Fuel Cell Research at the University of South Carolina

John W. Van Zee
University of South Carolina
Columbia, SC

Project ID # FCP_06_VanZee

Overview

Timeline

- Start - Feb 2007
- Finish – Oct 2009
- Percent complete - 90%

Budget

- Total project funding -$2,068,750
  - DOE - $1,655,000
  - Contractor - $ 413,750
- Funding received in FY06 - $0
- Funding for FY07 - $ 886,607
- Funding for FY08 - $1,182,143

Barriers

- A – Durability of seals, catalyst & catalysts supports
- B – Cost of catalysts, electrodes, & seals
- C – Performance in the presence of hydrogen contaminants and under transient temperature conditions

Partners

- Interactions/ collaborations
  - 14 Companies of NSF I/UCRC Center for Fuel Cells
  - DOE H2 Quality Team
  - Plug Power
- ORNL – subcontract

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Relevance

Objectives:

The **overall objective** of this project is to contribute to the goals and objectives of the Fuel Cell element of the Hydrogen, Fuel Cells and Infrastructure Technologies Program of the Department of Energy by enhancing and supplementing the fuel cell research efforts at the University of South Carolina. The project **research activities** focus on the following **technical objectives**:

- ❑ To synthesis and study of novel non-carbon materials that may serve as supports of catalysts. These supports should decrease support corrosion (relative to present-day carbon), reduce degradation of the catalysts, and remove the fraction of performance loss due to this mechanism (2015 target: <30 mV after 100 h @ 1.2V). (Barriers A-C; Task 2: electrodes)

- ❑ To develop an understanding and methodologies that help establish hydrogen quality standards related to PEM cell applications for transportation needs (Barriers A,C; Tasks 9: models for impurities)

Ref: DOE Barriers are: A-Cost, B-Durability, C-Performance, D-Transport, E,F-Thermal, air mgmt., G-Transient operation

Relevance

Objectives continued:

❑ To aid the development of development of durable, low cost seals for PEM stacks through the establishment of laboratory characterization methodologies and measurements and to develop life prediction methodologies. Accelerated tests protocols were explored and the results of these measurements will be related to the behavior observed in cells and stacks of our collaborators. (Barriers A-C; Task 6 Seals)

❑ To measure water isotherms for PBI-based membranes and to measure rates of water accumulation in these materials and cells so that advanced transport and computational fluid dynamic-based models of this high temperature membrane cell can be developed. Note that although these cells operate at 160-180°C, transient upsets or start-up conditions from ambient temperatures can affect the acid-PBI-water equilibrium that could lead to possible dilution of the H_3PO_4 electrolyte over a target 40,000 hour lifetime. (Barriers A,C,D,E,G; Task 8-stationary fuel cells; Task 9-models, Task 10-long term failure mechanisms)

Ref: DOE Barriers are: A-Cost, B-Durability, C-Performance, D-Transport, E,F-Thermal, air mgmt., G-Transient operation

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Approach-Overview

Four sub-projects were selected by DOE to address technology challenges of cost, durability and performance of PEM fuel cells and systems. **Specific goals** addressed include improving catalyst support durability, understanding hydrogen quality effects, understanding durability of seals, and quantifying the effects of water adsorption (gas-solid partitioning) during transient temperature changes in high temperature fuel cells using PBI-H_3PO_4 based membranes. The approach of each project is summarized here followed by sub-project specific slides with tasks.

1. **Supports:** Titania-based catalyst supports were synthesized and characterized. The characterizations included surface and spectroscopic methods, electrochemical and corrosion methods, and the stability analysis and performance studies of the supports loaded with catalysts.

2. **H_2 Quality**: Performance losses caused by fuel contaminants were measured for unique MEAs complimentary to work of NREL, ANL, SNRL, LANL and investigators at other universities involved in the DOE Hydrogen Quality team. Models were developed as part of an effort to isolate and understand contaminant adsorption /reaction/transport/performance relationships at low contaminant levels in PEM cells.

Approach-Overview (continued)

3. **Seals:** Materials were selected based on recommendations from industrial members of the National Science Foundation Industry /University Cooperative Research Center for Fuel Cells. Methods of aging of seal materials in simulated fuel cell environments and with various degrees of stress and deformation. The materials were characterized over extended time spans for mechanical stability and chemical stability including the leachant products. Stress relaxation and dynamic material analysis techniques were evaluated. We seek to contribute to US Fuel Cell Council working group on gaskets and seals. We intend to advance methods of controlled hydration and temperature characterization of elastomeric materials to establish a methodology for characterization of materials for seals in PEM stacks.

4. **Characterize PBI-H_3PO_4 membranes:** Water adsorption/de-sorption rates and isotherms were measured for PBI-H_3PO_4 based membranes. Water balance techniques are being completed to understand the accumulation of water as a function of temperature transients. These measurements will allow advances in the development of performance loss models at extended periods of operation (20,000-40,000 h).

Technical Accomplishments - Summary

The activities of the project contributed to the goals and objectives of the Fuel Cell element of the Hydrogen, Fuel Cells and Infrastructure Technologies Program of the Department of Energy through four sub-projects which report significant progress since beginning in February 2007. This project will end in October 2009.

- ❑ The development of **non-carbon catalysts supports** that display equivalent catalyst activity as Pt/C. The materials were dependent on Nb doping and additional studies should be performed to evaluate alternative levels of doping. Stability and durability of these supports are < 30 mV after 100 hours at 1.2 V for the high doping levels. Additional tests are being considered and proposed to study these effects. See sildes Technical accomplishment details for sub-project 1 sho

- ❑ The isotherms for concentrations of 0.1 ppm CO (current proposed standard is 0.2 ppm, Appendix C). and above were measured for Gore 57 series MEAs with relative high loadings (0.4 mg Pt/cm^2 anode and cathode). Lower loading MEAs are being acquired from commercial vendors and performance of these will be completed prior to the project end. Isotherm correlations suitable for predicting the performance loss are being published. Models to isolate performance loss mechanisms have been published. These models are useful for future experimental designs aimed at other contaminants and their synergistic effect with CO.

Technical Accomplishments – Summary continued

- The development of laboratory characterization methodologies for has advanced the understanding of stress-relaxation, chemical stability, leaching of contaminants, and materials selection for analysis of durable, **low cost seals for PEM stacks.** The sub-project project has developed collaborations through industrial members in the NSF Center for Fuel Cells, through the US Fuel Cell Council and with other investigators at universities. The work has been disseminated through publications and presentations. published

- Techniques and data have been developed for the measurement of isotherms and rate constants for the interaction of water vapor with PBI-H_3PO_4 based membranes and MEAs. These data will advance the understanding of performance loss due to transients (during start up and during upsets) in the stack temperature and current. These data provide a basis for model development.

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Collaborations

1. North American Fuel Quality Team organized by Dr. James Ohi (NREL) to addresses the impact of critical hydrogen fuel constituents as they affect the barriers of Durability, Cost, and Performance. These collaborations also include LANL, ANL, SRNL, University of Hawaii, University of Connecticut. This sub-project also participates in the US Fuel Cell Council Joint Hydrogen Quality Task Force. Oak Ridge National Laboratory (ORNL) tested the use of their spatially resolved mass spectroscopy techniques for understanding local distributions of contaminants.

2. Dana and Dow-Corning – providing materials as well as their knowledge in seal materials

3. General Motors corporation – correlation with their stack testing results with seal and gasket performance.

4. Plug Power collaborated on water-isotherm measurements for the PBI-H_3PO_4 based membranes and MEAs.

Future Work

(This project will end in October 2009)

1. **Non-Carbon supports –** the tasks of this sub-project are complete.

2. **Hydrogen quality –** measure additional CO isotherms and the interaction of CO with NH_3 on lower catalyst loaded Gore MEAs and requested by the H_2 Quality Team. Complete the analysis of isotherms and rate constants and disseminate results through presentations and submissions for publication.

3. **Gaskets and Seals -** the tasks for this project are complete. The project will be continued with the newly funded DOE award.

4. **PBI-H_3PO_4 isotherms -** verify isotherm and rate data with additional water balance measurements during transient temperature operation of single cells. Continue to disseminate results through presentations and submissions for publications.

Technical Accomplishments & Progress: Details for

Sub-Project 1: Development of Non-Carbon Catalyst Supports

Branko N. Popov and John W. Weidner

Department of Chemical Engineering
University of South Carolina

Technical Accomplishments and Progress: Details

Sub-Project 1: Non Carbon Supported Catalysts (100% completed)

OBJECTIVE: To synthesis and study of novel non-carbon materials that may serve as supports of catalysts. (2015 target: <30 mV after 100 h @ 1.2V). (Barriers A-C; Task 2: electrodes)

Task 1. Developed Titania-based Supports
- **Subtask 1.1 Synthesis of high surface area Nb doped TiO_2**
- **Subtask 1.2 Synthesis of high surface area Ti_4O_7 supports**
- **Subtask 1.3 Deposit catalysts – Form electrodes**

Task 2. Characterized Newly Developed Supports & Catalysts
- **Surface and Spectroscopy Methods:**
  (BET, Porosimetry, SEM, TEM, XRD, TGA, XPS, XAS)

Task 3. Characterized Electrochemical Behavior

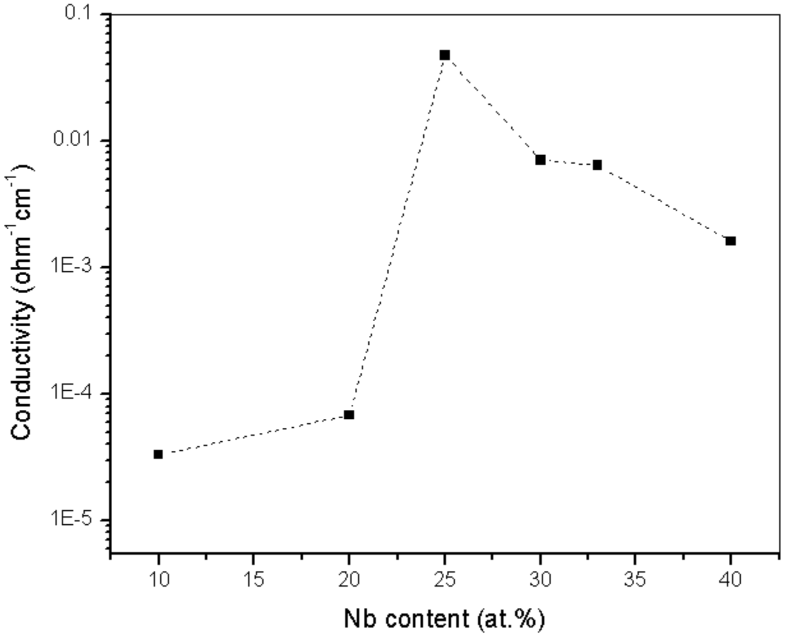
Task 4. Measure Corrosion Rates on Developed Supports & Catalysts

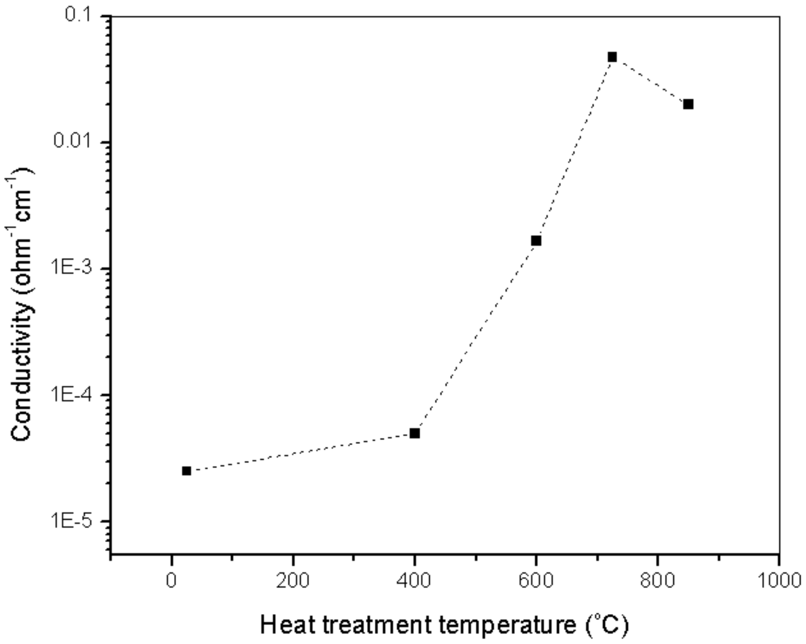
Task 5. Stability Analysis of the Loaded Catalysts with ADTs
(ADT = accelerated durability test)

Task 6. Presentations and Papers (submitted)

Sub-Project 1: Technical Accomplishments and Progress

Conductivity of Nb-Doped TiO_2 Support



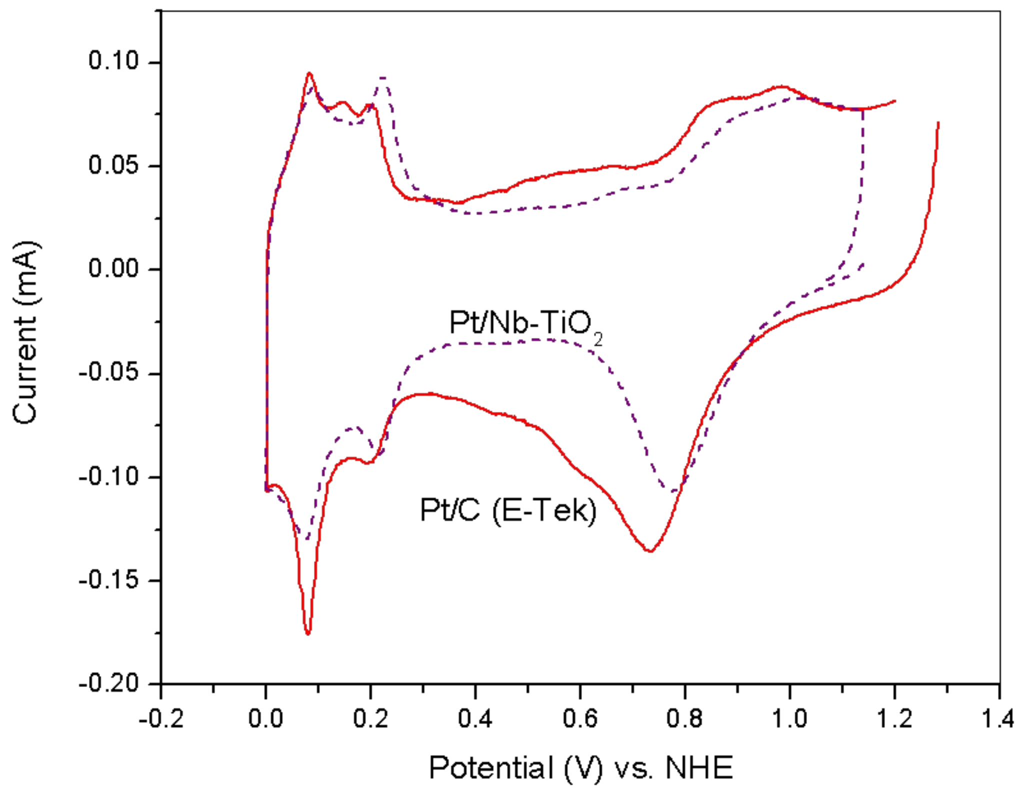


- ***The electrical conductivity shows a maximum for 25 at% Nb and 700 ^{o}C.***
- ***Increase in conductivity is due to the presence of Ti^{3+} and Nb^{2+}.***

Sub-Project 1: Technical Accomplishments and Progress

Pt Catalyst Supported on Nb-Doped TiO_2

Electrolyte: 0.5 M H2SO4; Sweep rate: 5 mV/s;Catalyst loading: 246 µg/cm2 (Pt/Nb-TiO2) 120 µg/cm2 (Pt/C)

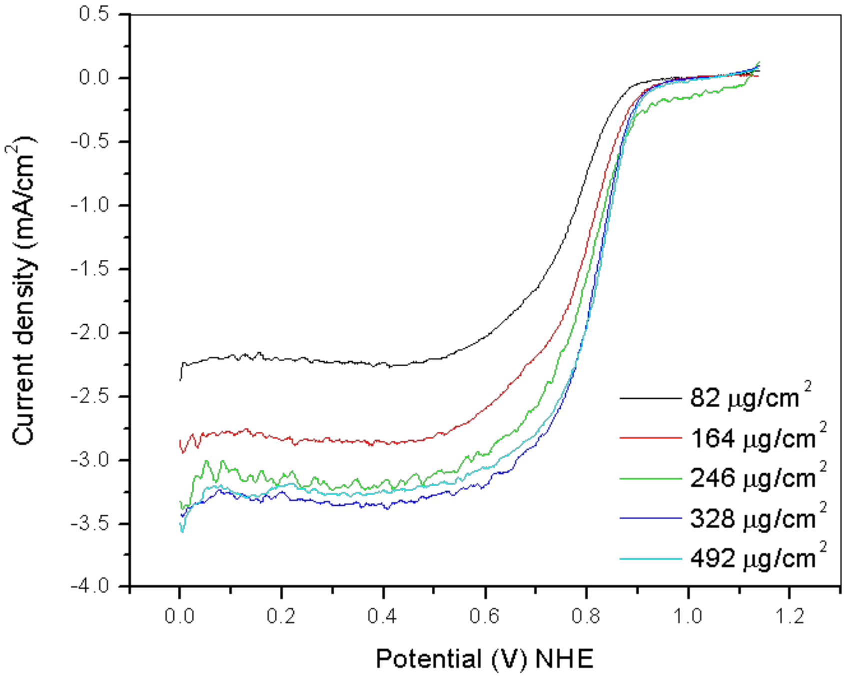


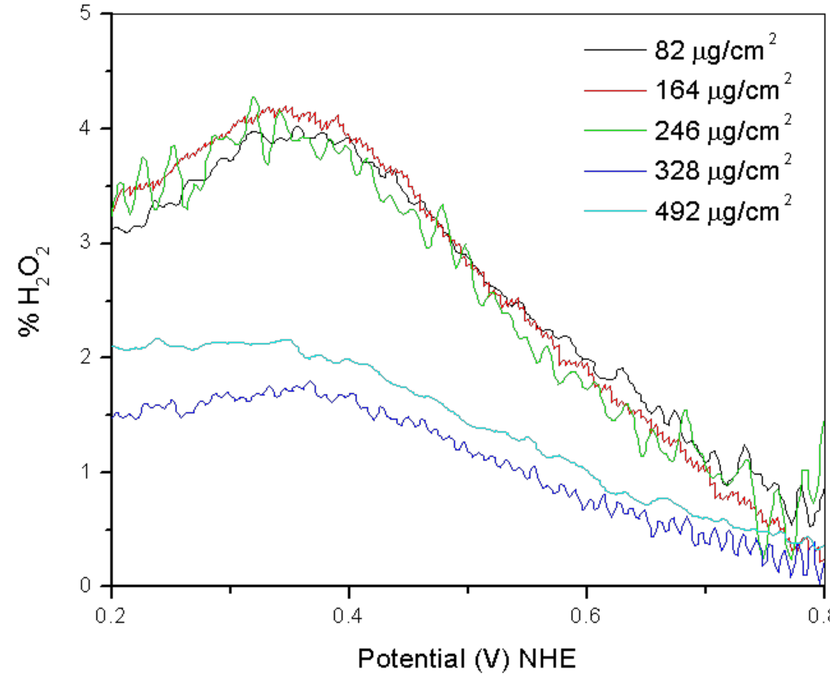
Conclusion: The electrochemical active surface area (ECSA) of Pt/Nb-TiO_2 is comparable to that of Pt/C.

Sub-Project 1: Technical Accomplishments and Progress

Pt/Nb-TiO_2 : LSV - Effect of Loading

Electrolyte: 0.5 M H_2SO_4 Scan rate: 5 mV/s





- ***The catalytic activity of Pt/Nb-TiO_2 is comparable to that of Pt/C.***
- ***The catalyst produces less than 4% H_2O_2.***

Summary Sub-Project 1: Technical Accomplishments

- A Nb-doped TiO_2 support with high surface area and electrical conductivity was developed by using a hydrothermal process.
- The synthesized support has a mesoporous structure and a surface area of approximately 80 - 150 $m^2\ g^{-1}$, which is much higher than that reported in the literature.
- Initial tests indicate low corrosion and comparable polarization for the ORR
- Initial tests indicate high turnover frequency for MeOH oxidation

Technical Accomplishments & Progress: Details for

Sub-Project 2: Hydrogen Quality

Jean St-Pierre and John W. Van Zee

Department of Chemical Engineering
University of South Carolina

Technical Accomplishments and Progress: Details

Sub-Project 2: Hydrogen Quality (90% completed)

OBJECTIVE: To develop an understanding and methodologies that help establish hydrogen quality standards related to PEM cell applications for transportation needs. Provide data for ANL model for CO as a "canary".

Task 1. Group Contaminants by Probable Mechanism

(Adsorption/Desorption, Reactive, Transport Through MEA)

Task 2. Study Effect of Temperature Distributions

Subtask 2.1 Predict temperatures in common cells

Subtask 2.2 Design new laboratory cells

Task 3. Perform Experiments for CO on Unique MEAs - Gore 57

Measure adsorption isotherms and rate constants (for CO, a marker compound, as agreed by H_2 quality team; Target = 0.2 ppm CO)

Task 4. Develop Models to Predict Performance Loss

Task 5. Explore with ORNL the Use of Intra-PEMFC Sensors

Task 6. Interact with H_2 Quality Team

Task 7. Present and Publish Results

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Technical Accomplishments and Progress: Details

Sub-Project 2: Hydrogen Quality Task 3 (90% completed)

Obtained *In-situ* Experimental Data for CO Poisoning Characterization

Obtained Polarization & Anode Overpotential data on Gore 57 MEAs:

- Operating conditions:
  - Tcell = 80 ˚C and 60 ˚C
  - Back pressure = 0/0 psig and 25/25 psig
  - Relative humidity = 75/25 % RH (A/C)
  - Stoic ratio = 1.2/2.0
- P_{co} = 10, 25, 50, 100 ppm - complete
- P_{co} = 0.2, 1.0, 2.5 ppm – complete
- O_2 crossover (internal air bleed) – in progress

Calculate isotherms and rate constants from these data – in progress

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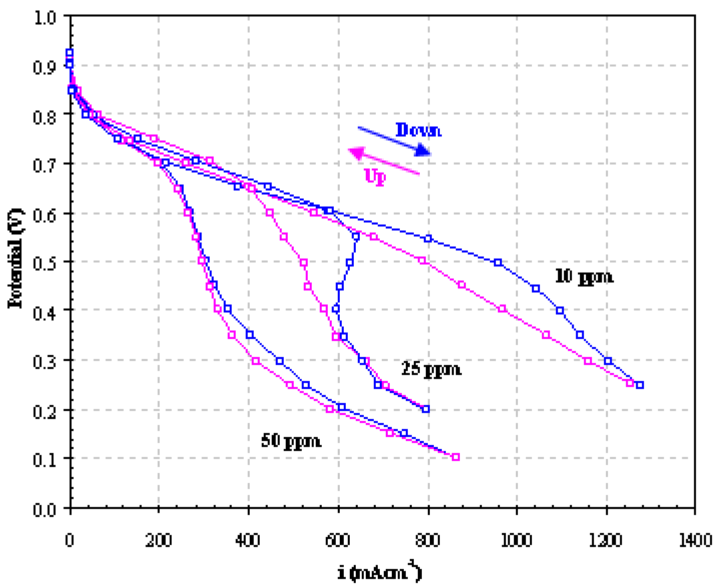
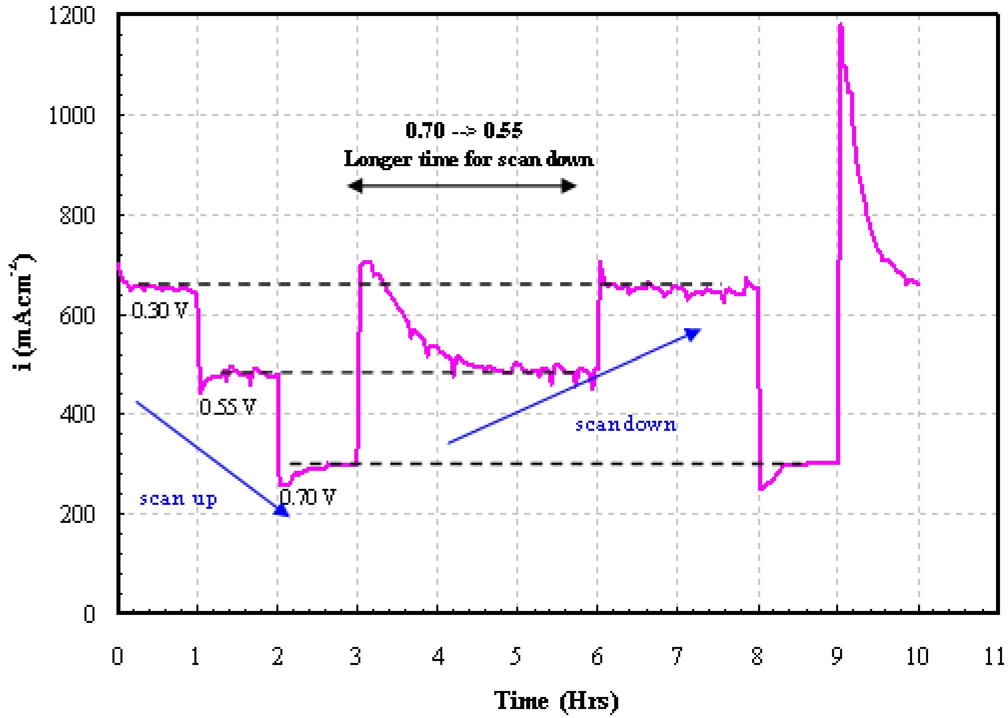
Technical Accomplishments and Progress: Details

Sub-Project 2: Hydrogen Quality (90% completed)

Conclusion: Steady state data, at low concentrations, require extended hold times and these times depend on direction. These hold times minimize hysteresis.



20 min hold too short for 25 ppm @ 80C and 0/0 psi

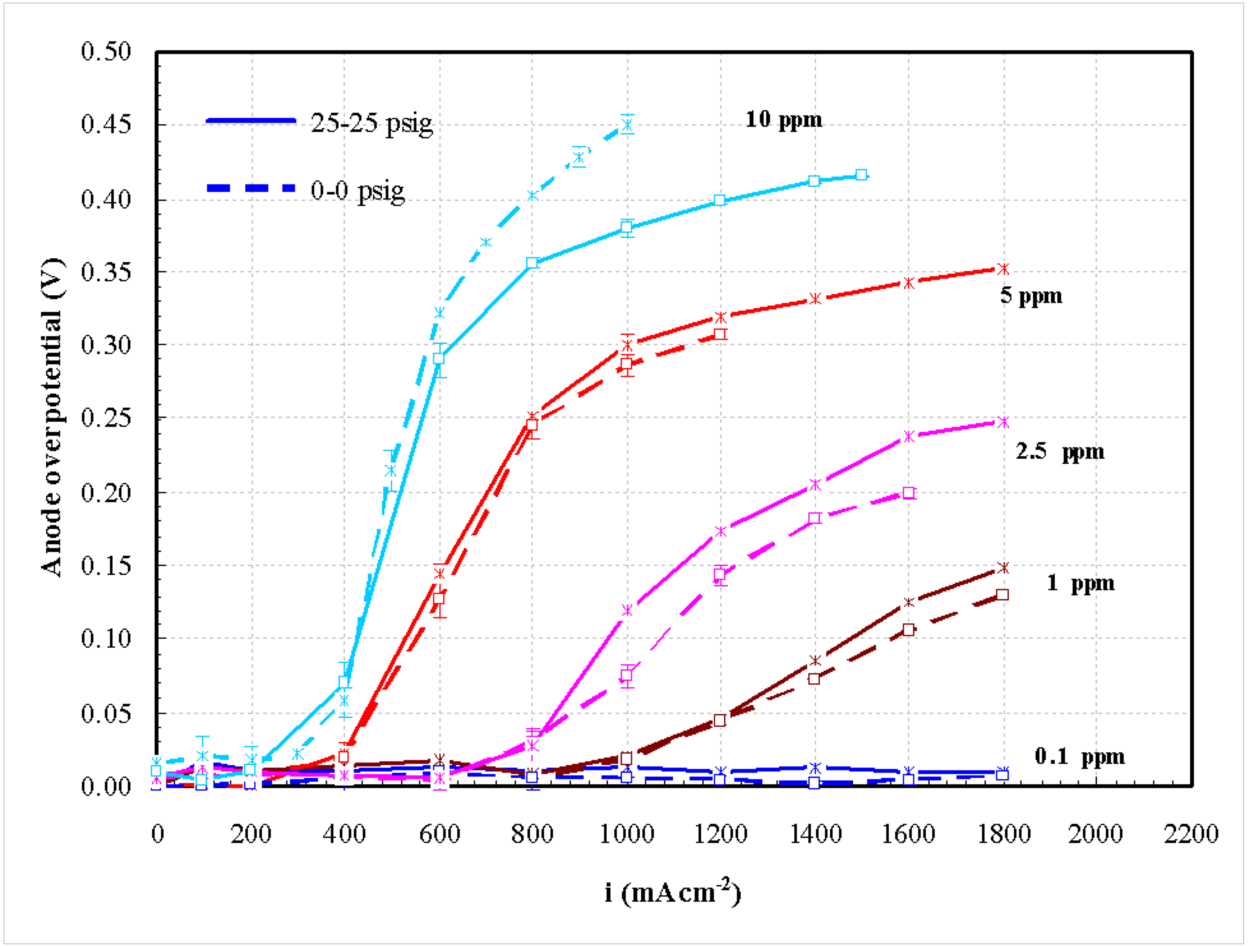


Technical Accomplishments and Progress: Details

Sub-Project 2: Hydrogen Quality (90% completed)

Effect of Pressure and Concentration of CO at 60 C

(T cell = 60 C, Gore 57 series MEA, A/C RH= 75/25 %, stoich = 1.2/2.0)

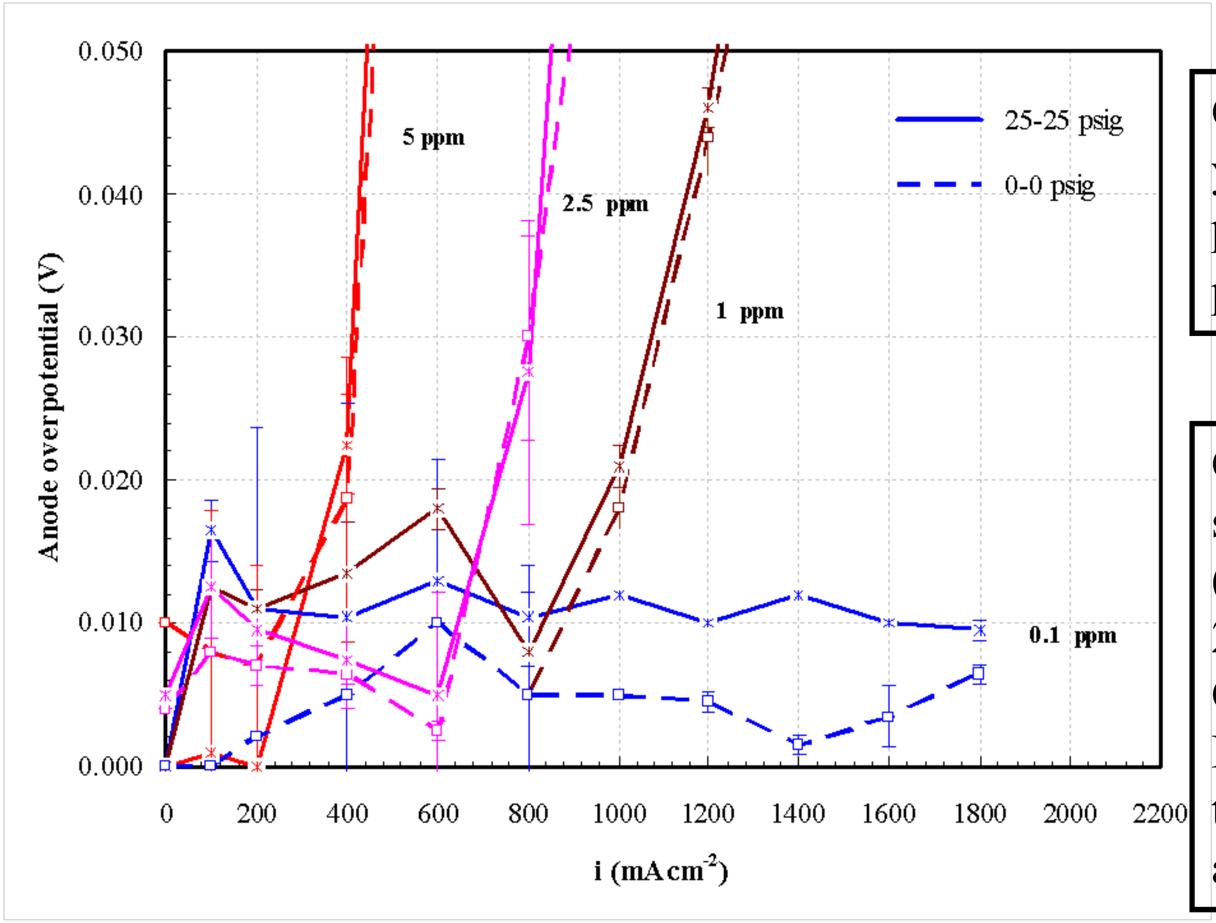


At P_{co}< 10 ppm, higher system pressure increases polarization but trend is reversed at higher partial pressures.

Technical Accomplishments and Progress: Details

Sub-Project 2: Hydrogen Quality (90% completed)

Expanded Low Overpotential Region of Previous Figure



Conclusion: 0.1 ppm CO yields ~ 10 mV polarization at 60 C at 25 psig.

Conclusion: Error bars show polarization ± 5 mV (the detection accuracy in 25 cm^2 cells) for 0.1 ppm CO at 60° C and 0 psig. Measurements at higher temperatures approach accuracy limits.

Summary for Sub-Project 2: Technical Accomplishments (Task is 90% complete- See Request by H_2 Quality team)

- Provided data on Gore 57 Series MEAs (0.4/0.4 mg Pt/$cm^{2)}$
  - Suitable for comparison with other MEAs & loadings
  - Over an operating range that allows parameter estimation
  - Complementary to other groups & modeling effort
  - Data for lower concentrations below Specificatsion
  - Consistent set of parameters for this MEA – in progress

- Future Work
  - Perform Comparison Measurements at 0.1/0.3 mg Pt/cm^2 (Recently Requested by H_2 Quality Team)
  - Perform Measurements for NH_3 /CO mixtures (Recently Requested by H_2 Quality Team)
  - Publish Isotherm Results to obtain Model Parameters
  - Continue to interact with H_2 Quality team

Technical Accomplishments & Progress: Details for

Sub-Project 3: Seals for PEMFCs

Bill Chao

Department of Mechanical Engineering
University of South Carolina

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Technical Accomplishments and Progress: Details

Sub-Project 3: Gaskets and Seals for PEMFCS (100% completed)

OBJECTIVE: To aid the development of development of durable, low cost seals for PEM stacks through the establishment of laboratory characterization methodologies and measurements and to develop life prediction methodologies.

Task 1. Selected Commercially Available Seal Materials.

Task 2. Aged Seal Materials

- **In simulated and accelerated FC environment**
- **With and without stress/deformation**

Task 3. Characterized Chemical Stability

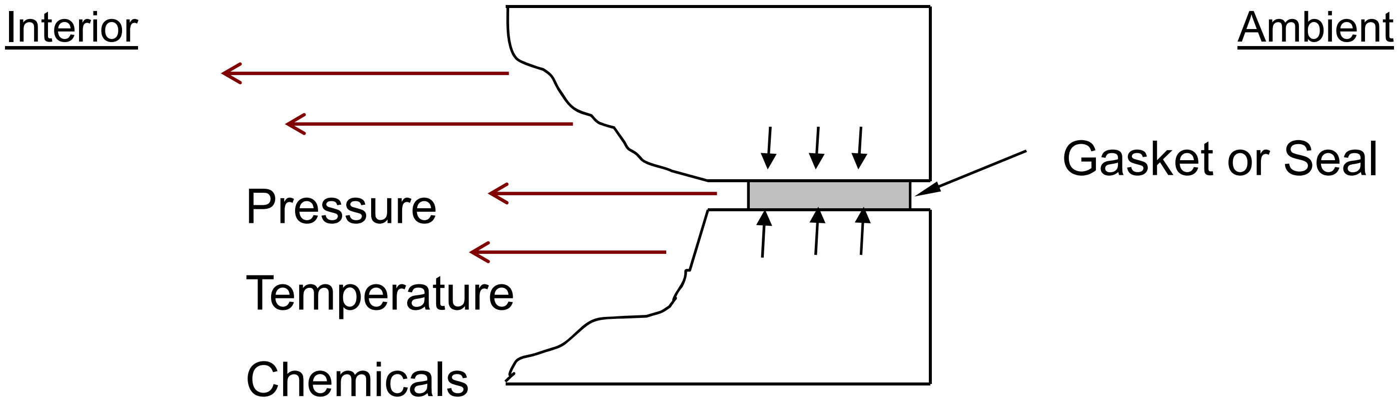
- **Perform both constant stress & constant displacement tests**
- **Assess the effect of applied stress/deformation on the rate of degradation**
- **Measure chemical/thermal stability will be assessed by various**

Task 4. Characterized Mechanical Stability

Task 5. Developed of Accelerated Life Testing Procedures

Task 6. Industrial Interaction and Presentations

Technical Accomplishments and Progress: Sub-Project 3:
Gasket/Seal as a structural member in Fuel Cells



Characteristics of gasket/seal :

Under compression, exposed to chemicals, high temperature, pressure, cyclic conditions, etc.

Loss of functionality : by cracking and /or stress relaxation

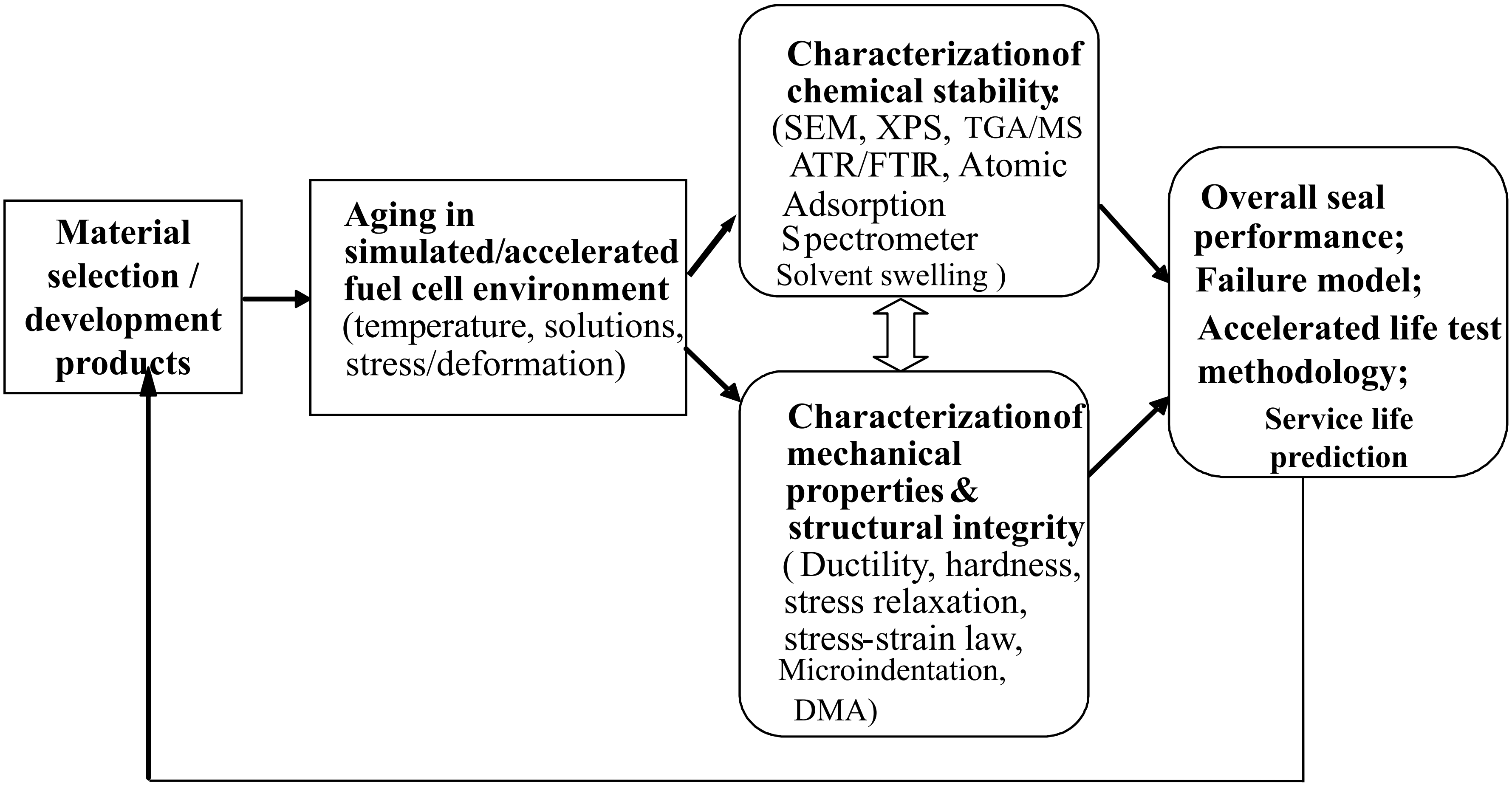
Cracking : due to corrosion under compression (Chemical stability)

Stress Relaxation : material degradation… loss its sealing ability (mechanical stability)

Leachants: detrimental sometimes (chemical stability)

Technical Accomplishments and Progress: Flow Chart of Studies

Sub-Project 3: Gaskets and Seals for PEMFCS (100% completed)



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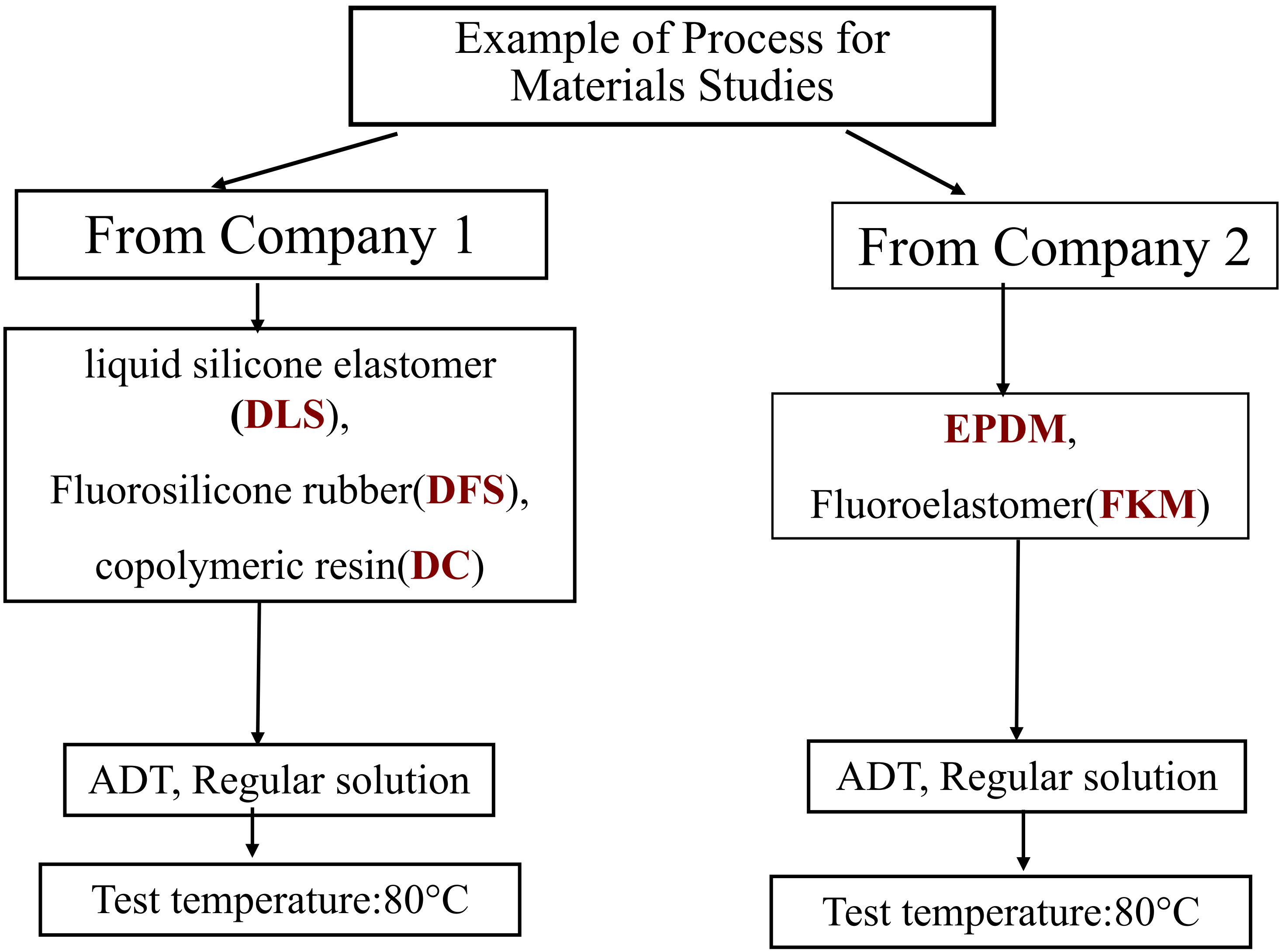
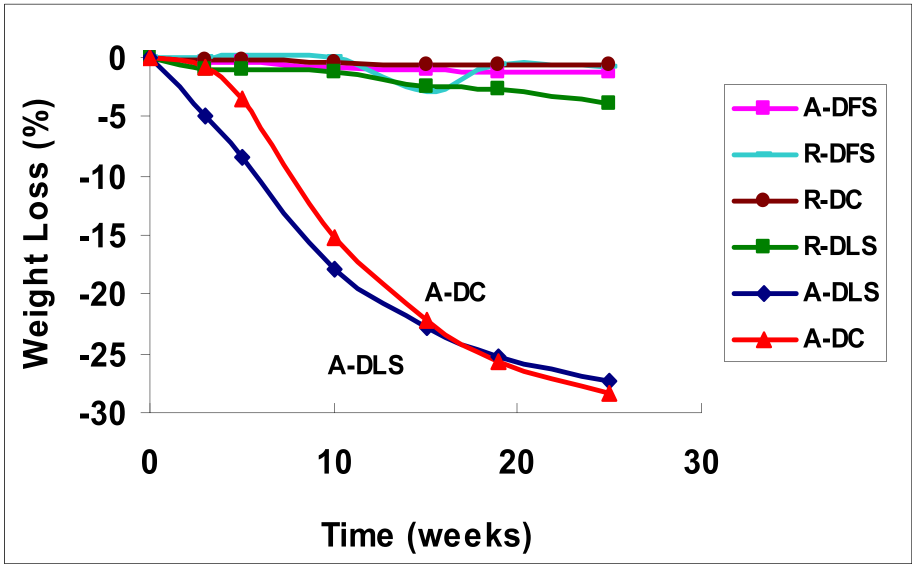
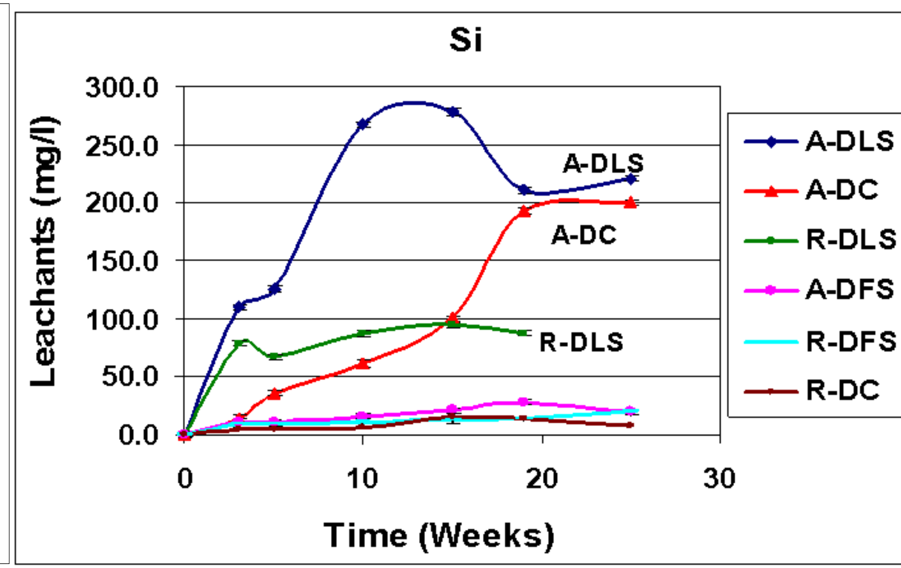
Sub-Project 3: Technical Accomplishments & Results



Sub-Project 3: Technical Accomplishments and Results

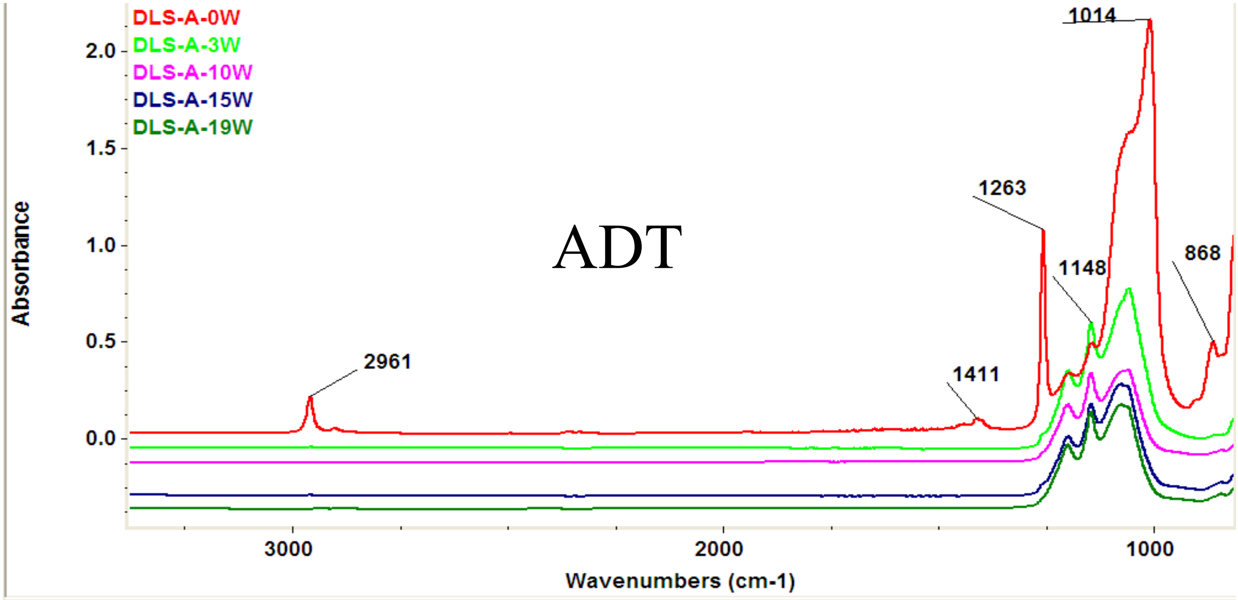
Weight loss and Chemical Leaching
A= Accelerated Solution, R= Regular Solution



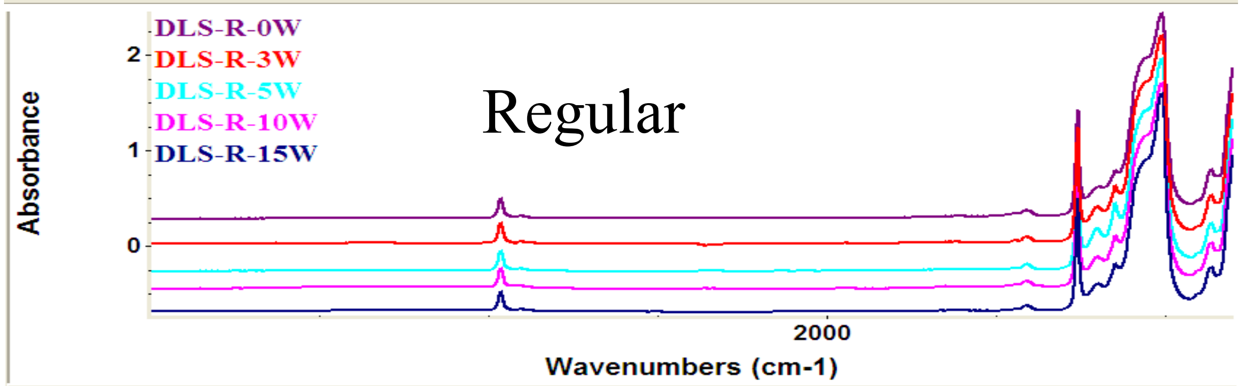


- A-DLS, A-DC and R-DLS→ more weight Loss and more Si leaching →Lost Si is the cause of weight loss
- No detectable Mg in all silicone elastomer
- The amount of Ca is in the range of 0-5mg/l
- The amount of Si is in the range of 5-300 mg/l

Sub-Project 3: Technical Accomplishments and Results
Example of ATR-FTIR Resutls for DLS Material



Chemical changes in backbone and crosslinked domain after 3week exposure



No significant Chemical Changes after 15 week exposure

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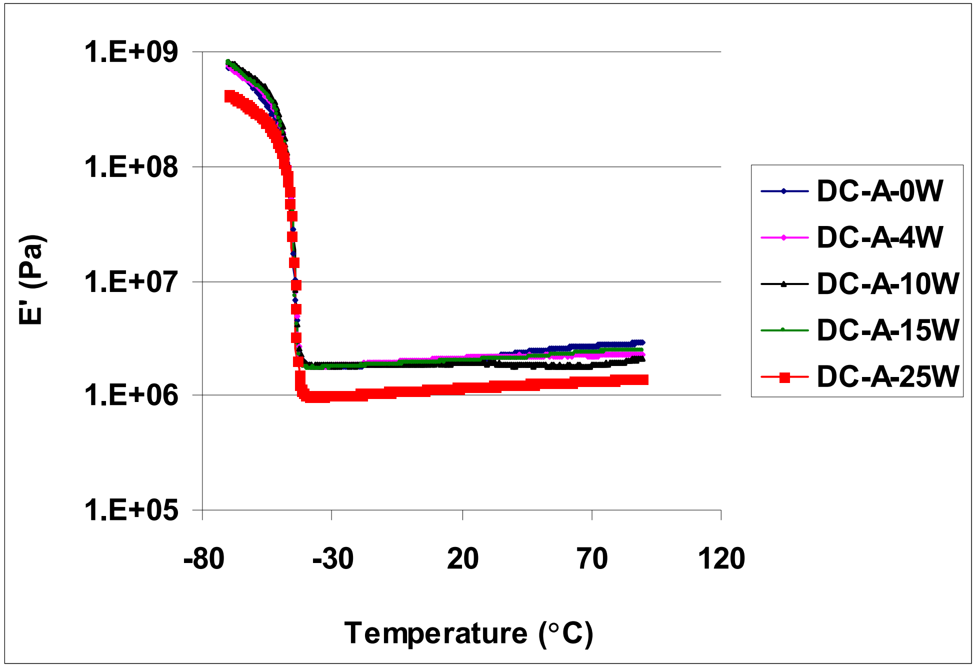
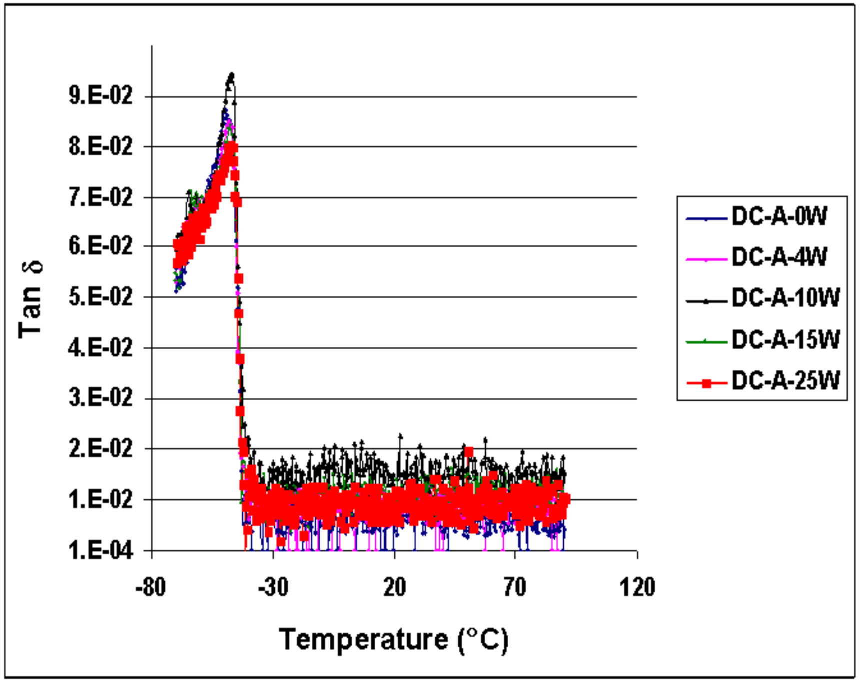
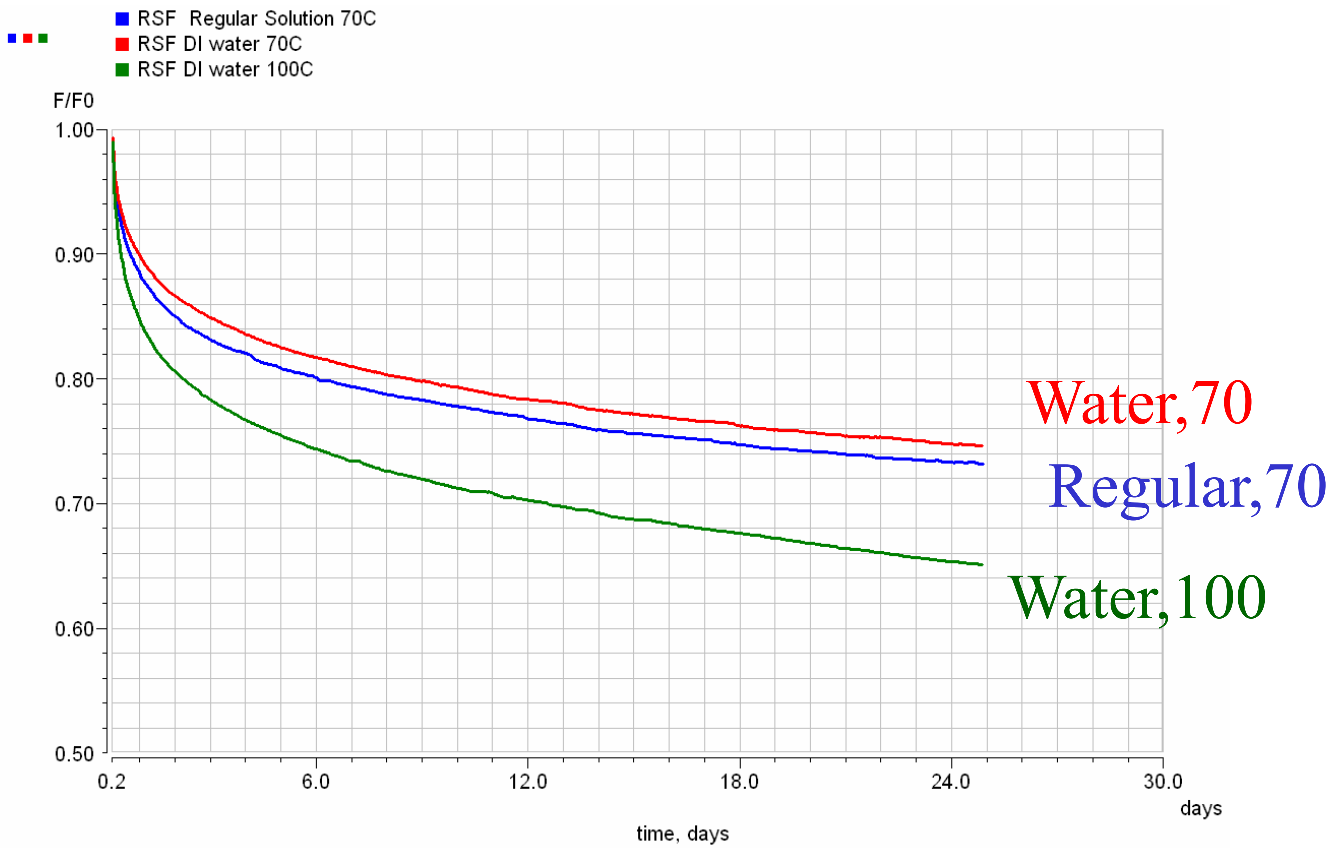
Elastic modulus E' and Tan δ for DC exposed to ADT solution (by DMA)





1. E' gradually decrease over time, especially at 25W (weeks) exposure
2. Tg remains at -47°C ± 1 °C
3. Constant oscillation after glass transition temperature for the loss modulus curves and Tan δ curves.

Compression Stress Relaxation curves of DLS at different temperature and different medium



- A combination of DI water and high temperature results in dramatic reduction of the retained seal force
- Acidic solution has minimal effect compared to water

Summary Sub-Project 3: Technical Accomplishments

1. **Optical microscope** and ESEM analysis to examine the degradation of surface.
2. **ATR-FTIR** test to elucidate the material surface chemical degradation.
3. **Atomic adsorption spectrometry** analysis to identify leachants from seals into the soaking solutions.
4. **Microindentation** test for assessing the mechanical properties of the gasket materials.
5. **New equipment purchased:**
   a. **DMA** for assessing the dynamical mechanical properties of the gasket materials.
   b. **Compression Stress relaxation** test system to monitor the retained seal force under fuel cell condition
6. **Data available for Developing** life prediction methodologies.
7. **Publications** in Journal and Conferences and discussions with members in the NSF Center for Fuel Cells.

Technical Accomplishments & Progress: Details for Sub-Project 4: PBI-H_3PO_4 isotherms

Tau Gu and Sirivatch Shimpalee

Department of Chemical Engineering
University of South Carolina

Technical Accomplishments and Progress: Details

Sub-Project 4: PBI-H_3PO_4 isotherms (90% completed)

OBJECTIVE: To measure water isotherms for PBI-based membranes and to measure rates of water accumulation in these materials and cells so that advanced transport and computational fluid dynamic-based models of this high temperature membrane cell can be developed.

Task 1. Design and Perform Steady State and Transient Experiments

- (a) obtain data for water content as f (T, Dew point)
- (b) obtain water balance data for water & acid balance as f (T) under load
- (c) obtain data for rates of water adsorption/desorption as f (T).

Task 2. Exercise Existing Computer Code to Predict Performance During Cycles

- (a) over a range of operating conditions
- (b) to determine model limitations
- (c) to compare predictions/behavior with existing data.
- (d) propose experiments required to improve the model

Task 3. Presentations and Publication

Sub - Project 4: Technical Accomplishments

1. Obtained $\lambda = f\left(P_{H_2O}, T\right)$ where $\lambda = \frac{moles\_of\_water}{moles\_of\_H_3PO_4}$
2. Measured extent acid loss to gas stream at open circuit.
3. Report and analyze weight change data relative to dry membrane mass.

Experimental Conditions

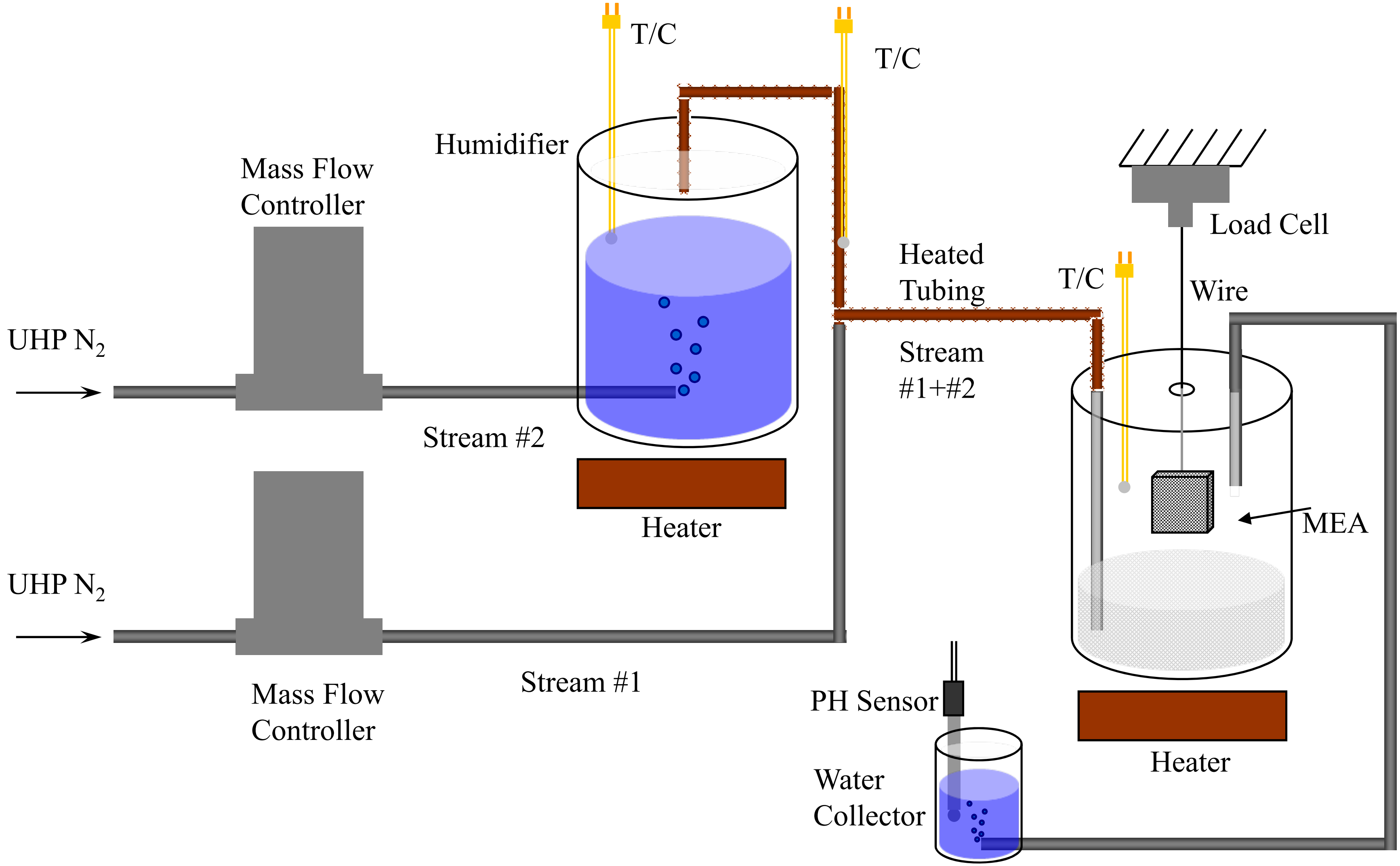
Temperatures: 160 ºC to 90 ºC

Sample size (nominal): 1 inch^2 (6.4516 cm^2)

Total nitrogen flow: 500 sccm,

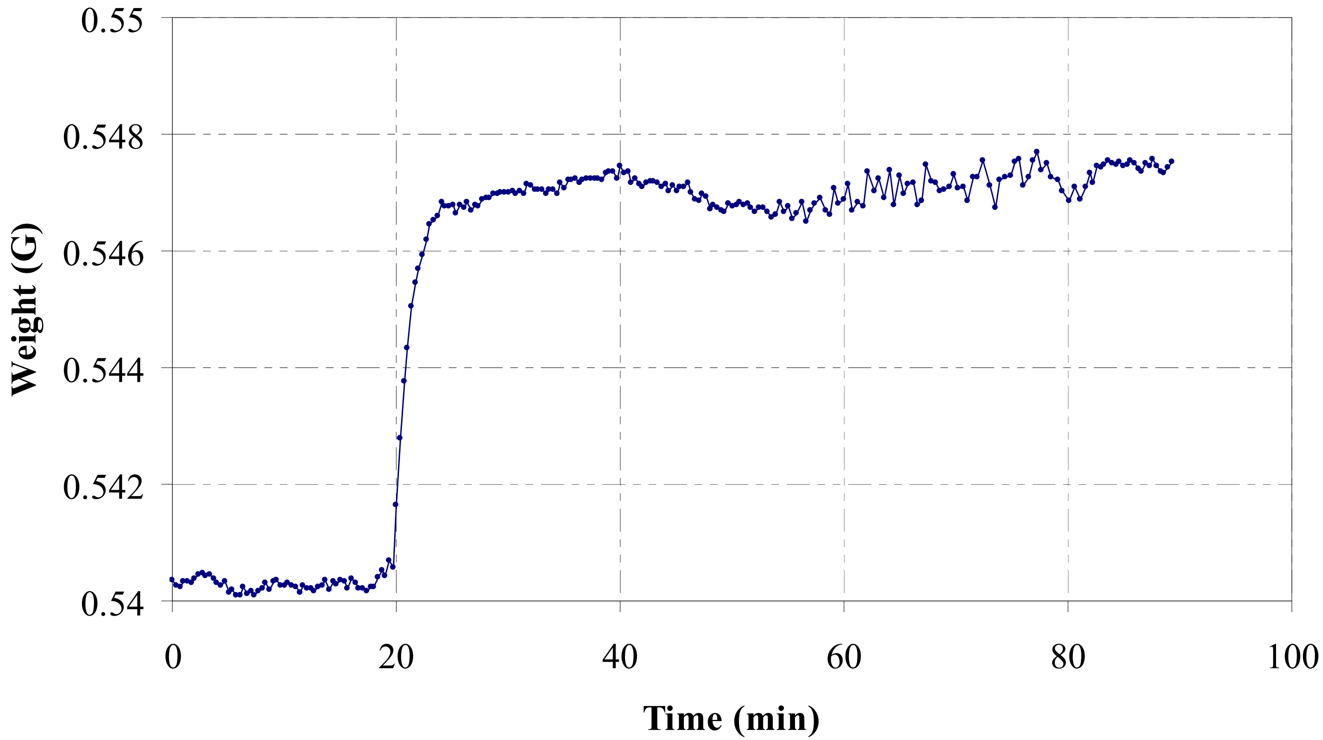
Water partial pressure scanning rate: 0.01 to 0.002 (kPa/101kPa/min)

Sub - Project 4: Technical Accomplishments
Recommended experimental set-up to measure isotherms



Sub-Project 4: Technical Accomplishments and Results

Response of water adsorption into the MEA for step change in inlet humidity (These type of data were used to determine isotherms and rate constants)



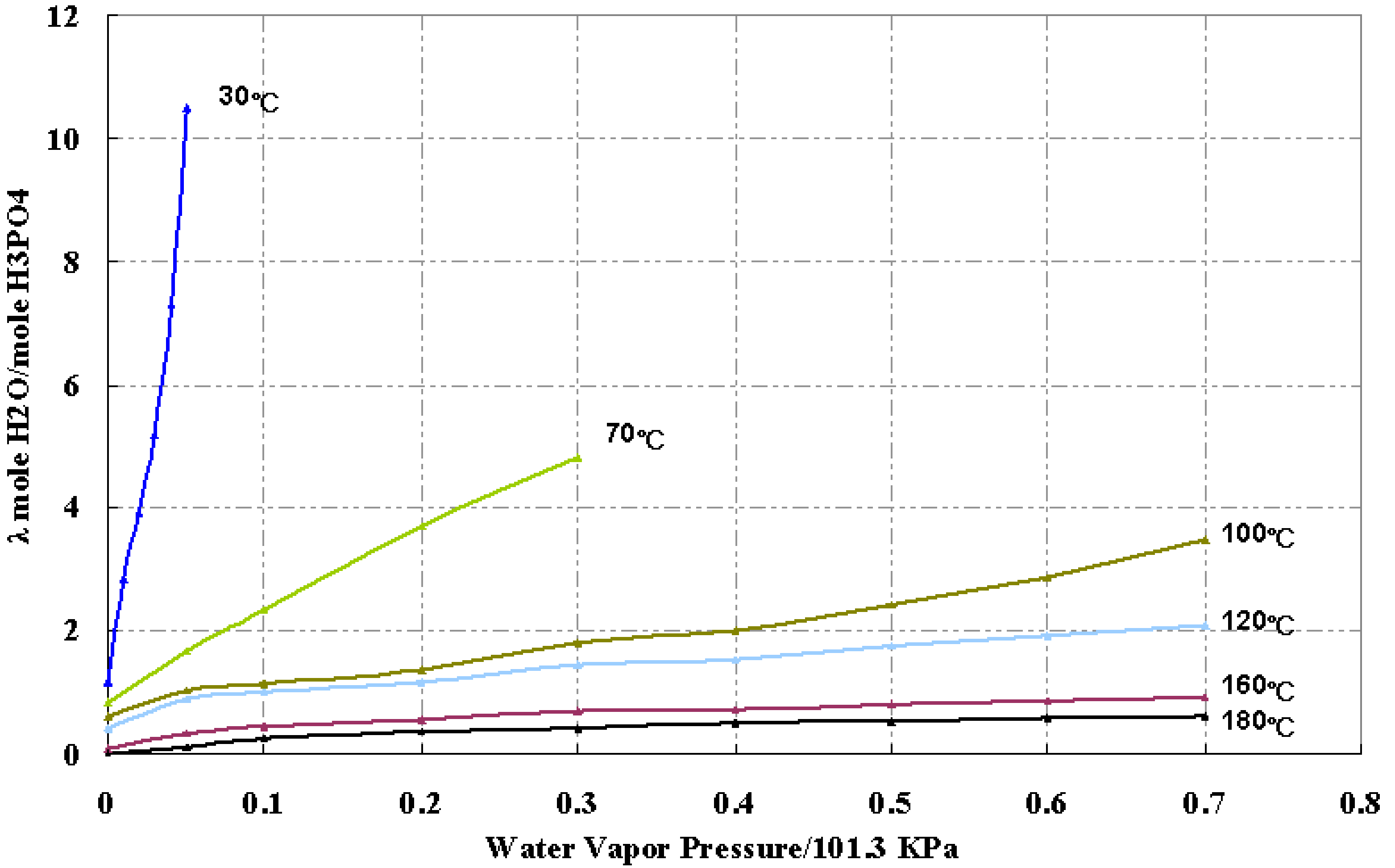
Container Temperature: 160 ^{o}C; Switching time: @20th minute

Initial humidity: 0.020 = 17.5 ^{o}C dew point

Final humidity: 0.156 = 55 ^{o}C dew point

Sub-Project 4: Technical Accomplishments and Results

Lambda as a function of temperature and dimensionless water vapor pressure



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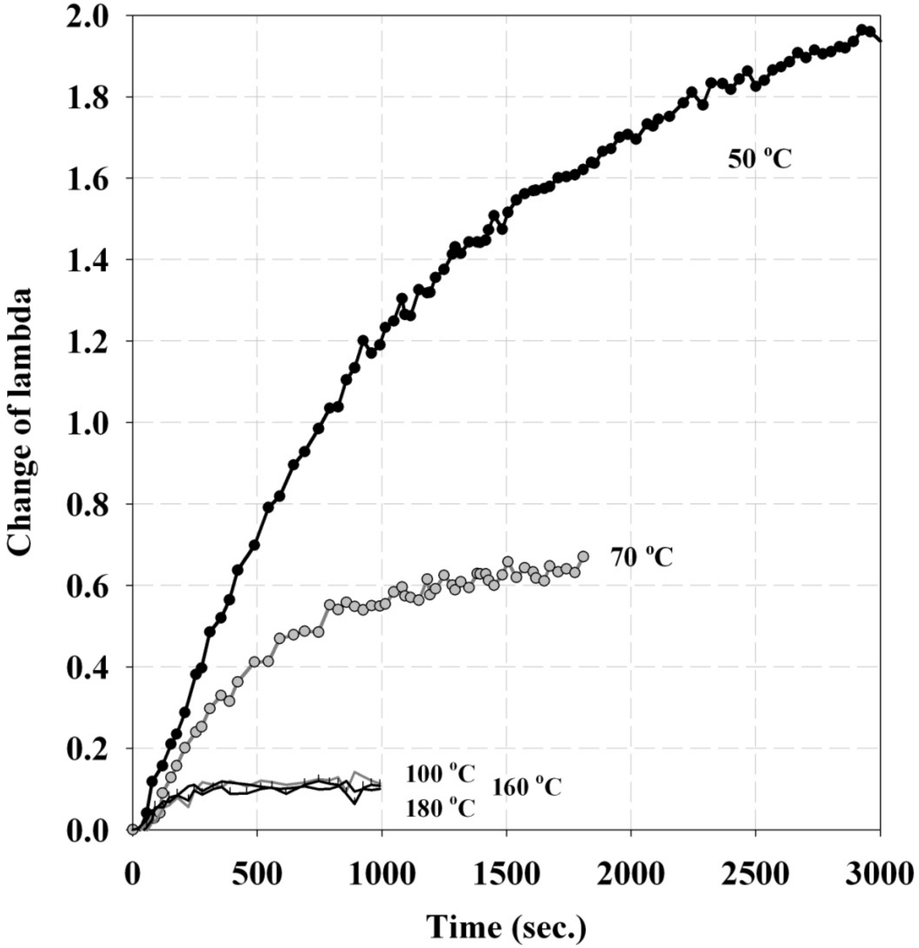
Project 4: Technical Accomplishments and Results

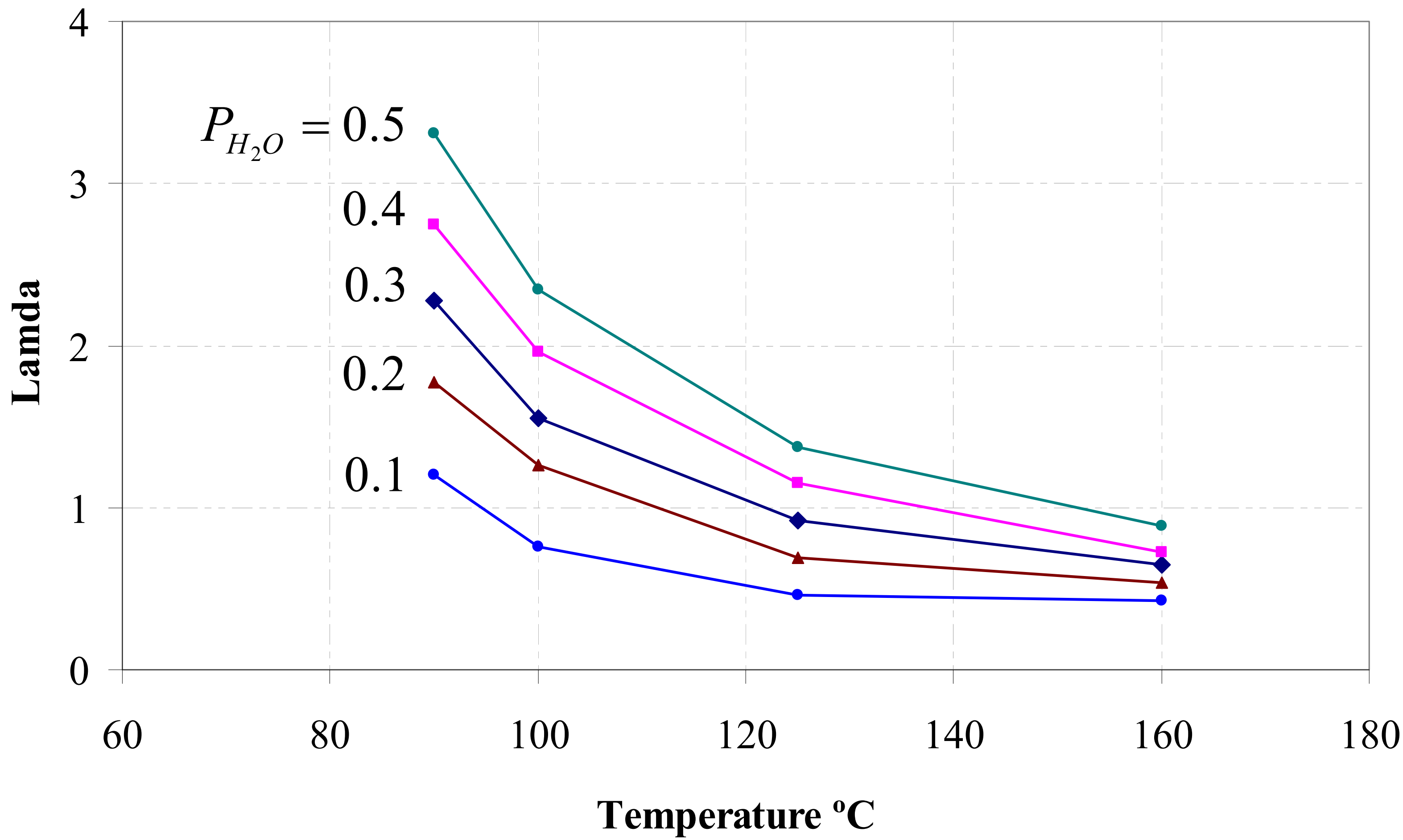
Rate of Change of lambda as a function of temperature



Conclusion: Rate of adsorption of water into PBI-H_3PO_4 MEA strongly depends on temperature at low temperatures. Rate of desorption (not shown here) is not as fast. Experimental data on cell/stack performance should report temperature excursions.

Sub Project 4: Technical Accomplishments and Results:

Effect of temperature on for various dimensionless water vapor pressures



Summary for Sub-Project 4: Technical Accomplishments

Task 1. Experiments

- (a) water content data obtained (complete)
- (b) water balance experiments (90% complete)
- (c) transient experiments & rate constants (complete)
- (d) publications and presentations (submitted)

Task 2. Exercise of Computer Code (90% complete)

- (a) data for water content as f (T, Dew point)
  allows for prediction of long-term water accumulation
- (b) verification data needed for water balance as f(T) under load
- (c) verification data cell needed for transient experiments
- (d) verification data needed for cathode carbon corrosion