PEM Fuel Cell Durability

2008 DOE Hydrogen Program Review

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FC26

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Overview

Timeline

2001: Project started as Fuel Cell Stack Durability on Gasoline Reformate

2004: Changed focus PEM H_2 Durability

2007: Ended. Restarted at $300k

Barriers

- Durability
- Cost
- Electrode Performance

Budget

- FY04: $900k
- FY05: $950k
- FY06: $1000k
- FY07: $0 → $300
- FY08: $300

Collaborators

- No Formal Partners
- ORNL (Karren More)
- LANL H_2 Storage Center
- Analysis:
  - Univ. New Mexico, Augustine Scientific, LANL MPA-MC
- Materials:
  - Gore, SGL, Cabot Fuel Cells

Objectives:
Quantify and Improve PEM Fuel Cell Durability

2010-2015 Technical Target: 5000 hours Durability (with cycling)

- **Define degradation mechanisms**
- **Design materials with improved durability**
- **Identify and quantify factors that limit PEMFC Durability**
  - Measure property changes in fuel cell components during life testing
    - Life testing of materials
      - Examine testing conditions, incl. drive cycle
    - Membrane-electrode durability
    - Electrocatalyst activity and stability
    - Electrocatalyst and GDL carbon corrosion
    - Gas diffusion layer hydrophobicity
    - Bipolar plate materials and corrosion products
  - Develop/apply methods for accelerated and off-line testing
- **Improve durability**

Approach to Durability Studies

- Fuel Cell MEA Durability Testing and Study
  - Constant voltage/current/power and power cycling (drive cycle)
    - VIR / cell impedance
    - Catalyst active area
    - Effluent water analysis
- *in situ* and post-characterization of MEAs, catalysts, GDLs
  - SEM / XRF / XRD (*ex situ* and *in situ*) / TEM / ICP-MS / neutron scattering / H_2 adsorption / Inverse Gas Chromatography / Contact Angle / total porosity / hydrophillic vs. hydrophobic porosity
- Develop and test with off-line and accelerated testing techniques
  - Potential cycling
  - Environmental component aging, testing and characterization
  - Component interfacial durability property measurements

Durability Testing Issues

- Testing times can be lengthy (and costly)
  - 5,000 hrs = ~ 7 months (automotive target)
  - 40,000 hrs = ~ 4.6 years (stationary system target)
  - ***Need relevant accelerated testing***
  - ***Need to close 'field / lab gap' or 'transfer function'***
    - ***Lab single cell → 'real' stacks → field data***

- Operating variables effect not fully understood
  - ***Many degradation mechanisms likely yet undefined***
  - Power transients - vehicle fuel cell/battery hybridization
  - Transient power, temperature, RH
  - Shut down / start-up

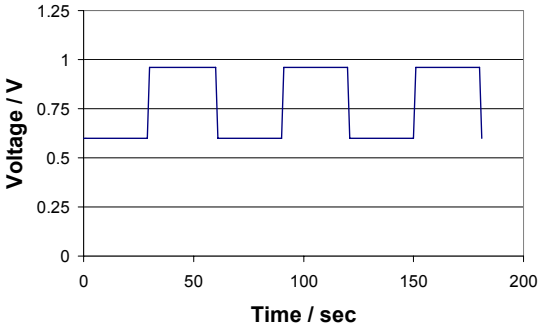
- Materials still being developed and improved
  - ***Need relevant accelerated testing***

Comparison of Accelerated Testing Methods

USFCC Accelerated Catalyst Test #1

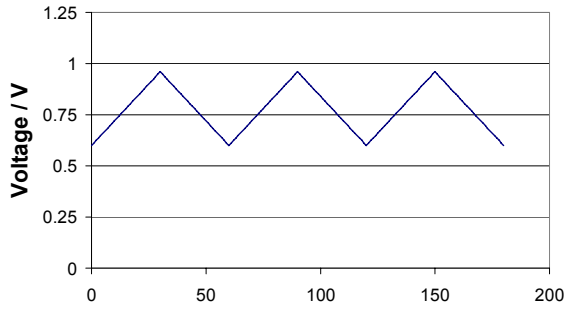
Step vs. Triangle Potential Cycle

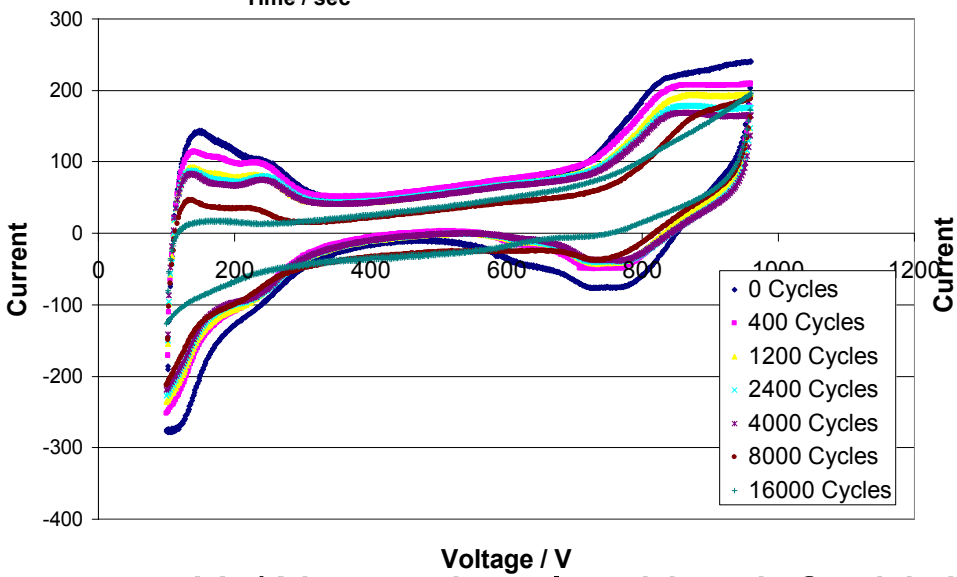
Step Potential Cycle

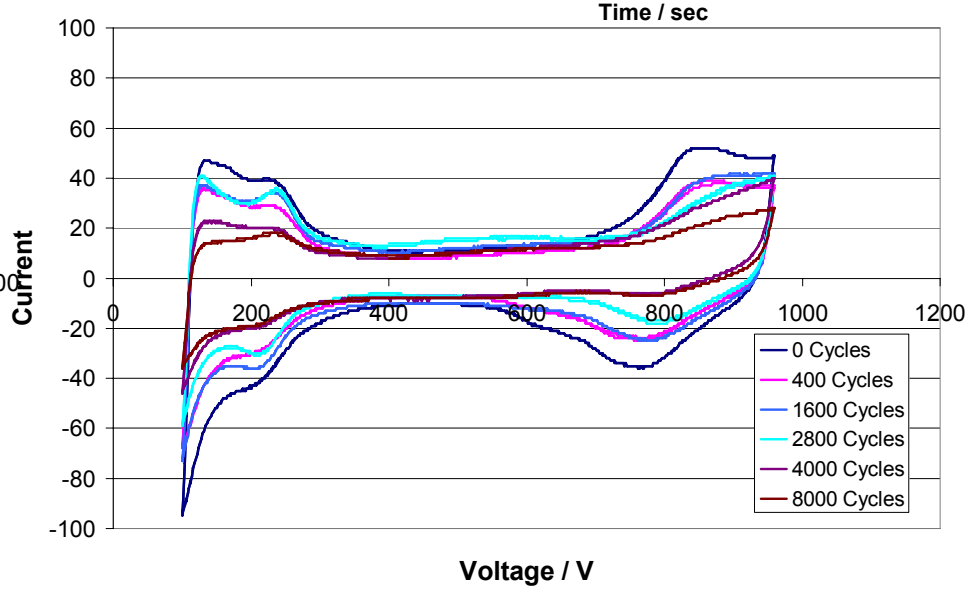


- Accelerated catalyst testing by potential cycling in H_2 / Air
- Voltage cycling: 0.6 and 0.96V (H2/Air)

Triangle Potential Cycle







- H_2/Air requires load bank for high current (can't use potentiostat).
- Some MEAs do not reach 0.96V OCP with standard load control
- Triangle potential sweep shows much faster degradation

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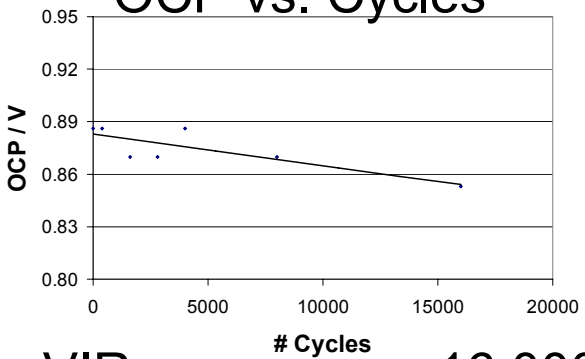
Comparison of Accelerated Testing Protocols

Test #1. Voltage cycling: 0.6 and 0.96V (H_2/air)
Step vs. Triangle Potential Cycle

Step Potential Cycle

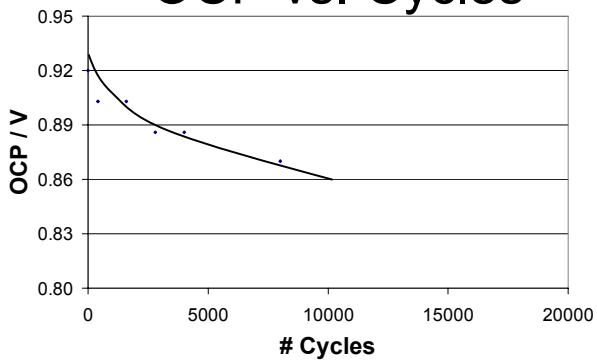
OCP vs. Cycles



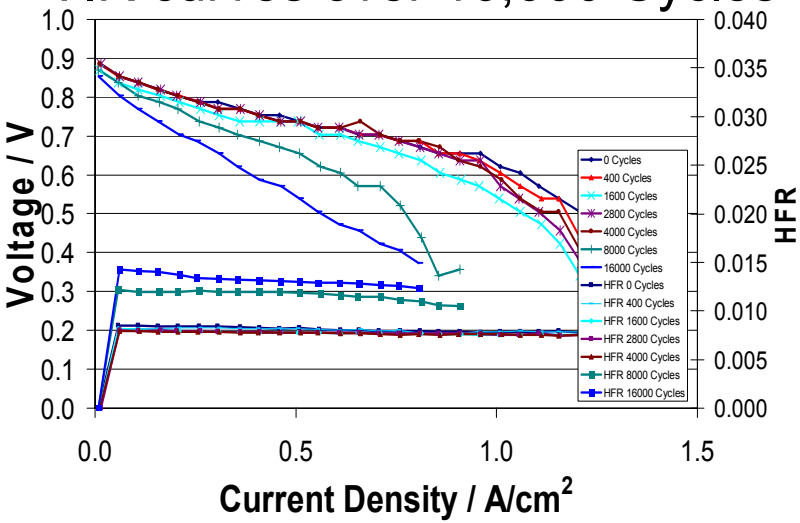
- OCP decreases with cycles
  - Varies potential limits
- Increase in sample HFR
- H_2/Air cycling not just catalyst degradation

Triangle Potential Cycle

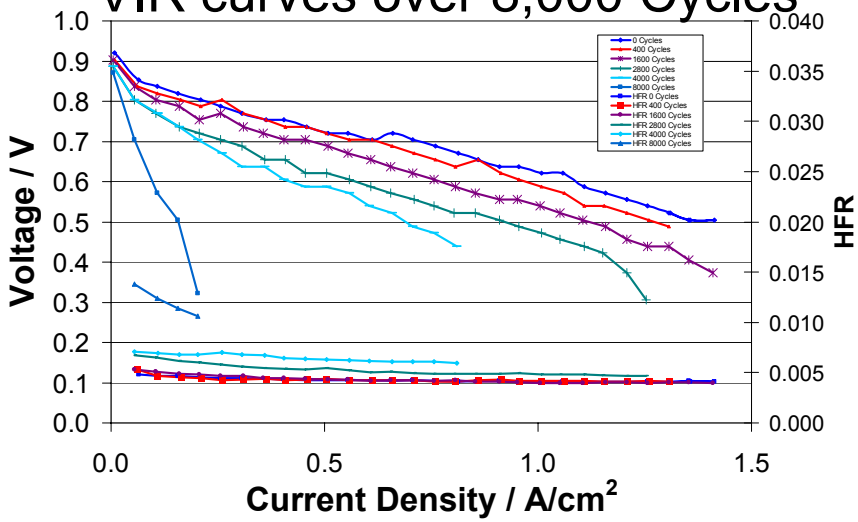
OCP vs. Cycles



VIR curves over 16,000 Cycles



VIR curves over 8,000 Cycles



- Difficulties with this test being consistent and repeatable
- Does not separate catalyst durability from other components

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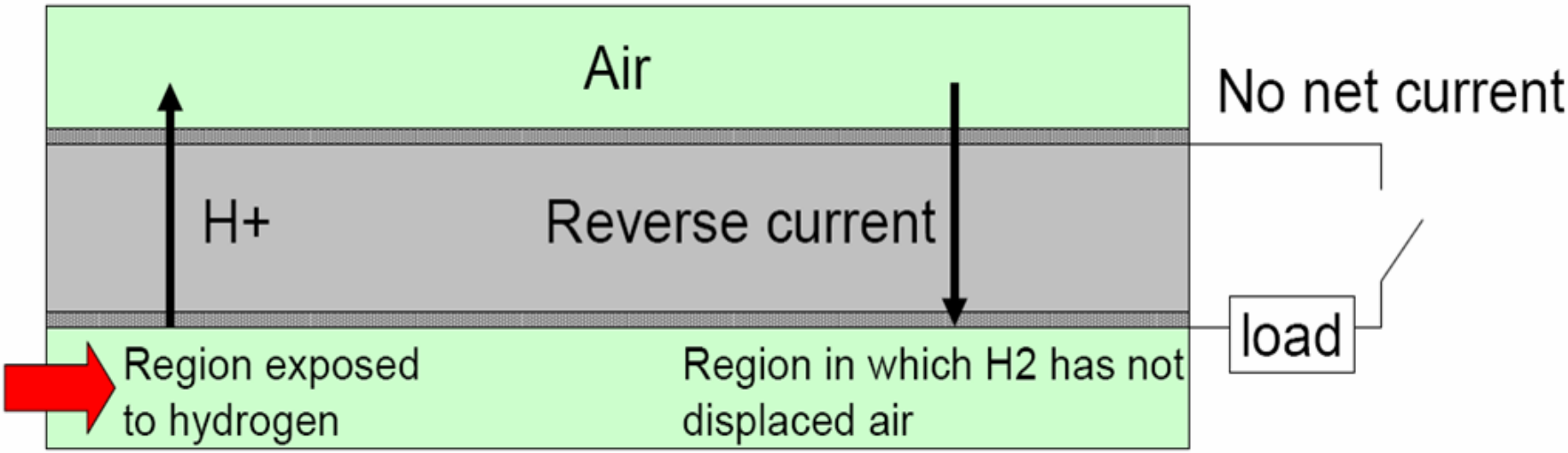
Shut-down/Start-up Effects

- 'Reverse Current' degradation
  - Non-homogeneous mixture of H_2 on anode
  - H_2/air portion of cell drives 'reverse current' elsewhere

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\qquad$ $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$

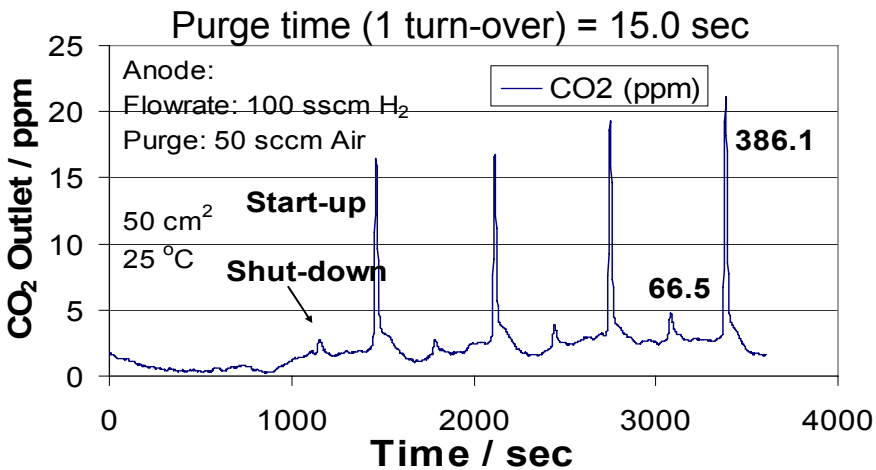


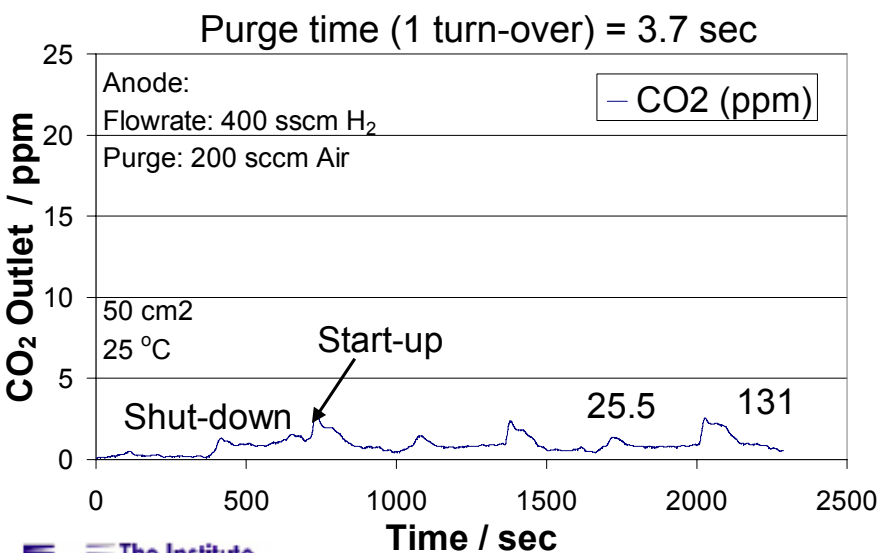
$H_2 \rightarrow 2H^+ + 2e^-$ $\qquad$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Modified from: Sathya Motupally, UTC Power

Stop-Start Cycling Effect on Carbon Corrosion

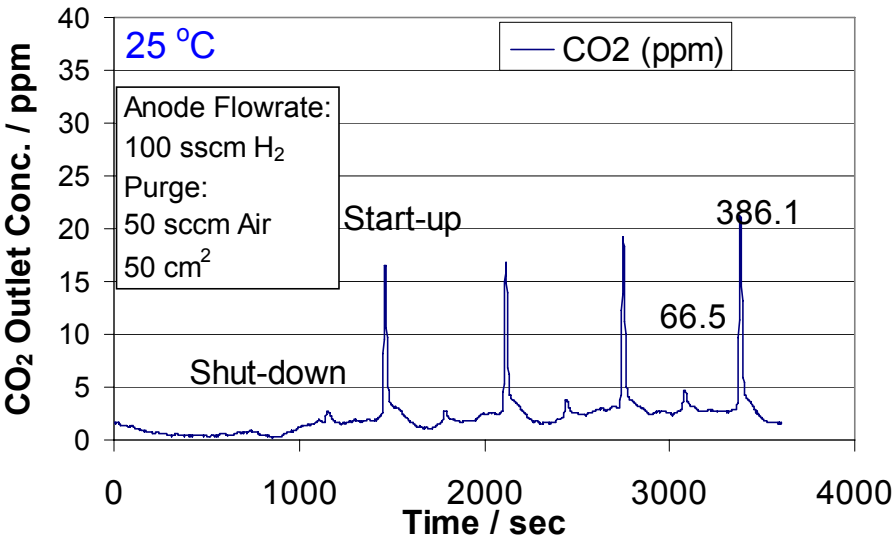
Anode Purge Rate Comparison

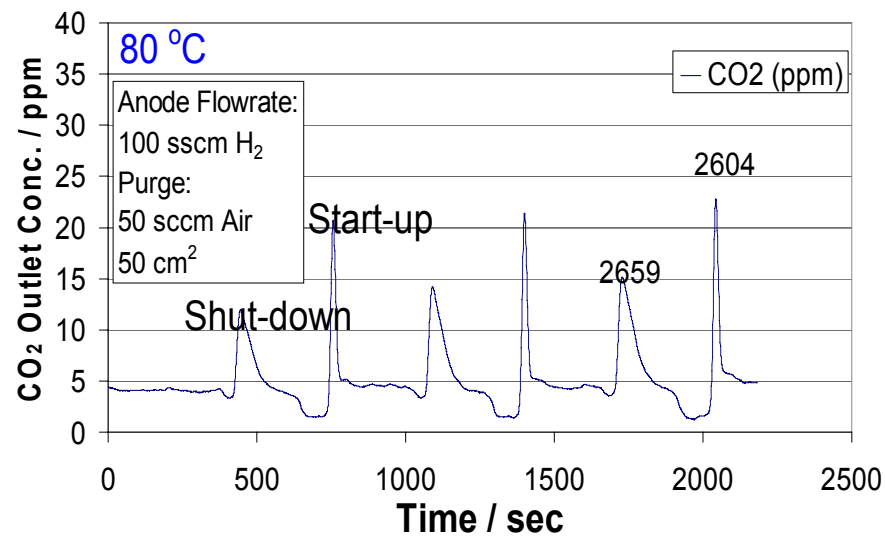


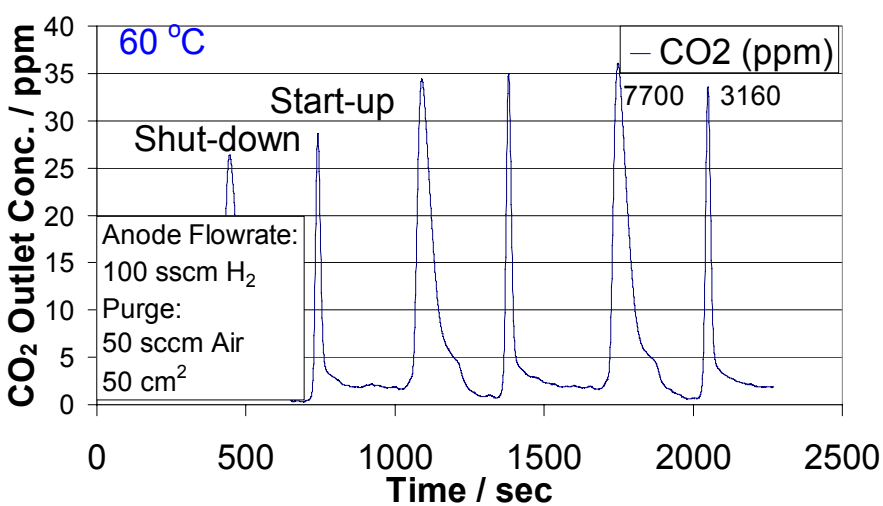


- Operation
  - OCV and dry air (250 sccm) continuously to cathode
  - Shut-down: anode dry air purge: 5 min.
  - Start-up: flow dry H_2 to anode: 5 min.
  - Measure CO_2 (and CO) evolution at cathode by NDIR (Non-dispersive Infrared)
- Results
  - Increasing anode gas change-over rate decreases CO_2 evolution
  - More CO_2 evolution at start-up compared to shut-down, 25 °C
  - Small amounts of CO produced

Temperature Effect on Carbon Corrosion During Stop-Start Cycling







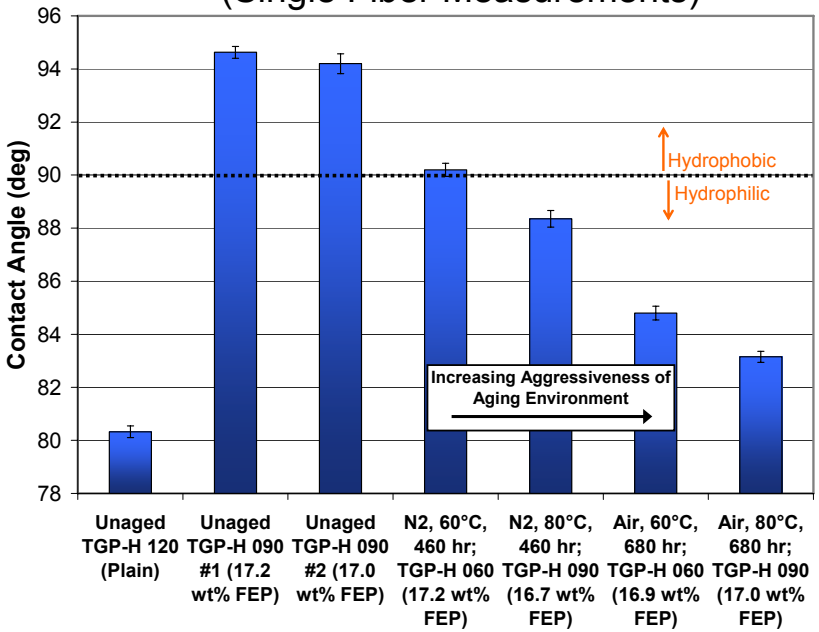
- CO_2 Evolution at Slow Purge Rate
  - 25 °C
    - Higher at start-up than shut-down
    - Much lower evolution than at 60 °C
  - 60 °C
    - Greatest evolution
    - Higher evolution at shut-down
  - 80 °C
    - Non-zero steady-state evolution
    - ~ Equal shut-down/start-up evolution

GDL Durability

Contact Angle Changes

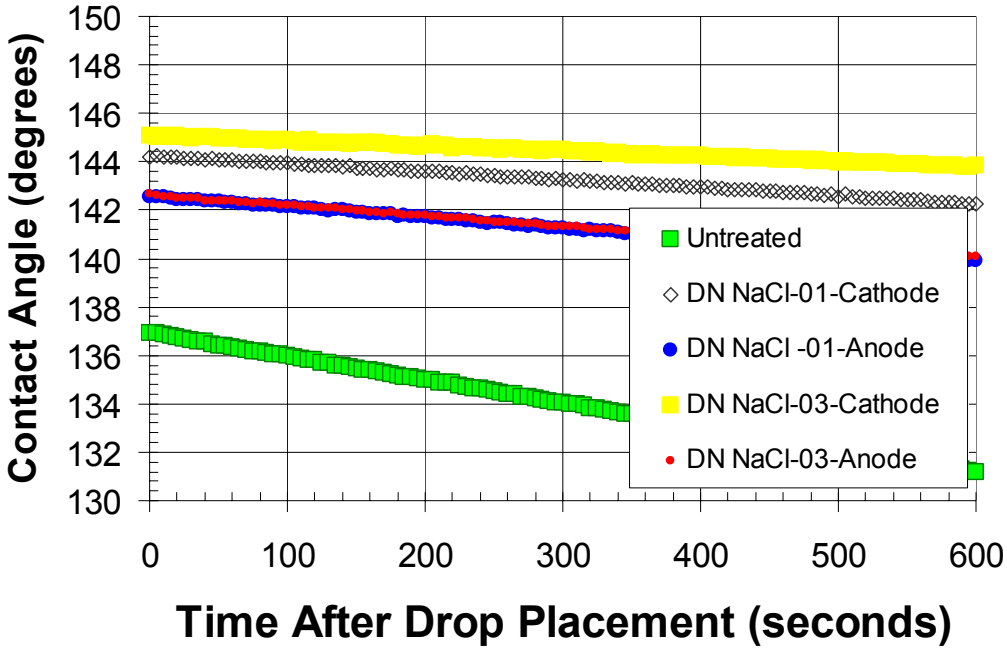
Contact angles with aging

(Single Fiber Measurements)



Contact angles with NaCl exposure

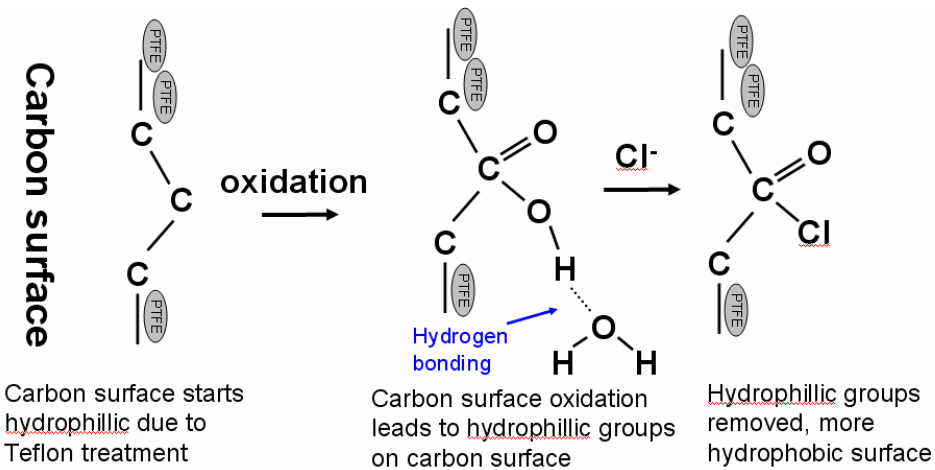
(Paper Sessile Drop Measurements)



- GDLs lose hydrophobicity with aging
- Exposure to NaCl make GDLs more hydrophobic
  - Also slows rate of water uptake

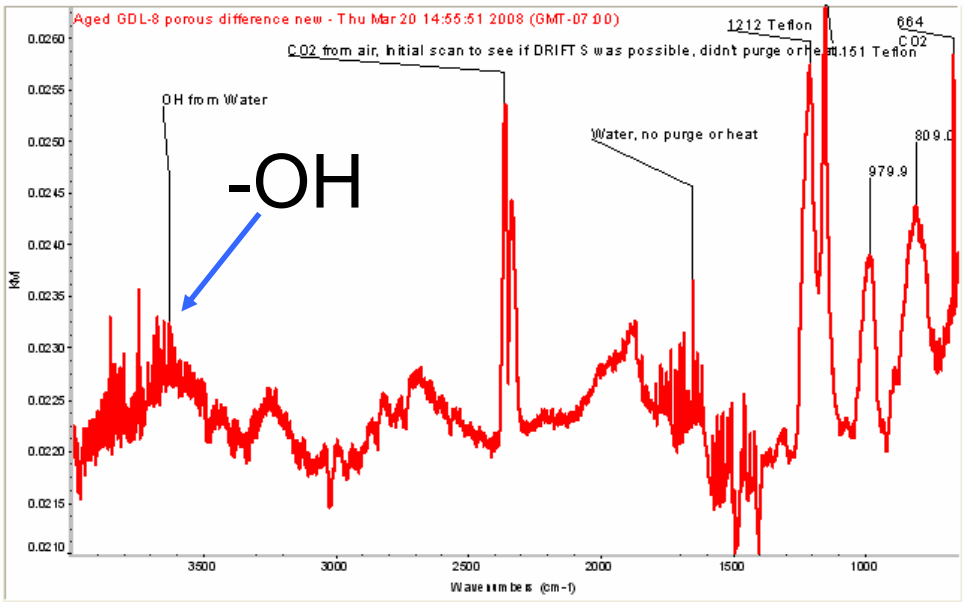
Surface Analysis of GDL Material

- Confirm –COOH surface species
  - Observe –OH and C=O IR
- Confirm acyl chloride
  - Reduction of –OH, and/or C-Cl



DRIFTS Spectra of Aged GDL

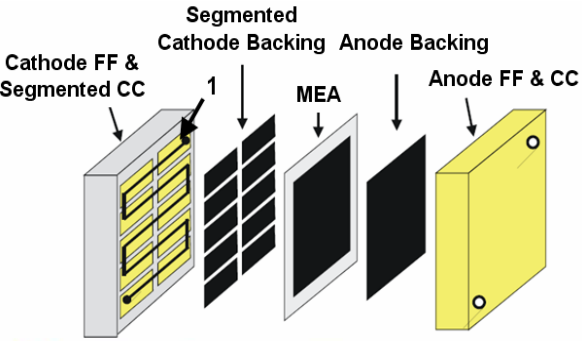
(Diffuse Reflectance Infrared Transmission Spect.)

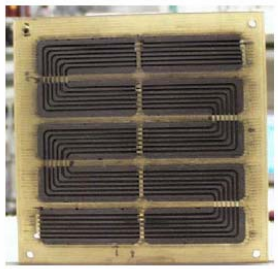


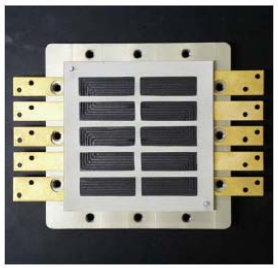
- -OH species identified
- Not yet satisfactorily identified surface species
- Using DRIFTS, will also explore Raman

Spatial Resolution of Durability:
Individual Fuel Cell Segments: VIRs over Time

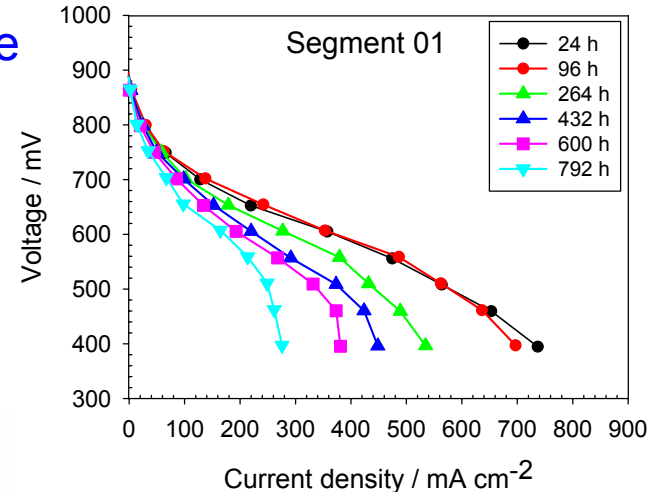
Segmented Cell Hardware

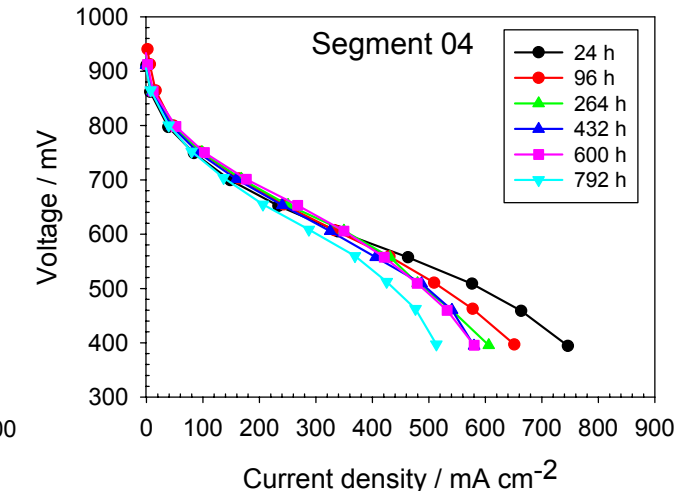


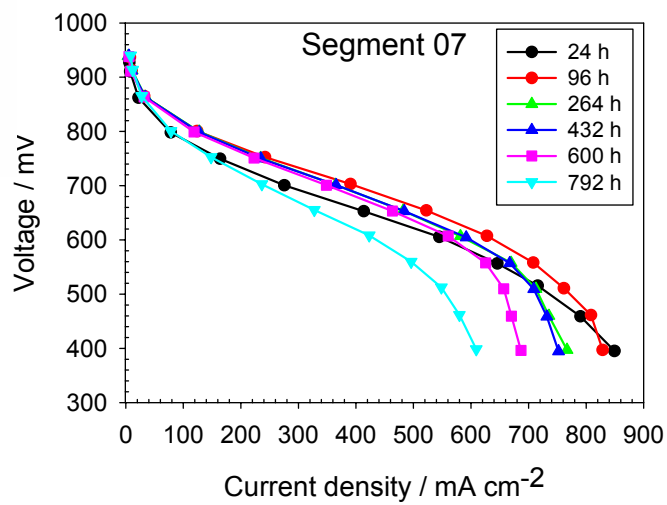


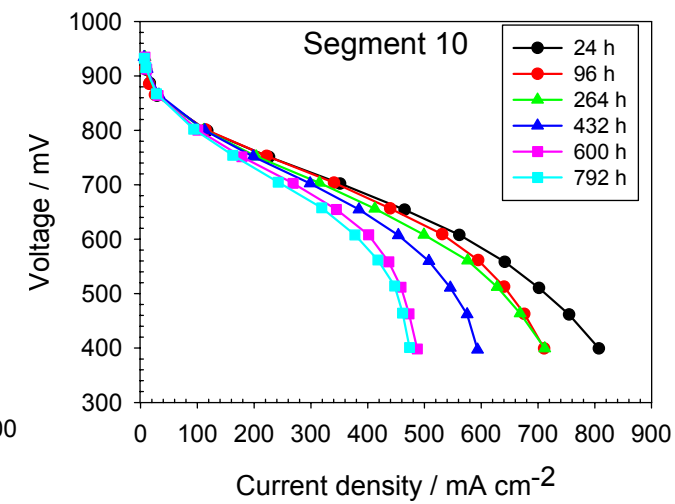


Segmented six parallel channel serpentine flow-field (left side) and segmented cathode hardware including gasket and current collector plates.
Segment-- 7.7 cm^2
Total– 77 cm^2



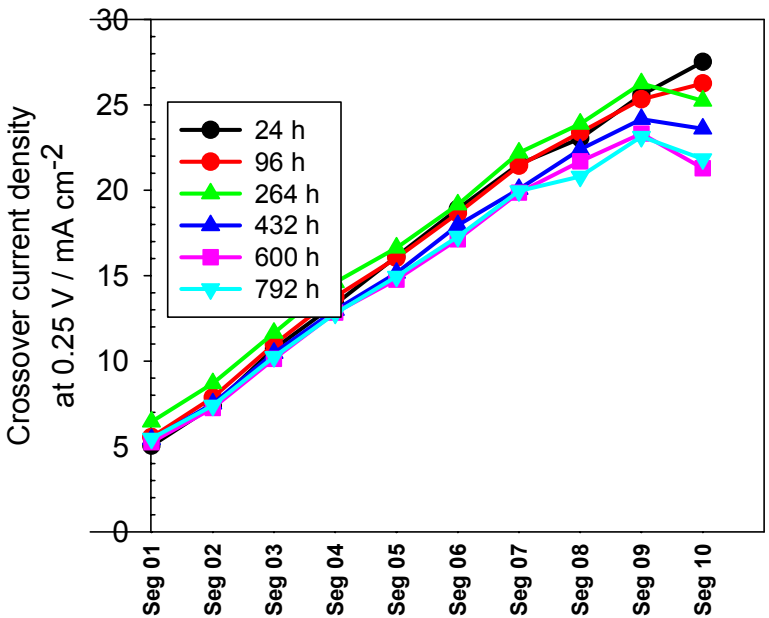


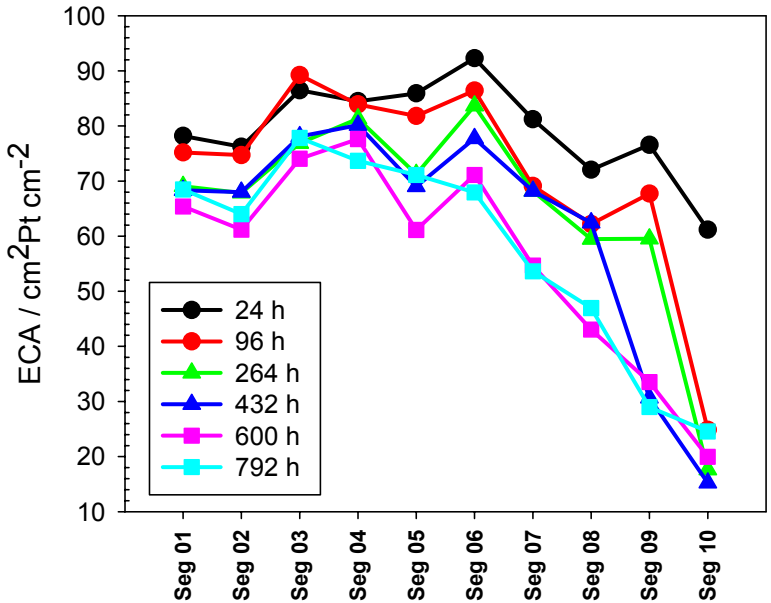




- Performance degradation greater at fuel cell inlet and near outlet

Crossover Current Density
Electrocatalyst Surface Area





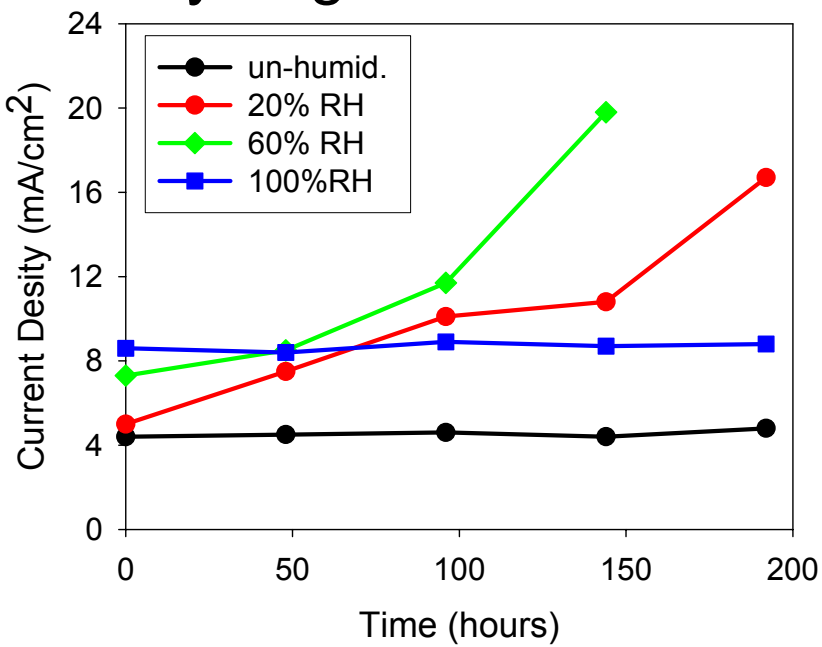
- H_2 cross-over per segment is ~ constant
- Unclear about segment 10

Note: Because of segmented flowfield traversing in series, each subsequent segment cross-over is cumulative for all previous segments

- Loss of electrocatalyst surface area (ECA) predominately at cathode outlet
  - (higher water content)
- Loss of ECA at inlet doesn't explain significant performance loss at inlet

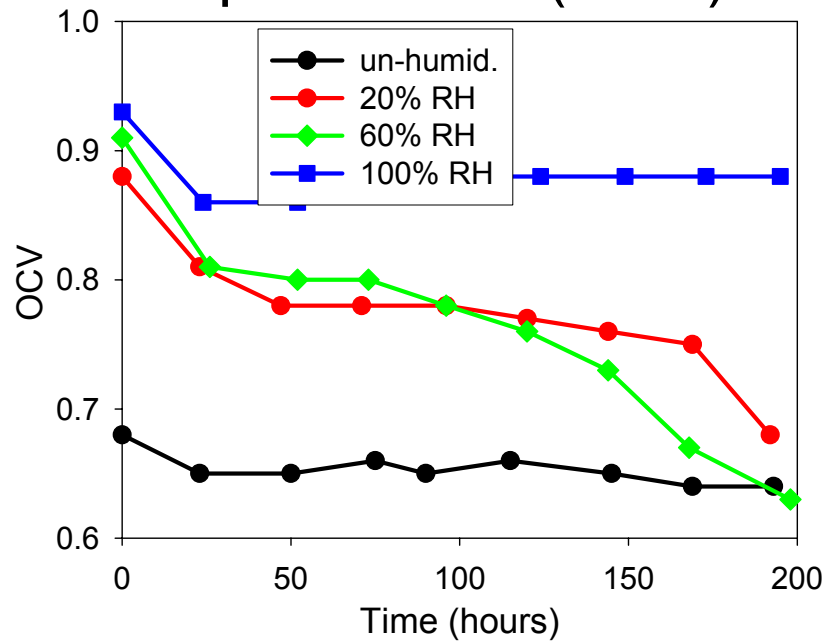
RH Effect on Membrane Degradation

Hydrogen Crossover



- Increase in H_2 crossover at medium RHs (20-60%)

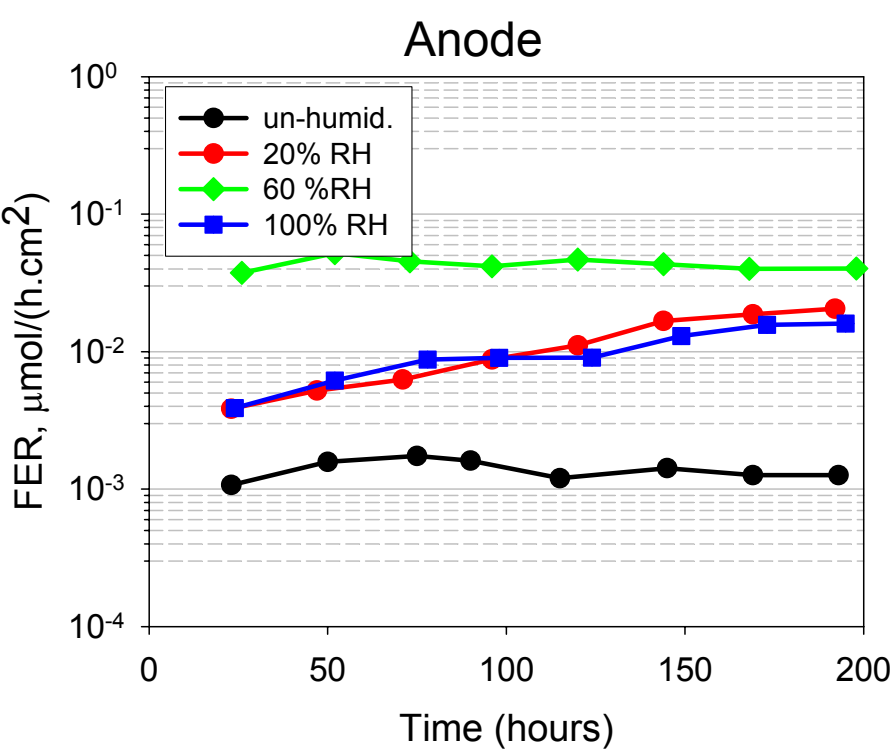
Open-Circuit (OCP)

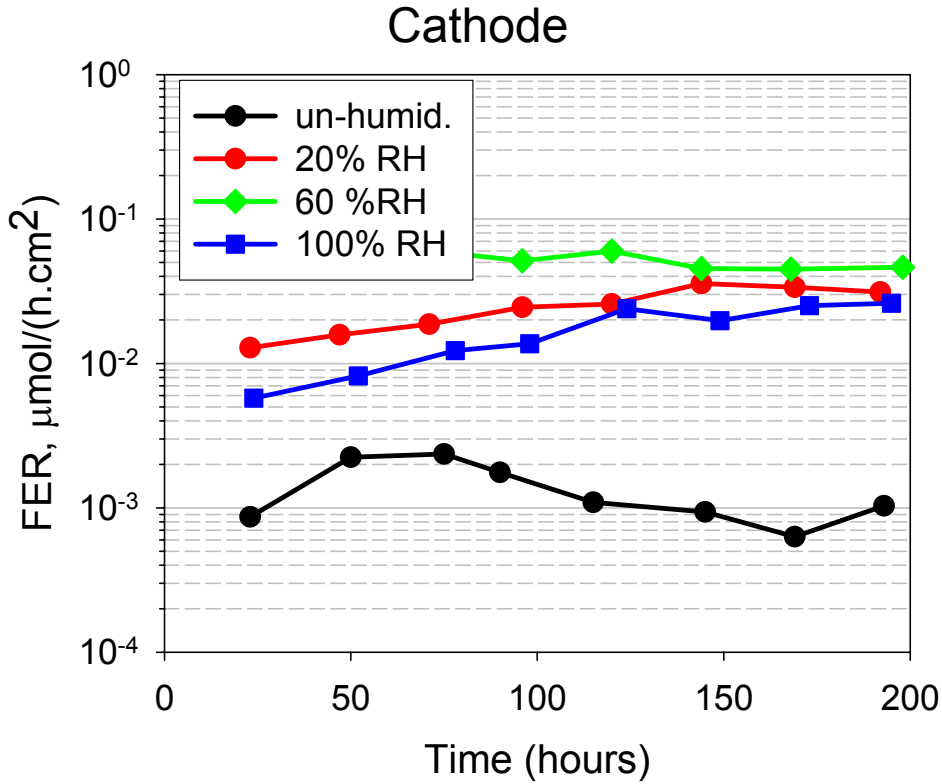


- Stable OCP at 100% RH
- OCP degrades at 20 & 60% RH
  - More H_2 and O_2 crossover results in greater H_2O_2 formation

H2, 500 sccm, 26psi; cathode: air/N2, 1000 sccm, 26psi.

Fluoride Emission Rate (FER)



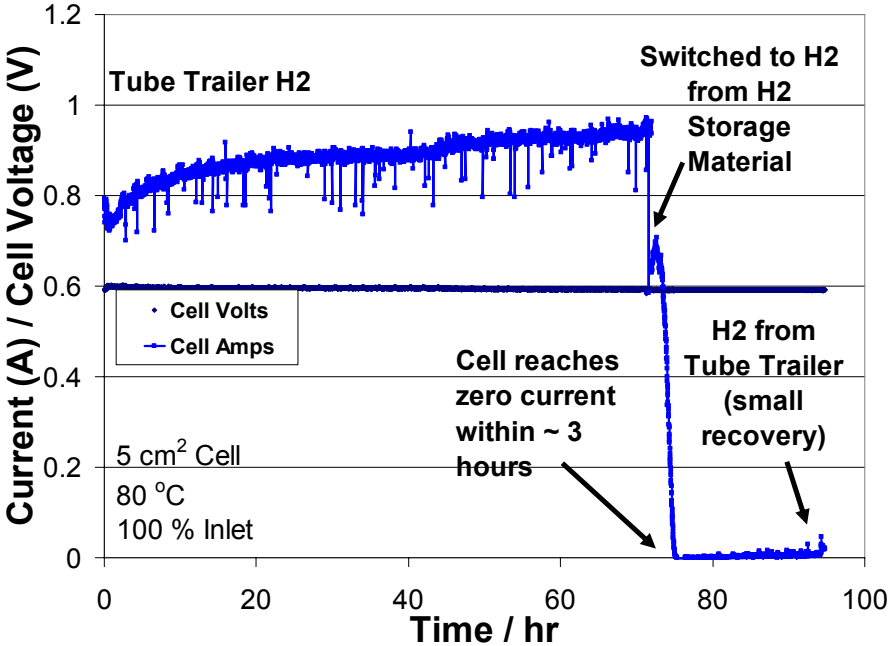


- Highest fluoride ion emission rate at 60% RH at anode and cathode
- 20% RH rate similar to 100% RH rate

Anode: H2, 500 sccm, 26psi; cathode: air, 1000 sccm, 26psi.

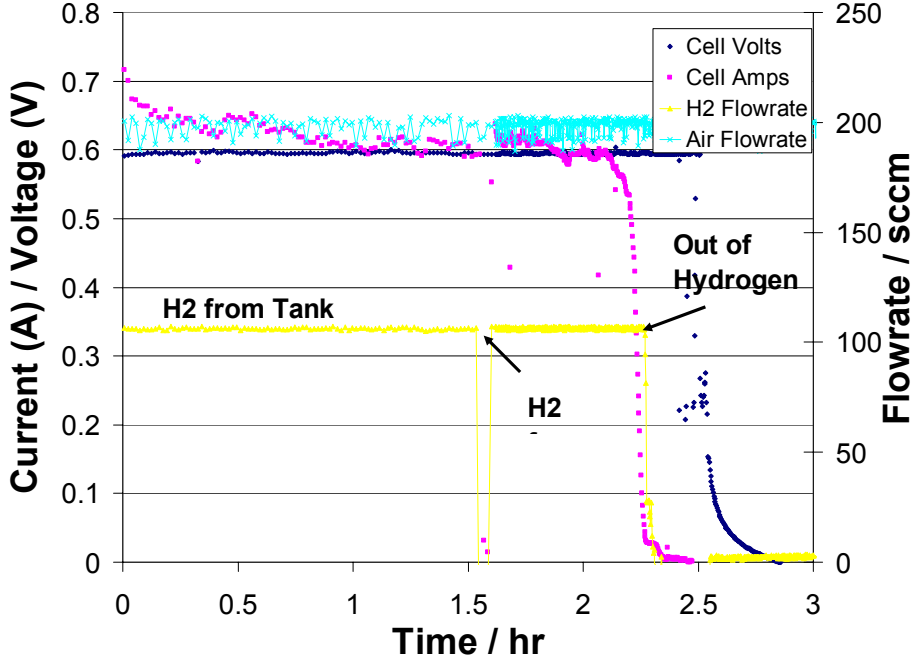
Durability Test with Hydrogen from Chemical Hydride

Test #1



- Immediate decrease in cell performance upon switching to H_2 from H_2 Storage Material
- Complete failure in 3 hours
- Gas analysis suggests B-N species

Test #2



- Cell gradually recovered ~ 80% over several days
- Used carbon filter in H_2 line
- No immediate decrease in performance
- Simple filtration may work

Milestones

PEM Fuel Cell Durability

Mon Yr	Milestone	
May 07	Shut-down / start-up protocol comparison of degradation rates	✓ Carbon corrosion
Dec 07	Electrocatalyst particle size growth measurements performed on 2010 and 2015 DOE target loadings	✓
Jan 08	Comparison of off-line potential square-wave cycling with fuel cell operation with square-wave cycling	✓ DOE/USFCC H2/Air H2/N2
Jun 08	Segmented Cell Operation	✓ S.S.
Sept 08	Peroxide formation results as function of Temperature, Operating potential and Electrocatalyst	

Summary - Durability Testing

- Durability testing remains difficult and time intensive
  - Time constraints led to accelerated type testing
  - Decay mechanisms required to define accelerated test protocols
    - Need to understand all degradation mechanisms
  - Need to correlate accelerated testing with real fuel cell life

- Operational variables important to component durability
  - RH, temperature, potential and potential cycling
  - Shut-down / start-up variations important to corrosion

- Components
  - Electrocatalyst (Particle growth)
  - Membrane (Chemical and mechanical degradation)
  - GDL (Hydrophobicity loss/gain, porosimetry losses)

Future Activities

- Not sure of future funding status (>FY08)
- MEA durability measurements
  - Drive cycle testing, operating effects (shut-down), spatial distribution
  - Identification of degradation mechanisms
- Accelerated testing and durability correlation
  - Correlate accelerated durability tests to fuel cell performance
  - Continue to develop accelerated tests for degradation mechanisms
- Component interfacial durability property measurements
  - GDL / MEA catalyst layer material interfacial contact

Remainder of FY08:

- Evaluate surface species leading to hydrophobicity changes
  - (both decreasing and increasing)
- Evaluate mechanisms leading to change in hydrophobicity
  - Examine Nafion / PTFE degradation and carbon bonding