Accelerated Testing Validation

Rangachary (Mukund) Mukundan Los Alamos National Laboratory May 15th 2013

> Project ID # FC016

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Project Overview

Timeline

- Project Start Date
 August 2009
- Project Duration
 - 4 Years (End: Sept '13)
- ≈ 90% complete

Budget

- Total project funding
 - -4 Years : \$4,159,790
 - DOE Cost : \$4,000,000
 - Cost Share : \$159,790
- Funding for FY12/FY13
 LANL
 + Partners (Industry)
 Other National Labs
 FY12/FY13 Total
 - \$ 397k, 750k
 - <u>\$ 300k, 250k</u> \$ 697k,1000k

Barriers

- Fuel cells: 2011 Technical Plan
- A. Durability

<u>Automotive</u>

5,000 hours (10% degradation)

Stationary

2017 : 40,000 hours (20% degradation) 2020 : 60,000 hours (20% degradation) <u>Bus</u>

1016 : 18,000 hours

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)

Los Alamos

- 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 : 18,000 hours (2016); 25,000 hours (ultimate); Status = 12,000 hours.

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

BALLARD

Approach





Approach - Milestones

Begin 08/09		M1 12/11	M2 03/12	M3/M4 04/12	M5/M6 12/12	M7 04/13	M8 06/13	M9/M10 09/13
<u>Mileston</u> M1: Com M2: Deve 03/2013	<u>es</u> plete failu eloped im	ure ana proved	lysis of multi-r	LANL AST san nodel and mu	nples <mark>(Compl</mark> e ulti-variable fi	ete 12/20 tting algo)11) prithm. (Comp	End 09/13 lete
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M9: Prop M10 : Fir to drive o	oose valida nal Statisti cycle of m	ated GI ical corr aterials	DL, men relation s with v	nbrane and st of AST and B arying lifetime	art/stop ASTs us data to ma es	s <mark>(80% co</mark> aterial pro	mplete) operty and AS ⁻	T lifetimes
	U.S.DOI	E FCT P	rogram A	MR and Peer E	valuation Meeti	ng May 1	5. 2013 • LO	, s Alamos

Materials Used

Accomplishments /Progress

- Gore[™] MEAs (AST: 2010 AMR, F/A: 2011 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 (AST: 2011 AMR, F/A: 2012 AMR)
- Ion Power MEAs (AST, F/A: 2012 AMR)
 - 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
 - G35 and Ni50Cr: Corrosion testing (coupons) and fuel cell testing (plate)
 - No degradation observed in short term testing in MEA (awaiting input from other LANL durability project)

M710 : Discontinued product. Lower chemical and mechanical durability sample

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

F/A = Failure Analysis



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
 - 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
- 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

Presented in 2011/2012 AMR

Drive Cycle Testing

Accomplishments /Progress

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Use 100% H_2 instead of 80% H_2

Only one station capable of RH control (bottle = 90°C, adjust dry and wet flows) Also performing cycles at the high RH conditions (Wet Cycling)

Potential Cycling AST Accomplishments /Progress



- 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
- 40% ECSA loss corresponds to approx. 20 mV voltage loss

5, 2013 • Los Alamos

Accomplishments /Progress

Correlation of AST and Drive Cycle

- 30,000 cycles ≈ 2000 hours of bus operation (Both P5 and HD6)
- 30,000 cycles ≈ 850 hours of US DRIVE Drive-Cycle
- 30,000 cycles ≈ 500 hours of wet drive cycle
- 5000 hours ≈ 175,000 cycles
- Need > 30,000 cycles for 5000 hour automotive durability

Catalyst	AST 30000 Cycles	Drive Cycle 30000 cycles
C510.2	53.80%	53.7%, 54.3%
C510.4	46.3%, 46.8%	46.60%



•Pt particle size increase.

- Consistent with potential cycling
 AST
- Larger Pt growth in drive cycle samples than AST samples
 6.5 nm after 30,000 cycles
 9.5 nm to 11.5nm after 1.2 V AST
 9.4 nm after 2000+ hours wet/dry cycle
 7.5 nm after 1200 hours wet cycle

5.6 nm after 300 hours wet cycle



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Carbon corrosion at low potentials Accomplishments /Progress







Significant carbon corrosion observed @ 0.9 V for high surface area carbon

Corrosion can be significantly accelerated using higher upper potentials and cycling instead of holds

FCTT adopting 1 – 1.5 V cycling

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Drive Cycle: Catalyst degradation (HSAC)^{Accomplishments}/Progress

HSAC : High surface area carbon

860 hrs wet drive cycle



1224 hrs wet drive cycle



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Pt band observed on cathode side of MEA. Band clearly visible after 2000 hours with high (0.4 mg.Pt/cm²) loaded catalyst

860 hours results in 10% thinning of catalyst layer, 1200 hours results in 25 % thinning and 2000+ hours in 50% thinning

Carbon Corrosion : Correlations

National Laboratory

Accomplishments /Progress



AMR 2012 Voltage loss Breakdown Analysis /

Accomplishments /Progress







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BERKELEY LAB

- LBNL modeling used for VLB
- Catalyst coarsening causes slight increase in cathode kinetic loses
- Little Ohmic changes

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- 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

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Voltage loss Breakdown Analysis Accomplishments /Progress



- Similar performance could be achieved for different distribution of resistance
- Manual supervision is required to allot appropriate weight to the various resistances
- Reaction distributions in the catalyst layers need adjustment
- Mass transport losses in ionomer, catalyst layer pores, GDL





Real Impedance (ohm cm²)

0.5

0.2

0

0

Real Impedance (ohm cm²)

0.5

1.5

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1

0.4

0.2

0

0

- Good agreement in the kinetic region 畿
- ✵ The second capacitance loop is associated with channel effects

1

✵ Modeling impedance gives an accurate determination of individual resistance

1.5

Simultaneous fitting of Air and HelOx data at different current densities 畿

Membrane ASTs

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AMR 2012

Drive Cycle: Membrane failure modes

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Baseline: 850+ hours wet cycling



- Both Wet/Dry and Wet cycles result in crossover increases and membrane failure
 - Little thinning observed in membrane (< 10% to none)
 - Consistent with field data from buses
 - Not compatible with OCV AST.

Baseline: 1200+ hours wet cycling



AST/Field correlation - Membrane

Accomplishments /Progress

HD6 Field Sample



P5 Field Sample



P5 sample after H₂/Air RH cycling AST





- RH cycling data being analyzed
- Membrane failure time decreases with increased time > 0.8 V
- Membrane failure time increases with increasing inlet RH



Membrane Degradation

Accomplishments /Progress



	vs. Field		
	Dry	Liquid	
RH Cycling Mechanical	Different	Similar	
Chemical AST	Similar	More Severe	
RHC @ OCV Mechanical / Chemical	Similar	Similar	

SAXS reveals similar membrane degradation in field samples as those aged under the combined mechanical/chemical cycle.



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

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AMR 2012

Drive Cycle: GDL Failure mode

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- Mass transport issues. Catalyst layer/GDL flooding
- Slightly higher flow rates can easily restore performance to almost BOL levels

Mass transport losses : HSAC

Accomplishments /Progress

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HSAC : High surface area carbon

3040 hours of drive cycle

1224 hours of wet drive cycle



Significant increase in mass transport losses

GDL degradation? Difficult to de-couple catalyst layer effects

Mass transport losses : LSAC

Accomplishments /Progress

LSAC : Low surface area carbon (Graphitized)





- Mass transport losses : Stopped Wet Drive cycle testing
 @ 382 hours. (Cannot sustain high currents, Cell Reversal)
 - Little thinning observed.

• 30-35% ECSA loss with 80% increase in Pt particle size

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Drive Cycle Testing: Varying GDLs

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Same MEA: Similar Catalyst Degradation and ECSA loss XPS confirms increase in C_xO_y peaks in aged GDLs (AST, Drive cycle, ex situ aged)

Collaborations

LANL (Rangachary Mukundan, Rodney Borup, John Davey, David Langlois, Dennis Torraco, Roger Lujan, Dusan Spernjak, Joe Fairweather and Fernando Garzon)

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

Ballard Power Systems (Paul Beattie, Greg James, Dana Ayota)
Analyze Bus Data; Deliver BOL MEAs used in Buses; Analysis of 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)

Durability working group (Start/Stop protocol)

Nancy University (Start/Stop segmented cell testing) Olivier Lottin (PI)

Summary/Future Work - I

- Initial AST (electrocatalyst, catalyst support, membrane chemical and mechanical) performed
 - Baseline materials from W.L. Gore, P5 and HD6 and Ion Power MEAs with three different catalyst supports
 - Failure analysis from all ASTs
- Bus Data analysis completed on P5 and HD6 bus stacks
 - Data on number of RH cycles and potential cycles from the buses are being analyzed
- Automotive drive cycle (FCTT) testing in progress on GM-RIT and quad-serpentine hardware
 - Baseline materials completed
 - Ion Power materials initiated.
 - GDL degradation issues have been addressed (need to be quantified)
 - Start/Stop will not be incorporated in drive cycle. The Durability Working Group protocol for start/stop is being studied separately.

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Summary/Future Work - II

- Start/Stops performed at Nancy University
 - Large spatial variations make average correlations difficult
 - Extremes will be studied
- Voltage loss break down modeling being refined
 - Down the channel effects being added to simultaneously fit impedance data
 - Models to be refined for better fit at > 1 A/cm² (GDL transport)
- NEW ASTs
 - GDL AST proposed. Surface oxidation of carbon observed in all samples. Degradation mechanism similar in drive cycle, AST and ex situ samples
 - Membrane mechanical/chemical AST found to reliably simulate field and drive cycle failure modes

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- 1 to 1.5 V carbon corrosion AST to be evaluated
- Compile all data in a Web site in addition to publications

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

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

W. L. Gore and Associates (MEAs)

SGL Carbon (GDLs)

Technical Backup Slides





1-D simplified model



- The model is 1-D, steady state
- Add in transient terms to do impedance

$$x_{i} = \overline{x}_{i} + \operatorname{Re}\left\{\widetilde{x}_{i} \exp(j\omega t)\right\}$$
T
Steady-state solution
$$Z = \frac{\widetilde{V}}{\widetilde{x}}$$

- Model is updated and leveraged from work in other LBNL projects
- Fitting parameters depend on AST, but are typically effective transport coefficients, surface area (if not measured), etc.

- Catalyst layer
 - Agglomerate model using Pt-oxide coverage terms and ionomer film

Yoon and Weber JES 158, B1007

- Gas transport mainly by Knudsen diffusion
- Diffusion media
 - Stefan-Maxwell diffusion
 - Liquid water with Darcy's law
 - Use capillary pressure and contactangle distribution model

Weber JPS 195, 5292

- This is being reevaluated
- Membrane
 - LBNL chemical-potential approach

Weber and Newman, in *Device and Materials Modeling in PEM Fuel Cells*, Paddison and Promislow, Eds, Springer, 157-198 (2009).





1-D simplified model

Inputs

- Operating/test conditions
- Cyclic voltammetry (active area)
- Electrochemical impedance
- Polarization curve

$$\begin{vmatrix} 1 & 0 & 0 & 0\\ \frac{\partial f_2}{\partial i_f} & -1 & \frac{\partial f_2}{\partial c_i} & \frac{\partial f_2}{\partial \gamma_k} \\ \frac{\partial f_3}{\partial i_f} & \frac{\partial f_3}{\partial V} & -1 & \frac{\partial f_3}{\partial \gamma_k} \\ \frac{\partial f_4}{\partial i_f} & \frac{\partial f_4}{\partial V} & \frac{\partial f_4}{\partial c_i} & -1 \end{vmatrix} \bullet \begin{vmatrix} \widetilde{i_f} \\ \widetilde{V} \\ \widetilde{C}_i \\ \widetilde{\gamma}_k \end{vmatrix} = \begin{vmatrix} \widetilde{i_f} \\ \widetilde{V} \\ \widetilde{C}_i \\ \widetilde{\gamma}_k \end{vmatrix}$$



Model > VLB 1-D simple model Modify to calculate/fit EIS profiles and polarization curves using physical equations Fit parameters to data

Outputs



Look for controlling dimensionless groups

 $\widetilde{x}_i = \widetilde{x}_i^{\text{Re}} + j.\widetilde{x}_i^{\text{Im}}$

 $\begin{vmatrix} J^{\text{Re}} & -J^{\text{Im}} \\ J^{\text{Im}} & J^{\text{Re}} \end{vmatrix} \bullet \begin{vmatrix} \widetilde{x}_i^{\text{Re}} \\ \widetilde{x}_i^{\text{Im}} \end{vmatrix} = \begin{vmatrix} G^{\text{Re}} \\ G^{\text{Im}} \end{vmatrix}$

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畿 Jacobian matrix from the steady state model is used to estimate the impedance in the frequency domain

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

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

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** 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.

Tech Team Protocol (Catalyst Support)

Table 2					
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	ve 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	Every 24 h	\leq 30 mV loss at 1.5 A/cm ² or rated			
0 to \geq 1.5 A/cm ^{2**}		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% H₂ (bal N₂)/O₂ {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.

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Tech Team Protocol (Membrane/Chemical)

Table 3 MEA Chemical Stability and Metrics Table revised December 10, 2009				
Test ConditionSteady state OCV, single cell 25-50 cm²				
Total time	500 h			
Temperature				
Relative Humidity	HumidityAnode/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	At least every 24 h	No target – for monitoring		
non-fluorine membranes				
Hydrogen Crossover	Every 24 h	$\leq 2 \text{ mA/cm}^2$		
$(mA/cm^2)*$				
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.

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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 $>2 \text{ mA/cm}^2$ 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	$\leq 2 \text{ mA/cm}^2$	
Shorting resistance**	Every 24 h	$>1,000 \text{ ohm cm}^2$	
* 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.

