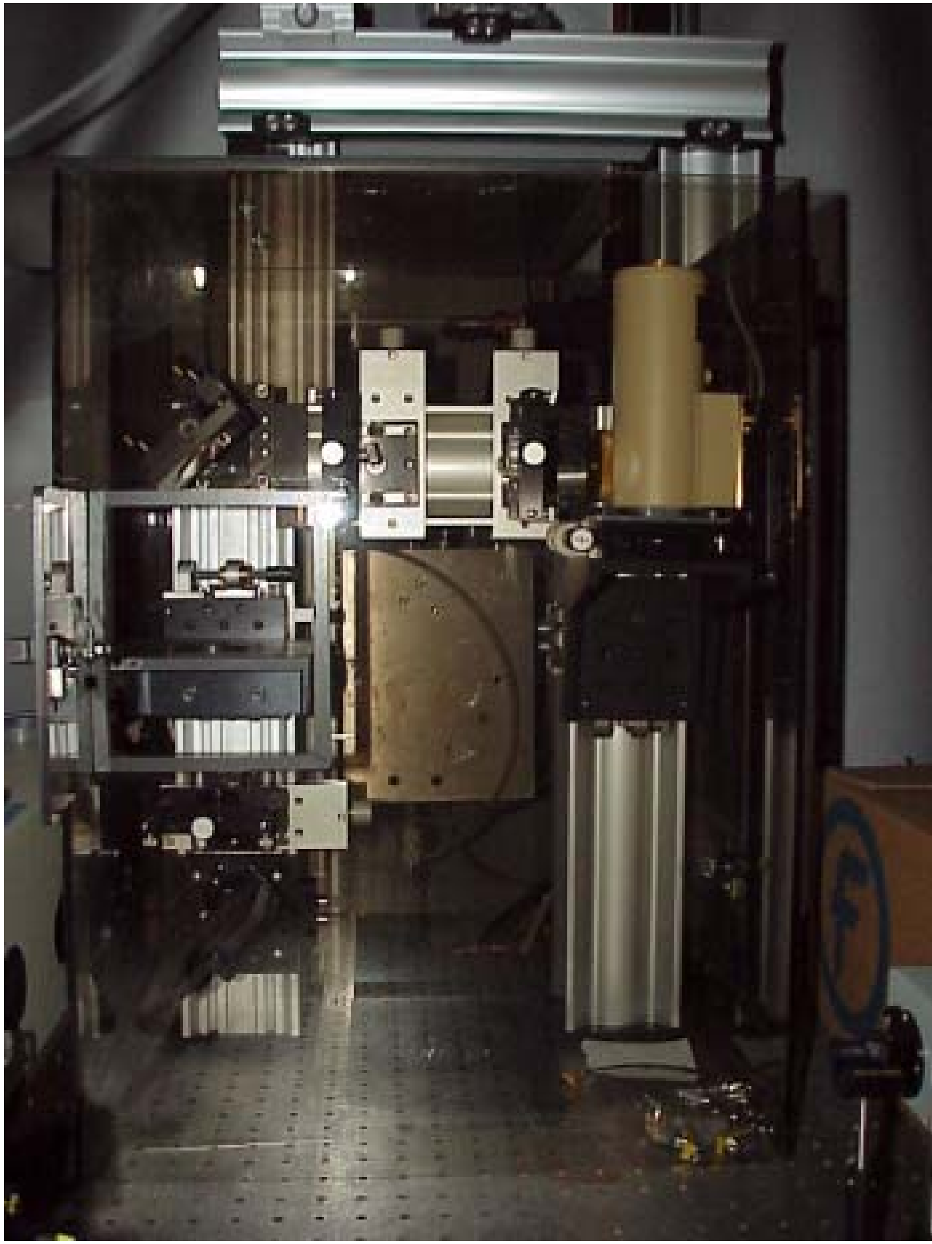

- Horizontal Orientation
- Increased Control
- Repeatability

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

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