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Membrane and MEA Accelerated Stress Test Protocols

Presented at High Temperature Membrane Working Group Meeting

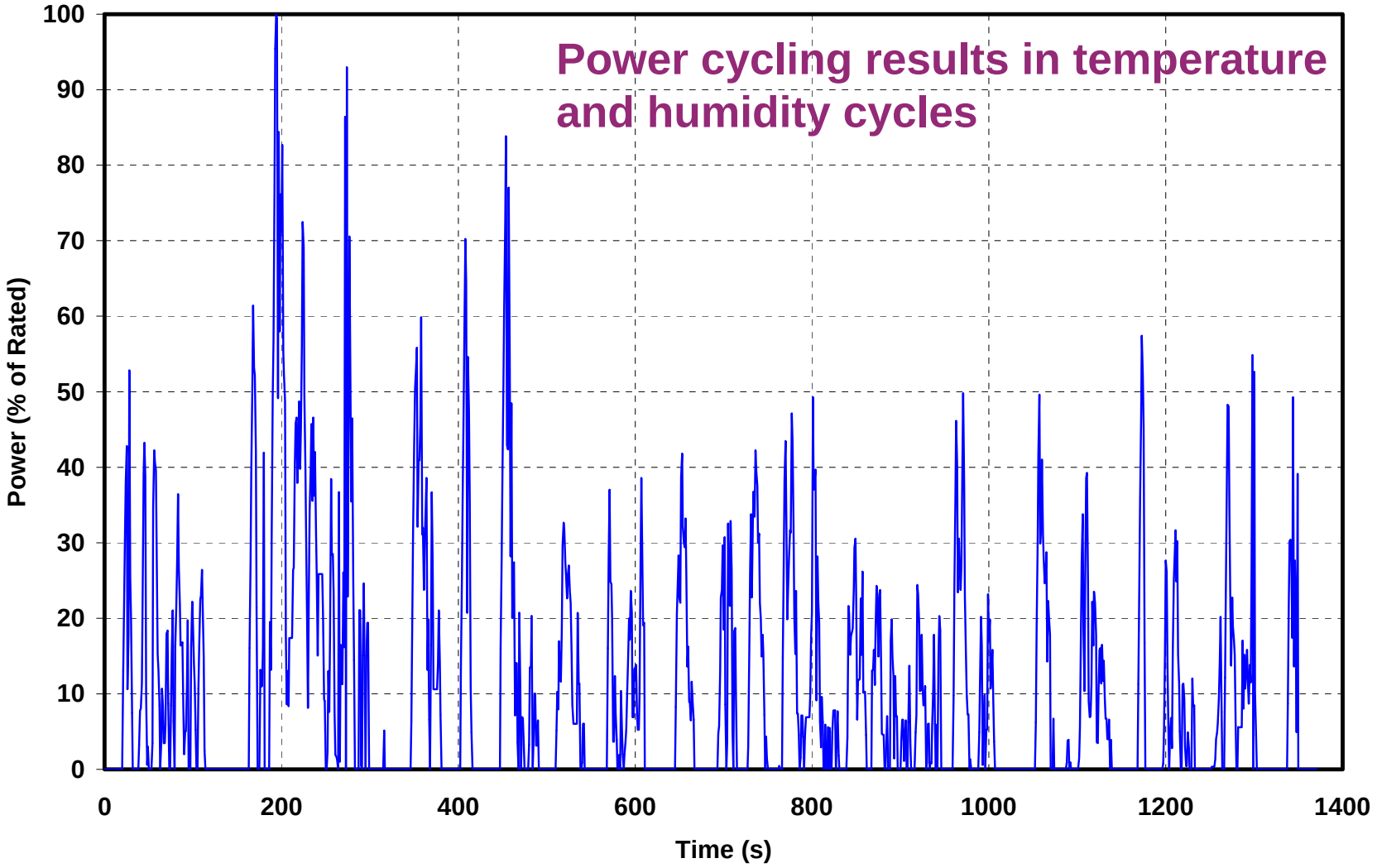
Washington, DC

May 14, 2007

T.G. Benjamin

Argonne National Laboratory

Federal Urban Driving Schedule (FUDS)



Degradation Mechanisms

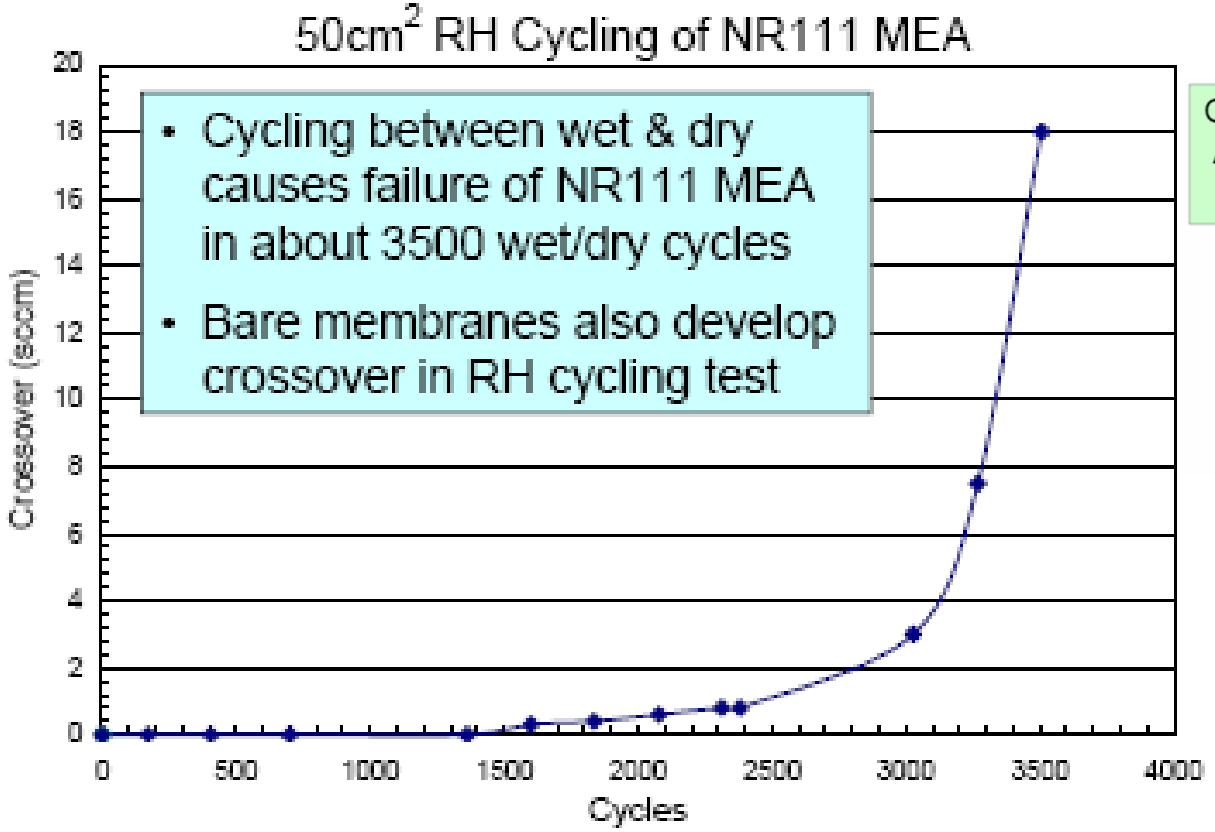
- **Mechanical cycling**
  - **Humidity cycling causes swelling and shrinkage, generating mechanical stresses in the membrane**
- **Chemical attack (by peroxy radical) causes ionomer damage and loss of functionality and integrity**

Mike Hicks, formerly of 3M and now of IdaTech, said,

- **Accelerated Stress Test Protocols are needed to reduce new product introduction cycle**
  - Can't wait 3 years to determine if product lasts 3 years
  - Need estimate of lifetime now
- **DOE 2010 stationary MEA lifetime target of 40,000 hours**
  - Should have started the life test in June 2005
- **Failure mode in accelerated test must be the same as the failure mode in "normal" operation.**

2nd MEA Manufacturing Symposium
Dayton, OH
August 23, 2006

RH Cycling: Results



- Cycling between wet & dry causes failure of NR111 MEA in about 3500 wet/dry cycles
- Bare membranes also develop crossover in RH cycling test

RH Test cycling accelerates mechanical failures in the absence of electrochemical degradation

Characterization of Perfluorosulfonic Acid Membranes for PEM Fuel Cell Mechanical Durability

Mike Budinski, Craig Gittleman, Yeh-Hung Lai, Brian Litteer & Dan Miller

General Motors Corporation
Fuel Cell Activities
Honeoye Falls, NY

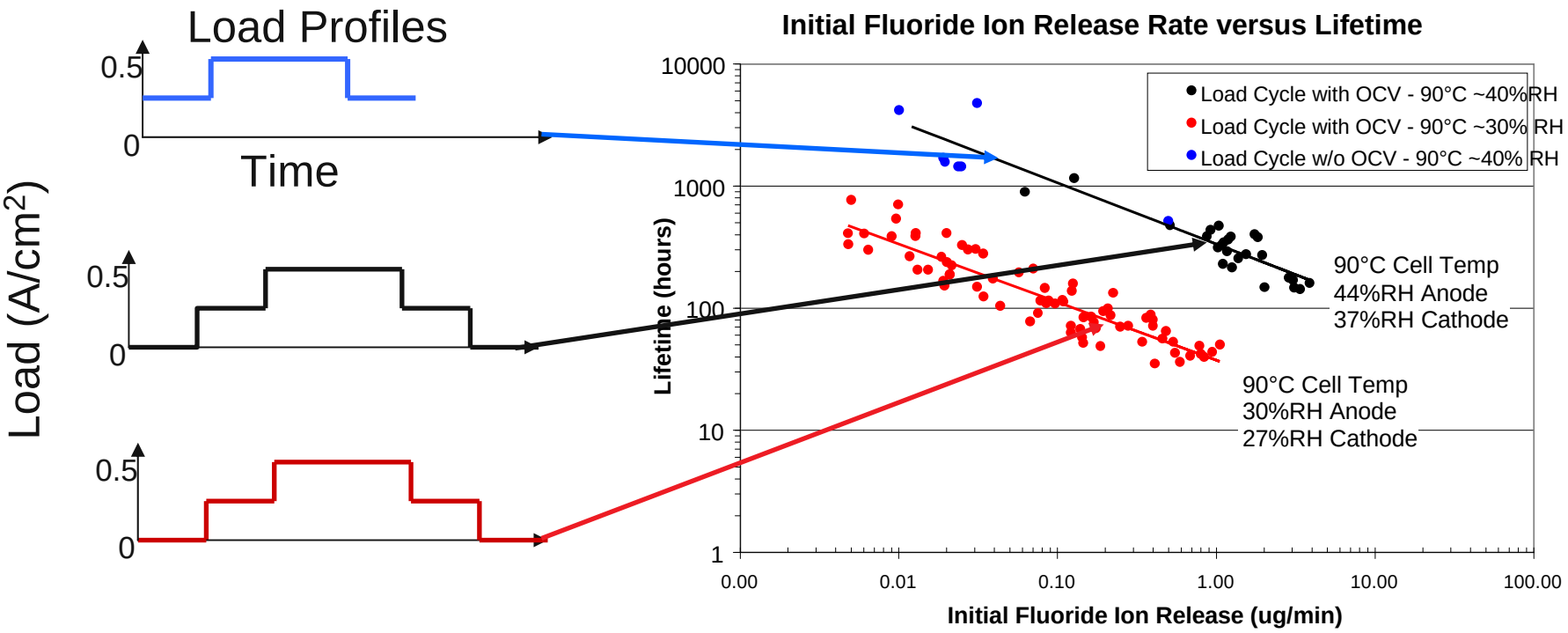
November 11, 2004

Annual AIChE meeting

Austin, TX

Accelerated Testing: Initial Fluoride Release vs. Lifetime

Cycle characteristics affect degradation.



Courtesy Mike Yandrasits, 3M

From DOE Solicitation DE-PS36-06GO96017 1/24/2006

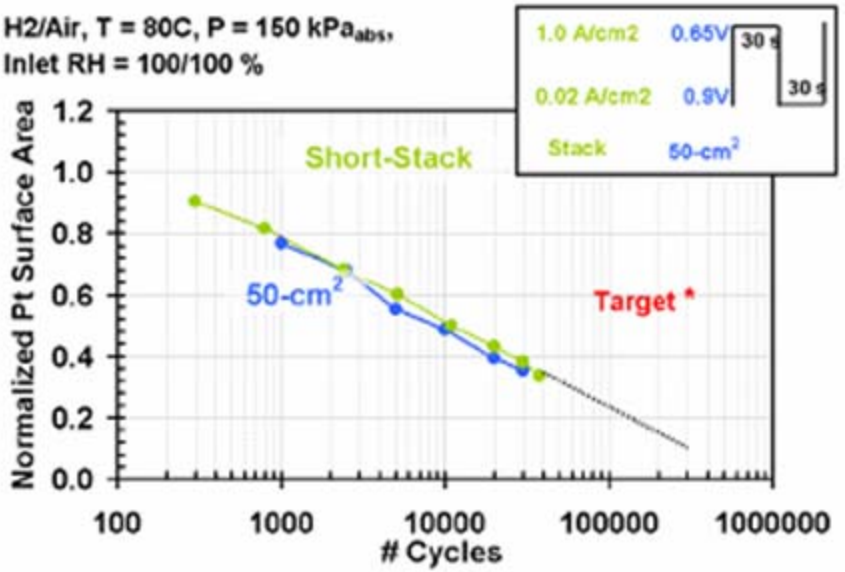
Pt Surface Area Loss Target

- catalysts must have ≤ 3 μV/hr degradation from Pt surface area loss during 5500 hrs of operation

→ ≤ 16.5 mV degradation in 5500 hrs

→ ≤ 16.5 mV degradation in 300,000 large-ΔV

→ Nominally ≤ 40% Pt surface area loss in 300,000 large-ΔV



GM

DOE MEA Chemical Stability

Table 3
MEA Chemical Stability and Metrics

Test Condition	**Steady state OCV, single cell 25 - 50cm^2**
Total time	200 h
Temperature	90ºC
Relative Humidity	Anode/Cathode 30/30%
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm^2 equivalent flow
Pressure, inlet kPa abs (bara)	Anode 250 (2.5), Cathode 200 (2.0)

Metric	**Frequency**	**Target**
F^- release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm^2)*	Every 24 h	≤20 mA/cm^2
OCV	Continuous	≤20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring

*Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical hydrogen crossover method

DOE Membrane Mechanical Cycle

Table 4
Membrane Mechanical Cycle and Metrics

Cycle	**Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25 - 50cm^2**	
Total time	Until crossover >10 sccm or 20,000 cycles	
Temperature	80ºC	
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)	
Fuel/Oxidant	Air/Air at 2 slpm on both sides	
Pressure	Ambient or no back-pressure	
Metric	**Frequency**	**Target**
Crossover*	Every 24 h	≤10 sccm

*Crossover per USFCC "Single Cell Test Protocol" Section A3-1, pressure test method with 3 psig N_2

M. Mathias et al., ECS Interface Vol. 14 No. 3, 2005, pp. 24-35

US Fuel Cell Council (USFCC) Durability Task Force

The Mission of the USFCC Durability Task Force is to establish standardized non-application specific, accelerated test protocols to evaluate the durability of various fuel cell components.

Initial Focus

- Catalyst
  - *Platinum sintering, agglomeration, and dissolution*
  - *Carbon catalyst support oxidation/corrosion*
- Membrane
  - *Chemical degradation (Peroxy radical attack)*
  - *Mechanical degradation*

www.usfcc.com

DOE MEA Chemical Stability – USFCC Differences

Table 3
MEA Chemical Stability and Metrics

Test Condition	**Steady state OCV, single cell 25 - 50cm^2**	
Total time	200 h	
Temperature	90ºC	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air a	m^2 equivalent flow
Pressure, inlet kPa abs (bara)	Anode 250 (2.5), Cathode 200 (2.0)	
Metric	**Frequency**	**Target**
F$^-$ release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm^2)*	Every 24 h	≤20 mA/cm^2
OCV	Continuous	≤20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring

*Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method

H_2/O_2 or H_2/40% O_2

DOE Membrane Mechanical Cycle – USFCC Differences

Table 4
Membrane Mechanical Cycle and Metrics

Cycle	**Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25 - 50cm^2** 0 - 150% RH	
Total time	Until crossover >10 sccm or 20,000 cycles	
Temperature	80°C	
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)	
Fuel/Oxidant	Air/Air at 2 slpm on both sides	
Pressure	Ambient or no back-pressure	
Metric	**Frequency**	**Target**
Crossover*	Every 24 h	≤10 sccm

*Crossover per USFCC "Single Cell Test Protocol" Section A3-1, pressure test method with 3 psig N_2

USFCC and DOE Additional Differences

- **USFCC Draft Protocol includes Fenton's test as an *ex-situ* membrane chemical stability assessment.**

- **USFCC Draft Protocol also includes DuPont DD-4 which is a combined (alternating) humidity and load cycle.**

Ex-situ *Chemical Stability Test: Fenton's Test from USFCC Materials and Components Working Group meeting at the Fuel Cell Seminar 2006*

Goal: assess the relative oxidative stability of PEMs

The degree of degradation measured by polymer weight loss, fluoride ion evolution, change in ion exchange capacity (IEC), etc.

Recommended test conditions for PFSA membranes:

- 30% H_2O_2
- 20 ppm Fe^{+2}
- 85^{o}C
- 3 Cycles with fresh reagent, 18 hours per cycle
- Measure fluoride and weight loss

Chemical + Mechanical Stability Test - from USFCC Materials and Components Working Group meeting at the Fuel Cell Seminar 2006

Goal: combine chemical and mechanical degradation mechanisms in a single accelerated test

Test protocol recommended by DuPont

Two cycle modes are interchanged every 24 hrs:

Humidity cycle:

N_2 / N_2, 80 ºC

RH of inlet gases is cycled between 0 and 100% RH every 30 minutes

Load cycle:

H_2 / O_2; 50%RH, 80 ºC

Load cycled between 10 and 800 mA/cm^2 (7min/3 min)

Monitor crossover current density as a function of time

Stop test when > 10 mA/cm^2

Thanks for your attention and … Remember

- **The accelerated stress test protocols have not been generally correlated with actual life under "normal" operating conditions.**
- **The protocols are test cycles only. Conditioning procedures and analysis techniques are not described.**
- **Membranes other than PFSA may need different cycles.**
- **Visit www.USFCC.com for:**
  - **Existing USFCC Single Cell Test Protocol**
  - **Future USFCC Catalyst Stability Accelerated Stress Test Protocols (first draft)**
  - **Future Membrane/MEA Accelerated Stress Test Protocols**

And Remember

- **DOE Solicitation DE-PS36-GO95020 – "High Temperature, Low Relative Humidity, Polymer-Type Membranes" – says**

"Applicants should also show that the material can be expected to meet durability targets in the aggressive environment of a fuel cell, i.e., the material must have good chemical stability and be resistant to oxidation by peroxide."

- **Funding Opportunity DE-PS36-06GO96017 - Research and Development of Fuel Cell Technology for the Hydrogen Economy - says**

"Additionally, the material must demonstrate the ability to meet the cost and durability targets in the aggressive environment of the fuel cell, and have good mechanical and chemical stability under highly oxidizing conditions."