Improved Accelerated Stress Tests Based on FCV Data

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UTC POWER

MAY 11, 2011

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Project ID: FC015

Overview

Timeline

- Start Date: December 2009
- Finish Date: November 2011
- Status: 65% Complete

Budget

- Total funding $3,847,218
- Cost share 20%
- Spend on-plan

GFY '09	$778,015
GFY '10	$1,638,508
GFY '11	$1,430,694

Barriers

(2007 RD&D for auto FC)

- ❑ >5,000 hr stack durability (with cycling)
  - Include all materials (e.g. membrane, seals)
  - UTC bus fleet target >15,000 h stack life
- ❑ <10% Performance decay
  - Start-stop / transient operation
- ❑ ASTs used to avoid costly durability testing

Partners

United Technologies Research Center

Los Alamos National Laboratory EST. 1943

Oak Ridge National Laboratory
Managed by UT-Battelle for the Department of Energy

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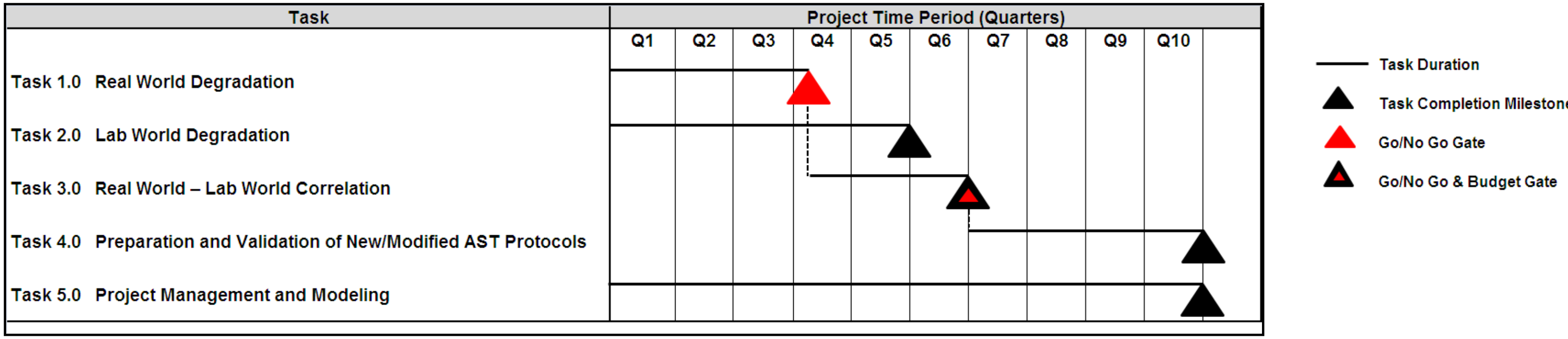
Relevance

Program Objectives	Current Gaps	2009-2010 Objectives
Comparison of conditions & materials in bus field operation vs. DOE ASTs	DOE ASTs not calibrated with real world degradation	**Task 1** - Analyze performance data and characterize degraded materials from 2850 hr stacks in bus service **Task 2** - Analyze data and degraded materials run in DOE ASTs (same as in bus stacks)
Develop acceleration factors for DOE AST mechanisms → recommend modifications	DOE ASTs may over- or under-accelerate mechanisms → inadequate material selections	**Task 3** - Correlate results for all current DOE ASTs: 1) PGM decay 2) Carbon corrosion 3) Membrane mechanical 4) Membrane chemical
Identify life-limiting mechanisms not addressed by DOE AST's → recommend new AST's	Validated GDL specific AST; Validated integrated membrane mechanical/chemical AST;	**Task 4** – Prepare and Validate New/Modified AST Protocols

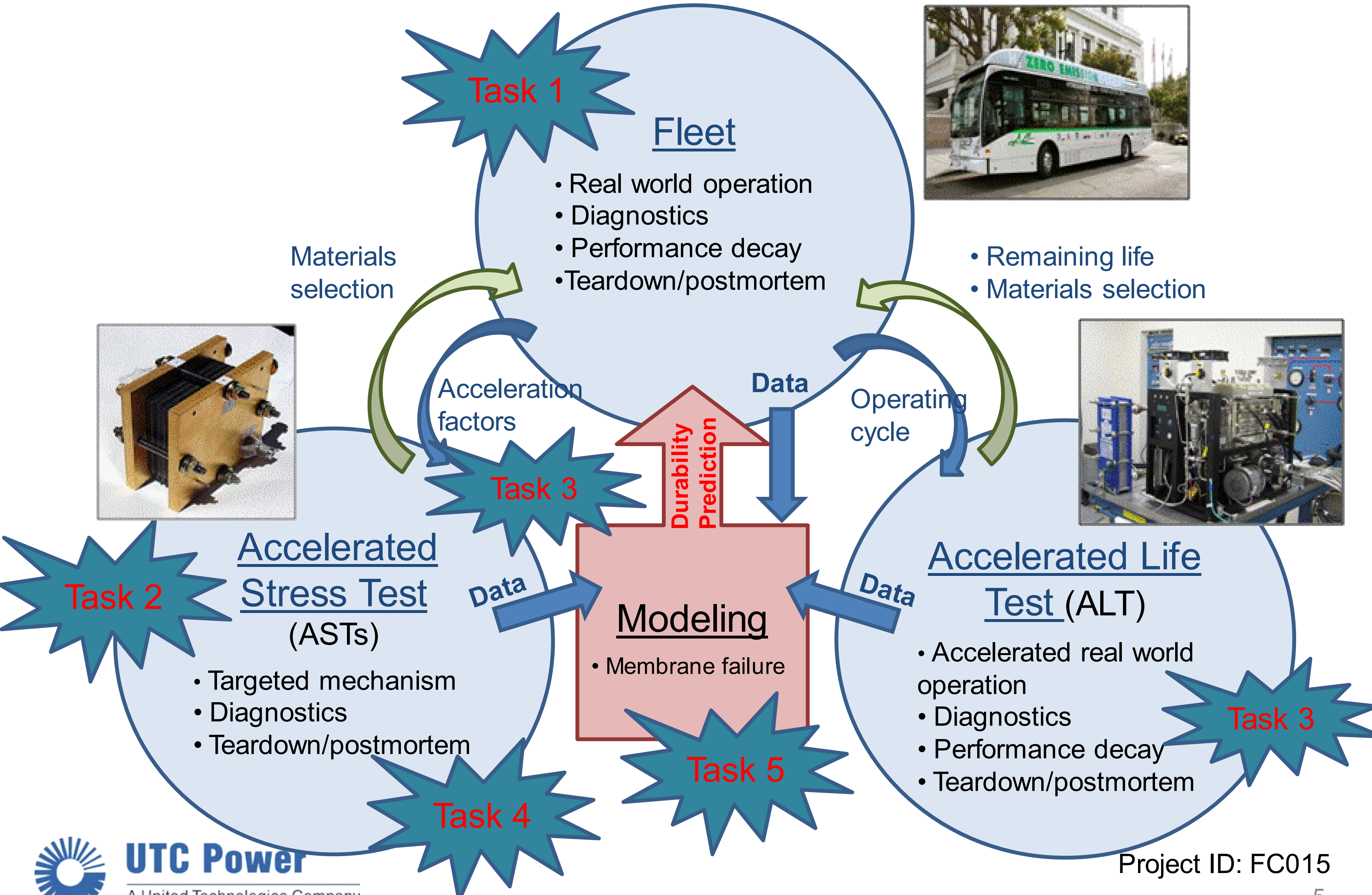
This work is funded under DOE Project # DE-EE0000468

Approach



Task	Progress	Status
1.0. Real world degradation	• Completed bus operating cycle analysis • Completed characterization of field-operated bus stack (2850 h) for all 4 decay mechanisms covered by current AST's	100% complete
2.0. Lab world degradation	• Completed all 4 DOE AST on the same materials as the bus stack • Post-mortem characterization completed	100% complete
Go / No Go Gate 1	• Correlate all observed degradation to field operating conditions → sufficient degradation in field conditions	100% complete
3.0. Real – Lab correlation	• Acceleration factors determined for all existing DOE mechanisms • New degradation mode found and accelerated test proposed • New breadboard unit developed and running accelerated life test (ALT)	100% complete
Go/No Go Gate 2	•Gap in DOE AST's identified for isolation of GDL oxidation effects •Modeling and DMA used to understand chemical + mechanical membrane degradation	100% complete
4.0 Preparation and Validation of New/Modified AST Protocols	•Integrated membrane chemical/mechanical AST underway •Ex-situ GDL oxidation AST development proposed	10% complete
5.0 Project Management and Modeling	•Further development of membrane hydration strain model ongoing	25% complete

Approach



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Collaborations

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Oak Ridge National Laboratory — Managed by UT-Battelle for the Department of Energy

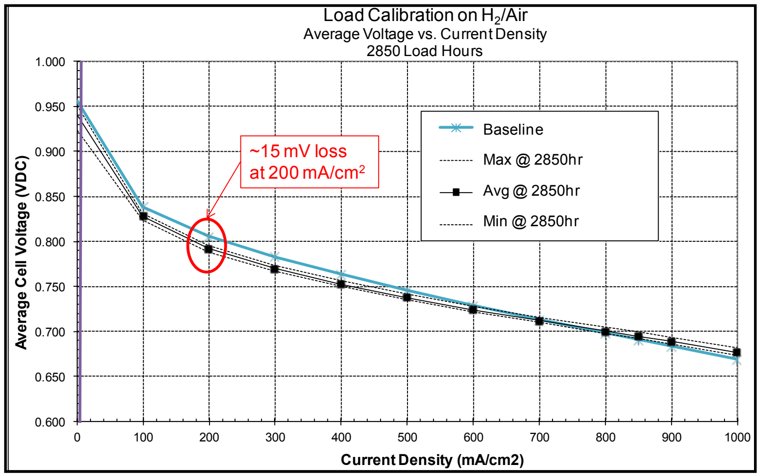
United Technology Research Center (Industry)
- Membrane hydration strain modeling
- Material characterization

Los Alamos National Laboratory (Federal)
- AST development
- Subscale fuel cell and electrochemical testing

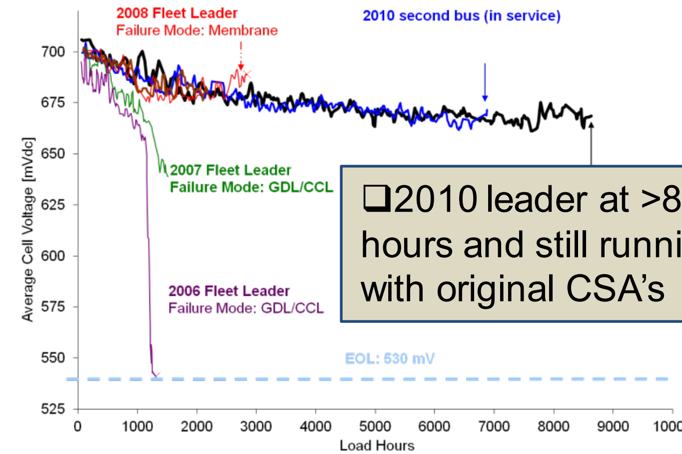
Oak Ridge National Laboratory (Federal)
- Material characterization

Technical Accomplishments
Real World Performance Degradation

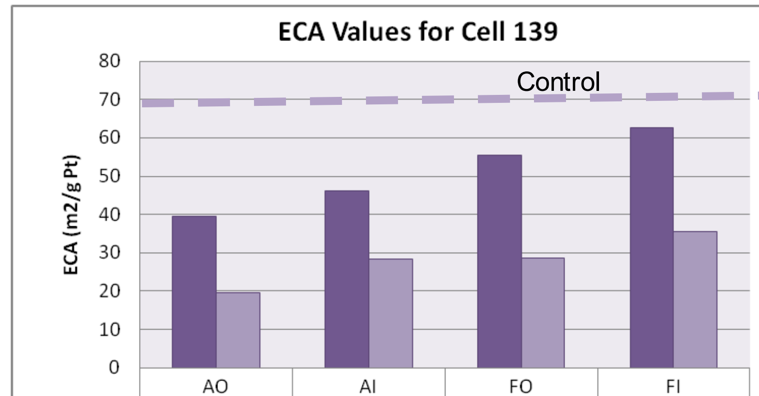
Real World Conditions
Reactants: H_2(dry)/Air(ambient)
Average Temperature: 63 C
Cycle Frequency: 100-120 cycles/hr
Operating time: 2800 hours
Cumulative cycles: 300,000 cycles



UTC 2008 fleet leader at BOL and EOL
~ 15 mV loss @ 0.2 A/cm^2
~50% Platinum area loss



❑2010 leader at >8500 hours and still running with original CSA's



	AO	AI	FO	FI
Anode	39.64	46.24	55.34	62.7
Cathode	19.56	28.27	28.7	35.61

ECA measurements performed on subscale sections at indicated locations (calculated particle size shown in red)

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Technical Accomplishments

PGM AST

Lab ASTs by LANL on UTC 2008 fleet leader BOL components in 50 cm^2 cell

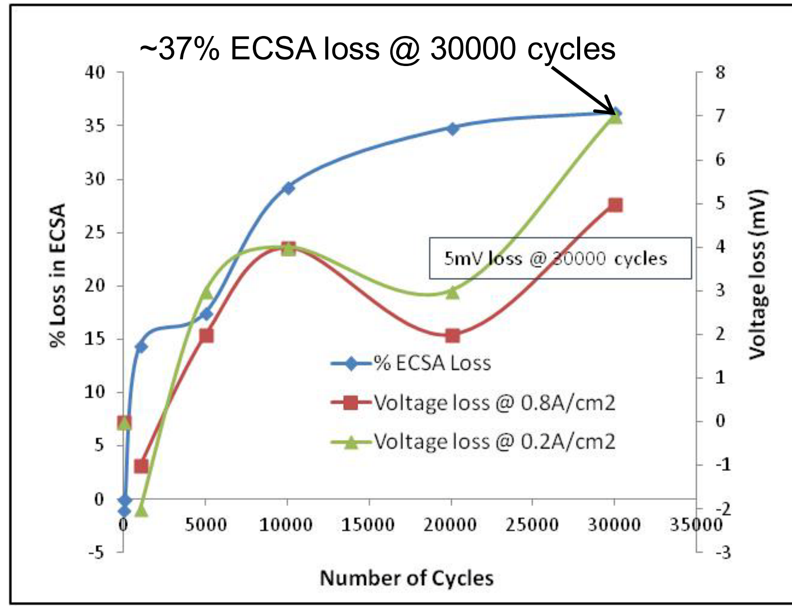
AST Conditions

Reactants: H_2(100%)/N_2(100%)

Average Temperature: 80 C

Cycle Frequency: 112 cycles/h

Cycle Range: 0.6 – 1.0 V (Triangle)



Voltage and ECA loss during potential cycling AST

Observed @ 30k cycles	DOE Target @ 30k cycles
~37% ECA loss	≤40% loss of initial area
~7 mV loss @ 0.2 A/cm^2 ~5 mV loss @ 0.8 A/cm^2	≤30 mV loss at 0.8 A/cm^2
~20% loss of activity	≤40% loss of activity

- Potential cycling AST has acceleration factor of ~8X vs. fleet operation

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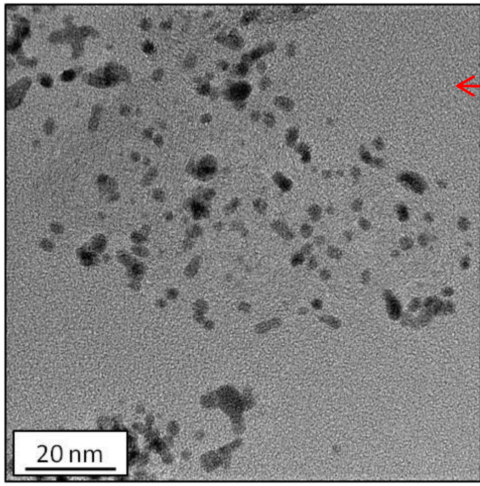
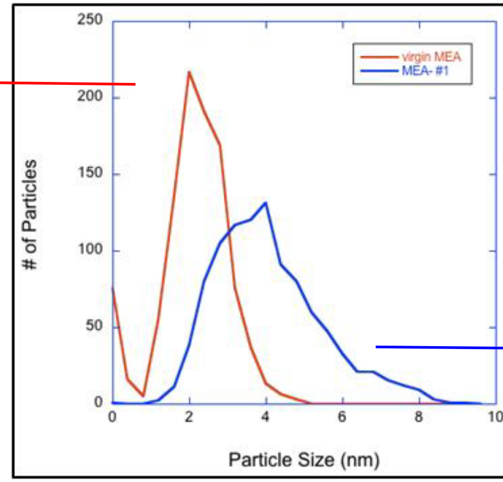
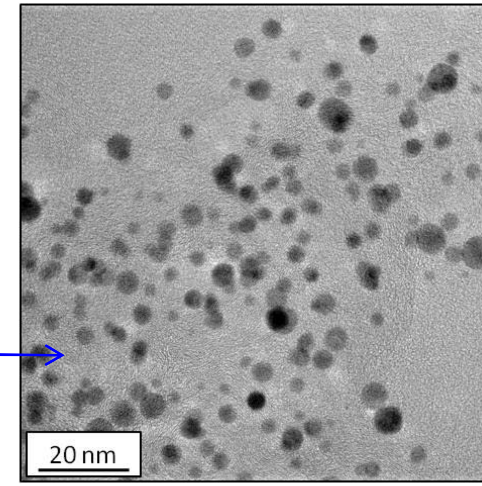
Technical Accomplishments

TEM Analysis on UTC 2008 fleet leader

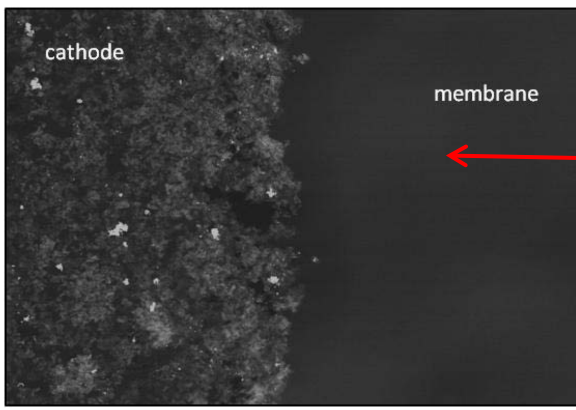


Baseline





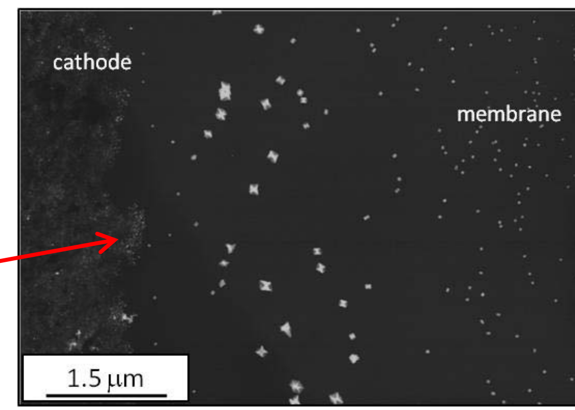
Air Inlet - 2850 hr



Baseline cathode = ~2nm
2850 hr cathode = ~4nm

No Pt observed in membrane of virgin MEA

Pt precipitation in membrane adjacent to cathode



❑TEM analysis shows particle agglomeration and platinum precipitation within the membrane adjacent to cathode catalyst layer

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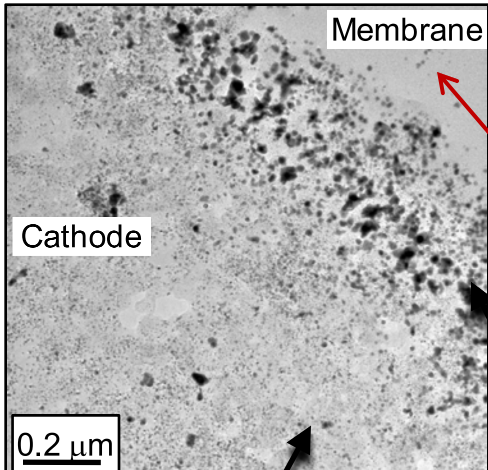
Technical Accomplishments

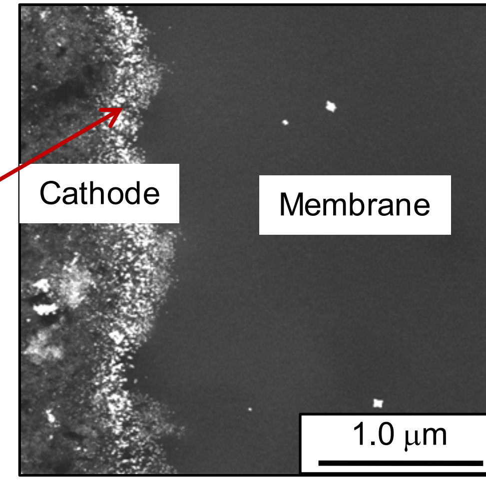
TEM analysis of MEA subjected to PGM AST

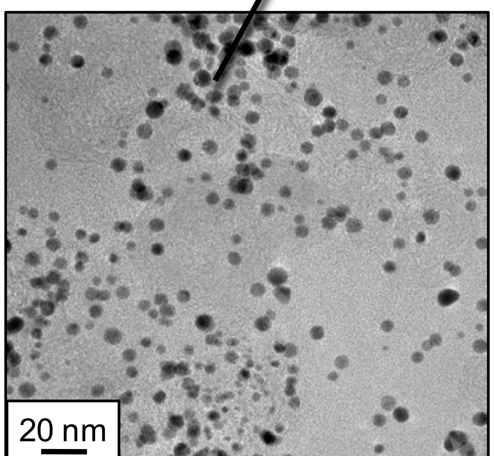
TEM

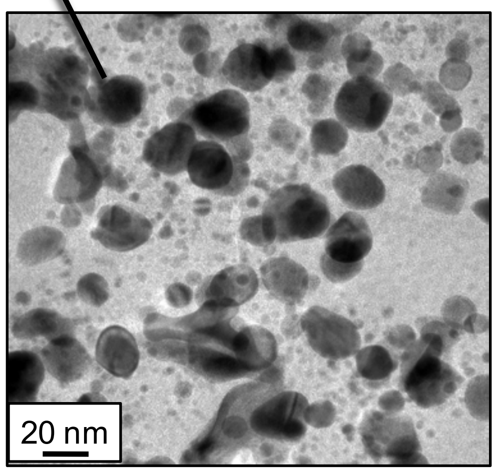


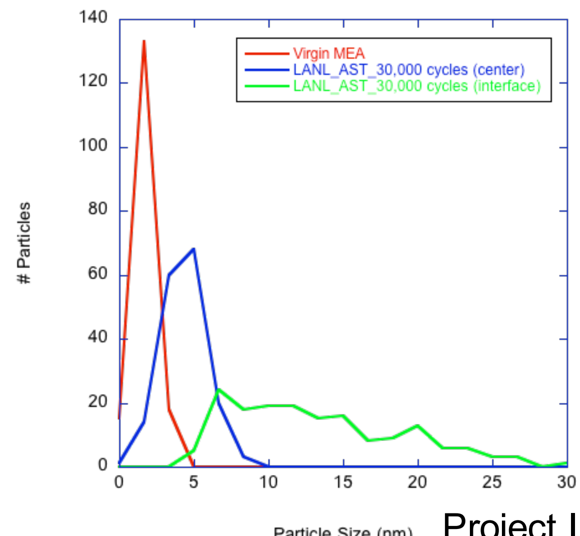
- After AST, formation of large Pt single crystals at cathode - membrane interface observed with little Pt precipitation observed within membrane
- This can be explained by difference in gas compositions; Platinum will precipitate in membrane under H_2/Air and just outside of membrane under H_2/N_2

HAADF-STEM









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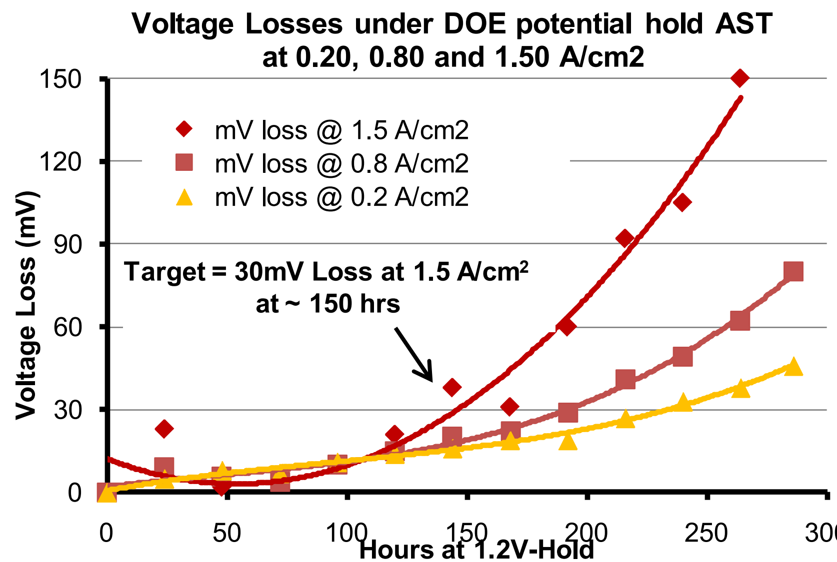
Technical Accomplishments

Carbon Corrosion AST

AST Conditions
Reactants: H_2(100%)/N_2(100%)
Average Temperature: 80 C
Cycle Period: 24 h
Cycle Range: 1.2 V

Observed @ 285 hr	DOE Target @ 400 hr
~40% mass activity	≤60% mass activity
>150mV @ 1.5 A/cm^2	≤30mV @ 1.5 A/cm^2
~50% ECA loss	≤40% ECA loss

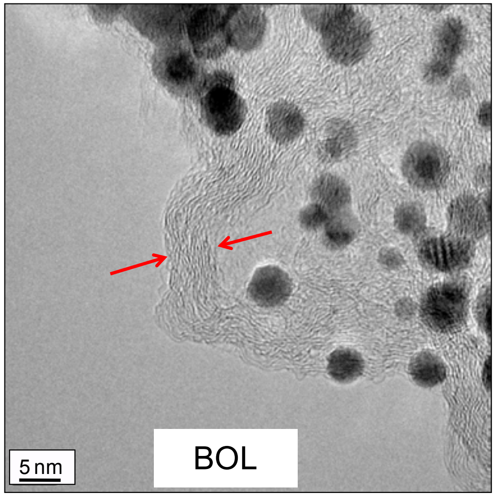


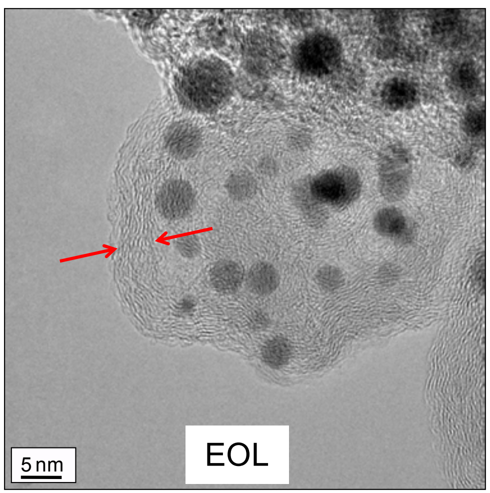
Summary
Severe carbon corrosion under Lab AST
Damaging potentials avoided in 2008 fleet leader
2006 and 2007 fleet leaders suffered from carbon corrosion

Technical Accomplishments

Real World and AST Carbon Morphology

UTC 2008 Fleet Leader



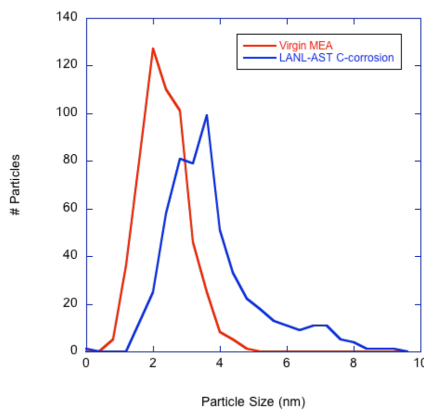


UTC 2008 fleet leader at BOL and EOL

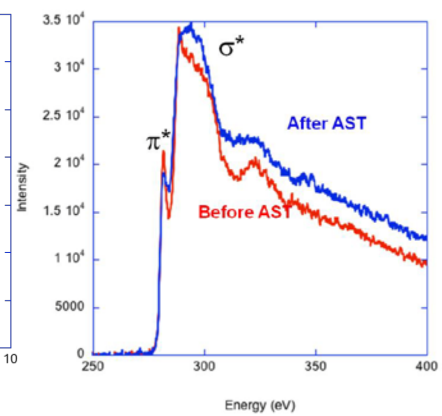
- Small voltage loss @ 1.0 A/cm^2
- Effective system mitigations for start-stop decay → Minor carbon corrosion in real-world operation

AST

- Cathode electrode thinning (20-70%)
- Platinum particle growth
- Increased σ carbon bonds
- AST effective for C corrosion

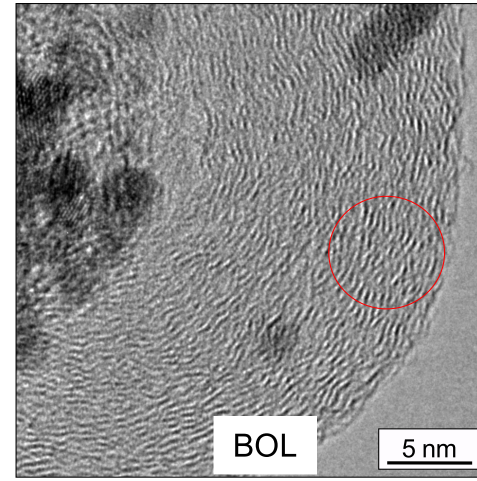


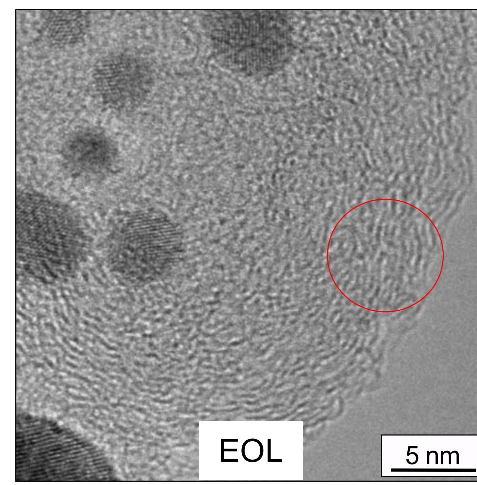
Pt particle growth: ~2.0nm in baseline to ~3.8nm after AST



Increased σ carbon bonds after AST

AST





Graphitic structure disorganized

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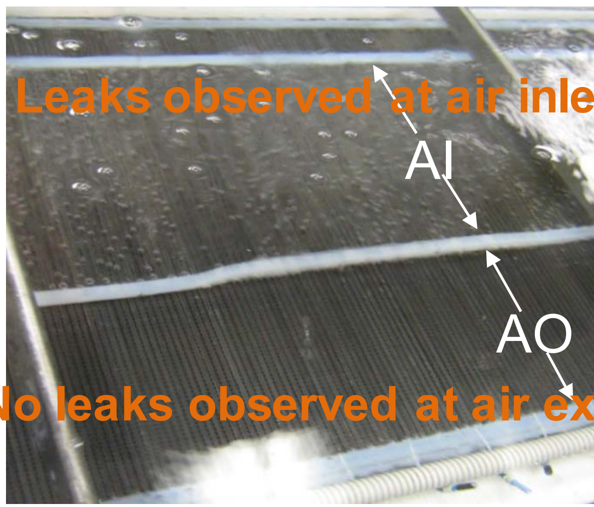
Technical Accomplishments

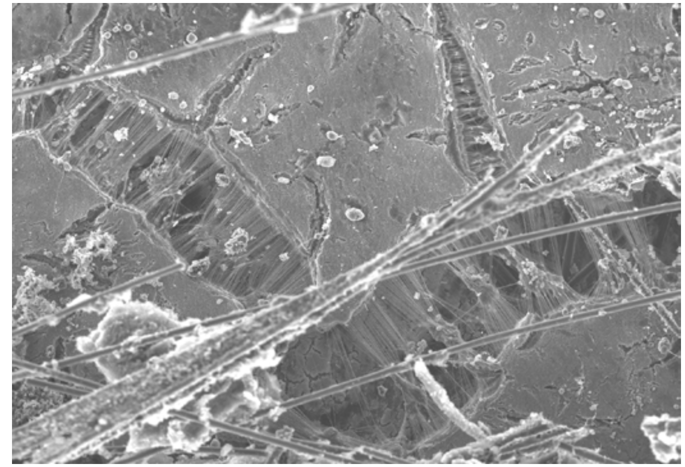
Real World Membrane Mechanical Damage

Real World Conditions
Reactants: H_2 / Air
Average Temperature: 63 C
Cycle Frequency: 100-120 cycles/hr
Humidity range: 50-100% (ΔRH=50%)
Total Time: 2800 hours
Total Cycles: 300,000 cycles

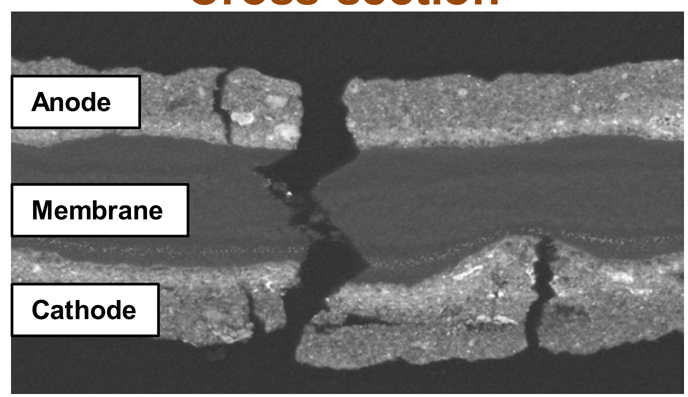


- In fleet operation, membrane failed after 2800 hours at air inlet due to membrane hydration strain cycling induced by load-flow cycling

Surface image



Cross-section



SEM micrographs confirming membrane failure at the air inlet

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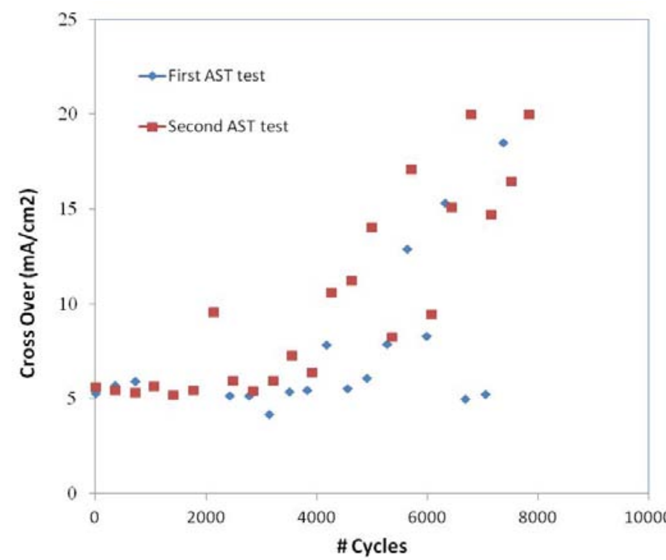
AST Membrane Mechanical Damage

Lab AST Conditions

Reactants: Air / Air
Average Temperature: 80 C
Cycle Frequency: 15 cycles/h
Humidity range: 0-100% (ΔRH=100%)

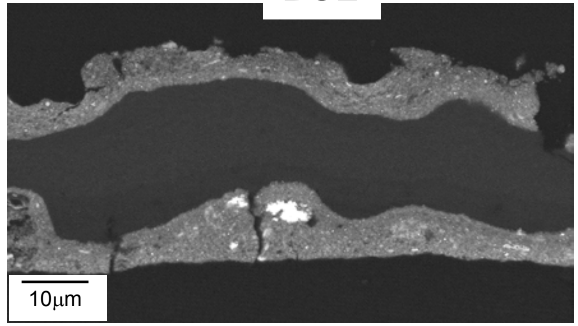
H$_2$ Crossover



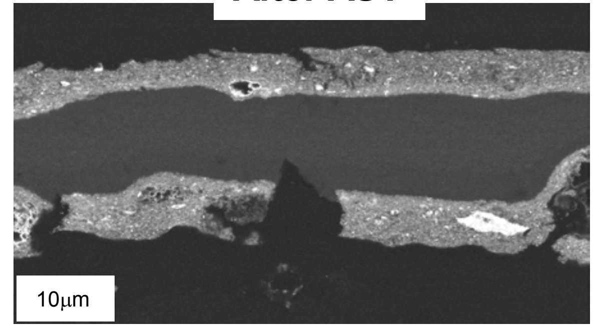
	DOE AST Target @ 20000 cycles	Observed @ 7000 cycles
Crossover	<2 mA/cm^2	20 mA/cm^2
Shorting Resistance	> 1000 ohm cm^2	~1400 ohm cm^2

- Membrane mechanical AST resulted in acceleration factor of ~6X vs. fleet operation with same failure mode

BOL



After AST

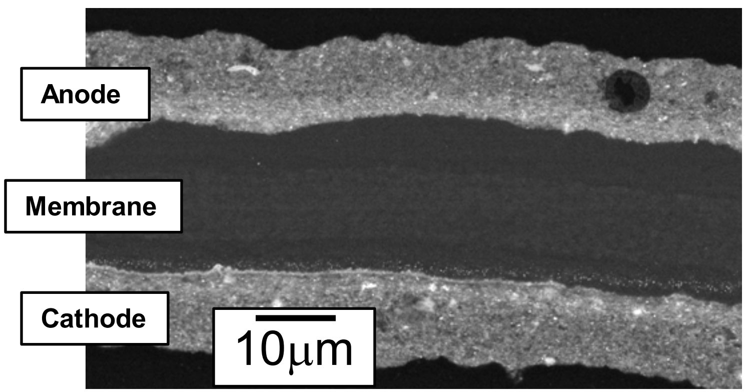


Structural damage observed in membrane and catalyst layers

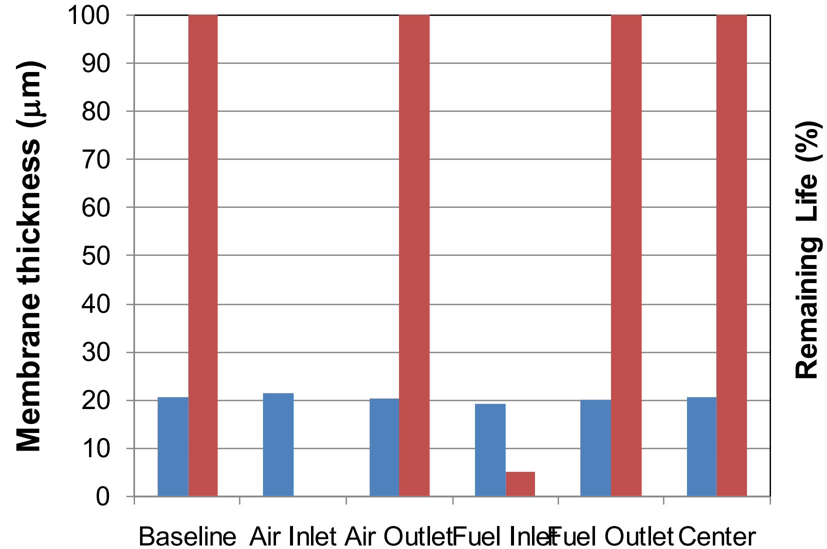
Technical Accomplishments

Real World Membrane Chemical Damage

Real World Conditions
Reactants: H_2 / Air
Average Temperature: 63 C
Time at high voltage: 30%
Humidity: 100%



No detectable chemical attack



Membrane thickness measurements and DMA testing of remaining life results of BOL and EOL at various locations in the active area

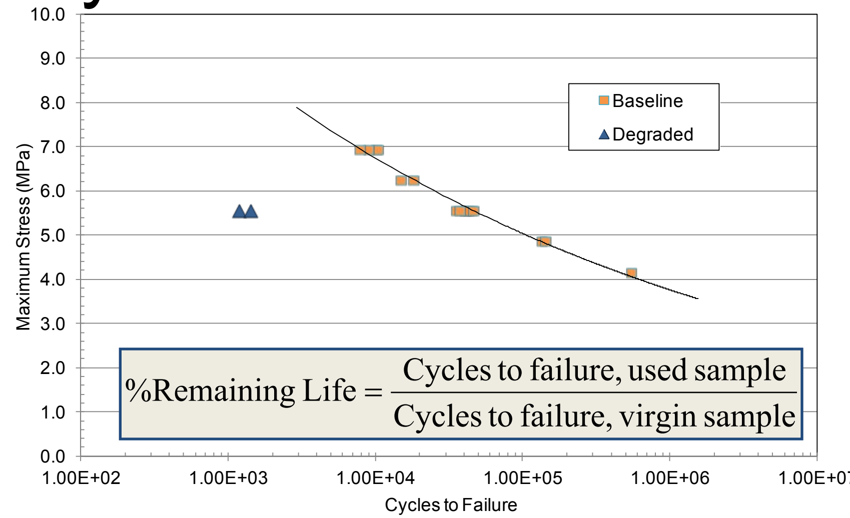
- No membrane thinning observed in real world application; Significant mechanical degradation observed at reactant inlets due to membrane hydration strain cycling

Technical Accomplishments

AST Membrane Chemical Decay

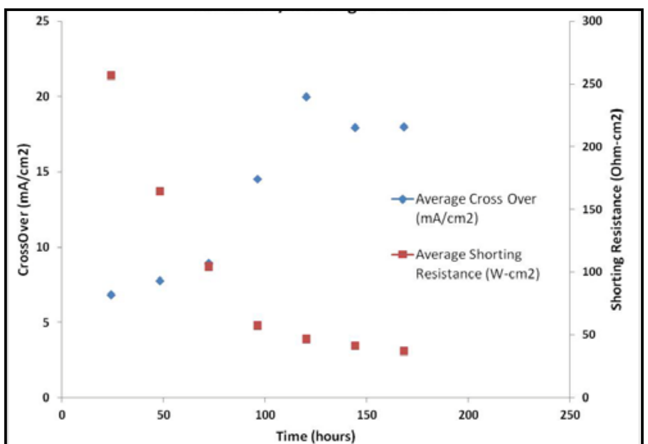
AST Conditions
Reactants: H_2 / Air
Average Temperature: 90 C
Voltage: Open Circuit
Humidity: 30%

	DOE Target @ 500 hr	Observed @ 200 hr
Crossover	≤ 2 mA/cm^2	~ 20 mA/cm^2
OCV loss	≤ 20%	~ 20%
Shorting Resistance	< 1000 Ω- cm^2	~ 250 Ω-cm^2

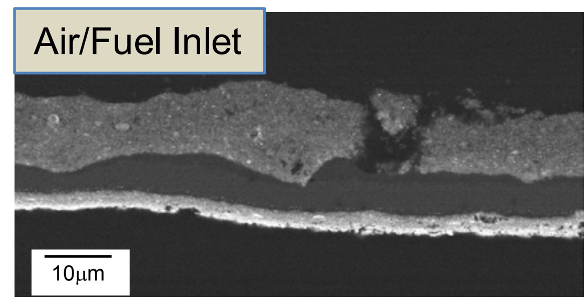


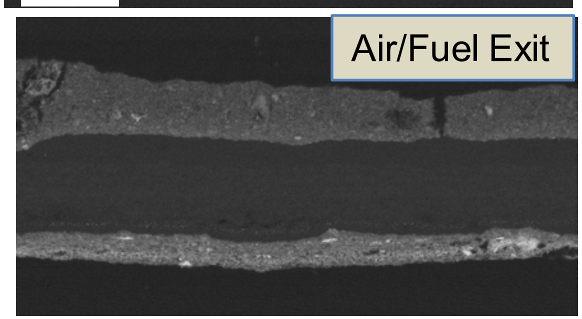
$$\%\text{Remaining Life} = \frac{\text{Cycles to failure, used sample}}{\text{Cycles to failure, virgin sample}}$$

Crossover/Shorting Resistance



- Significant membrane thinning observed after membrane chemical decay AST; DMA technique useful for estimating remaining life





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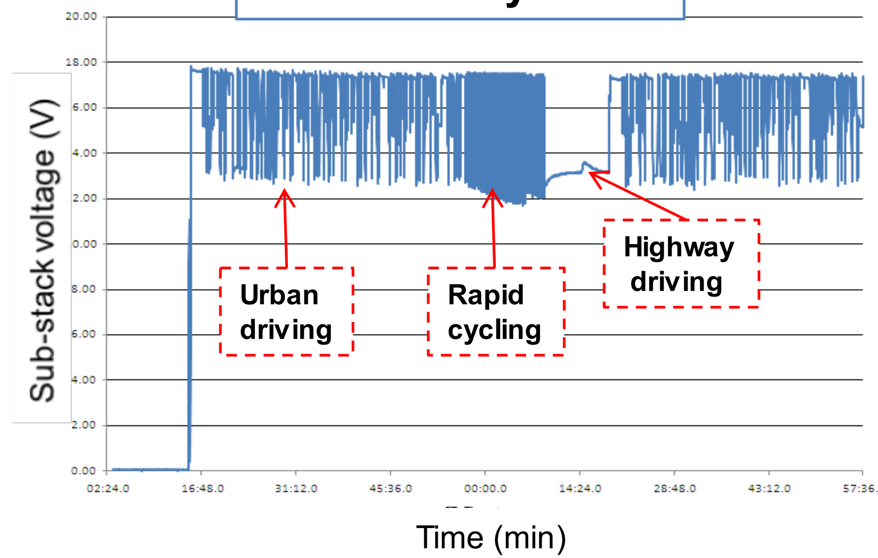
Technical Accomplishments

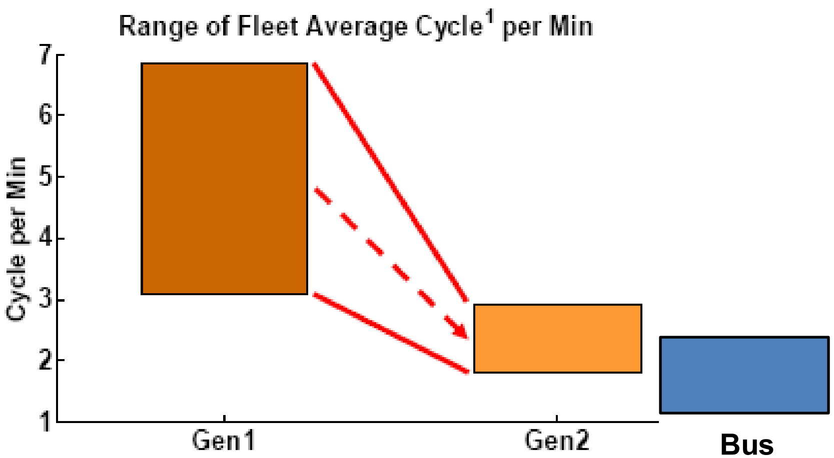
ALT Rig

Stack format	Failure mode	Expected completion
2008 leader	Membrane	May 2011
2010 leader + advanced UEAs	Unknown	Nov 2011

Transit cycle

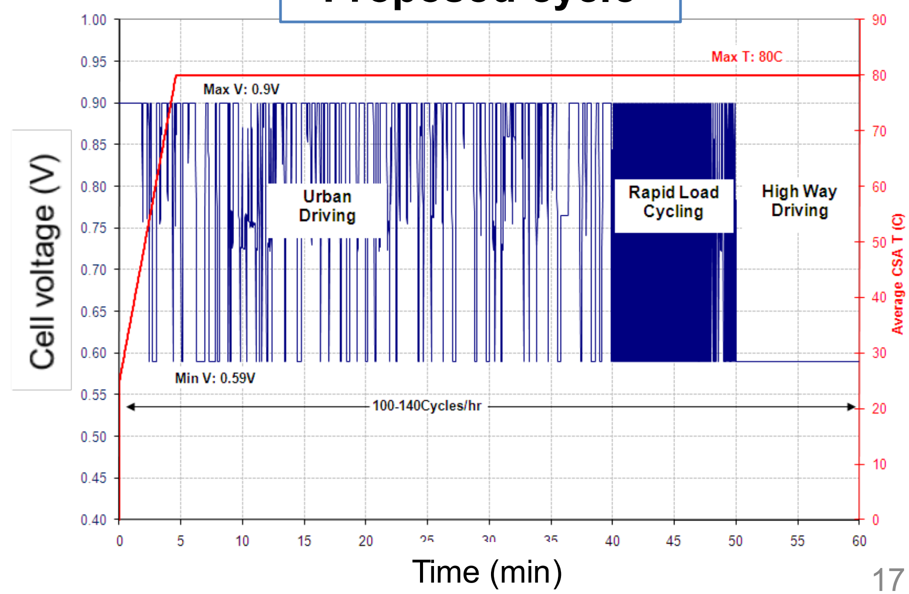


Auto cycle



from "Controlled Hydrogen Fleet and Infrastructure Analysis" TV001, K. Wipke of NREL, 2010 AMR

Proposed cycle



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Technical Accomplishments

Summary of Real World to AST Comparisons

Mechanism	Real Cycle	Real Diagnostics	AST Cycle	AST Diagnostics	Correlation
Pt Dissolution/ sintering	2850 hrs 100 cycles/h 0.6 to 0.9 V	~2% V loss @ low power ~60% ECA loss	30 kcyc 112.5 cycles/h 0.6 – 1.0 V_{nhe}	~1% V loss @ low power ~37% ECA loss	-High AST-Real correlation -Low impact on Real World perf -May depend on 0.4 mg Pt/cm^2
Carbon Corrosion	~500 cycles H_2 / Air fronts from S/S cycles (mitigated)	Negligible performance loss @ 1.0 A/cm^2	250 hrs Continuous hold @1.2 V_{nhe}	90 mV performance loss @ 1.0 A/cm^2	-No AST-Real correlation -AST effective for C corrosion -High impact on performance if S/S mitigations not employed
Membrane Mechanical	2850 hrs 100 cycles/h ΔRH: 40-50%	High RPS response & visible leakage across stack	6000 cyc ΔRH: 0- >100% 15 cycles/h	>15 mA/cm^2 (vs 2 mA/cm^2 BOL)	-High AST-Real correlation -High impact on Real World perf
Membrane Chemical	~850 hrs H_2/Air @ V_{idle} 63°C 100%RH	Minimal membrane thinning	100 hr H_2/air 90°C 30%RH OCV	>15 mA/cm^2 (vs 2 mA/cm^2 BOL)	-Low AST-Real correlation -AST effective for membrane chemical degradation -Combined chemical-mechanical

Future Work

Task	Description	Status	Owner	Comments
Task 4	4.1 Develop new AST protocols	Underway	UTC Power / LANL	• Identified following opportunities: 1) Integrated membrane chemical / mechanical AST[Q2/2011] 2) Validated failure time prediction using DMA[Q3/2011] 3) GDL oxidation AST[Q3/2011] 4) Validate the ALT breadboard degradation[Q4/2011] 5) Evaluate proposed FCTT load / RH cycle AST[Q2/2011]
	4.2 Test BOL cells with new AST's	Underway	UTC Power / LANL	• ALT currently testing BOL materials at UTCP[Q3/2011]
	4.3 Validate new AST protocols	Not started	All	• LANL testing of developed protocols[Q3/2011] • Employ analyses and techniques already developed for new AST's[Q3/2011]
Task 5	5.1 Further development of membrane hydration strain model	Underway	UTRC	•Include modeling of composite structures[Q3/2011] •Include effect of flow field design on membrane hydration strain[Q4/2011]

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PROJECT SUMMARY

Relevance: Development of validated accelerated test protocols for all identified failure modes will decrease need for expensive, time consuming durability testing

Approach: Perform fuel cell diagnostics and materials characterization on real world samples and samples that have been subjected to accelerated test protocols; Identify any failure modes not being addressed by current DOE AST protocols and develop and validate new AST's for those failure modes;

Technical Accomplishments and Progress:

-Completed characterization of field-operated bus stack (2850 h) for all 4 decay mechanisms covered by current AST's;

-New breadboard unit developed and running accelerated life test (ALT)

-Gap in DOE AST's identified for isolation of GDL oxidation effects

-DMA used to estimate remaining life

Technology Transfer/Collaborations: Active partnerships with LANL and ORNL in AST validation, development of new AST's, and material characterization . Technology transfer through team meetings, presentations and publications.

Proposed Future Research: Develop validated ex-situ GDL oxidation test; Validate combined membrane chemical/mechanical AST; Validate use of DMA as lifetime prediction tool;

Technical Back-up Slides

Technical Accomplishments

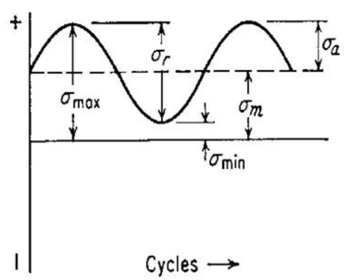
Real World versus AST

	Task 1 – Real-World			Task 2 – Lab-World		
Decay Mechanism	Real-World Cycle	Real-World Diagnostics	Real-World Post-test Analysis	Lab AST Cycle	Lab AST Diagnostics	Lab AST Post-test Analysis
Pt Dissolution/ sintering	H_2/Air 63°C 100%RH 100 cycles/h 0.6 – 0.9 V	Performance ΔV @ 0.2A/cm² ECA loss	SEM XRD HRTEM	H_2/N_2 80°C 100%RH 112.5 cycles/h 0.6 – 1.0 V_{nhe}	Performance ΔV @ 0.2A/cm² Mass activity & ECA loss	SEM XRD HRTEM
Carbon Corrosion	H_2 / Air fronts during start-up (25 C) and shutdown (65 C) (mitigated); Air-Air Time	Performance ΔV@1.0 A/cm²	SEM HRTEM EELS	H_2/N_2 80°C 100%RH 1.2 V_{nhe}	Performance ΔV@1.5A/cm² CO_2 release Mass activity loss	SEM HRTEM EELS
Membrane Mechanical	H_2/Air 63°C ΔRH: 40-50% 100 cycles/h	Crossover diagnostics (RPS)	SEM, DMA (BOL & EOL)	Air/Air 80°C ΔRH: 0→100% 15 cycles/h	H_2 cross-over Shorting	SEM, DMA (BOL & EOL)
Membrane Chemical	H_2/Air 63°C 100%RH V_{idle} for ~30% load time	Crossover diagnostics (RPS)	SEM, DMA (BOL & EOL)	H_2/air 90°C 30%RH OCV	FER H_2 cross-over Shorting	SEM, DMA (BOL & EOL)

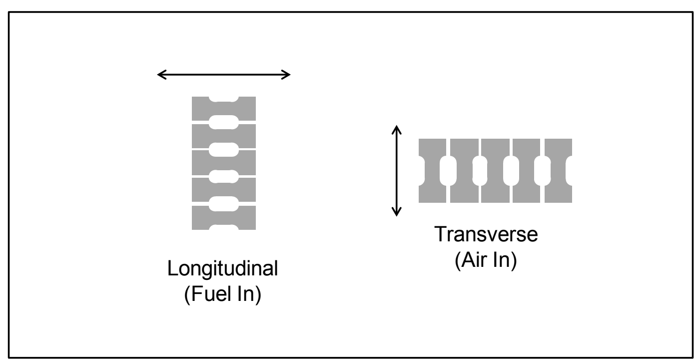
Experimental – dynamic mechanical analysis (DMA)

Sample: MEA
Conditions:

- 60°C
- 90%RH
- 10Hz
- $\sigma_{Min} = 20\%\sigma_{max}$



Sampling configuration:



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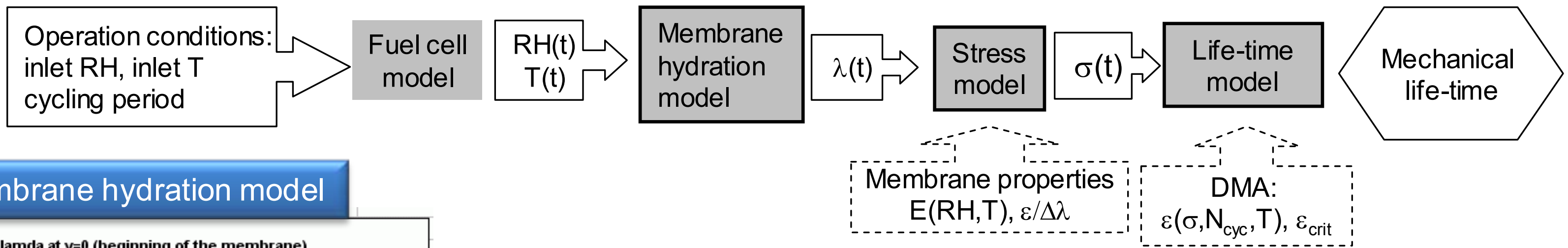
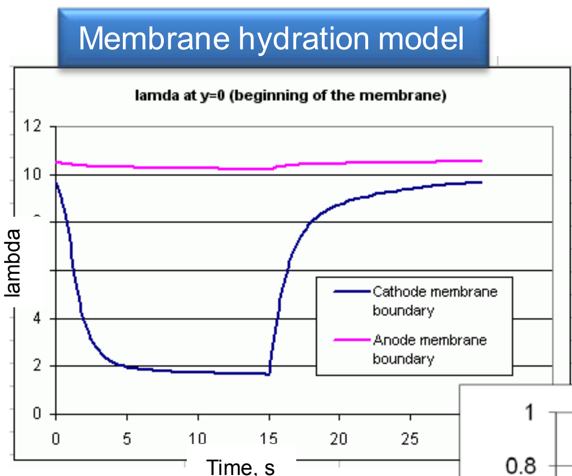
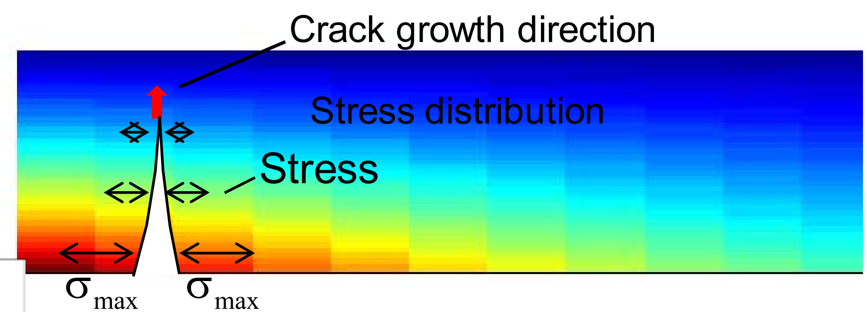
Technical Accomplishments

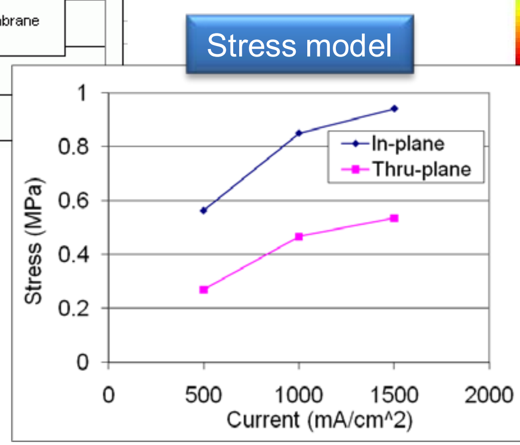
Membrane Hydration-induced Stress Model

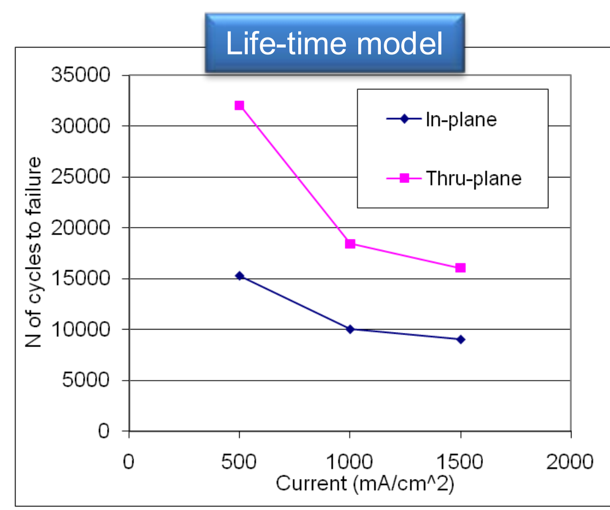
Membrane Mechanical Decay Model:











Developed modeling framework to relate fuel cell operation to membrane property changes and predict mechanical failure

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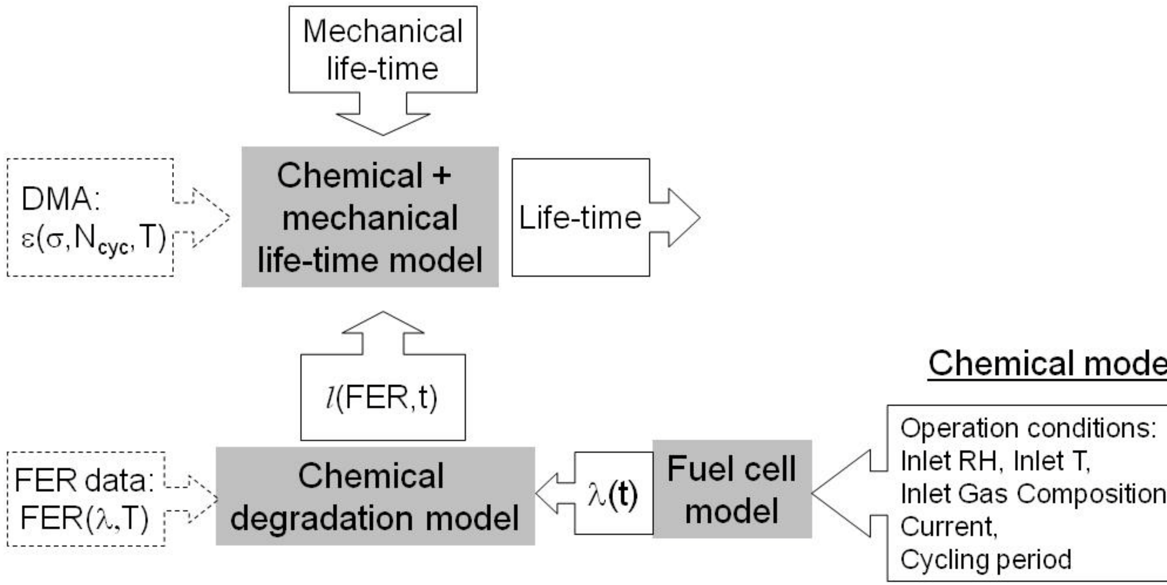
Motivation for Membrane Chemical + Mechanical



	Through plane	In plane
Maximum stress, Mpa	0.41	0.81
Cycles to failure:Mechanical	142463.76	70840.79
Cycles to failure: Chemical + Mechanical	45208.29	30679.42

"Model for Prediction of Abrupt Failure of PEMFC Membranes" in preparation to **Journal of the Electrochemical Society**, November 2010.

Motivation for Diffusion Layer AST

GDL Corrosion

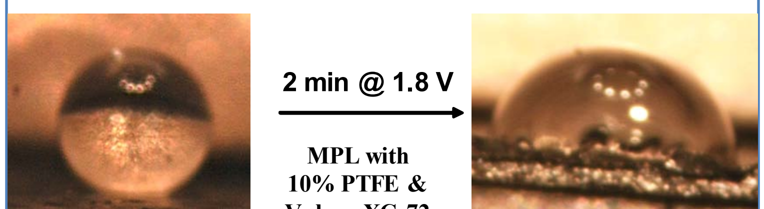
- Occurs at all normal cathode potentials
- Can be partially oxidized to form surface oxide groups

$$C + H_2 0 \rightarrow C - OH + H^+ + e^-$$

  - Results in change in surface hydrophobicity
- Can be fully oxidized to form gas

$$C + 2H_2 0 \rightarrow CO_2 + 4H^+ + 4e^-$$

  - Results in change in structure
- Cycling vs holding at fixed potentials leads to different results



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