



2008 DOE Hydrogen Program Review

Hydrogen Production and Fuel Cell Research

University of South Florida
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Arlington, Virginia

Project ID #
PDP 13

Participants and Projects

Participants

- **PI/Co-PI:** Yogi Goswami, Lee Stefanakos
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- **Ph.D. Graduate students:** M. Schmidt, P. Algarin, S. Vakkalanka, J. Fedock

Projects

Hydrogen Production and Fuel Cell (PDP 13)

- Thermochemical H₂ Production
- H₂ Production from Biomass
- Photoelectrochemical H₂ Production
- Photocatalytic H₂ Production
- PEM Fuel Cell Research (Freeze Degradation)
- PEM Fuel Cell Research (Electrolyte Development)

Hydrogen Storage (Please see STP 31)

Thermochemical H₂ Production

Overview

Timeline

Start: October 2005

End: August 2009

Percent Completed: 80%

Barriers

- **3.1.4.2.5 U,V,X**

- High Temperature Thermochemical Technology
- High Temperature Robust Materials
- Coupling Concentrated Solar Energy and Thermochemical Cycles

Objectives

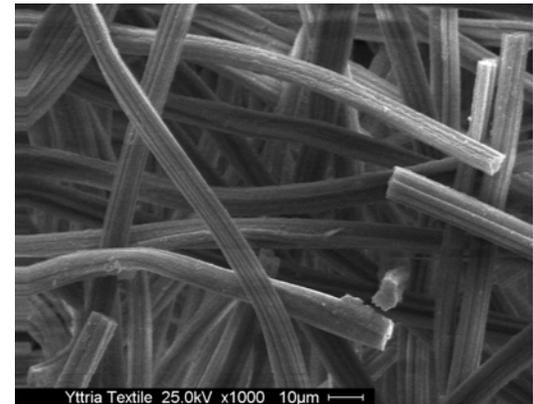
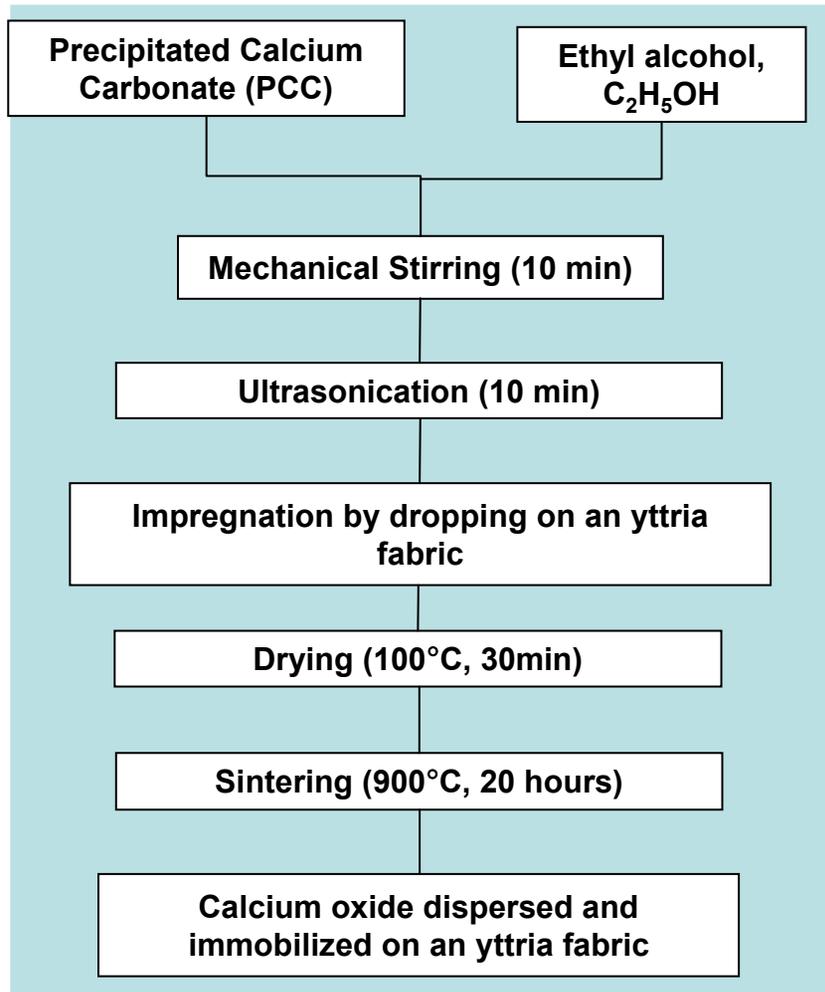
- Investigate a feasibility of UT-3 thermochemical cycle theoretically and experimentally
- Develop a calcium oxide reactants with favorable characteristics and better performance
- Conduct kinetic studies of gas-solid reactions to examine and improve cyclic stability and performance of solid reactants
- Lower hydrogen production cost by increasing hydrogen yield with an improved solid reactant

Approach

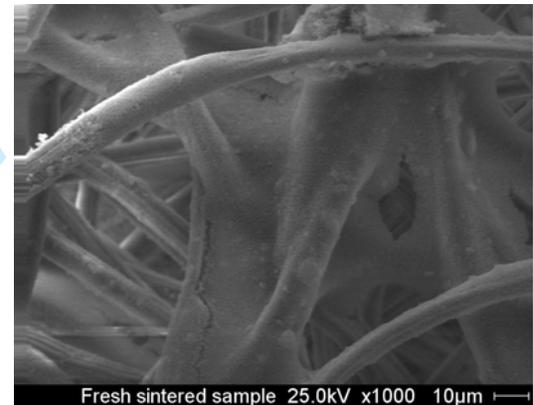
- Thermodynamic simulations for theoretical optimal operation conditions
- Development of calcium oxide solid reactants dispersed and immobilized on an yttria fabric via a simple and inexpensive preparation process
- Chemical kinetic studies to evaluate and improve the cyclic life, reaction rates and conversion of the solid reactants using lab-scale apparatus
- A parametric study to determine the effect of inert material amounts in the solid reactants, incomplete conversion and heat recovery on the efficiency.

Accomplishments

- ◆ A durable calcium oxide reactant immobilized on an yttria fabric was fabricated via a new developed inexpensive and straightforward process.



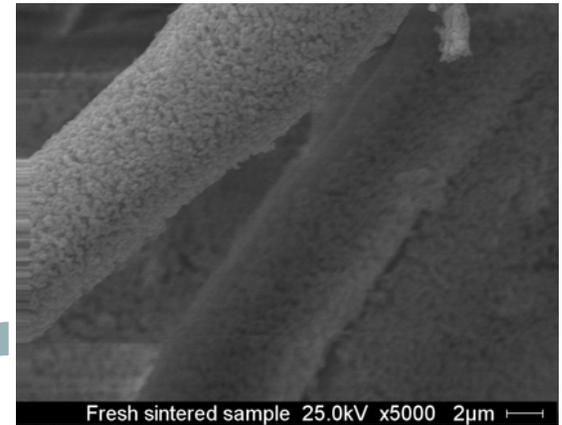
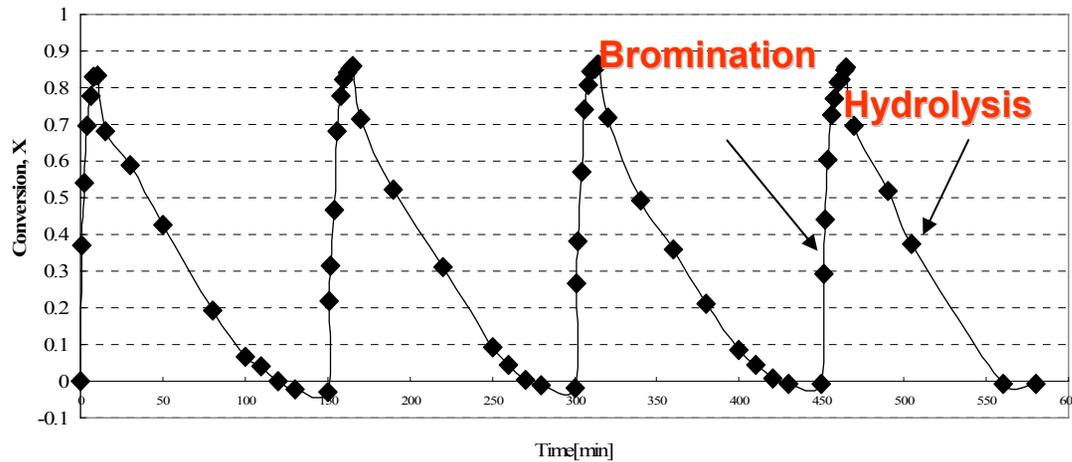
Bare yttria fabric



Fresh calcium oxide fabric

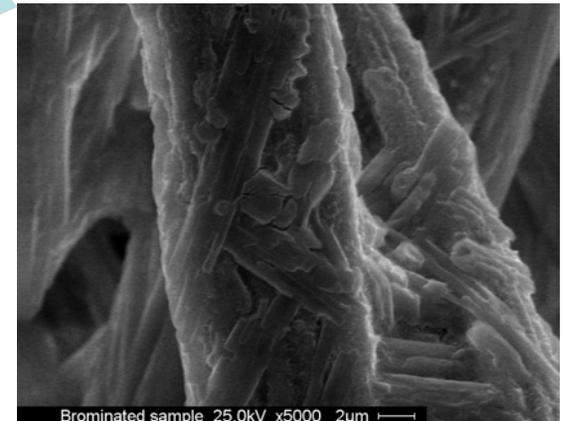
Accomplishments (cont'd.)

- ◆ The calcium oxide reactant on the yttria fabric had continuous higher reactivity (~ 85%) in the bromination reaction during four cycles.



Bromination

Hydrolysis



Summary and Future Work

- **Objective** : Investigate various aspects of the UT-3 cycle in order to improve the process performance
- **Approach** : Understand the reaction kinetics, solid reactant behavior and process thermodynamics
- **Technical Accomplishments and Progress:**
 - Thermodynamic simulations to find optimal operation conditions. (Completed)
 - Installation of laboratory scale facility for kinetic studies. (Completed)
 - Development of a preparation process for immobilization of calcium oxide particles on a yttria fabric with favor characteristics for solid-gas reactions. (Completed)
 - The preliminary characterization of calcium oxide fabrics using XRD and SEM (Completed)
 - The continuous higher bromination conversion (~ 85%) of the calcium oxide fabric during four cycles. (Completed)
- **Proposed Future Research**
 - Conduct long-term cyclic kinetic studies of the calcium oxide fabric
 - Develop an immobilization process for Fe-reactants
 - Study kinetics of Fe-reactants
 - Evaluate the practical process efficiency

H₂ Production from Biomass

Overview

Timeline

Start: October 2005

End: August 2009

Percent Completed: 85%

Barriers

• **3.1.4.2 V,W**

- Feedstock cost and availability
- Capital cost
- Efficiency of biomass gasification
- Improve H₂ yields

Objectives

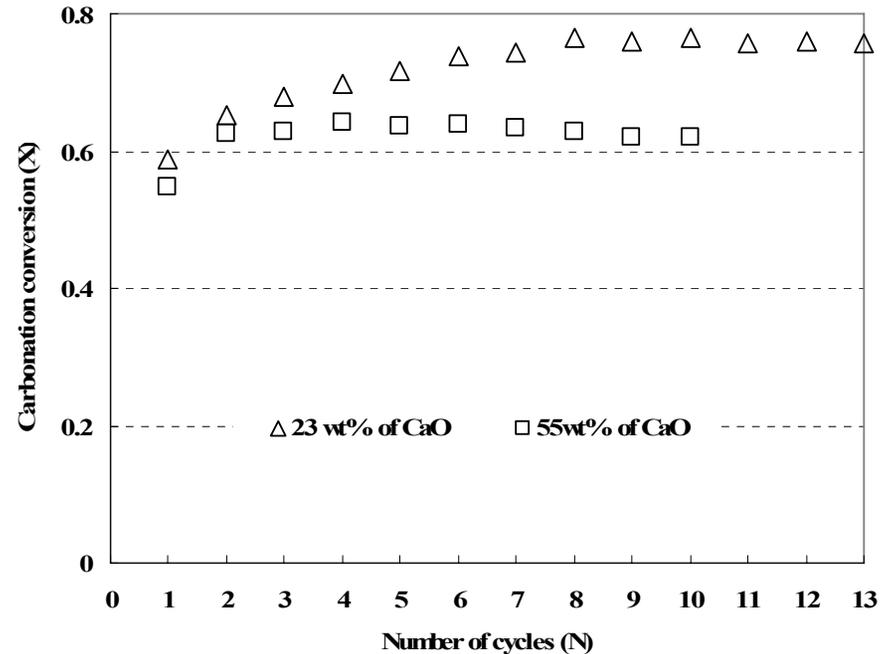
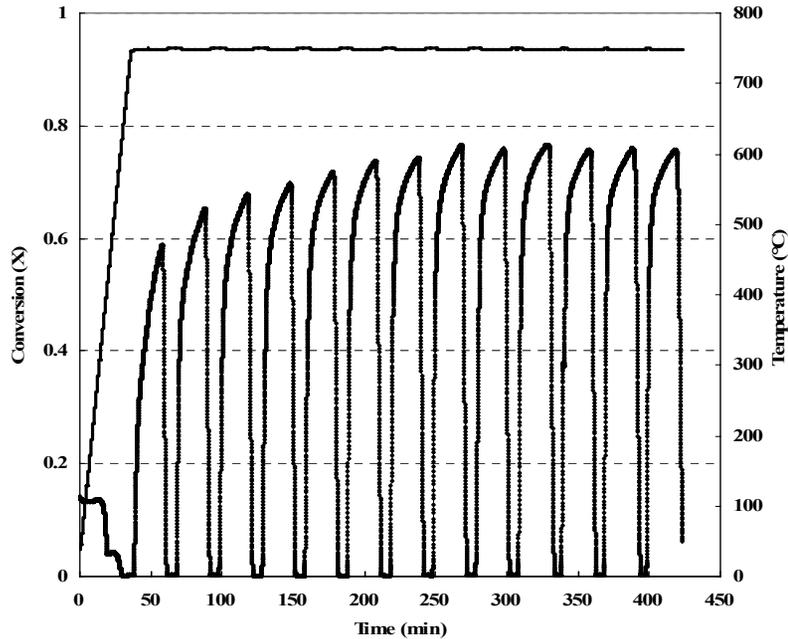
- Improve H₂ yield and process efficiency by
 - better heat integration
 - alternate gas clean-up approaches
- Reduce capital cost by combining process (gasification, reforming and shift) steps and operations
- Conduct theoretical studies of sorbent enhanced biomass gasification
- Improve gasification efficiency by developing a model-based controller for a biomass gasifier
- Develop experimental set-up
- Experimentally determine effect of sorbent addition on H₂ (& CO, CO₂) yields
- Conduct energy analysis of biomass gasification

Approach

- **Task 1: Thermodynamic studies (complete)**
 - Determine process conditions for maximum thermodynamic H₂ yield
 - Develop ASPEN models for conventional & sorbent based biomass gasification
- **Task 2: Experimental studies (complete)**
 - Fabricate test set-up
 - Conduct tests with and without sorbent to find H₂, CO & CO₂ yields
- **Task 3: Energy analysis (complete)**
 - Study energy consumption of conventional & sorbent enhanced gasification
 - Identify energy efficient methods for regenerating spent sorbent
- **Task 4: Development of calcium oxide absorbent (in progress)**
 - Develop a simple and effective preparation process for the calcium oxide absorbent to enhance cyclic performance
 - Evaluate the cyclic performance of CO₂ capture

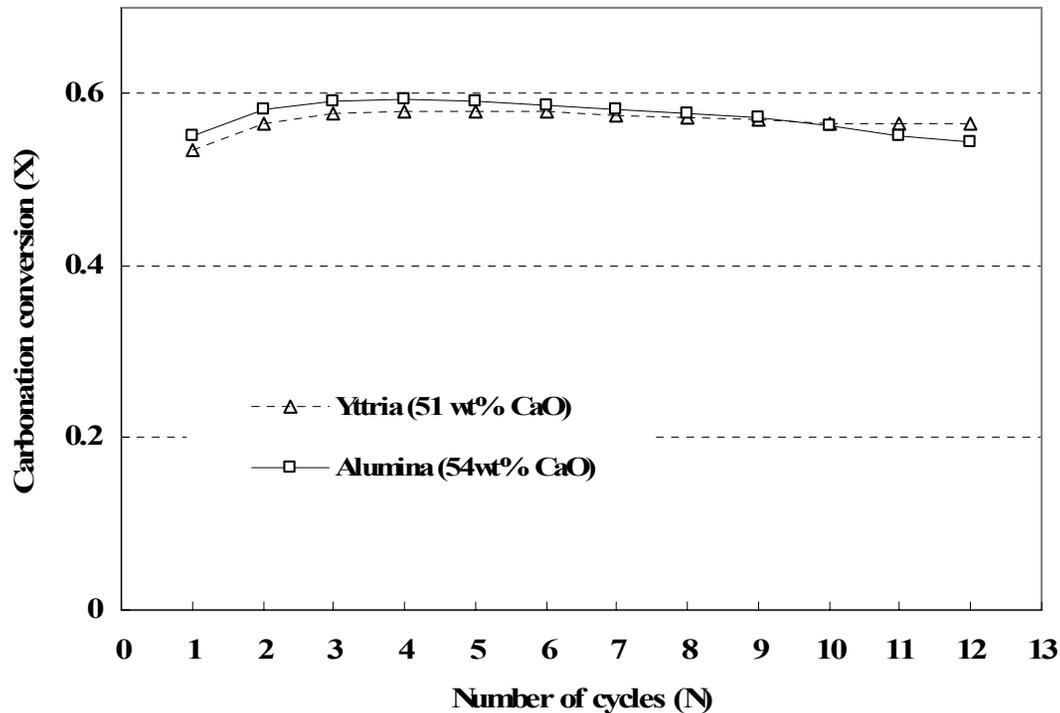
Accomplishments

Cyclic carbonation-calcination reactions (mild calcination, 750°C with N₂)



- ◆ A new procedure for the immobilization of calcium oxide on a ceramic fiber was developed for carbon dioxide absorbents in biomass gasification
- ◆ The sample with 23 wt% calcium oxide content attained about 75% carbonation conversion after 13 carbonation-calcination cycles and the carbonation conversion of the sample with 55 wt% calcium oxide reached about 62% after 10 cycles.

Accomplishments (cont'd.)



- ◆ Under the more severe calcination condition, at 850°C and 20 wt% CO₂ in N₂, the carbonation conversion of the calcium oxide sample using yttria fabric was maintained at 56% through the 12 cycles while those of the sample using alumina dropped by about eight percents from the maximum, 59%, after 12 cycles possibly due to the formation of Ca₁₂Al₁₄O₃₃ by the reaction between calcium oxide and alumina.

Summary and Future Work

◆ Summary

- Sorbent enhanced biomass gasification has proven to have great promise in hydrogen production from biomass due to:
 - Increased total gas and hydrogen yields
 - Reduced reactor temperature at comparable yields
 - Reduced heat duty of gasifier
 - Improved carbon conversion efficiency
- It could lead to significant savings both in operating and material costs.
- The new type calcium oxide absorbent dispersed and immobilized in ceramic-based fibrous fabric was fabricated via a newly developed immobilization method.
- The prepared sample showed superior performance in cyclic carbonation-calcination reactions under the various conditions.

◆ Proposed future research

- Considerable improvements in absorbent materials and possible incorporation of catalysts may be required
- A more detailed energy analysis including absorbent regeneration is required.

Photoelectrochemical H₂ Production

Objectives

Overall	To produce Hydrogen in the \$ 0.70 – 2.00/kg range Photocatalyst efficiency (sunlight to hydrogen) 14% Photocatalyst cost (\$/m ²) 70 Membrane cost(\$/m ²) 50
Current	To develop tandem solar cells to meet the above efficiency and cost objectives. Current emphasis is on development of the p-window contact for CdSe in the CdSe/Si(CIGS) tandem structure

Approach

- **Device Structures**

- CdSe/Si – intermediate term, hybrid
- CdSe/CIGS – long term, thin-film, low cost

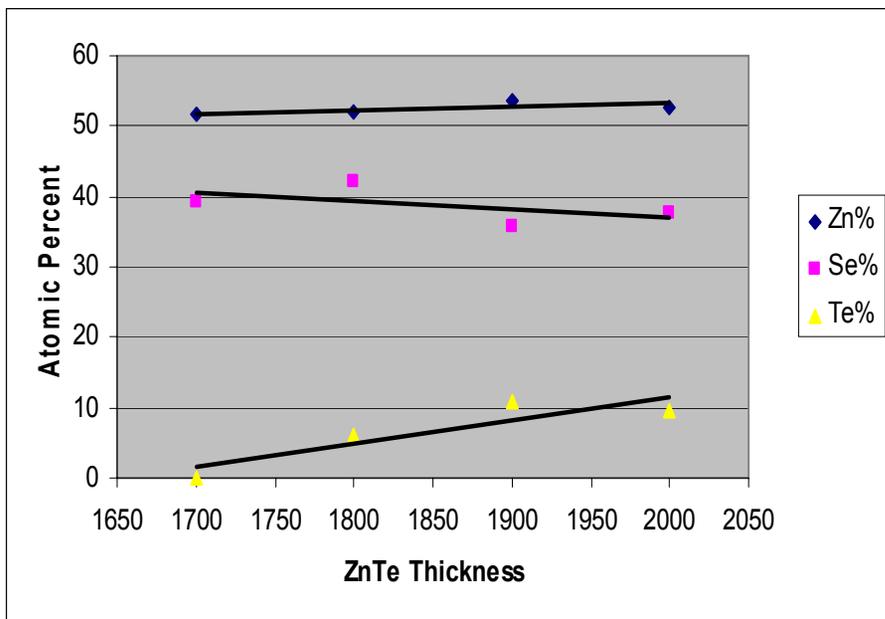
- **Key Technology Limitation**

- High efficiency, transparent p-window/CdSe/n-window device
- The p-window is limiting performance because of low V_{oc}

- **Current Focus**

- Development of ZnSe and ZnTeSe as p-windows
- Improving doping efficiency to increase V_{oc} by use of ion source implantation of nitrogen

Accomplishments



- Ion source implantation of N interferes with stoichiometry control in $\text{ZnSe}_x\text{Te}_{1-x}:\text{N}$ ρ -window contacts except at low Te levels
- Use of ZnTe / ZnSe:N superlattice structures allows better control at higher Te levels

Composition of $\text{ZnSe}_x\text{Te}_{1-x}:\text{N}$ films; Deposited Se thickness: 1000Å and ZnSe thickness: 2000Å.

Structure	Zn	Se	Te
Super Lattice	52.6	17.7	29.7
Co-evaporated	51.8	44.9	3.3

Film composition for $\text{ZnSe}_x\text{Te}_{1-x}$ window layers in devices

Photoelectrochemical H_2 Production

Accomplishments (cont'd.)

P-Window Configuration	V _{oc} (mV)
Standard ZnSe	340
Coevaporated ZnSeTe	180
Superlattice ZnSeTe	410

Voc's for various p-window configurations

- Both co-evaporated and superlattice ZnSe_xTe_{1-x} p-window contacts have been doped with nitrogen
- Doping levels for holes up to 10¹⁶/cm³ have been observed
- Devices have been fabricated with both co-evaporated and superlattice contacts
- A 50 mV increase in Voc is observed for the superlattice structures due to a 75 meV downward movement of the Fermi level caused by improved doping

Summary and Future Work

- Significant improvement in window p-layer doping has been accomplished
- Concomitant improvement in Voc has been realized
- Additional techniques will be pursued to further improve doping and Voc
 - Direct doping of $\text{ZnSe}_x\text{Te}_{1-x}$ p-window contacts with Cu
 - Co-doping of $\text{ZnSe}_x\text{Te}_{1-x}$ p-window contacts

Photo-catalytic H₂ Production

Overview

Timeline

- Start date: May 2005
- End date: August 2009
- Percent complete: 70%

Technical Targets

- Design and synthesis of photocatalytic materials that meet DOE 2010 Photoelectrochemical Hydrogen Production targets:
 - Chemical conversion process efficiency (EC), >10%*
 - Durability, >1000*

Barriers

- **3.1.4.2**
 - **P:** Materials Efficiency
 - **Q:** Materials Quality
 - **R:** System Efficiency

Objectives

Photocatalytic H₂ Production

- Improve Photocatalytic Efficiency
- Extend Light Absorption of TiO₂ into the Visible Spectrum by Nitrogen Doping and metal doping
- Determine the Relationship between the Materials Characteristics and Photocatalytic Activity

Approach

Novel Nitrogen Doping Process

We are developing three-step TiO₂ thermochemical treatment procedure that includes:

- N-doping by thermal treatment in a NH₃ atmosphere
- thermal treatment in an inert atmosphere to form TiO_{2-x}N_x at the interface TiO₂ and TiN, and
- re-oxidation in order to transform TiN into TiO_{2-x}N_x

Approach (cont'd.)

Novel Nitrogen Doping Process

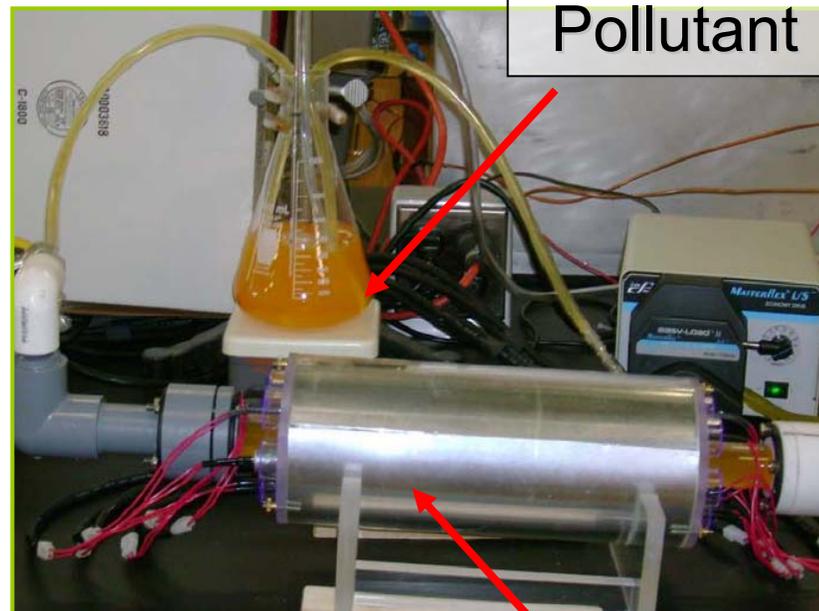
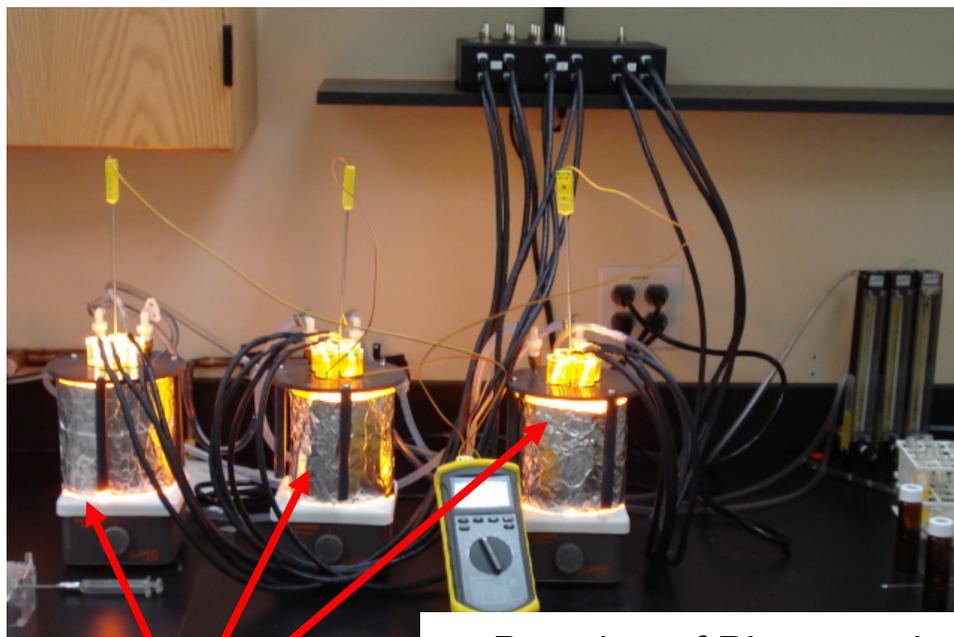


Untreated TiO_2



Thermochemically
Modified TiO_2
(Final Product)

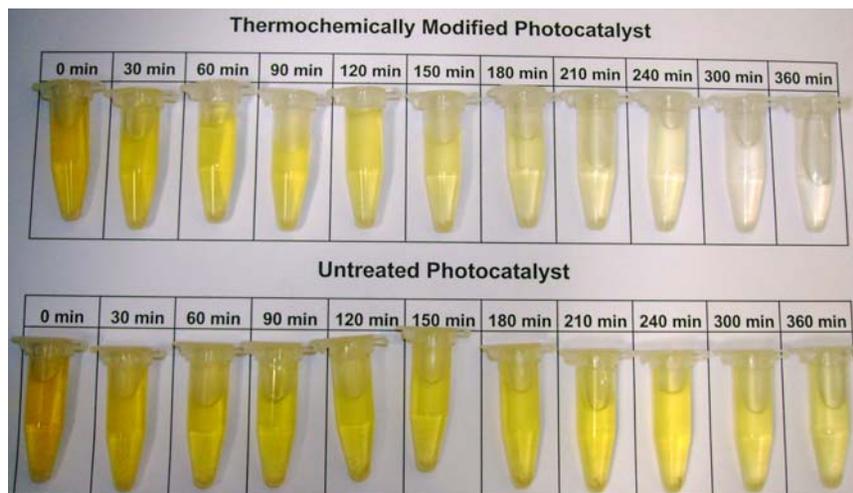
Photocatalytic Reactor Systems



Pollutant

Tubular UV Reactor

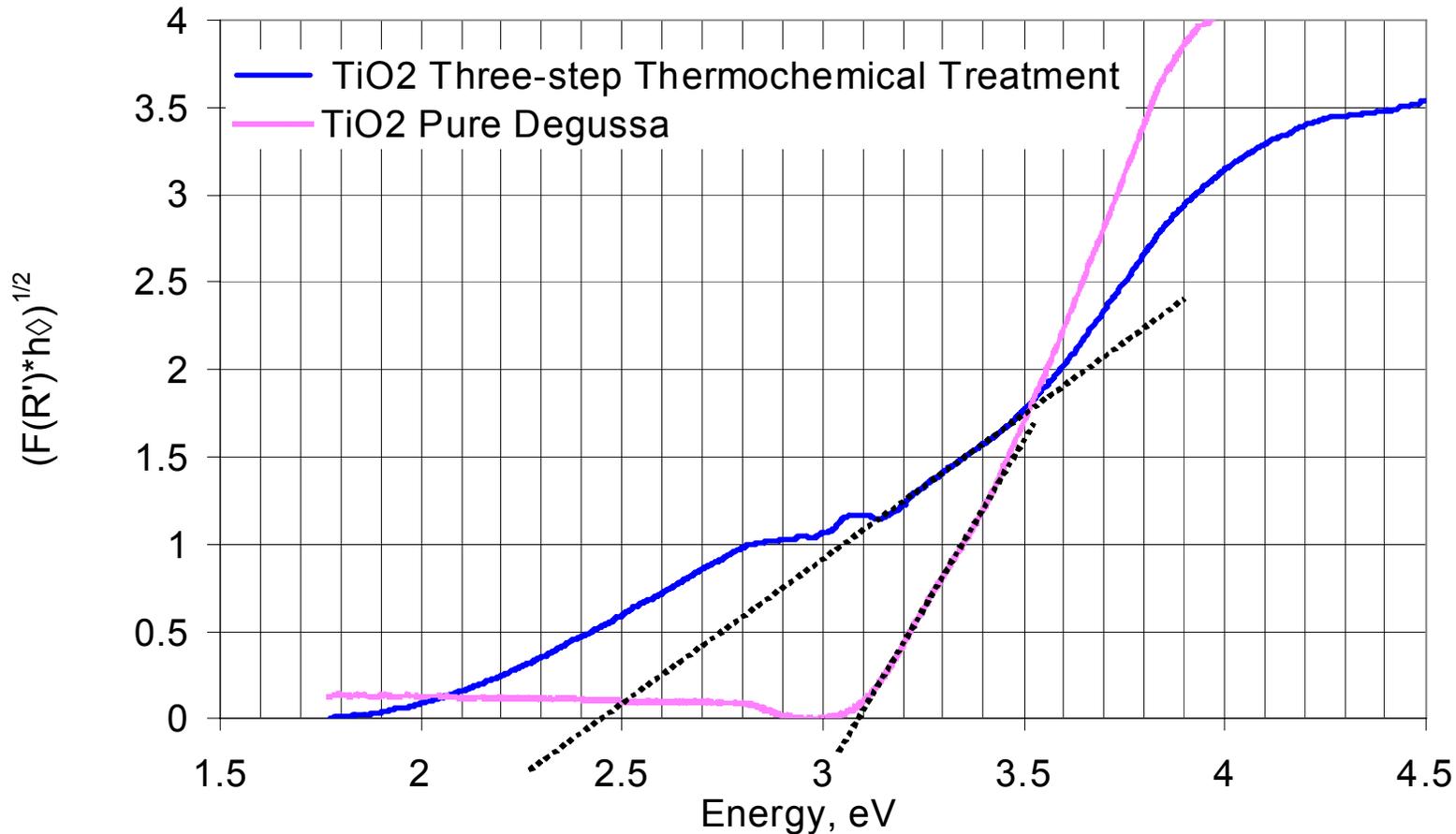
Duration of Photocatalytic Treatment by Simulated Solar Spectrum Irradiation



Simulated Solar Spectrum Photocatalytic Reactors

Accomplishments

- Developed N-doped TiO₂ material having optical absorption edge at 510 nm (~2.4 eV)



Future Work

Photocatalytic H₂ Production

- Improve Photocatalytic Efficiency of N-doped TiO₂ by metal ion doping (Ag, Cu) or alloying (V)

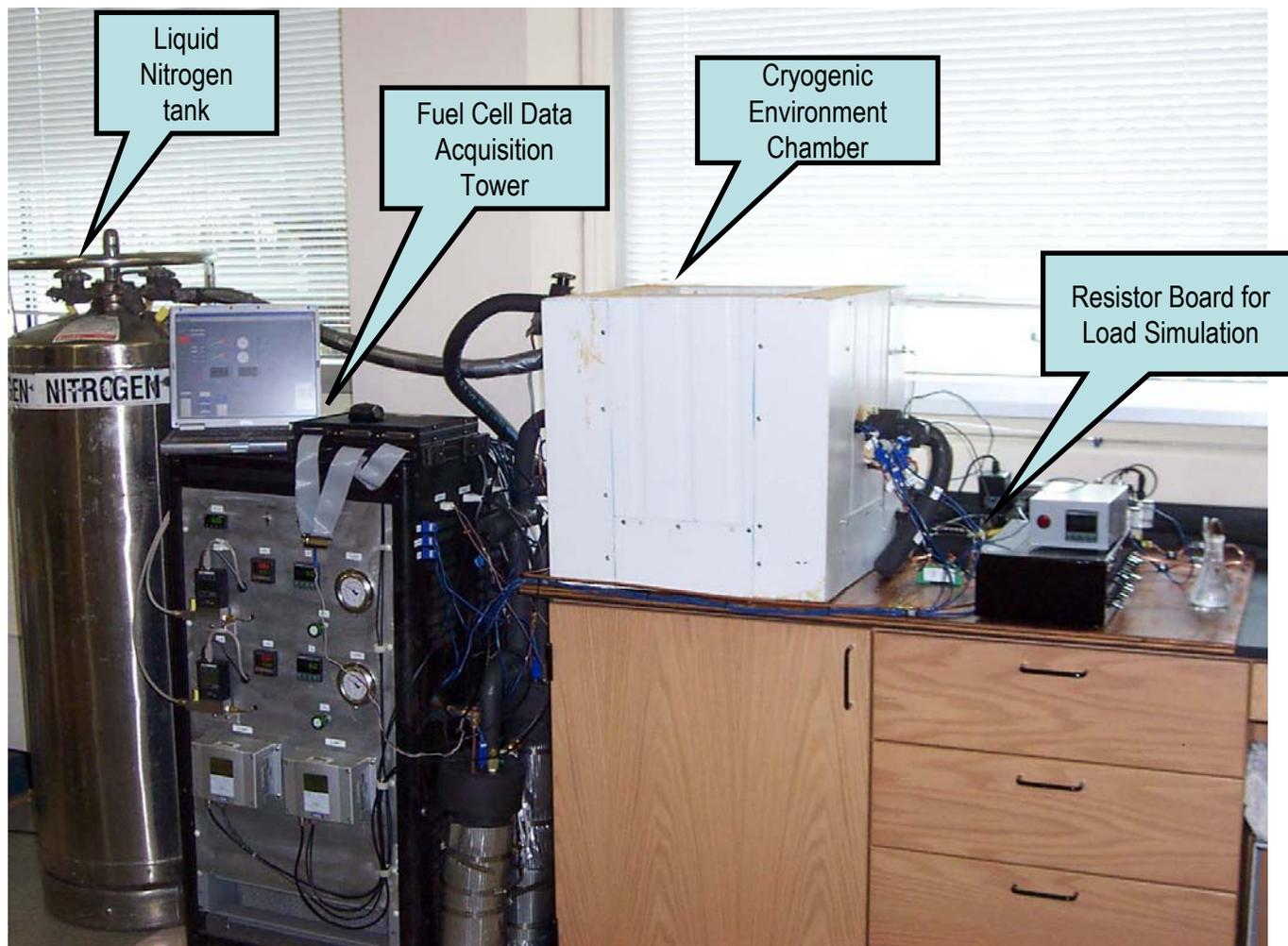
- Determine the Relationship between the Materials Characteristics and Photocatalytic Activity

PEM Fuel Cell Freeze Degradation

Objectives

- Design and manufacture a climate chamber capable of being integrated in to the current test station to simulate sub-zero climate conditions
- Quantify the amount of performance degradation experienced after subsequent freeze/thaw cycles over a range of potentially destructive operating conditions
- Analyze the degraded membrane to determine the probable cause of the cell's performance loss by the use of Scanning Electron Microscope (SEM), Electron Dispersion Spectroscopy (EDS), and (BET) porosity scanning techniques

The Fuel Cell Test Center



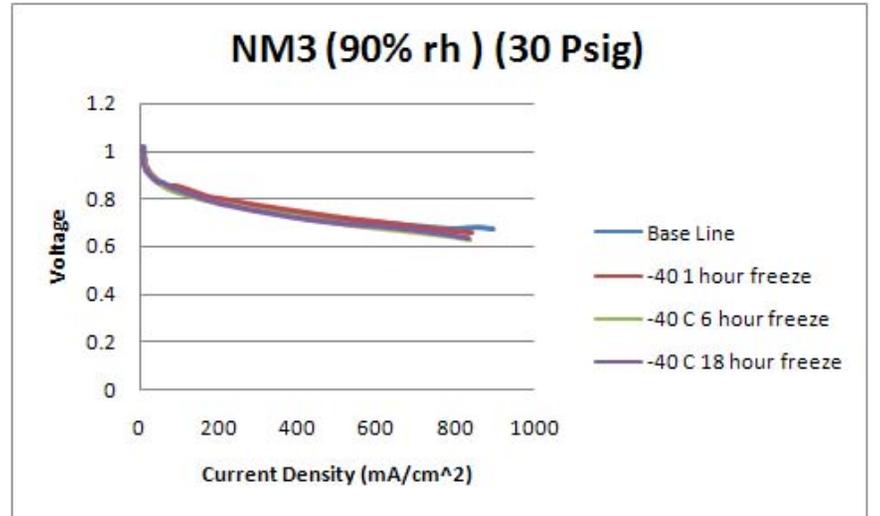
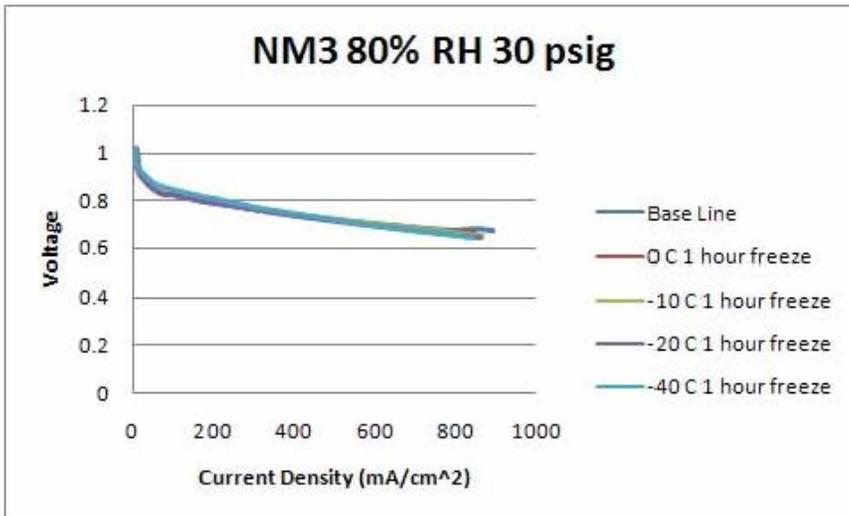
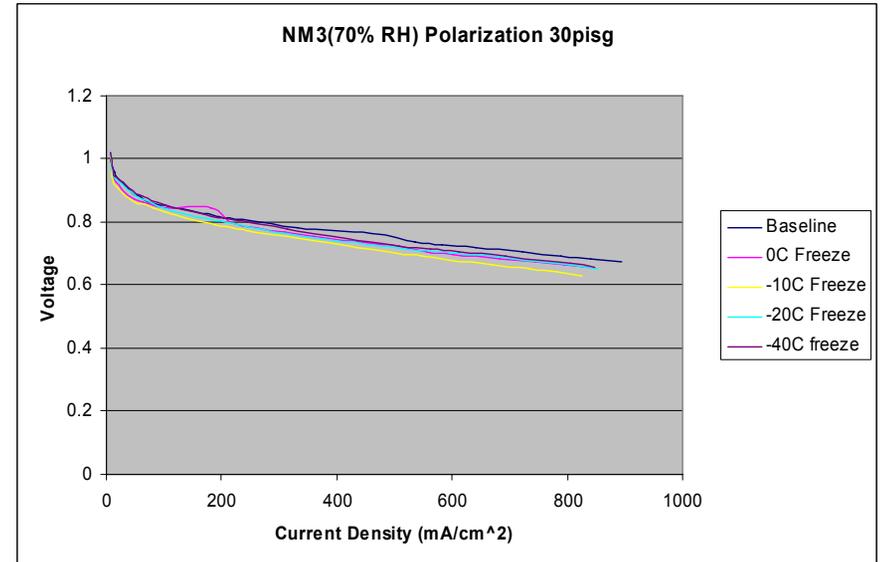
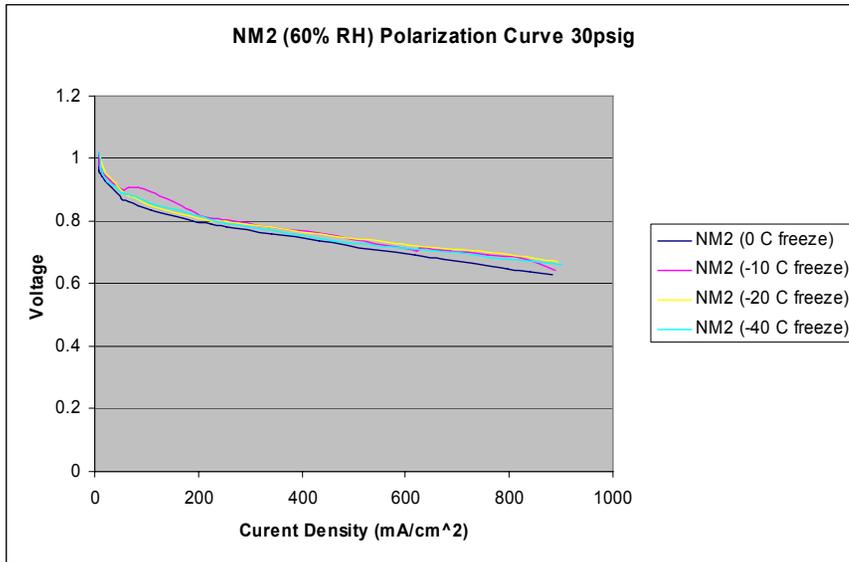
Approach

- In order to determine amount of performance that is lost due to a freeze/thaw cycle, critical data is collected before and after each cycle in order to construct valuable performance maps.
- Current focus has been to determine effectiveness of dehumidifying the cell before freezing as a possible mitigation strategy for future applications.
- Cells are exposed to differing amounts of de-humidification before exposure to varying temperature extremes in order to determine the cell's operational range

Accomplishments

- Certain membranes has shown a type of performance endurance limit to the freeze degradation.
- Membranes that were operated with (un-humidified) oxygen as the cathodic fuel experienced little degradation while exposed to temperatures ranging from 0 to -40 degrees Celsius for periods up to six hours.
-
- The small amount of the initial degradation has been related to the amount of water present in the membrane during the freeze/thaw cycle and the duration of exposure to sub-zero temperatures

Accomplishments (cont'd.)



Summary and Future Work

- **Objective:** To quantify a Polymer Electrolyte's Membrane performance degradation after being thermally cycled between operational regions that have been identified as potentially destructive
- **Current Results:** Have found today's current fuel cell technology to be more robust than expected with relatively minimal amount of power degradation measured which offers great hope for this technology to become a viable energy resource in the near future
- **Future Work:** Will continue to analyze previously utilized membranes to determine the root cause of the freeze degradation.
- This will help facilitate appropriately designed critical parameters such as the graphite plate fuel distribution pattern and the membrane's electrode assembly constituents

Development of PEM Electrolytes

Overview

Timeline

- Start date: October 2004
- End date: May 2008
- Percent complete: 100%

Partners

- University of South Florida
- University of Florida

Barriers

- **3.4.4.2**
 - **E:** Durability of distributed power generation systems
 - **O:** Cost of fuel cell stack component materials
 - **R:** Thermal and water management in high temperature membrane electrolytes

Objectives

- Lower the cost of fuel cell-generated electricity by decreasing the cost per unit power for PEM electrolytes
- Improve long-term chemical stability of PEM electrolytes operating at ≤ 120 °C
- Maintain or improve high proton conductivity of PEM electrolytes
- Minimize water content necessary to support high proton conductivity

Approach

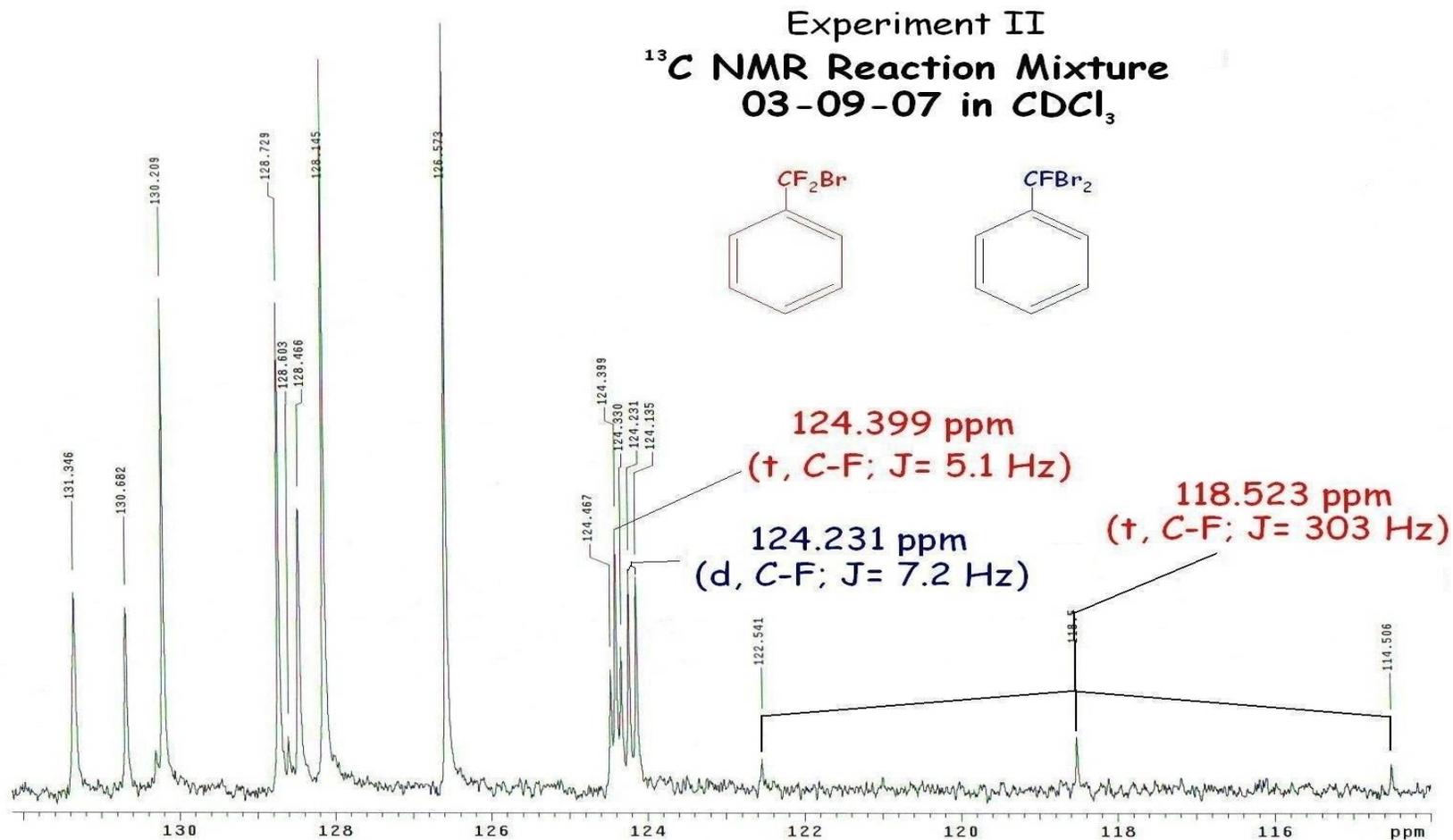
- Develop synthetic method for fluorosulfonation of hydrocarbon polymers to promote proton conductivity and oxidative stability, but with minimum amounts of fluorine (i.e., “strategic fluorination”) to control costs
- Develop accelerated test apparatus to evaluate prototype PEM’s

Accomplishments

- Successfully performed fluorosulfonation of trifluoromethylbenzene monomer (TFMB) or α,α,α -trifluorotoluene.
- Attempted fluorosulfonation of the diamino derivative; determined that amines react with BBr_3 starting material, preventing diazotization and conversion to the hydroxide.
- Converted amines to amides to protect against BBr_3 reaction; studies on acetanilide showed that the methyl amide will still react with BBr_3 , forming the diacetanilido boron bromide.
- Identified difluoro and dihydroxy derivatives of TFMB that should be polymerizable once fluorosulfonation of the difluoro monomer is accomplished.

Accomplishments (cont'd.)

^{13}C NMR spectrum of mono- and dibrominated TFMB



Summary

- Attempting to make the fluorosulfonic acid of PEEK polymer to serve as a conductive, stable, inexpensive membrane electrolyte in fuel cells.
- Successfully produced the fluorosulfonic acid of trifluoromethylbenzene monomer
- Next step will be to produce the fluorosulfonic acid monomer with polymerizable side groups.