Stack Durability on Hydrogen and Reformate

2004 Hydrogen and Fuel Cells Merit Review Meeting

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This presentation does not contain any proprietary or confidential information.

Technical Objectives:
Quantify and Improve PEM Fuel Cell Durability

- Identify and quantify factors that limit PEMFC Durability
  - Measure property changes in fuel cell components during long term testing
    - Membrane-electrode durability
    - Electrocatalyst activity and stability
    - Gas diffusion media hydrophobicity
    - Bipolar plate materials and corrosion products
  - Develop and apply methods for accelerated and off-line testing
- Improve durability

- Component Technical Barriers Addressed:
    - Durability (Barrier P)
    - Electrode Performance (Barrier Q)
    - Stack Material & Manufacturing Cost (Barrier O)

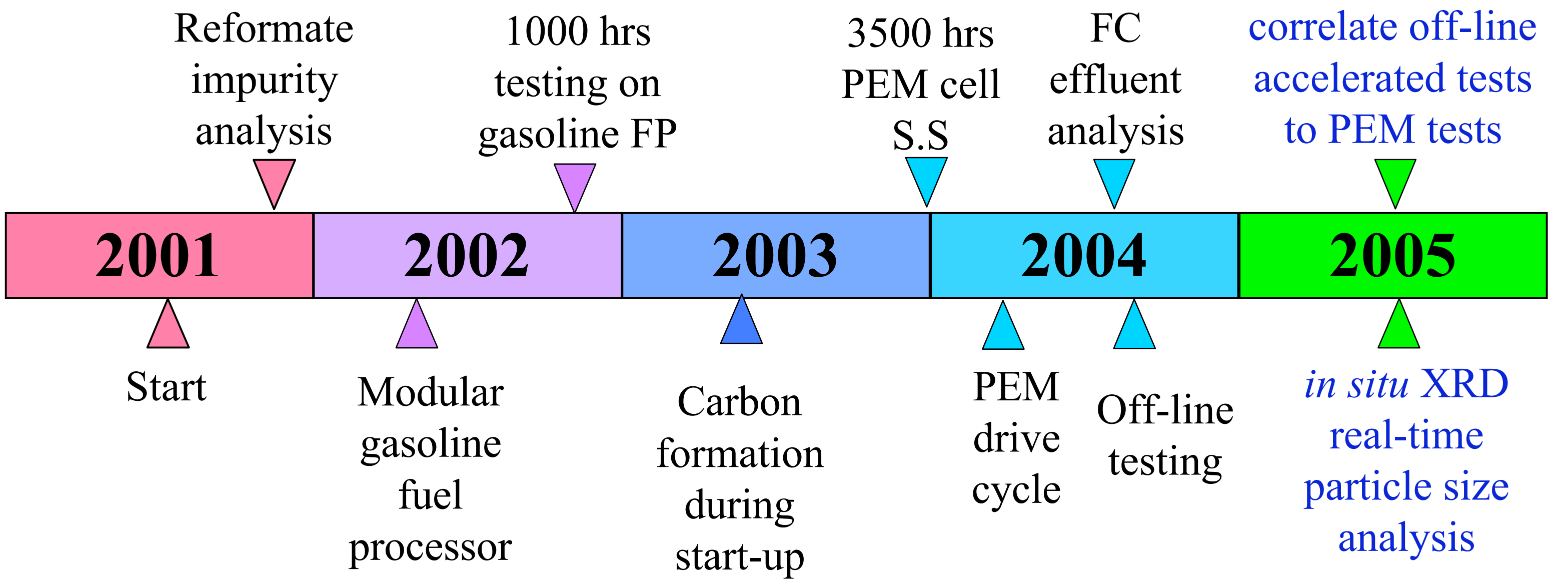
- DOE Technical Target for Fuel Cell Stack System (2010)
    - Durability 5000 hours
    - Precious metal loading (0.2 g/rated kW)
    - Survivability (includes thermal cycling and realistic driving cycles)

Approach to Durability Studies

- PEM fuel cell durability testing
  - 5 cm^2, 50 cm^2 and full size active area (200 cm^2) / 12 cell stack
  - Testing: simulated vehicle drive cycle and steady-state testing
    - VIR / cell impedance
    - catalyst active area
    - effluent water analysis
- *in situ* and post-characterization of membranes, catalysts, GLDs
    - SEM/EDAX / XRF / XRD / TEM / ICP-MS / neutron scattering / H_2 adsorption
- Develop and test with off-line and accelerated testing techniques
  - Potential sweep methods
  - Environmental/leachate chamber
  - Corrosion tests

Fuel Cell Durability Testing Timeline

Project initiated in 2001 as Fuel Cell Stack Durability on Gasoline Reformate
Beginning FY2004 concentration on PEM H_2 Durability



	2004 Milestones
Dec 03	Complete water analysis of impurities developed during testing.
Nov 03	Incorporate drive cycle into durability testing.
Jan 04	Initiate off-line durability accelerated testing procedure.
Jan 04	Incorporate Teledyne Stack into H_2 durability testing.

Response to Reviewer Comments at 2003 DOE Review Meeting

Stack Durability on Hydrogen and Reformate and Testing of Fuels in Fuel Cell Reformers

2003 presentation concentrated on Fuel Effects on Fuel Reforming, so most comments not applicable

- Redirected to work on H_2 PEM durability

Reviewer comments relevant after redirection:

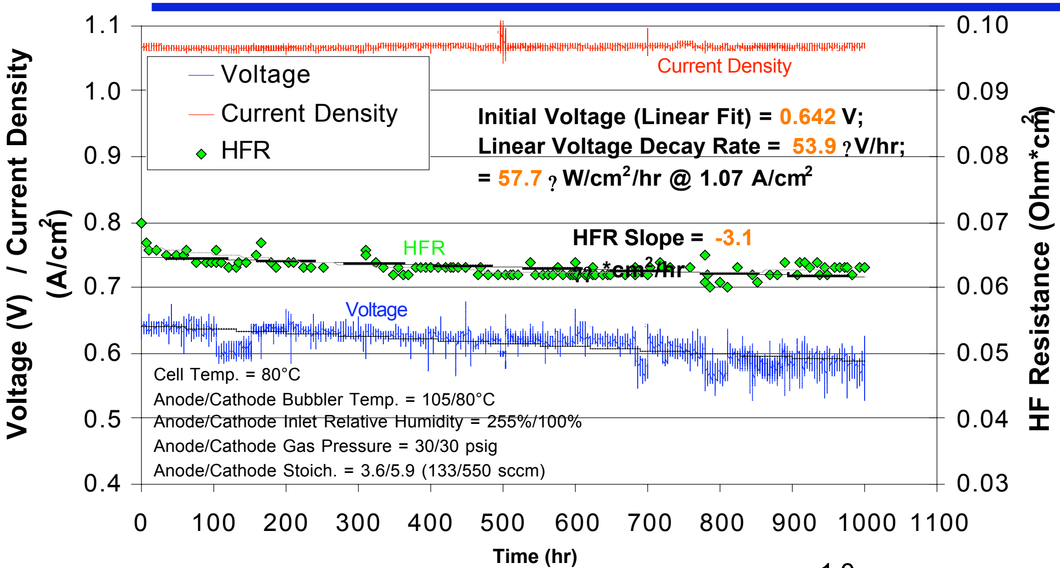
• The durability objective of this project is very important and I hope it will be actively addressed.

• I especially like the proposal of operating the system in a duty cycle operating mode.

• Introduction of drive cycle dynamics and start-up for next year is a plus …

• **Need more fundamental work.**

1000 hr Steady-State Test (5 cm^2)



Constant current

Temperature = 80 °C

MEA geometric active area = 5.0 cm^2

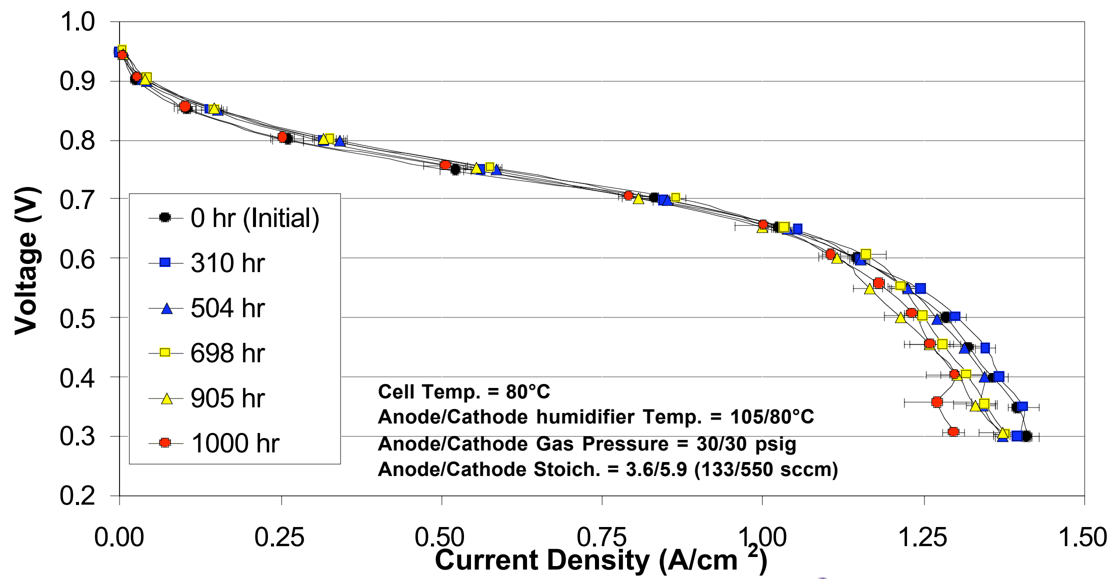
Anode catalyst: 20% Pt/C

Cathode catalyst: 20% Pt_3Cr/C

Loadings of 0.20 ± 0.01 mg Pt/cm^2

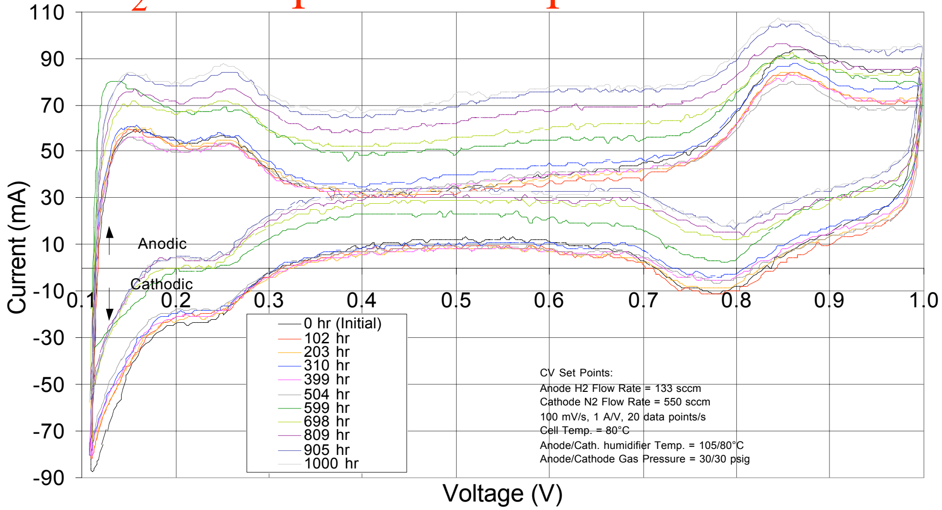
N112 membrane.

Comparison of Polarization Data During MEA 1000-hr Durability Test



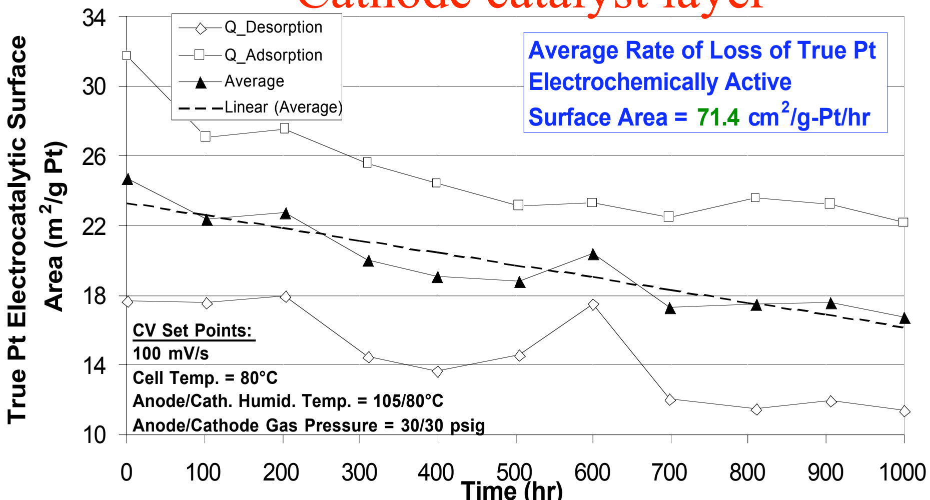
Analysis of Steady-State 1000-hr Test

H_2 Adsorption-Desorption CV Scans

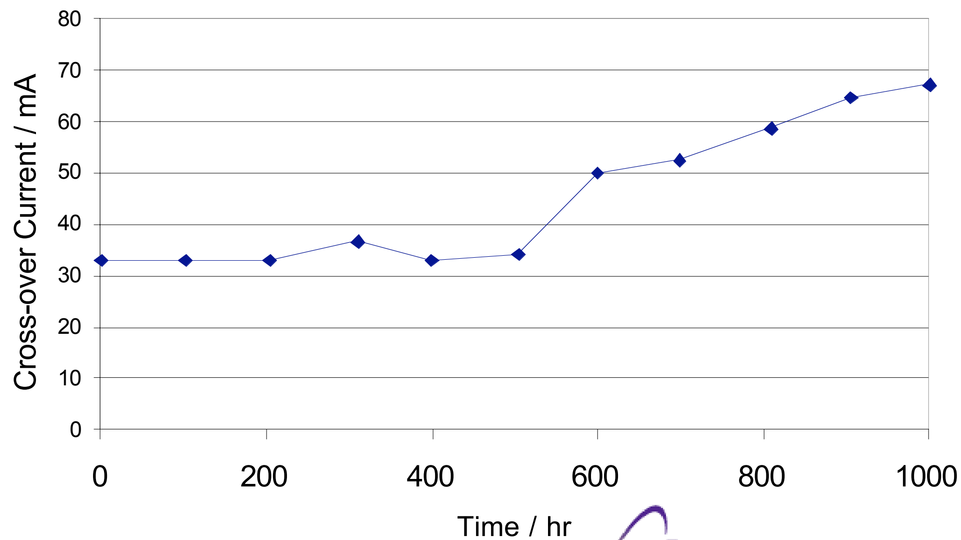


- During 1000-hr steady-state constant current durability test
  - Catalyst surface area decreases
  - Hydrogen cross-over increases

Cathode catalyst layer



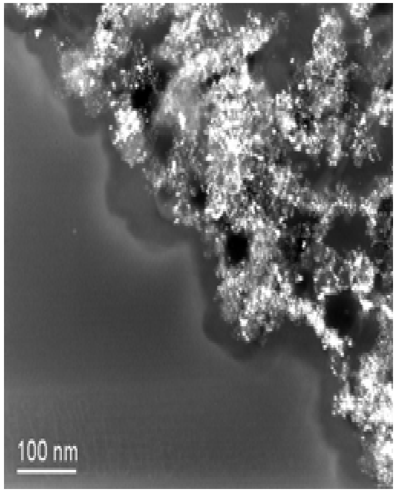
Hydrogen cross-over Current



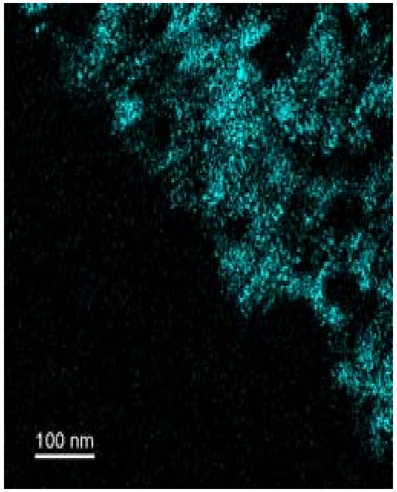
X-ray Maps of Tested MEA (Cathode)
(Steady State Testing for ~ 1000 hrs)

- After life test, a layer approximately 50-100nm thick develops at the interface of membrane and cathode catalyst layer
- This layer is enriched in S and depleted in F with respect to the rest of the membrane
- The fresh MEA had a uniform S and F composition across the membrane/anode interface

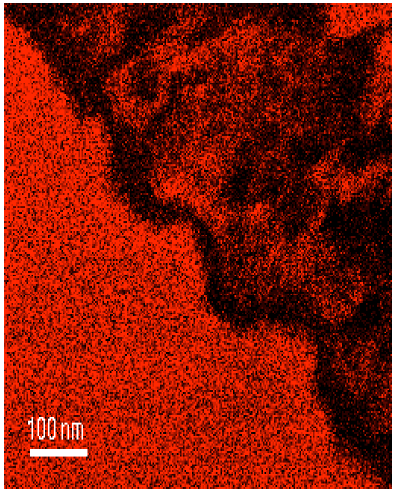
Z-contrast



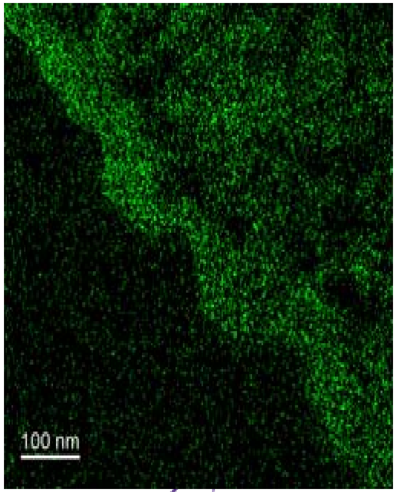
Platinum



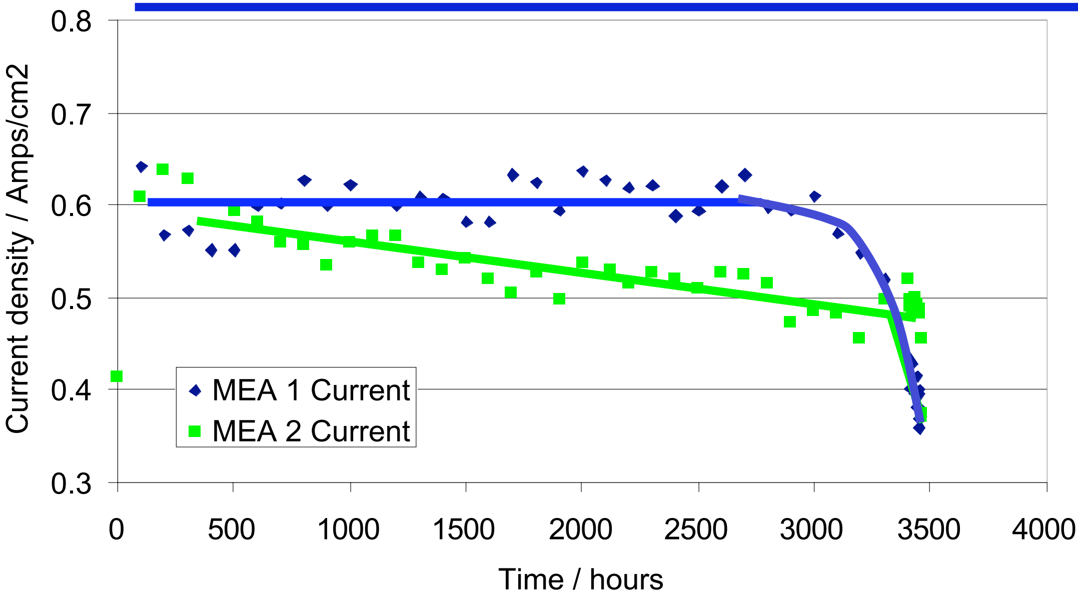
Fluorine



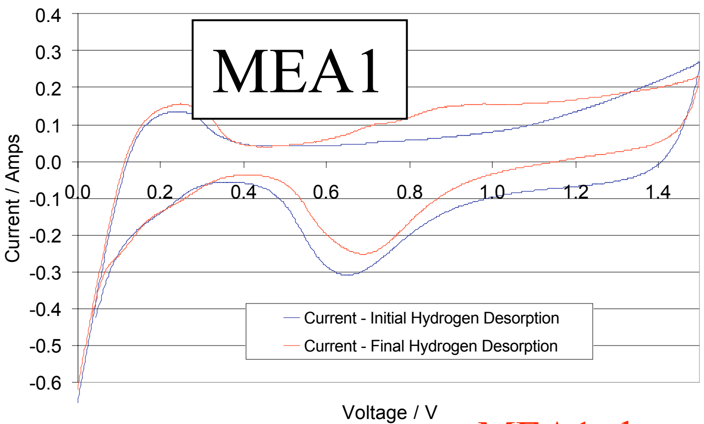
Sulfur



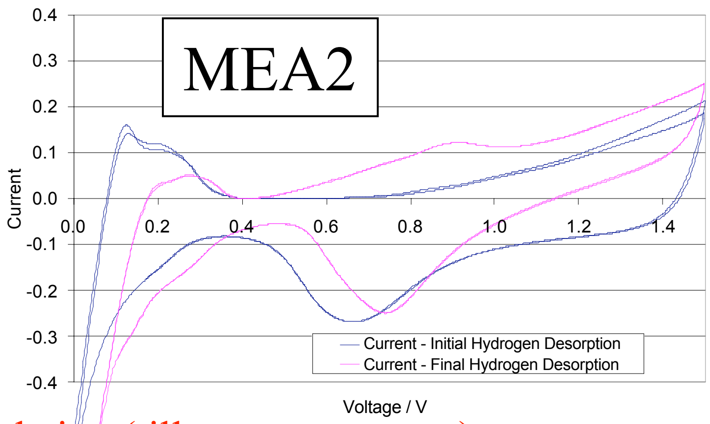
3500 hrs Life Tests (50 cm^2)



Constant Voltage: 0.6 V
Pt/Pt: 0.2 mg/cm2
N112
Cell Temp. = 80°C
Anode/Cath Humid. Temp = 105/80 ^oC
Anode/Cath Gas Press. = 15/15 psig
MEA1 Degradation:
~ 0 microamps / hr - (for 3000 hrs)
MEA2 Degradation:
~ 2 microamps / hr - (for 3000 hrs)



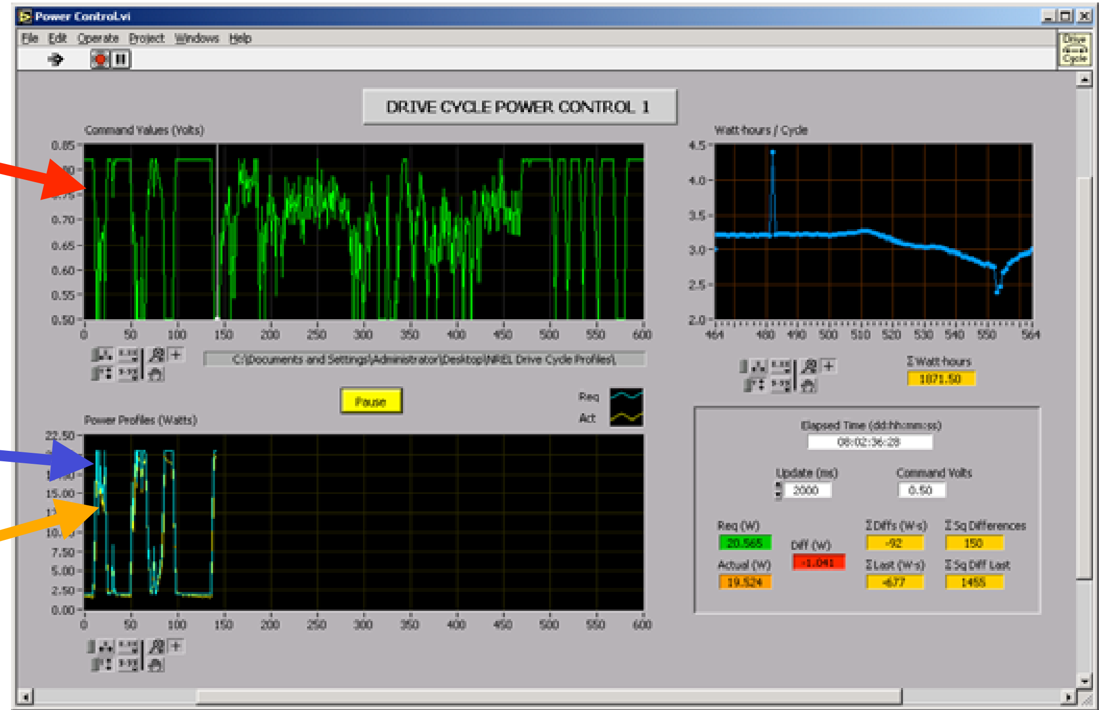
Surface area Reduction
MEA1:
Anode: 0%
Cathode: 14%
MEA2
Anode: 75%
Cathode: 86 %
Particle size same



MEA1 shows little/no performance degradation (till crossover starts)
MEA2 shows gradual performance degradation
cross-over developed in both MEAs at about 3000 hours

Fuel Cell Drive Cycle Testing

Voltage control profile:
Volt vs. Time (sec)



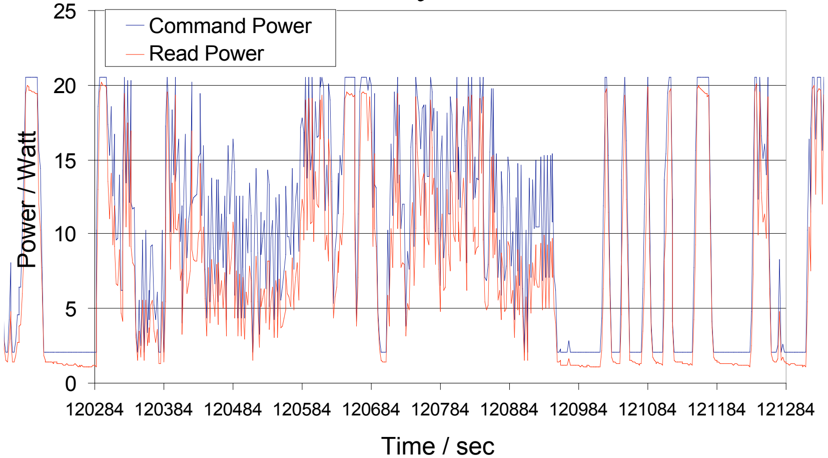
Power control profile
and
Power response profile
Watts vs. Time (sec)

1 cycle occurs over 20 minutes

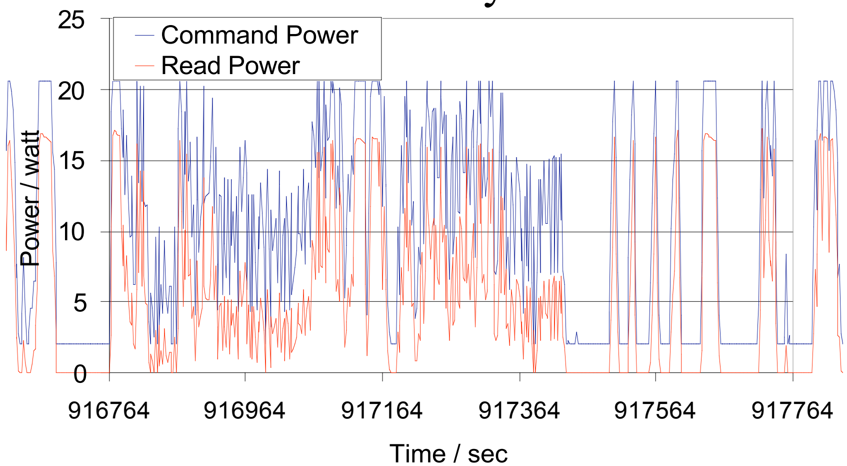
- Drive cycle ‘controls’ power
  - Uses fuel cell VIR to calculate voltage for a power level
  - Actively controls voltage to get power from VIR
- Current hardware with Labview control
  - 50 cm^2 single cell, Pt/Pt: 0.2 mg/cm^2, N112, Cell Temp. = 80°C
  - constant humidification and constant anode/cathode flowrates

Initial/Final Drive Cycle Comparison

~100 cycle



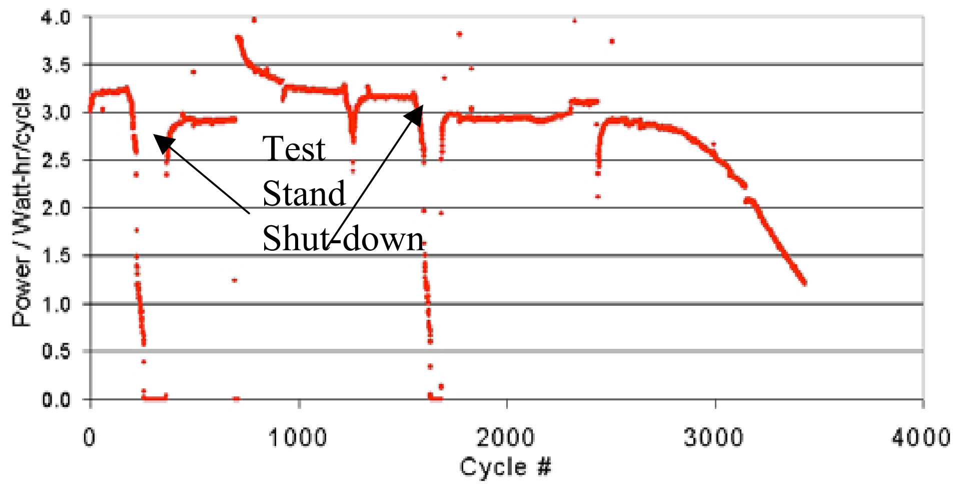
~ 3500 cycle



Blue is Control Power Cycle

Red is MEA Power Response

Power per cycle over 1200 hrs



Reduction in H_2 adsorption after testing:

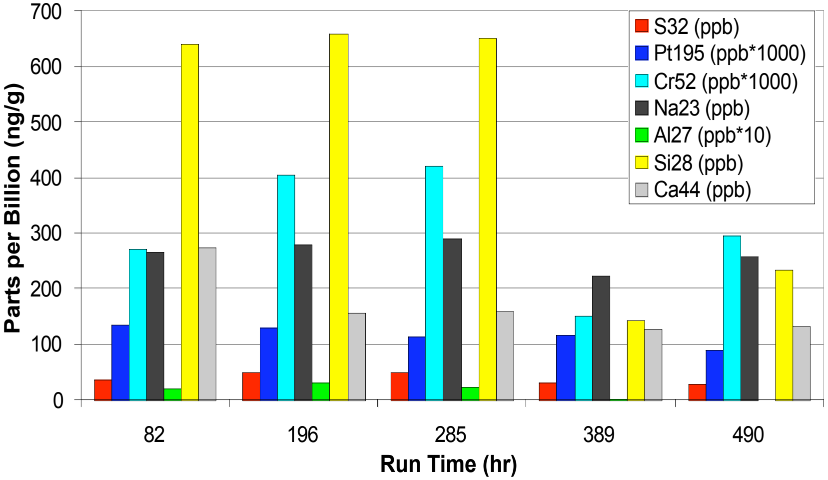
Anode: 31%

Cathode: 57%

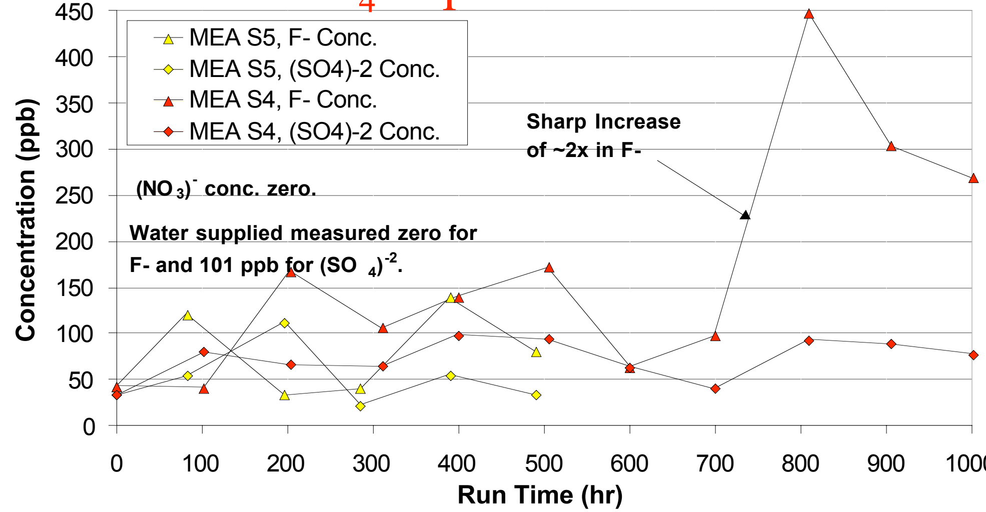
Fuel Cell Water Effluent Analysis

(S.S. constant current testing / Pt/PtCr 5 cm^2)

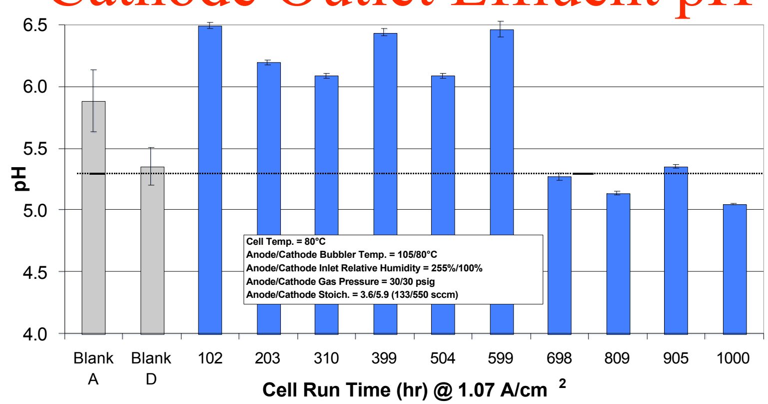
ICP-MS Analysis of Cathode Outlet Water through ~500 hr



Cathode Effluent F$^-$ and SO_4^{-2} Species Concentrations:



Cathode Outlet Effluent pH



Change in concentration of fluoride (F$^-$) and sulfate (SO_4^{-2}) anions

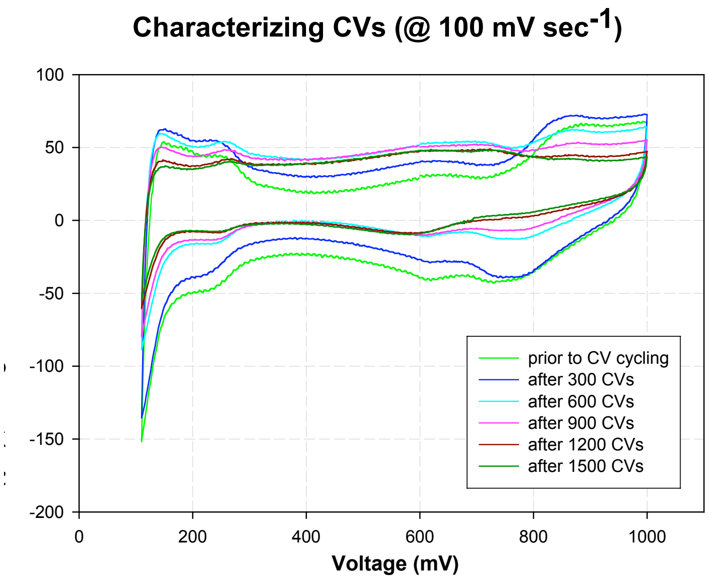
Sharp increase in F- may coincide with cross-over formation

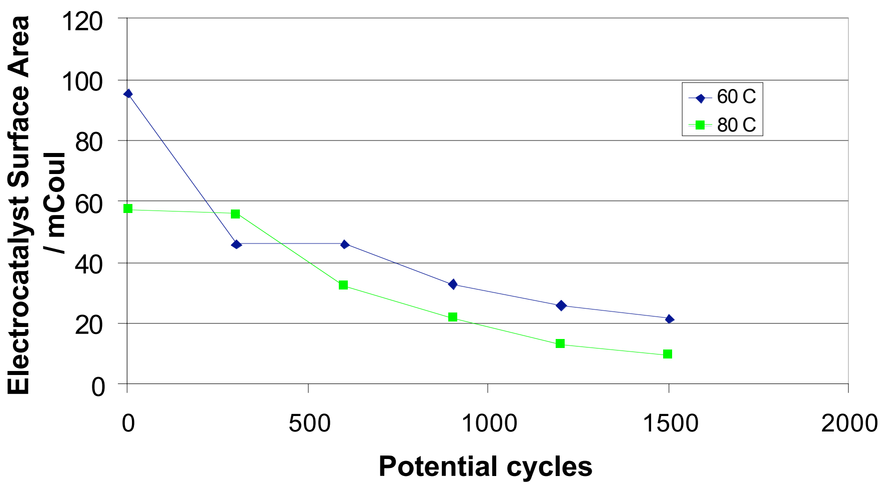
Change in pH also corresponds with increased crossover

Off-line Testing:
MEA Potential Cycling

- Obtain predictive, accelerated life test of PEMFC MEA, electrocatalysts.

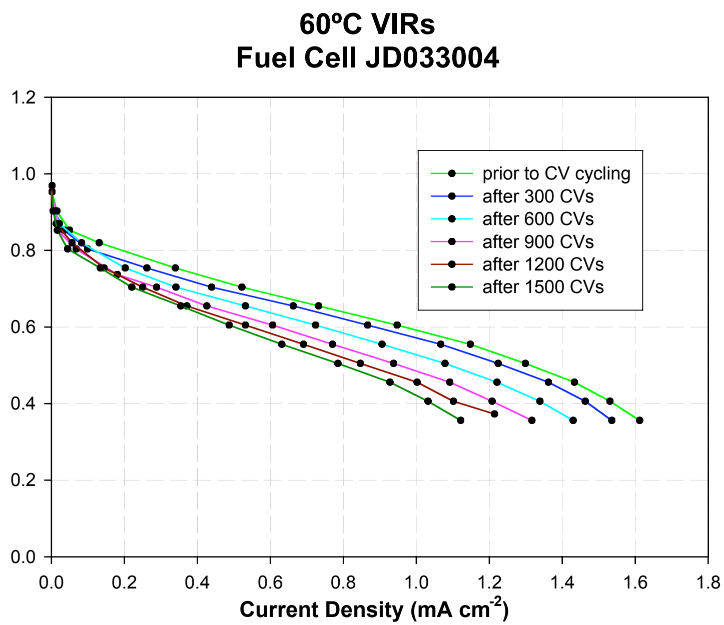
Within several hundred potential cycles of the MEA electrode, electrocatalyst surface area is decreased, as is MEA performance

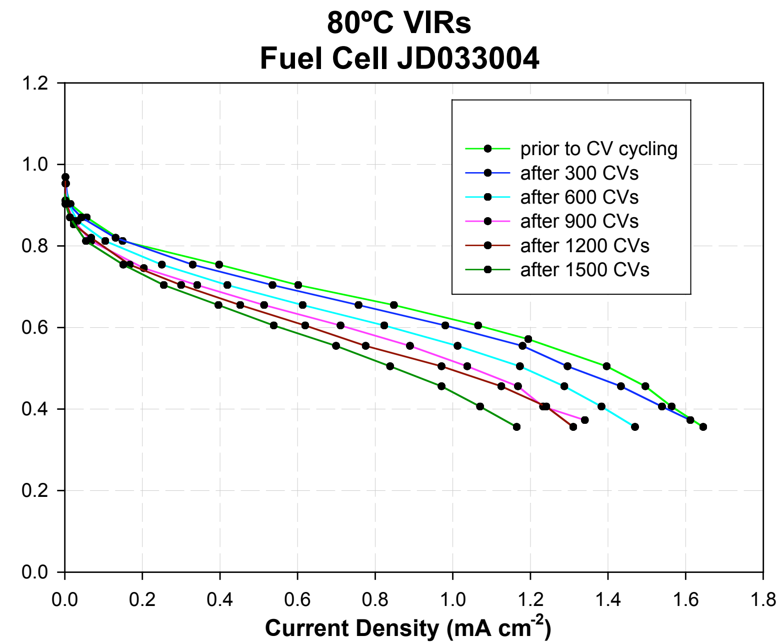




- Voltage cycling 0.1 V to 1.0, 1.2 V
- T_{cell} = 80 °C
- Anode humidifier = 105 °C
- Cathode humidifier = 80 °C

Potential Cycling of MEAs





XRD: Pt crystallite size

ANODE: 2.3 nm

CATHODE: 7.4 nm

XRD: Pt crystallite size

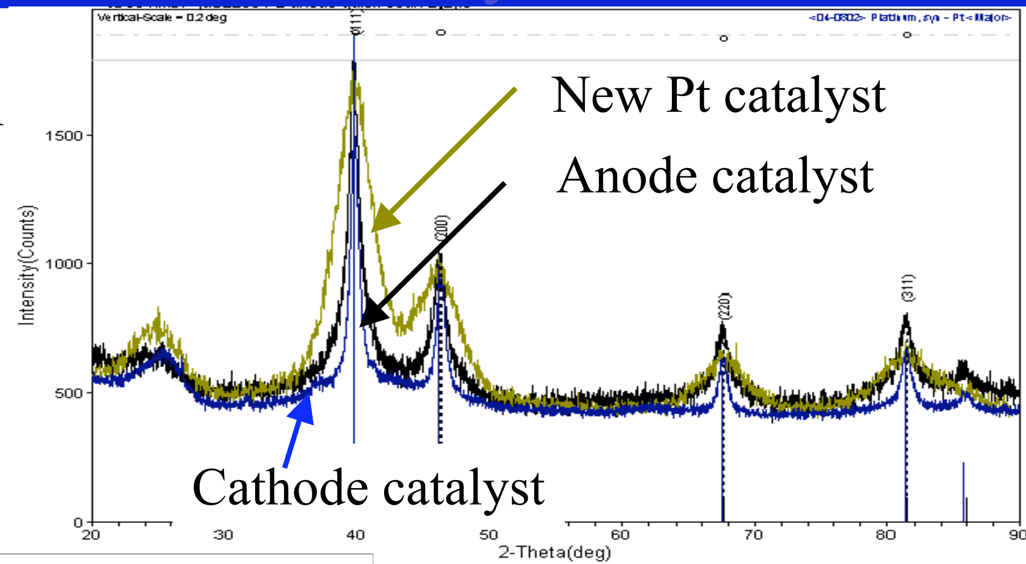
ANODE: 4.8 nm

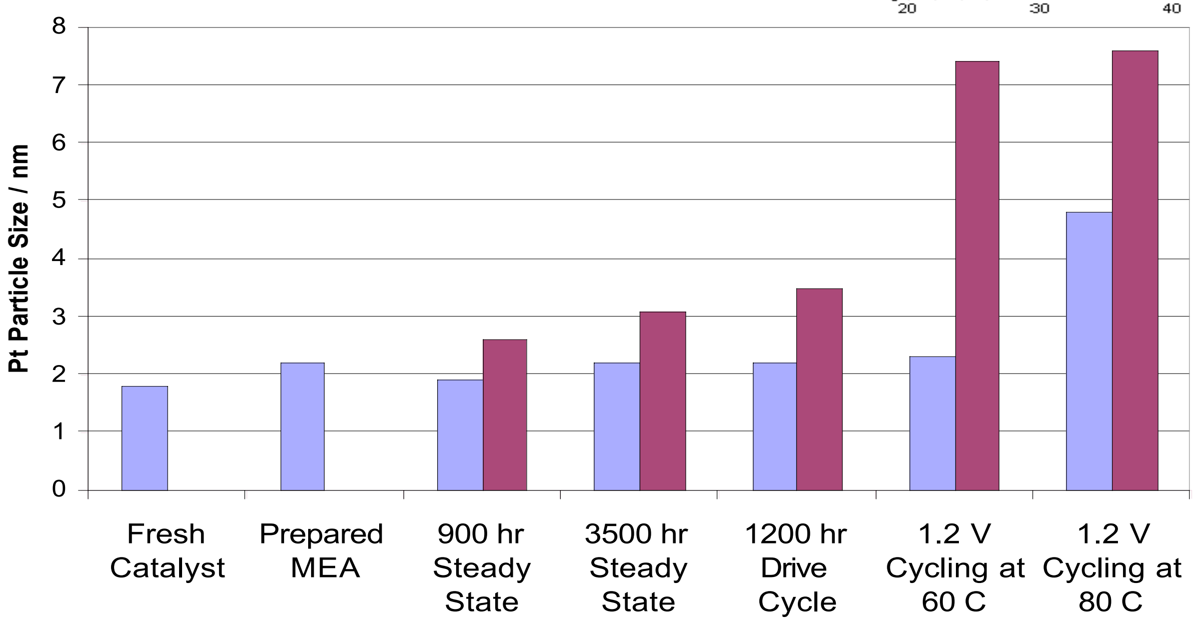
CATHODE: 7.6 nm

Electrocatalyst Size Growth

XRD analysis of electrocatalysts

- Electrocatalyst particle growth
  - Z with time
  - Z with drive cycle
  - Z with potential cycling
  - Z Temperature

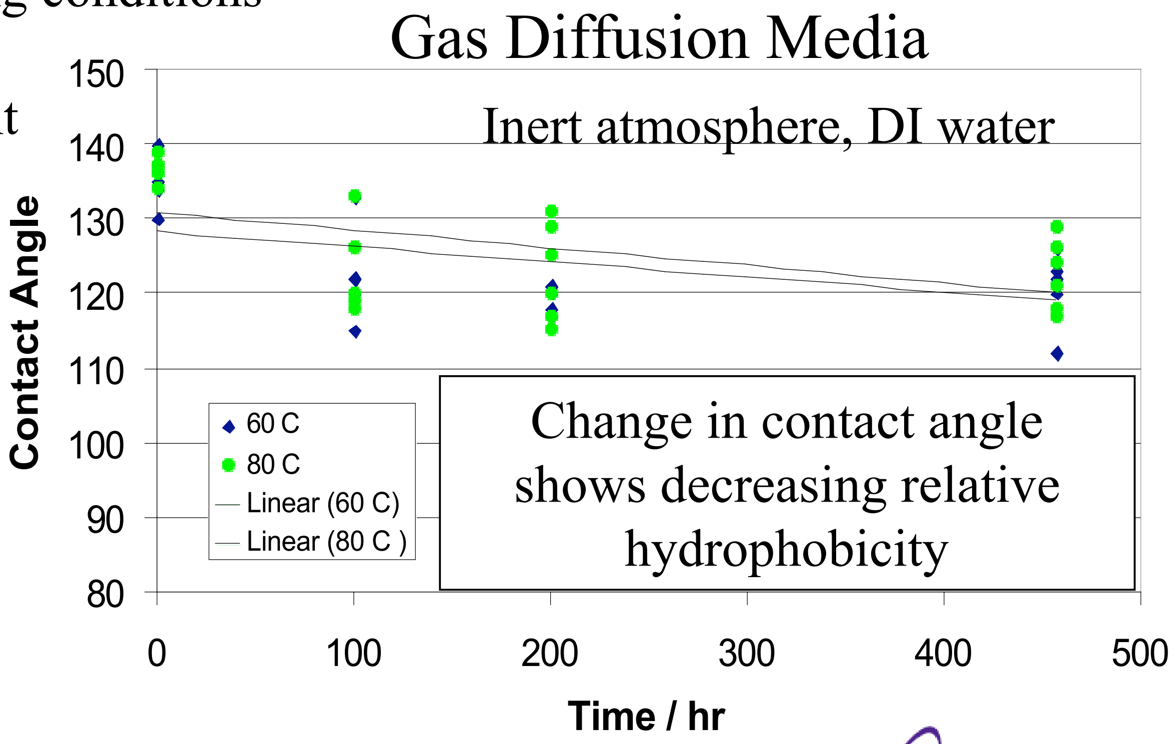




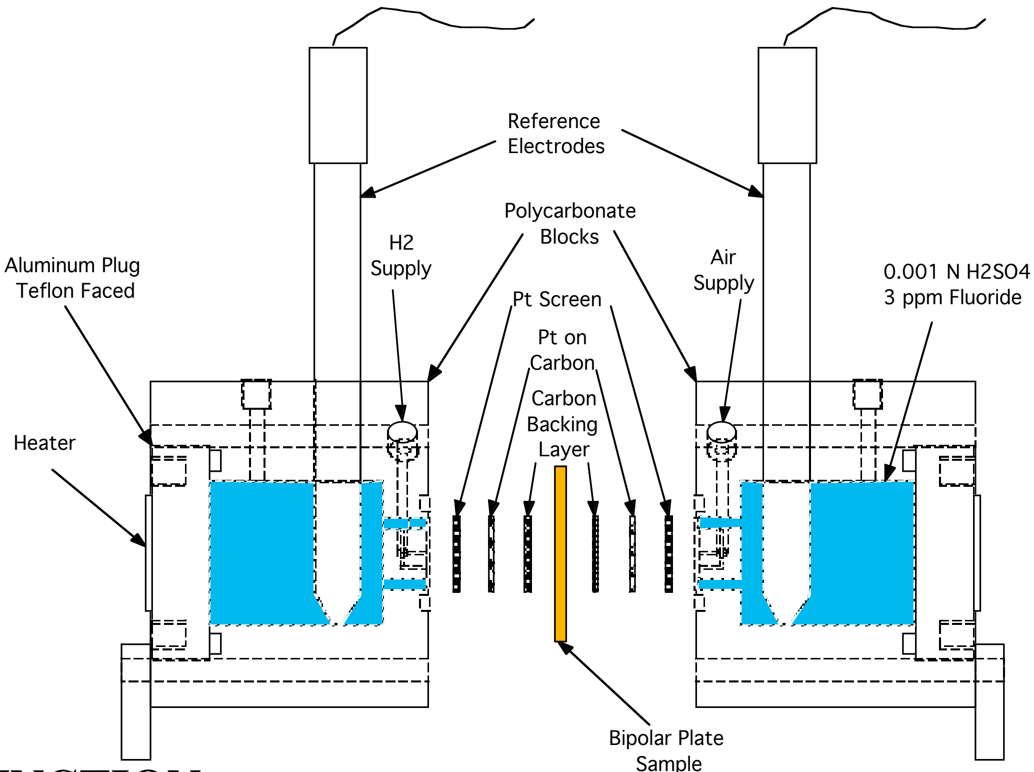
Off-line Testing: Enviromental / Leachate Chamber

- Isolation of components and separation of degradation effects
  - GDL, MEA, bipolar plates, gaskets, electrocatalysts
- Obtain predictive, accelerated life test for prospective individual components.
- Correlate PEMFC effluent water with components found in the off-line testing

- Simulate PEMFC operating conditions
  - Temperature
  - Chemical environment



Bipolar Plate Corrosion Test Cell



STATUS

- Developed in 1999 to 2000 with DOE funding
- Patented in 2002
- Tested candidate bipolar plate materials for Mike Brady (ORNL)
- Loaned, licensed cells to Ballard (2001 to 2003).
- Technology available for licensing

FUNCTION

- Simulates the bipolar plate environment (Temperature, anode and cathode potentials and acidity)
- Provides in-situ indication of contact resistance changes arising from corrosion film growth
- Electrolyte samples indicate production of soluble ions.

Interactions/Collaborations

- National Technical Presentations/Publications
  - Fuel Cell Seminar, ECS, JECS submission
- Fuel Cell Materials
  - MEAs (3M, Gore, LANL)
  - GDLs (Spectracorp, Toray, SGL, ETEK)
- Stack: Teledyne Energy Systems
- Characterization
  - ORNL (Douglas Blom and Karren More)
  - UNM (Plamen Atanassov)
  - LANL - NMT Division (Dave Wayne), C Division (Pat Martinez), LANSCE (Jaroslaw Majewski)
- Drive Cycle NREL (Tony Markel)

Project Safety

Management Safety Controls:

Hazard Control Plan (HCP) - Hazard based safety review
Integrated Work Document (IWD) - Task based safety review
Integrated Safety Management (ISM)
Define work → Analyze Hazards → Develop Controls → Perform Work → Ensure Performance

Engineering Controls:

Hydrogen and carbon monoxide room sensors
Electrically and computer interlocked with the test stand power, the gas supplies
H_2 sets off the CO sensors, (set at 30 ppm)
Limits H_2 far from the explosive limit

Safety Related Lessons

There have been no safety related incidents (& related projects).
Use of gas sensors, test stand interlocks limit hydrogen hazards.

Summary/Findings

- Steady-state and drive cycle testing of MEAs
  - MEA degradation quicker with drive cycle testing compared with S.S. testing
  - H_2 cross-over increases with time for both S.S. and cycling
  - Electrocatalyst active surface area decreases
  - Platinum particle size growth observed
    - higher particle growth with cycling, time
  - Change in conc. of fluoride (F^-), sulfate (SO_4^{-2}) anions, pH
    - coincides with increased cross-over ('hole') formation
  - A layer 50-100nm thick developed at the cathode/membrane interface
    - Layer is enriched in S and depleted in F in comparison to the membrane

- Off-line (accelerated) degradation techniques
  - High catalyst sintering during potential sweeps to high potentials
  - Temperature effect on anode catalyst sintering
  - GDL hydrophocity shows little change in DI water
  - Neutron scattering shows promise for delineating PTFE/Nafion degradation
  - Corrosion cell for bipolar plate testing

Future Plans

Remainder of FY 2004:

- correlate potential cycling tests to drive cycle testing
- correlate increase in F^- and SO_4^{-2} with cross-over in membrane

FY 2005:

- Membrane / MEA degradation
  - examine Nafion bonding via neutron scattering
  - simulate membrane cross-over by inducing penetrations
- Gas Diffusion Media
  - continue off-line testing determining hydrophobicity degradation
  - determine PTFE/graphite (GDL) bonding interaction changes
- Catalyst Durability / characterization
  - examine some Pt alloys for particle size growth
  - *in situ* XRD → real-time particle size analysis during simulated fuel cell operation