DOE Hydrogen Program

Fuel Cell Research at the University of South Carolina

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

Project ID #
FC47

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Overview

Timeline

- Start - Feb 2007
- Finish – Dec 2008
- Percent complete - 65%

Barriers

- Barriers addressed
  - A - Durability
  - B - Cost
  - C - Performance

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 - $1,182,144

Partners

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

OBJECTIVES

Project 1- Non Carbon Supported Catalysts

- Develop novel materials (e.g., Nb doped) for
  - improved corrosion resistance
  - improved fuel cell components

Project 2 -Hydrogen Quality

- Develop a fundamental understanding of
  - performance loss induced by fuel contaminants
  - durability loss fuel induced by contaminants

Project 3 -Gaskets for PEMFCs

- Develop a fundamental understanding of
  - the degradation mechanisms of existing gaskets
  - the performance of improved materials

Project 4 -Acid Loss in PBI-type High Temperature Membranes

- Develop a fundamental understanding of
  - acid loss and acid transport mechanisms
- Predict performance and lifetime as a function of load cycle

Approach: Project 1: Non Carbon Supported Catalysts

Task 1. Development of Titania-based Non-carbon 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. Characterization of the Developed Supports & Catalysts

Surface and Spectroscopy Methods:

(BET, Porosimetry, SEM, TEM, XRD, TGA, XPS, XAS)

Task 3. Electrochemical Characterization

Task 4. Corrosion Studies on Developed Supports & Catalysts

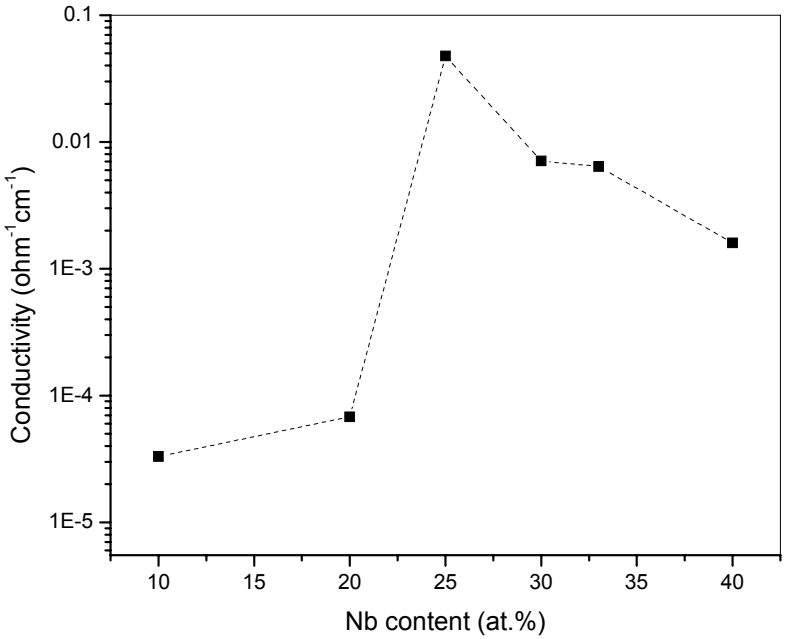
Task 5. Stability Analysis of the Loaded Catalysts with ADT

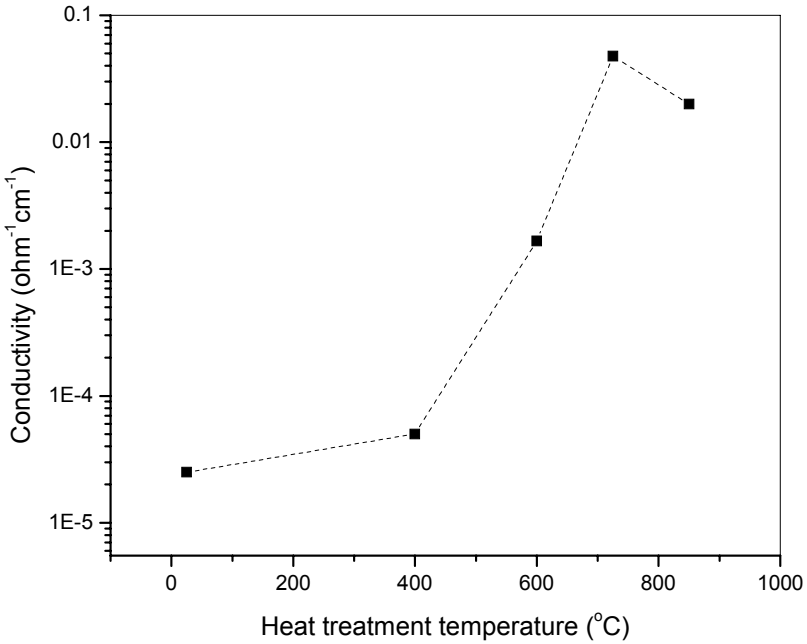
(ADT = accelerated durability test)

Task 6. Industrial Interaction and Presentations

Project 1: Technical Accomplishments/Progress/Results

Conductivity of Nb-Doped TiO_2 Support

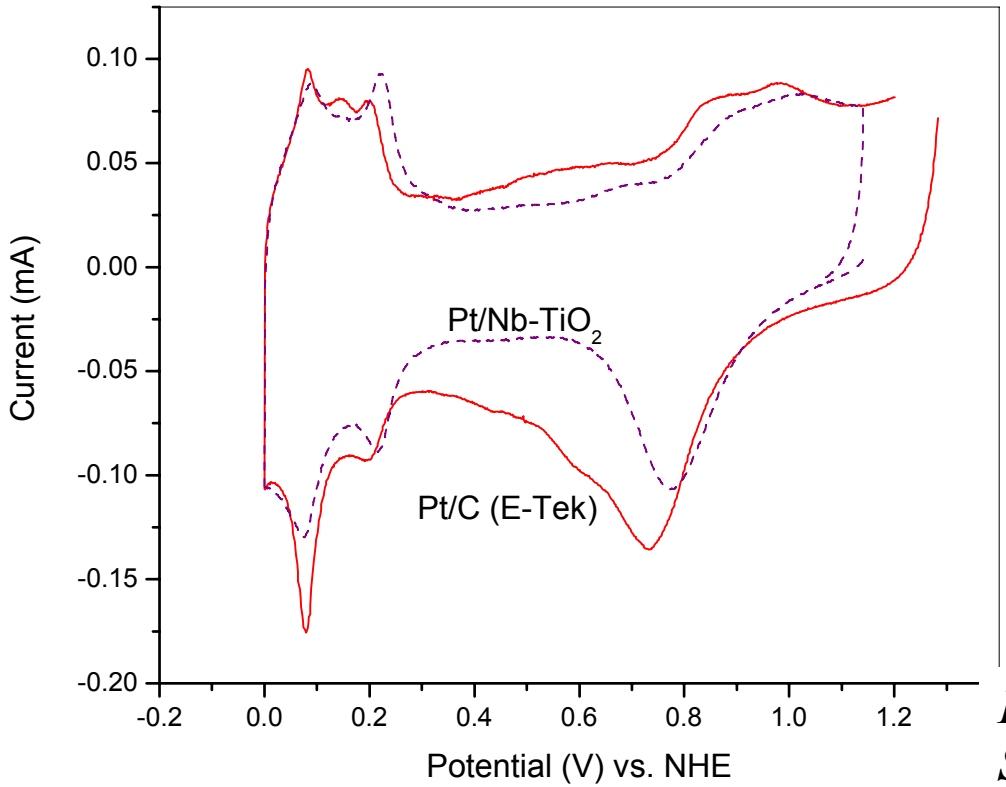




- ***The electrical conductivity shows a maximum for 25 at% Nb and 700 ^{o}C.***
- ***Increase in conductivity is due to the presence of Ti^{3+} and Nb^{2+}.***

Project 1: Technical Accomplishments/Progress/Results

Pt Catalyst Supported on Nb-Doped TiO_2

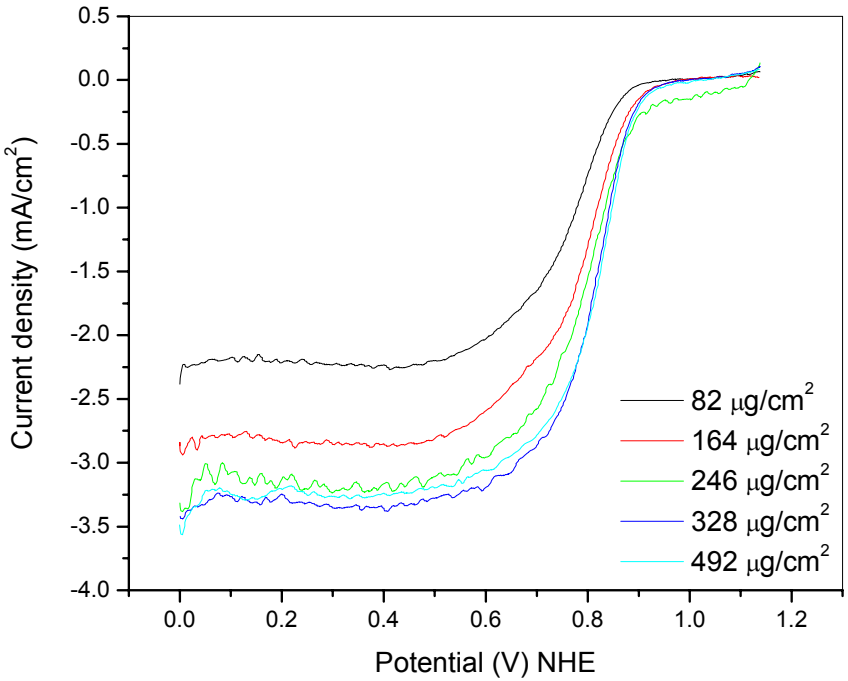


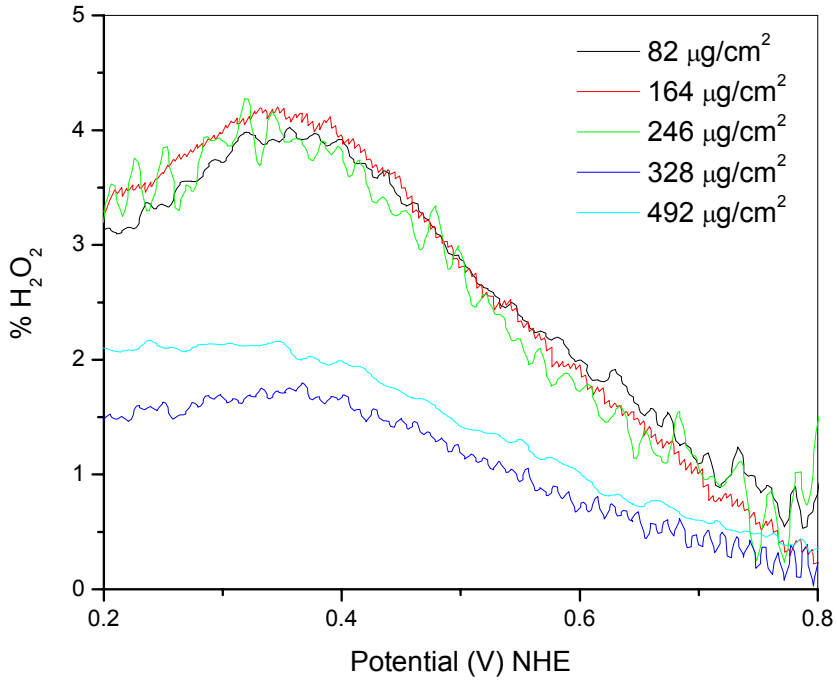
The electrochemical active surface area (ECSA) of Pt/Nb-TiO_2 is comparable to that of Pt/C.

Electrolyte: 0.5 M H_2SO_4
Sweep rate: 5 mV/s
Catalyst loading: 246 µg/cm² (Pt/Nb-TiO_2)
120 µg/cm² (Pt/C)

Project 1: Technical Accomplishments/Progress/Results

$Pt/Nb\text{-}TiO_2$: LSV - Effect of Loading

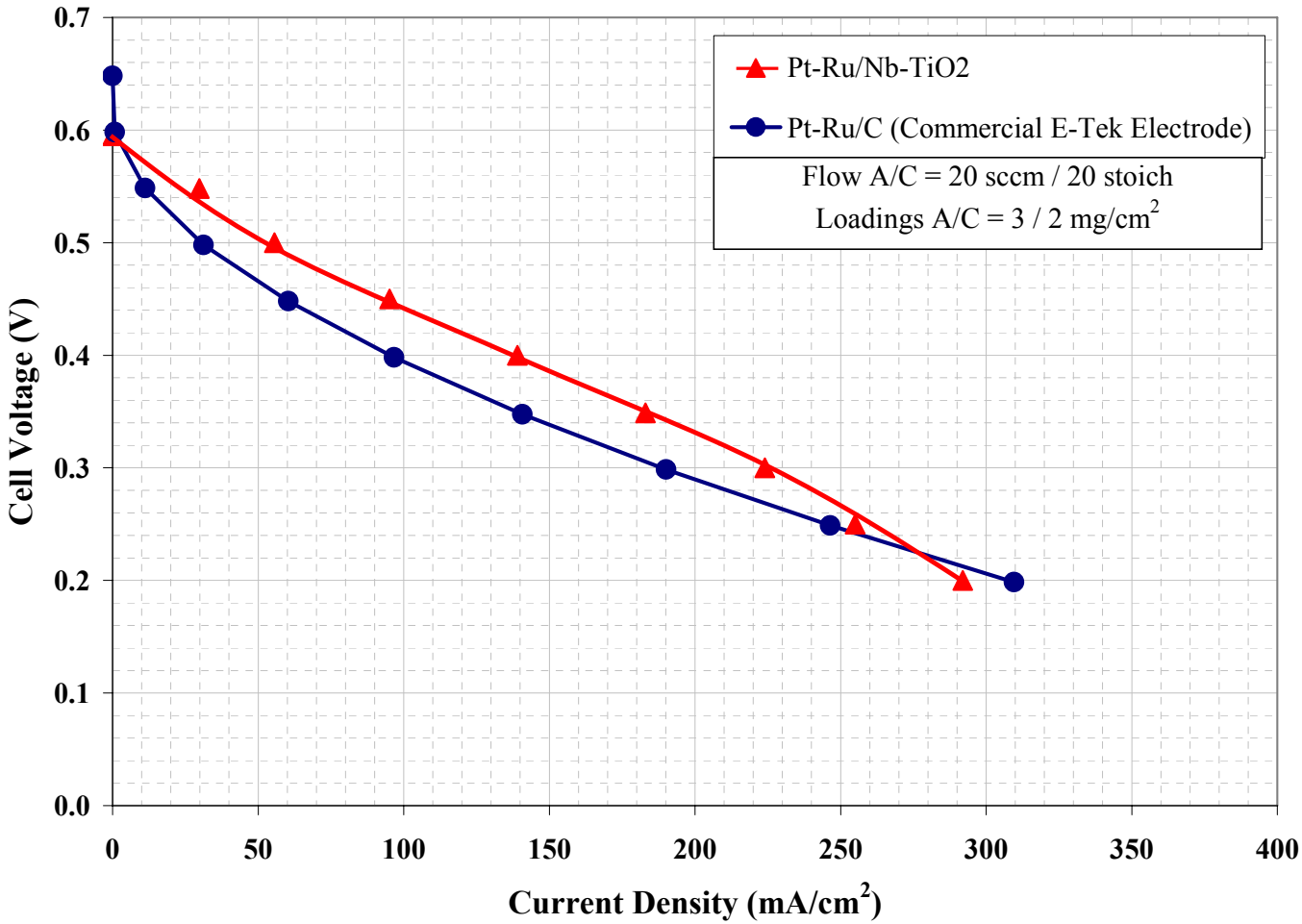




- ***The catalytic activity of $Pt/Nb\text{-}TiO_2$ is comparable to that of Pt/C.***
- ***The catalyst produces less than 4% H_2O_2.***

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

Project 1: Technical Accomplishments/Progress/Results
Opportunities for DMFC



B. L. García, R. Fuentes, and J. W. Weidner, Electrochem. and Solid-State Letters, 10 (7) B108.

Summary 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**

Approach: Project 2: Hydrogen Quality

Task 1. Group Contaminants by Probable Mechanism
(Adsorption/Desorption, Reactive, Transport Through MEA)

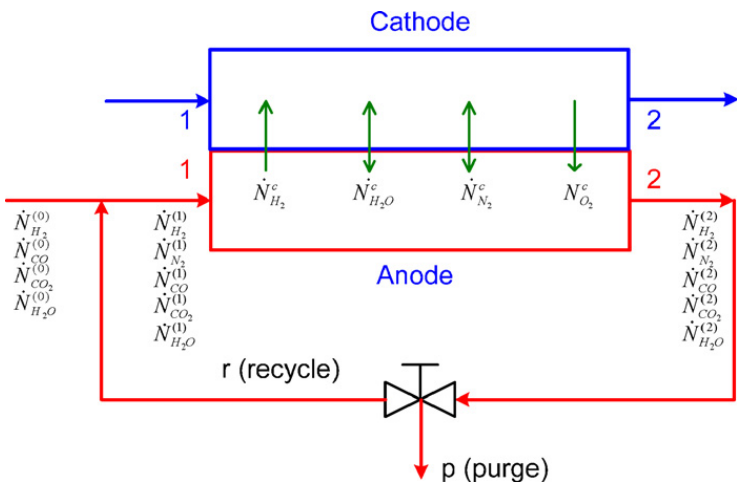
Task 2. Study Effect of Temperature Distributions
- **Subtask 1.1 Predict temperatures in common cells**
- **Subtask 1.2 Design new laboratory cells**
- **Subtask 1.3 Measure temperature distributions**

Task 3. Design & Perform Experiments by Mechanism
- **Sub Task 3.1 Determine independent adsorption isotherms and rate constants (for CO, a marker compound, as agreed by H2 quality team)**
- **Sub Task 3.2 Extend the methodology to other species**

Task 4. Predict Long-term Effects
Task 5. Exploratory Study with ORNL: Intra-PEMFC Sensors (see Additional Slides)
Task 6. Interact with H2 Quality Team
Task 7. Presentations of Results

Approach: Project 2: Hydrogen Quality- Task 3

- Provide data on Gore 57 Series MEAs
  - Suitable for comparison with other MEAs & loadings
  - Over an operating range that allows parameter estimation
  - Complementary to other groups & modeling effort
  - Provide fundamental parameters for ANL's recirculation model
- Contribute data & techniques to the H2 Quality Team Model
  - ANL model (R. K. Ahluwalia, X. Wang, *J. Power Sources*, 162 (2006) 502, 171 (2007) 63, 180 (2008) 122)



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Approach: Project 2: Hydrogen Quality- Task 3

In-situ Experimental Data for CO Poisoning Characterization

Obtain Polarization & Anode Overpotential data:

- 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 – in progress
- O_2 crossover (internal air bleed) – in progress

- Determine isotherms and rate constants from these data

Fig. 2.1 Hysteresis profiles for CO at 10, 25 and 50 ppm with 20 minutes of holding time.

(Tcell = 80 C, back pressure = 0/0 psig)

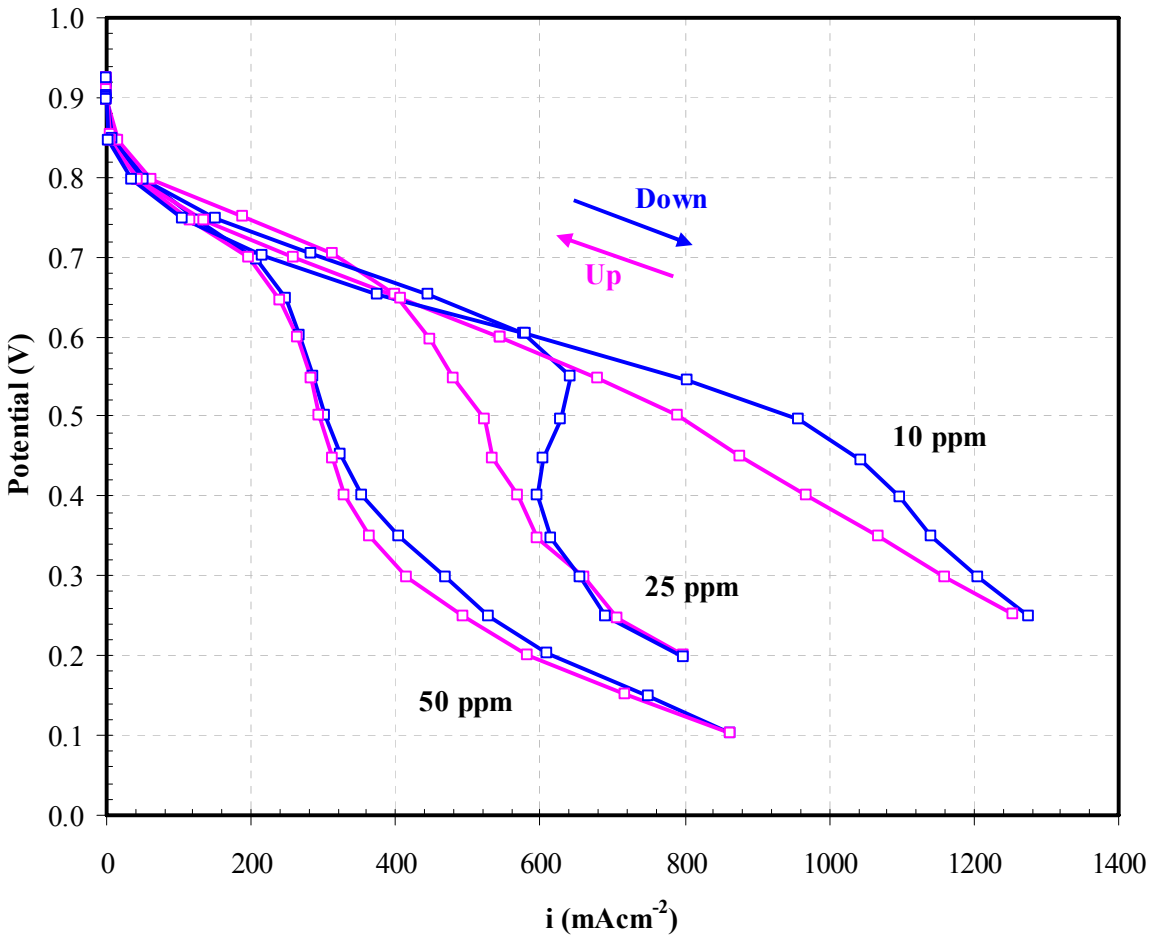


Figure 2.2. Current density versus time for 25 ppm CO at potential = 0.30, 0.55 and 0.70, scanning up-down until reaching steady state.

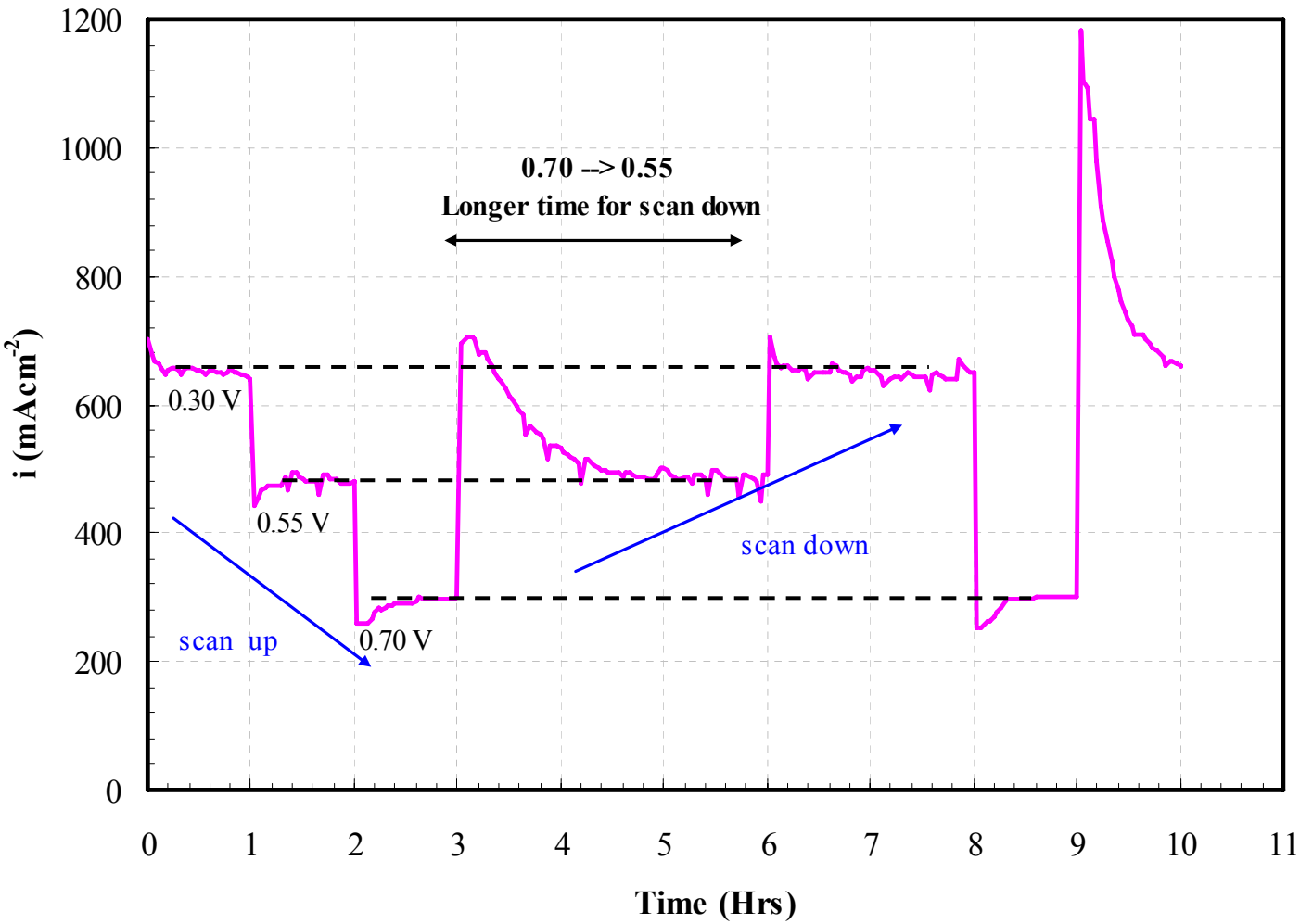


Fig. 2.3. Polarization with CO for Tcell = 80° C & 0 psig.

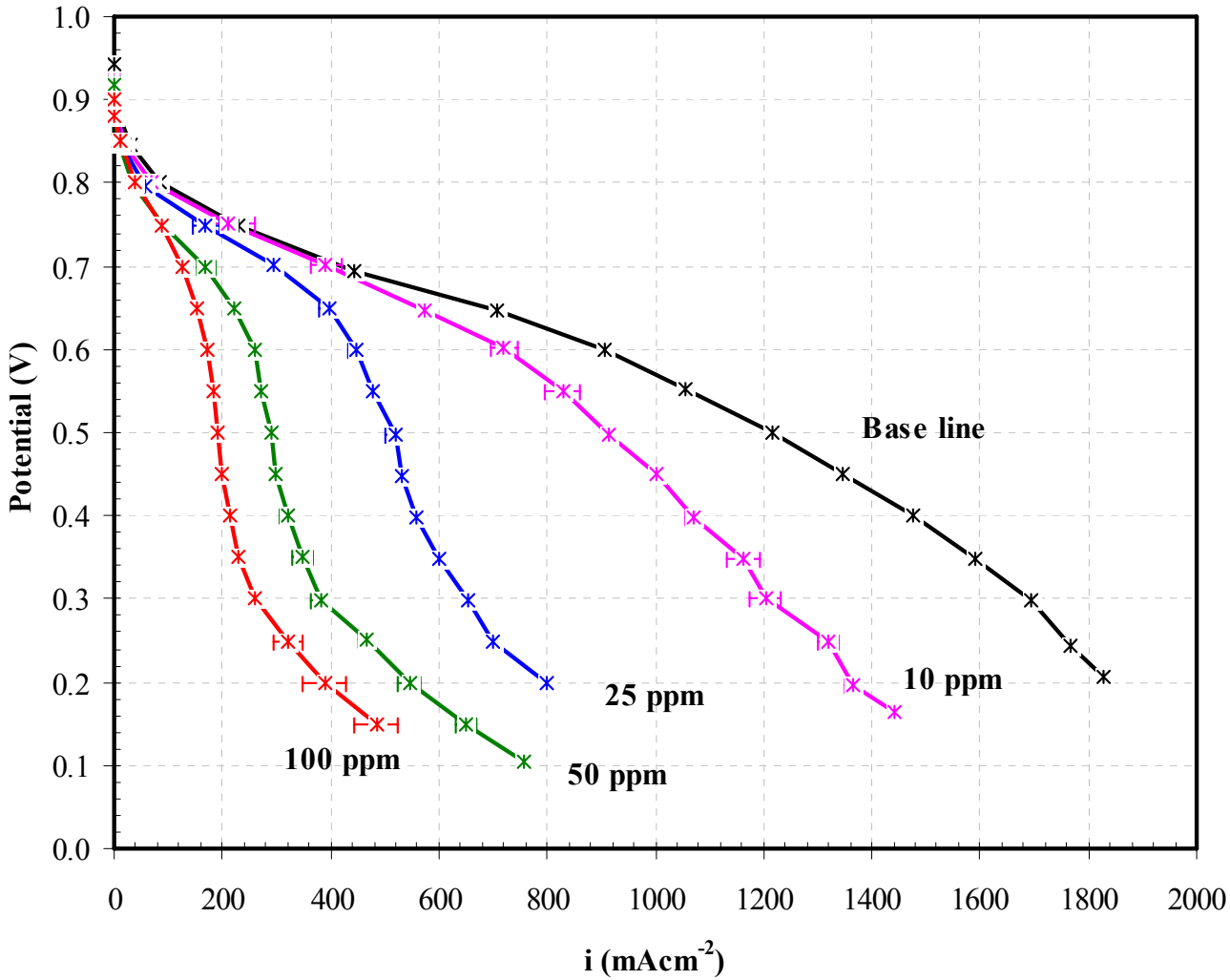


Fig. 2.4. Anode overpotential for CO at 80° C & 0 psig.

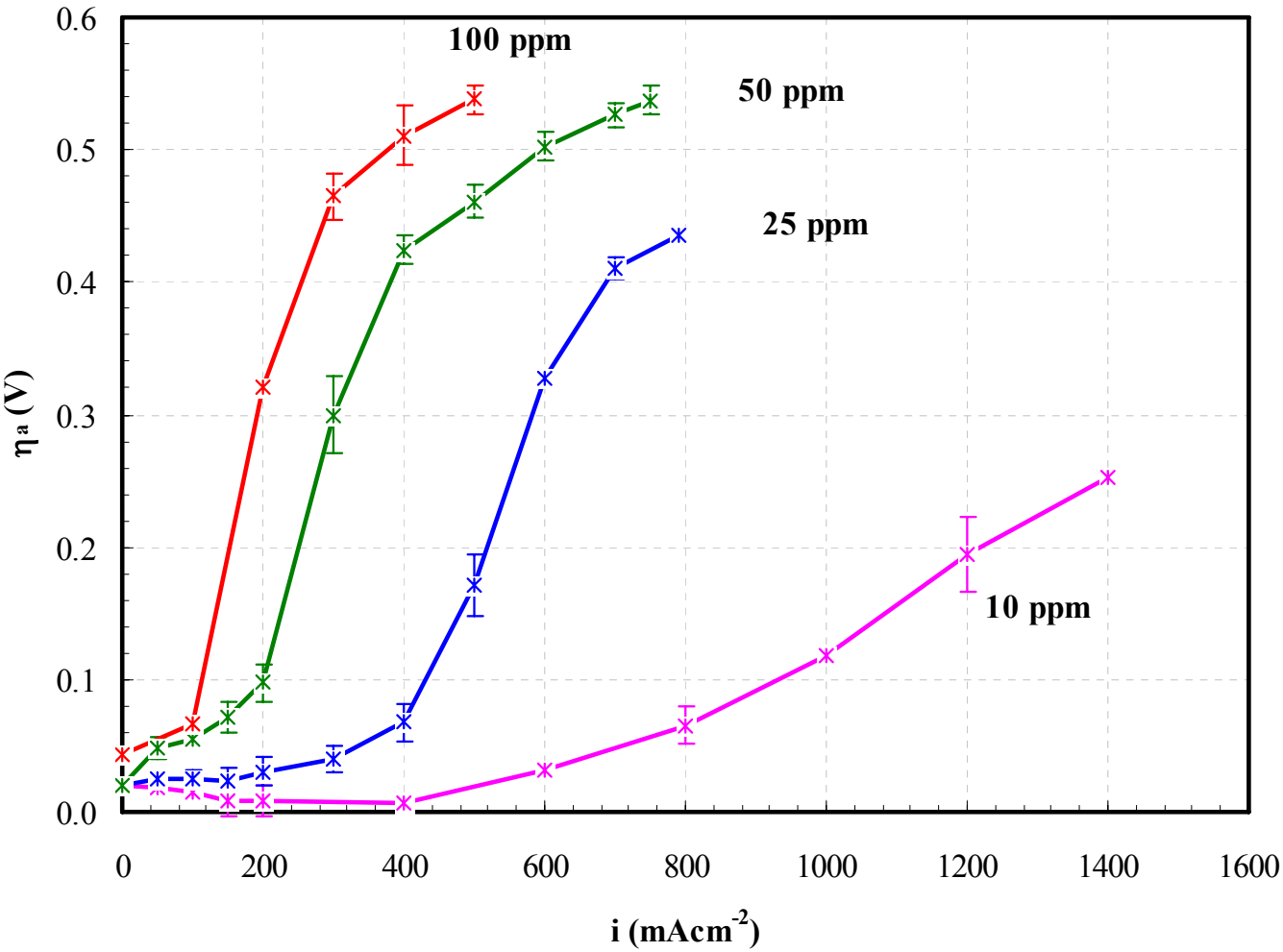


Fig. 2.5. Temperature dependence of anode overpotential at 25 psig.

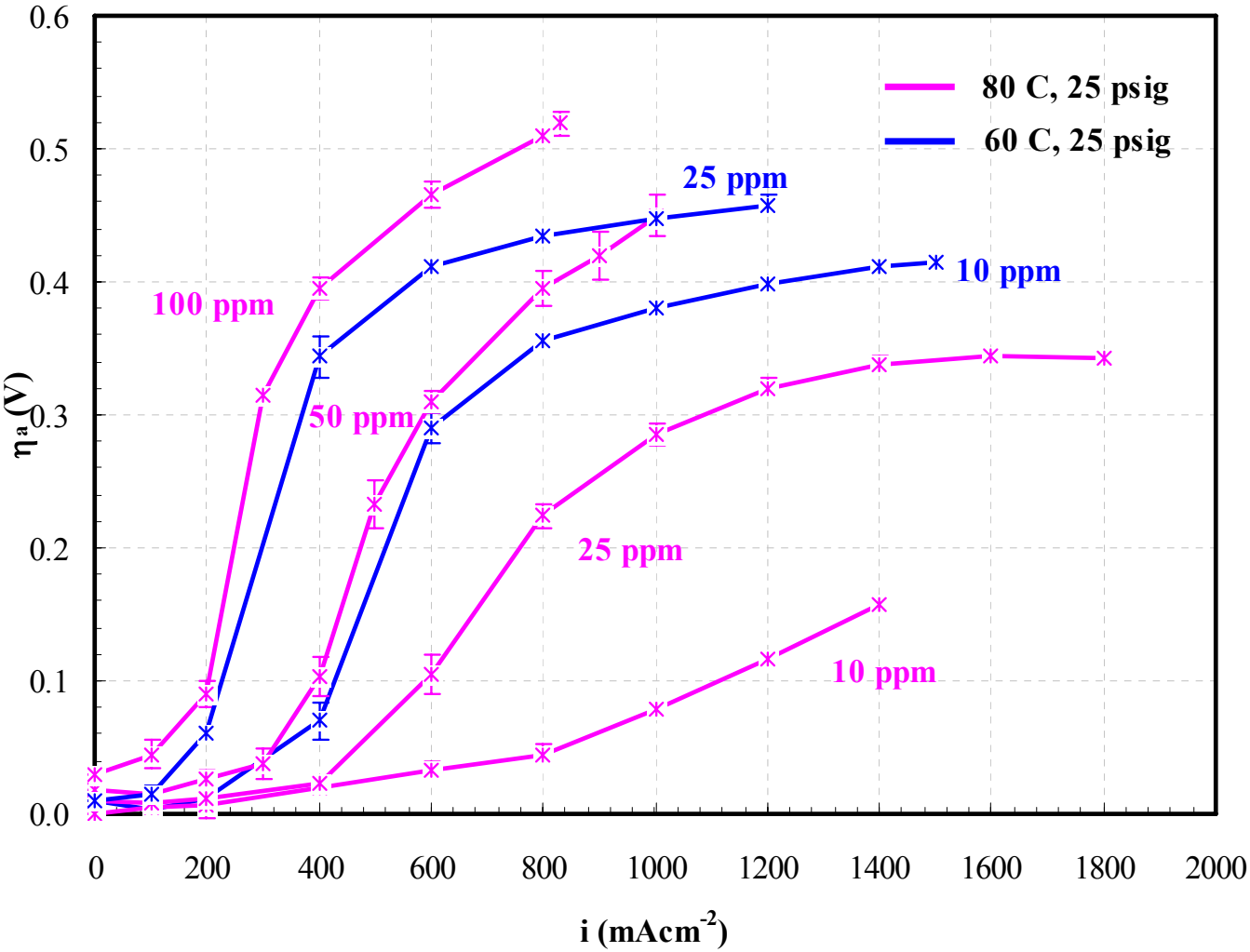
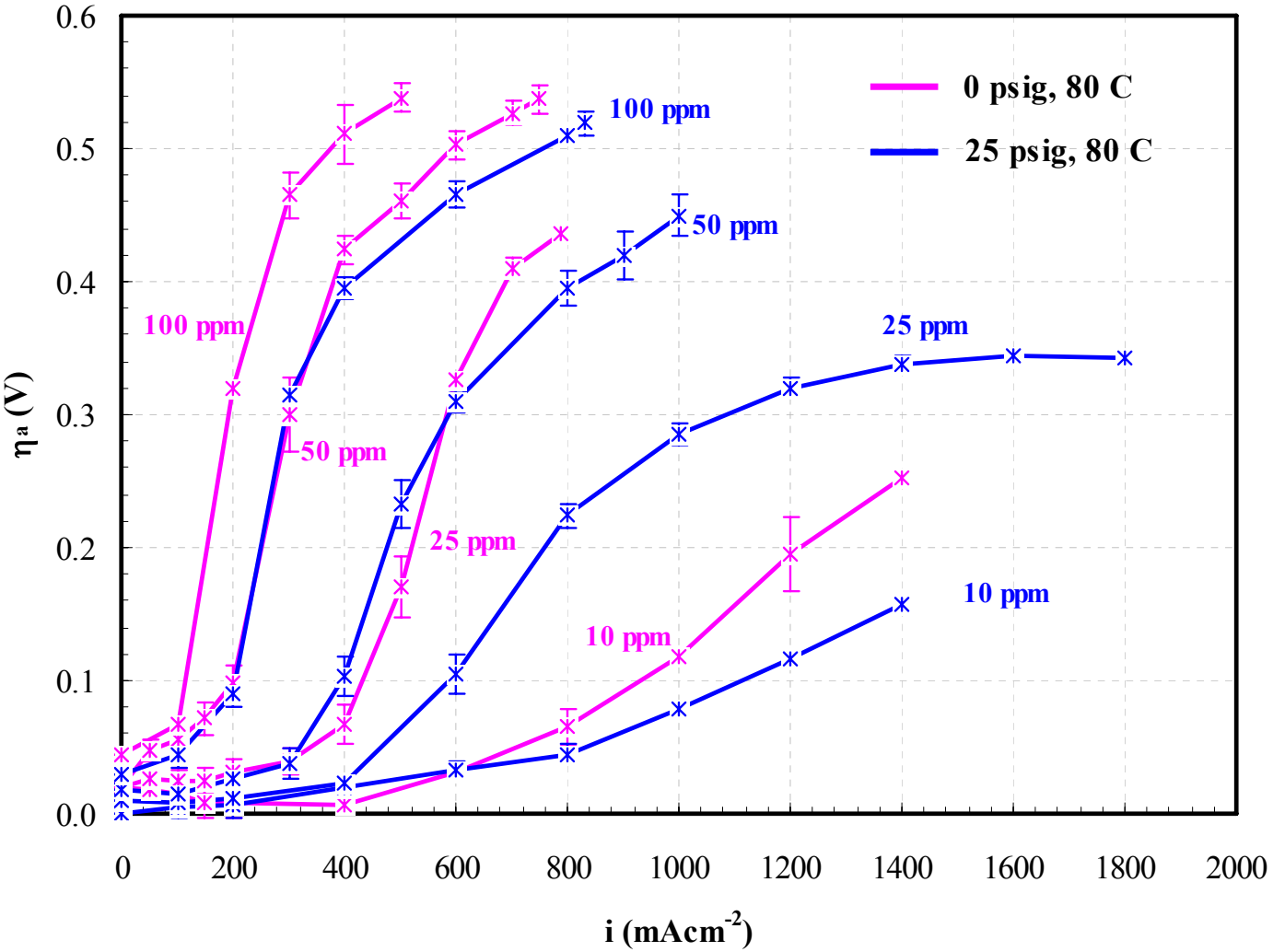


Fig. 2.6. Pressure dependence of anode overpotential at 80 C



Summary Project 2: Technical Accomplishments

- Provided data on Gore 57 Series MEAs
  - 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 - in progress
  - Consistent set of parameters for this MEA – in progress

- Future Work
  - Develop techniques to understand the effect of loading
  - Extend methodology to other contaminants (NH_3 & H_2S)
  - Develop consistent methodology for obtaining parameters
  - Continue to interact with H2 Quality team

Approach: Project 3- Gaskets for PEMFCs

Task 1. Selection of Commercially Available Seal Materials. (95 % complete)

Task 2. Aging of Seal Materials

In simulated and accelerated FC environment

With and without stress/deformation

Task 3. Characterization of Chemical Stability

Perform both constant stress & constant displacement tests

Assess the effect of applied stress/deformation on the rate of degradation

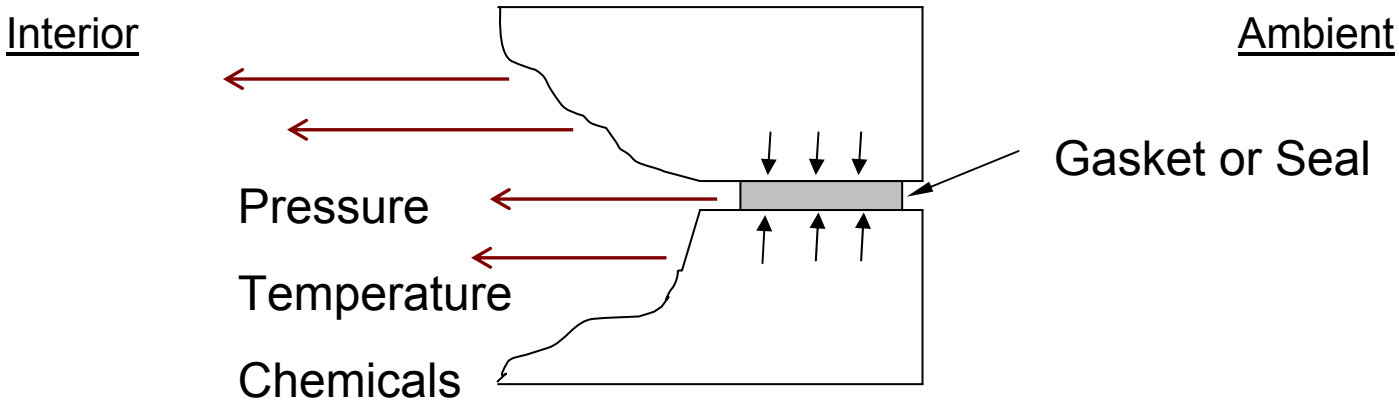
Measure chemical/thermal stability will be assessed by various

Task 4. Characterization of Mechanical Stability

Task 5. Development of Accelerated Life Testing Procedures

Task 6. Industrial Interaction and Presentations

Approach: 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.

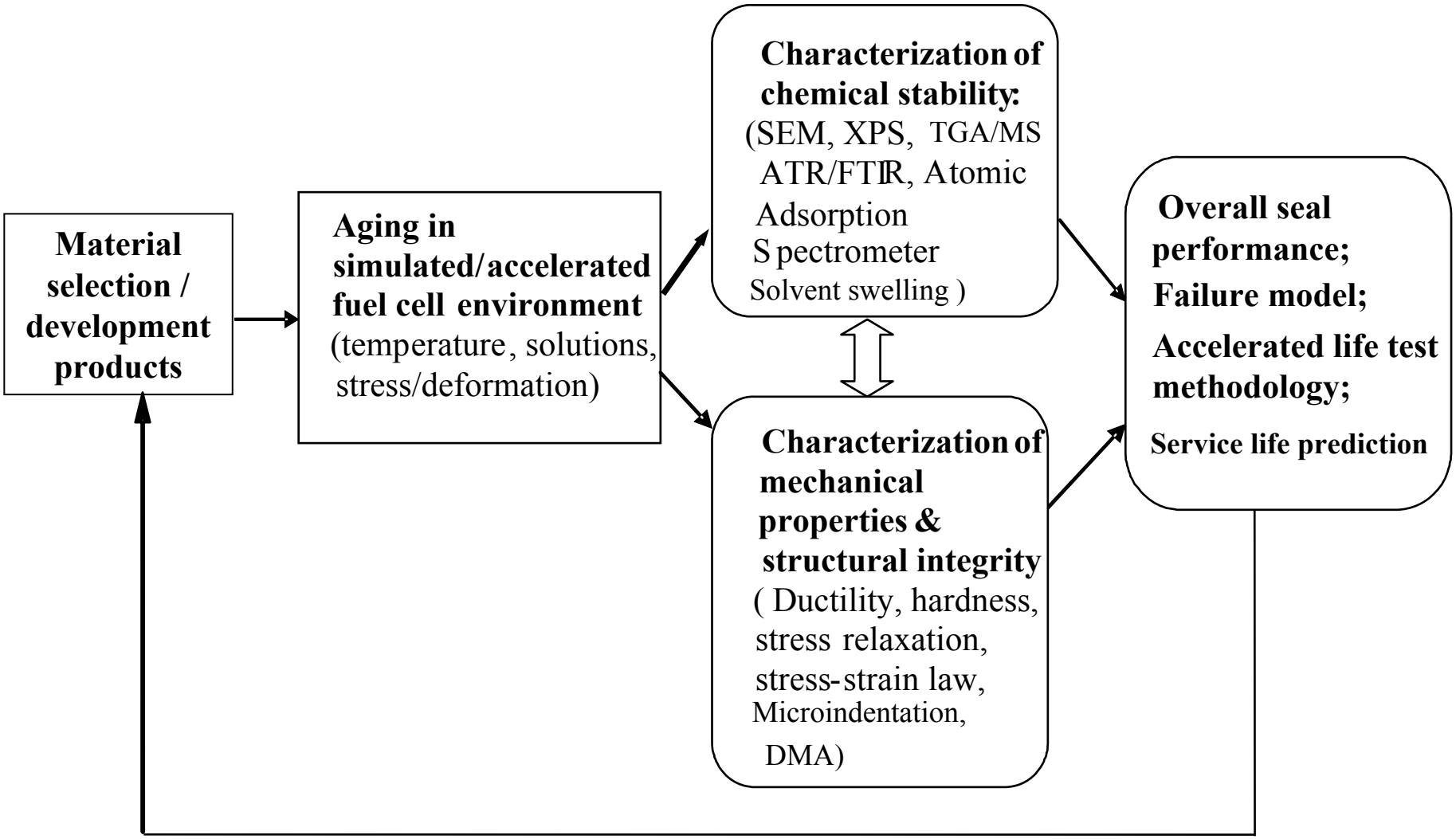
Loss of functionality : by cracking and /or stress relaxation

Cracking : due to corrosion under compression (Chemical stability)

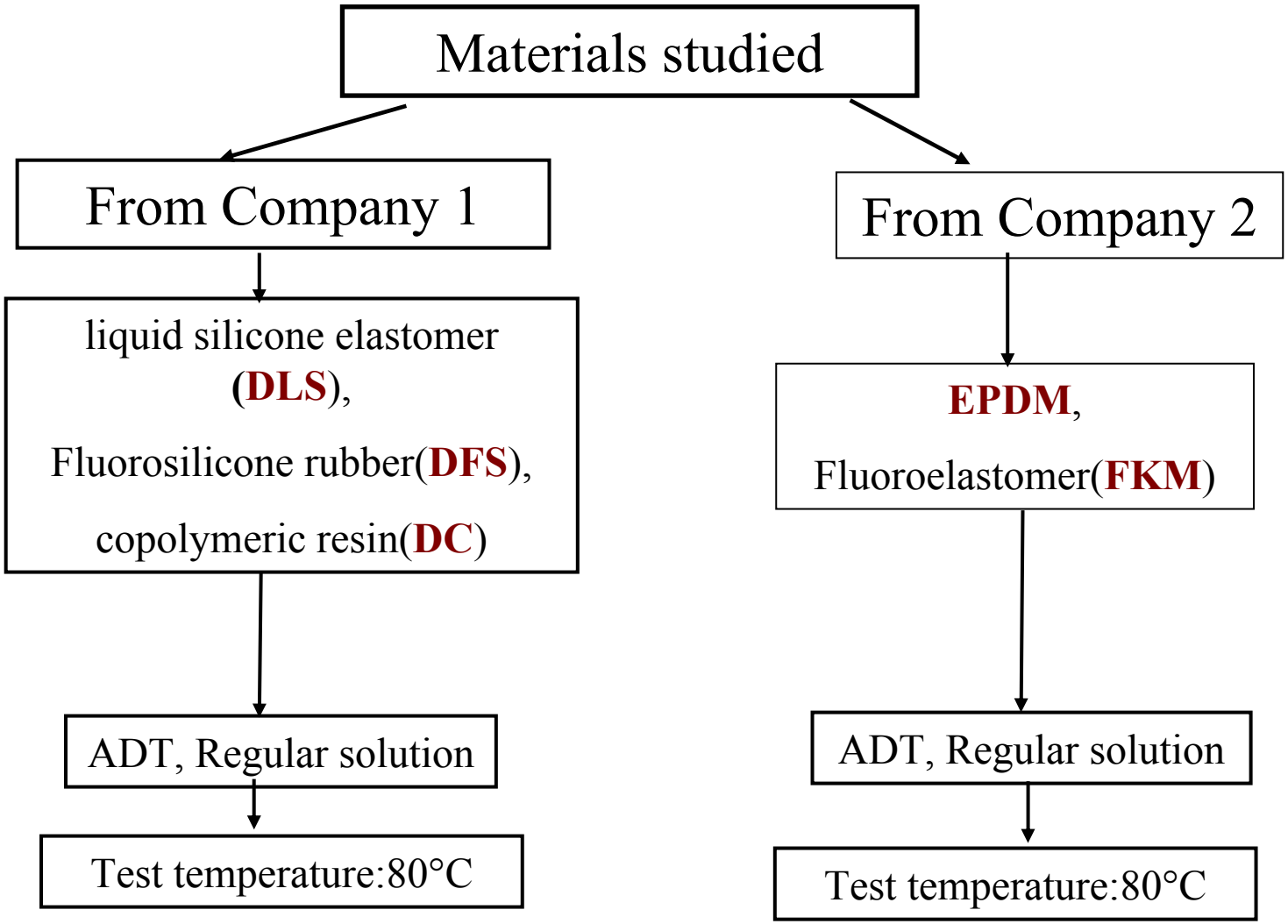
Stress Relaxation : material degradation… loss its sealing ability (mechanical stability)

Leachants: detrimental sometimes (chemical stability)

Approach: Project #3: Flow Chart of Studies



Project 3: Technical Accomplishments/Progress/Results

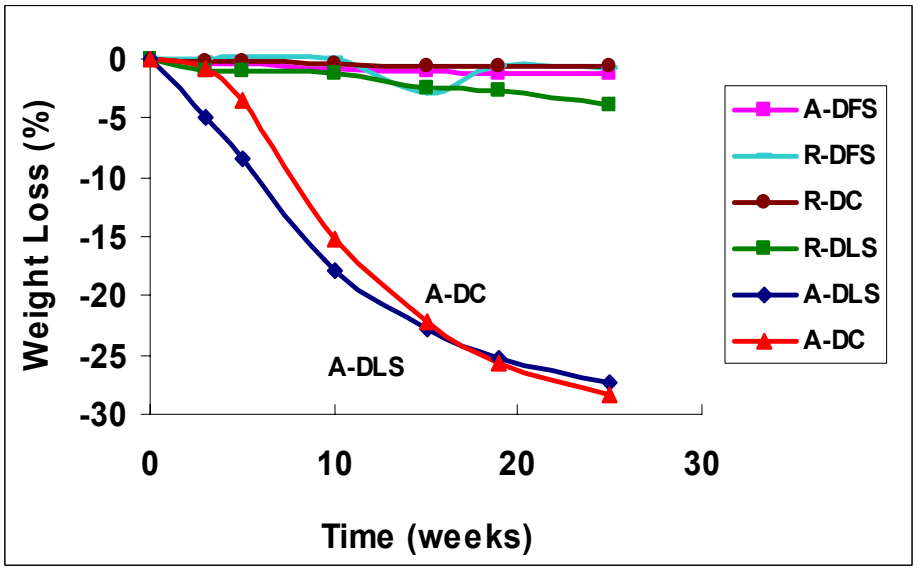


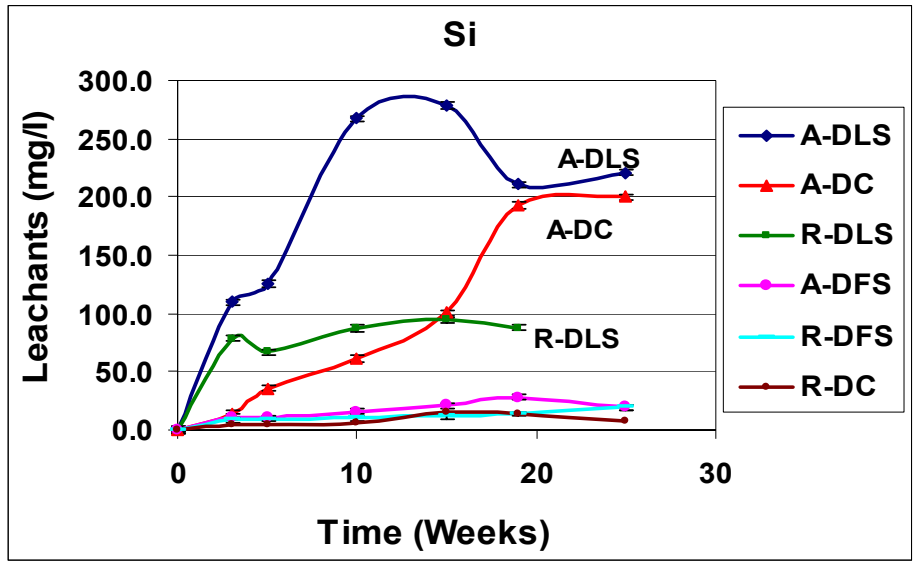
Labels for samples from Company # 1

- In ADT solution
  (accelerated durability test)
  - A-DLS
  - A-DFS
  - A-DC
- In regular solution
  - R-DLS
  - R-DFS
  - R-DC

Project 3: Technical Accomplishments/Progress/Results

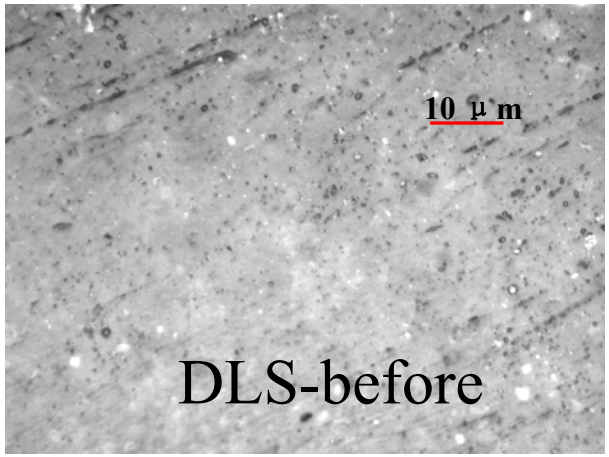
Weight loss and chemical leaching

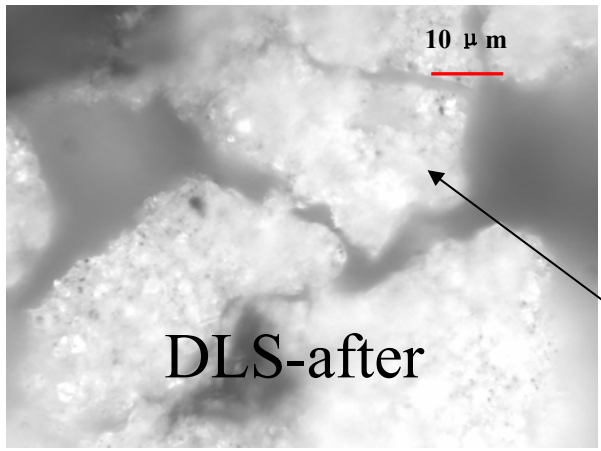




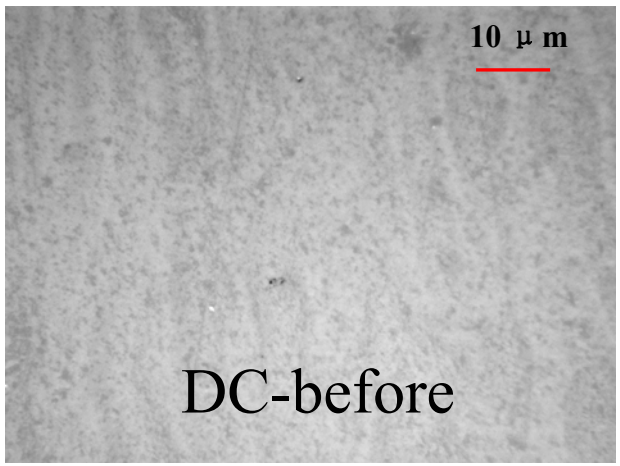
- A-DLS, A-DC and R-DLS→ more weight Loss and more Si leaching →Lost Si is the cause of weight loss
- No detectable Mg in all silicone elastomer
- The amount of Ca is in the range of 0-5mg/l
- The amount of Si is in the range of 5-300 mg/l

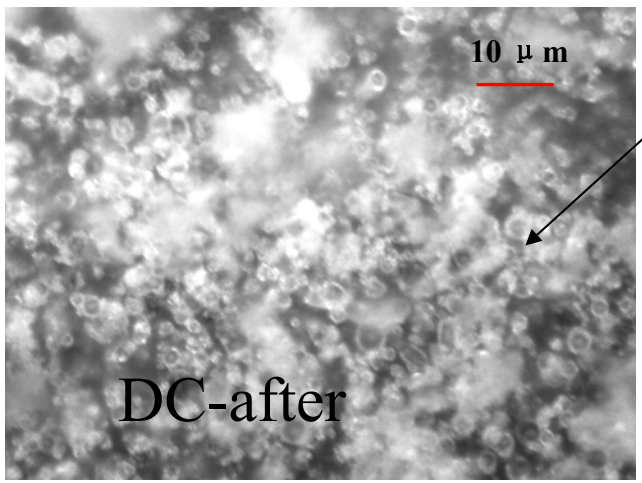
Optical image of DLS and DC before and after exposure to ADT solution for 10 weeks



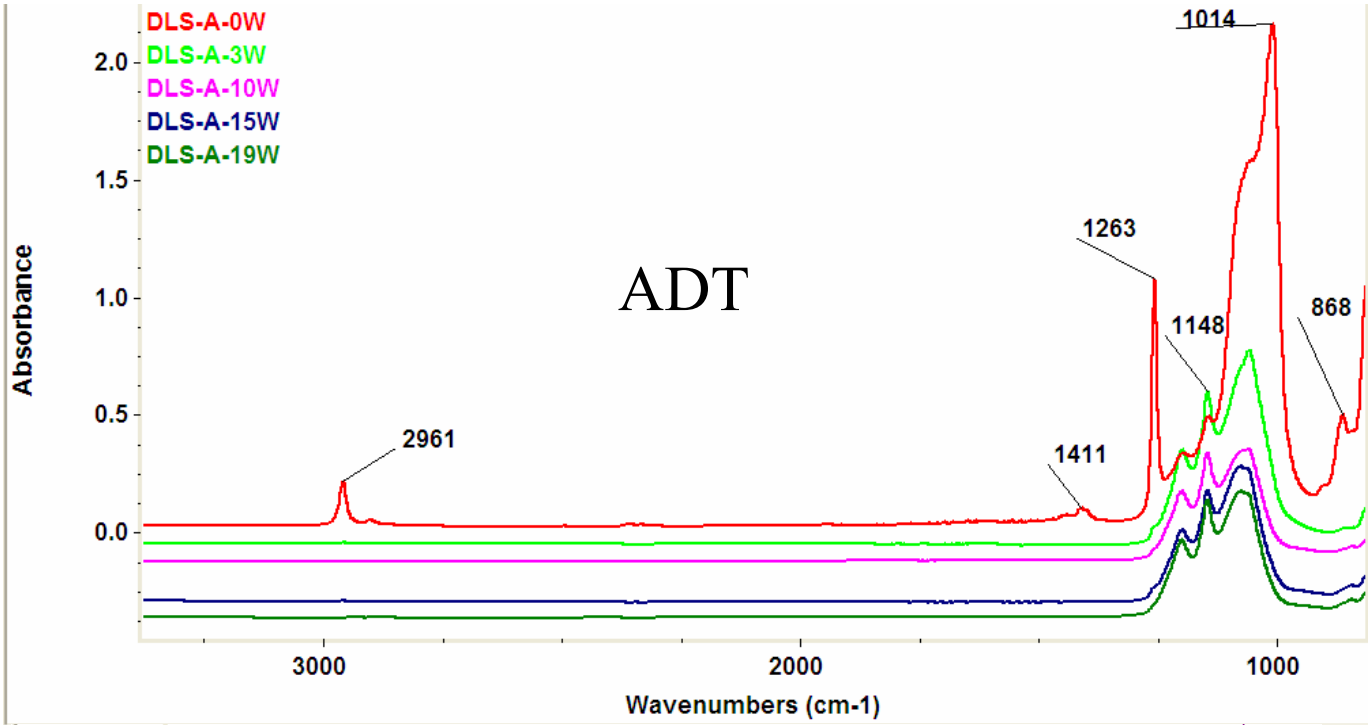


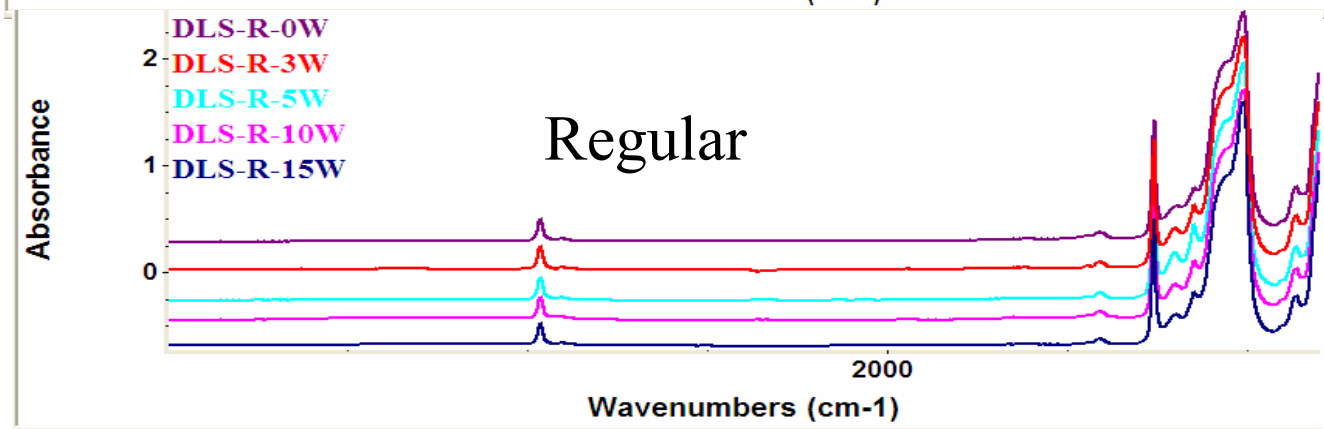
Crystal-like accumulation





Project # 3: ATR-FTIR for DLS





Chemical changes in backbone and crosslinked domain after 3week exposure

No significant Chemical Changes after 15 week exposure

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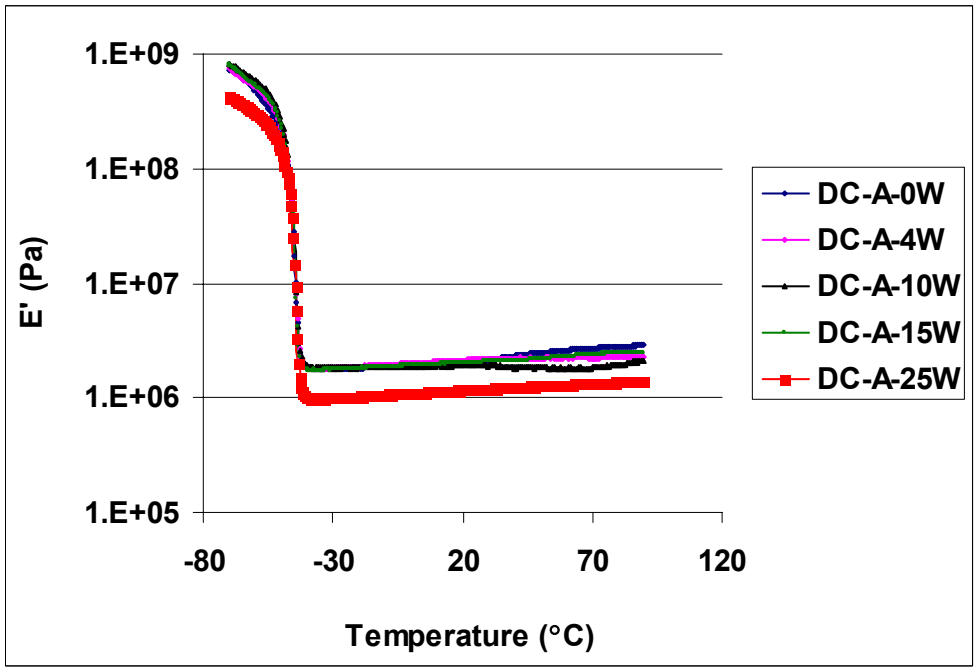
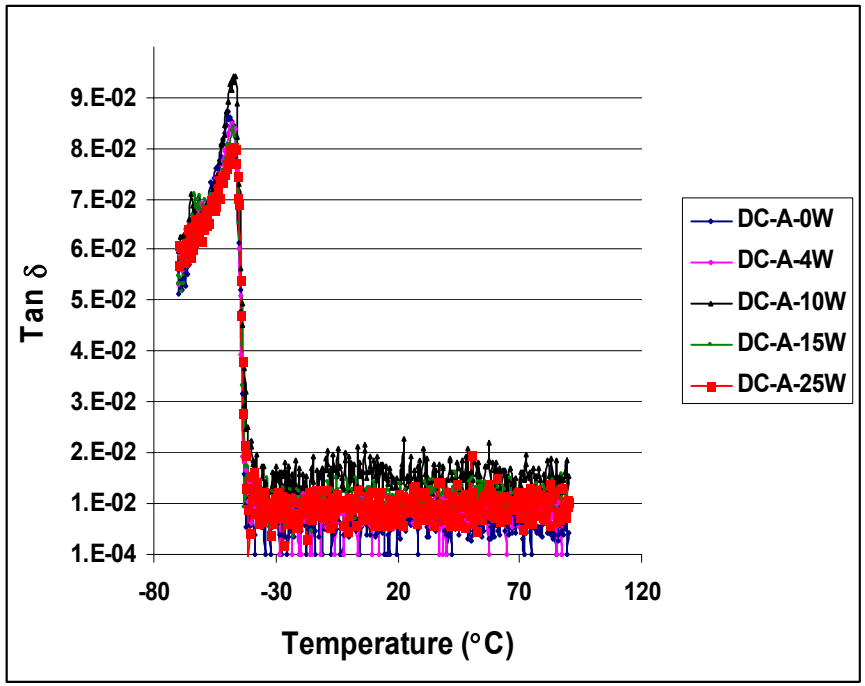
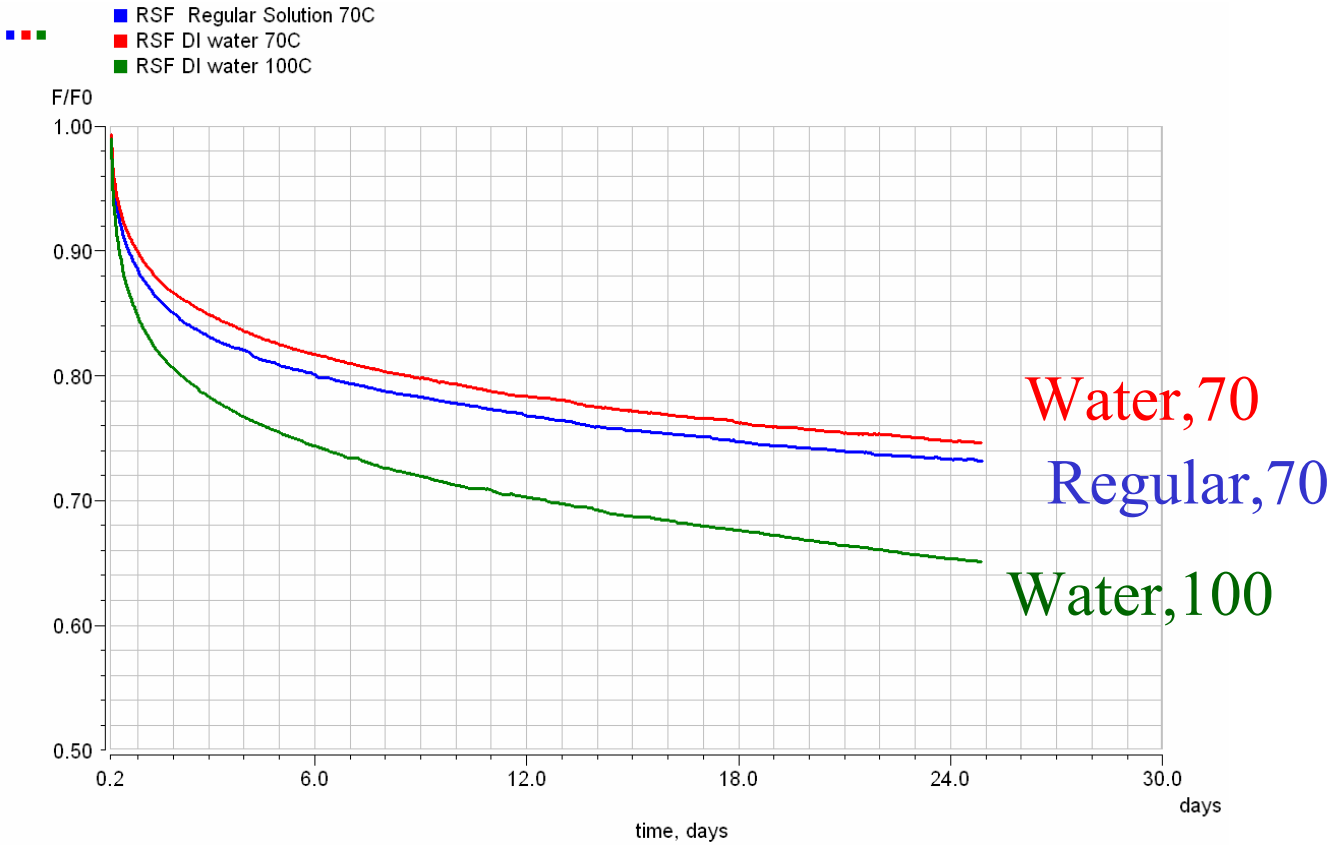
Elastic modulus E' and Tan δ for DC exposed to ADT solution (by DMA)





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 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. **Developing** life prediction methodologies.
7. **Publications** in Journal and Conferences and discussions with members in the Center for Fuel Cells.

Approach: Project 4 - Acid Loss in PBI-type High Temp. Membranes (interaction with Plug Power)

Task 1. Exercise Existing Computer Code

(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 2. Additional Experiments and Model Modification

(a) obtain data for water content as f (T, Dew point)

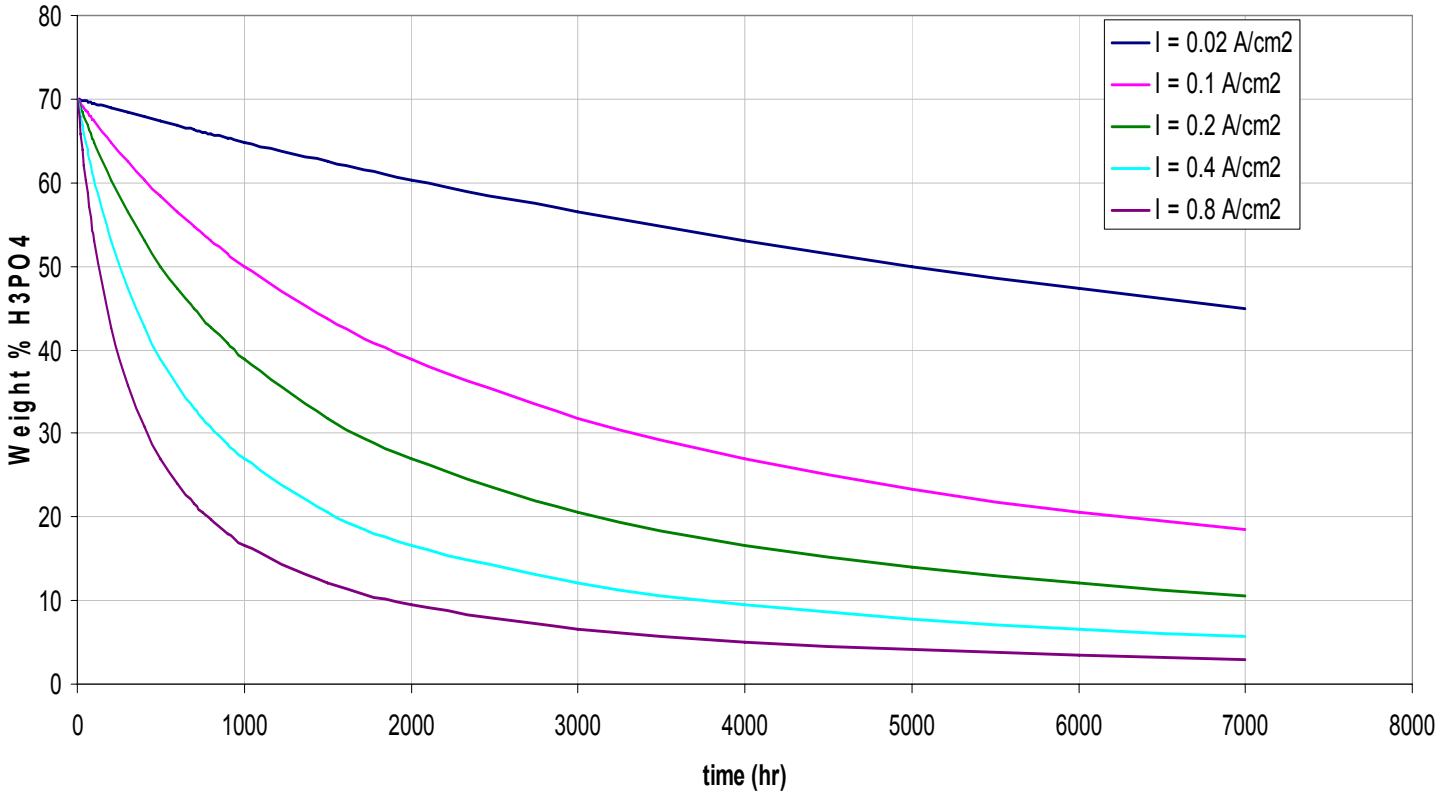
(b) obtain data for water & acid balance as f (T) under load

Task 3. Presentations and Publication

Project 4: Technical Accomplishments/Progress/Results:

Change of wt % depends on water/membrane equilibrium

(Predictions below assume all water remains in MEA-unlikely but how much?)



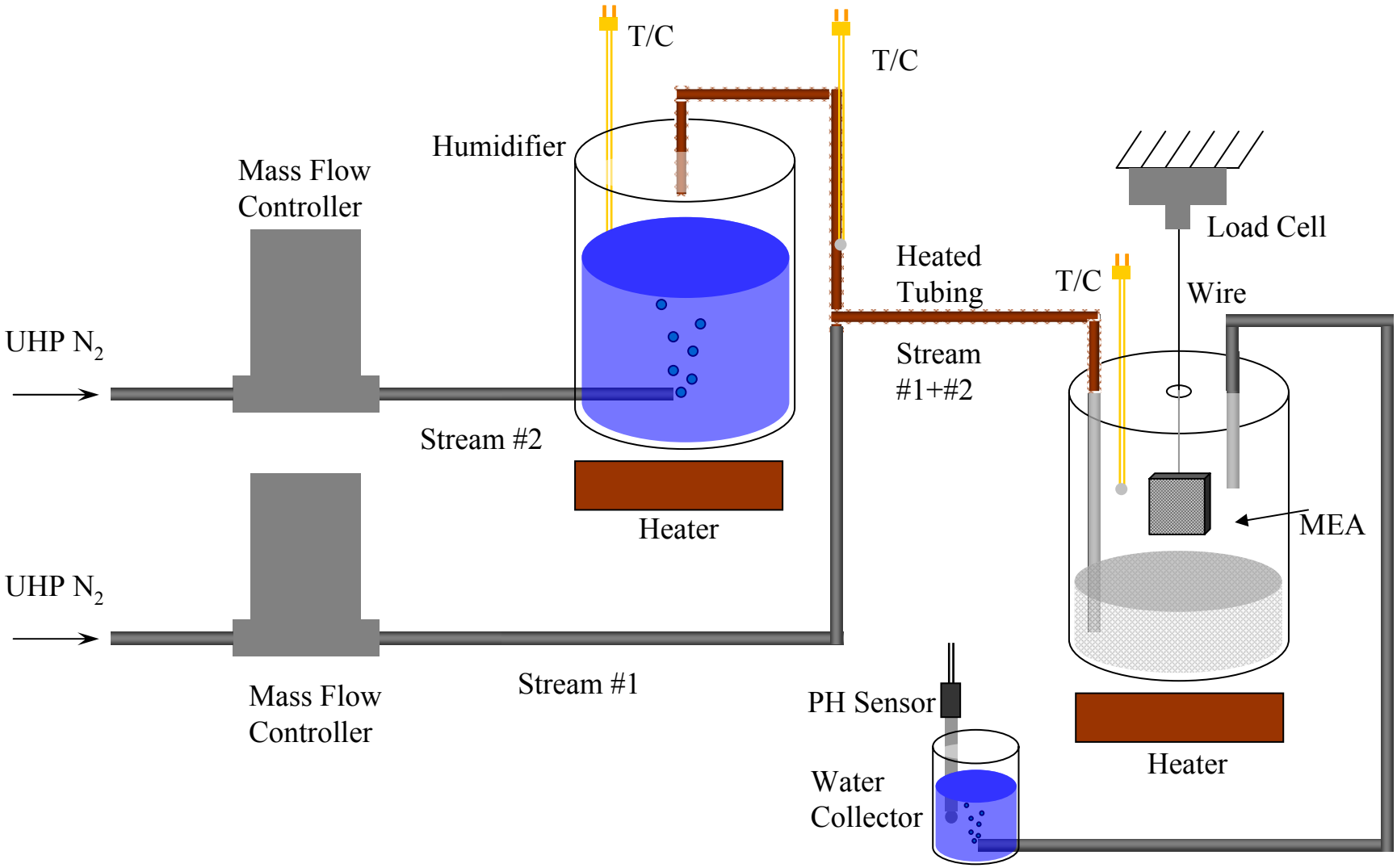
Project 4: Technical Accomplishments/Progress/Results

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

Experimental Conditions

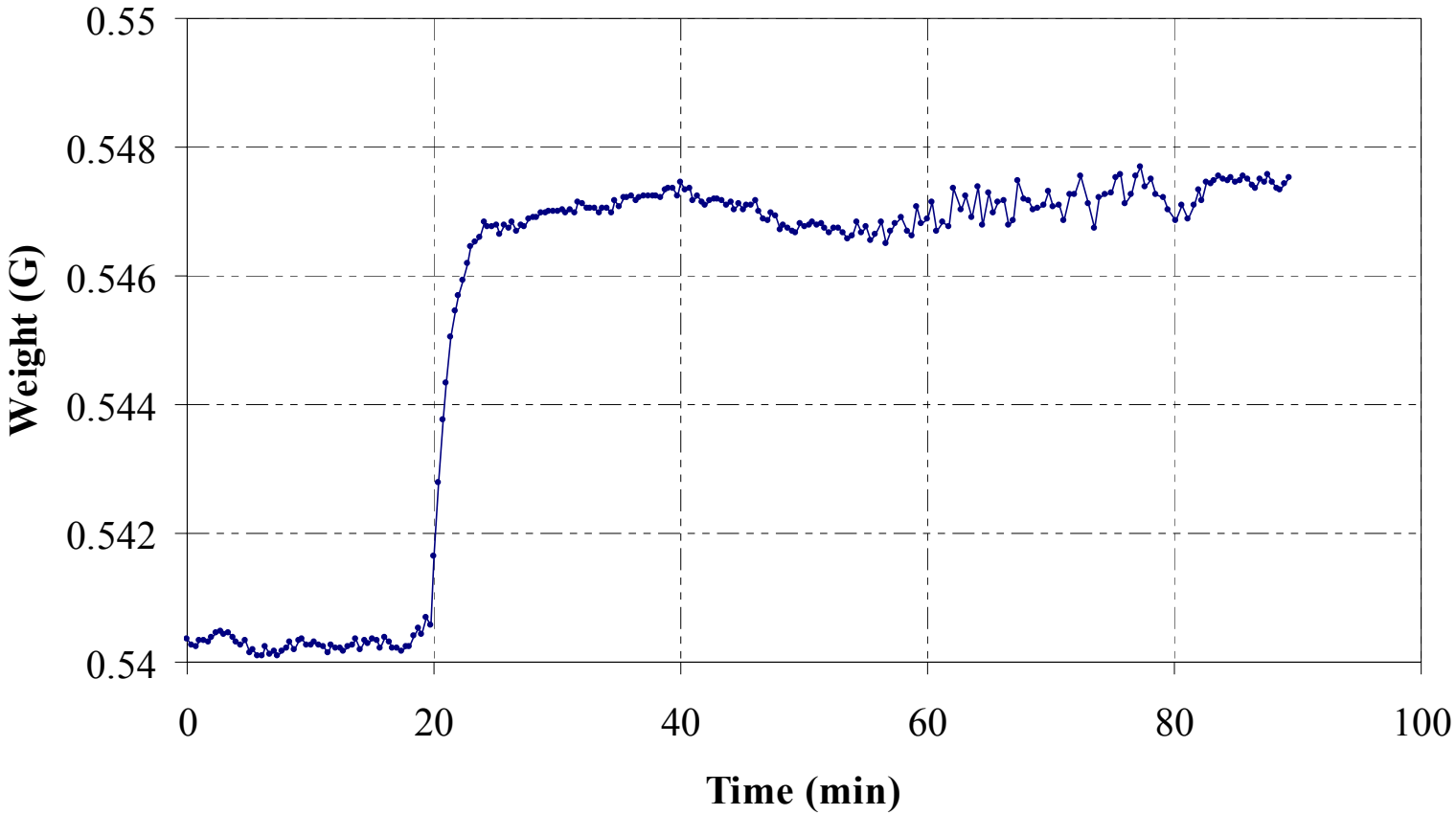
Temperatures:	160 ºC to 90 ºC
Sample size (nominal):	1 inch² (6.4516 cm²)
Total nitrogen flow:	500 sccm,
Water partial pressure scanning rate:	0.01 to 0.002 (kPa/101kPa/min)

Figure 4.2. Schematic experimental setup to measure water euilibrium.



Project 4: Technical Accomplishments/Progress/Results

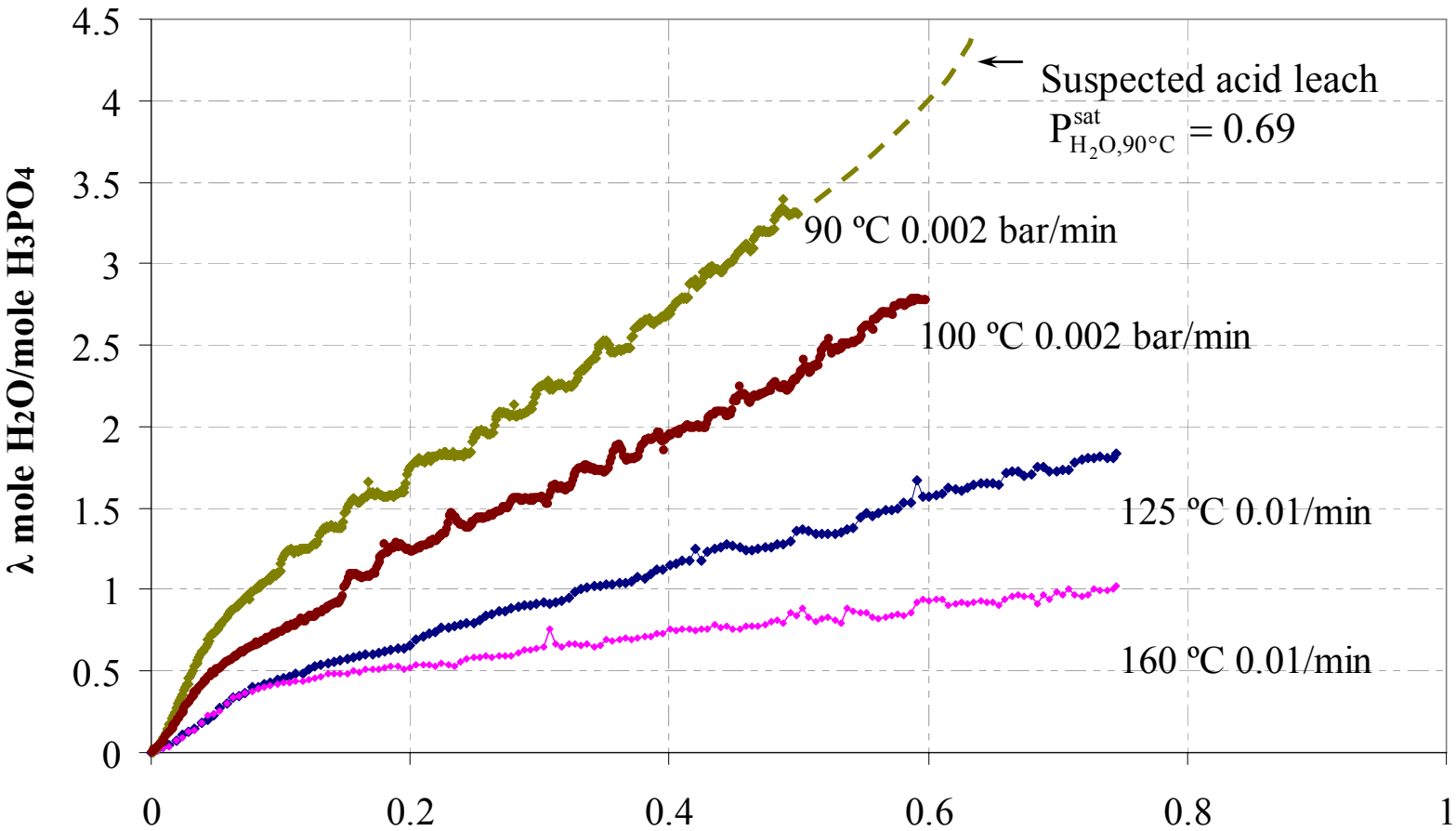
Response of water absorption into the MEA with step change in inlet humidity.



Container Temperature: 160 °C; Switching time: @20th minute
Initial humidity: 0.020,17.5 °C dew point
Final humidity: 0.156,55 °C dew point

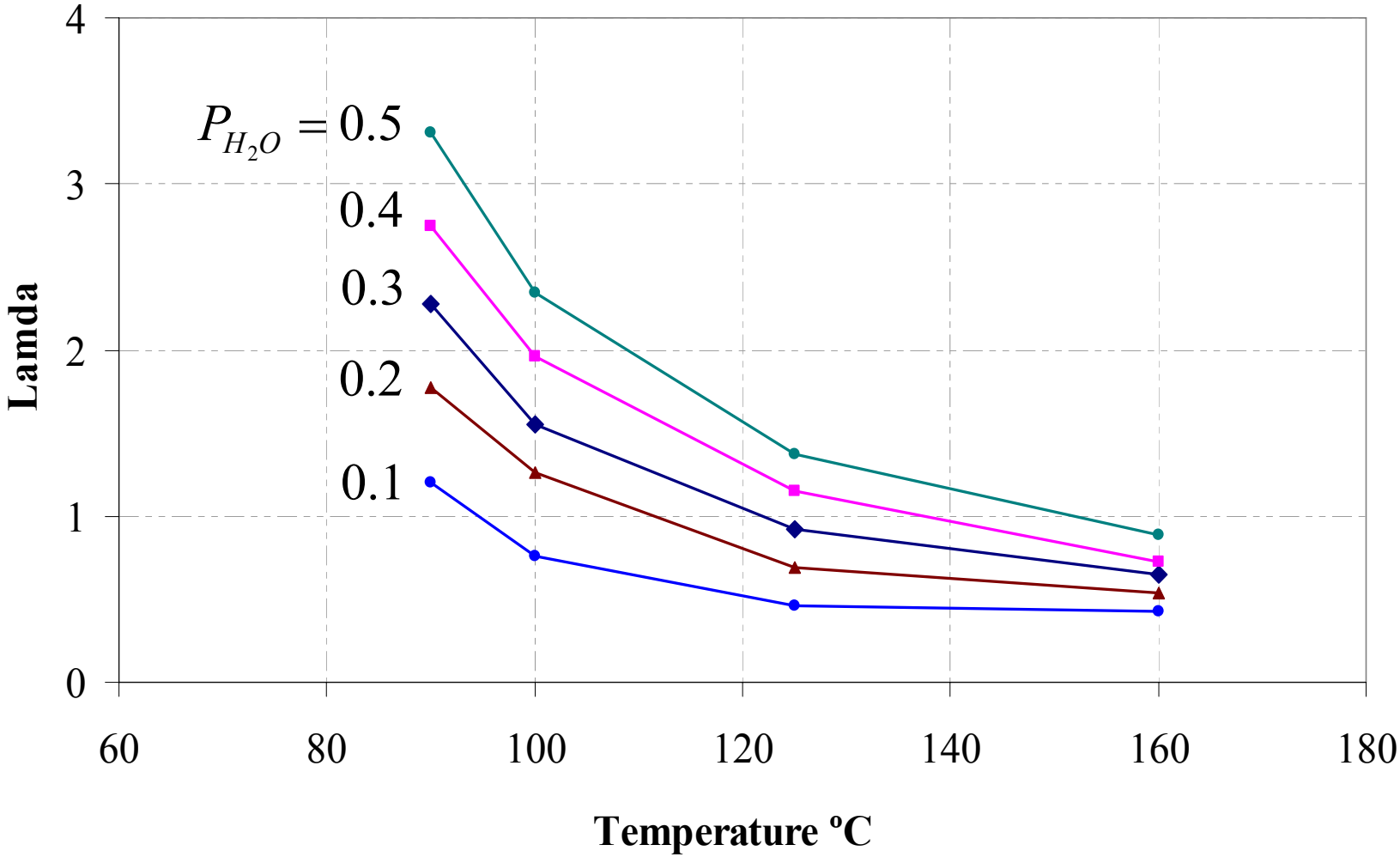
Project 4: Technical Accomplishments/Progress/Results

Figure 4.4A. Change of lambda (mol fraction of water/phosphoric acid) with dimensionless water vapor pressure.



Project 4: Technical Accomplishments/Progress/Results

Figure 4.4B. Change of λ (mole of water/mole of phosphoric acid) with temperature.



Project 4: Technical Accomplishments/Progress/Results

Task 1. Exercise of Computer Code showed that

(a) data obtained for water content as f (T, Dew point)

(b) data need for water balance as f (T) under load

(c) data needed for cathode carbon corrosion

(d) data needed for transient experiments

Task 2. Experiments and Model Modification

Subtask 2.1 – water content data obtained

Subtask 2.2 – water balance experiments underway

Subtask 2.3 - transient experiments underway

Acknowledgements (Senior Collaborators)

Project 1: B. N. Popov, J. W. Weidner

Project 2: J. St-Pierre, T. Gu

Spaci-MS: ORNL: T. J. Toops, W. P. Partridge

Project 3: Y. J. Chao, C. T. Williams, Company Reps.

NSF- Center for Fuel Cells

Project 4: S. Shimpalee, T. Gu

Plug Power: B. Du, R. Pollard