# Fuel Cell Research at the University of South Carolina

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Project ID # FC47

# Overview

## Timeline

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

## 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

## Barriers

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

## 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**

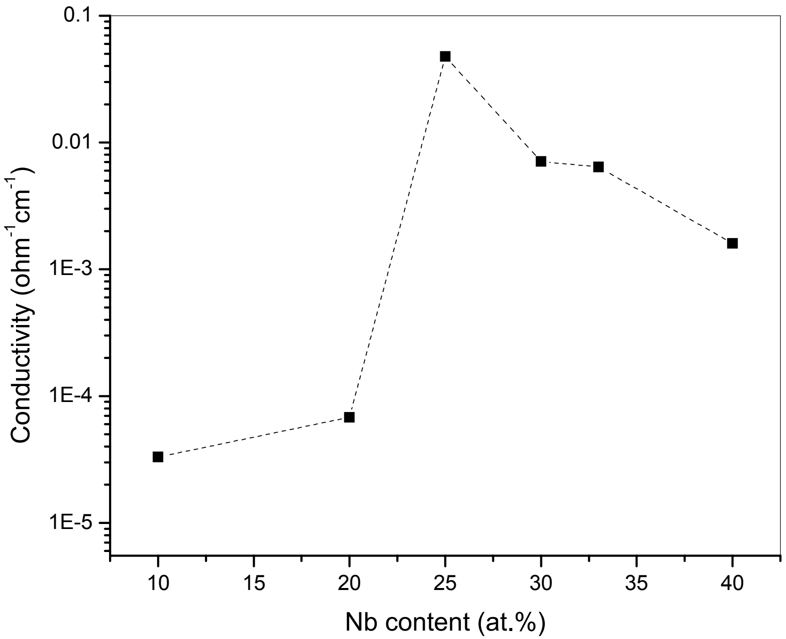
**Task 5. Stability Analysis of the Loaded Catalysts with ADT**

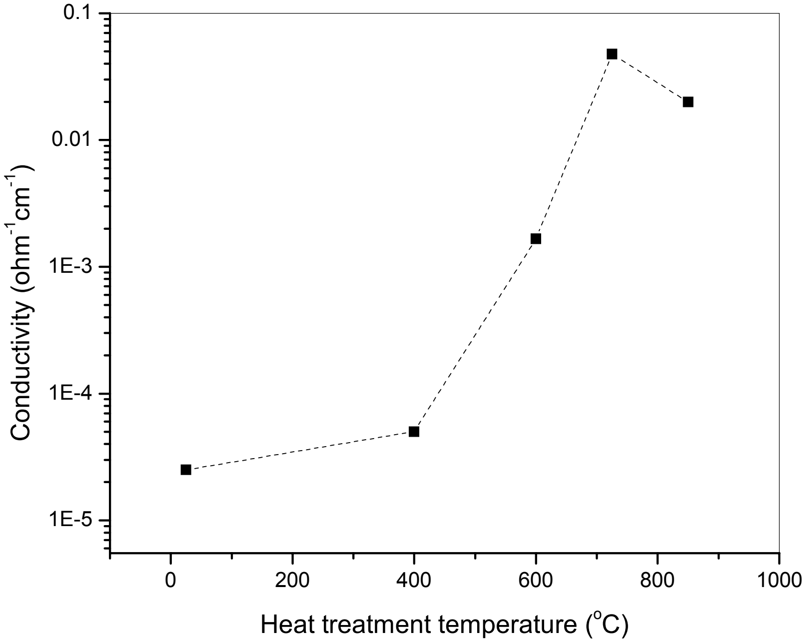
**(ADT = accelerated durability test)**

**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 $Nb^{2+}$.***



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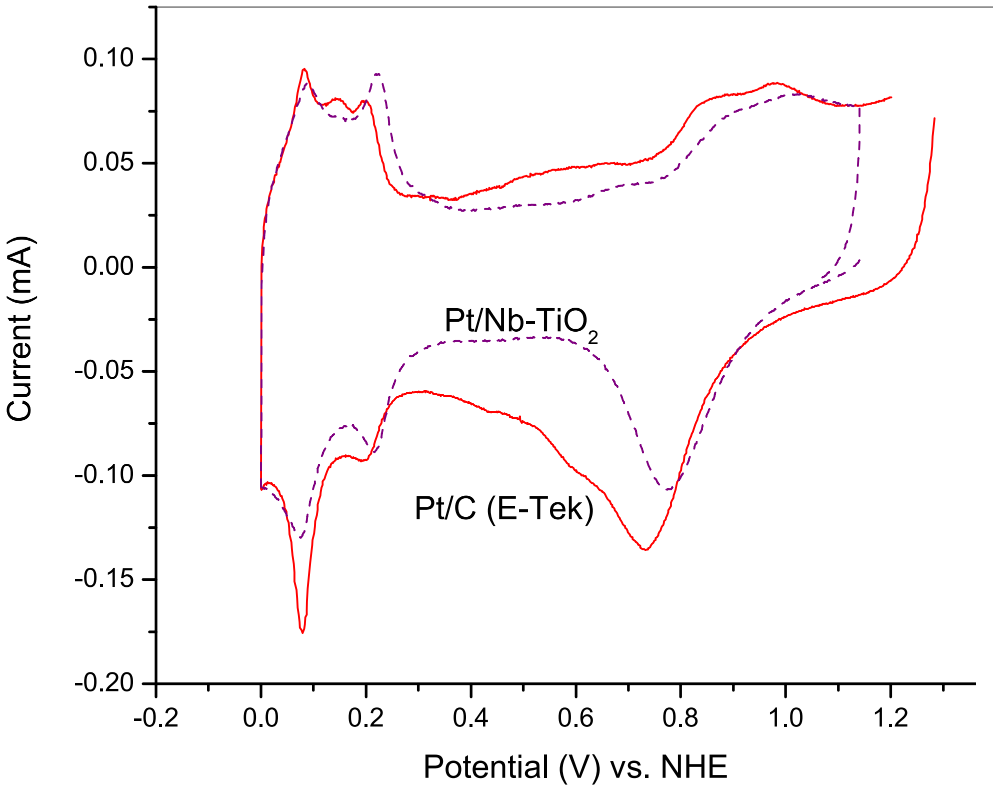
# Project 1: Technical Accomplishments/Progress/Results

## 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)***



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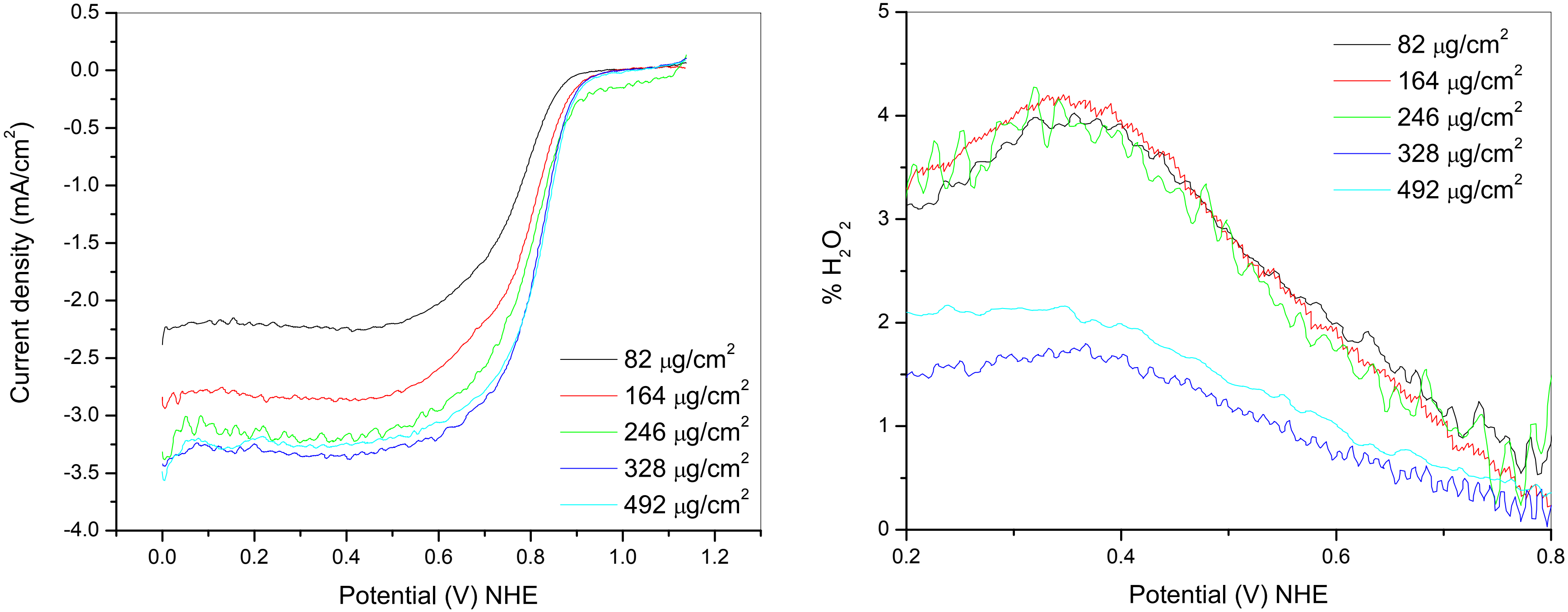
# Project 1: Technical Accomplishments/Progress/Results

## Pt/Nb-$TiO_2$ : LSV - Effect of Loading




- *The catalytic activity of Pt/Nb-$TiO_2$ 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***



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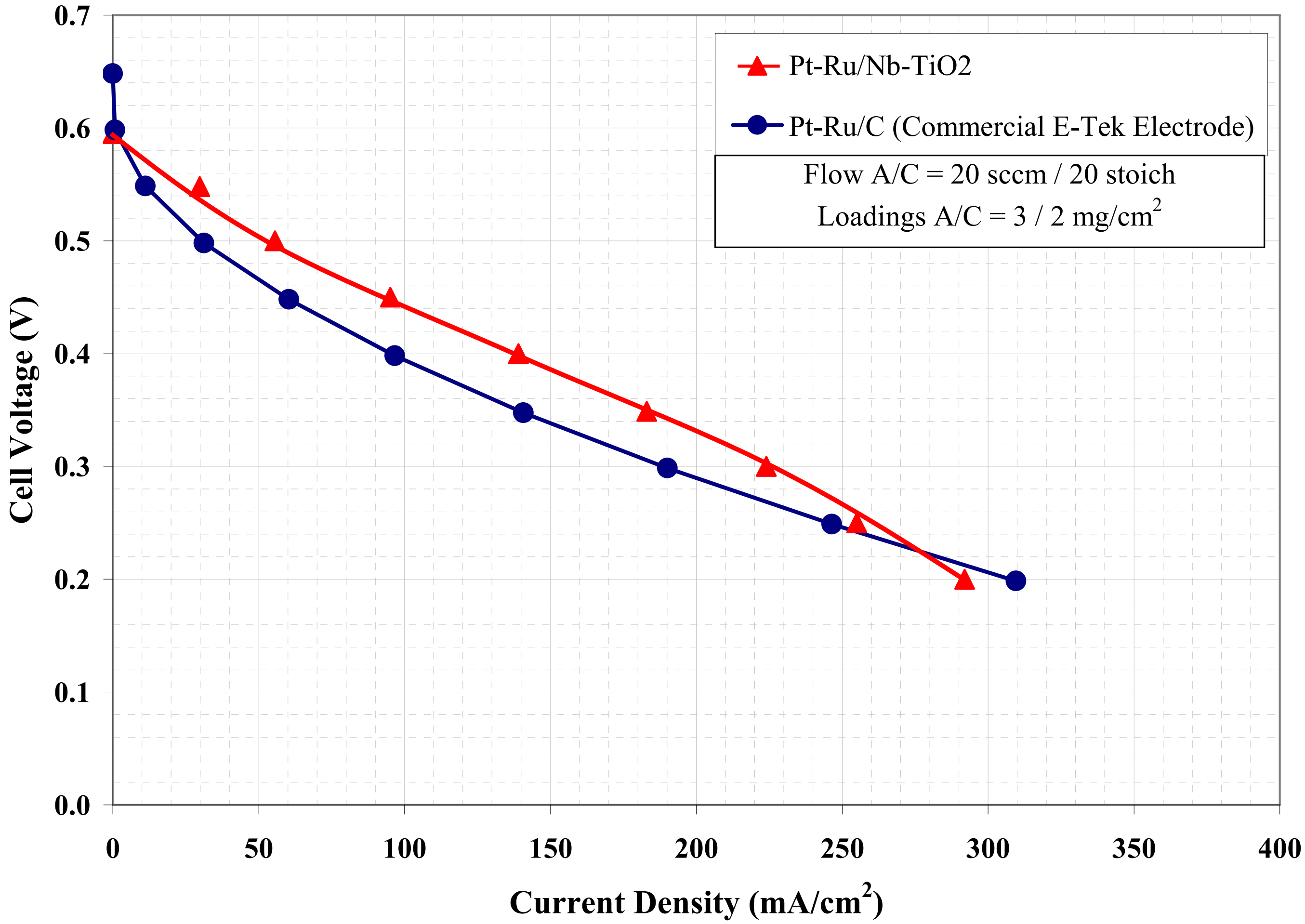
# Project 1: Technical Accomplishments/Progress/Results

## 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)**

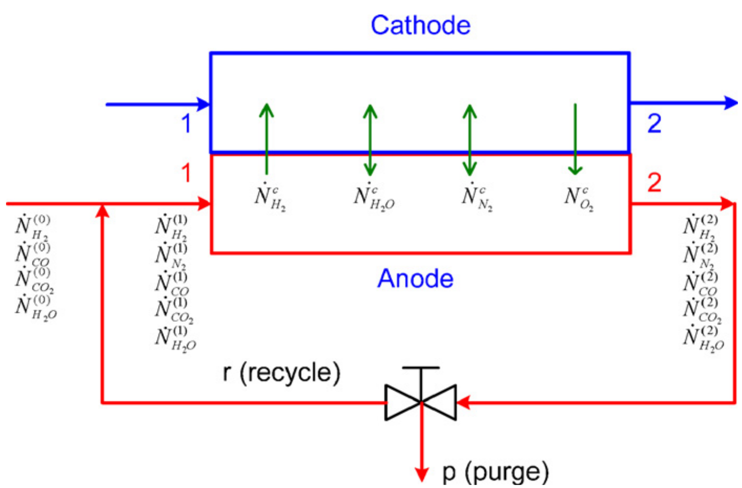
**Task 2. Study Effect of Temperature Distributions**
- **Subtask 1.1 Predict temperatures in common cells**
- **Subtask 1.2 Design new laboratory cells**
- **Subtask 1.3 Measure temperature distributions**

**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)



# 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



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# 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)**

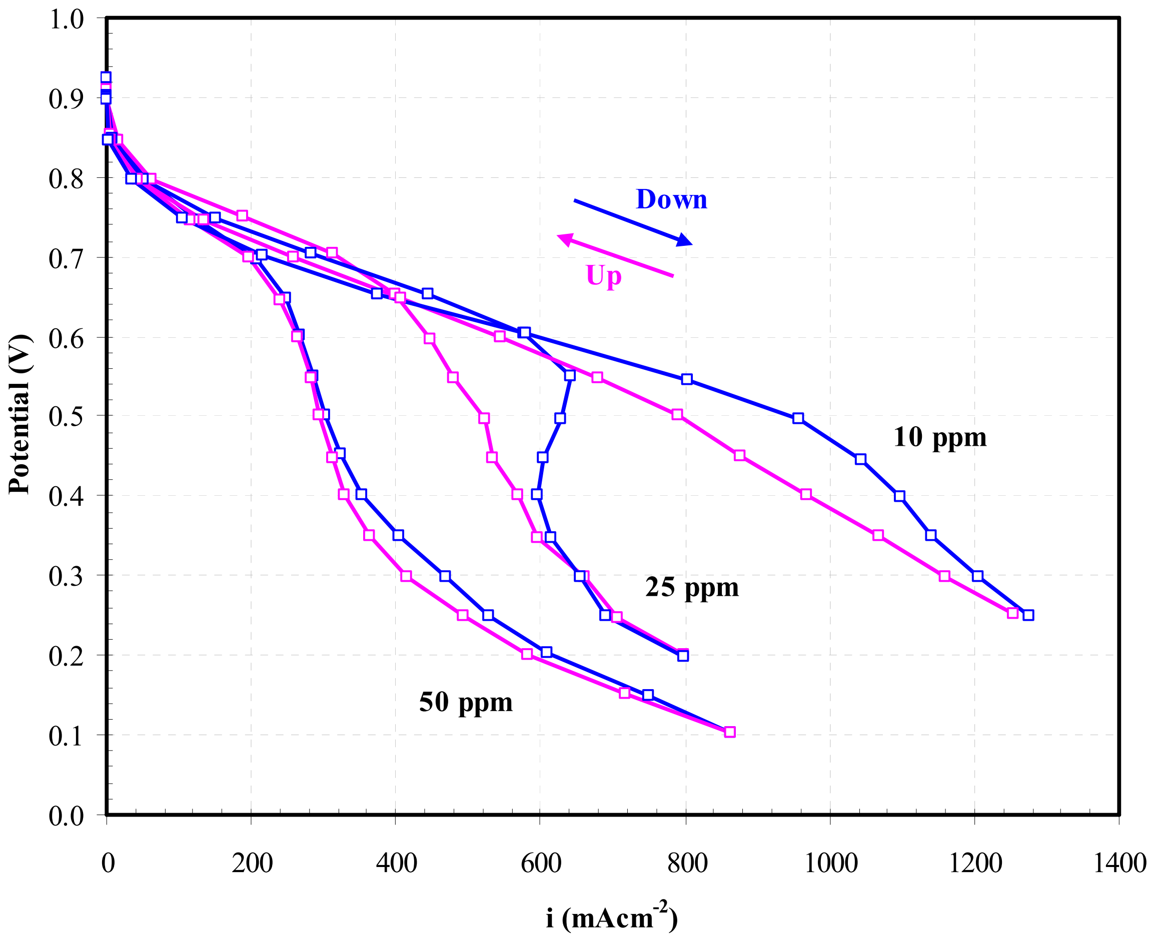
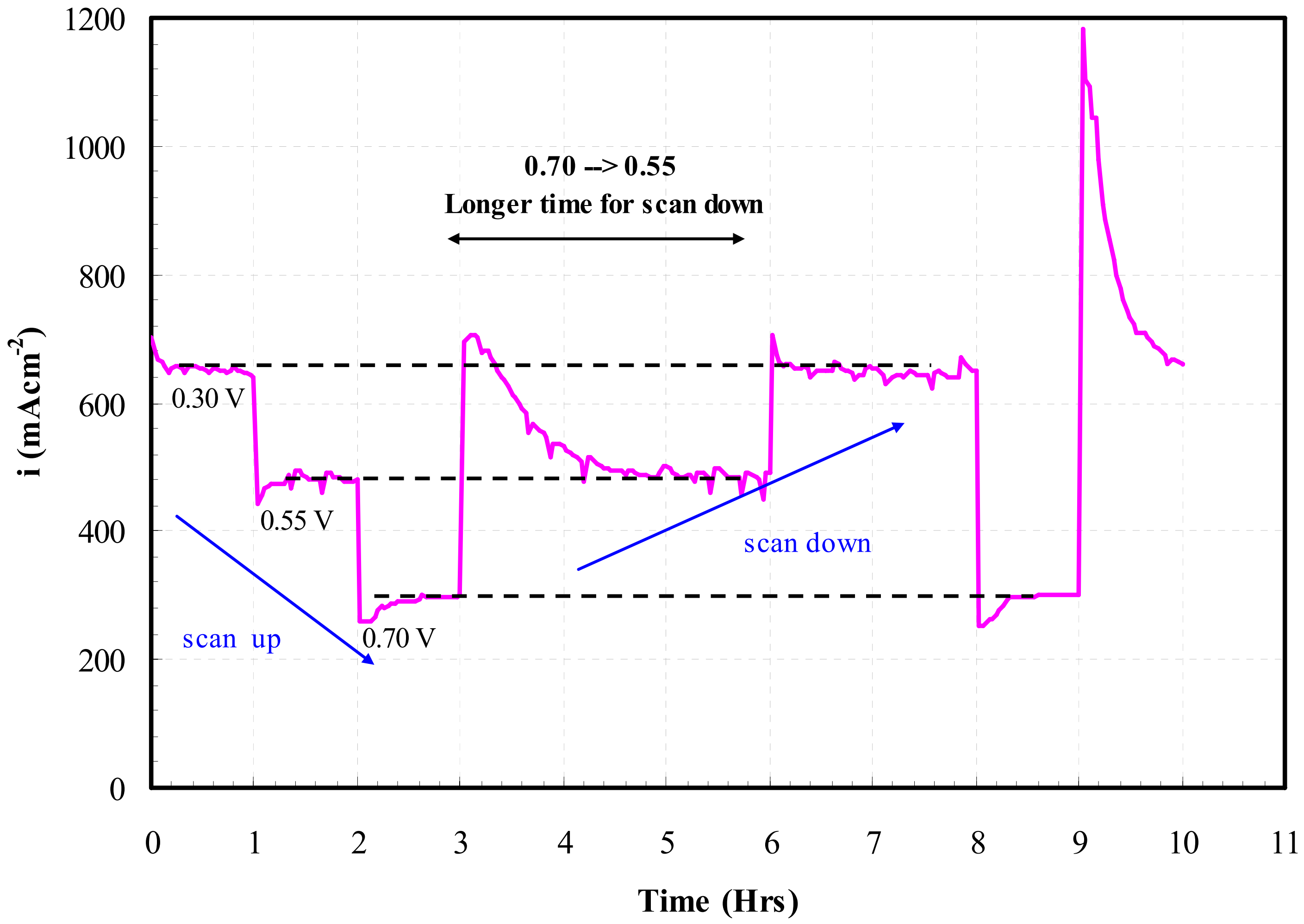
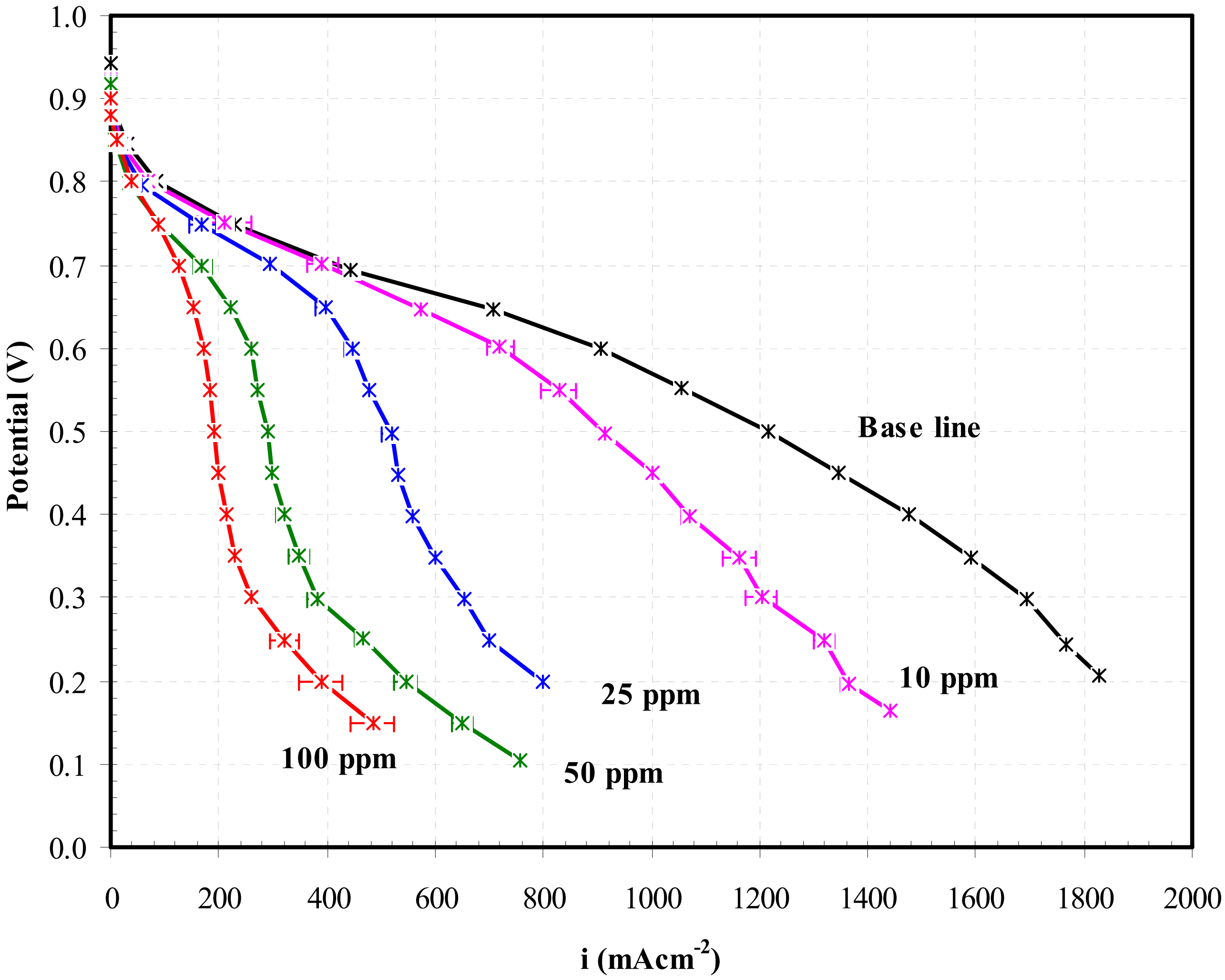


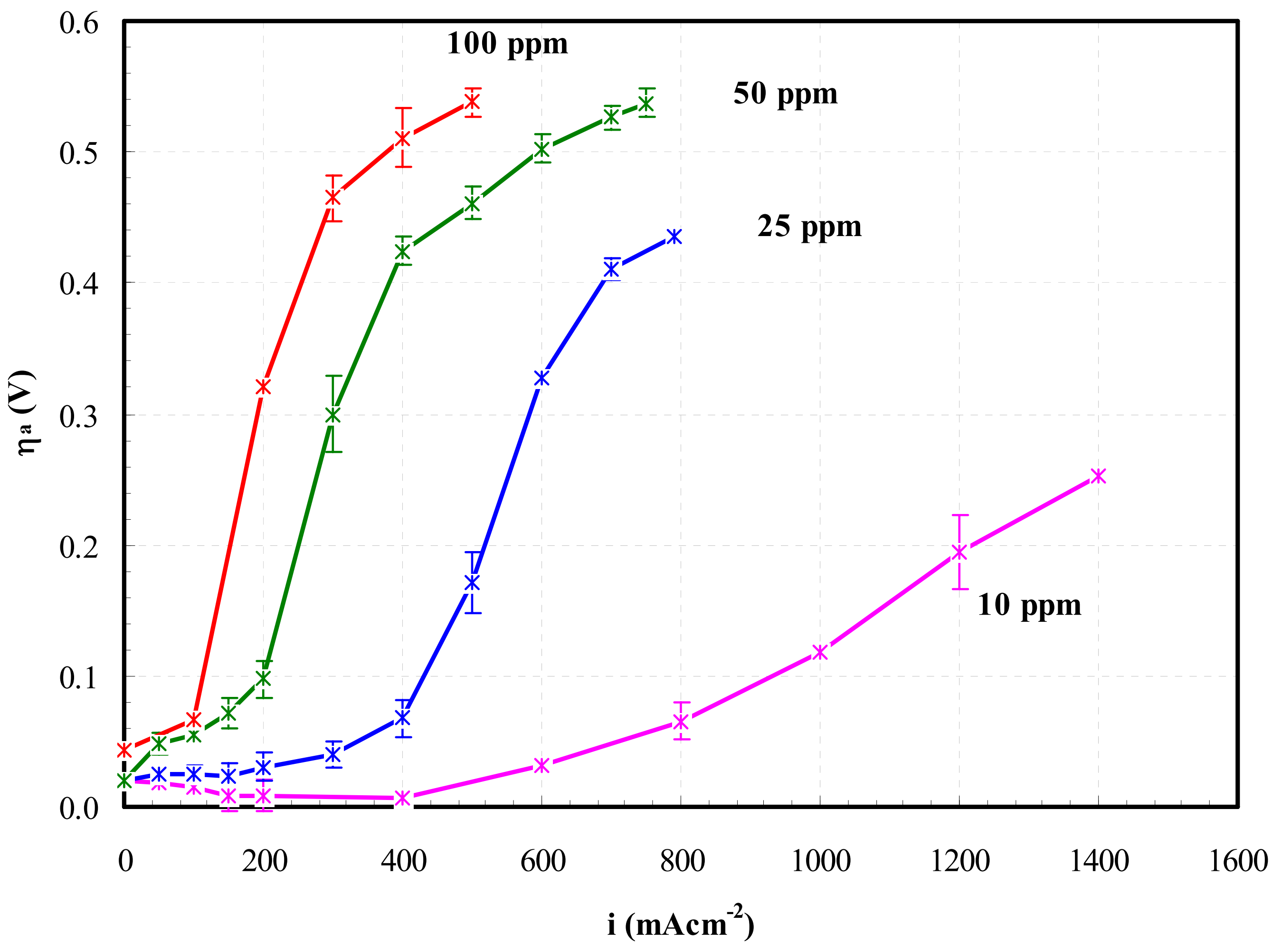
**Figure 2.2. Current density versus time for 25 ppm CO at potential = 0.30, 0.55 and 0.70, scanning up-down until reaching steady state.**



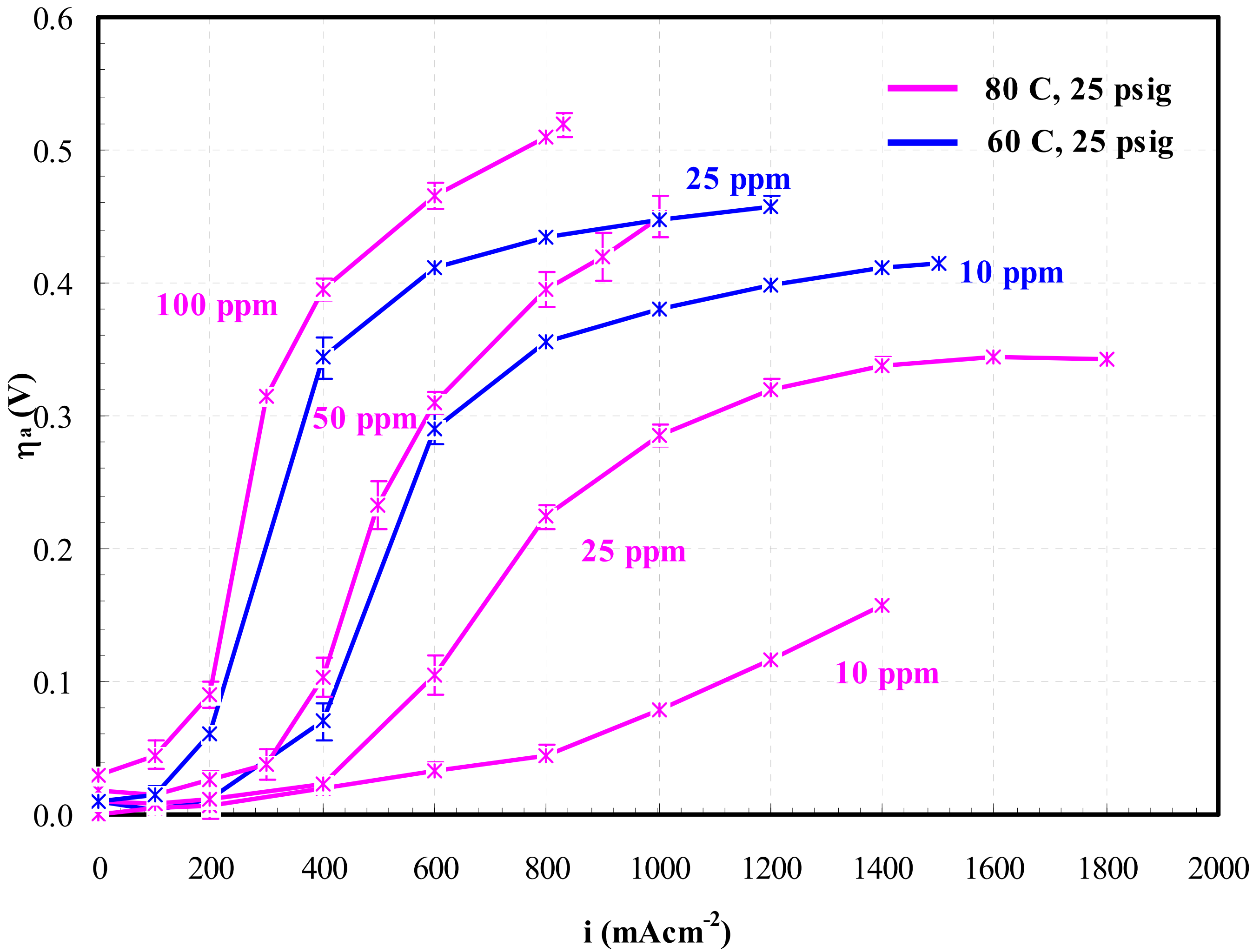
# Fig. 2.3. Polarization with CO for Tcell = 80° C & 0 psig.



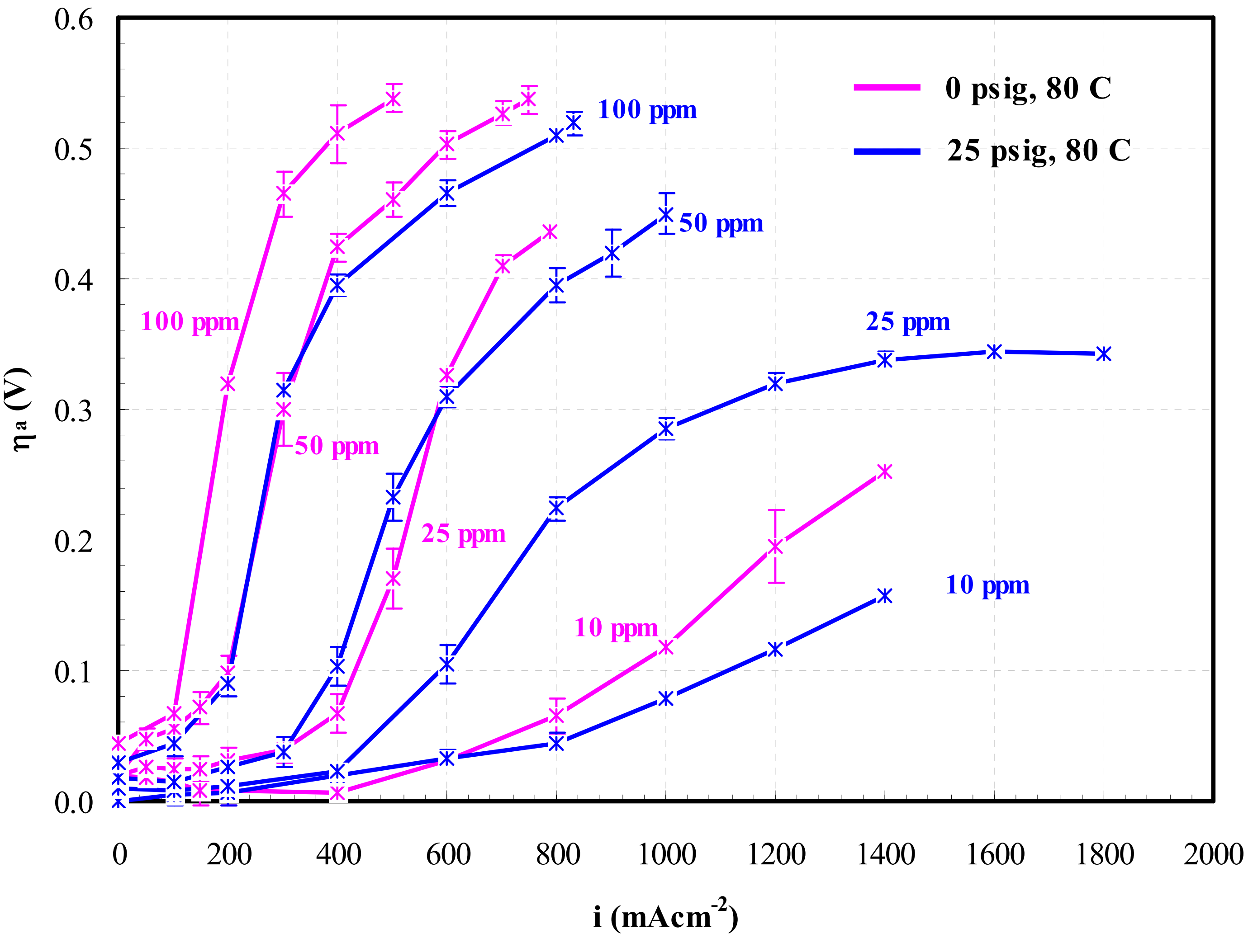
# Fig. 2.4. Anode overpotential for CO at 80° C & 0 psig.



# 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**

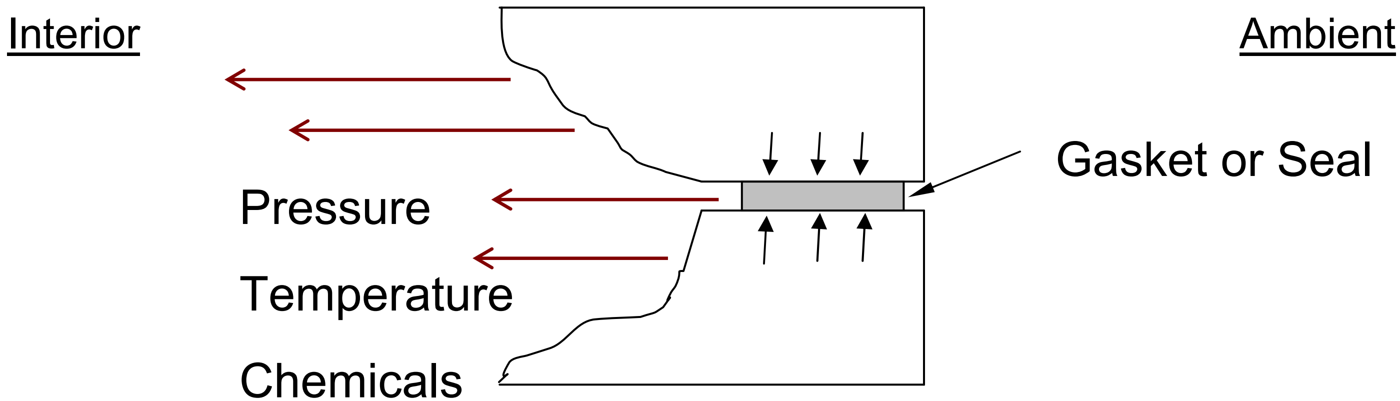
**Task 3. Characterization of Chemical Stability**
- **Perform both constant stress & constant displacement tests**
- **Assess the effect of applied stress/deformation on the rate of degradation**
- **Measure chemical/thermal stability will be assessed by various**

**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)



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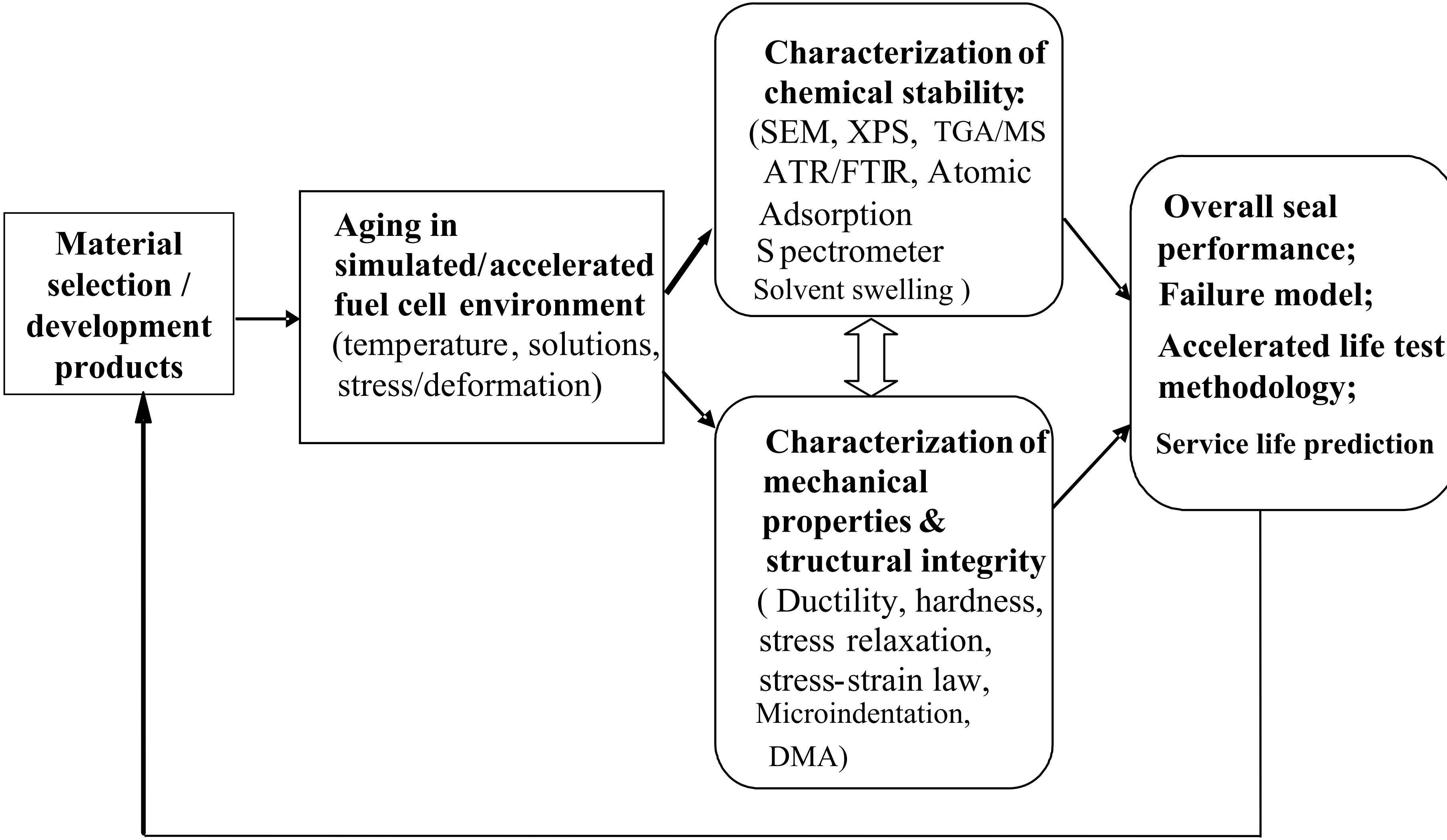
# Approach: Project #3: Flow Chart of Studies



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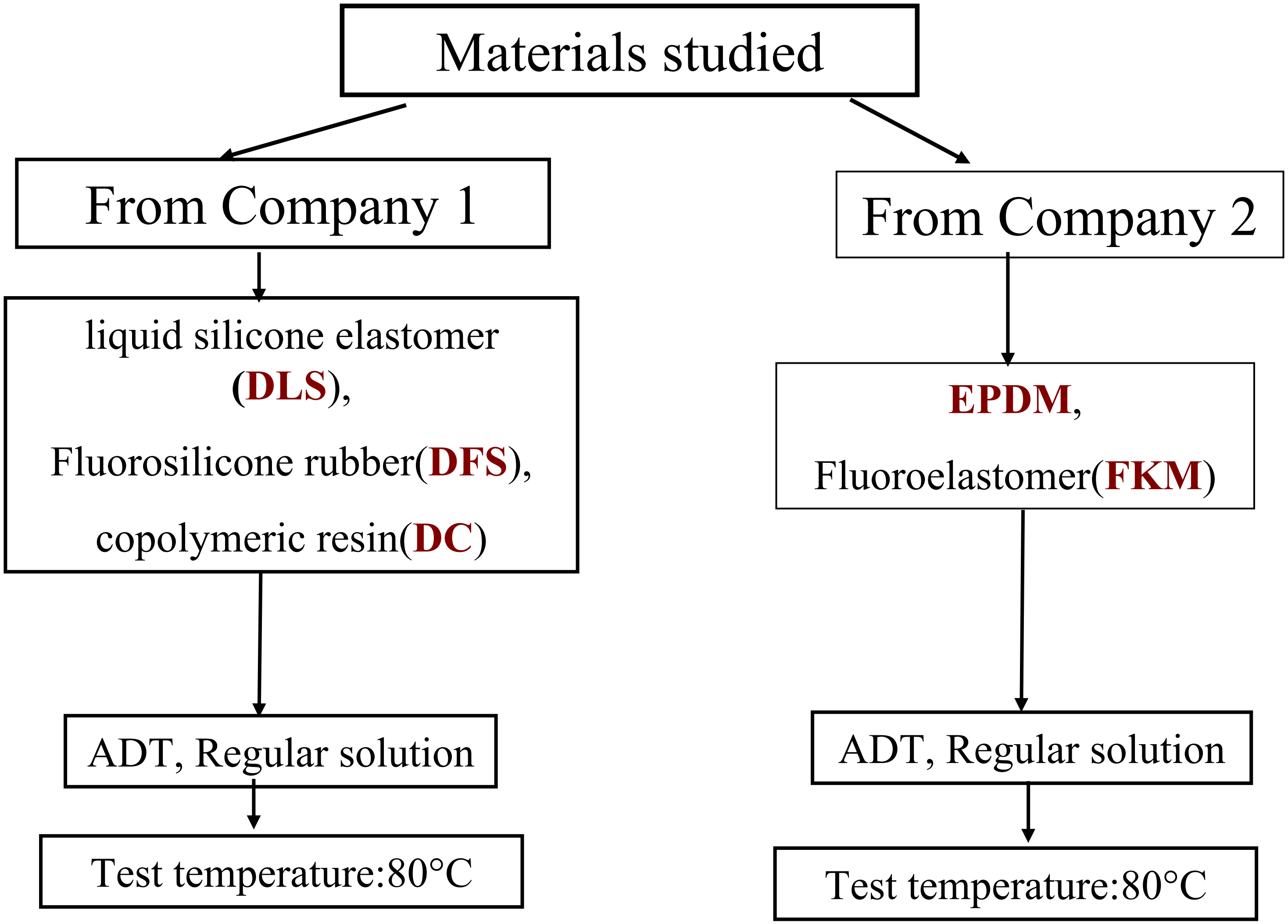
# Project 3: Technical Accomplishments/Progress/Results



# Labels for samples from Company # 1

- In ADT solution
  (accelerated durability test)

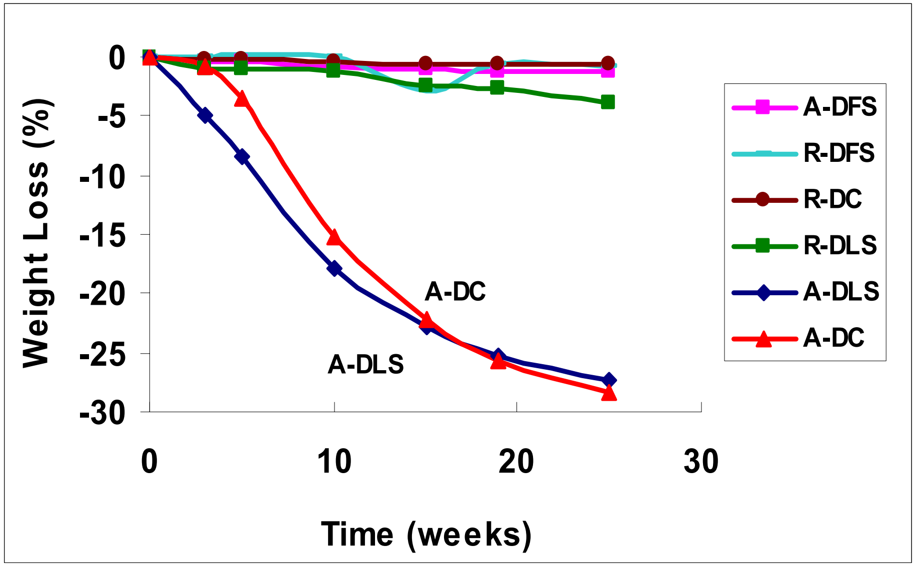
- A-DLS
- A-DFS
- A-DC

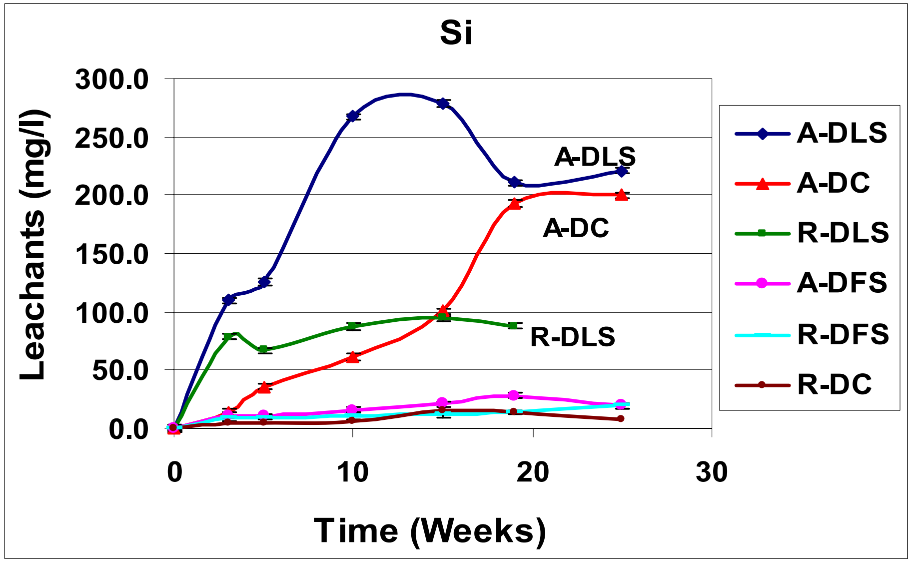
- In regular solution

- 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



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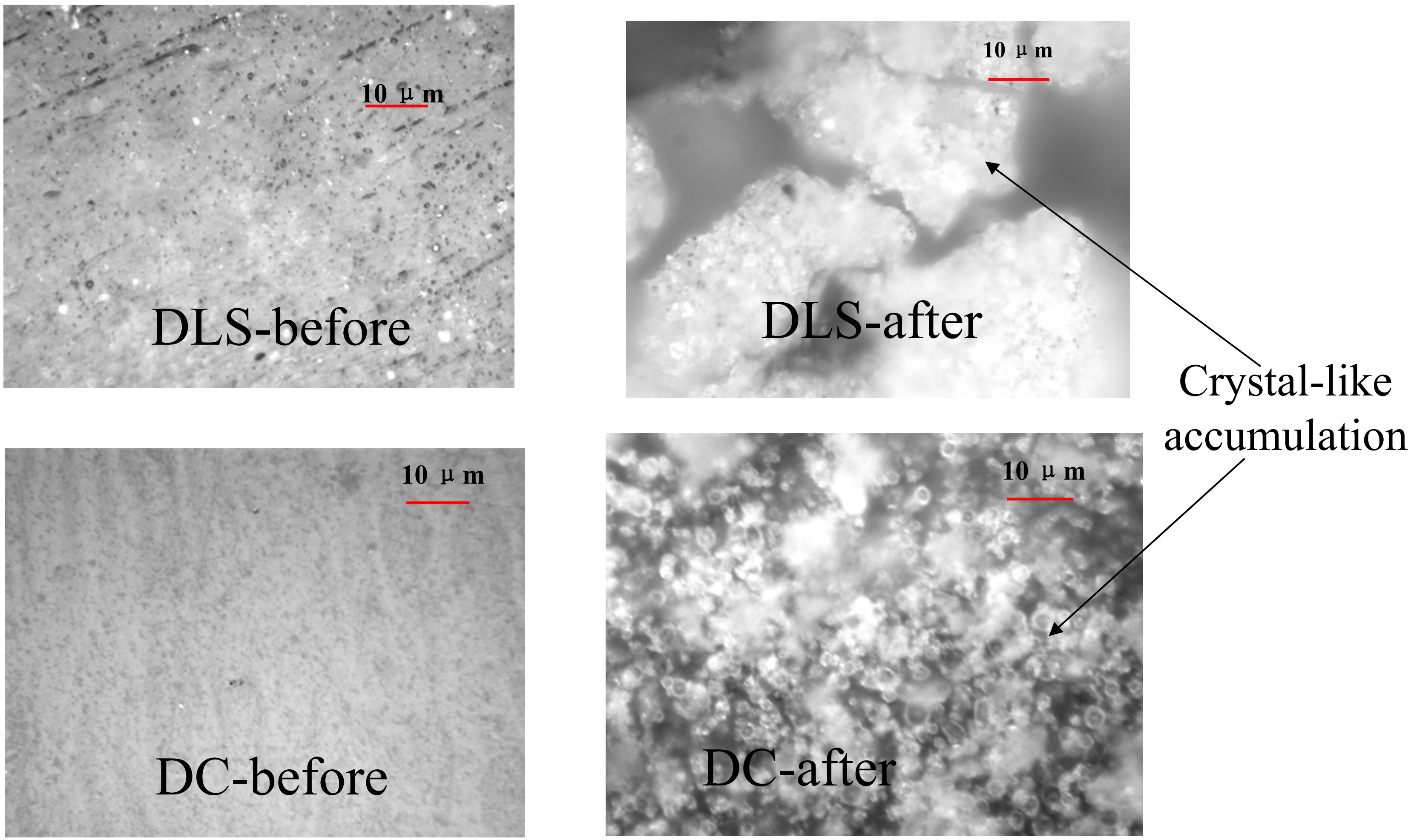
# Optical image of DLS and DC before and after exposure to ADT solution for 10 weeks



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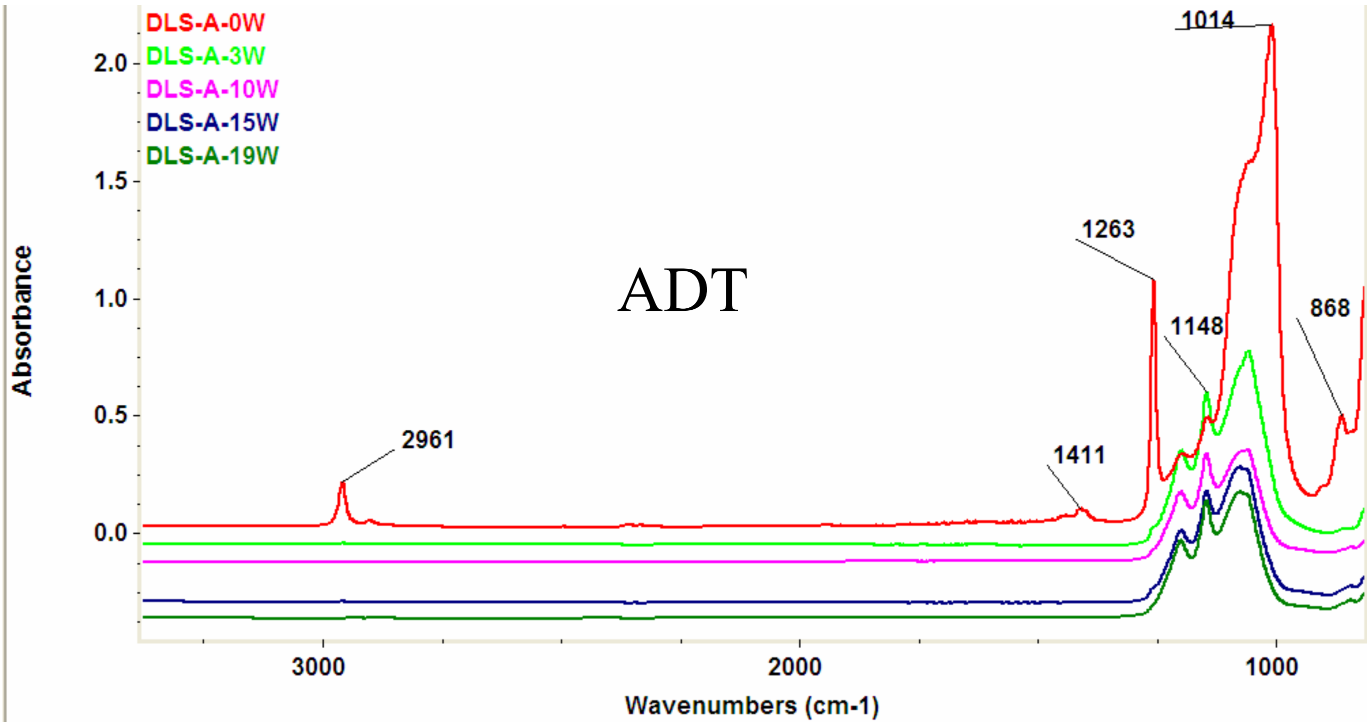
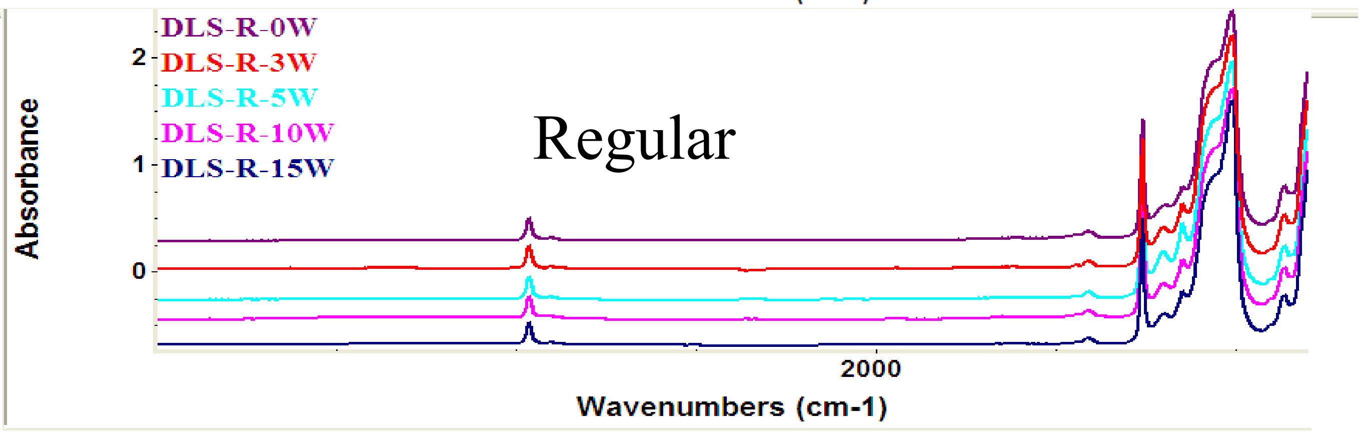
# Project # 3: ATR-FTIR for DLS




Chemical changes in backbone and crosslinked domain after 3week exposure




No significant Chemical Changes after 15 week exposure



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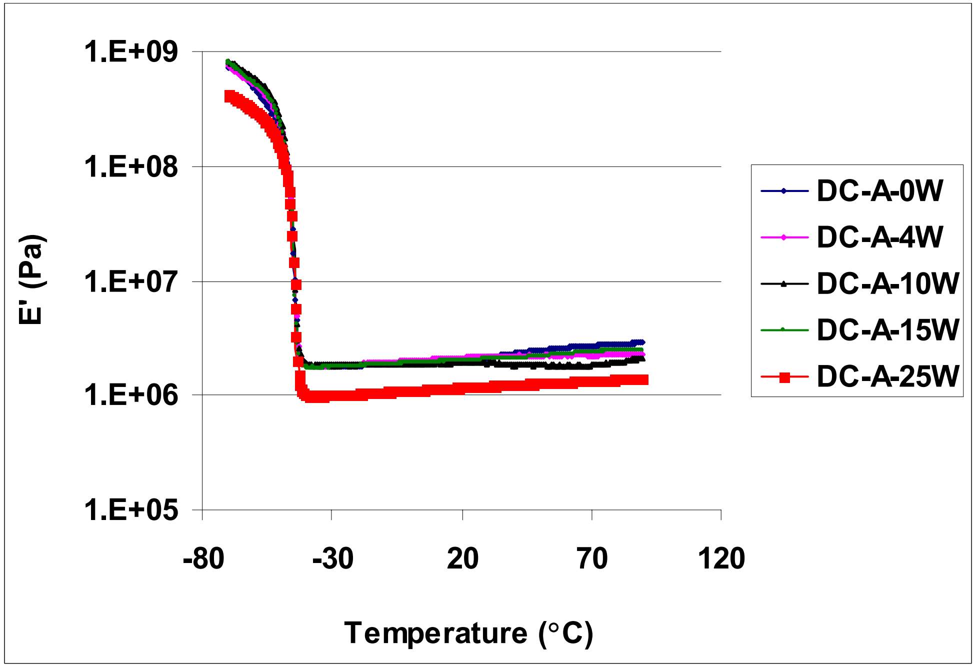
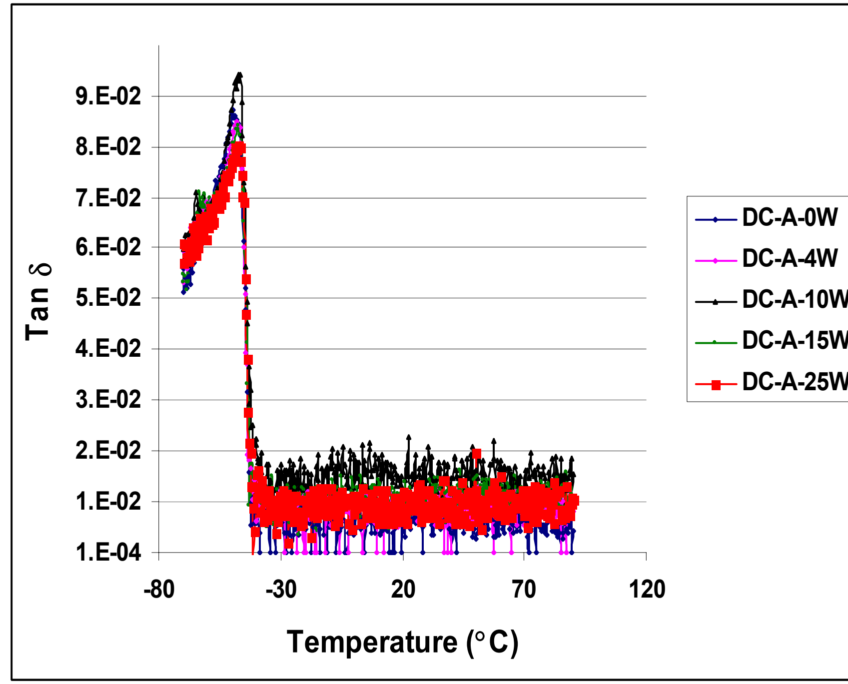
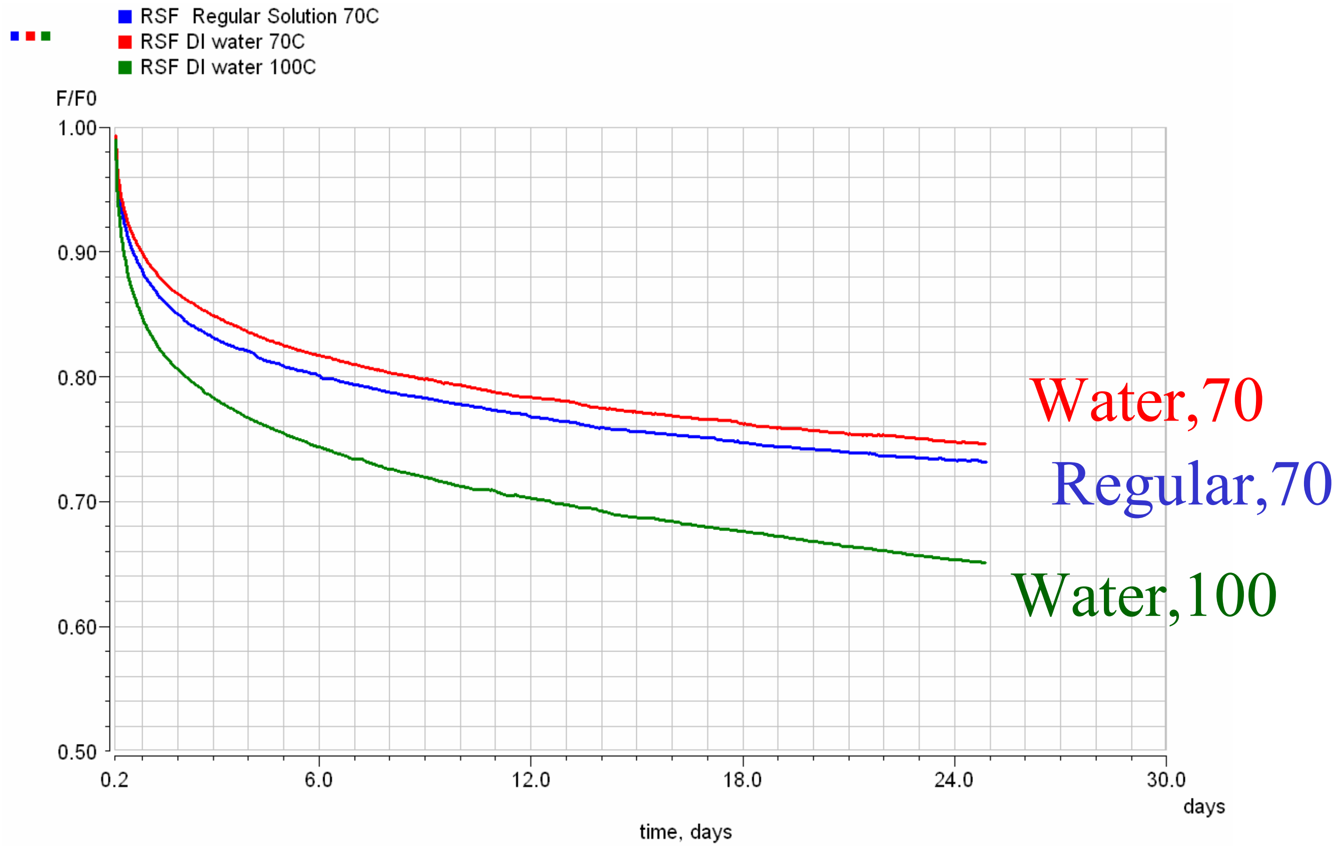
# Elastic modulus E' and Tan δ for DC exposed to ADT solution (by DMA)




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**

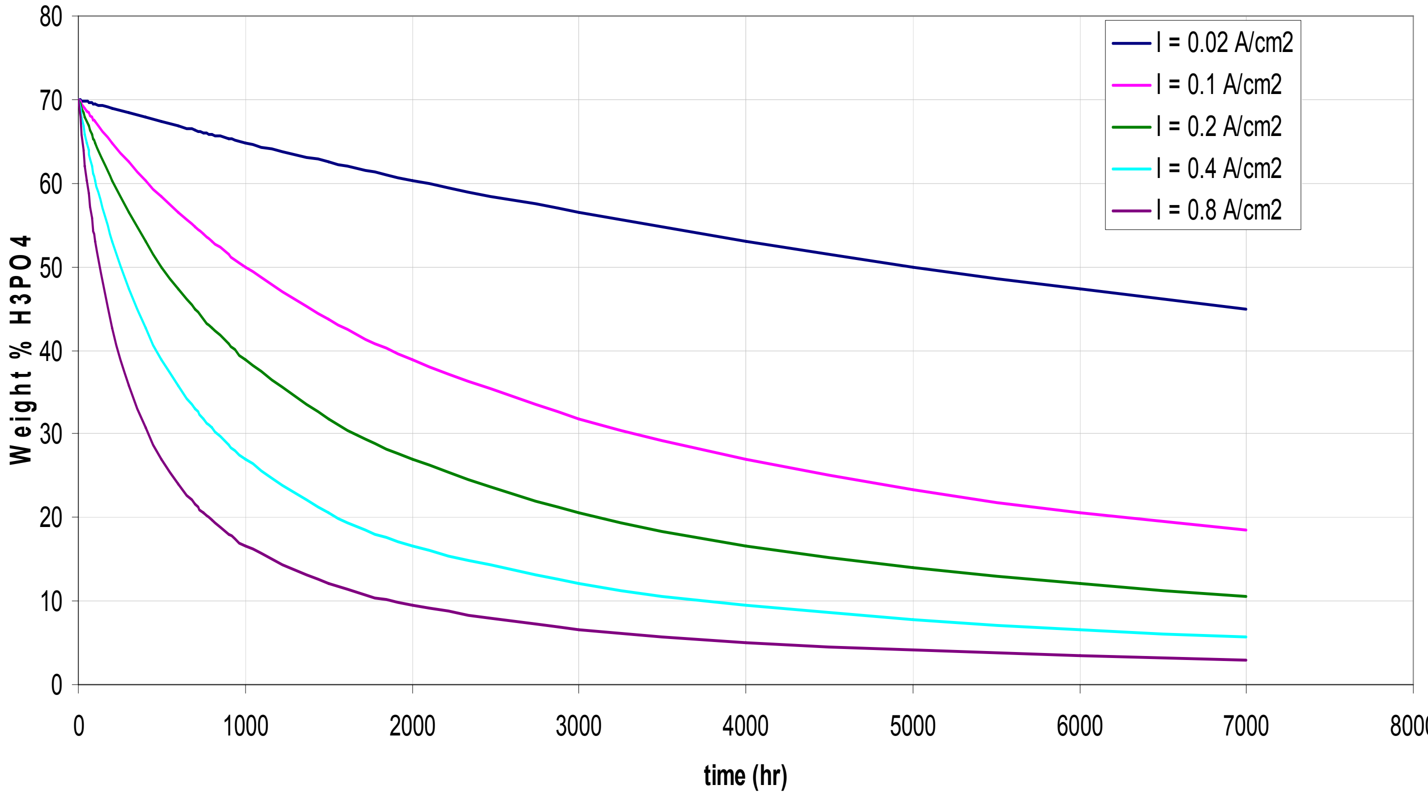
- **(a) obtain data for water content as f ( T, Dew point)**
- **(b) obtain data for water & acid balance as f ( T) under load**

**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?)



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# 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 inch$^2$ (6.4516 cm$^2$) |
| Total nitrogen flow: | 500 sccm, |
| Water partial pressure scanning rate: | 0.01 to 0.002 (kPa/101kPa/min) |



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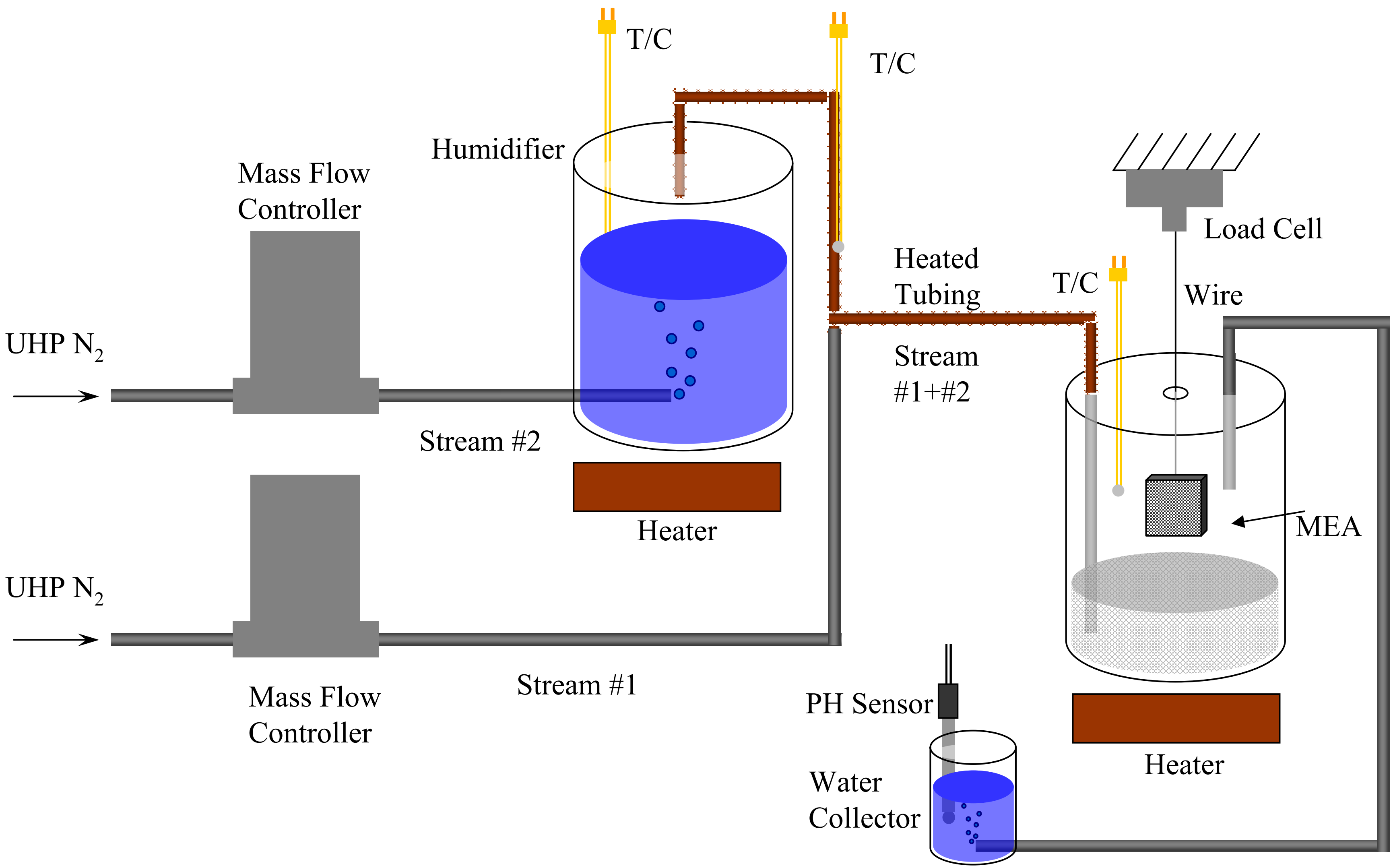
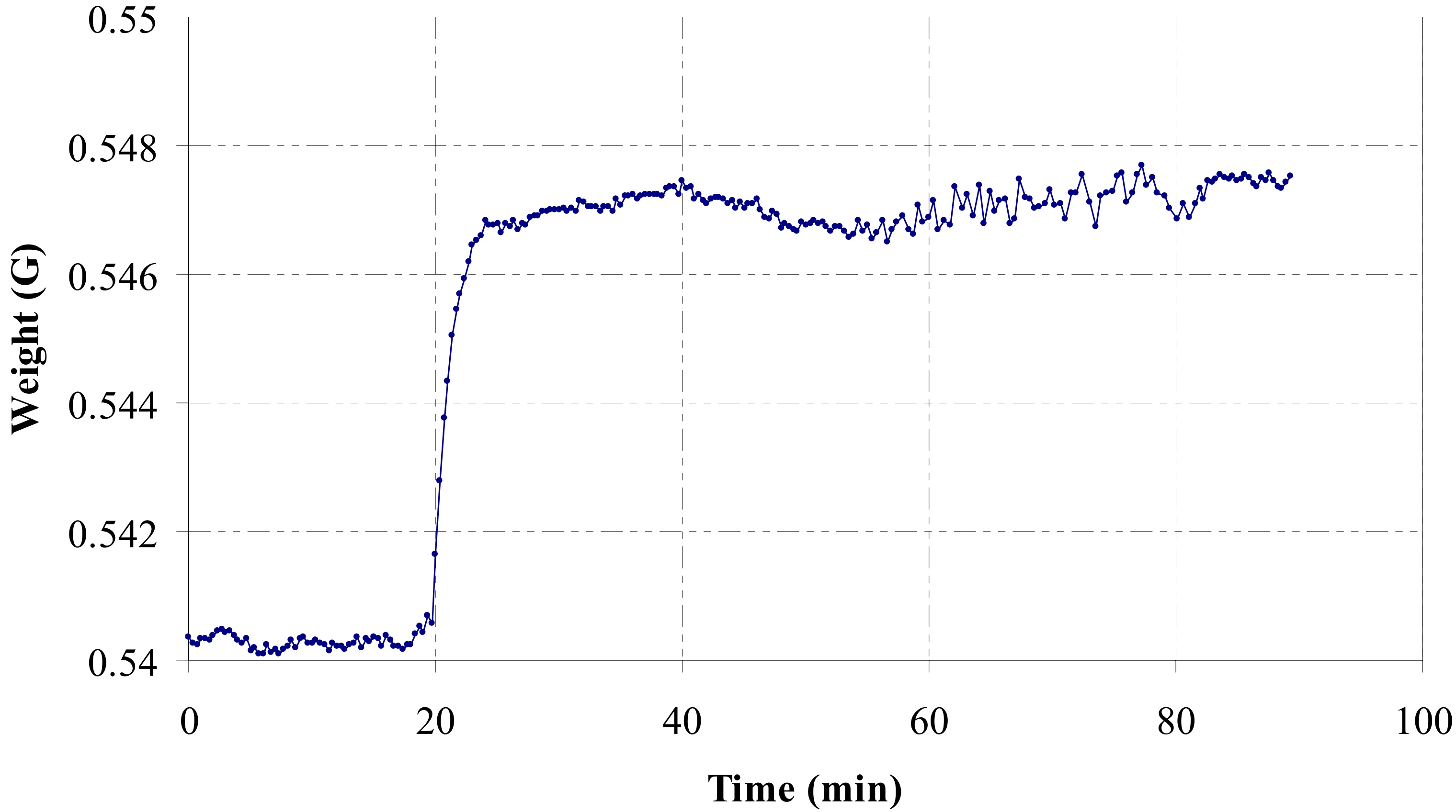
Figure 4.2. Schematic experimental setup to measure water euilibrium.



# Project 4: Technical Accomplishments/Progress/Results

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



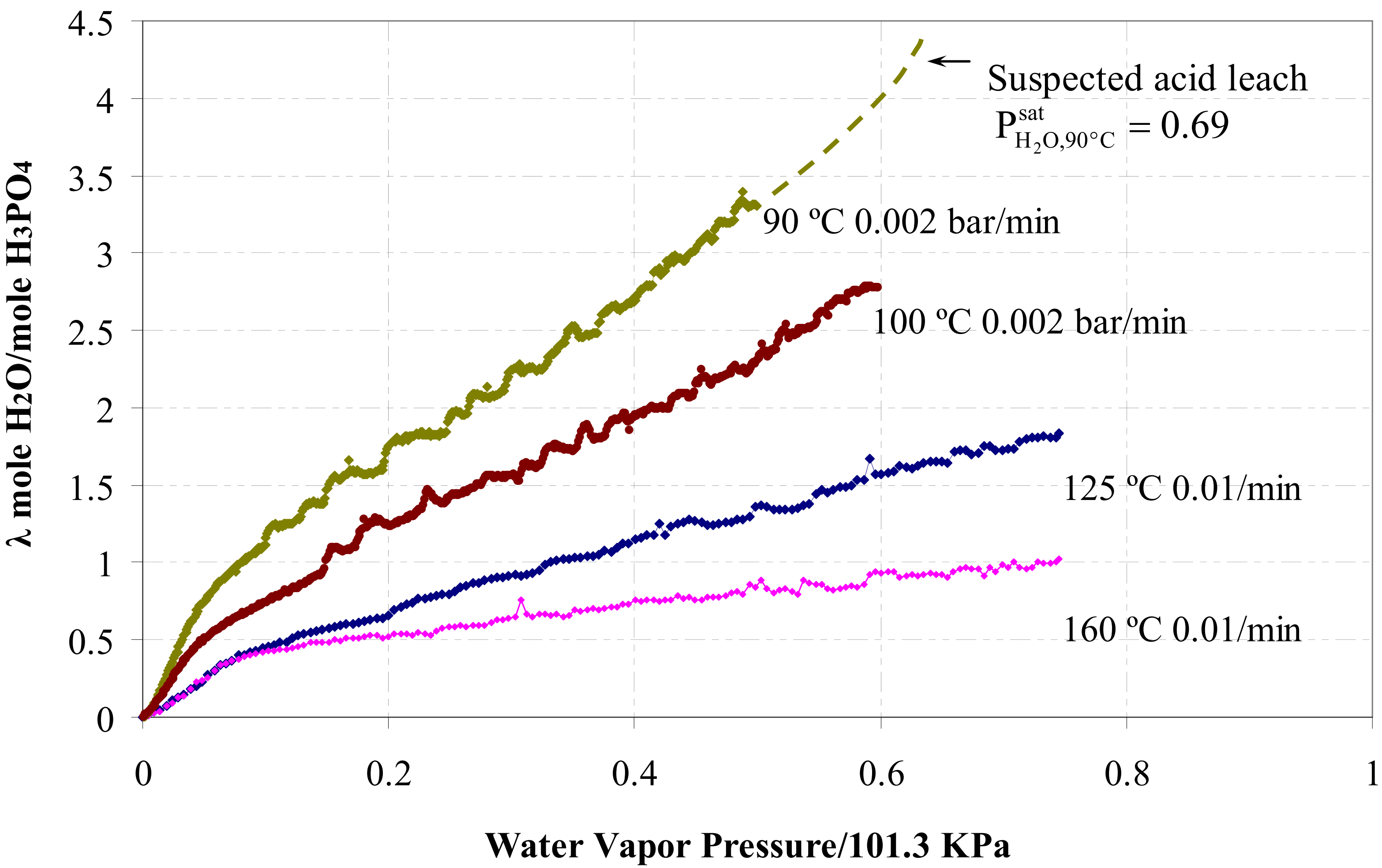

Container Temperature: 160 $^oC$; Switching time: @20th minute

Initial humidity: 0.020,17.5 $^oC$ dew point

Final humidity: 0.156,55 $^oC$ dew point

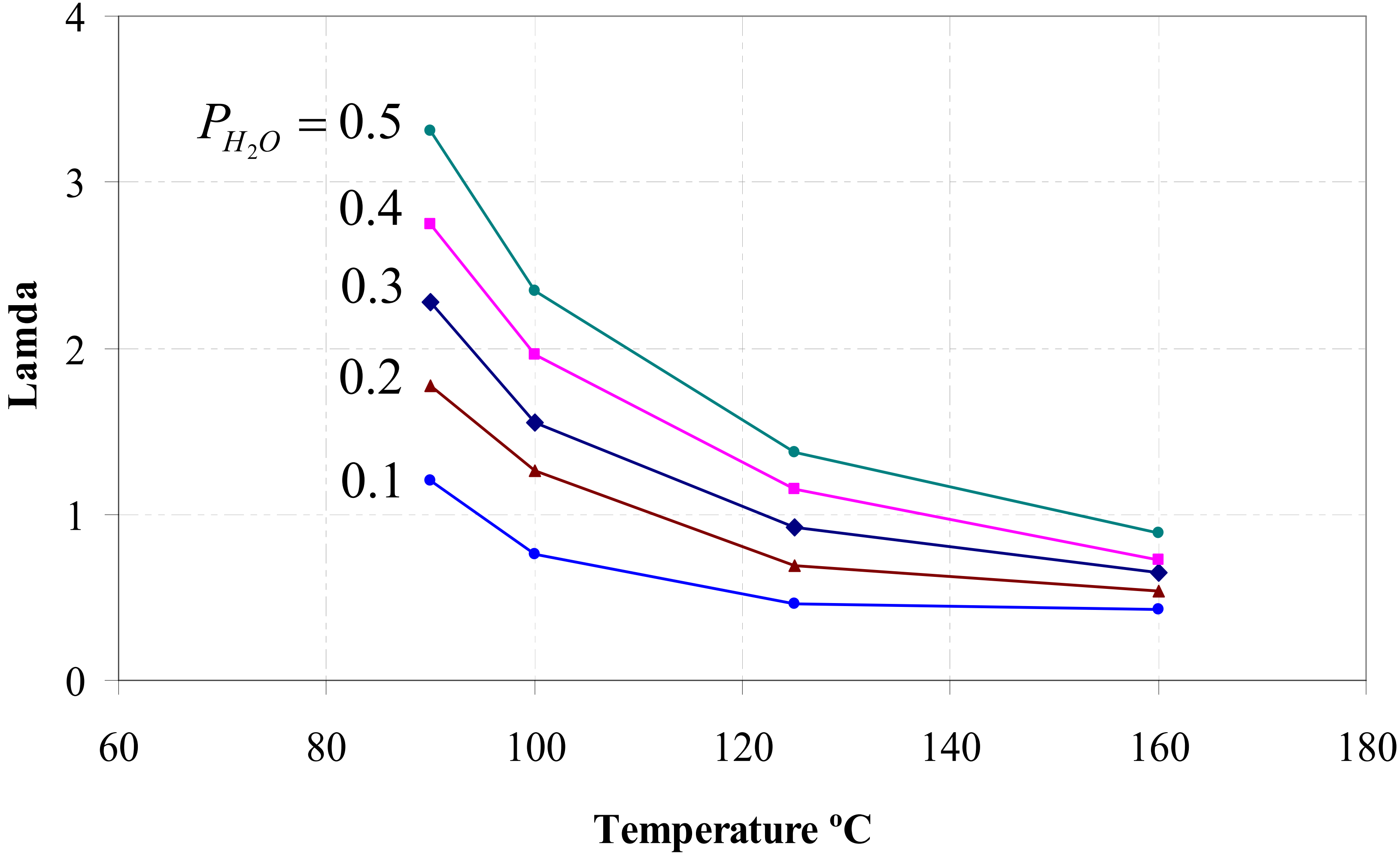
# Project 4: Technical Accomplishments/Progress/Results

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**