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

Budget

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

Barriers

- Durability
- Cost
- Electrode Performance

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

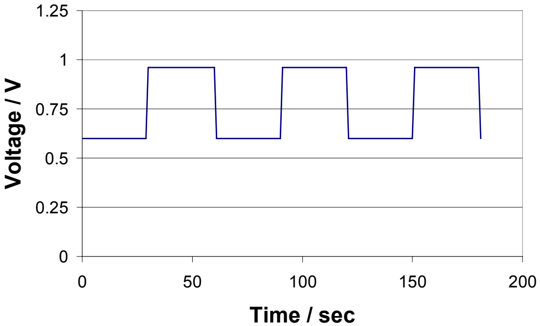
- Materials still being developed and improved
  - ***Need relevant accelerated testing***

Comparison of Accelerated Testing Methods

USFCC Accelerated Catalyst Test #1

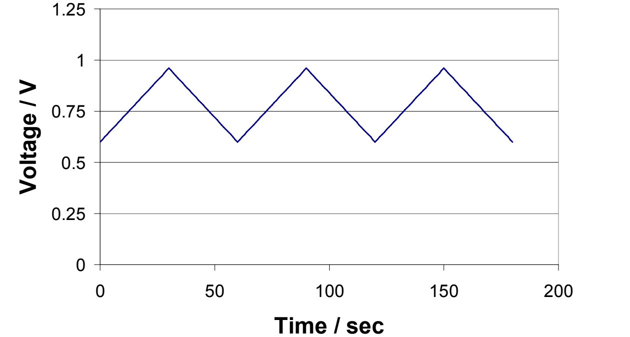
Step vs. Triangle Potential Cycle

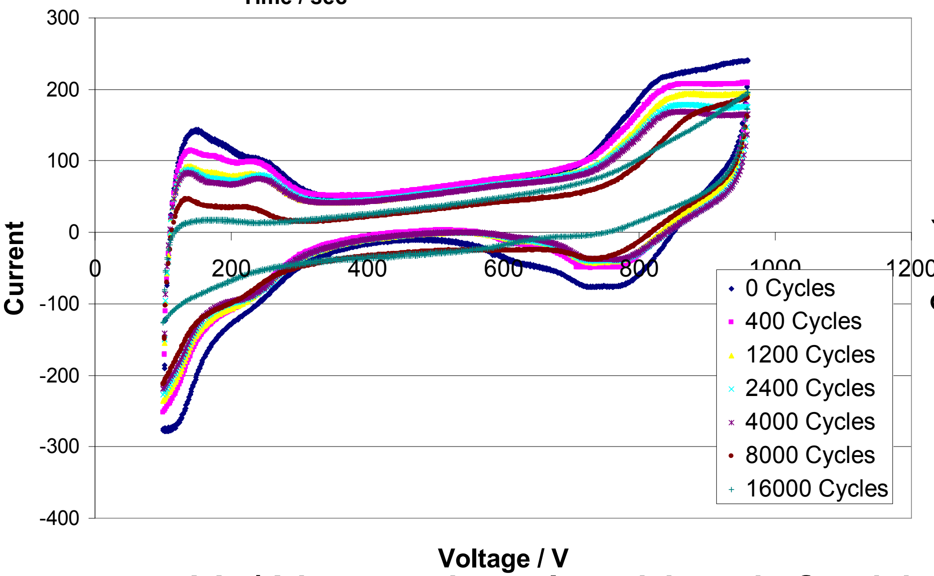
Step Potential Cycle

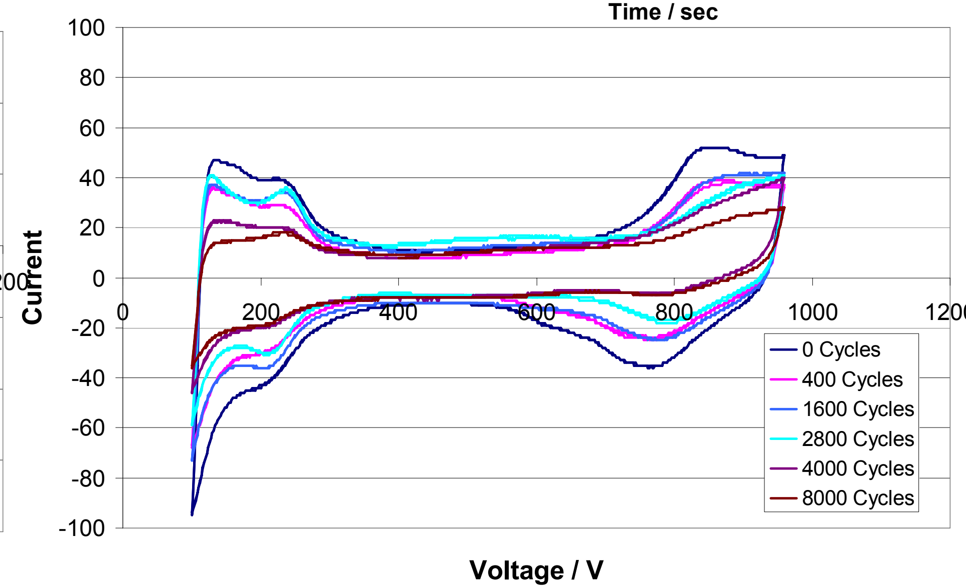


- Accelerated catalyst testing by potential cycling in H_2 / Air
- Voltage cycling: 0.6 and 0.96V (H2/Air)

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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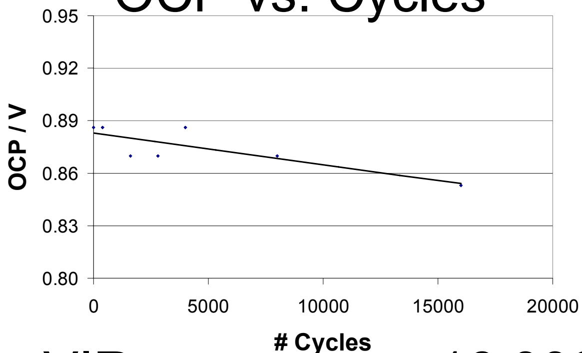
Comparison of Accelerated Testing Protocols

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

Step Potential Cycle

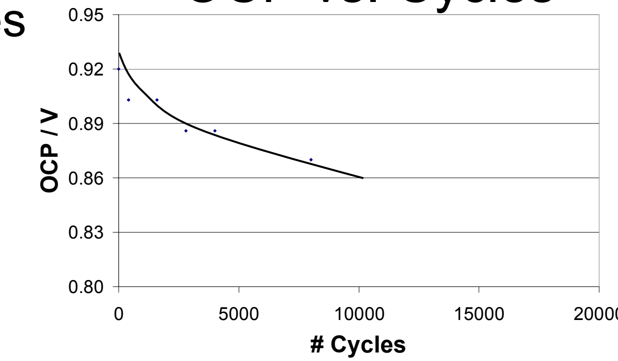
OCP vs. Cycles



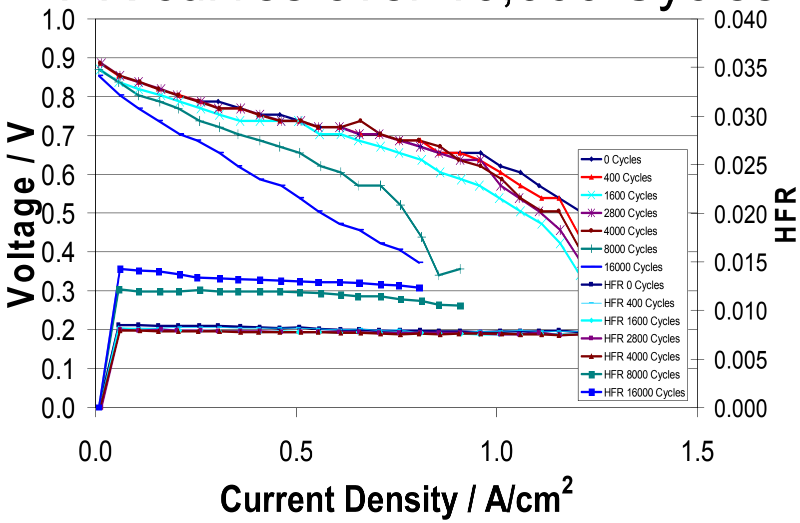
- OCP decreases with cycles
  - Varies potential limits
- Increase in sample HFR
- H_2/Air cycling not just catalyst degradation

Triangle Potential Cycle

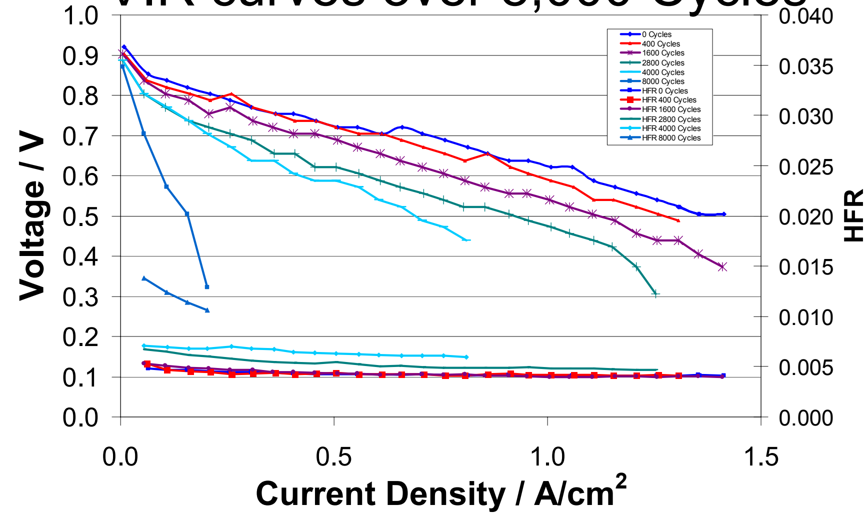
OCP vs. Cycles



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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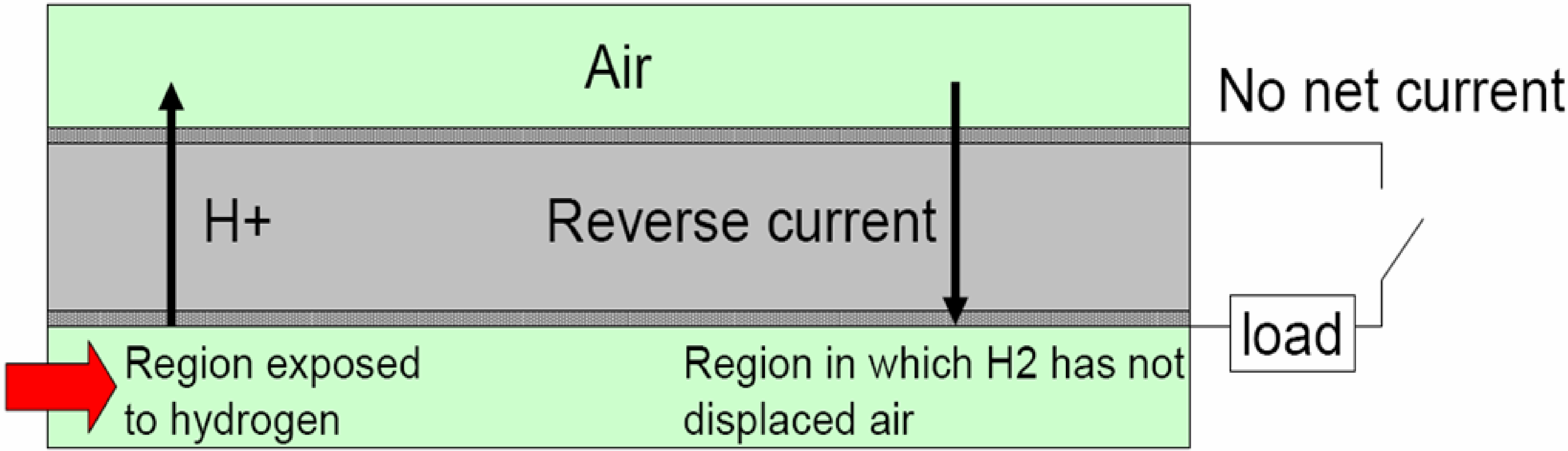
Shut-down/Start-up Effects

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

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



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

Modified from: Sathya Motupally, UTC Power

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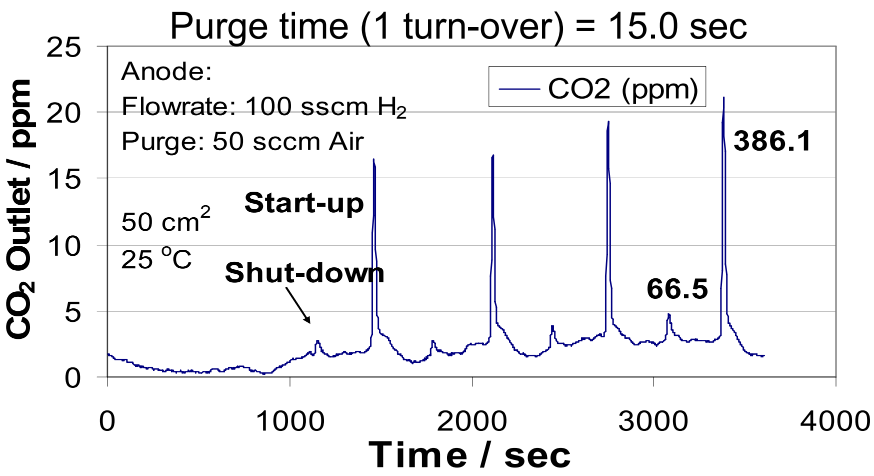
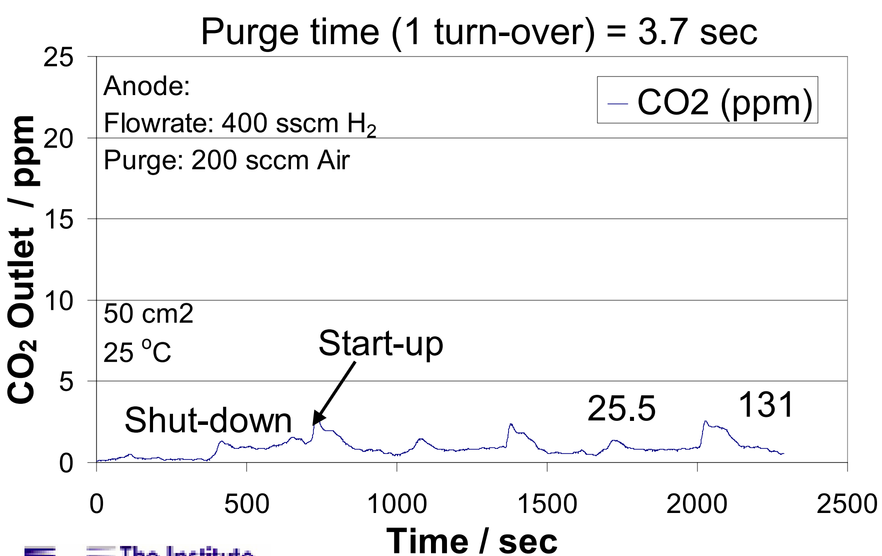
Stop-Start Cycling Effect on Carbon Corrosion

Anode Purge Rate Comparison

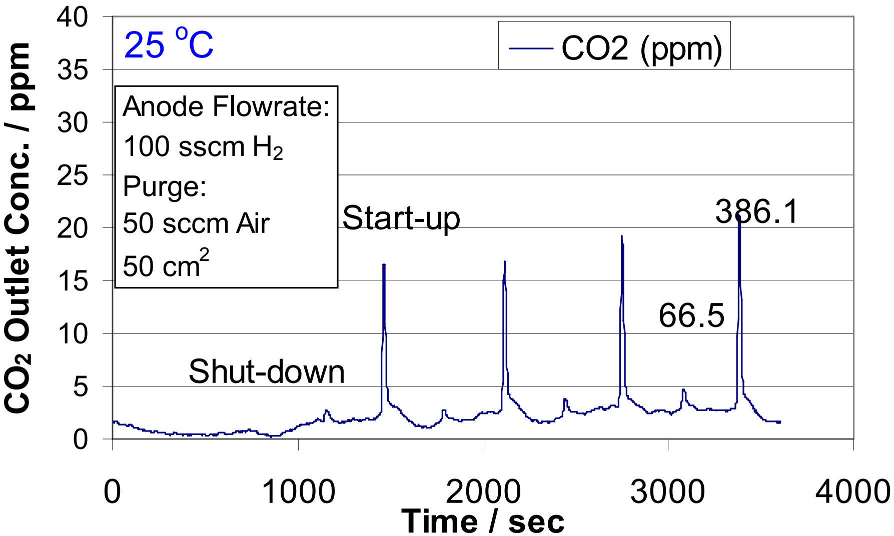


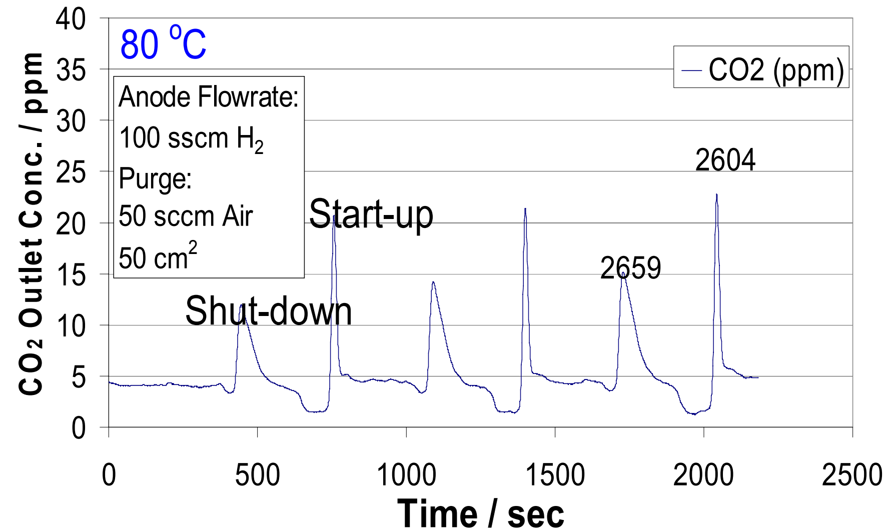


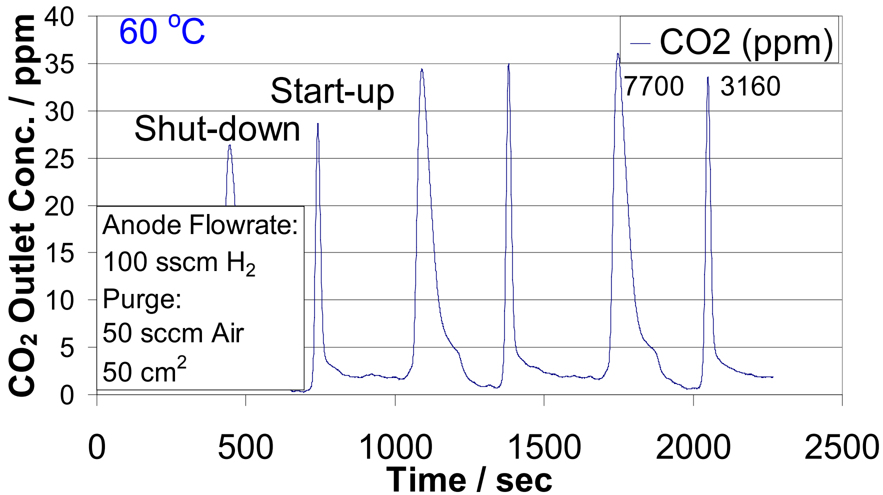
- Operation
  - OCV and dry air (250 sccm) continuously to cathode
  - Shut-down: anode dry air purge: 5 min.
  - Start-up: flow dry H_2 to anode: 5 min.
  - Measure CO_2 (and CO) evolution at cathode by NDIR (Non-dispersive Infrared)

- 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



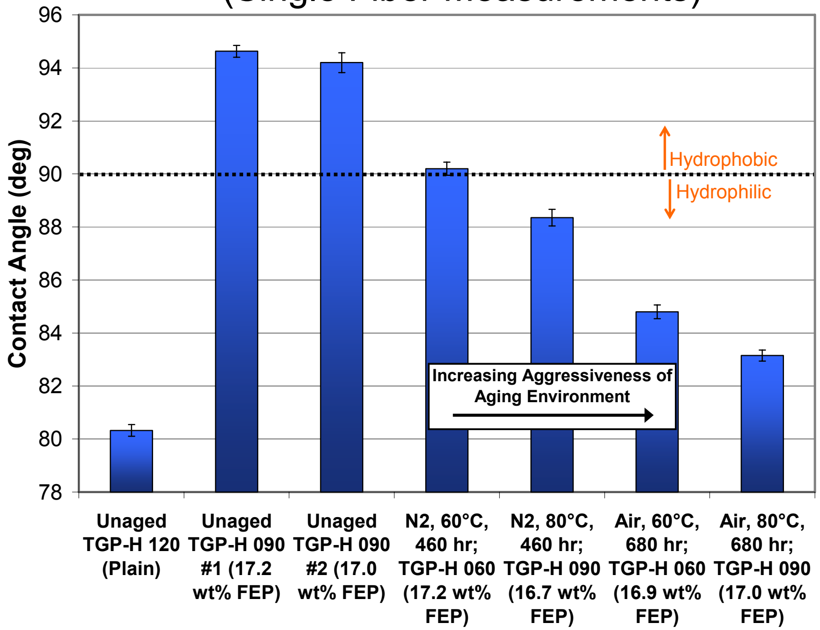




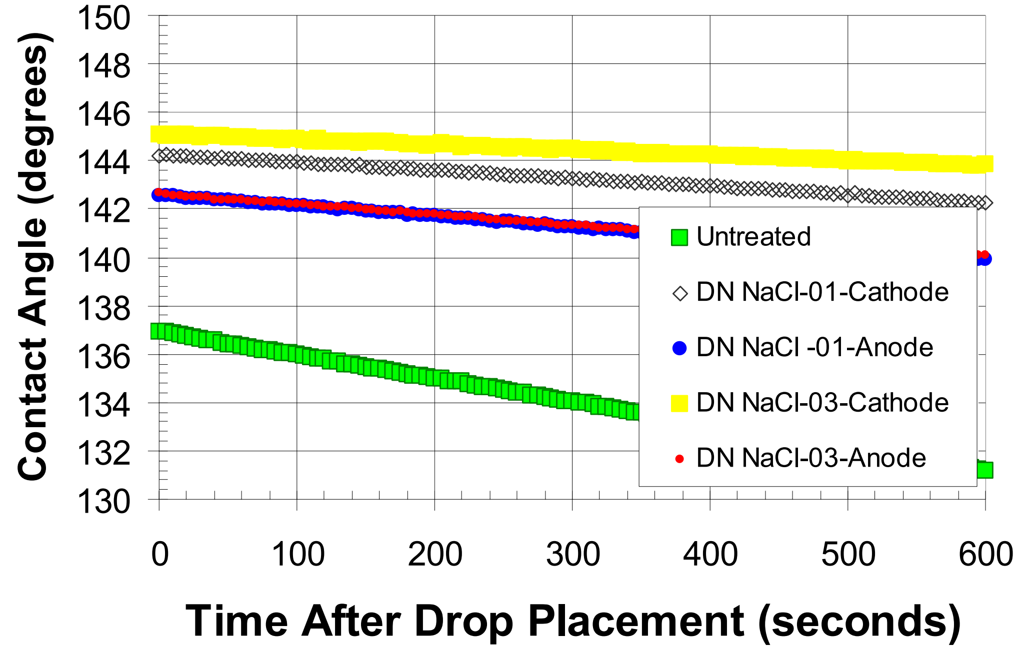
- CO_2 Evolution at Slow Purge Rate
  - 25 °C
    - Higher at start-up than shut-down
    - Much lower evolution than at 60 °C
  - 60 °C
    - Greatest evolution
    - Higher evolution at shut-down
  - 80 °C
    - Non-zero steady-state evolution
    - ~ Equal shut-down/start-up evolution

GDL Durability
Contact Angle Changes

Contact angles with aging
(Single Fiber Measurements)



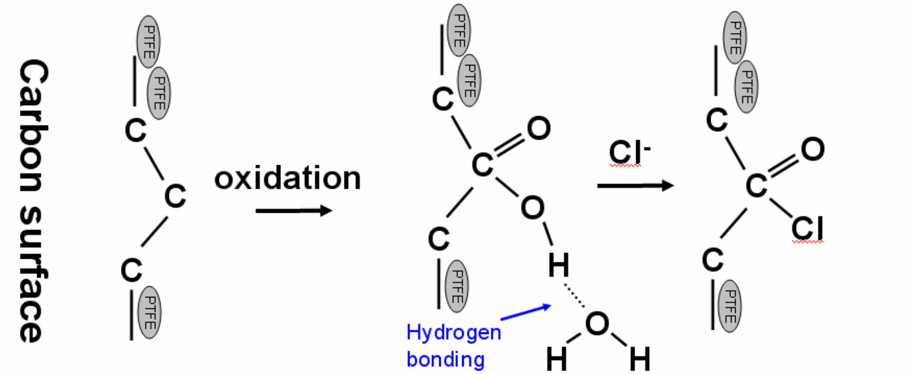
Contact angles with NaCl exposure
(Paper Sessile Drop Measurements)



- 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



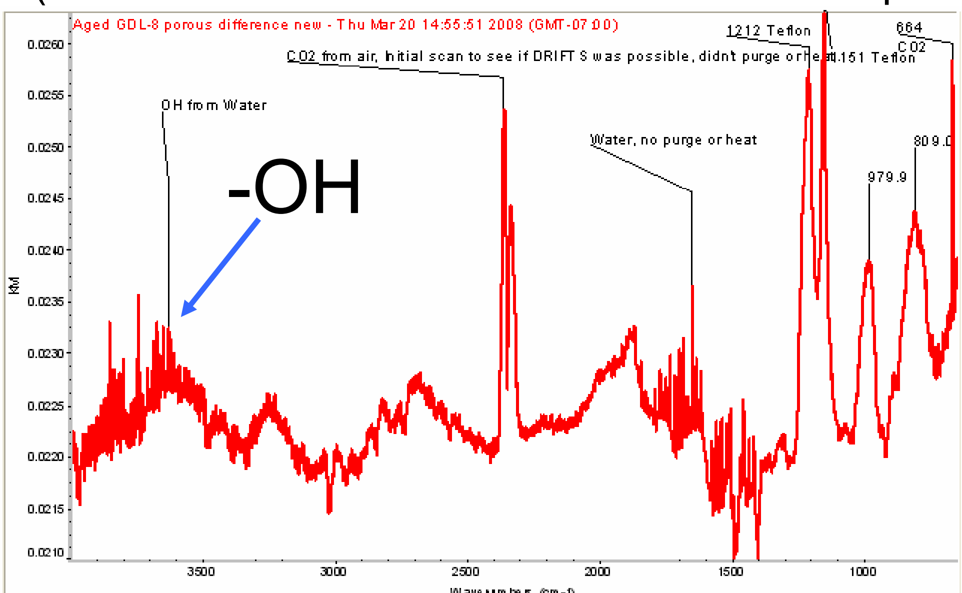
Carbon surface starts hydrophillic due to Teflon treatment

Carbon surface oxidation leads to hydrophillic groups on carbon surface

Hydrophillic groups removed, more hydrophobic surface

DRIFTS Spectra of Aged GDL

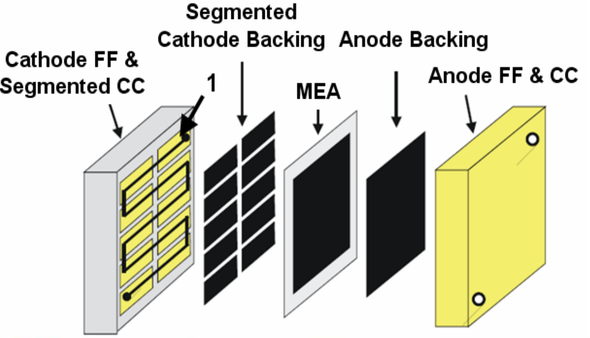
(Diffuse Reflectance Infrared Transmission Spect.)

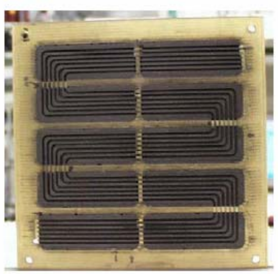


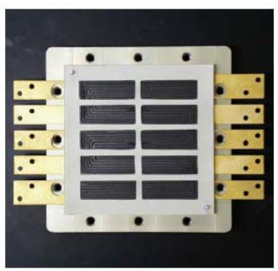
- -OH species identified
- Not yet satisfactorily identified surface species
- Using DRIFTS, will also explore Raman

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

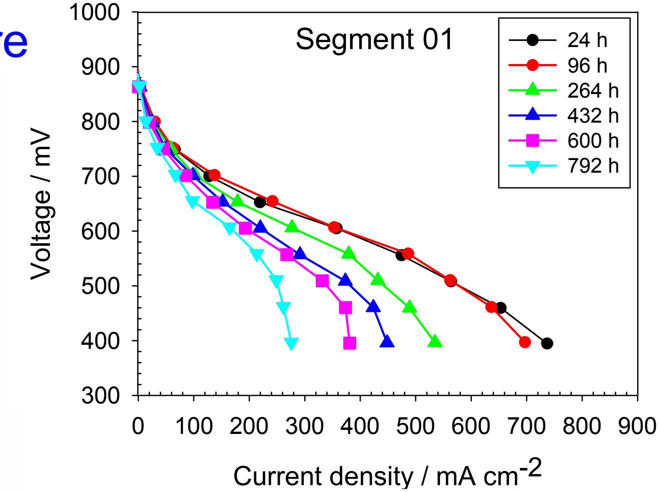
Segmented Cell Hardware

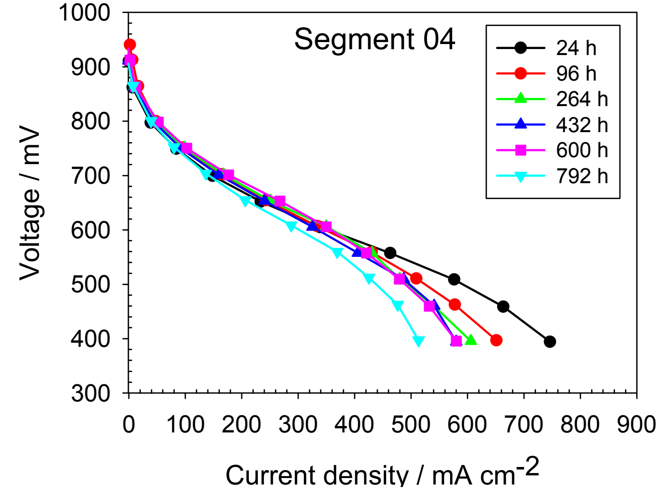


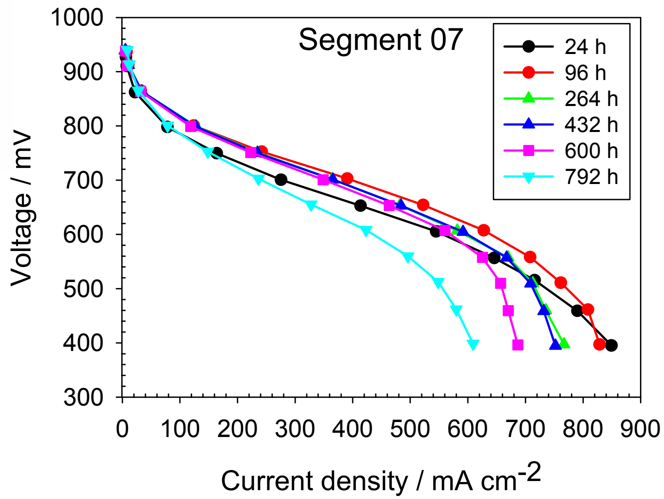


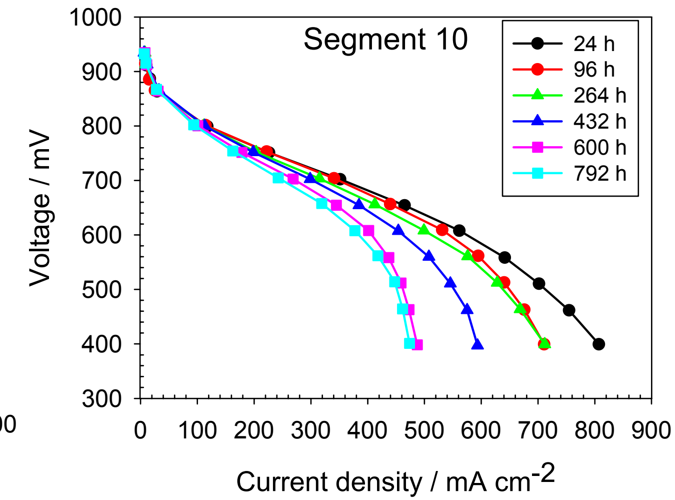


Segmented six parallel channel serpentine flow-field (left side) and segmented cathode hardware including gasket and current collector plates.
Segment-- 7.7 cm^2
Total– 77 cm^2



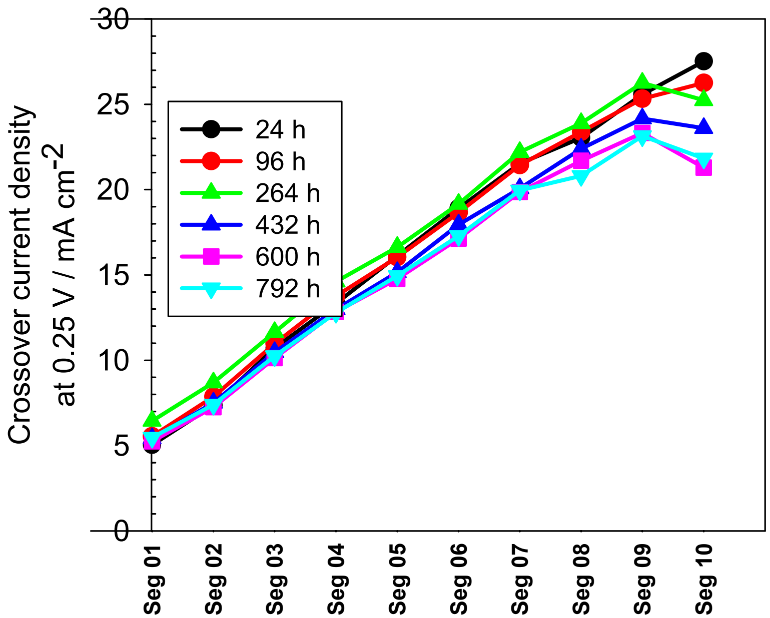


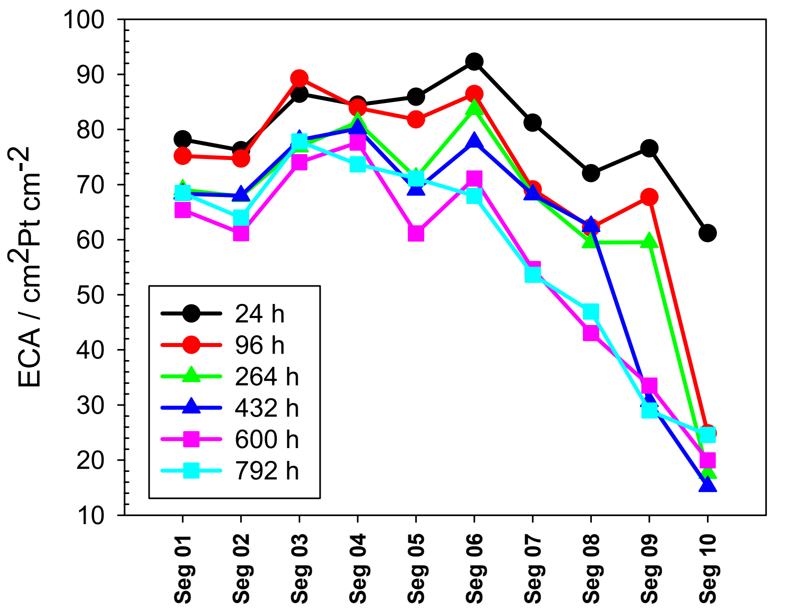




- Performance degradation greater at fuel cell inlet and near outlet

Crossover Current Density Electrocatalyst Surface Area





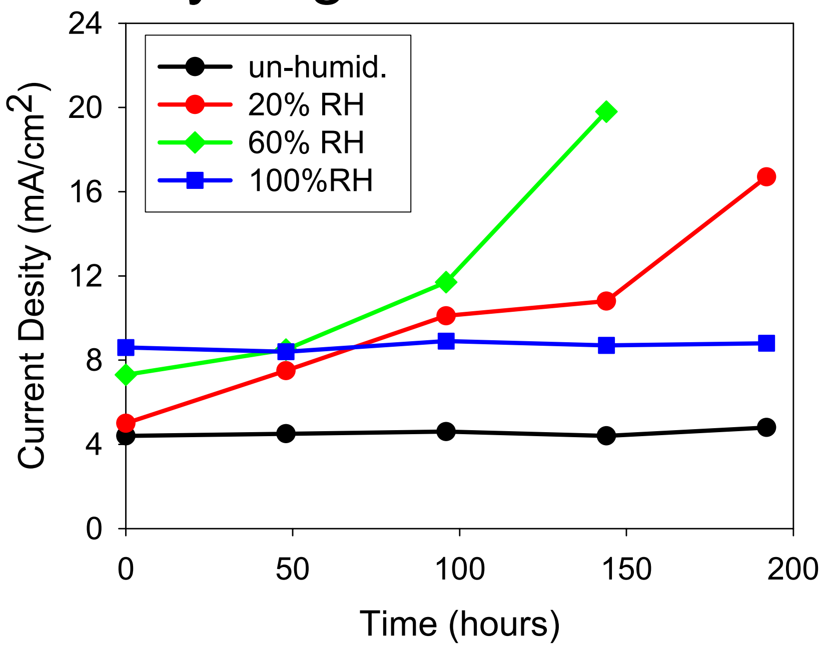
- H_2 cross-over per segment is ~ constant
- Unclear about segment 10

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

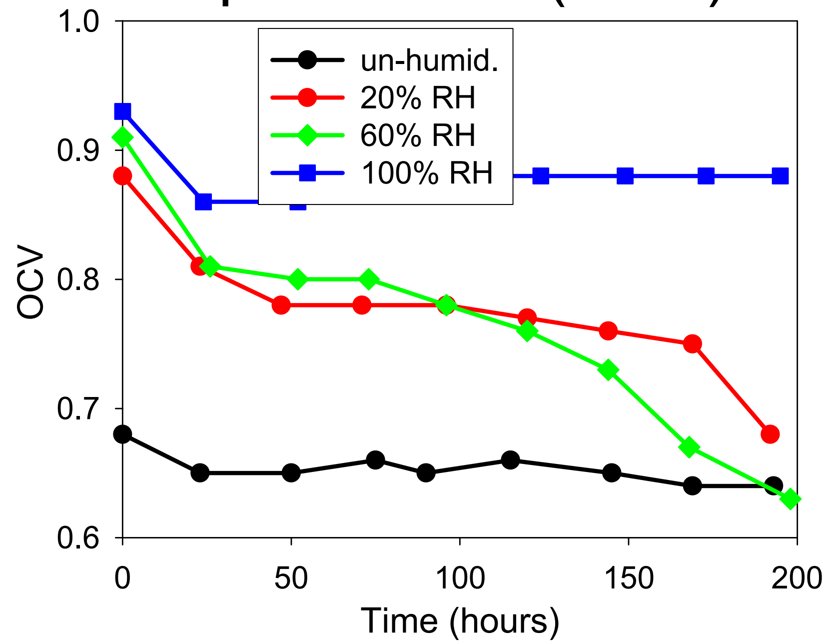
- Loss of electrocatalyst surface area (ECA) predominately at cathode outlet
  - (higher water content)
- Loss of ECA at inlet doesn't explain significant performance loss at inlet

RH Effect on Membrane Degradation

Hydrogen Crossover



Open-Circuit (OCP)



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

- 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.

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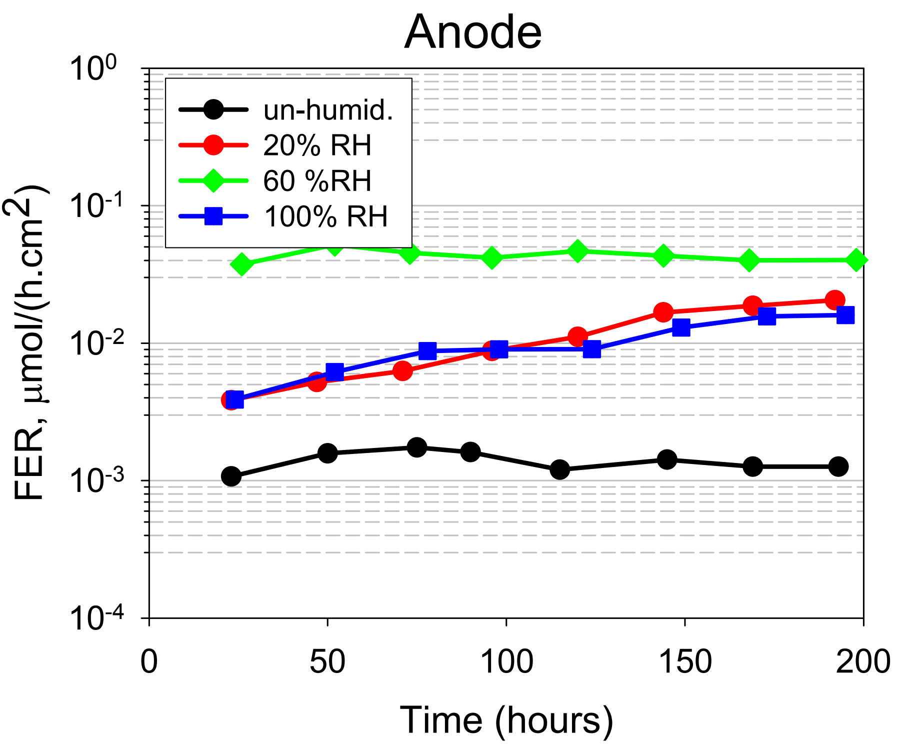
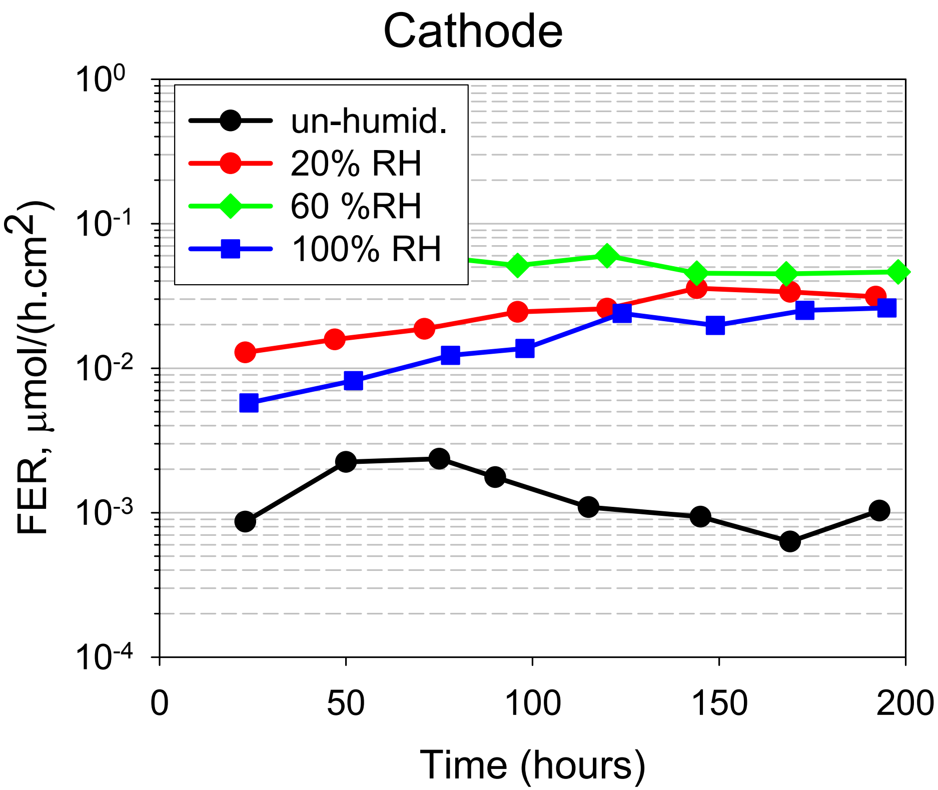
Fluoride Emission Rate (FER)





- 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.

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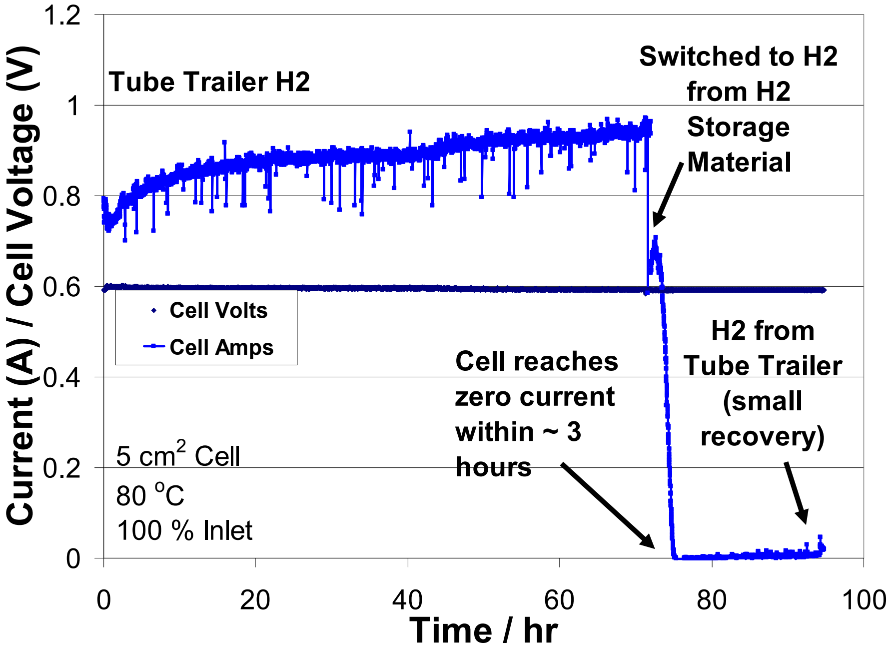
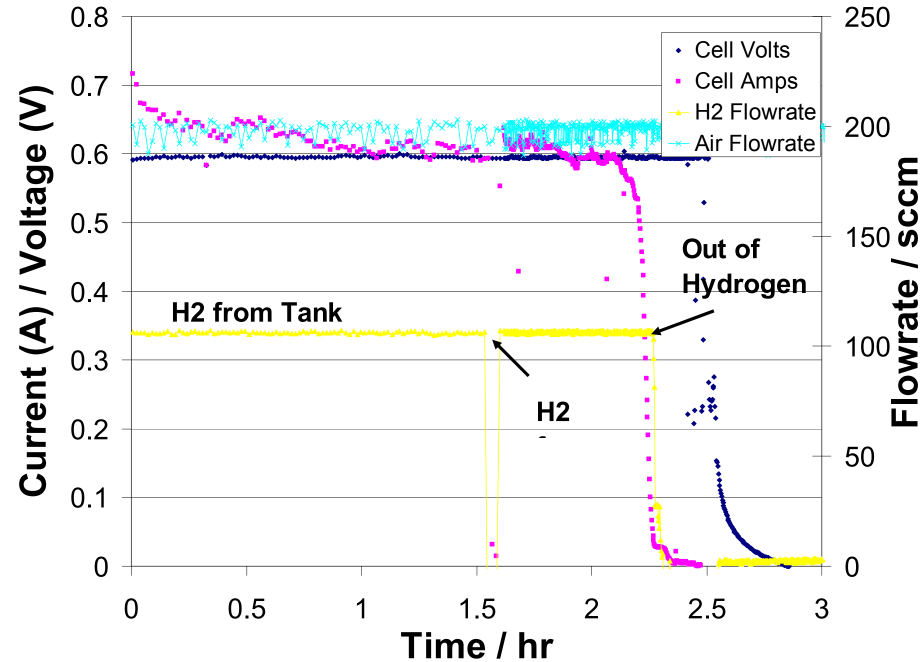
Durability Test with Hydrogen from Chemical Hydride

Test #1



Test #2



- 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

- 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