Accelerated Testing Validation

Rangachary (Mukund) Mukundan
Los Alamos National Laboratory

May 16th 2012

Project ID #
FC016

Los Alamos

Project Overview

Timeline

- Project Start Date
  - **August 2009**
- Project Duration
  - **4 Years (End: Sept '13)**
- ≈ 70% complete

Budget

- Total project funding
  - 4 Years : $4,159,790
  - DOE Cost : $4,000,000
  - Cost Share : $159,790
- Funding for FY11/FY12

LANL	$ 578k, 397k
National Labs & Industry	$ 238k, 300k
FY11/FY12 Total	$1096k, 880k

Barriers

Fuel cells: 2011 RD&D Plan

A. Durability

Automotive

5,000 hours (10% degradation)

Stationary

2017 : 40,000 hours (20% degradation)

2020 : 60,000 hours (20% degradation)

Accelerated testing protocols need to be developed to enable projection of durability and to allow for timely iterations and improvements in the technology.

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.

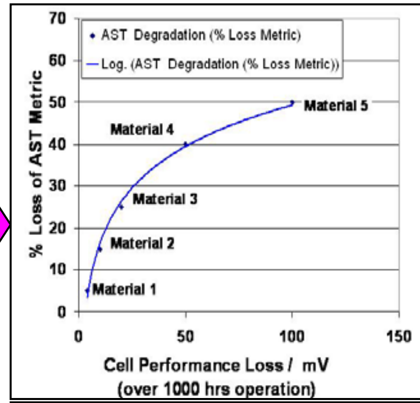
Importance of Accelerated Stress Test (AST)

- 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

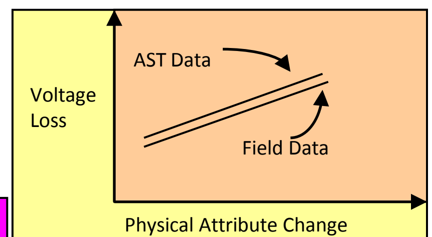
GDL
- Impedance, Hydrophobicity

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 FCHEA (USFCC) and USDOE-FCTT

Approach - Milestones

Begin 08/09	M1/M2 12/10	M3 10/11	M4 12/11	M5 04/12	M6/M7 09/12	M8 09/13
			G1 01/12		G2 09/12	End 09/13

Milestones

M1: Ballard provides initial breakdown analysis of Bus Stack (Complete 12/2010)
M2 : LANL completes initial AST testing on Ballard MEAs (Complete 12/2010)
M3: LBNL completes initial VLB (Complete 10/11)
M4: Complete failure analysis of LANL AST samples (Complete 12/2011)
M5: Complete failure analysis of Ballard samples (Complete 04/2012)
M6: Complete AST testing on a high SA and a low SA carbon (80% complete)
M6 : Complete Drive cycle testing with start up / shut down (tests initiated)
M7 : Propose GDL AST (Validation in progress)
M8 : 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 to life cycle and bus data – Redirect AST based on results (developing membrane AST, re-examine C-corrosion AST)
G2 : Go/ No go on Freeze AST for MEA interfaces (NO GO based on FCTT input)

Materials Used

- Gore® MEAs (Presented at 2010 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

M710 : Discontinued product. Lower chemical and mechanical durability sample

- Ballard P5 and HD6 MEAs (Presented at 2011 AMR, F/A presented here)
- Ion Power MEAs (In progress)
  - 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

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

- GDL
  - SGL 24BC (5% PTFE-substrate/23% PTFE MPL)
  - Varying PTFE content and substrate porosity
- Bipolar plates
  - G35 and Ni50Cr: Corrosion testing (coupons) and fuel cell testing (plate)

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

Lack of Automotive data

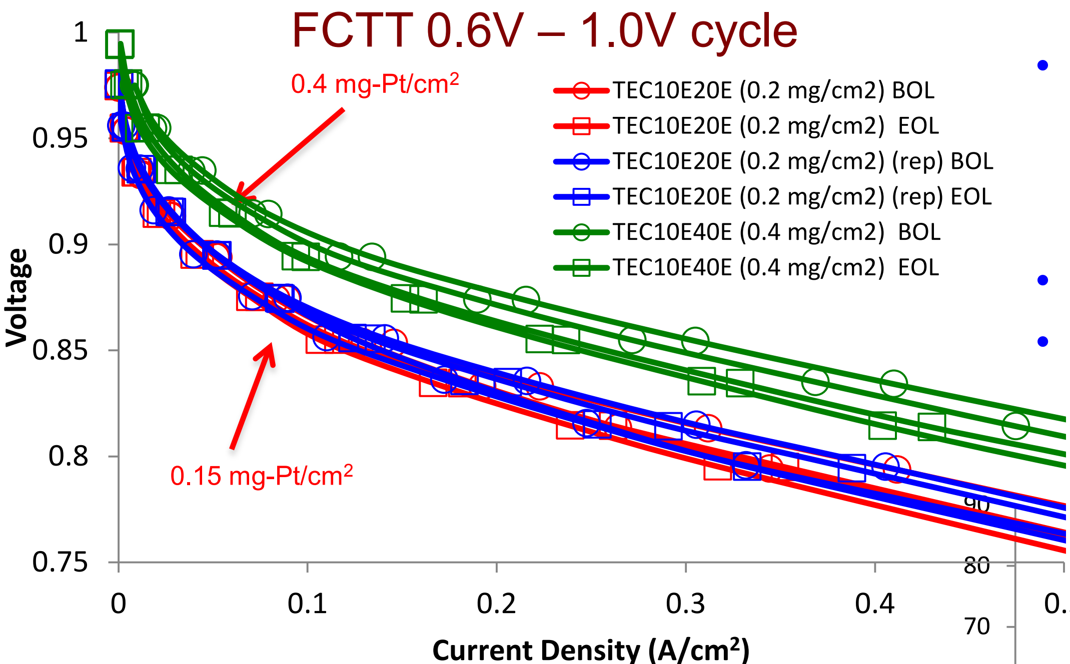
No publicly available automotive field data? Anyone want to share automotive data?

Stressors

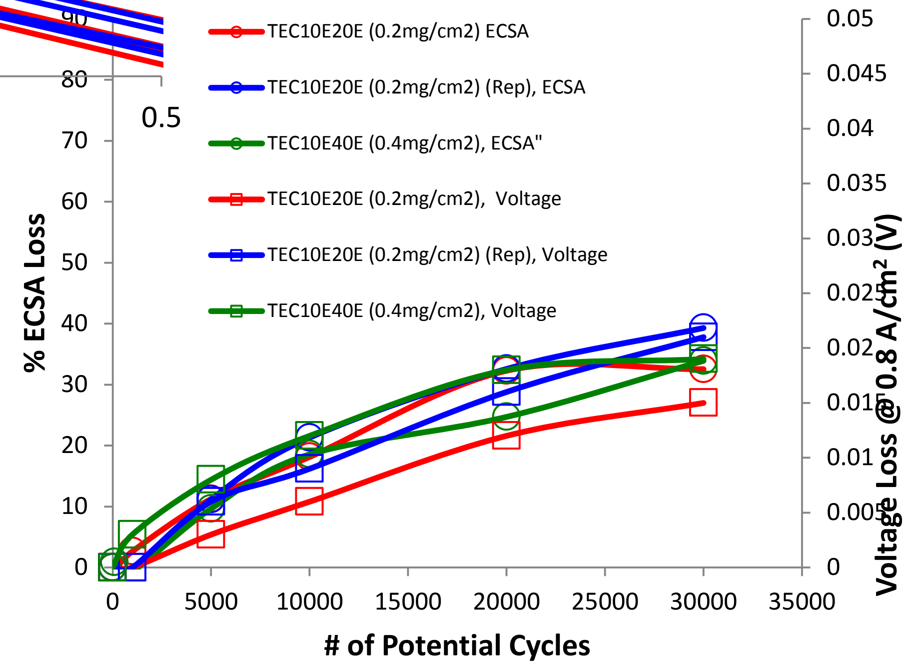
- HD6 showed much higher resistance to transfer leaks and performance degradation
- From operational stressor analysis, when compared to P5, HD6 had:
  - Greater frequency of higher potential
  - Lower average operating temperature
  - Higher relative humidity
  - Lower air/air start-ups
- P5 buses, 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

Effect of loading on Electro-catalyst Stability



- All catalysts tested (TEC10E20E, TEC10E40E, TEC10V40E, TEC10EA40E) meet ECSA, MA and voltage loss targets
- Good reproducibility
- Decreasing catalyst loading leads to performance loss, but similar degradation rates



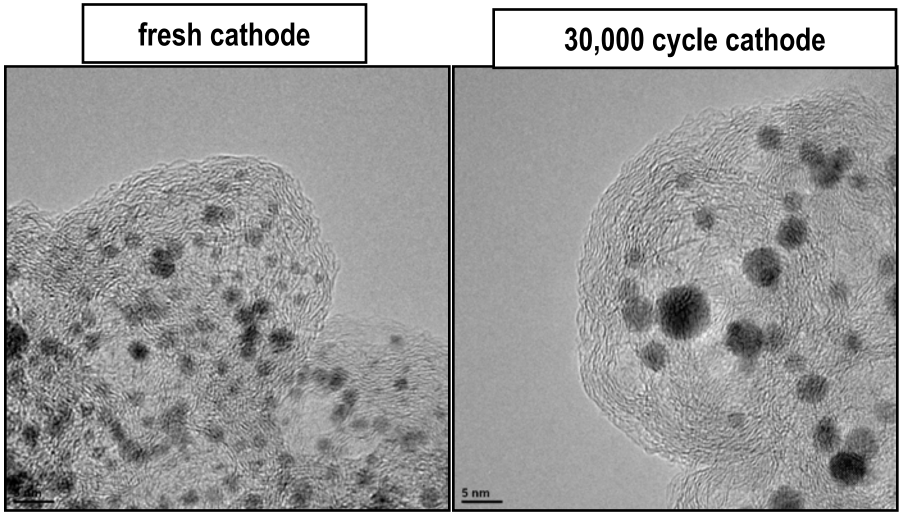
- ECSA loss correlates well with mass activity and performance losses

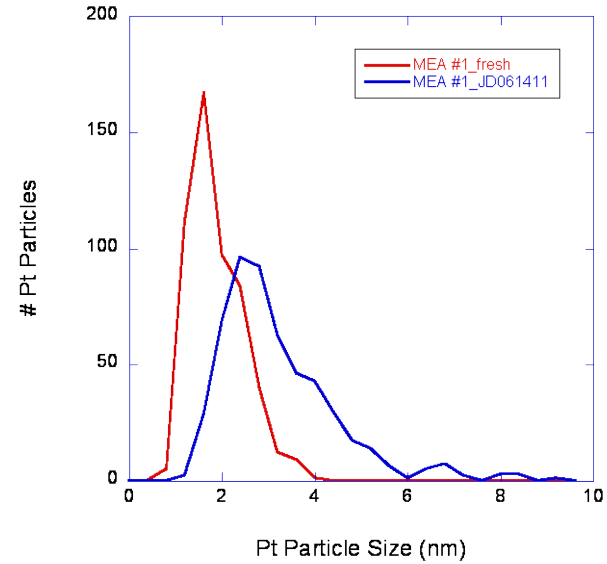
ECSA loss : Avg = 35%; Std Dev = 3.6%
Voltage loss @ 0.8 A/cm^2 = Avg = 18mV; Std Dev = 3mV

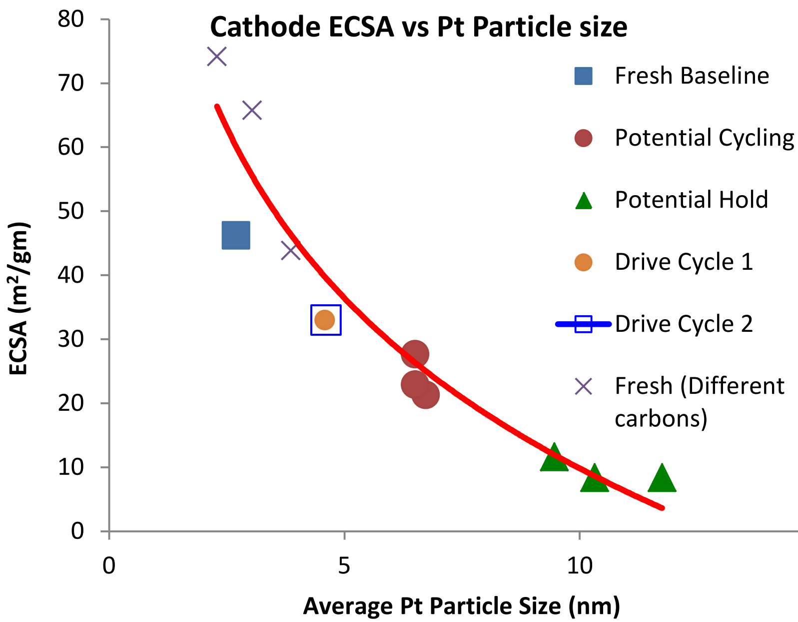
- Some catalyst layer thinning observed

Los Alamos

Correlation of ECSA and Pt-particle size



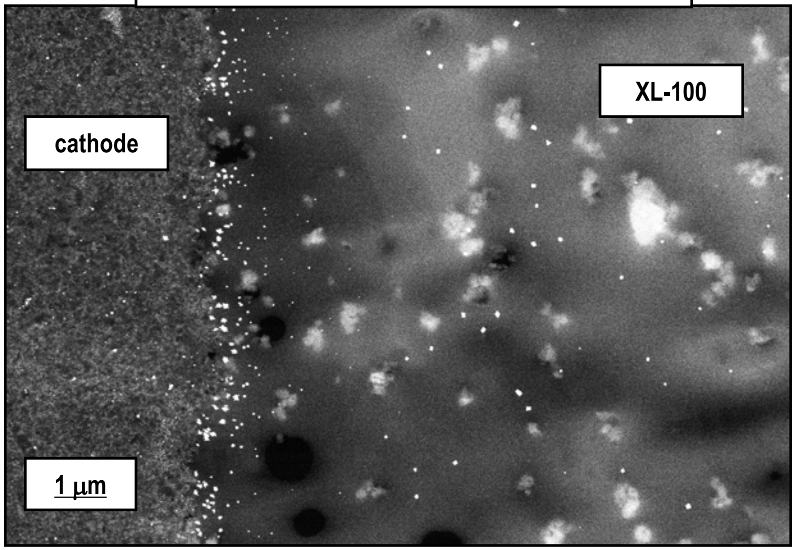


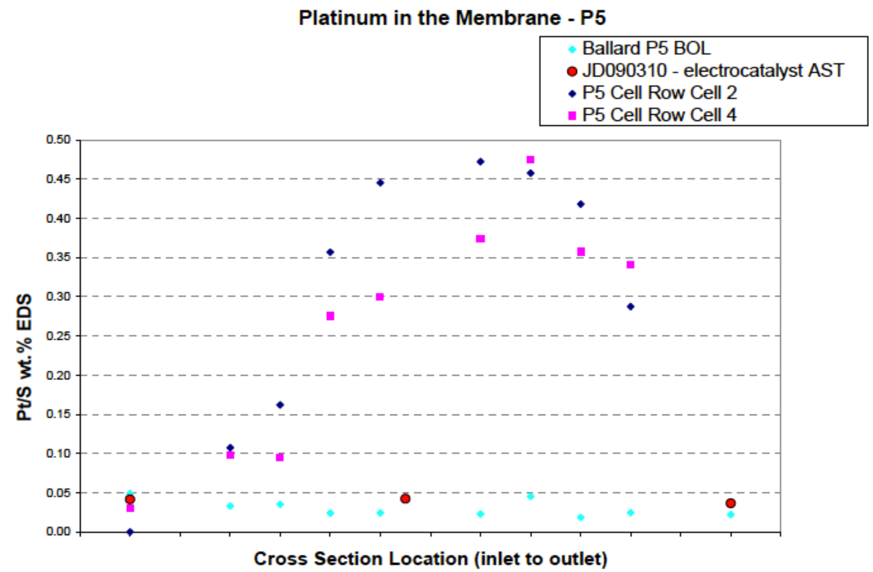


- Pt particle size growth observed in both TEM and XRD
- Correlates with decreasing ECSA
  - Observed in both electro-catalyst (potential cycling) and carbon corrosion (high potential hold) AST
- Mass activity, voltage loss, and increased impedance in kinetic region observed

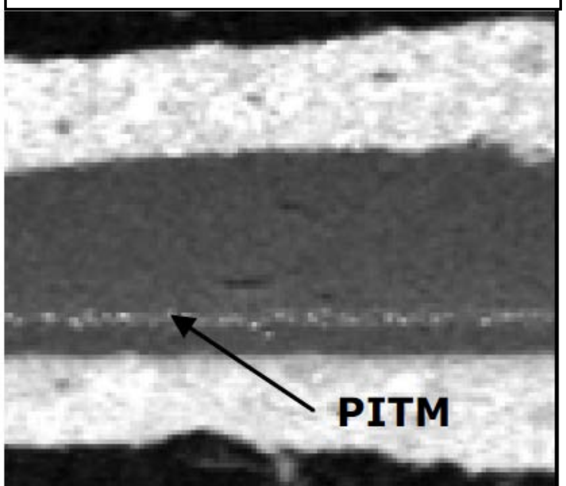
AST underestimates Pt in Membrane

Platinum in membrane from AST sample



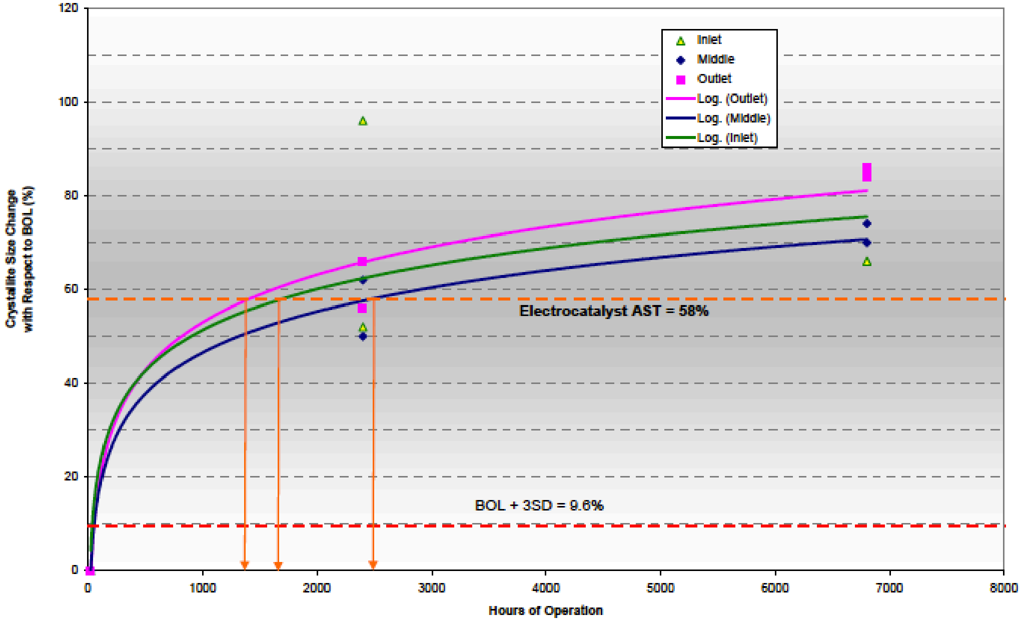


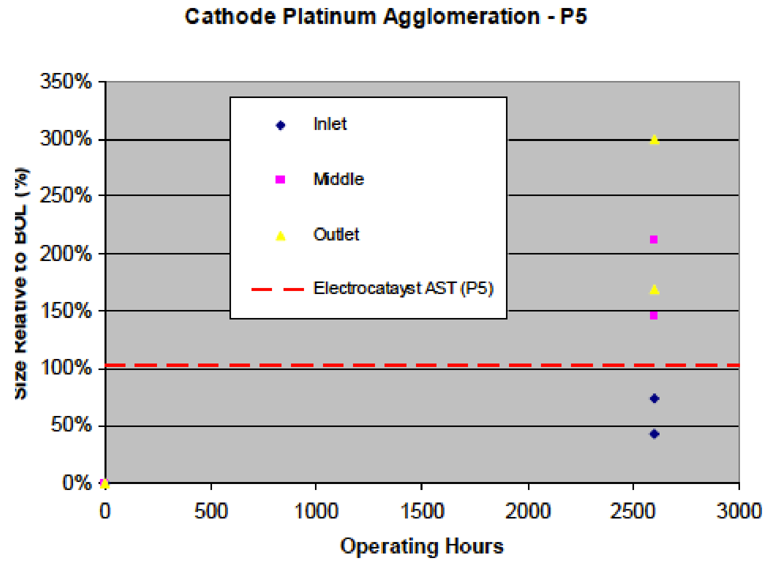
Platinum in membrane from field sample



- Pt observed in membrane (PITM) in both field and AST samples
- H_2/N_2 tests do not simulate this degradation mechanism accurately
  - Field samples have PITM at least 1 order of magnitude greater than AST samples
  - Increases from inlet to outlet
  - Plateaus at ≈ 2500 hours of operation

AST/Field correlation-electro-catalyst

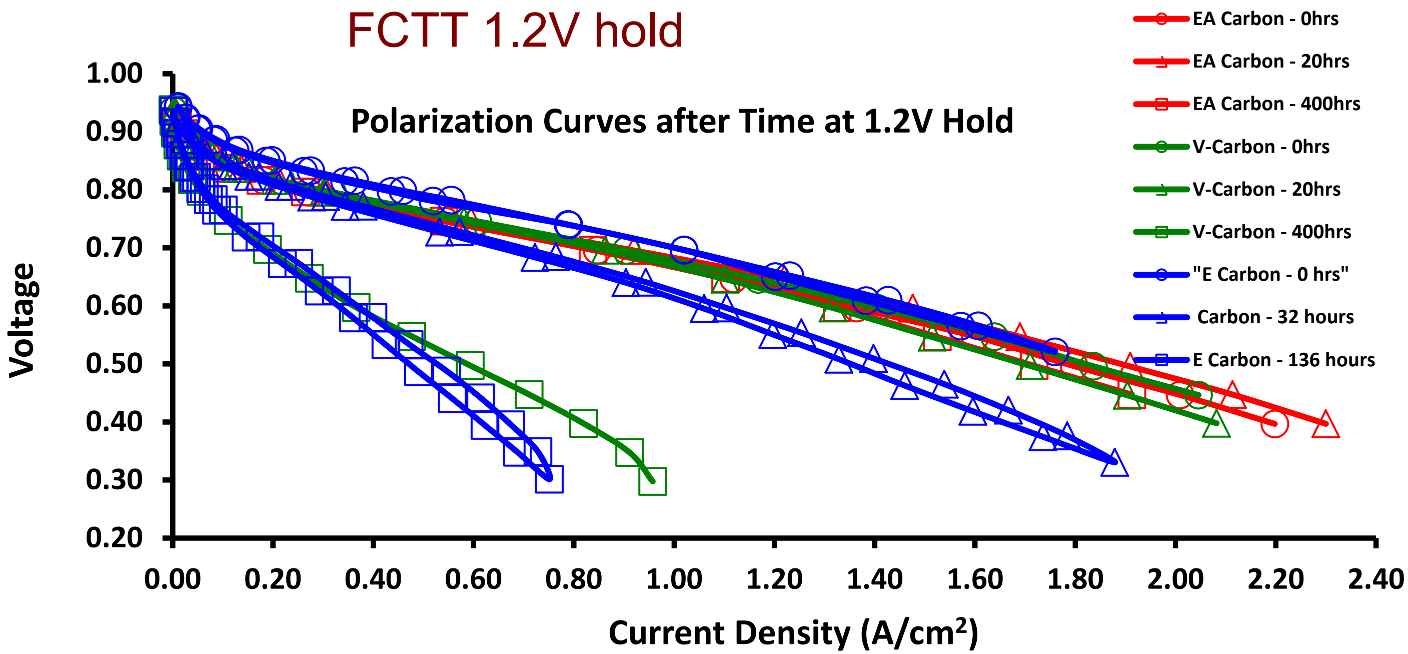




- Significant Pt particle agglomeration variations in field samples from inlet to outlet
- HD6 AST showed a 58% increase in ECSA with respect to BOL. HD6 module sample showed similar ECSA growth (average from inlet to outlet) at around 1900 hours of operation
- P5 AST showed a 102% increase in ECSA with respect to BOL. P5 field samples at 2600 hours showed larger (157%) ECSA growth than AST samples

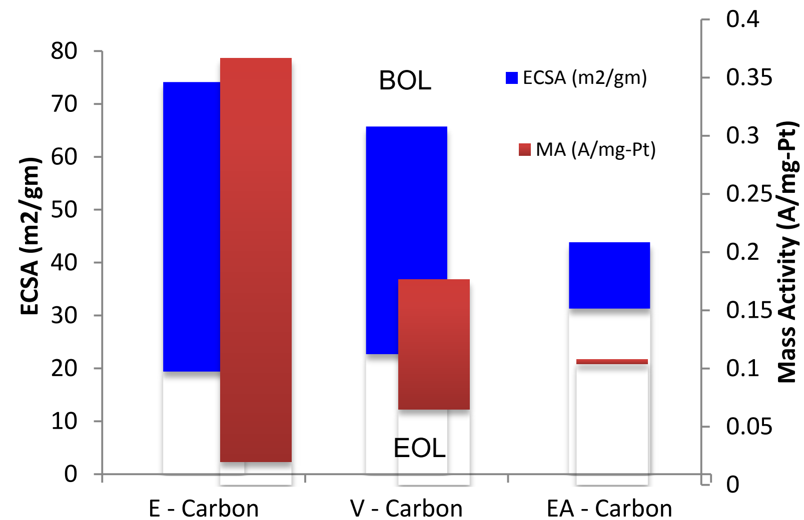
30,000 cycles ≈ 2000 hours of operation

Effect of Graphitization on Carbon Corrosion



- Only EA carbon meets ECSA and MA targets
- 30mV @ 1.5 A/cm²
  - EA @ 240 hrs
  - V @ 32.5 hrs
  - E @ < 4 hrs

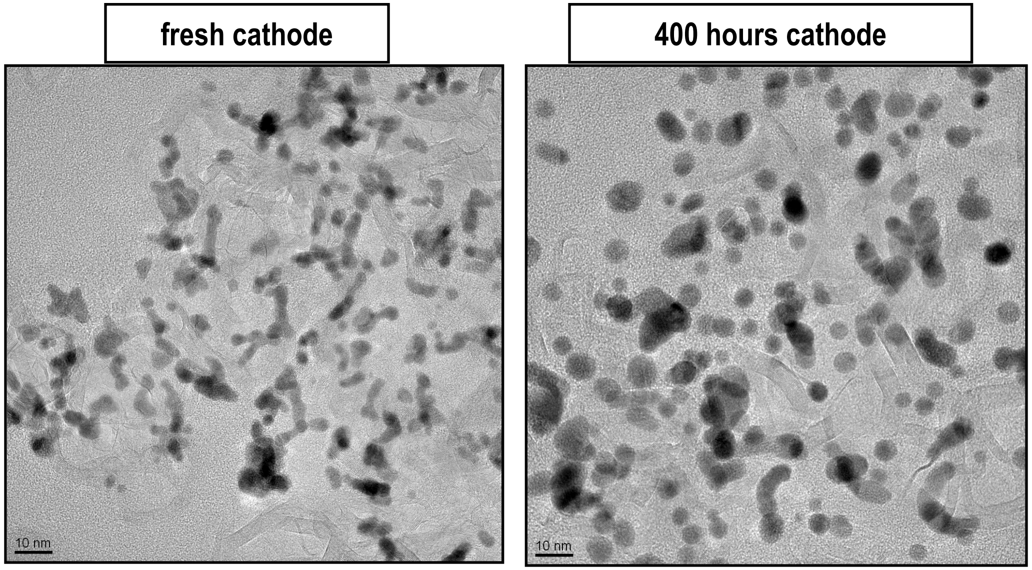
- Significant improvement in durability with decreasing surface area (more graphitization)
- Results in lower performance from all metrics
- Direct comparison of voltage losses not performed due to differing loadings

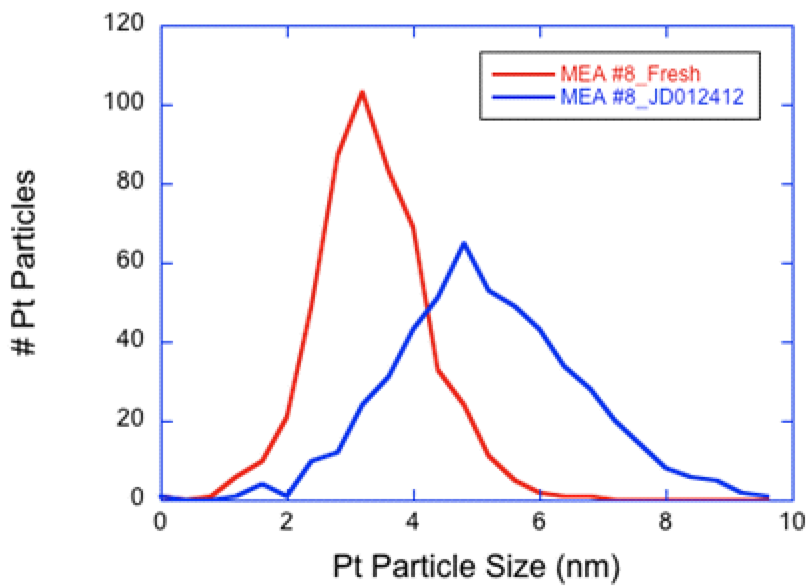


Los Alamos

Pt growth during Carbon Corrosion

Accomplishments /Progress



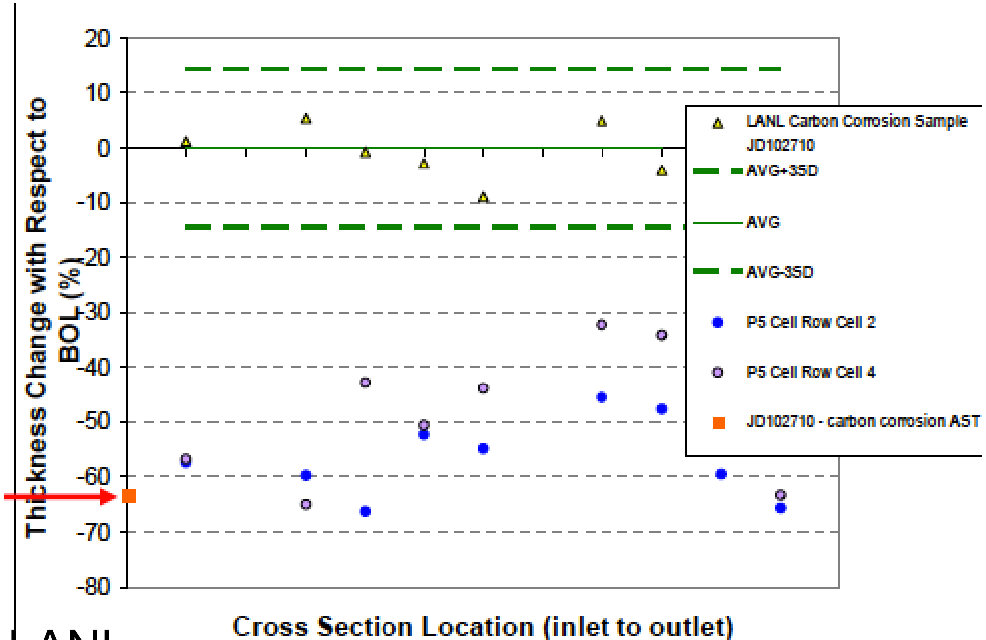


- Both E-type and V-type carbons show evidence of extensive C-corrosion
  - Catalyst layer thinning
  - Pore collapse
  - Change in carbon structure
- In EA carbon there is significant Pt coarsening even though there is little evidence of C- corrosion (Electro-catalyst ripening @ 1.2V hold)

	BOL (thickness/ μm)	EOL (thickness/ μm)	BOL (particle_size/ nm)	EOL (particle_size/ nm)
E-type	25	7	2.94	3.68
V-type	10	4	3.04	8.47
EA-type	14	12	3.87	6.28

20% Pt/C shows smaller Pt growth than the 40% Pt/C

AST/Field correlation - Carbon Corrosion

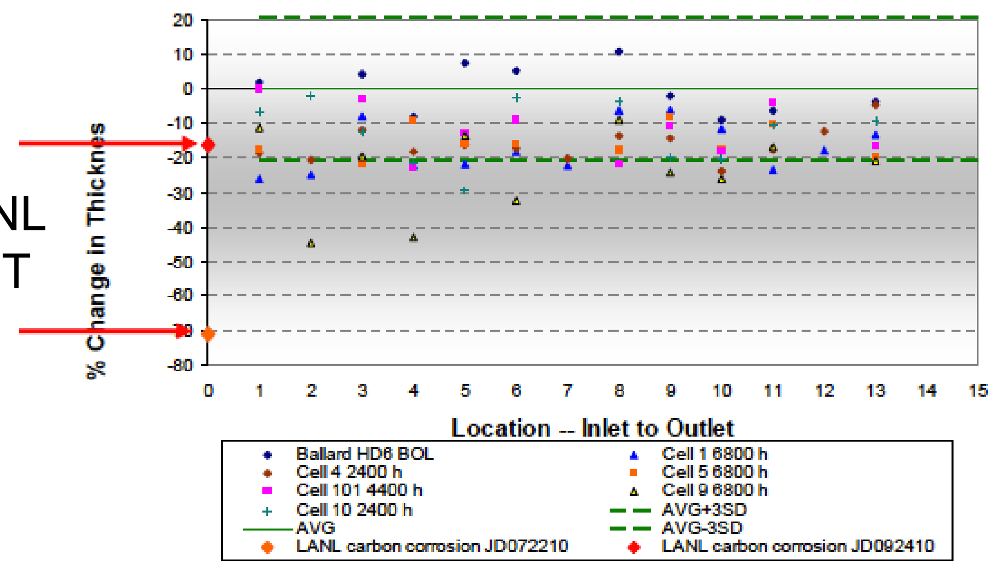


LANL AST

P5

1.2V AST sample (400 hours) shows similar catalyst layer thinning (≈ 60%) as field data (30% - 70% variation)

LANL AST

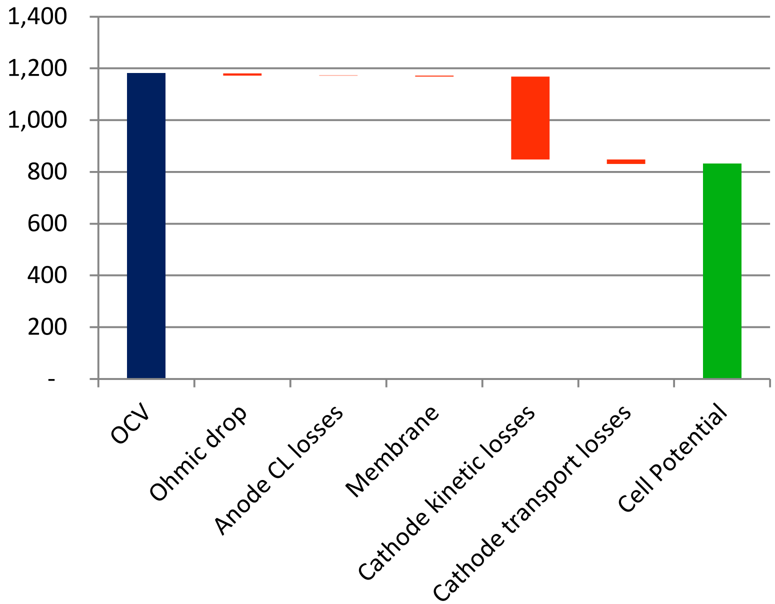


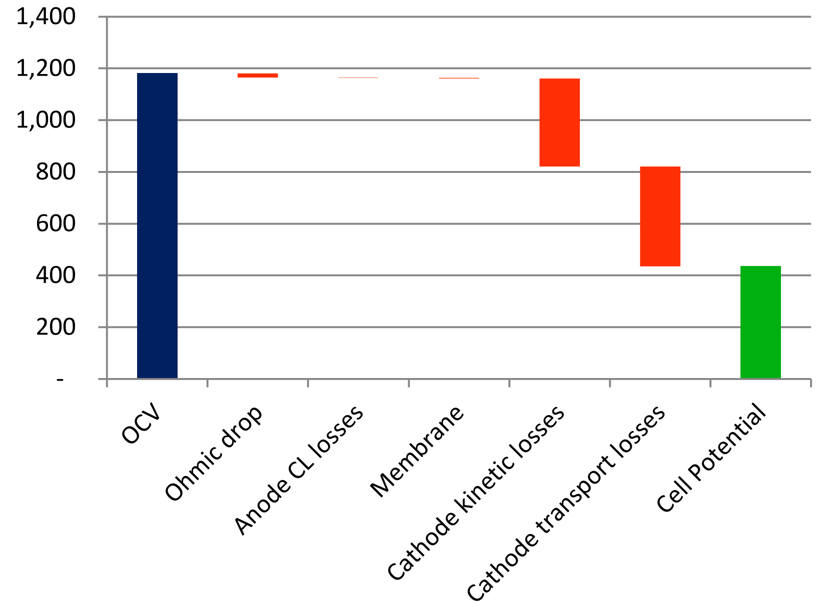
HD6

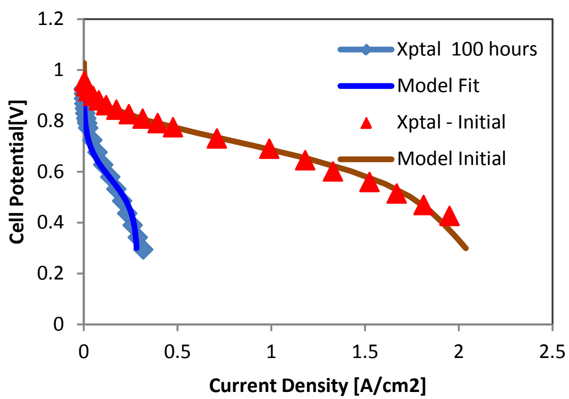
1.2V AST sample (400 hours) shows no catalyst layer thinning similar to field data

Higher voltages (up to 1.8V) result in significantly more degradation

Voltage loss Breakdown Analysis

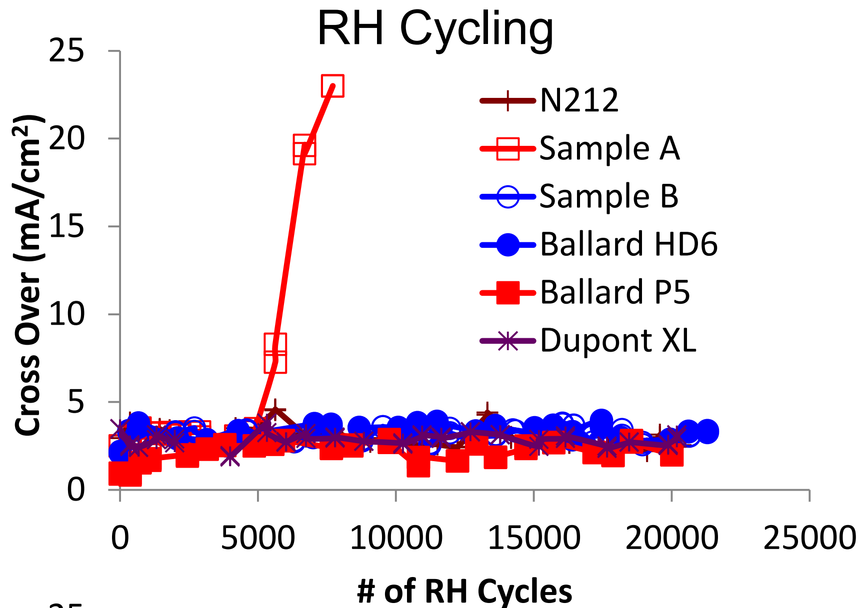


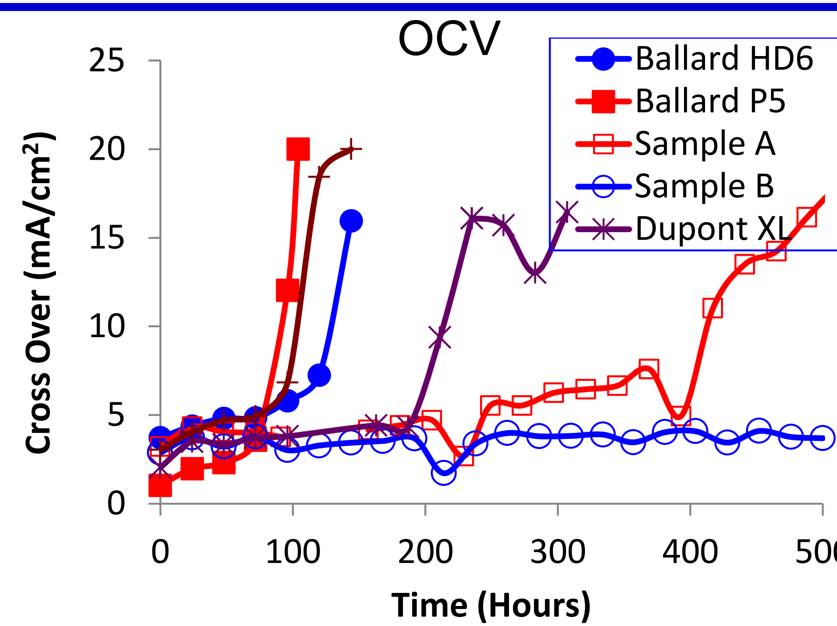


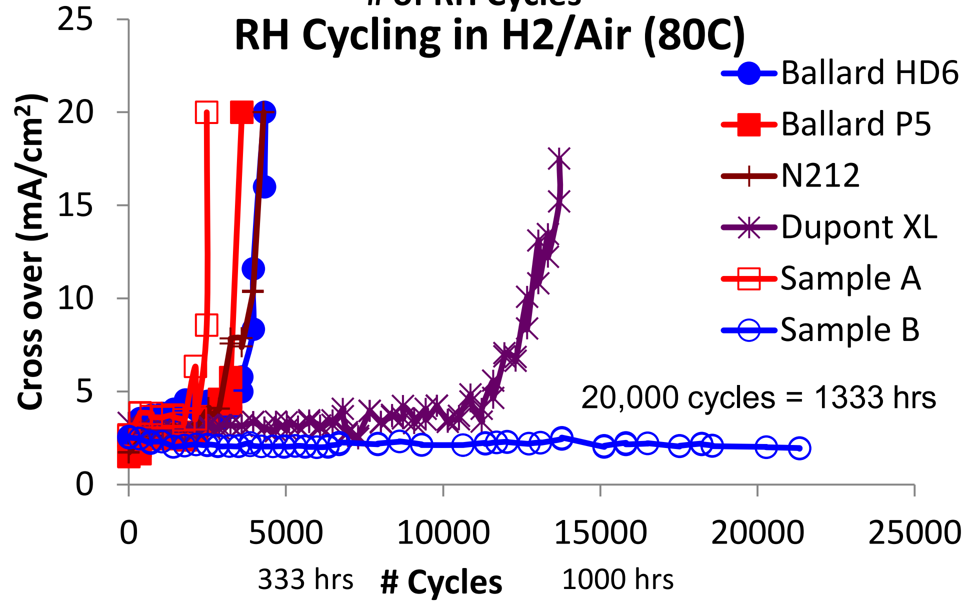


- LBNL modeling used for VLB
- Catalyst coarsening causes slight increase in cathode kinetic loses
- Little Ohmic changes
- Major loss is cathode transport losses consistent with collapse of cathode structure
- Will be compared with drive cycle testing using multiple catalyst layers to get statistical correlations

Membrane ASTs



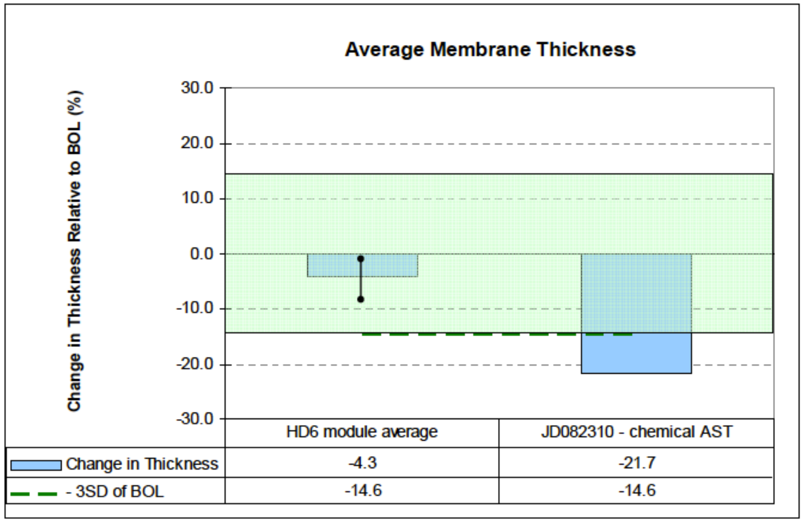


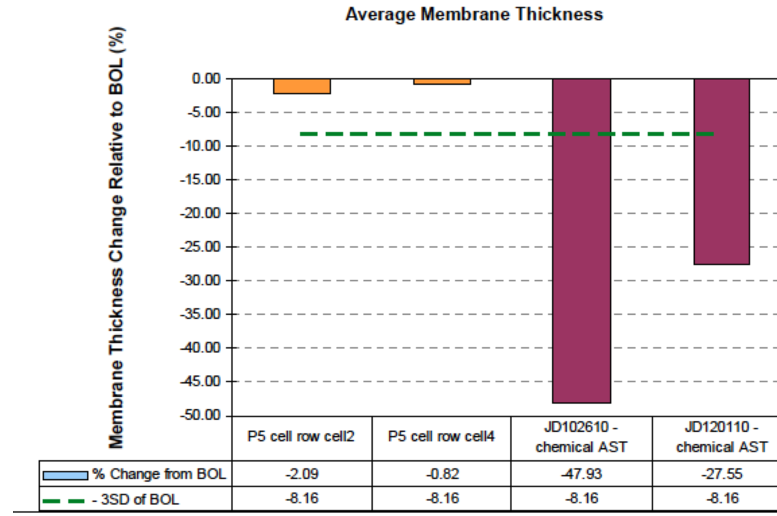


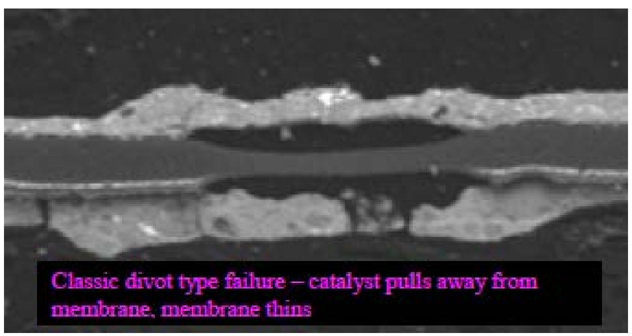
- RH cycling test does not have ability to distinguish between most PFSA membranes
- OCV testing too severe for bus applications
- Combined mechanical/chemical AST has ability to distinguish between MEAs, needs further acceleration.

Los Alamos

AST/Field correlation - Membrane







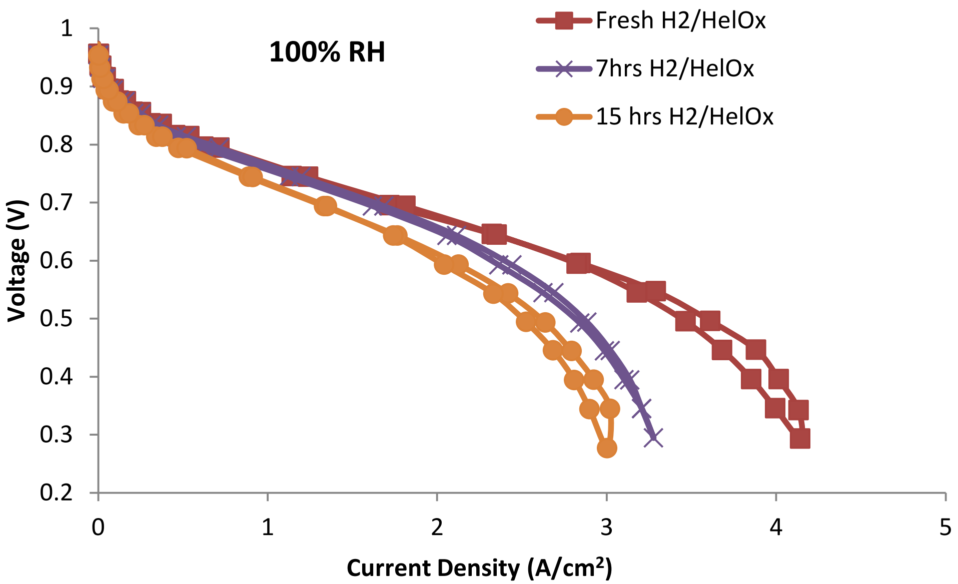
Field

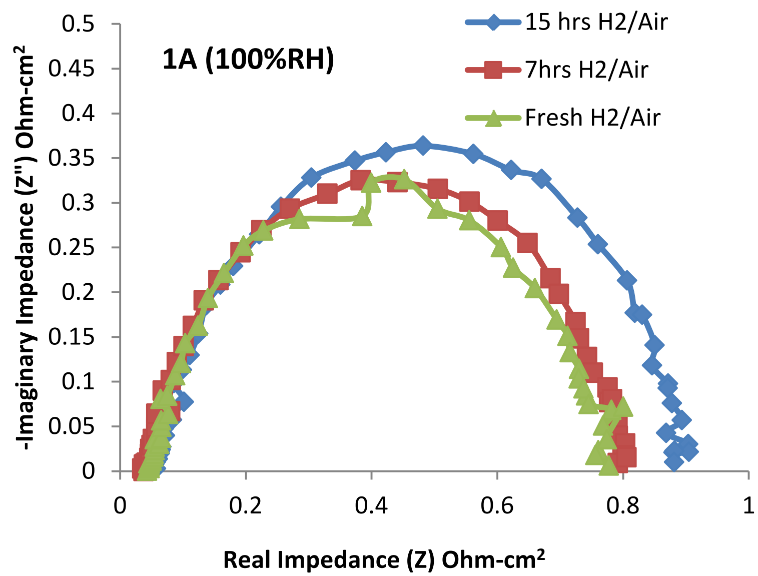
AST

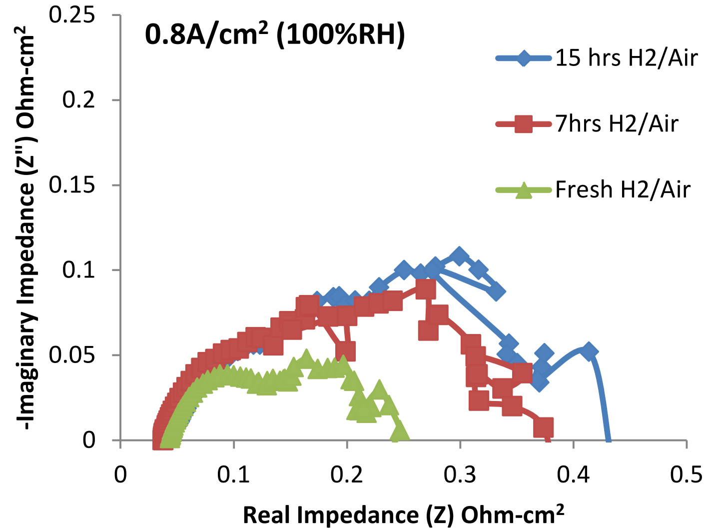
- OCV test shows severe membrane thinning whereas very little observed in the field
- Mechanical AST simulates field failure in both P5 and HD6
- Inlets and Outlets of field MEAs show damage similar to AST samples.

Los Alamos

Develop GDL AST







- Collaborative development with UTC to examine observed field GDL degradation
- GDLs aged at 95°C in 30% H_2O_2
  - (Original procedure from Decode project, Peter Wilde: SGL Carbon)
  - Simulates loss of hydrophobicity
  - Substrate pore volume increases
- Low current/ low RH performance similar
- Degradation in high current/high RH performance

Los Alamos

Collaborations

LANL (**Rangachary Mukundan, Rodney Borup, John Davey, David Langlois, Dennis Torraco, Roger Lujan, 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, Dana Ayota)

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

LBNL (Adam Weber, Siva Balasubramanian, Wonseok Yoon)

- 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, Karren More)
Deliver metal bipolar plates/TEM

W. L. Gore and Associates Inc., and SGL Carbon (materials suppliers)

Summary/Future Work - I

- Initial AST (electrocatalyst, catalyst support, membrane chemical and mechanical) performed
  - Baseline materials from W.L. Gore, P5 and HD6 (Completed)
  - Ion Power MEAs (In progress)
  - Failure analysis (Baseline, Ballard completed, IP in progress)
- Bus Data analysis completed on P5 and HD6 bus stacks
  - Failure analysis of HD6 and P5 stacks will be completed by June 2012
- Automotive drive cycle (FCTT) testing initiated on GM-RIT hardware
  - Baseline materials in progress, SU/SD will be incorporated
  - Parametric study in progress (Dr. Borup's project)
- Modeling of Voltage loss break down completed
  - Baseline materials and Bus AST complete
  - IP MEAs in progress

Summary/Future Work - II

- GDL AST testing complete
  - Validation in progress
  - Bipolar plate data from Dr. Borup's project
- Membrane combined mechanical/chemical cycling AST performed
  - Needs further acceleration for state of the art MEAs
- Other carbon corrosion ASTs to be examined
  - 0.9V to 1.3V (JARI)
  - 1 to 1.5V cycling (Nissan/NREL)
- Correlation of material properties with degradation rates
  - Pt particle size and ECSA/kinetic losses
  - Mass transport losses and electrode/GDL morphology
  - Membrane mechanical testing and electrolyte damage
  - Membrane thinning observed in initial FCTT drive cycle

Acknowledgements

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

US DRIVE 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

Modeling Methodology

1-D simplified model

- Voltage Loss Breakdown
  - Have a master program that does a multivariable regression over the various data for both pre and post AST
    - 1-D model that does polarization curve, oxygen gain, impedance, etc.
      - Input parameters for both BOL and EOL coming from as much characterization data as possible
      - Changes from BOL to EOL first tried based on expected effects of AST
  - 1D model for polarization curve, etc. working but not for full impedance
    - Requires some simplification of possible pseudo-steady-state variables\phenomena to remain tractable but should be doable using full numerical approach
- Correlations
  - Use statistics to tie changes in properties between AST and real world
    - Input from the VLB analyses, teardown results
  - Do a sensitivity analysis using the 1D model to predict expected impacts of parameters within the expected property-change range
- Lifetime
  - Implement a Monte-Carlo approach to test parameter and multi-parameter interactions and changes and to help predict general lifetime effects

DOE Tech Team Protocol (Pt Catalyst)

Table 1
Electrocatalyst Cycle and Metrics
Table revised March 2, 2010

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 Fuel Cell Tech Team Polarization Protocol in Table 5.

*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

DOE Tech Team Protocol (Catalyst Support)

Table 2
Catalyst Support Cycle and Metrics
Table revised March 2, 2010

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$40% 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 Fuel Cell Tech Team Polarization Protocol in Table 5

*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

DOE Tech Team Protocol (Membrane/Chemical)

Table 3
MEA Chemical Stability and Metrics
Table revised December 10, 2009

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 150 (1.5), Cathode 150 (1.5)	
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.

** Measured at 0.5V applied potential, 80°C and 100% RH N_2/N_2. Compression to 20% strain on the GDL.

DOE Tech Team Protocol (Membrane/Mechanical)

Table 4 Membrane Mechanical Cycle and Metrics (Test using a MEA) Table revised December 10, 2009		
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.

** Measured at 0.5 V applied potential, 80°C and 100% RH N_2/N_2. Compression to 20% strain on the GDL.