

2009 DOE Hydrogen Program Review

Hydrogen Production and Fuel Cell Research

University of South Florida
Presenter: D. Yogi Goswami

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Arlington, Virginia

Project ID #
PDP_28_Goswami

Overview

Participants

- **PI/Co-PI:** Yogi Goswami, Lee Stefanakos
- S. Srinivasan (CERC), N. Kislov (CERC) D. Morel (EE), C. Linkous (FSEC, UCF)
- **Graduate students:** D. Latchman, Li Steven

Budget

Total Project Cost = \$6,172,694

DOE Share = \$4,938,155

USF Share = \$1,234,539

Projects

Hydrogen Production and Fuel Cell (PDP 28)

- 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 23)

Overview

Timeline

Start: October 2005

End: August 2009

Percent Completed: 85%

Barriers

- 3.1.4.2.5 U,V,X

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

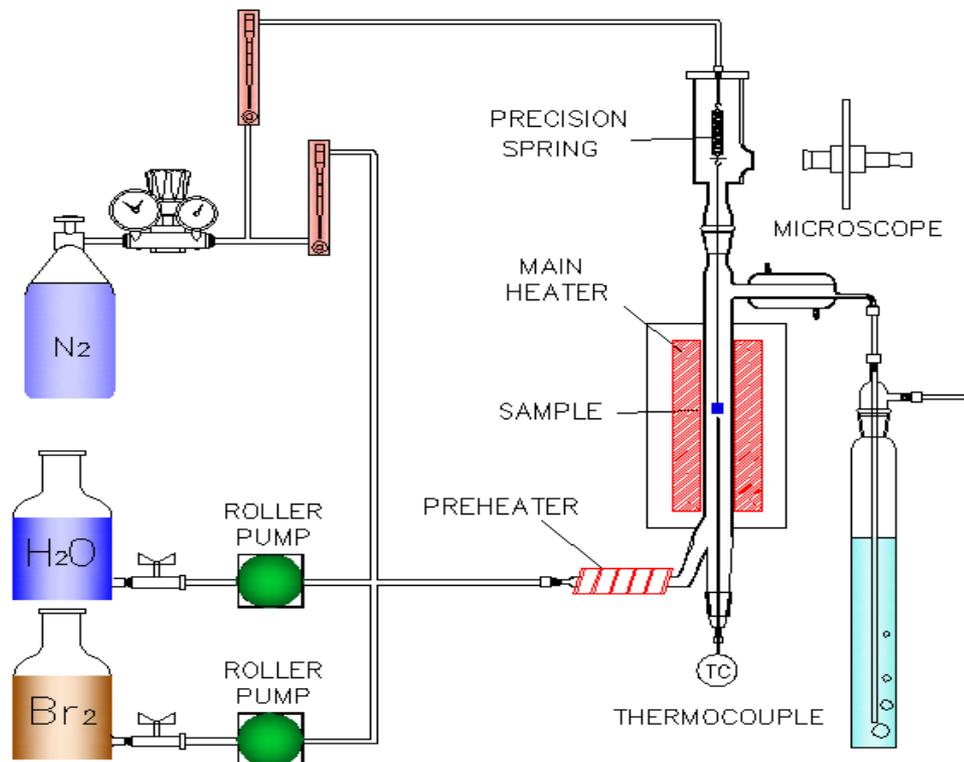
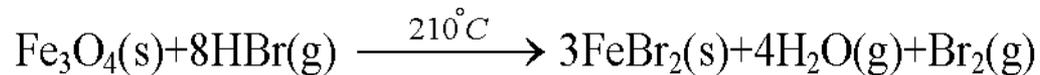
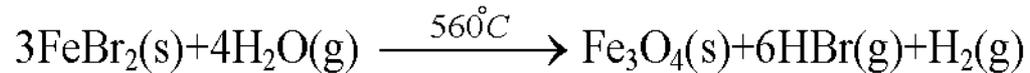
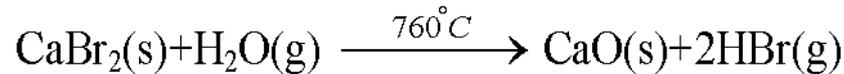
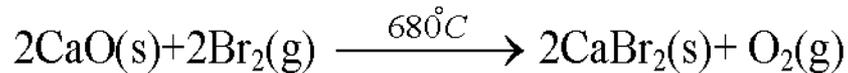
Objectives

- 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

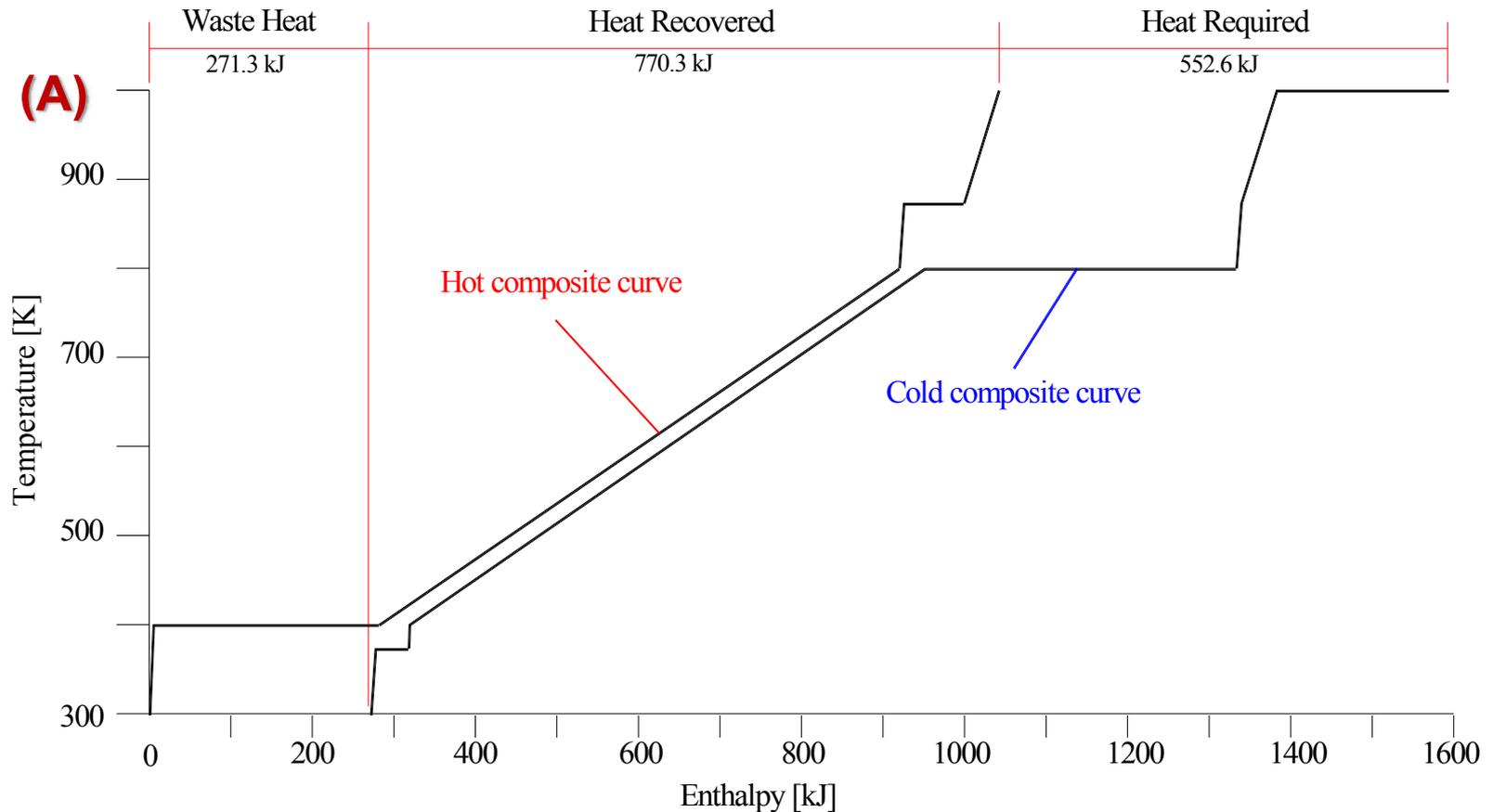
- Evaluation of characteristics of calcium and iron oxide solid reactant to improve their formulation
- Chemical kinetic studies to evaluate and improve the solid reactant's cyclic life, reaction rates and conversion using lab-scale apparatus
- Experiments on the feasibility of UT-3 thermochemical cycle for hydrogen production
- Fabrication and evaluation of porous calcium oxide (CaO) and iron oxide (Fe_3O_4) reactants which have an enduring structure and favorable characteristics in cyclic transformations between oxide and bromide forms.

UT3 Thermochemical Cycle



Accomplishments

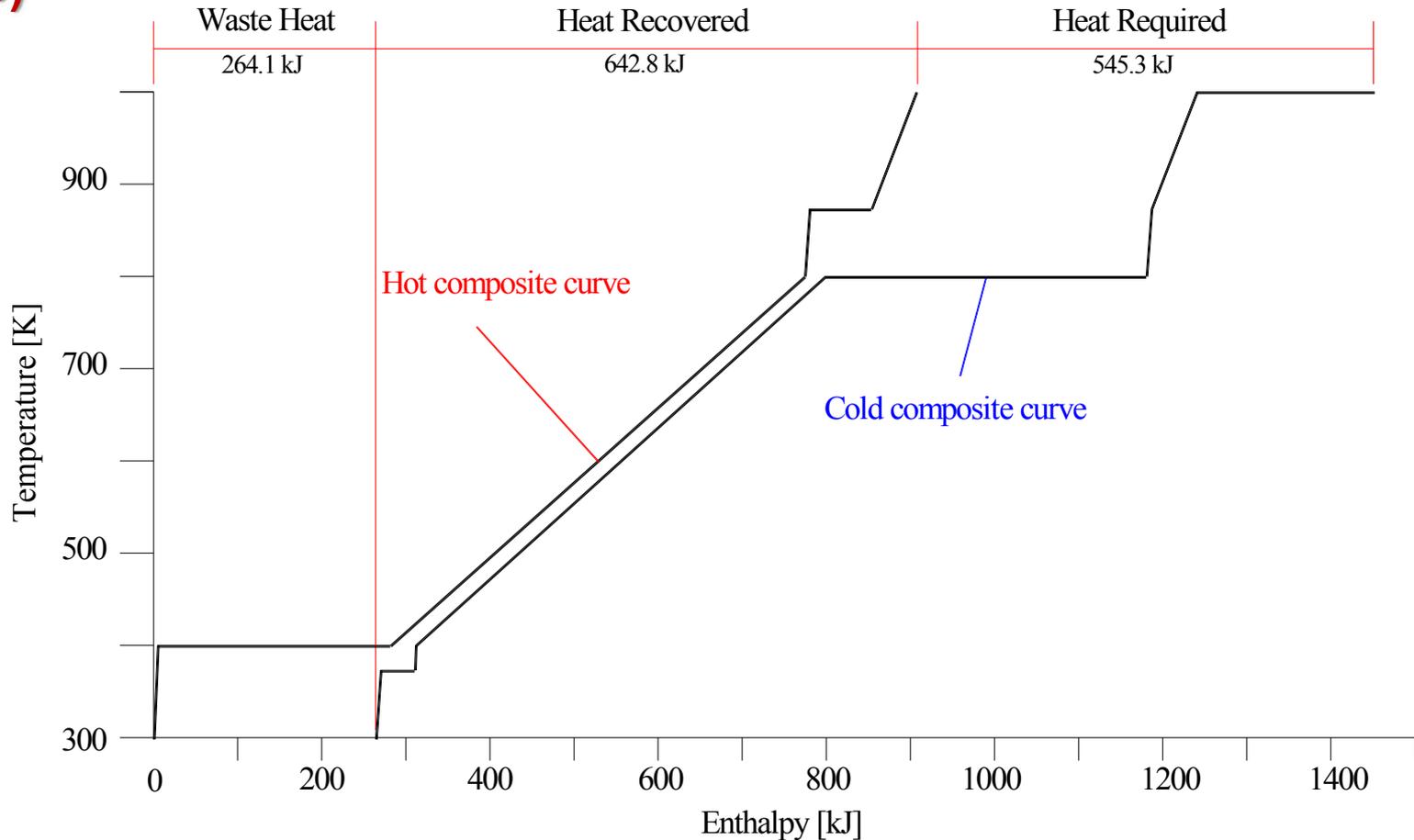
- Thermal efficiency of the UT-3 Process was evaluated considering inert materials, heat recovery and incomplete conversion.
- In order to determine feasible heat recovery in the process, pinch analysis was employed in this thermodynamic analysis.



Thermochemical H₂ Production

Accomplishments

(B)



. Combined composite curves for (A) Pellet and (B) Fabric samples

Accomplishments (cont'd.)

	Pellets (other researches [1, 2])		Fabrics (this study)	
	No recovery	Heat recovery	No recovery	Heat recovery
Thermal energy for reactions	593.5 kJ/mol	593.5 kJ/mol	593.5 kJ/mol	593.5 kJ/mol
Total energy for heating	729.4 kJ./mol	729.4 kJ./mol	594.7 kJ./mol	594.7 kJ./mol
Recovered thermal energy	-	770.3 kJ/mol	-	642.8 kJ/mol
Thermal efficiency	21.6%	51.8%	24.1%	52.4%

Thermal efficiencies including inert material & incomplete conversion

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:**
 - Practical process efficiency was determined using the experimental results and theoretical thermodynamic analysis. It was found that the effect of heat recovery and inert materials cannot be disregarded in the calculation of thermal efficiency of the cycle. To increase the efficiency, heat recovery must be used and the use of the inert materials should be minimized.
- **Proposed Future Research**
 - The cause of the delay of the hydrolysis reaction with higher calcium oxide contents will be investigated.
 - Development of a new preparation method for iron oxide.

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

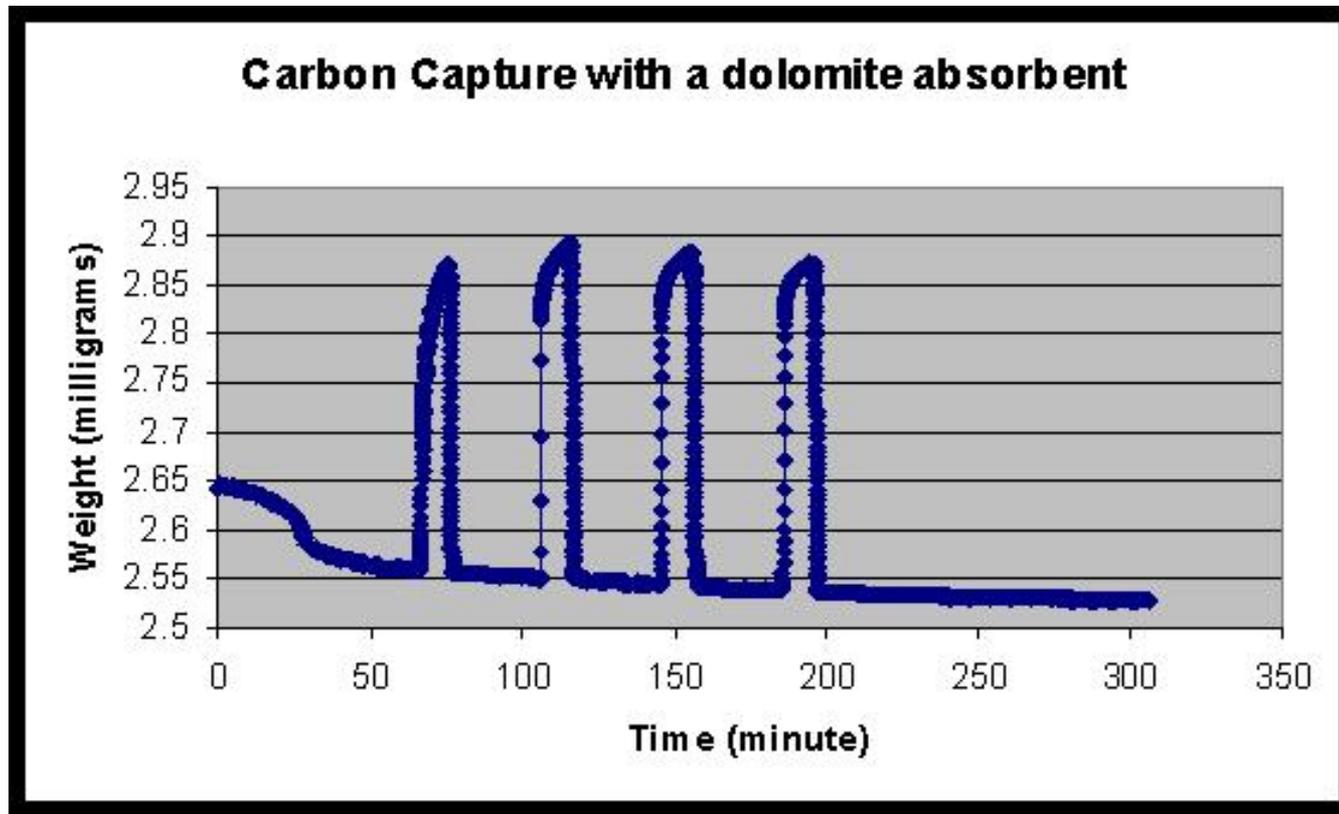
- Improve H₂ yield and process efficiency by
 - better heat integration
 - alternate gas clean-up approaches
- Reduce capital cost by combining process (gasification, reforming and shift) steps and operations
- Conduct theoretical studies of sorbent enhanced biomass gasification
- Improve gasification 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

- Biomass feedstock common to Florida such as pine mulch was steam gasified in a batch type reactor. The effects of temperature and presence of sorbent (calcium oxide) and form of sorbent (powder vs pellets) on the hydrogen yield were experimentally investigated. The initial experimental studies have shown a significant improvement in hydrogen and overall gas yield in presence of sorbents. In order to enhance cyclic performance of the sorbents, a simple and effective immobilization technique of the calcium oxide sorbent in fibrous ceramic mat as a substrate was developed and the cyclic performance was evaluated.

Accomplishments

- Dolomite on alumina fabric was used in the preparation of the absorbent sample.
- Two samples were prepared of dolomite applied to alumina fabric and Ytria fabric.
- The two samples were then analyzed using the Thermogravimetric Analysis (TGA).



Cyclic carbonation and calcinations of dolomite on Alumina fabric

Summary and Future Work

◆ Summary

- Carbon dioxide can be captured by dolomite type material using the inexpensive preparation method developed by the University of South Florida.

◆ Proposed future research

- Additional experimental studies on calcium oxide absorbents to increase calcium oxide loading.
- Longer cyclic experiments with more severe calcination condition, higher temperature under high concentration of carbon dioxide, will be carried out.
- Study of different materials to be used as the carbon dioxide sorbent material
- Comparison of the calcium oxide versus the dolomite absorbent materials.

Task 3

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

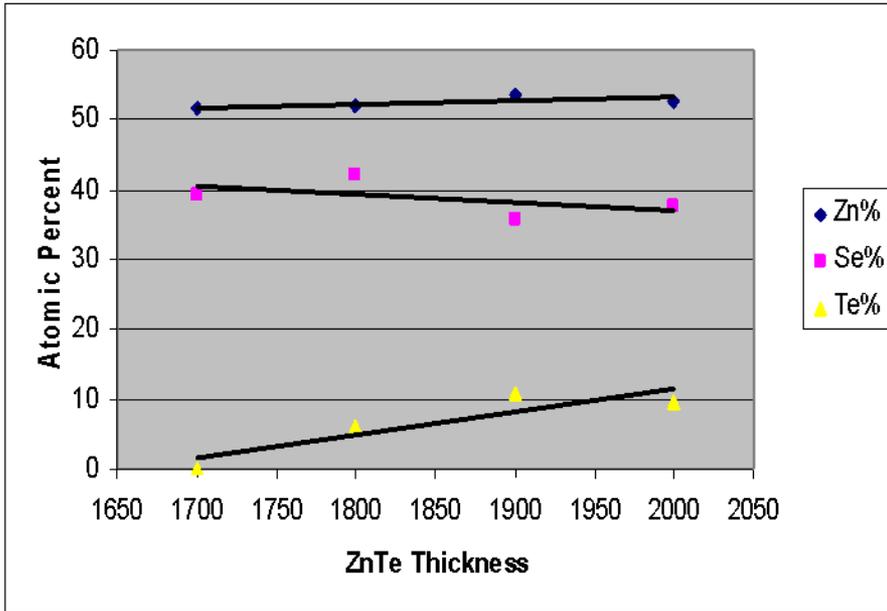
- **Key Technology Limitation**

- 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

Task 4

Photo-catalytic H_2 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

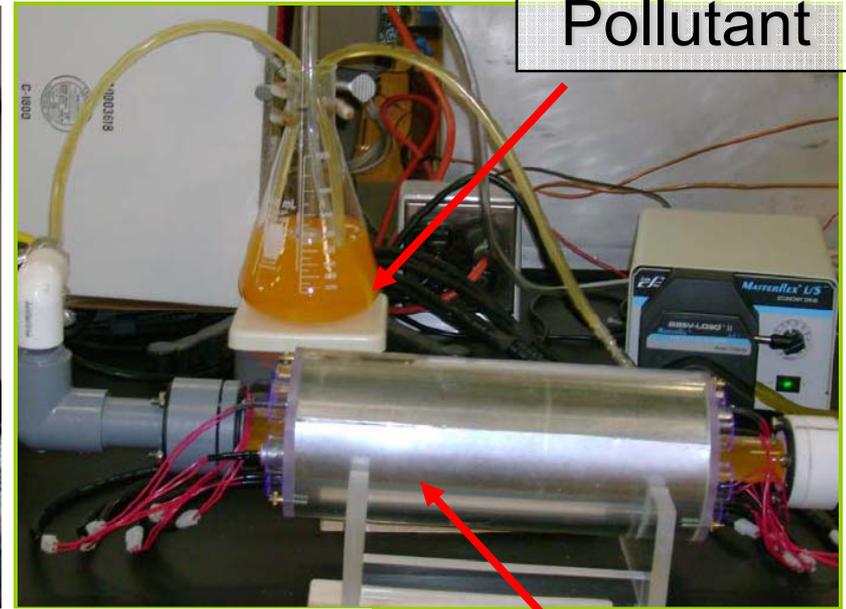
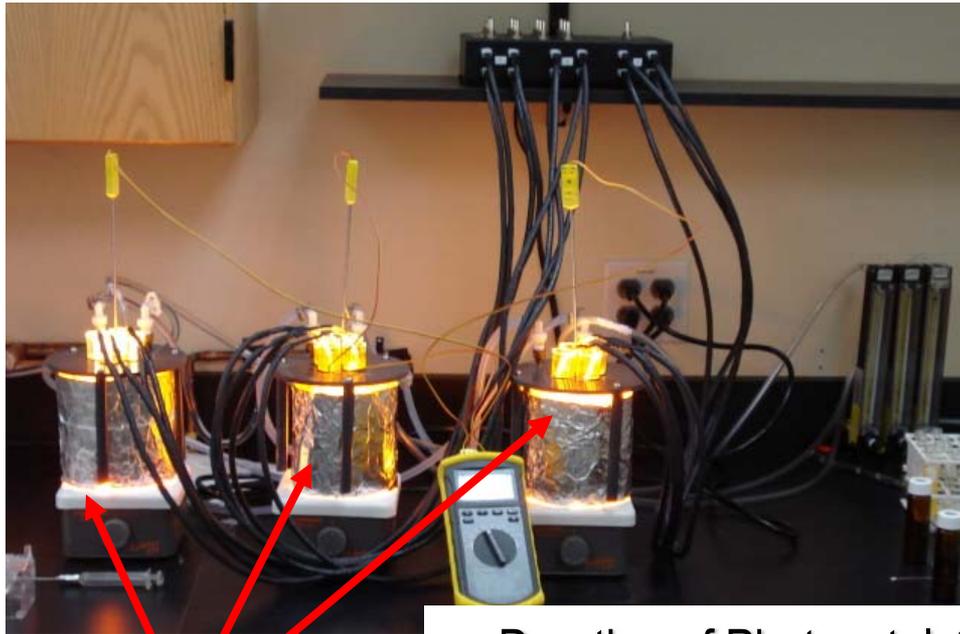


Untreated TiO_2



Thermochemically
Modified TiO_2
(Final Product)

Photocatalytic Reactor Systems

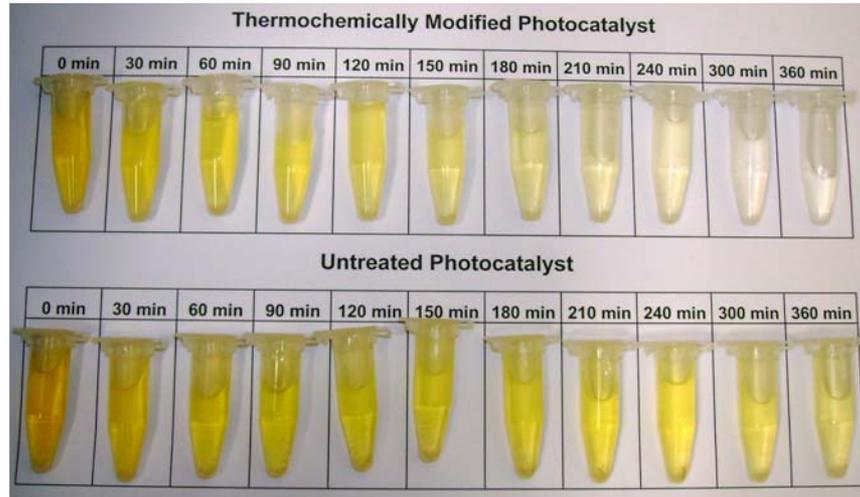


Pollutant

Tubular UV Reactor

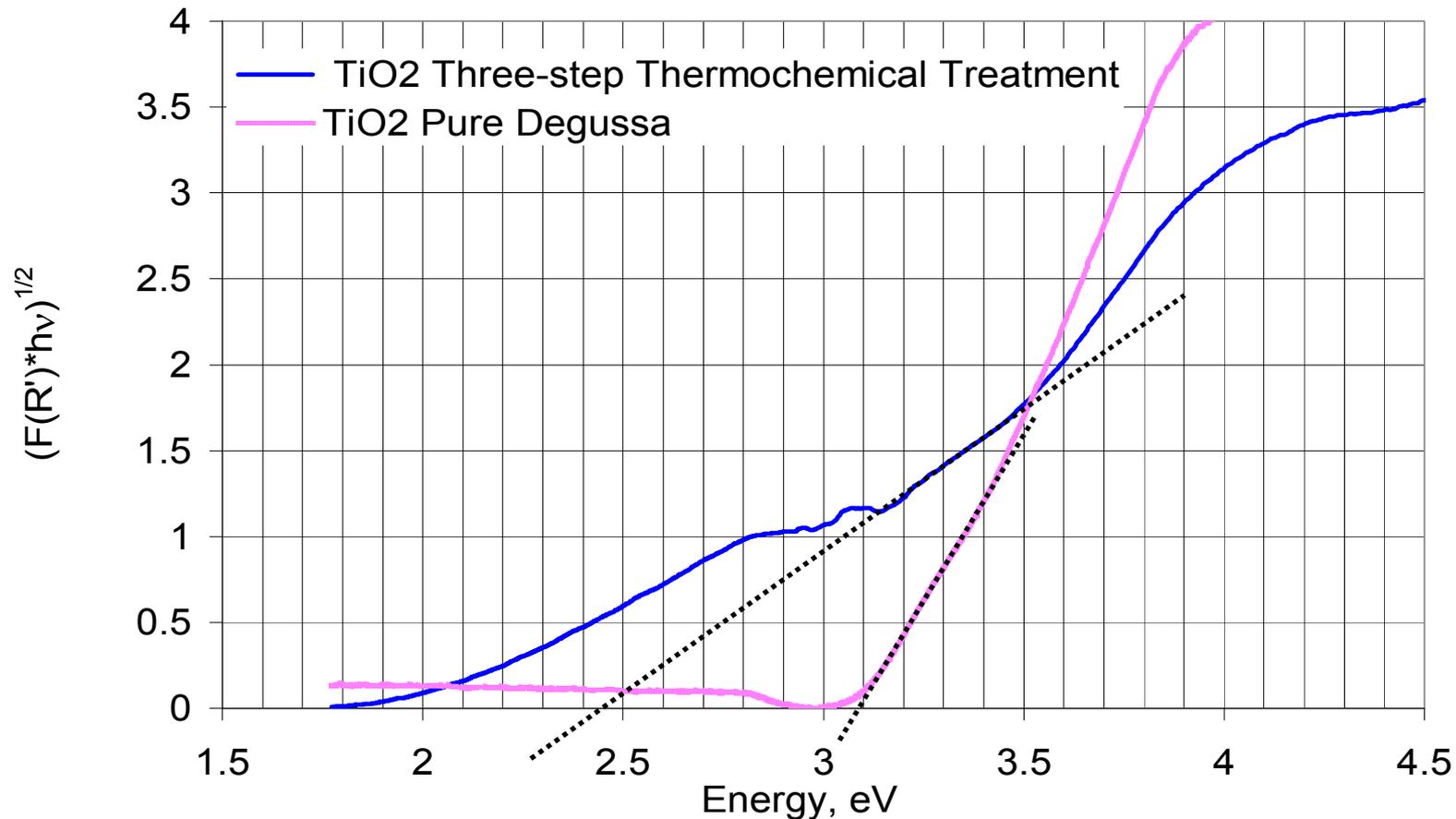
Simulated Solar Spectrum Photocatalytic Reactors

Duration of Photocatalytic Treatment by Simulated Solar Spectrum Irradiation



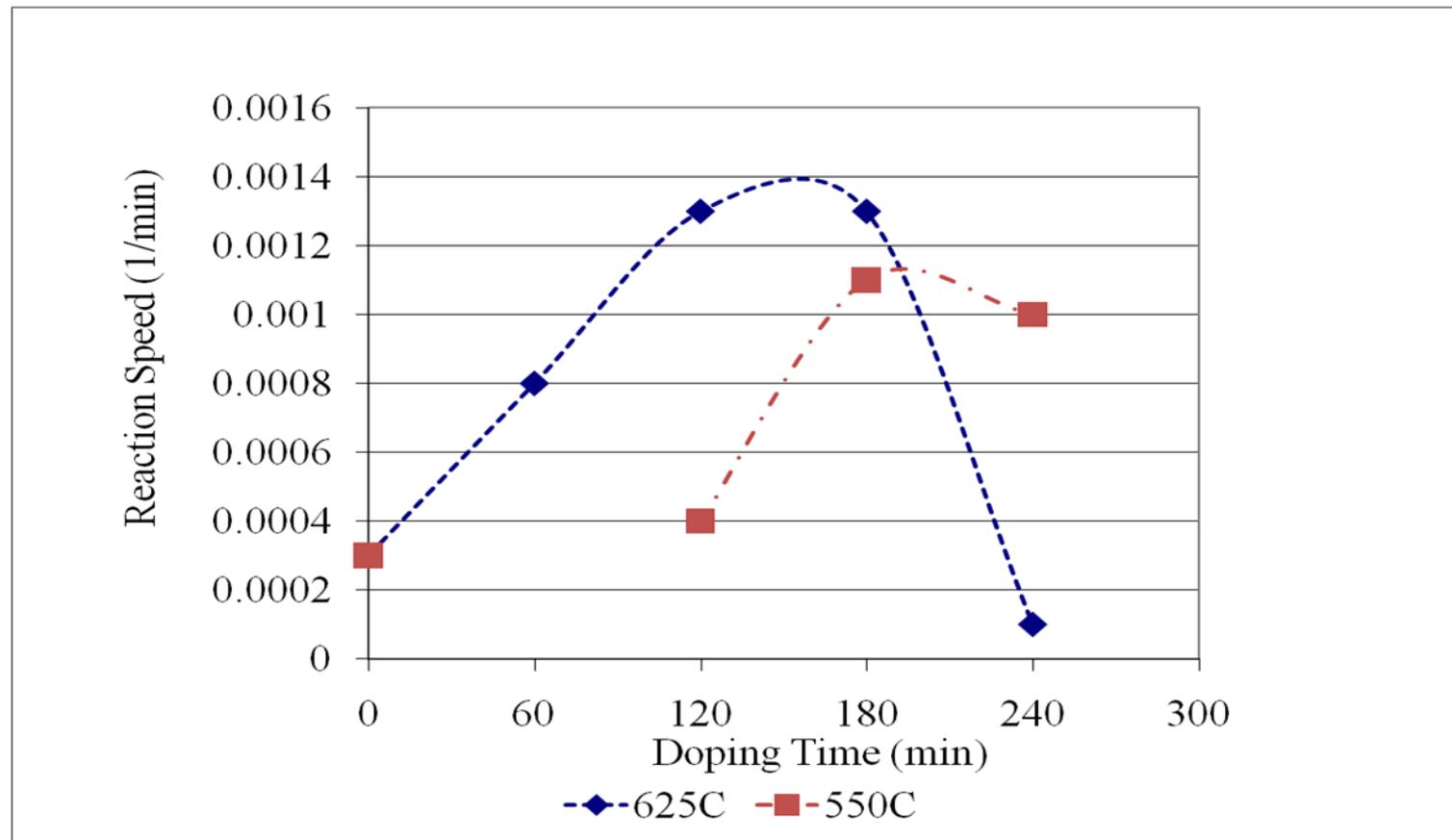
Accomplishments

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



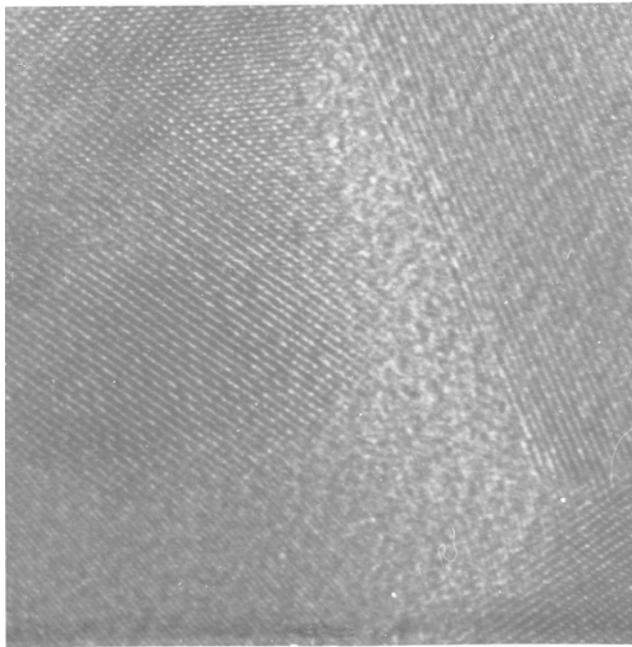
Accomplishments

- Dependence of initial rate of Methyl Orange degradation on the TiO_2 catalysts treated thermo-chemically at 625 °C and 550 °C.

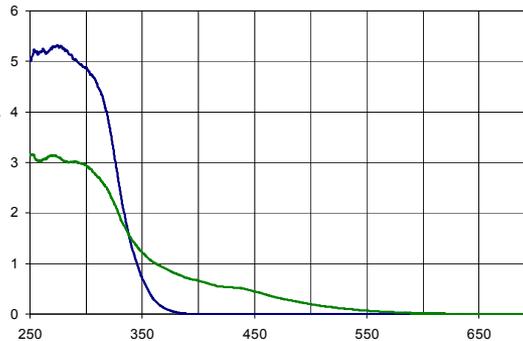


Accomplishments

HRTEM of Pure Degussa P-25 TiO₂

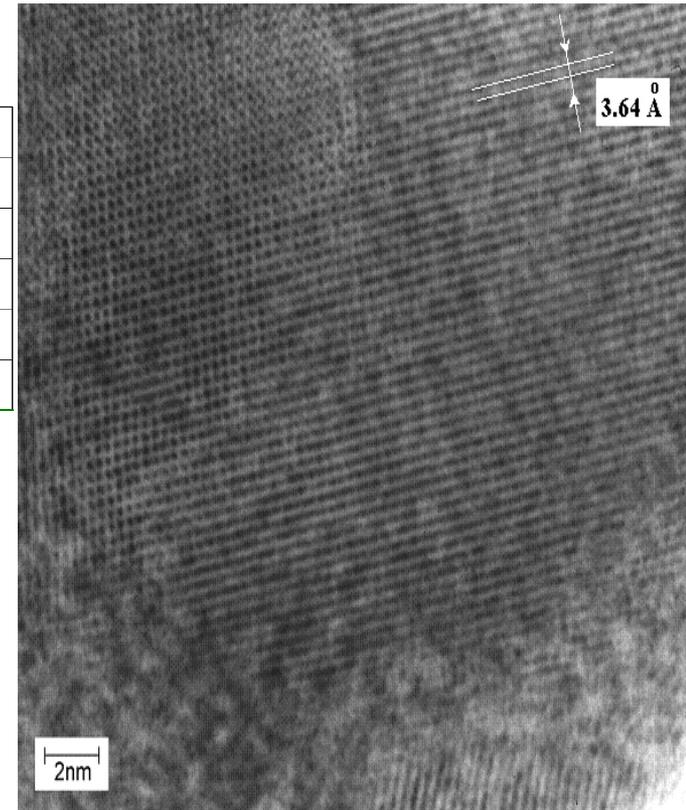


Optical Absorption (Kubelka-Munk a.u.)



— Pure Degussa P-25 TiO₂ — 164B TiO₂ NH₃ 6h

UV Spectra



HRTEM of Thermochemically NH₃ Treated Degussa P-25 TiO₂ Converted to Ti₉O₁₇

Photo-catalytic H₂ Production

Summary and Future Work

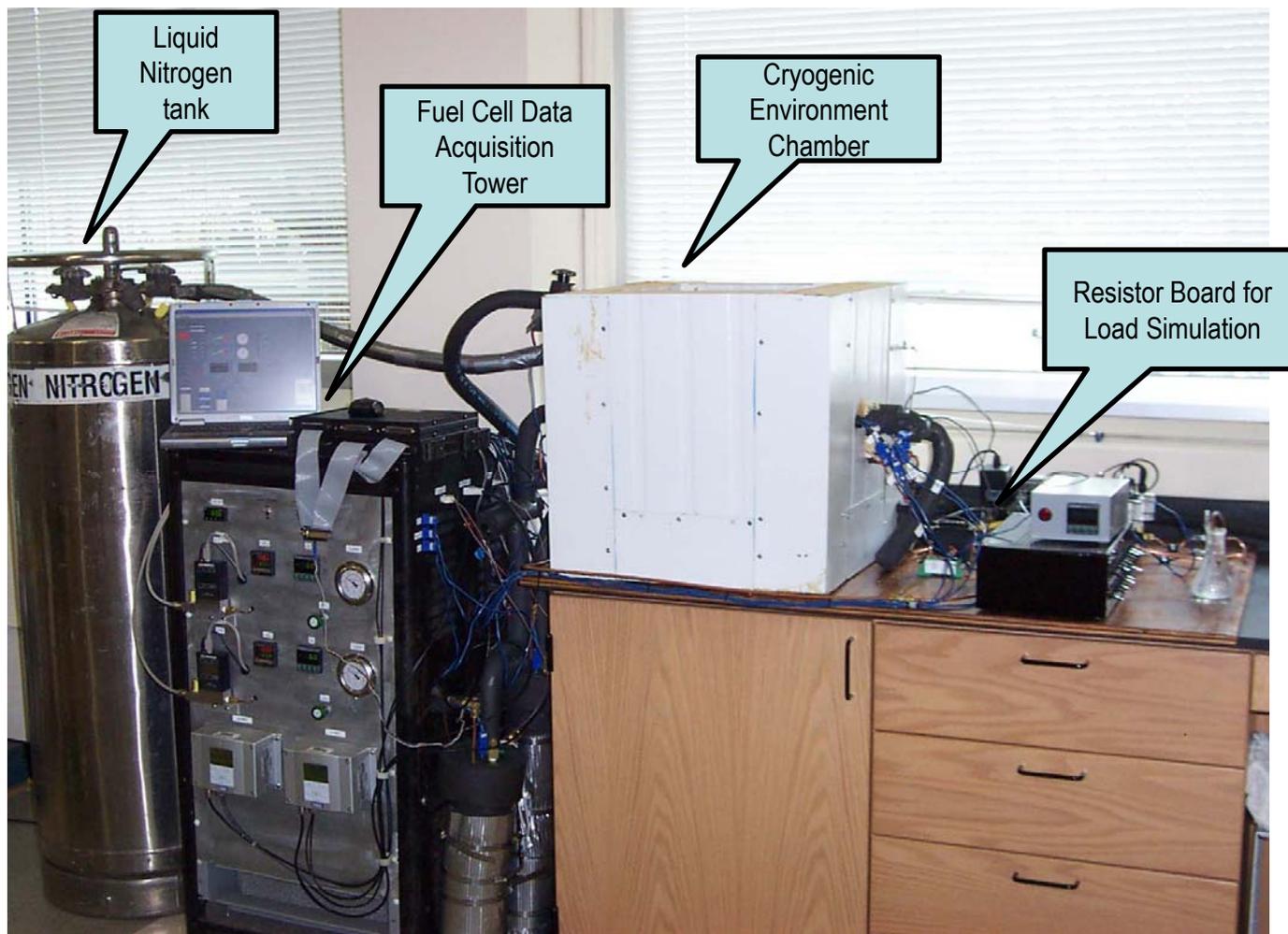
Photocatalytic H₂ Production

- Thermochemical anhydrous ammonia treatment of TiO₂ based photocatalysts have the potential to create an efficient and inexpensive visible-light photocatalyst, which, on a commercial, scale is much more advantageous as compared with sputtering and ion implantation techniques
- 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
- Optimization of nitrogen loading in to the TiO₂ for the effective photocatalytic performance will be studied. Based on our preliminary studies it is inferred that the surface and microstructure of the nitrogen doped TiO₂ will be compared and correlated with the overall photocatalytic activity. Silver co-precipitation of N-doped TiO₂ will be investigated.

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

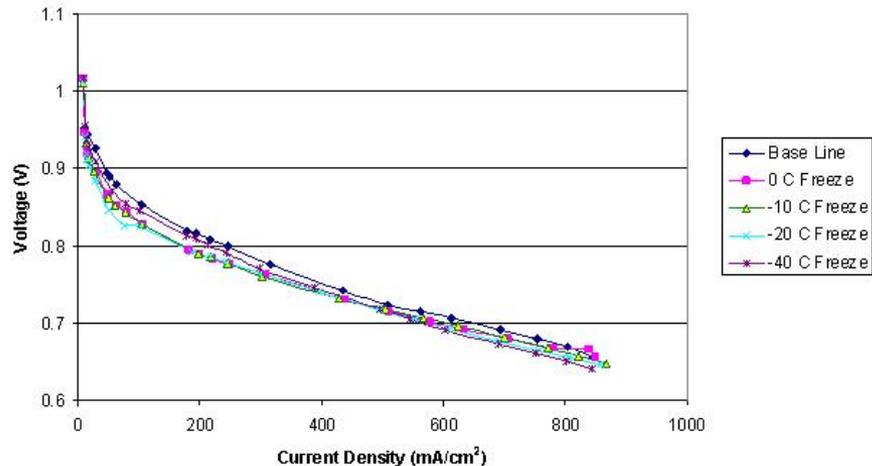
- In order to determine amount of performance that is lost due to a freeze/thaw cycle, critical data is collected before and after each cycle in order to construct valuable performance maps.
- Current focus has been to determine effectiveness of dehumidifying the cell before freezing as a possible mitigation 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

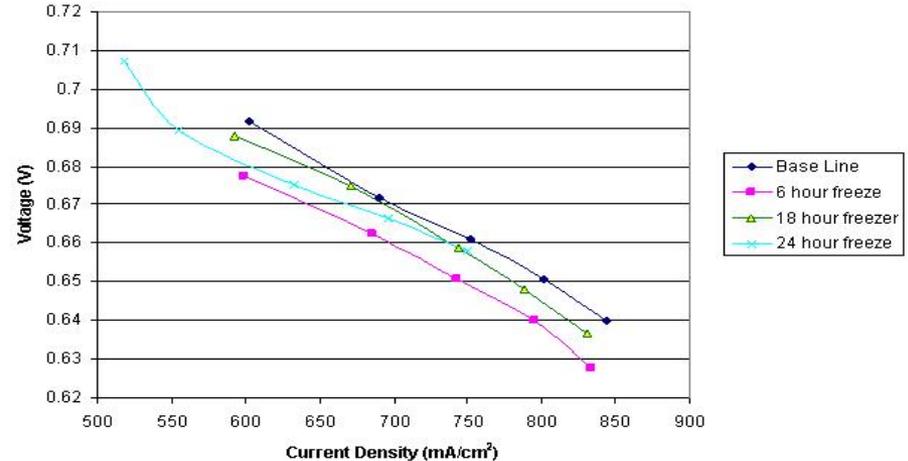
- Certain membranes has shown a type of performance endurance limit to the freeze degradation.
- Membranes that were operated with (un-humidified) oxygen as the cathodic fuel experienced little degradation while exposed to temperatures ranging from 0 to -40 degrees Celsius for periods up to six hours.
-
- 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.)

Polarization Curve 80% RH



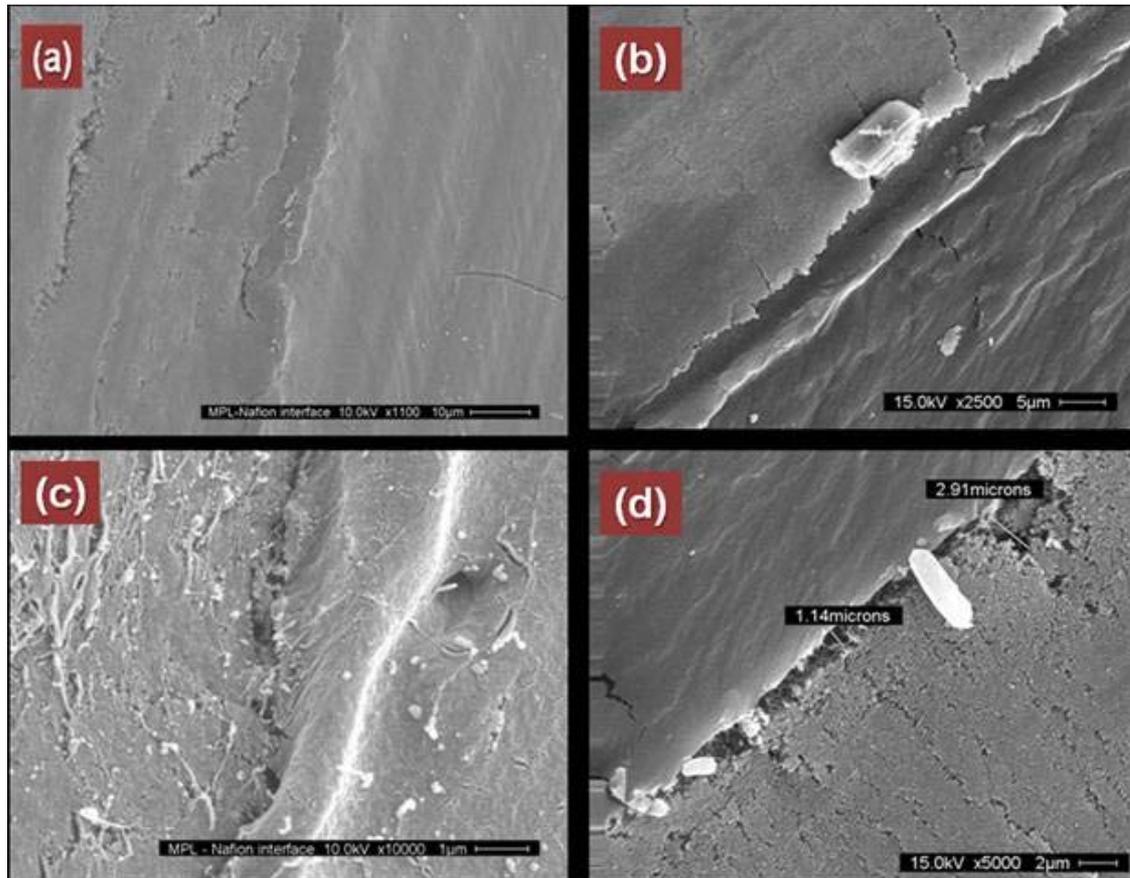
Polarization Curve



Polarization curve illustrates the power curves for a membrane which was dehumidified by flowing 80% relative humidity gas through the cell for ten minutes prior exposure to the experimental storage temperature for one hour

The effect of freeze/thaw cycle duration has upon the amount of degradation experienced by the cell. Note: This graph only represents a small portion of the entire polarization curve to better portray the performance loss.

Accomplishments (cont'd.)



(a) Control (OS1) proton exchange – M.P.L. interface x1100; (b) NM3 proton exchange – M.P.L. interface x2500; (c) Control (OS1) proton exchange – M.P.L. interface x10,000; (d) NM3 proton exchange – M.P.L. interface x5,000

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

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

- ❑ Decrease cost per unit power for proton exchange electrolyte membranes
- ❑ Improve long-term chemical stability of fuel cell PEM electrolytes operating at ≤ 120 °C
- ❑ Maintain or improve high protonic conductivity of PEM electrolytes
- ❑ Minimize water content necessary to support high conductivity under stated conditions

Approach

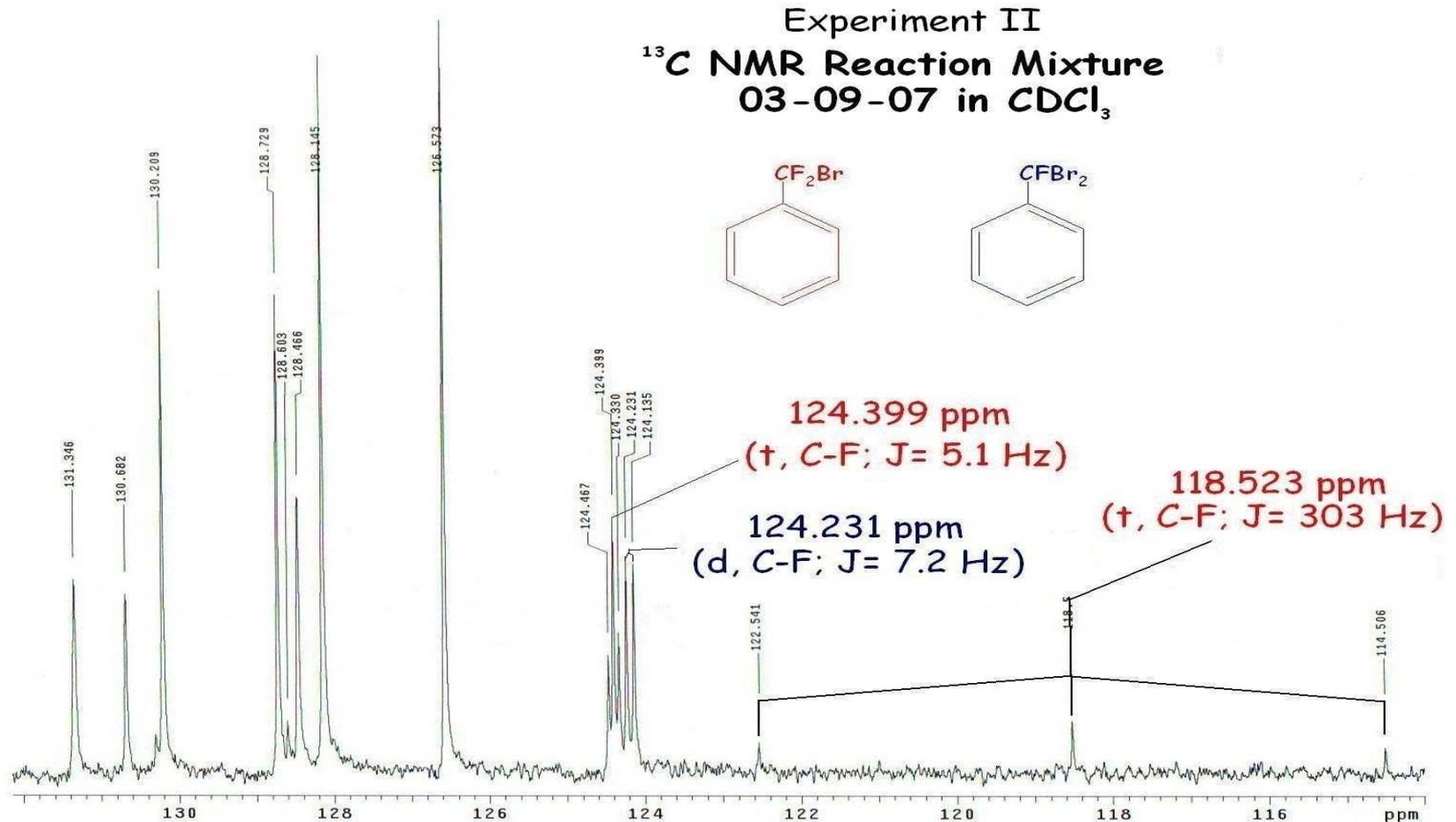
- Develop synthetic method for fluorosulfonation of hydrocarbon polymers to promote proton conductivity and oxidative stability, but with minimum amounts of fluorine (i.e., “strategic fluorination”) to control costs
- Develop accelerated test apparatus to evaluate prototype PEM’s

Accomplishments

- Successfully prepared via cross-linking chemistry a membrane based on highly sulfonated (water soluble) SPEEK, with an equivalent weight of 534 g/equiv.
- Developed a synthetic approach for fabricating a proton exchange membrane made from the fluorosulfonic acid of PEEK. The procedure begins with bromination of the bis-acetamide derivative of 2,5-diaminobenzotrifluoride. Have successfully performed the amidization, the monobromination, and the sulfatodehalogenation of the starting material.
- Developed multiple characterization methods for monitoring peroxide attack.

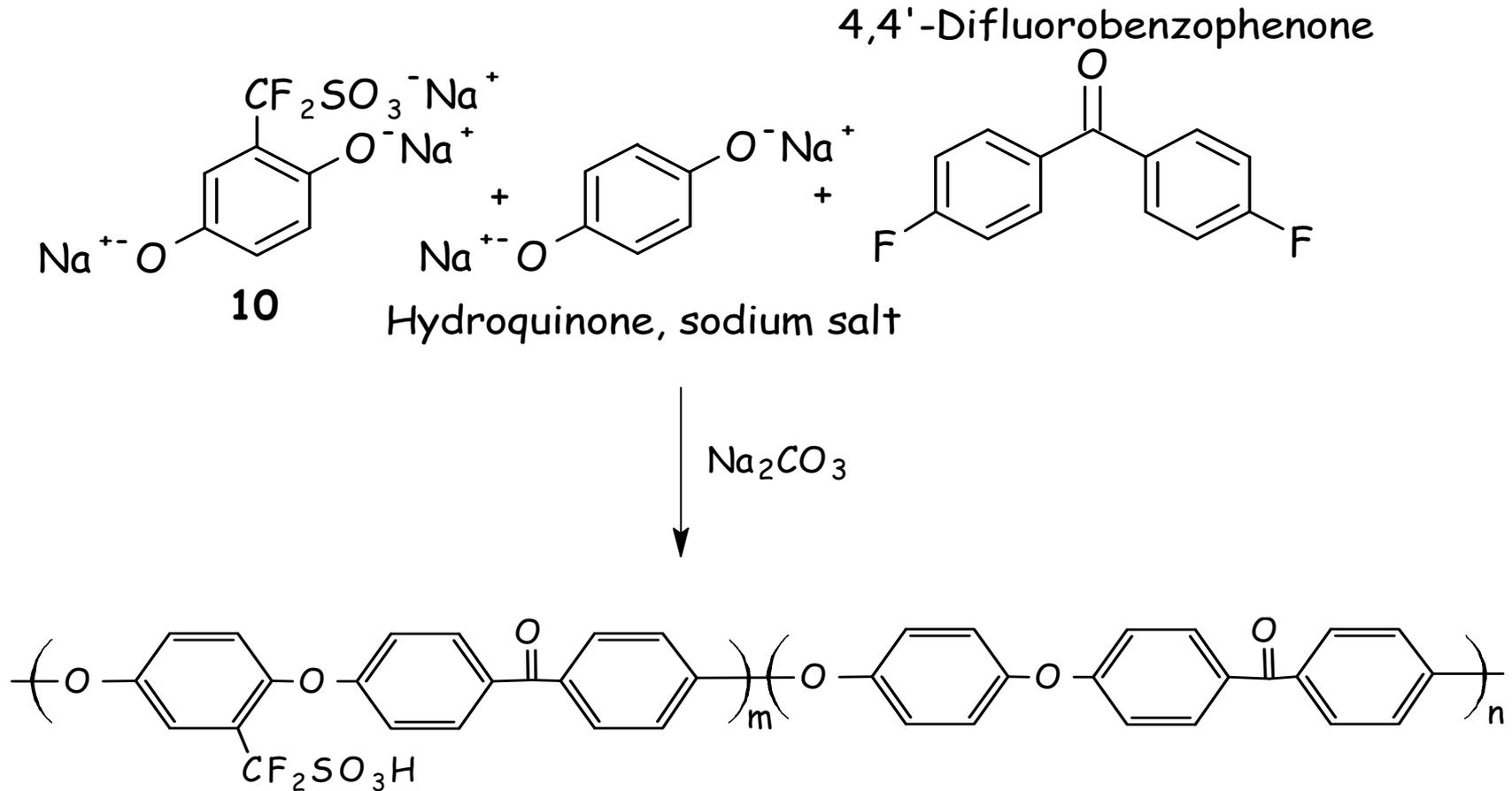
Accomplishments (cont'd.)

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



Accomplishments (cont'd.)

Synthetic scheme for preparation of fluorosulfonated PEEK (F-SPEEK)



Summary

- Water uptake is an important attribute of all membrane electrolytes, as it is related to mechanical strength, creep, and dimensional stability. Thus some means of controlling water uptake by a hydrophilic sulfonic acid polymer is desirable. This is particularly important for SPEEK, which at high degrees of sulfonation (i.e., low equivalent weight) has demonstrated substantial water uptake, on order of 10's of water molecules per sulfonic acid unit. We have attempted to control water uptake in SPEEK membranes by performing cross-linking reactions on the finished polymer. Water-soluble SPEEK (85% degree of sulfonation, or 418 g/eq EW), benzene dimethanol, and various transition metal chloride catalysts were cast together to form a membrane that was heated at 200 °C for 10 min. The resulting insoluble membrane was shown to have conductivity comparable to an uncross-linked SPEEK membrane over a range of relative humidifies.