Accelerated Testing Validation

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Project ID #
FC016

Project Overview

Timeline

- Project Start Date
  - **August 2009**
- Project Duration
  - **4 Years (End: Sept '13)**
- ≈ 15 % complete

Budget

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

LANL	$550k
Partners (Univ. & Ind.)	$239k
Other National Labs	$234k
FY10 Total	$1023k

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 Systems (System Integrator)
- Ion Power Inc. (Materials Supplier)
- ORNL (Metal Bipolar Plates)
- LBNL (Modeling)

Relevance

Importance of Accelerated Stress Test (AST)

- Allows faster evaluation of new materials and provides a standardized test to benchmark existing materials
- 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

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

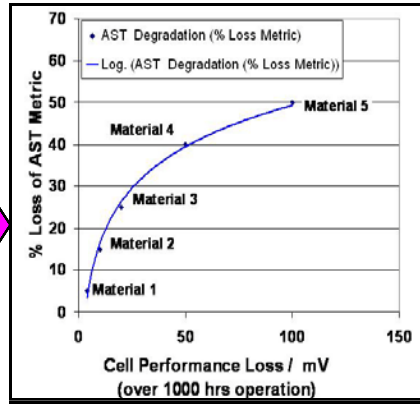
Technical Targets

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.

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, morphology, composition, loading

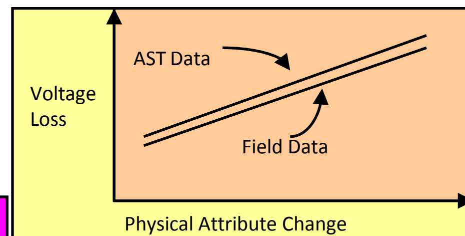
Membrane
Cross-over, shorting resistance, HFR, thickness
GDL
- Impedance, Hydrophobicity

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 (LBNL)

- 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

Begin 08/09 | M1 03/10 | M2/M3 09/10 | M4 09/11 | M5 09/12 | M6 09/13

G1 01/12 | G2 09/12 | End 09/13

<u>Milestones</u>

M1 : Ballard delivers BOL Bus MEAs (04/2010)

M2 : Develop GDL AST

M3 : Report summarizing bus data (voltage degradation, operating conditions)

M4 : Complete initial AST testing

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

Co-ordinate with USCAR Tech Team and USFCC fuel cell council

<u>Go/No go Decision</u>

G1 : Initial Correlation of AST vs drive cycle and bus data – Redirect AST based on results

G2 : Go/ No go on Freeze AST for MEA interfaces

Materials Used

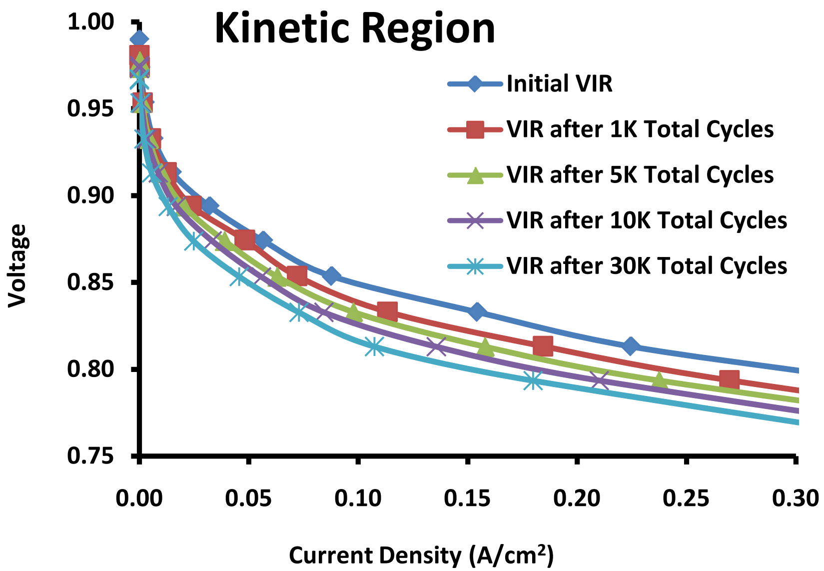
Progress

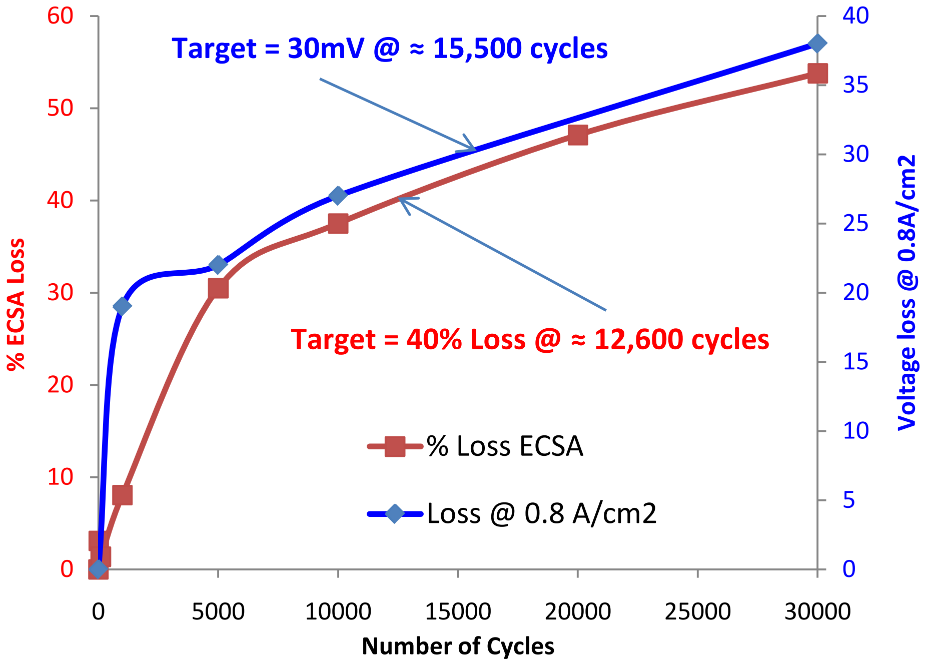
- Gore™ Primea® MESGA MEA A510.1/M720.18/C510.2
- Gore™ Primea® MESGA MEA A510.2/M720.18/C510.4
- Gore™ Primea® MESGA MEA A510.1/M710.18/C510.2
- Agreement with Gore
  - LANL can perform analysis on commercial M710 based MEAs
  - LANL can perform catalyst analysis (particle size distribution by XRD) on 510 series catalysts
  - Gore will perform SEM/TEM for catalyst layer thicknesses and microstructure on M720 based MEAs
- Ion Power
  - Ability to do unfettered analysis on custom MEAs
- GDL
  - SGL 24BC (5% PTFE-substrate/23% PTFE MPL)
- Single serpentine flow field
  - Explore others (Multiple-serpentine, GM water transport project, UTC water transport plates, Nuvera Metal Mesh) for RH cycling

Catalyst Cycling AST

Progress

Cycling in H_2/N_2 from 0.6V to 1V @ 50mV/sec (Details in supplemental slides)

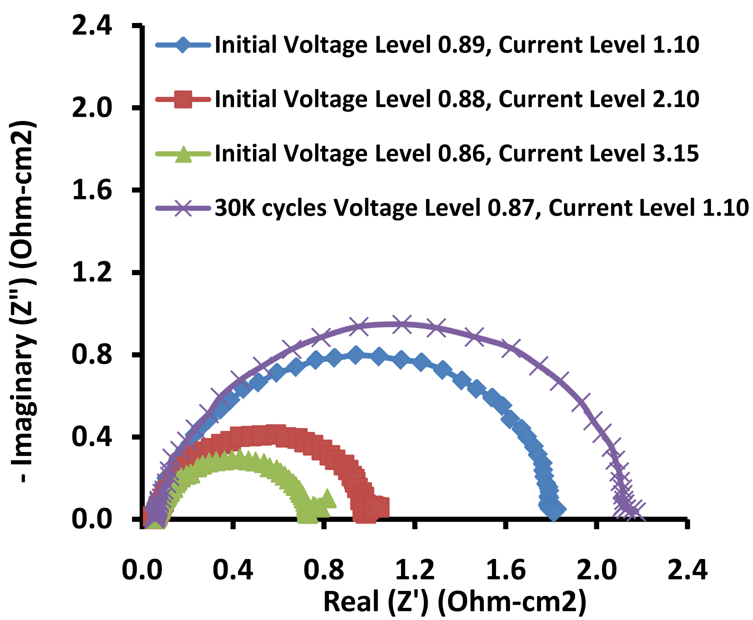


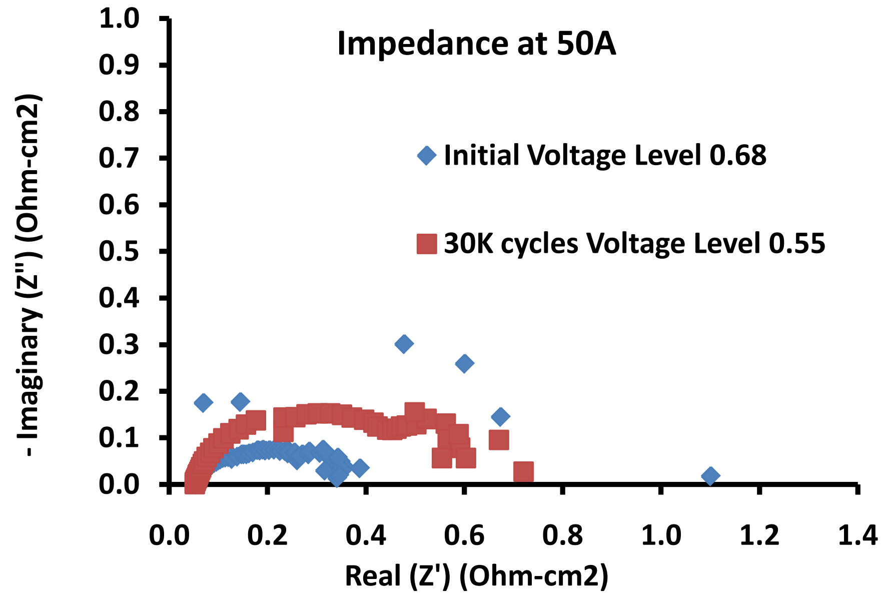


- Clear losses in kinetic region correlated with ECSA and Mass activity losses
- Mass activity loss = 47% from initial to final (Target = 40%)
- Refine correlations between ECSA, Voltage loss and MA targets

Catalyst Cycling Impedance

Progress

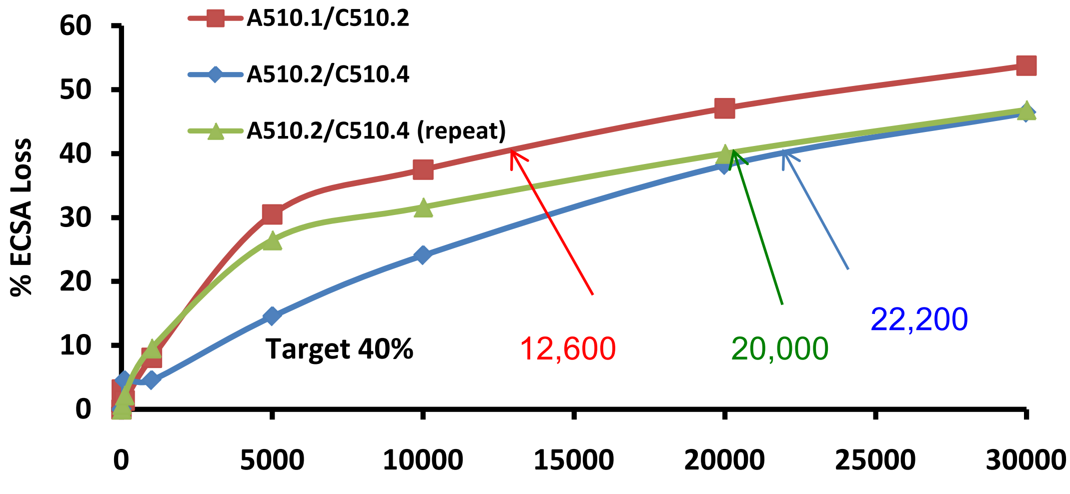


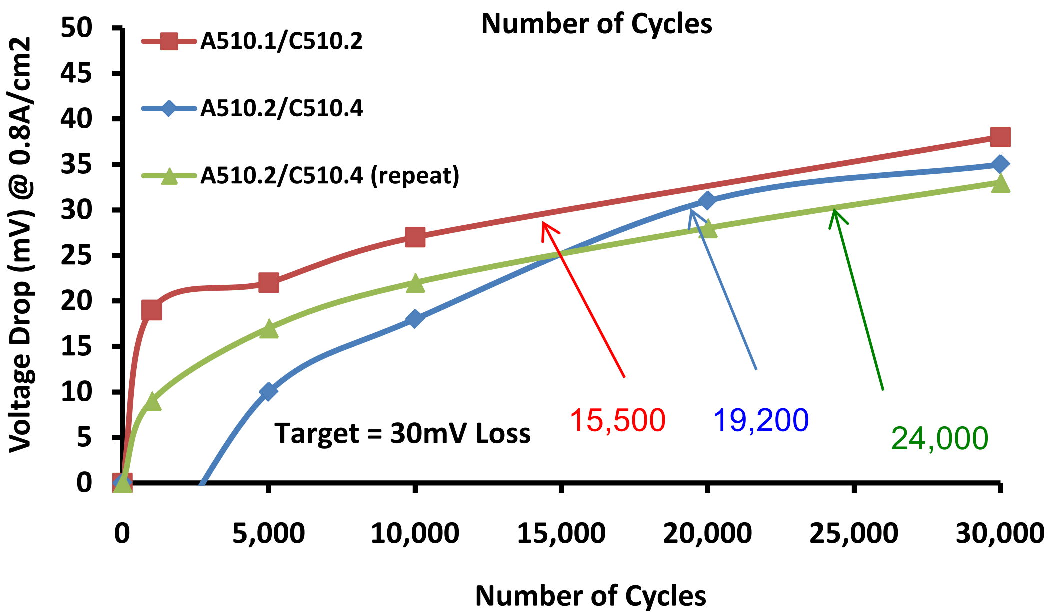


- Significant increase in charge transfer resistance
  - After 30,000 cycles : CT resistance at 0.87V increases 138%
- Slight increase in mass transport resistance
  - After 30,000 cycles : MT resistance increases 40% at 50A

Catalyst Cycling Metrics

Progress



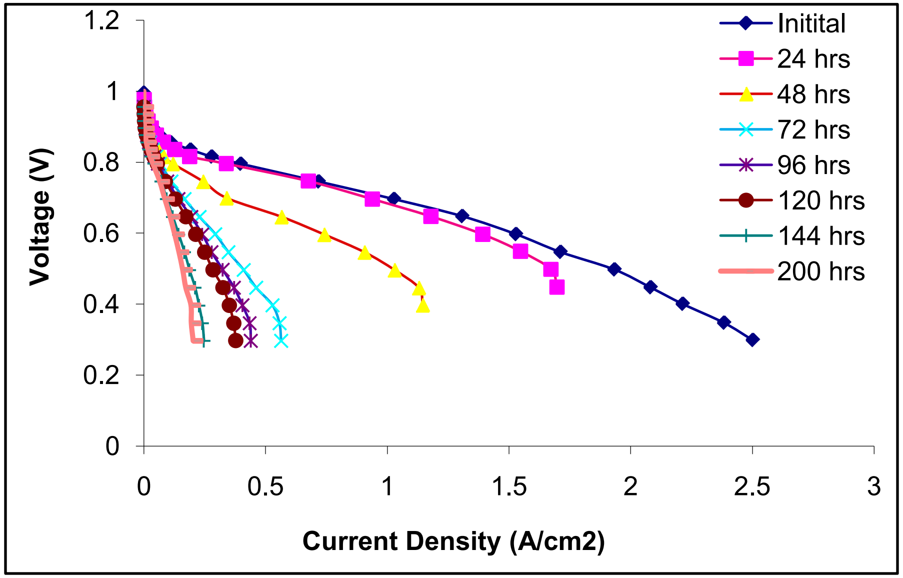


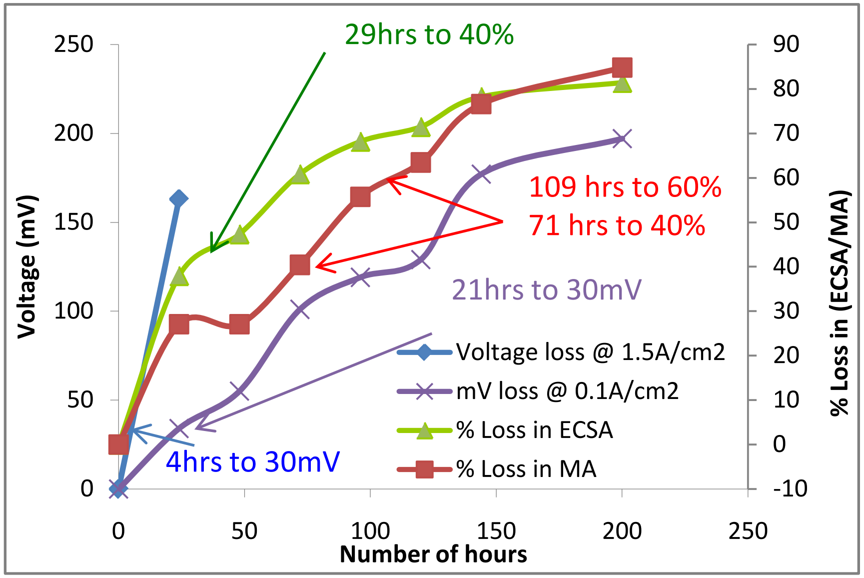
- Performance loss accelerated at lower loadings
- Reasonable repeatability
- Reasonable agreement between ECSA and voltage loss metric (monitor mass activity more frequently)
- Initial values slightly different due to different testing times before starting experiments

Carbon Corrosion AST

Progress

Hold @ 1.2V in H_2/N_2 (Details in supplemental slides)

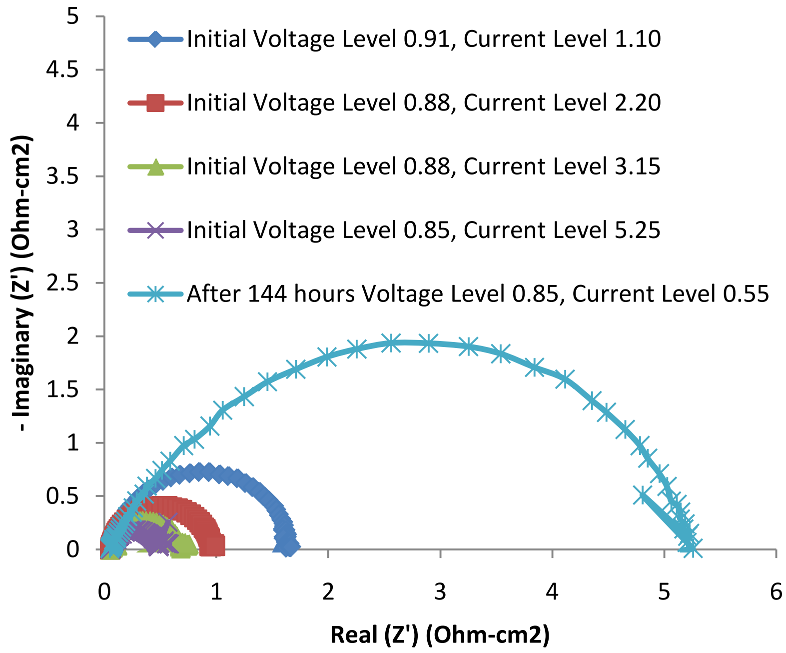


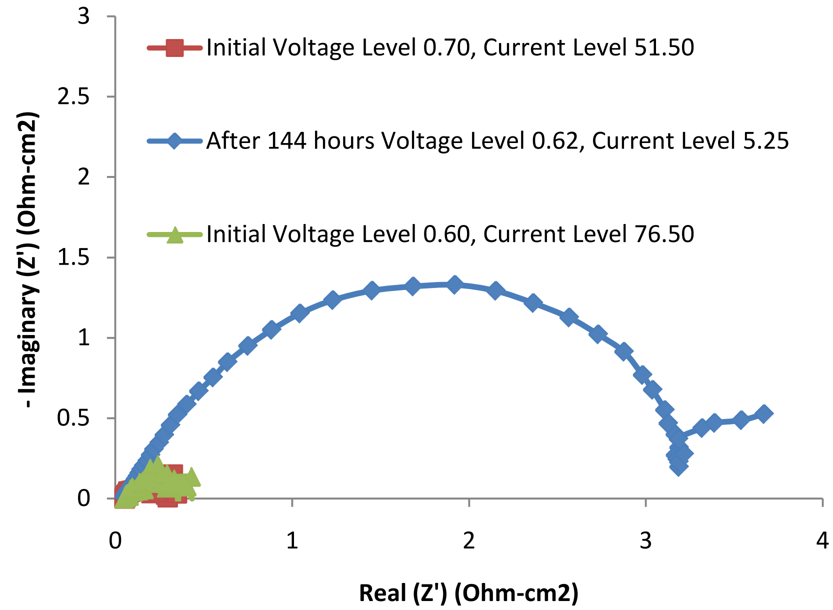


- C-corrosion resistance is very low on the 510 catalyst layer
- Better correlations needed between the various metrics
- VIR degradation >>> ECSA loss due to mass transport losses
- Mass activity loss correlates with ECSA loss reasonably well
- Monitor low frequency impedance to track mass transport losses?

Carbon Corrosion Impedance

Progress

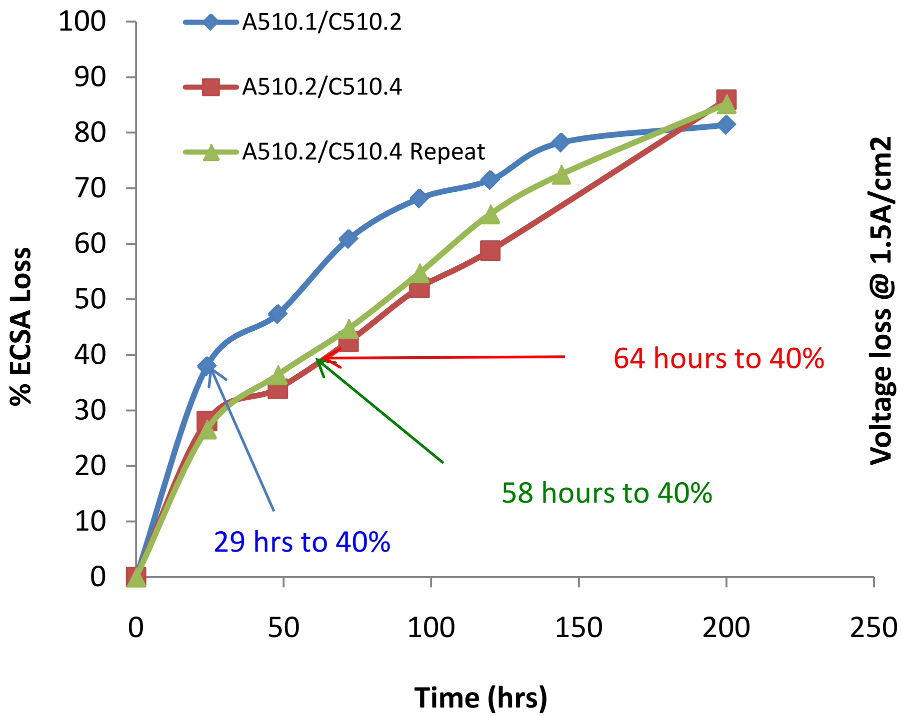


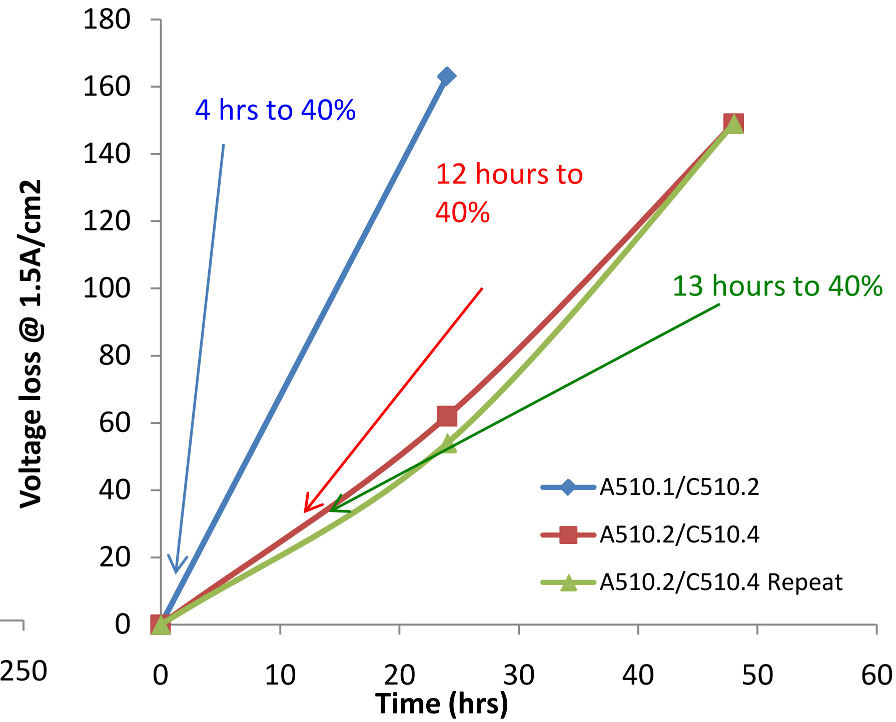


- Significant increase in charge transfer resistance
  - After 144 hours: CT resistance at 0.85V increased by 866 %
- Significant increase in mass transport resistance
  - After 144 hours: MT resistance at $0.1 A/cm^2$ > initial MT resistance at > $1 A/cm^2$

Carbon Corrosion Metrics

Progress



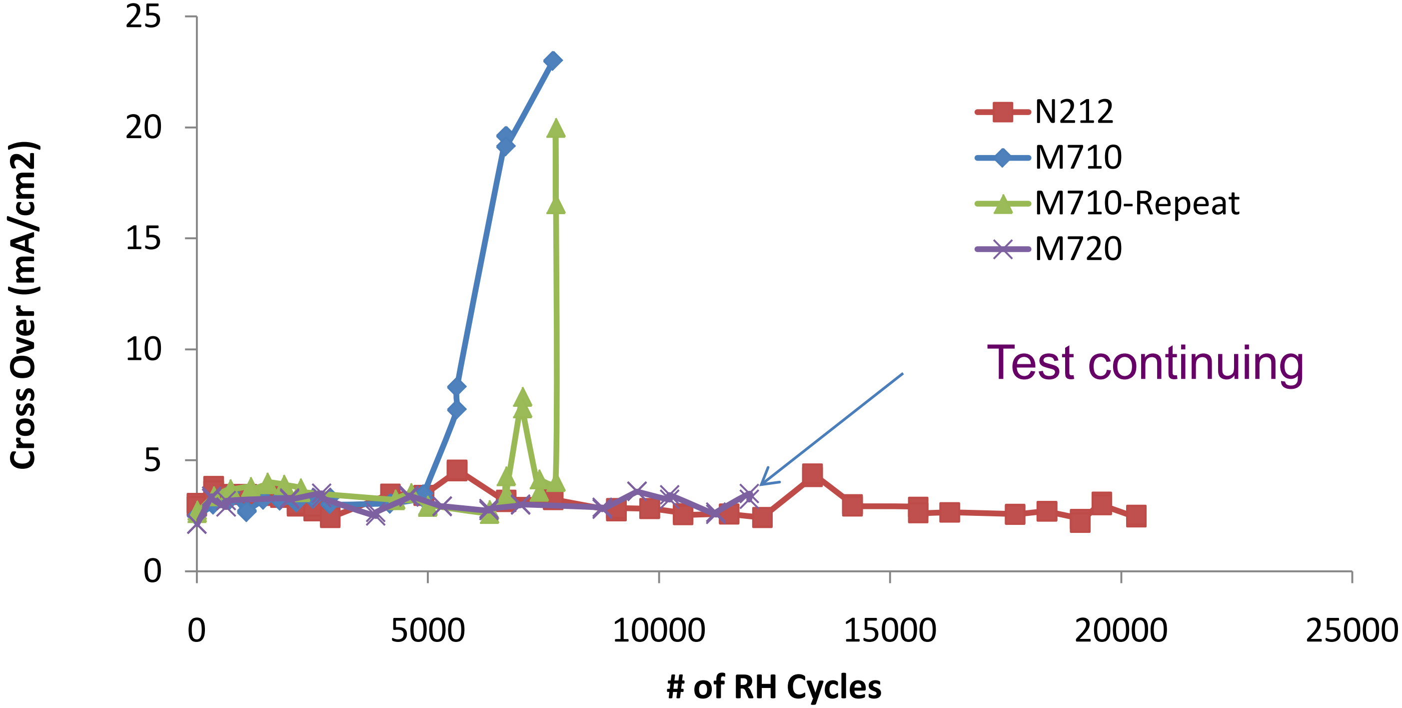


- Performance loss accelerated at lower loadings
- Reasonable repeatability
- Need better metrics to correlate with voltage loss

RH Cycling Metrics

Progress

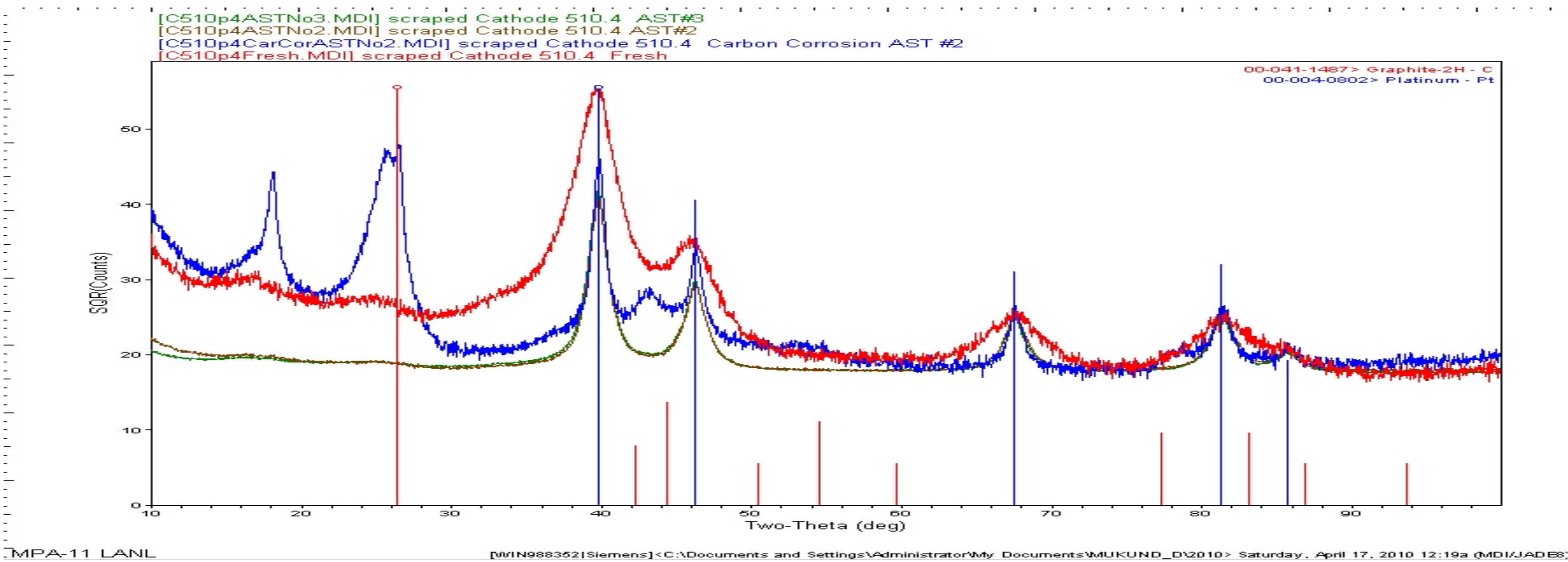
Cycle: 0%RH and 90°C dewpoint: 2 min. each (Details in supplemental slides)

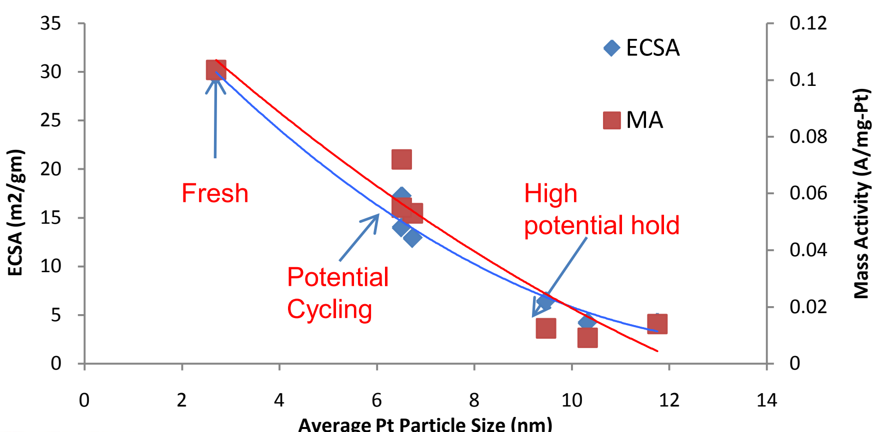


- Gore™ M720 has significantly better durability than M710
- N212 has excellent durability
- Good reproducibility of failure point (not so for rate of failure)
- Target (2mA/cm^2 @ 30°C) – Need target at 80°C (3-4mA/cm^2?)

Characterization

Progress





- Particle size growth correlates to ECSA and Mass activity loss (quadratic fits are shown by the solid lines)
- Anode grows from 2.5nm to 3.5nm
- Will be used to compare AST to real world and drive cycle data

Accomplishments (Partners)

Progress

BALLARD®

Attribute	P5 Bus MEA	HD6 Bus MEA
Bus Cycle	Site Specific	Orange County Transit Authority Cycle
Technology Vintage	2002	2007
Total Catalyst Loading	1.05 mg/cm^2	1 mg/cm^2
Membrane Thickness	50 micron	25 micron
Time to Failure	2,500 – 4,000 hours	~ 6,000 hours
Failure Modes	Performance Degradation & External Leak; Minor Transfer Leak	Transfer Leak
Samples to LANL by April 30th	16	16

Ion Power, Inc

- Contract signed March 2010
- Preparing custom MEAs for LANL and initiated degradation testing

ornl
OAK RIDGE NATIONAL LABORATORY

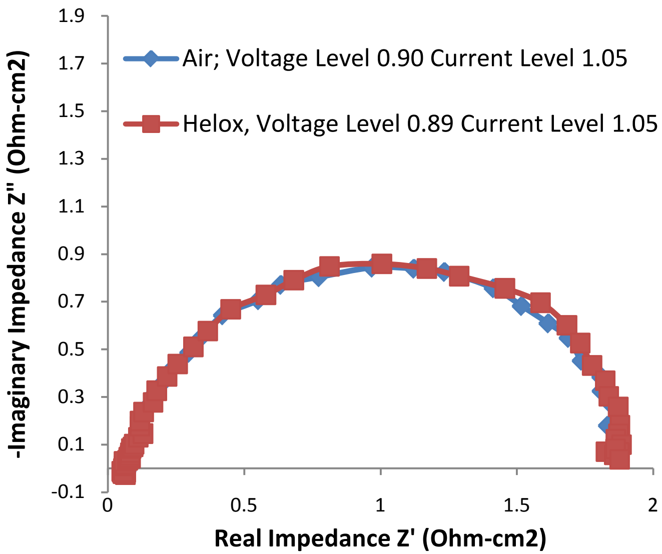
- Preparing coupons and 25 cm^2 nitrided metal bipolar plates (July 2010)
- Hastelloy G35, Ni-50Cr and Fe-20Cr-4V

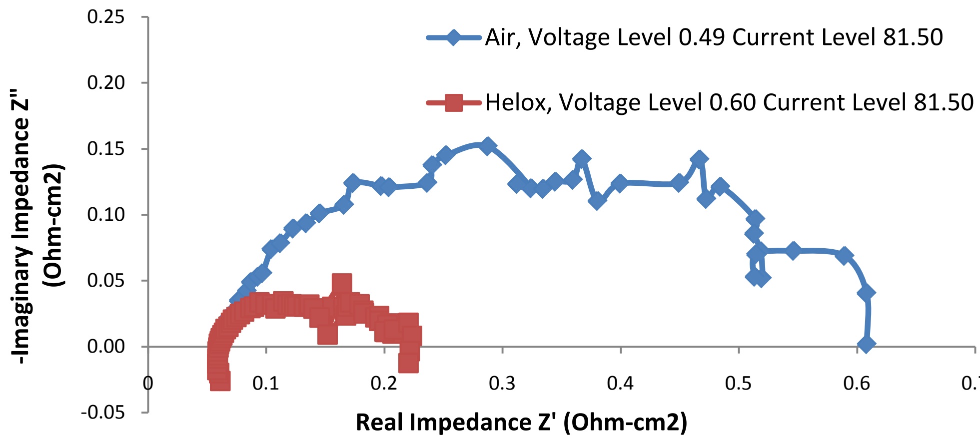
The Institute for Hydrogen and Fuel Cell Research

Los Alamos

Accomplishments (Partners)

Progress





- Modeling
  - Using simplified 1-D model to capture general impacts of changing property
    - Physics-based equations
      - Transport in the membrane
      - Porous electrode
      - Simplified GDL model using breakthrough capillary-pressure parameter and modified GDL length to account for land/channel
    - Developing EIS profiles from physical equations

Berkeley Lab

The Institute for Hydrogen and Fuel Cell Research

Los Alamos

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

Proposed Future Work

Task Schedule, by Quarters (Q) with Milestones (M), Decision Points (G), Deliverables (D)

Q / Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1a				M1												
1b						M2										
1c						D1		G1 M3								
1d												G2 M4				M5
1e						M6										
1f						D2				M7						
2a(i)						M8										
2a(ii)												M9				
2a(iii)																M10
2a(iv)																
2a(v)					As Needed											
2b(i – ii)		D3 M11		M12		M13				M14		M15				M16
3a								M17								
3b							M18						M19			M20
3c									G3							M21
4a																D4
4b	As needed in support of USFCC AST Durability Round Robin															

Task 1. AST Testing (Will initiate combined mech/chem testing of membrane, vary potentials in the catalyst cycling AST)

Task 2: Cell life testing (Start with GM provided protocol)

Task 3: Correlation of AST to Life Data (Modeling work initiated on VLB)

Task 4: Development of New ASTs / Verification of Existing AST (GDL ASTs initiated)

Summary

- All 4 DOE_FCTT ASTs initiated
  - Catalyst durability highly dependent on loading
  - Need for better metrics to monitor mass transport losses in carbon corrosion AST (low frequency impedance)
  - Catalyst particle size correlates well with ECSA, MA, and voltage loss and will be used to relate to “real-world” data
  - Catalyst layer thickness and/or porosimetry data will be used to track carbon corrosion
  - Material sets with varying durabilities have been tested
  - GDL ASTs and modeling of VLB initiated
- BPS started manufacturing of 50 cm^2 MEAs that were used in the bus stack and also analysis of field data
- Catalyst layers with better carbon corrosion durability to be tested

Acknowledgements

Nancy Garland
(Fuel Cell Technologies Program –
Technologies Development Manager)

Craig Gittleman and Jim Waldecker for guidance on ASTs

W. L. Gore and Associates (MEAs)

SGL Carbon (GDLs)

Supplemental Slides

DOE Tech Team Protocol (Pt Catalyst)

Table 1
Electrocatalyst Cycle and Metrics
Revised April 2008

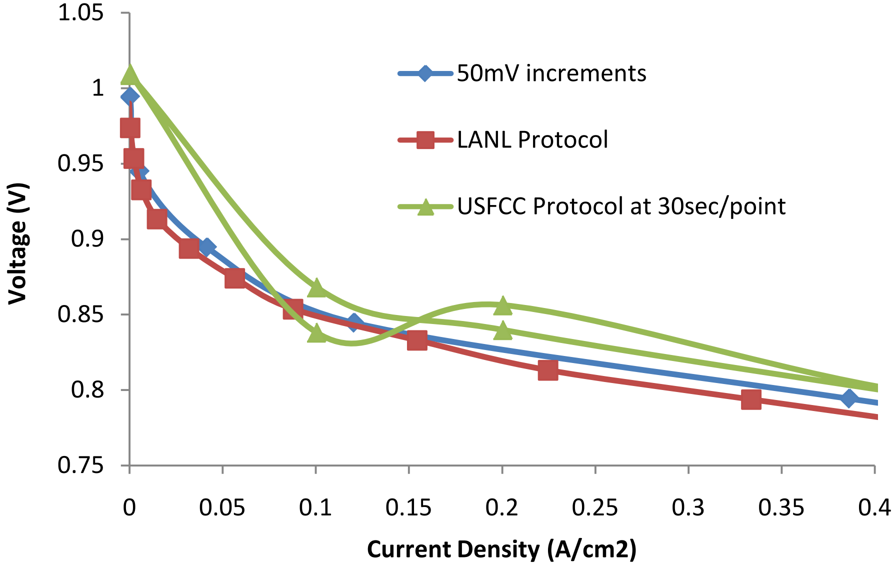
Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-50 cm^2	
Number	30,000 cycles	
Cycle time	16 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/N_2 (H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell	
Pressure	Atmospheric pressure	
Metric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

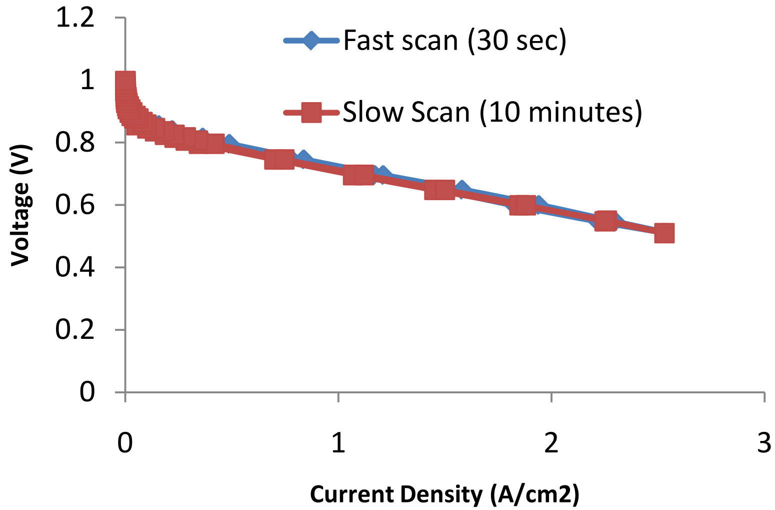
*Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H_2 (bal N_2)/O_2 {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

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

Modified Polarization Curve

- USFCC Polarization curve is not appropriate

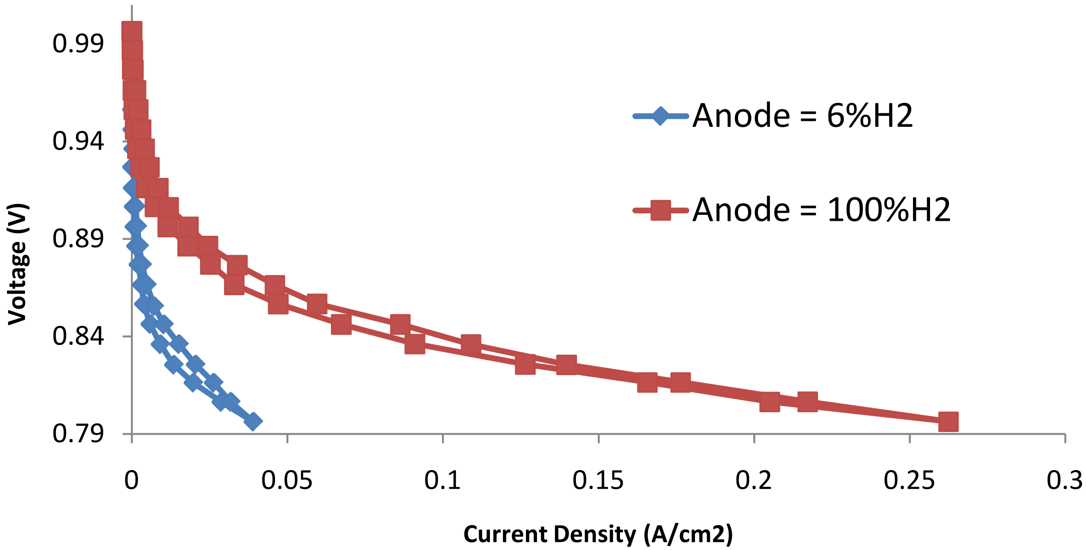




Cell Temp = 80^{o}C. Anode and Cathode inlet RH = 100% (Not 50%).
Anode and Cathode Outlet Back Pressure = 28.7psig (Los Alamos) = 40 psia
H_2 Flow : Minimum = 42 sccm and 1.2 stoich (50cm^2 cell) = stoich flow for 0.1A/cm^2
Air flow : Minimum = 166 sccm and 2.0 stoich (50 cm^2 cell) = stoich flow for 0.1A/cm^2
2way scan: First range = 1V to 0.8V @ 20mV steps @ 30sec/step
Second Range = 0.8V to 0.3V @ 50mV steps @ 30sec/step

USFCC protocol misses most of the information in the kinetic region
There is no need to increase dwell time to 20 minutes a point

Modified Mass Activity



- Perform mass activity measurement in H_2 instead of 6%H_2
  - Do not want anode to be a limiting factor
  - H_2(900mV$_{IR\text{-}free}$) = 0.08- 0.13 A/mg-Pt (6 different samples)
  - 6%H_2(857mV$_{IR\text{-}free}$) = 0.035 A/mg-Pt (0.1mg/cm^2 Anode) and 0.058 A/mg-Pt (0.2mg/cm^2 Anode)
- Use fixed flow rates of gases (500 sccm)

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	≤60% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm^2**	Every 24 h	≤30 mV loss at 1.5 A/cm^2 or rated power
ECSA/Cyclic Voltammetry	Every 24 h	≤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

Fuel Cell Tech Team

Comments

- Concerns with obtaining "real world" freeze data
- Not enough "real world" data points in bus fleet

Actions

Eliminate freeze work and redirect money to obtain more real world data (Fork lifts)