Accelerated Testing Validation

Rangachary (Mukund) Mukundan
Los Alamos National Laboratory
May 11th 2011

Project ID #
FC016

Project Overview

Timeline

- Project Start Date
  - **August 2009**
- Project Duration
  - **4 Years (End: Sept ’13)**
- ≈ 40% complete

Budget

- Total project funding
  - 4 Years : $4,159,790
  - DOE Cost : $4,000,000
  - Cost Share : $159,790
- Funding for FY10/FY11

LANL	$550k, 550k
Partners (Industry)	$239k, 280k
Other National Labs	$234k, 251k
FY10/FY11 Total	$1023k,1081k

Barriers

Fuel cells: 2007 Technical Plan

A. Durability

Automotive : 5,000 hours
Stationary : 40,000 hours

- Degradation mechanisms not well understood
- Develop Mitigation strategies
- Simultaneously meet cost and durability targets

Partners

- Ballard Power (System Integrator)
- Ion Power (Materials Supplier)
- ORNL (Metal Bipolar Plates)
- LBNL (Modeling)

Objectives/Barriers - Relevance

The objectives of this project are 3-fold

1. Correlation of the component lifetimes measured in an AST to real-world behavior of that component.
2. Validation of existing ASTs for Catalyst layers and Membranes
3. Development of new ASTs for GDLs, bipolar plates and interfaces

Technical Targets

Automotive : Durability with cycling: 5,000 hours (2010/2015): 2005 Status (2000 hours for stack and 1000 hours for system)

Stationary : Durability: 40,000 hours (2011): 2005 Status = 20,000 hours

Bus Data will have intermediary targets in terms of lifetime.

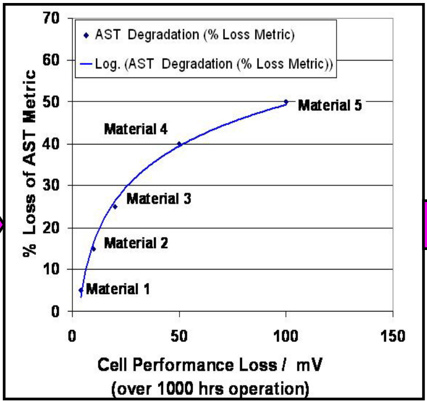
Importance of Accelerated Stress Test (AST)

- Allows faster evaluation of new materials and provides a standardized test to benchmark existing materials
- Accelerates development to meet cost and durability targets
- Different ASTs are available (DOE-FCTT, USFCC and JARI)
  - Lack of correlation to “Real World” Data
  - No tests available for GDLs and other cell components
  - Value of combined vs individual tests

Approach

Materials

- BPS provides materials used in Bus Stack
- W. L. Gore provides commercial MEAs
- Ion Power provides custom MEAs
- SGL carbon provides commercial GDL materials
- ORNL provides metal bipolar plates



LANL performs DOE-FCTT ASTs
Develops GDL, bipolar plate ASTs

Characterization

Fuel Cell Performance

VIR, Impedance, HelOx, Modeling

Catalyst

- ECSA, Mass activity, particle size, layer thickness, composition, loading

Membrane

Cross-over, shorting resistance, HFR, thickness

GDL

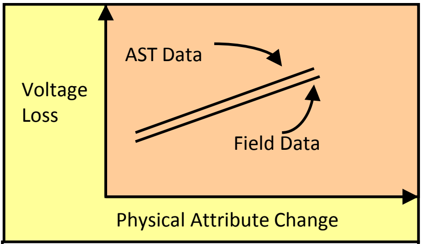
- Impedance, Hydrophobicity

BPS Bus Fleet Data

- Voltage degradation distribution data from P5 fleet & HD6 Module
- Cell Data (36 Cells)
- MEA Characterization (108 MEAs)

LANL Drive Cycle Testing

- Automotive drive cycle testing
- RH, Temp, Pressure effects



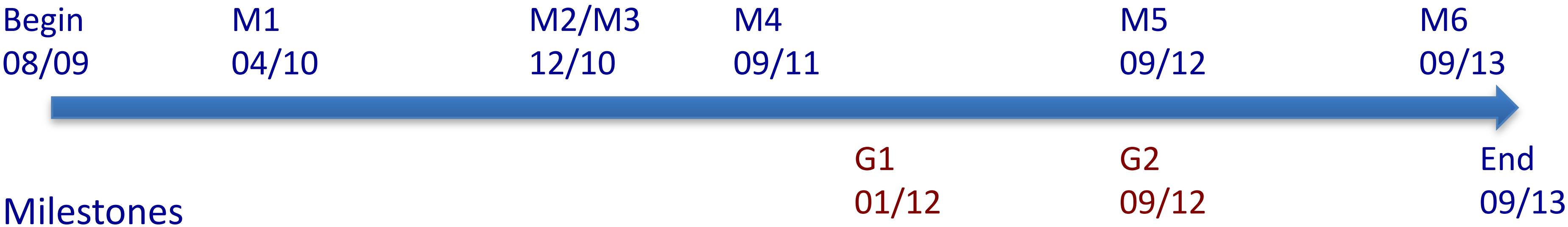
Statistical Correlation

- Relate field and AST data to physical attribute change
- Good correlation if AST slope similar to “Real World Data” slope

Goals

- Recommend improved catalyst and membrane ASTs that correlate to real world data
- Recommend ASTs for GDL and bipolar plate materials
- Co-ordinate efforts with USFCC and USDOE-FCTT

Approach - Milestones



Milestones

M1 : Ballard delivers BOL Bus MEAs (Complete 04/2010)
M2: Ballard provides initial breakdown analysis of Bus Stack (Complete 12/2010)
M3 : Complete initial AST testing on Ballard MEAs (Complete 12/2010)
M4: Develop GDL ASTs
M5 : Complete Drive cycle testing with start up / shut down
M6 : Final Statistical correlation of AST and Bus data to material property and AST lifetimes to drive cycle of materials with varying lifetimes

Go/No go Decision

G1 : Initial Correlation of AST of life cycle and bus data – Redirect AST based on results
G2 : Go/ No go on Freeze AST for MEA interfaces (NO GO based on FCTT input)

Materials Used

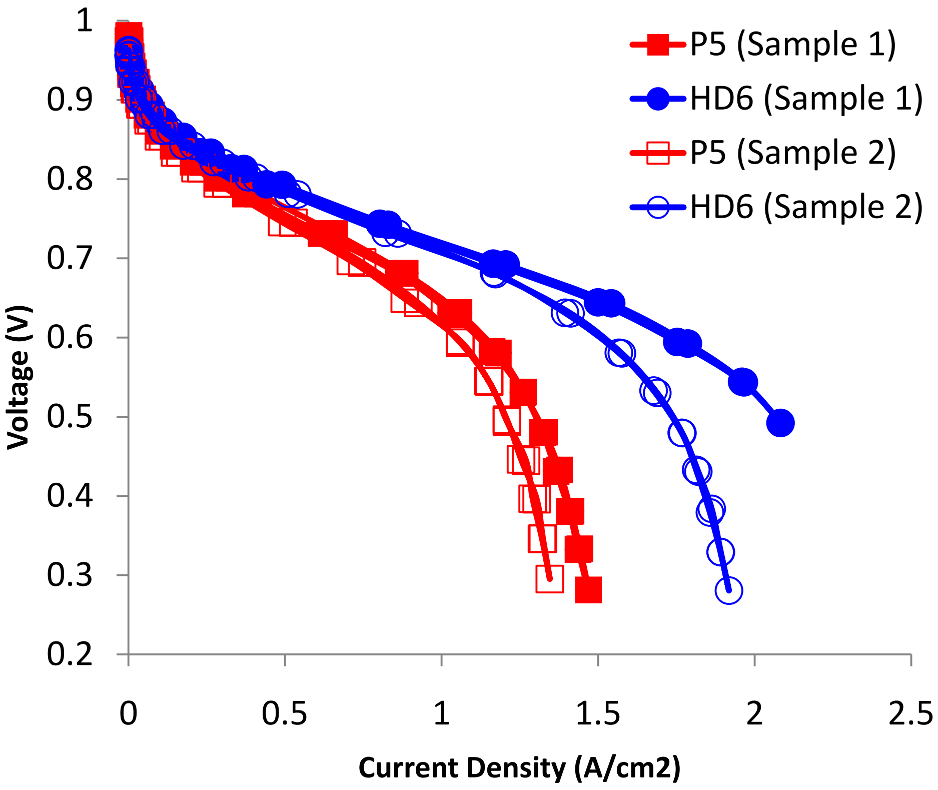
- Gore™ MEAs (Presented at last year AMR)
  - Gore™ Primea® MESGA MEA A510.1/M720.18/C510.2
  - Gore™ Primea® MESGA MEA A510.2/M720.18/C510.4
  - Gore™ Primea® MESGA MEA A510.1/M710.18/C510.2
- Ballard P5 and HD6 MEAs (Current data)
  - MEAs delivered 04/2010
  - DOE FCTT ASTs completed 12/2010

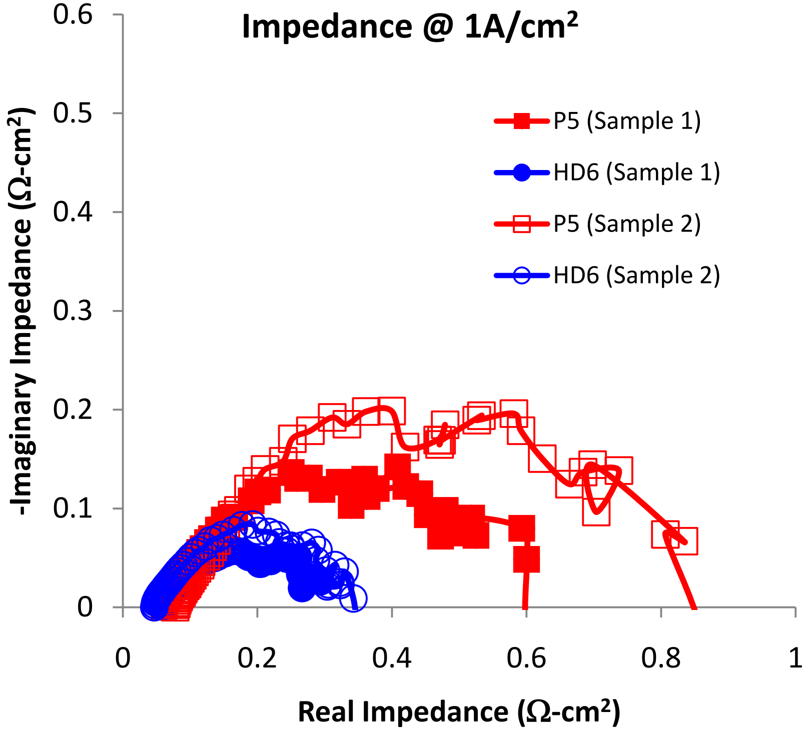
M710 : Discontinued product. Lower chemical and mechanical durability sample

M720 : technology circa 2005. Higher chemical and mechanical durability sample

- Ion Power MEAs (In progress – 03/2011)
  - Dupont XL membranes
  - Tanaka Catalysts
    - TEC10E50E, TEC10E40E, TEC10E20E (High Surface area carbon 50 wt%, 40 wt% and 20 wt% Pt)
    - TEC10V40E, TEC10V20E (Vulcan carbon 40 wt%, 20 wt% Pt)
    - TEC10E40EA Low Surface area carbon 40 wt% Pt
- GDL
  - SGL 24BC (5% PTFE-substrate/23% PTFE MPL)
  - Varying PTFE content and substrate porosity
- Bipolar plates (07/2010)
  - G35 and Ni50Cr: Corrosion testing (coupons) and fuel cell testing (plate)

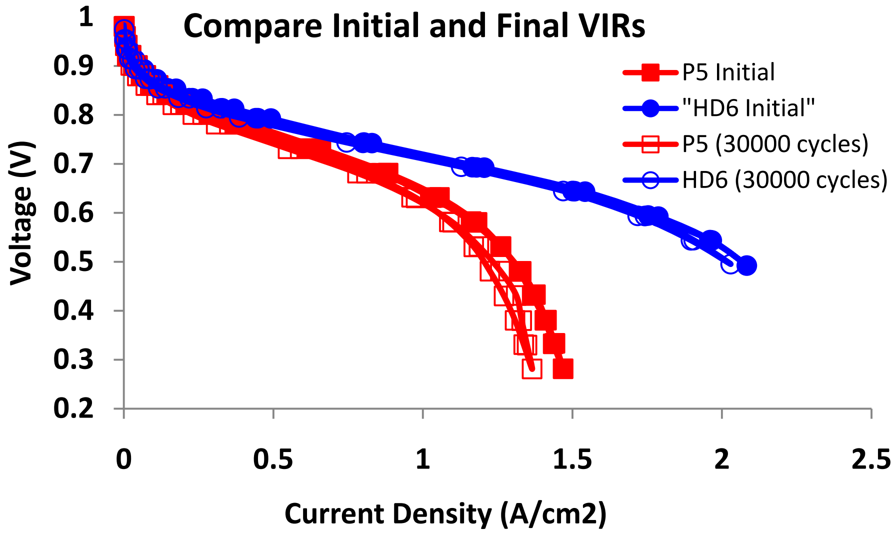
Ballard MEAs (BOL Data)



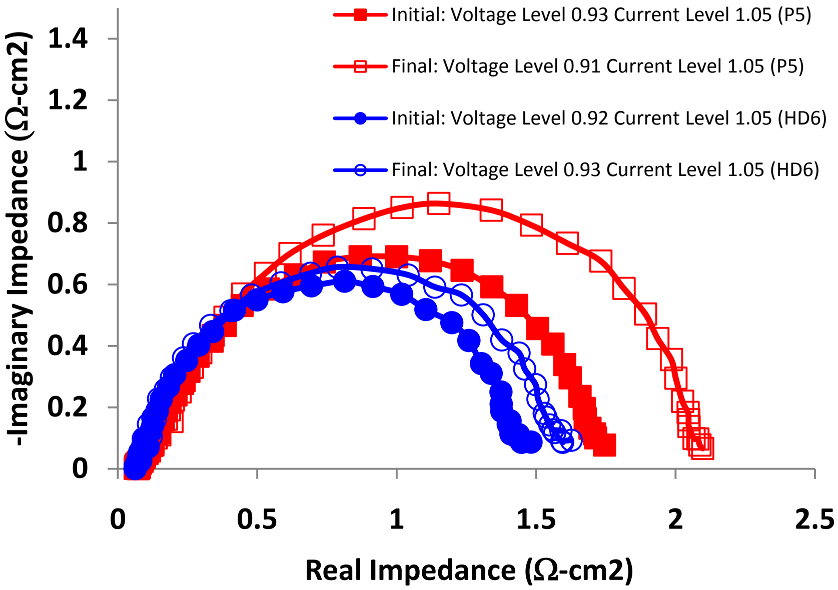


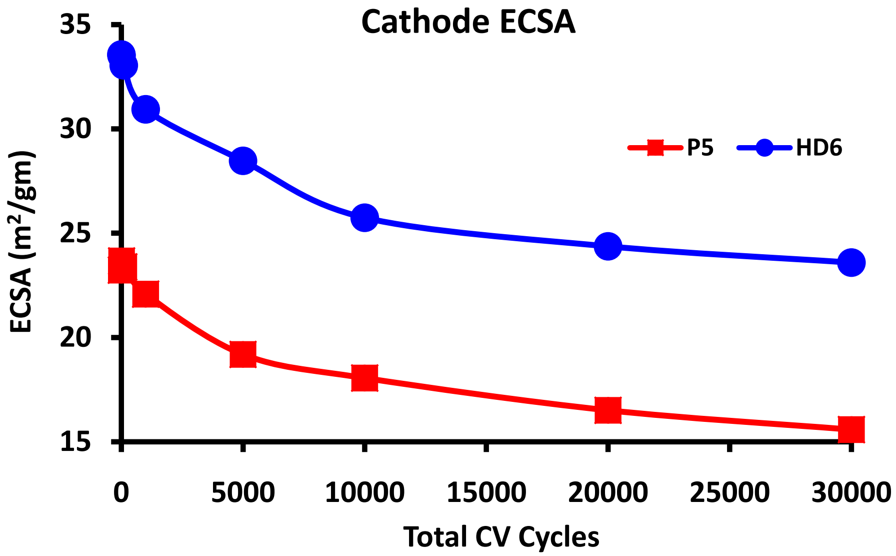
P5 (2002): 1.05mg/cm², 50μm membrane
HD6 (2007): 1mg/cm², 25μm membrane
HD6: Better performance.
Slight improvement in kinetic region and ohmic region
Significant improvement in mass transport region

Potential Cycling AST



Compare Initial and Final VIRs

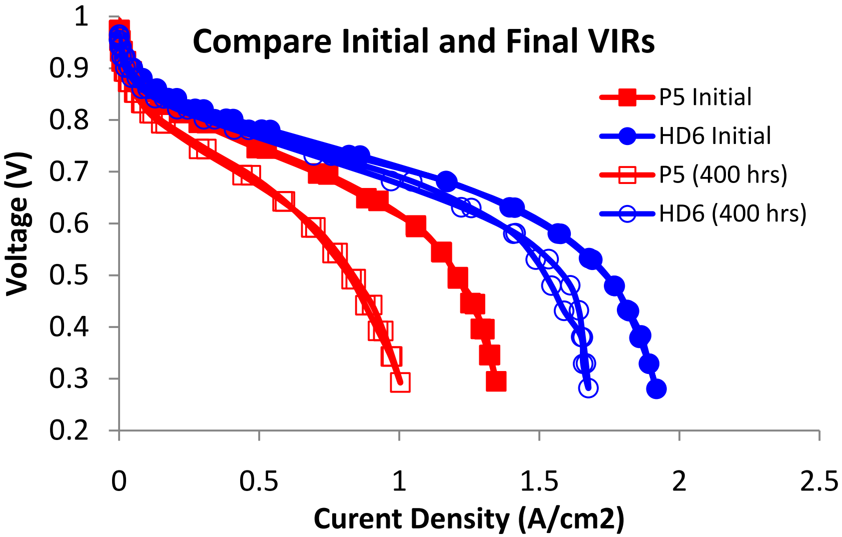


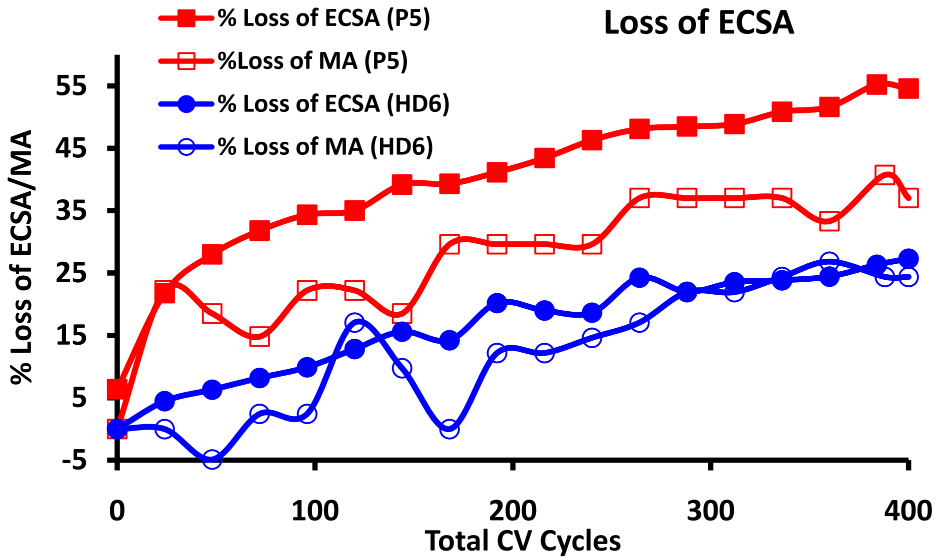


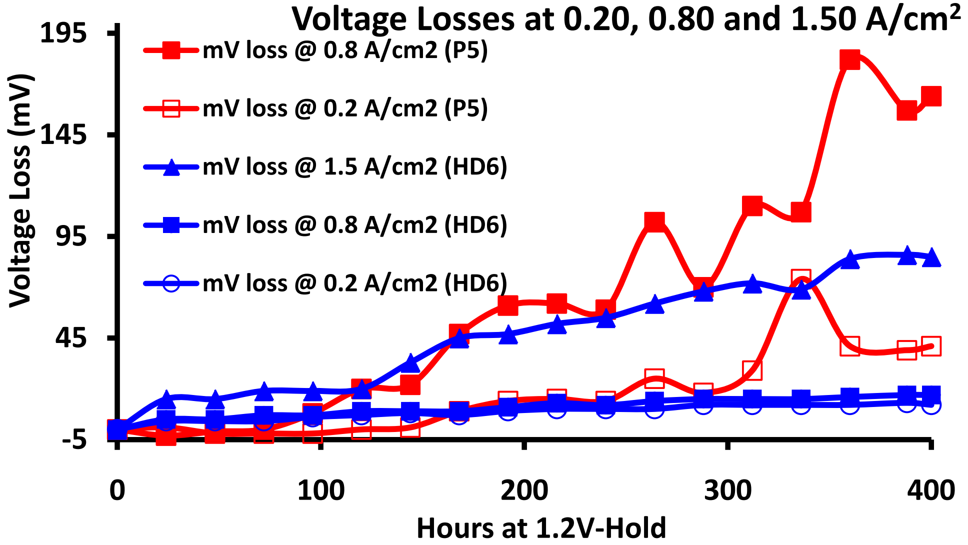
Cathode ECSA

HD6 has better performance
HD6 has slightly better durability towards potential cycling
HD6 Mass transport resistance does not change with cycling
Slight increase in P5 mass transport resistance with cycling

High Potential Hold AST







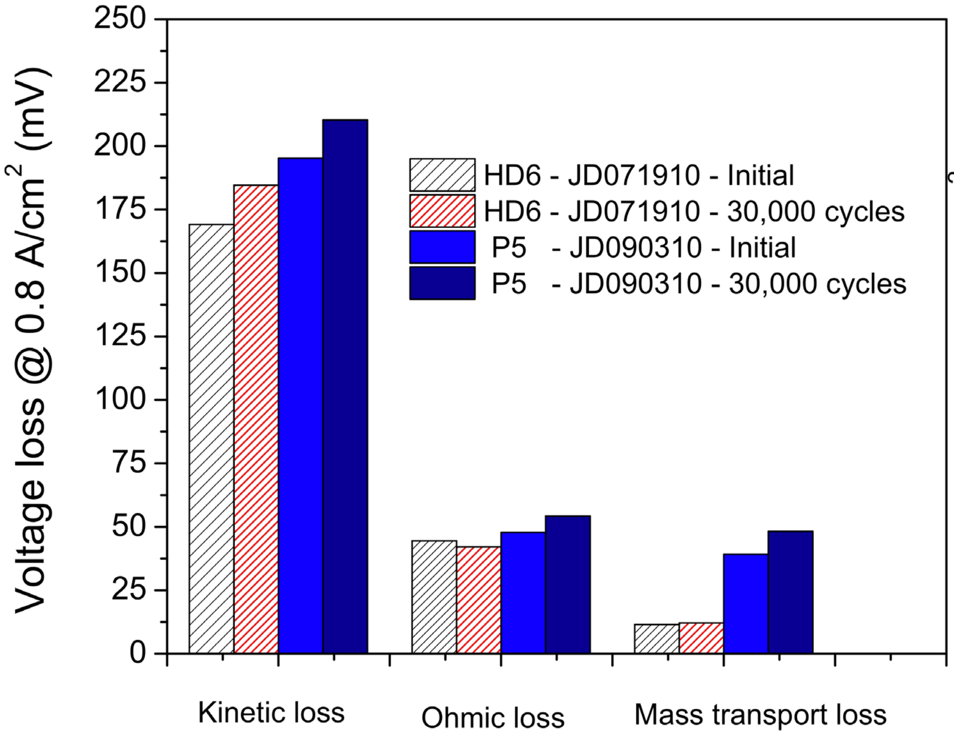
Some kinetic losses and significant mass transport losses

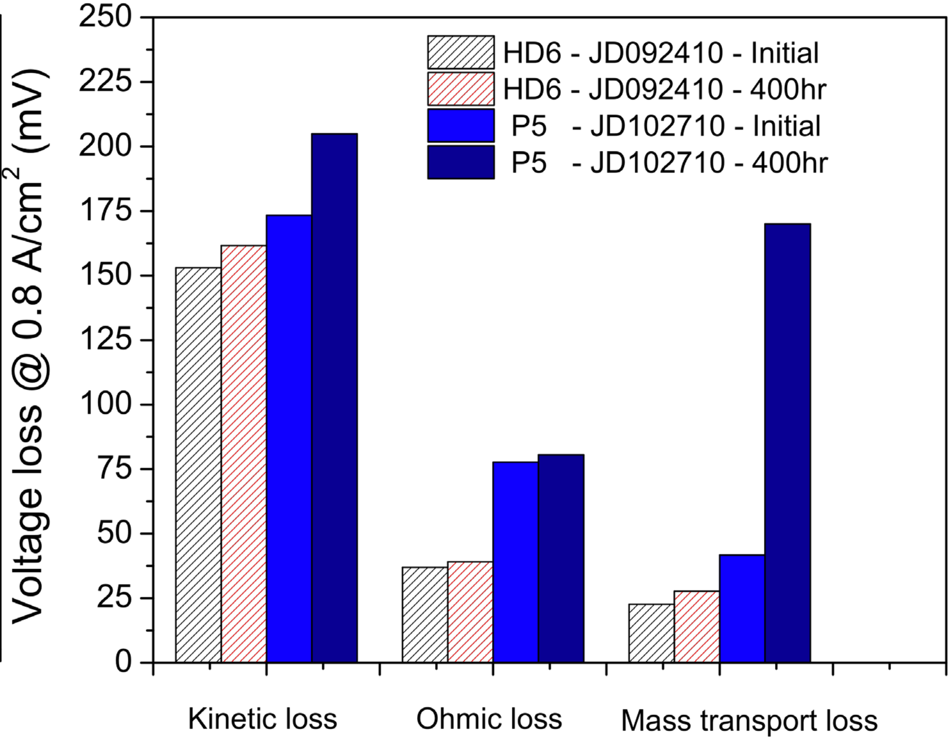
Greater losses in P5

P5 (40% ECSA @ 177hrs, 30mV loss @ 0.8A/cm2 @ 150hrs)

HD6 (30mV loss @ 1.5A/cm2 @ 140 hrs)

Voltage loss Breakdown





LBNL modeling used for VLB

P5 shows significant mass transport losses due to carbon corrosion (Failure Analysis [F/A] in progress to relate to physical property)

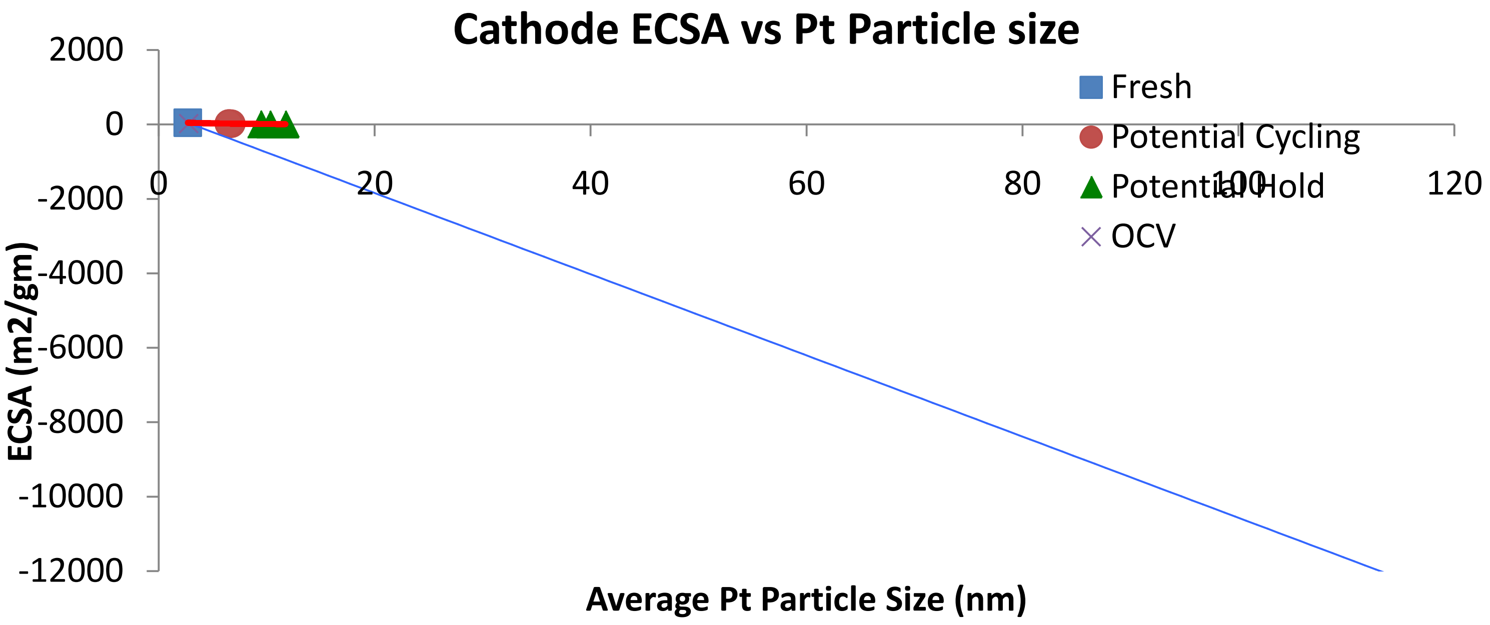
Little Ohmic changes

More kinetic losses in P5

Some carbon corrosion in catalyst cycling AST

Correlation (Performance/Property)

Accomplishments /Progress

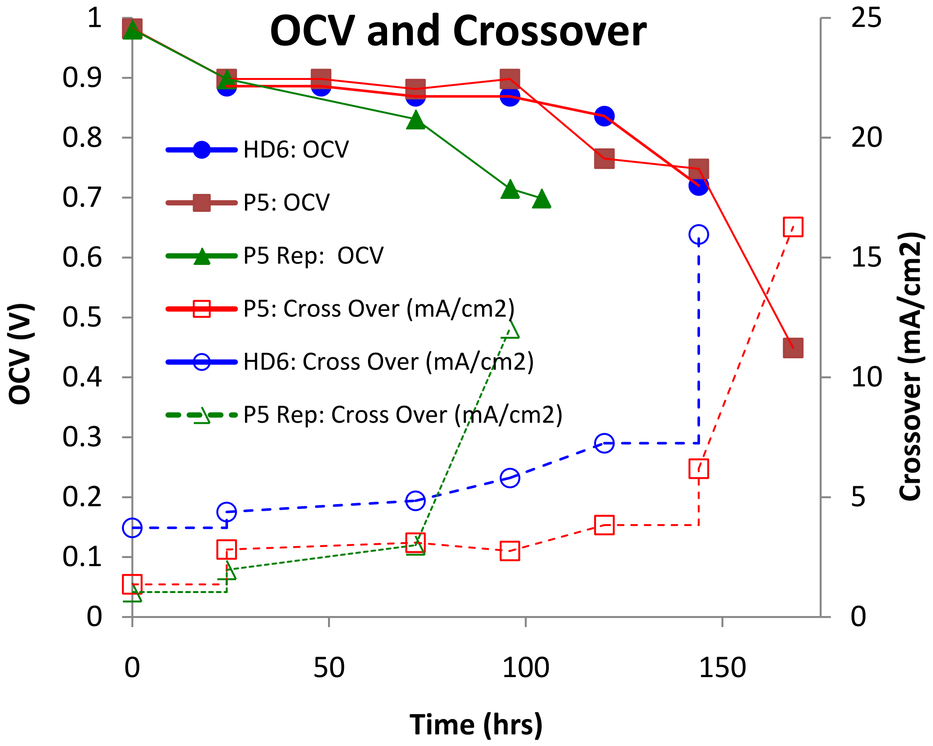


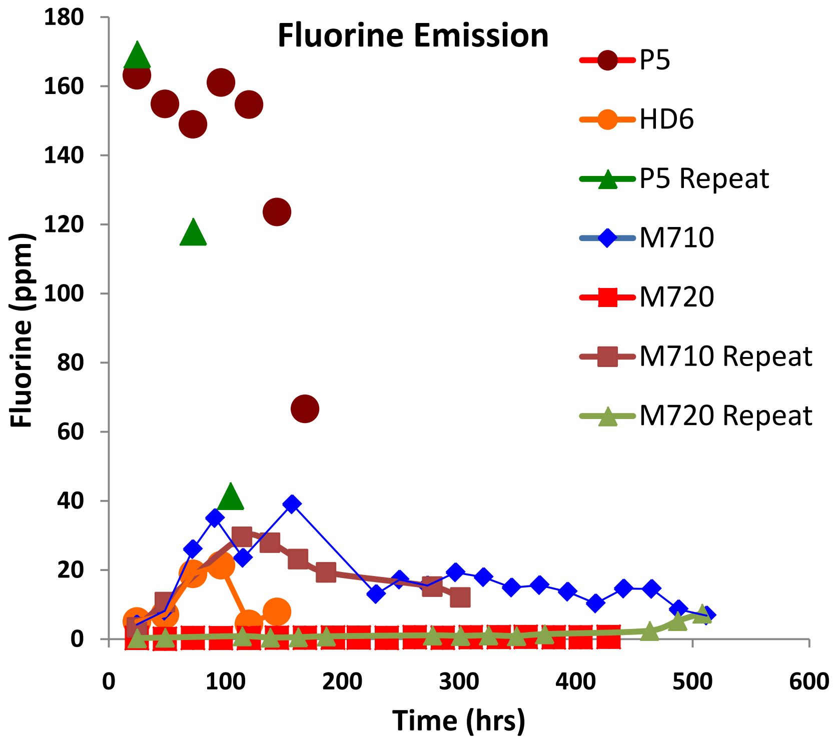
Good correlation between Pt-particle size and ECSA
Irrespective of mechanism

Baseline data sharing with other projects
ECSA can also be affected by ionomer degradation (Input from other LANL degradation project)

OCV AST

Accomplishments /Progress



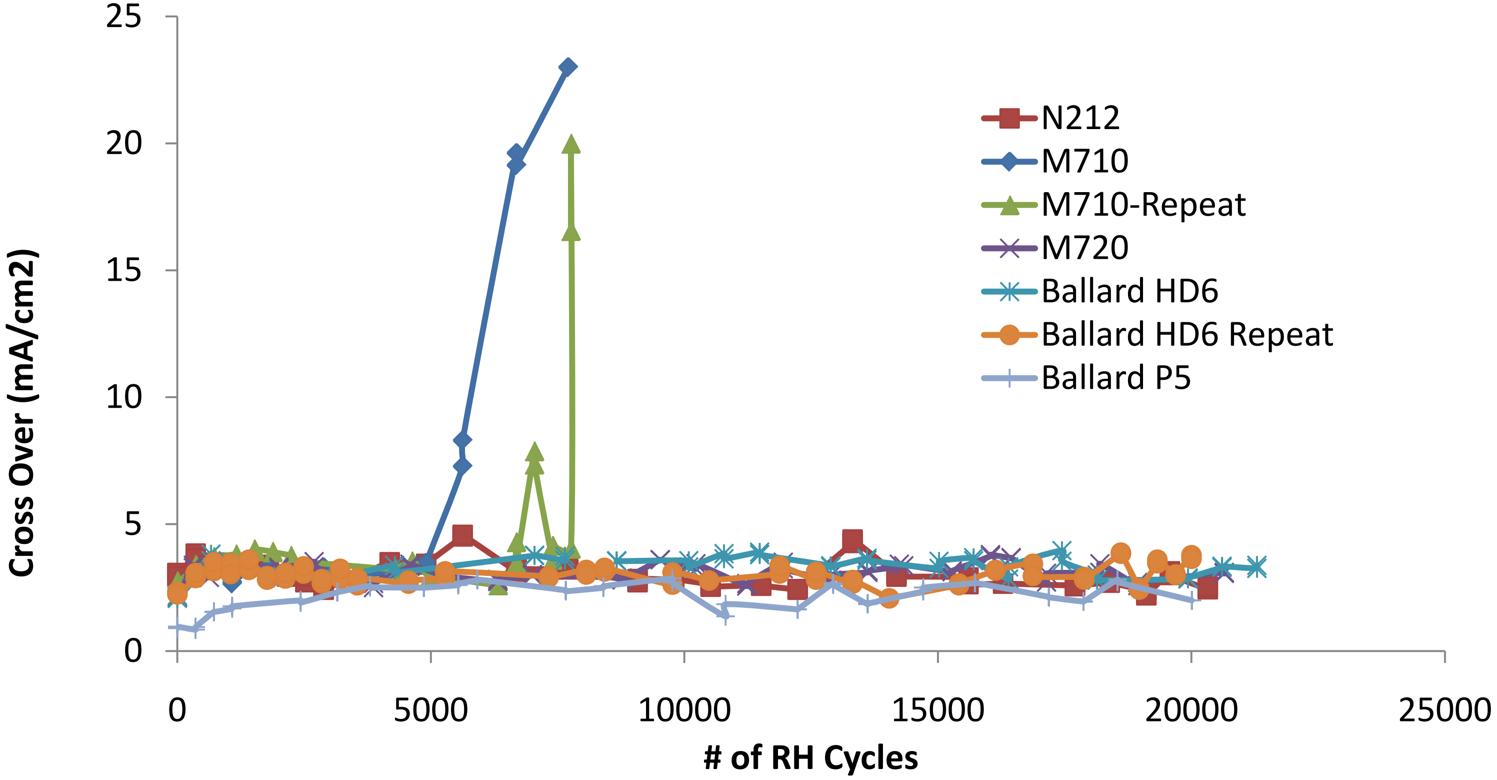


High sample-sample variation in cross over and OCV data.
Little change in HFR. Edge failures observed.
Consistent Fluorine emission rates : Will be used with F/A analysis for correlations
Ability to distinguish between W.L. Gore's lower and higher durability membranes

Los Alamos

RH Cycling AST

Accomplishments /Progress



RH cycling test has ability to distinguish between W.L. Gore's lower and higher durability membranes

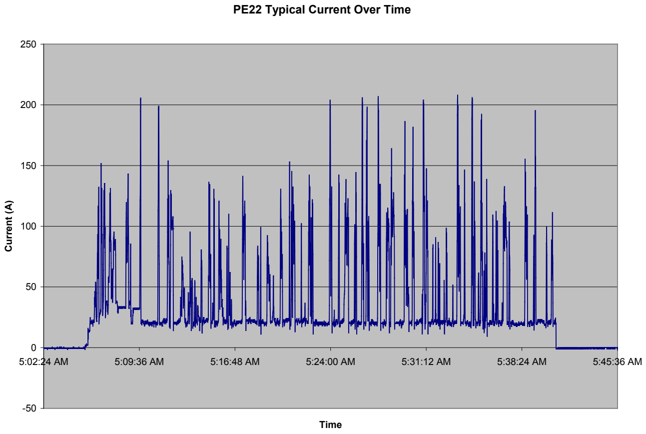
N212 and Ballard MEAs have similar durability

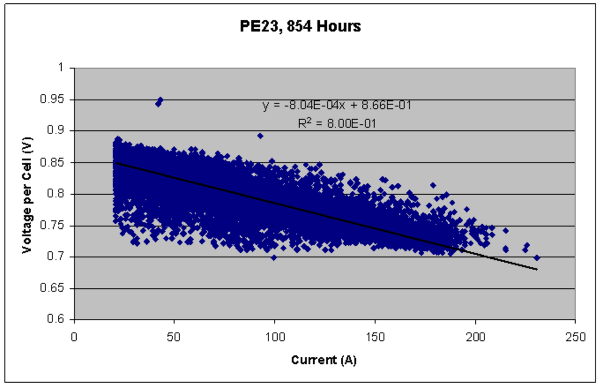
Good reproducibility of failure point (not so for rate of failure)

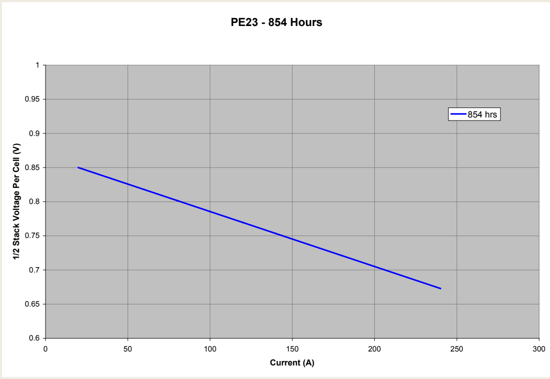
Field Data

- History of P5 Stacks are as follows:
  - PE4 with 2,769 hours of operation
  - PE22 with 3,360 hours of operation
  - PE24 with 2,597 hours of operation
  - All 3 buses operated in Hamburg for their life
- HD6 Stack is designated as follows:
  - SN5096 with 6,842 hours of operation
  - Stack was system tested in lab under Orange County Transit Authority (OCTA) cycle
  - Due to pull outs of MEAs from stack will have failure analysis (FA) data at ~2,400 hours, 4,300 hours and 6,842 hours

Field Data : Analysis


PE22 Typical Current Over Time


PE23, 854 Hours


PE23 - 854 Hours

<u>Current vs Time</u>

Highly dynamic behavior in field operation seen by current requests

<u>Voltage vs Current</u>

Leads to large scatter in data points which needs to be further processed to get useful data

<u>Averaged Pol. curve</u>

In this presentation, took average of points to calculate stressors and performance

Field Data hard to analyze due to high dynamics
To make use of field data, had to reduce stressor signals such as Voltage, Temperature, and Relative Humidity to averages

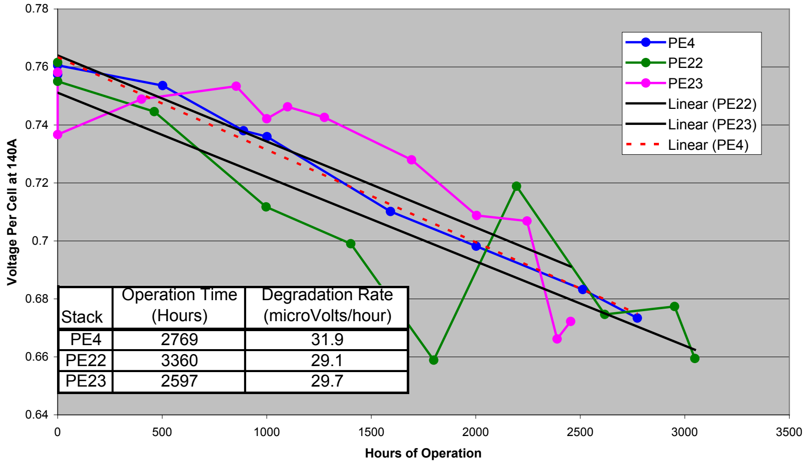
Field Data : Failure Modes

- Two failure modes of interest were Voltage Degradation and Membrane Transfer Leak
- P5 data
  - Data over a sample stretch of 1-2 hours were analyzed to define performance degradation
  - 8-10 time periods per stack were analyzed to ensure enough points to develop a good average performance degradation rate
  - Additionally, overall data were analyzed to determine the number of stack soak times that would cause an air – air condition
  - Membrane transfer leak initiation was not available from the recorded data therefore only BOL and EOL data available
- HD6 data
  - As part of the overall duty cycle, polarization tests were periodically performed to give 26 points over ~ 6,900 hours to draw degradation rate from
  - Membrane transfer leaks were monitored on the same frequency as the polarization tests

Voltage Degradation Rates

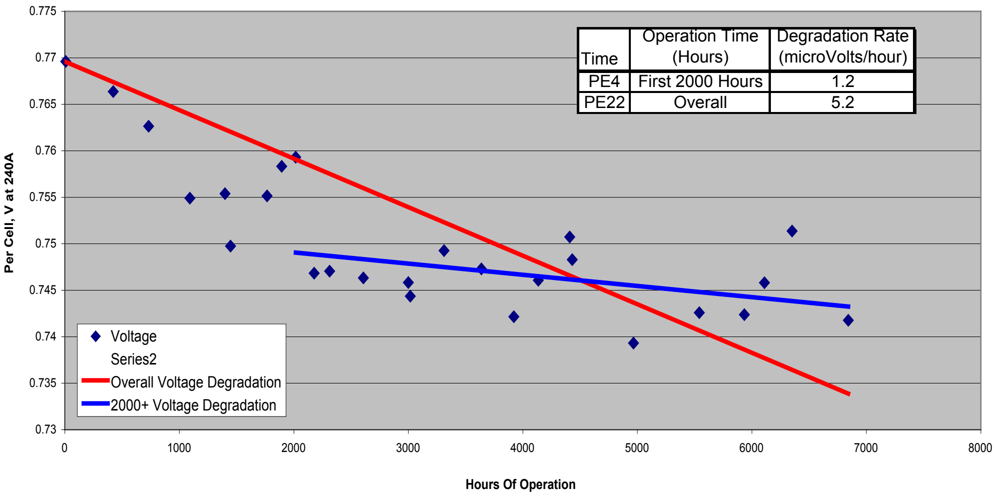
Accomplishments /Progress

Half-Stack Performance at ~0.5 A/cm2
for PE4 (H-0519), PE22 (H-0352) and PE23 (H-0470)



Stack	Operation Time (Hours)	Degradation Rate (microVolts/hour)
PE4	2769	31.9
PE22	3360	29.1
PE23	2597	29.7

HD6 75 KW DV Module
Stack Degradation @ ~0.5 A/cm2



Time	Operation Time (Hours)	Degradation Rate (microVolts/hour)
PE4	First 2000 Hours	1.2
PE22	Overall	5.2

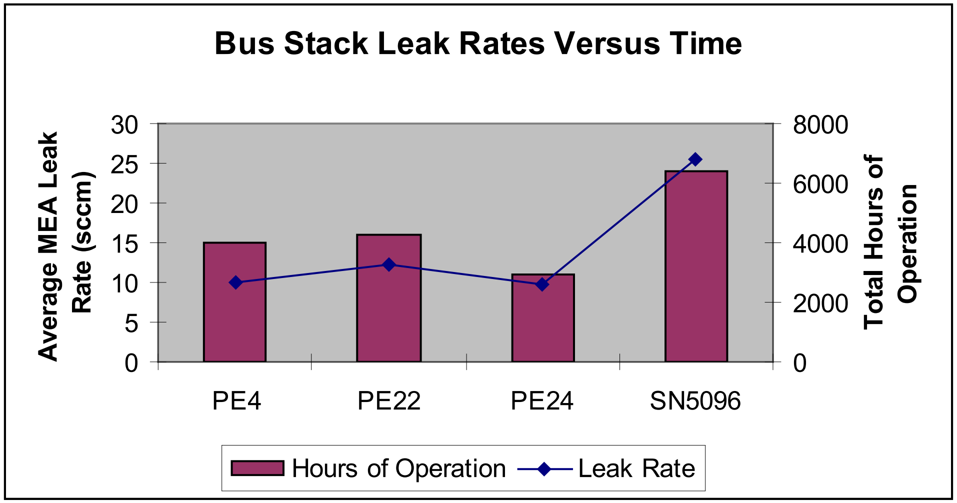
All the P5 bus stacks have a similar voltage degradation rate of ~ 30 microVolts/cell/hr

- There is variability sample point to sample point which likely is an indication of the variability of recoverable performance degradation in service

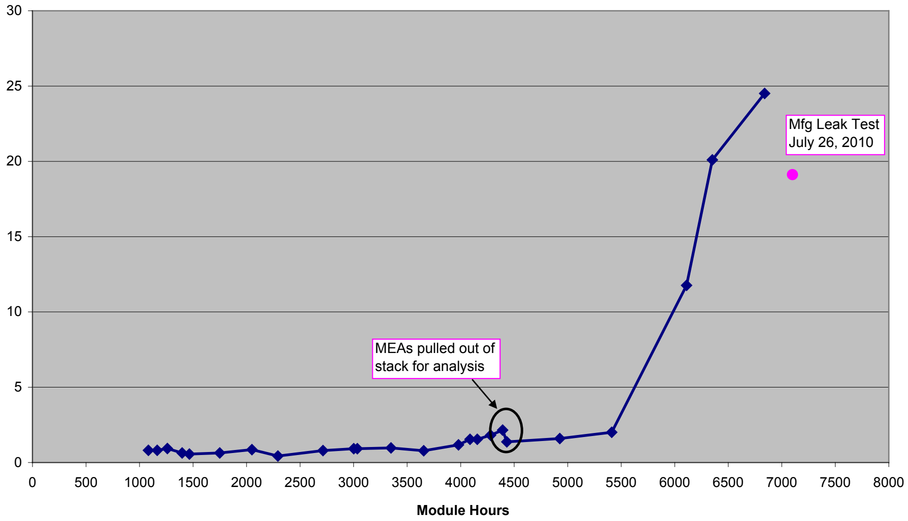
The HD6 voltage degradation rate overall was much lower than P5 at ~ 5.2 microVolts/cell/hr but has two distinct trends

- Over first 2000 hours, degradation rate measured 9.6 uV/hr/cell
- Over 2000 to 7000 hours, degradation rate measured at 1.2 uV/hr/cell
- Note, as HD6 was operated in lab, which allows for higher confidence in voltage measurements as cycle was interrupted to get clean data

Leak Rates Versus Time



HD6 75 KW DV Module
Oxidant to Fuel Transfer Leak Rate @ 0.5barg N2
Stack SN 5096



P5 bus showed no trend of operational hours versus EOL transfer leak rate

Sample analysis of 10 cell blocks from 2 P5 stacks indicated that transfer leaks were in the majority if not every MEA that was operated in the bus – very strong wear out characteristics

HD6 showed an extensive shift in time. A high transfer leak initiation with high propagation starting to occur around 5,500 hours of operation.

Stressors

- HD6 showed much higher resistance to transfer leaks and performance degradation
- From operational stressor analysis, when compared to P5, HD6 had:
    - Greater frequency of higher potential
    - Lower average operating temperature
    - Higher relative humidity
    - Lower air/air start-ups
- P5 buses, while running on different routes, showed fairly consistent stressor levels.
- PE23 shows slightly better life characteristics than other P5 stacks
    - Lower number of air/air start-ups only tangible difference in stressors analyzed
- Higher RH in PE22 (more voltage loss and less transfer leak rate)

Operational Stressor	PE4 (H-0519)	PE22 (H-0352)	PE23 (H-0470)	HD6 DV Module
Voltage (%cycle >0.8V/cell)	52	48	53	57
Temperature (%cycle >70C)	54.8	76.3	66.1	12.5
# Air/air starts per Hour	0.130	0.124	0.101	<0.015
Total # of Air/Air Starts	361	417	263	<100
Humidity (%cycle in RH range)	55 b/w 84-92%RH	50 b/w 90-98%RH	55 b/w 86-94%RH	100% >95%RH
Hours of Operation	2769	3360	2597	6842
Degradation Rate (BOL to EOL) at ~0.5 A/cm2 (uV/cell/hr)	**31.4**	**33.5**	**26.3**	**5.2**
mV/cell lost over life (@ ~0.5 A/cm2)	87	113	68	20
Transfer Leak Rate	15ccm/cell @2.7k Hrs	16ccm/cell @3.3k Hrs	11ccm/cell @2.6k Hrs	24ccm/cell @6.8k Hrs

Collaborations

LANL (**Rangachary Mukundan, Rodney Borup, John Davey, Roger Lujan, Dennis Torraco, and Fernando Garzon)**

- Co-ordinate project
- Perform all ASTs and Drive cycle testing
- Materials Analysis of BOL and EOL materials

Ballard Power Systems (Greg James)

- Analyze Bus Data
- Deliver BOL MEAs used in Buses
- Analysis of EOL MEAs

LBNL (Adam Weber)

- Detailed Voltage loss break-down
- Statistical correlation of materials properties to lifetimes and AST metric loss of materials with differing durabilities

Ion Power (Steve Grot)

Deliver MEAs with varying durability

ORNL (Mike Brady)

Deliver metal bipolar plates

W. L. Gore and Associates Inc., and SGL Carbon to supply materials

Summary/Future Work - I

- Initial AST (electrocatalyst, catalyst support, membrane chemical and mechanical) performed
  - Baseline materials from W.L. Gore (completed)
  - P5 and HD6 (Initial tests complete, repeats in progress)
  - Ion Power MEAs (initiated)
  - Failure analysis (in progress)
- Bus Data analysis completed on P5 and HD6 bus stacks
  - Failure analysis of HD6 and P5 stacks initiated
- Hardware obtained for drive cycle testing
  - MEAs delivered in March to initiate drive cycle testing
  - Parametric study (Temperature, RH, pressure)
- Modeling of Voltage loss break down initiated
  - Kinetic, Ohmic and Mass transport losses identified
  - Mass transport models to be refined

Summary/Future Work - II

- Bipolar plate ASTs to be completed in summer
- GDL ASTs to be initiated
    - Awaiting input from 2 other DOE funded projects
- Other ASTs including combined mechanical/chemical cycling, and 0.6V – < 1 V (input from other LANL durability project) potential cycling to be tested later this year
- Correlation of material properties with degradation rates
    - Pt particle size and ECSA/kinetic losses (identified)
    - Mass transport losses and electrode/GDL morphology
    - Crossover/Fluorine emission and membrane thickness
- F/A from Field data to help correlate AST and Field data

Acknowledgements

Nancy Garland
(DOE – EERE – Fuel Cell Technologies – Technology Development Manager)

Fuel Cell Tech Team (Craig Gittleman and Jim Waldecker) for guidance on ASTs

W. L. Gore and Associates (MEAs)

SGL Carbon (GDLs)

Technical Backup Slides

1-D simplified model

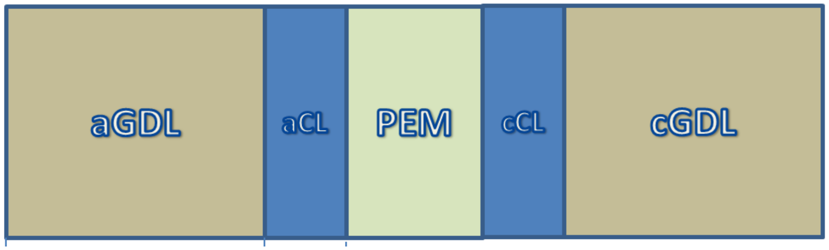
- Modeling methodology
  - Utilize data were measured and have submodels to determine other parameters
  - Model can do full impedance from underlying physics

$$x_i = \bar{x}_i + \mathrm{Re}\left\{\tilde{x}_i \exp(j\omega t)\right\}$$

Steady-state solution   Complex function

$$Z = \frac{\tilde{V}}{\tilde{i}}$$

  - Fit model parameters to full suite of experimental data
    - Impedance
    - Polarization curve
      - HelOx and other conditions
  - Typical fitting parameters are effective diffusion coefficients and ionomer-film oxygen resistivity



- The model is 1-D and focuses currently on the cathode
- Catalyst layer
  - Agglomerate model using Pt-oxide coverage terms and ionomer film
  - Gas transport mainly by Knudsen diffusion
- Diffusion media
  - Modeled using Stefan-Maxwell diffusion
    - Currently single phase but are beginning to implement simplified two-phase treatment

DOE Tech Team Protocol (Pt Catalyst)

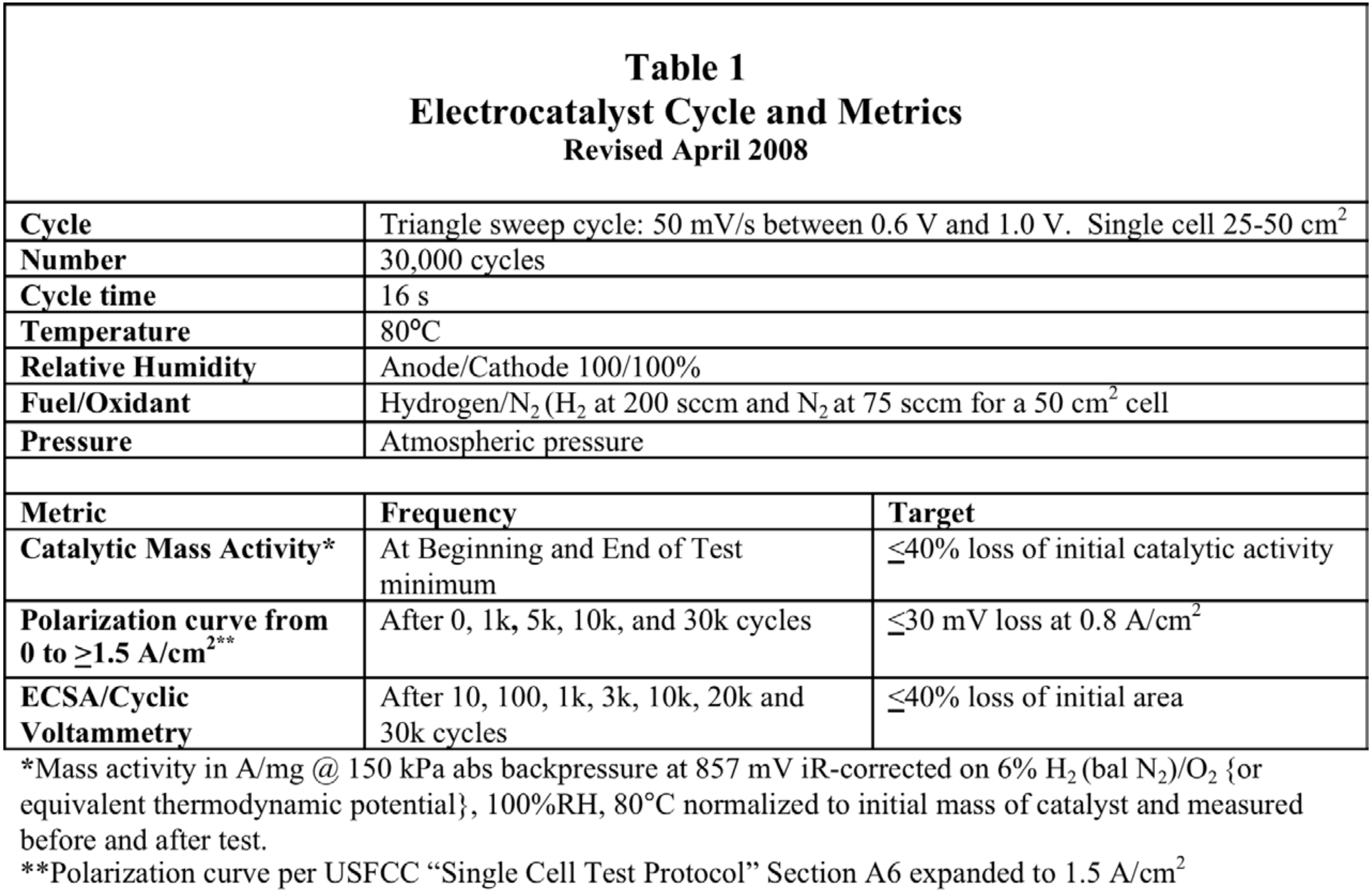


Table 1
Electrocatalyst Cycle and Metrics
Revised April 2008

Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-50 cm^2
Number	30,000 cycles
Cycle time	16 s
Temperature	80°C
Relative Humidity	Anode/Cathode 100/100%
Fuel/Oxidant	Hydrogen/N_2 (H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell
Pressure	Atmospheric pressure

Metric	**Frequency**	**Target**
Catalytic Mass Activity*	At Beginning and End of Test minimum	$\leq$40% loss of initial catalytic activity
Polarization curve from 0 to $\geq$1.5 A/cm^{2}**	After 0, 1k, 5k, 10k, and 30k cycles	$\leq$30 mV loss at 0.8 A/cm^2
ECSA/Cyclic Voltammetry	After 10, 100, 1k, 3k, 10k, 20k and 30k cycles	$\leq$40% loss of initial area

*Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H_2 (bal N_2)/O_2 {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

**Polarization curve per USFCC "Single Cell Test Protocol" Section A6 expanded to 1.5 A/cm^2

DOE Tech Team Protocol (Catalyst Support)

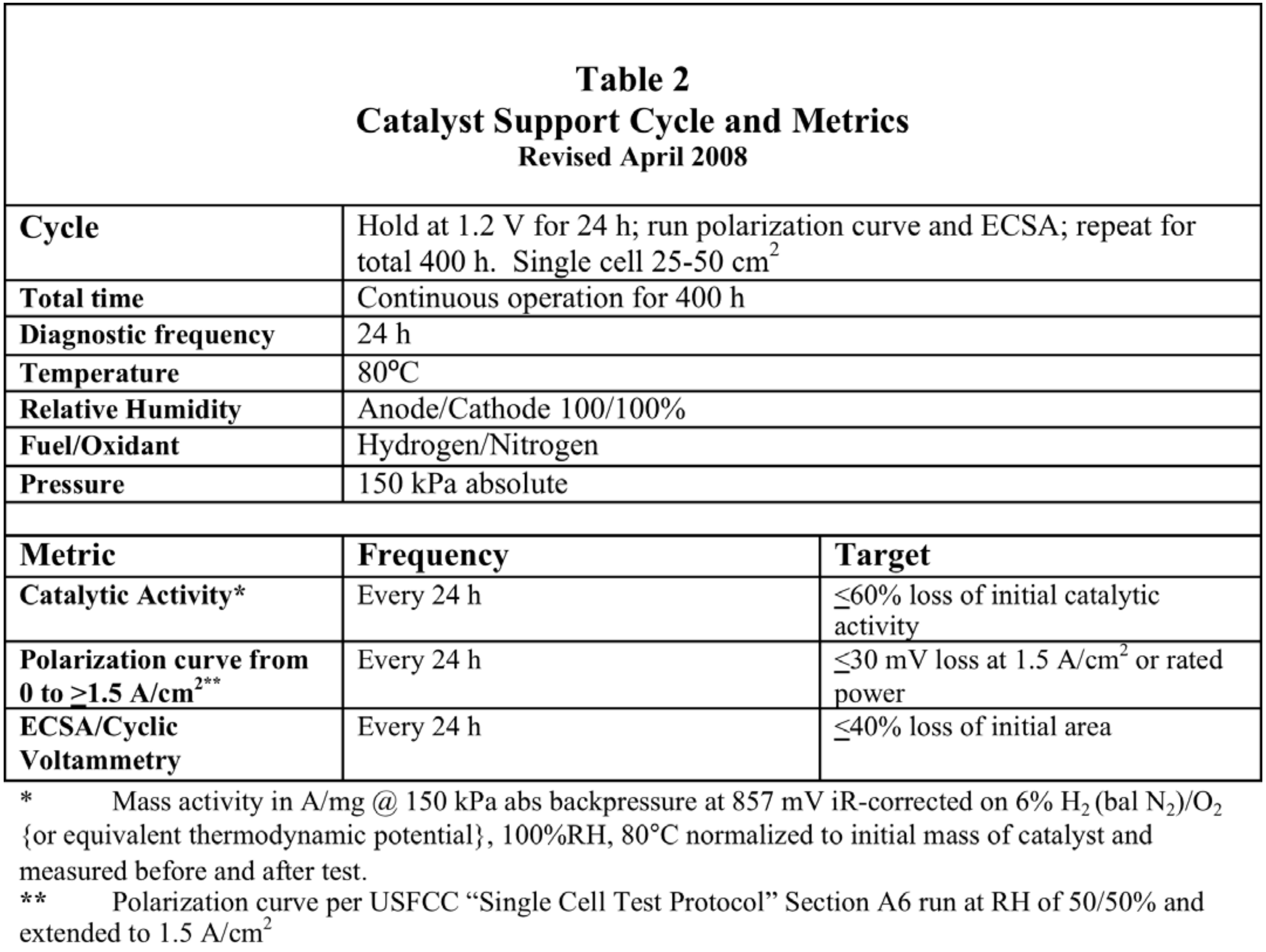


Table 2

Catalyst Support Cycle and Metrics

Revised April 2008

Cycle	Hold at 1.2 V for 24 h; run polarization curve and ECSA; repeat for total 400 h. Single cell 25-50 cm^2
Total time	Continuous operation for 400 h
Diagnostic frequency	24 h
Temperature	80°C
Relative Humidity	Anode/Cathode 100/100%
Fuel/Oxidant	Hydrogen/Nitrogen
Pressure	150 kPa absolute

Metric	**Frequency**	**Target**
Catalytic Activity*	Every 24 h	$\leq$60% loss of initial catalytic activity
Polarization curve from 0 to $\geq$1.5 A/cm^{2**}	Every 24 h	$\leq$30 mV loss at 1.5 A/cm^2 or rated power
ECSA/Cyclic Voltammetry	Every 24 h	$\leq$40% loss of initial area

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H_2 (bal N_2)/O_2 {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

** Polarization curve per USFCC "Single Cell Test Protocol" Section A6 run at RH of 50/50% and extended to 1.5 A/cm^2

DOE Tech Team Protocol (Membrane/Chemical)

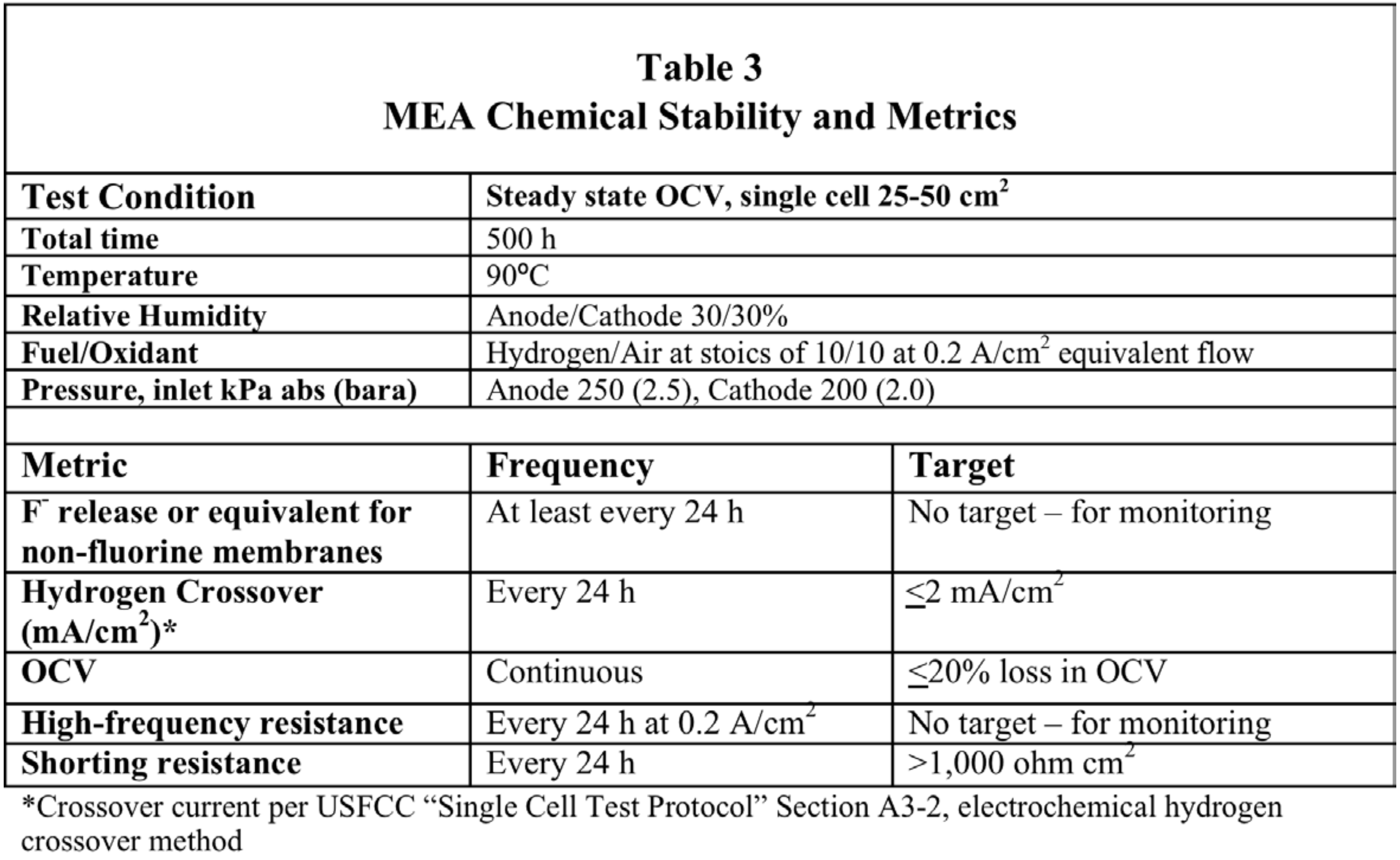


Table 3
MEA Chemical Stability and Metrics

Test Condition	**Steady state OCV, single cell 25-50 cm^2**
Total time	500 h
Temperature	90°C
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	$\leq$2 mA/cm^2
OCV	Continuous	$\leq$20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring
Shorting resistance	Every 24 h	>1,000 ohm cm^2

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

DOE Tech Team Protocol (Membrane/Mechanical)

Table 4
Membrane Mechanical Cycle and Metrics
(Test using a MEA)

Cycle	**Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50 cm^2**
Total time	Until crossover >2 mA/cm^2 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	$\leq$2 mA/cm^2
Shorting resistance	Every 24 h	>1,000 ohm cm^2

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