Improved Accelerated Stress Tests Based on FCV Data

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UTC POWER

May 15, 2012

UTC Power
A United Technologies Company

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This work is funded under DOE Project # DE-PS36-08GO98009

Overview

Timeline

- Start Date: December 2009
- Finish Date: May 2012
- Status: 90% Complete

Barriers

(from the Multi-Year Research, Development and Demonstration Plan)

- ❑ >5,000 hr stack durability w/ less than 10% performance decay
- ❑ ASTs used to avoid costly durability testing
- ❑ UTC bus durability target of 15,000 hours

Budget

Total funding: $3.847M

- DOE: $3.078M (includes $617K to the National Labs – ORNL & LANL)
- Cost share: $769K

Total DOE Funds Received: $3.078M

FY11 DOE Funding: $884K

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	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 ASTs → recommend new ASTs	Validated GDL specific AST; Validated integrated membrane mechanical/chemical AST;	**Task 4** – Prepare and Validate New/Modified AST Protocols

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Collaborations

Partners

United Technologies Research Center

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

Los Alamos National Laboratory EST. 1943

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

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

Oak Ridge National Laboratory (Federal)
- Material characterization

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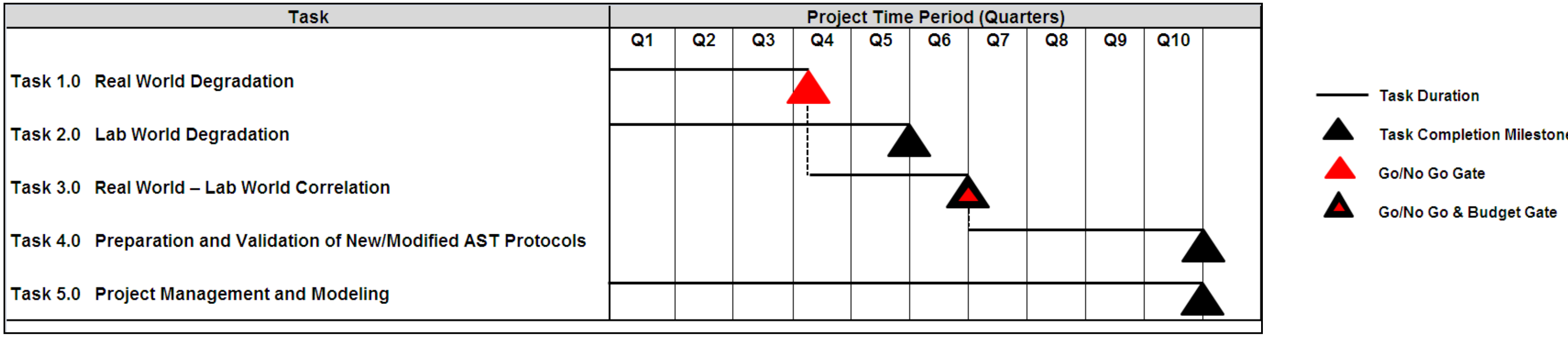
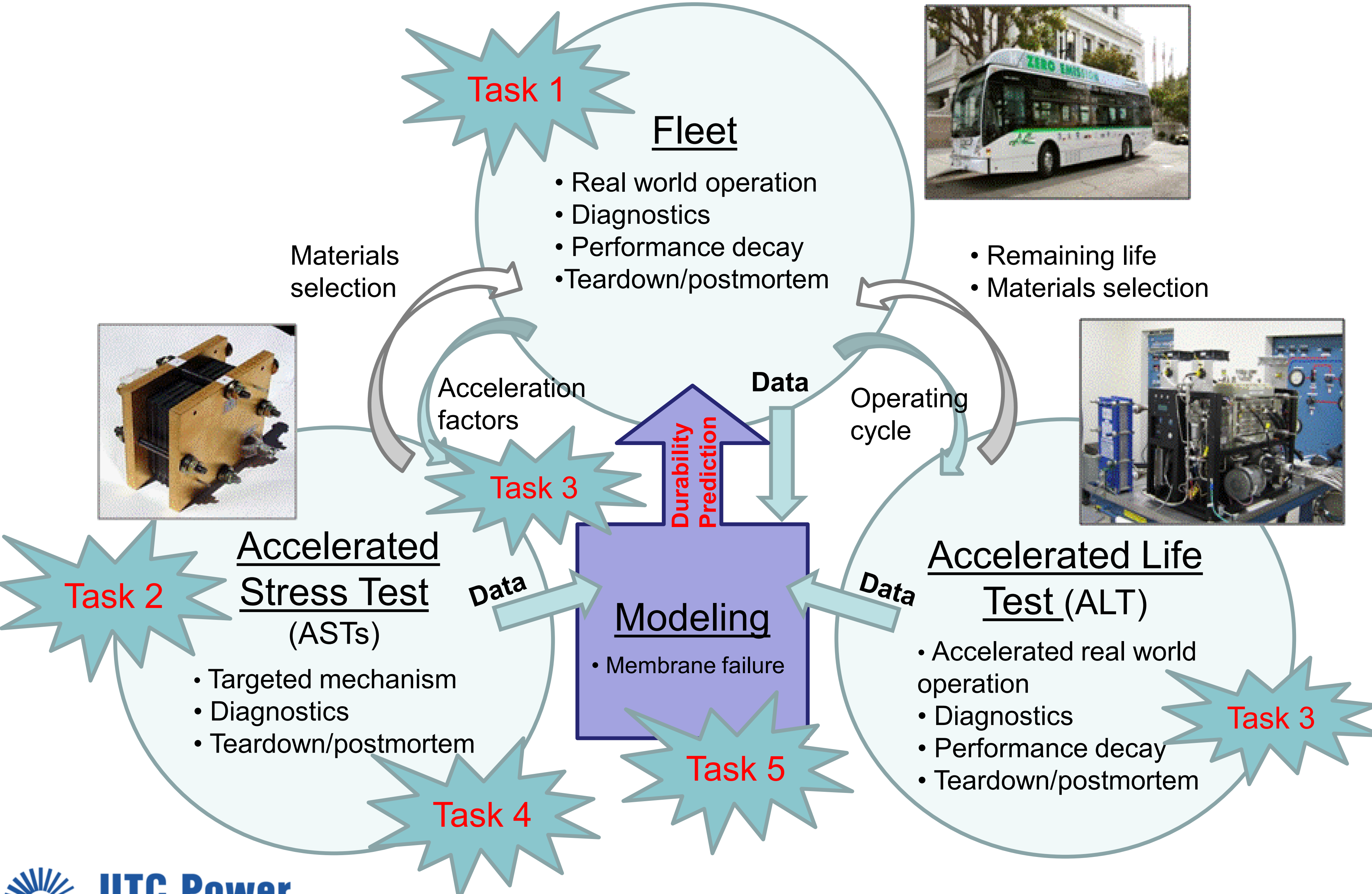
Approach



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 ASTs	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 ASTs identified for isolation of GDL oxidation effects •Modeling & DMA used to understand chem. + mech. membrane degradation	100% complete
4.0 Preparation and Validation of New/ Modified AST Protocols	•Integrated membrane chemical/mechanical AST completed •Ex-situ GDL oxidation AST development underway	90% complete
5.0 Project Management and Modeling	•Further development of membrane hydration strain model completed	100% complete

Approach



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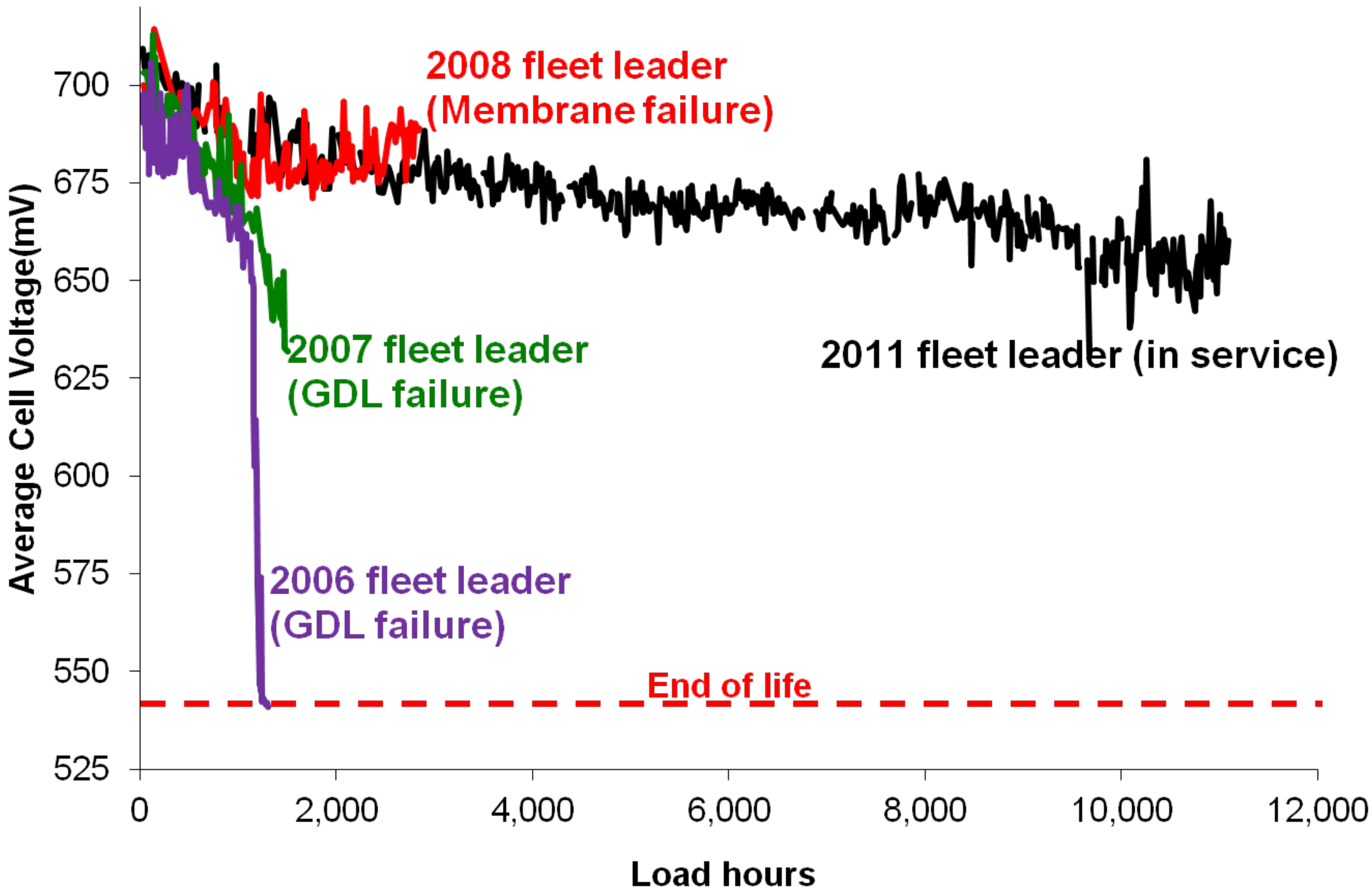
Approach
Real world versus AST

	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/cm^2 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/cm^2 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/cm^2	SEM HRTEM EELS	H_2/N_2 80°C 100%RH 1.2 V_{nhe}	Performance ΔV@1.5A/cm^2 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)

Technical Accomplishments

UTC fleet data



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Technical Accomplishments

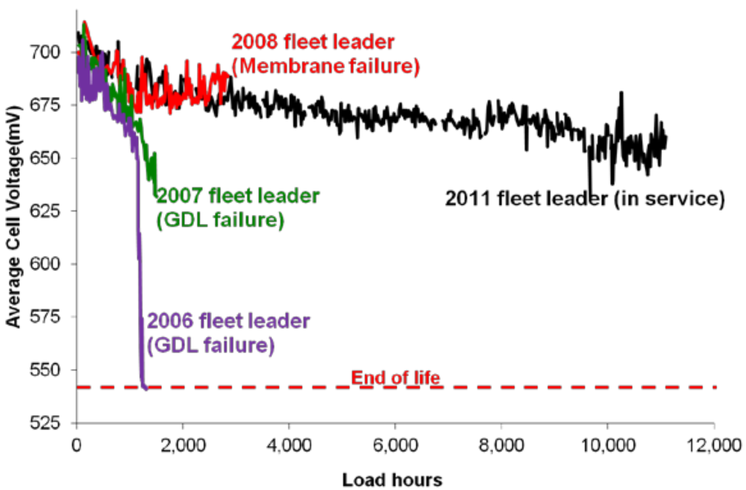
Carbon corrosion AST(Air-air cycling)

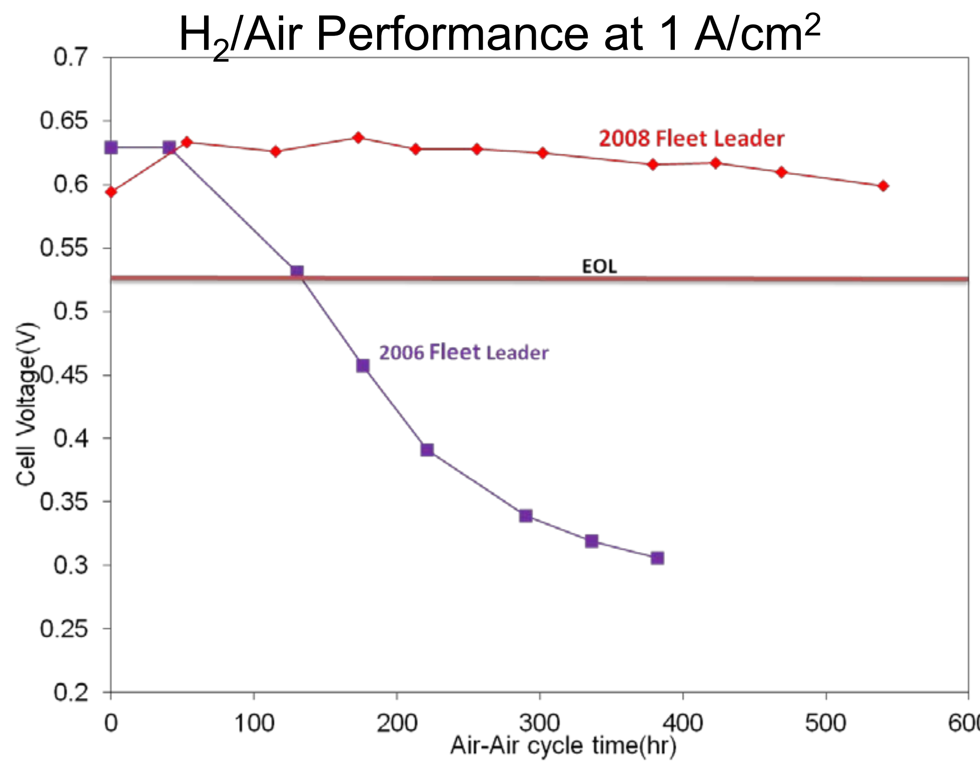
Air-air cycling AST shows ~10X acceleration factor from lab to field

Implementing GDL which showed 10X improvement in Air-air cycling AST allowed fleet durability improvement from 1000 hours to 2800 hours, at which point it failed due to membrane failure

Relatively time consuming test for newest material set

Coolant inlet temperature (ºC)	65ºC		
Reactant flow cycle	Time	Anode Reactant	Cathode Reactant
	5 minutes	H_2	H_2
	5 minutes	N_2	N_2
	1 hour	Air	Air
	5 minutes	N_2	N_2
Applied external resistance	<0.2 mOhm		





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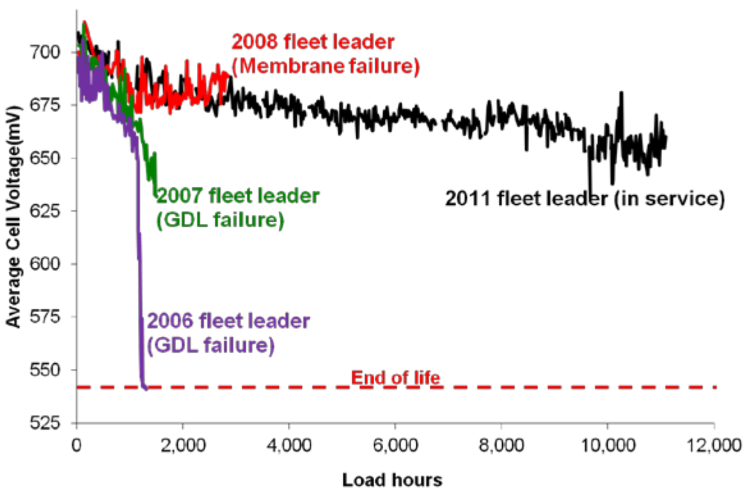
Technical Accomplishments

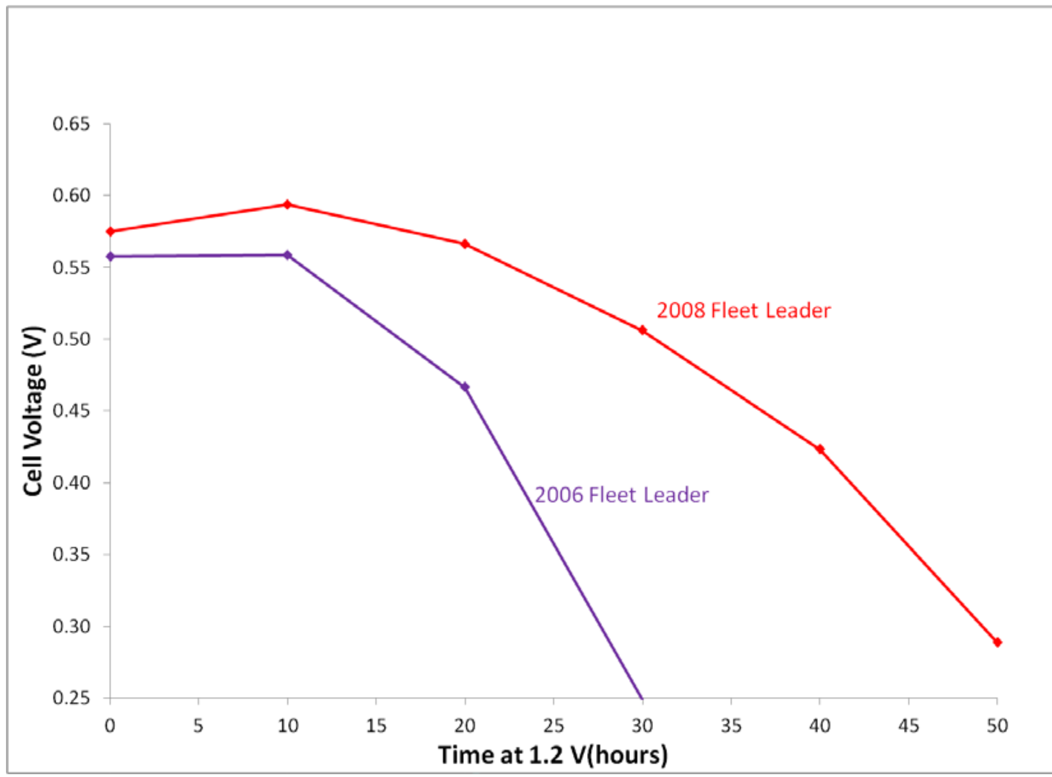
Carbon corrosion AST(1.2 V hold @ 80ºC)

1.2 V hold at 80ºC is a 50X accelerated test

2008 fleet leader GDL (same as 2011 fleet leader GDL) shows 2X improvement in carbon corrosion AST over 2006 fleet leader; In field, improvement was greater than 7X

Coolant inlet temperature (ºC)	80ºC
Anode Reactant	4% H_2 in N_2
Cathode Reactant	N_2
Applied Voltage	1.151 V vs Ref (1.2 V vs H_2)





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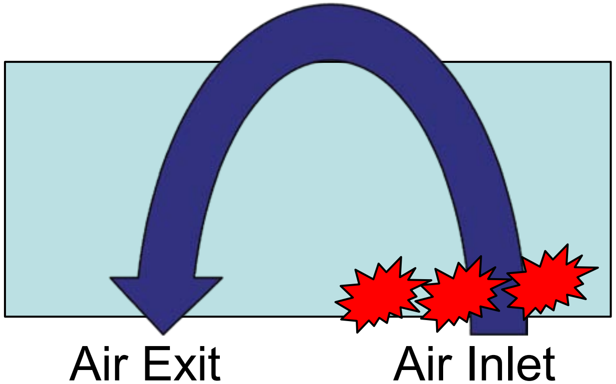
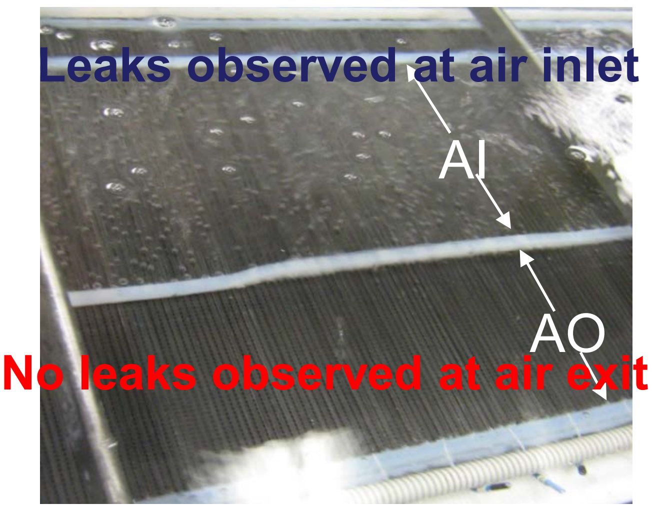
Real world membrane mechanical damage

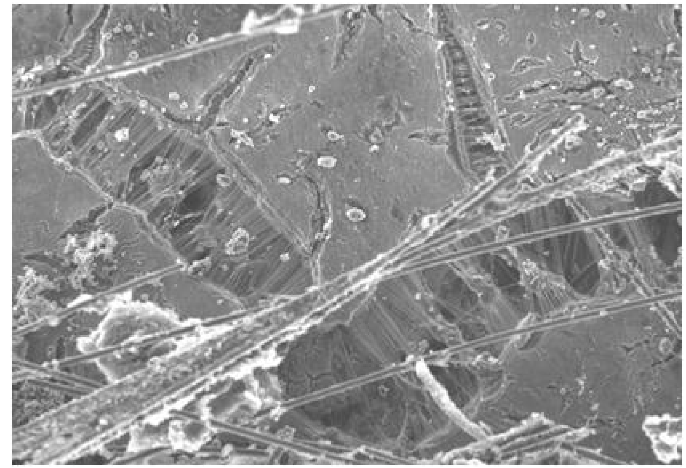




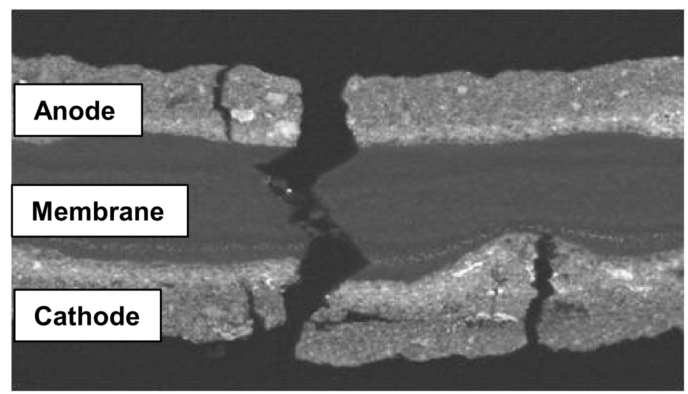
Water submerge test showing air inlet

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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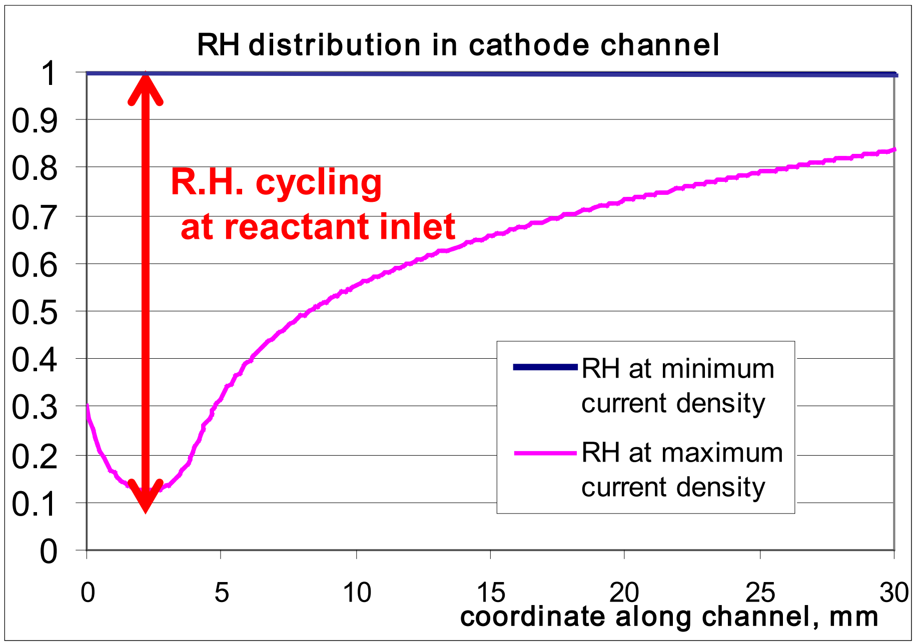
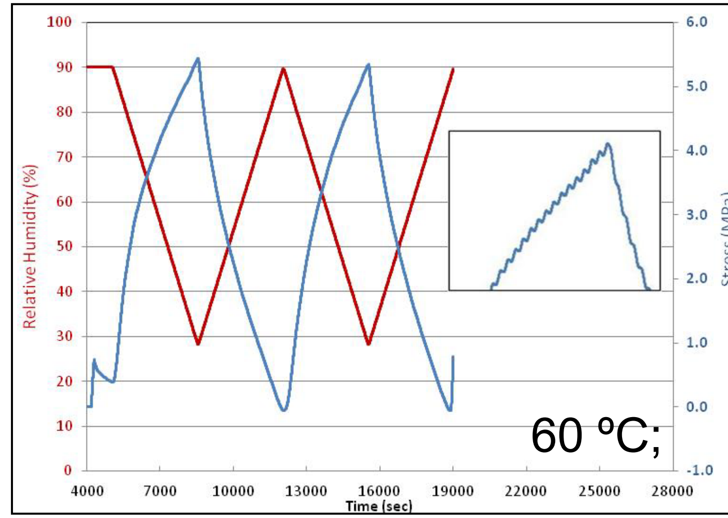
Technical Accomplishments

Failure mechanism of 2008 fleet leader

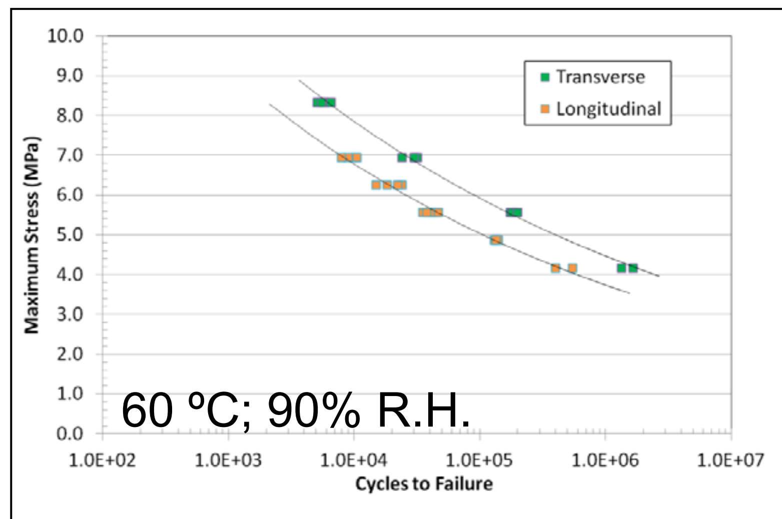
Current density cycling → **Relative humidity cycling** → **Stress cycling** → **Mechanical failure**



Model of Channel R.H. during load cycling



Stress during R.H. cycling at constant strain



S-N curve for 2008 fleet leader

T.T. Aindow and J. O'Neill, Journal of Power Sources, Volume 196, Issue 8, 15 April 2011, Pages 3851-3854

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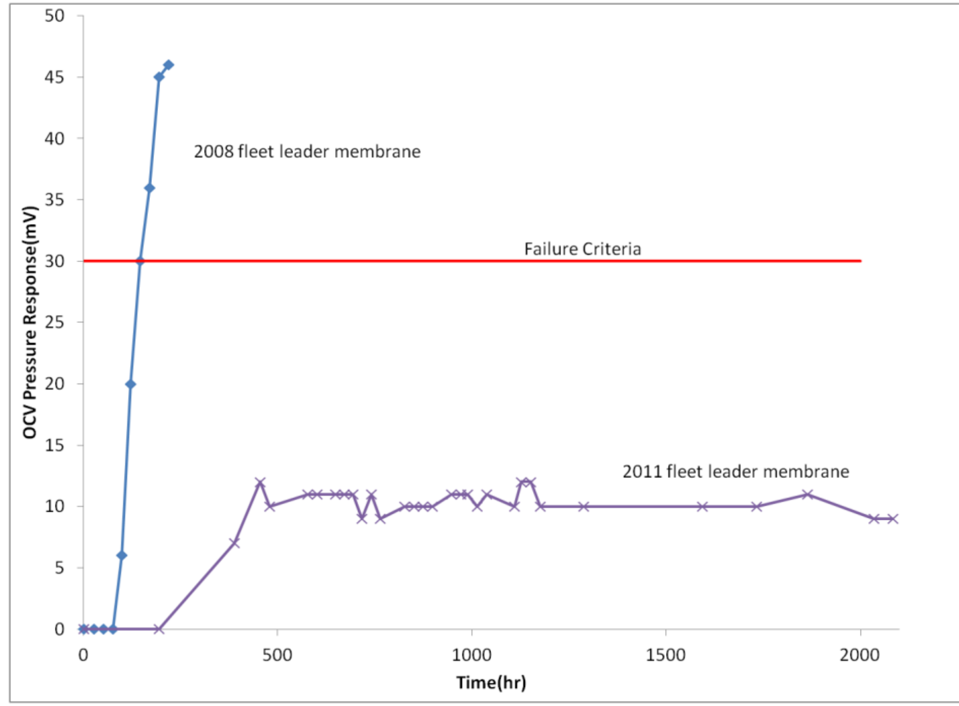
Technical Accomplishments

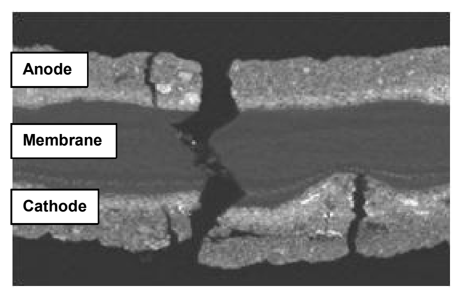
Modified membrane mechanical damage AST

Coolant inlet temperature (ºC)	80ºC	
Anode reactants	Hydrogen, 80% utilization(SR = 1.25)	
Cathode reactants	Air, 60% utilization (SR = 1.66)	
Load cycle	**Time**	**Current density**
	20 sec	10
	15 sec	800 or 1500 mA/cm^2
OCV Pressure Response	Measure cell voltage difference at open circuit when the anode to cathode cross-pressure is changed from 0 kPa to 15 kPa	

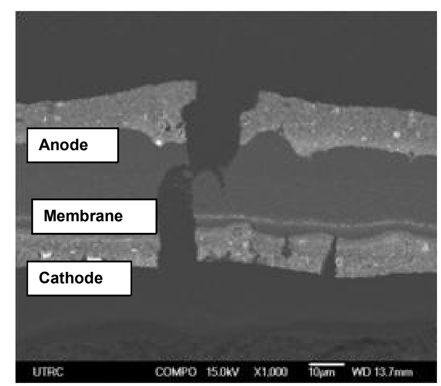


Membrane mechanical AST resulted in acceleration factor of ~20X vs. fleet operation with same failure mode

Implementation of more durable membrane enabled fleet durability to increase from 2800 hours to 10,000 hours



2008 Fleet Leader, 2800 hours



Lab AST

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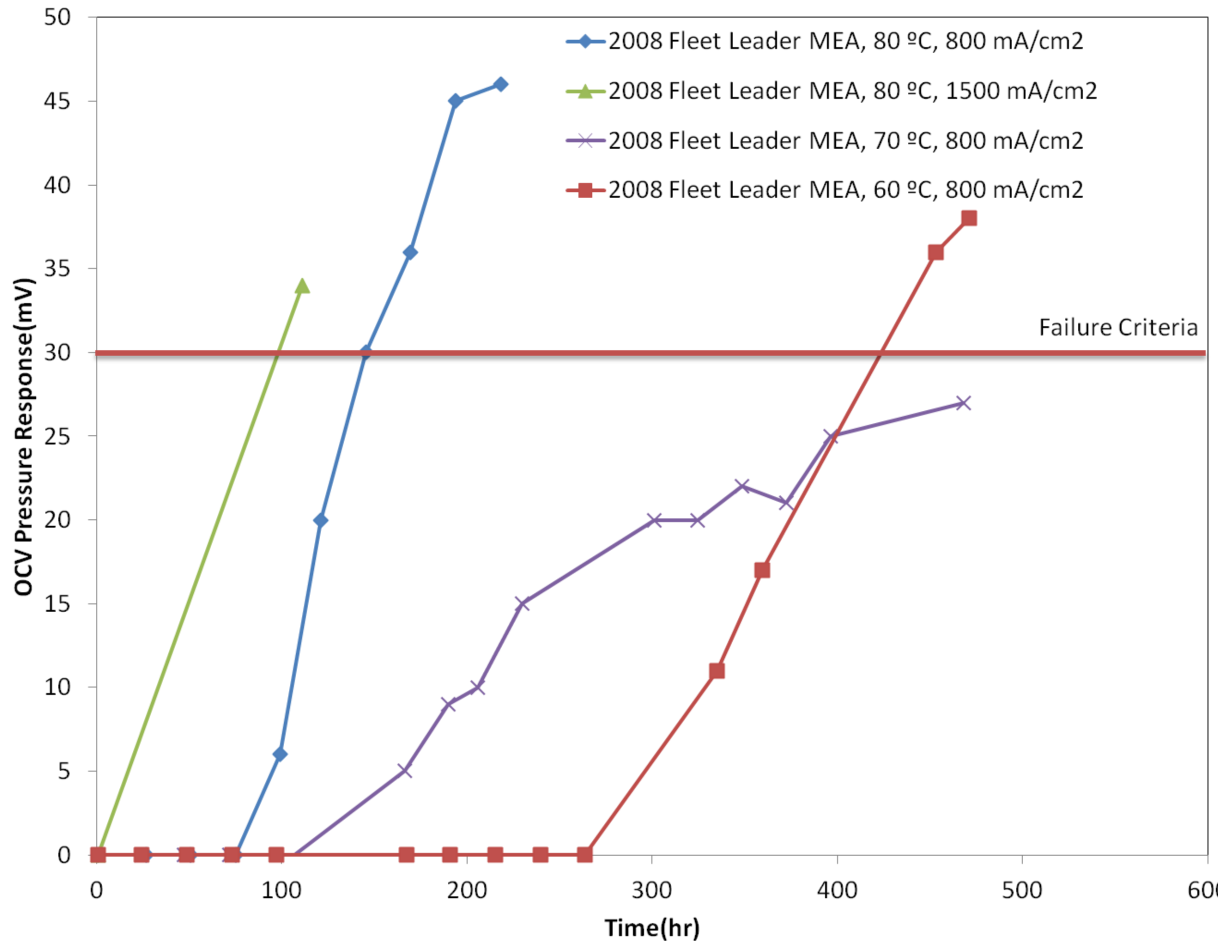
Technical Accomplishments

Effect of operating conditions

Increasing temperature from 60 to 80ºC decreased lifetime by factor of 4

Doubling current density from 800 mA/cm^2 to 1500 mA/cm^2 decreased lifetime by 20%



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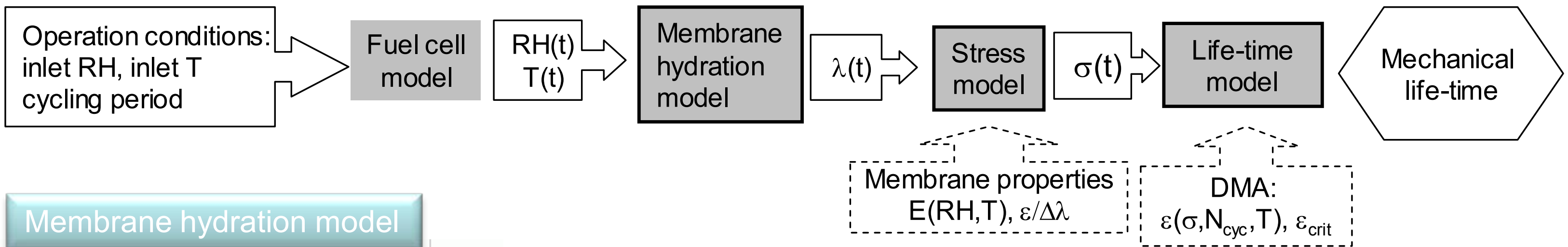
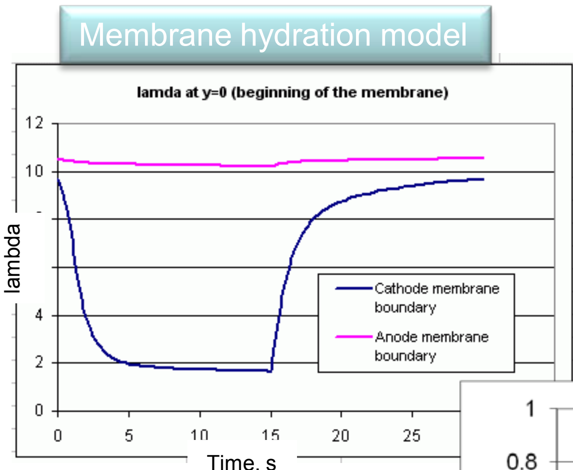
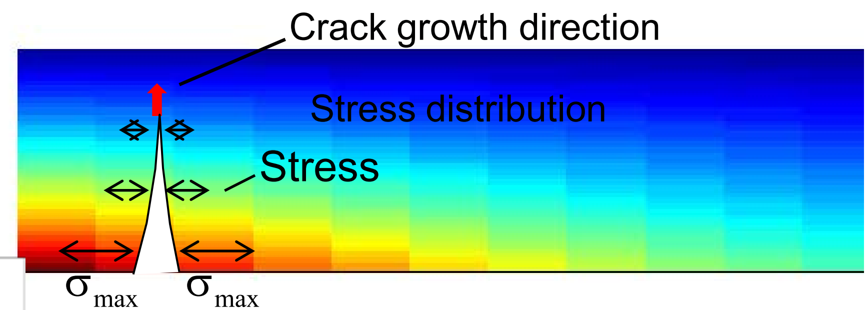
Technical Accomplishments

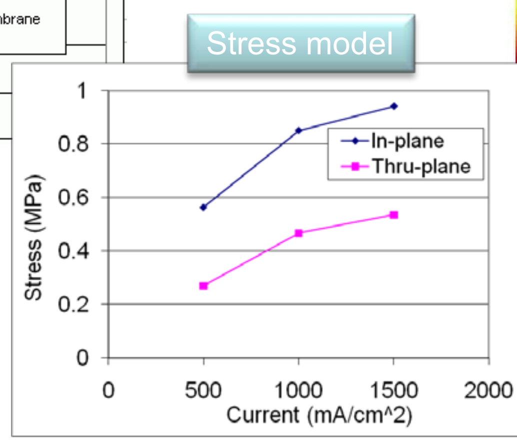
Membrane hydration-induced stress model

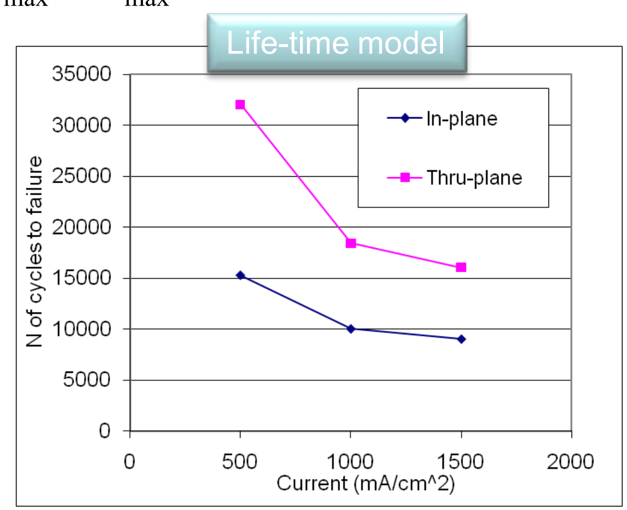
Membrane Mechanical Decay Model:











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

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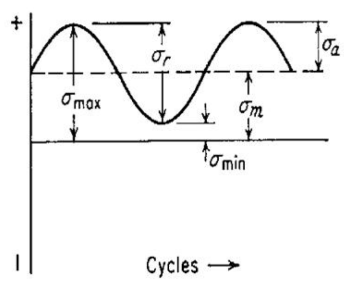
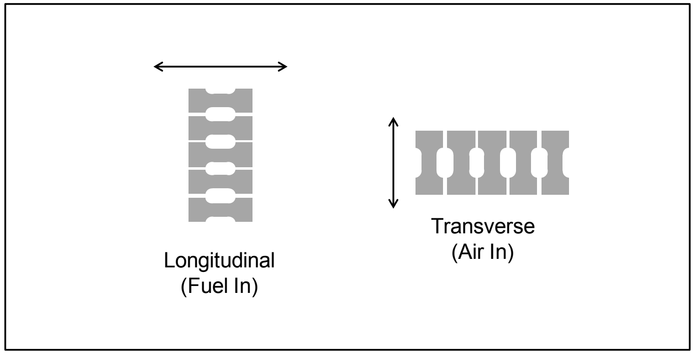
Technical Accomplishments

Using DMA as rapid membrane screening tool

Sample: MEA
Conditions:
Temperature: Variable
90%RH
10Hz
$\sigma_{Min} = 20\% \sigma_{max}$



Sampling configuration:



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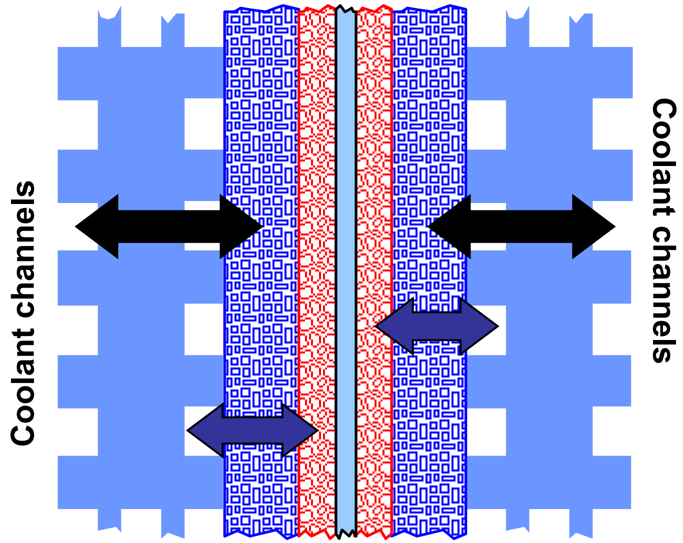
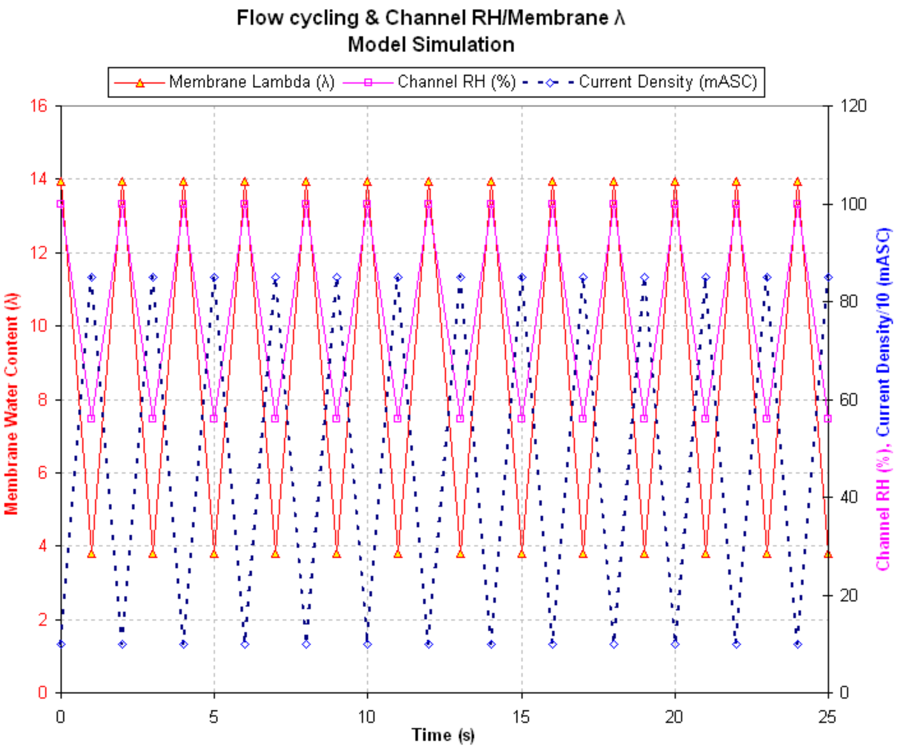
Using DMA as rapid membrane screening tool



Water transport plate used in UTC PEMFC



Load cycling → ΔRH → dimensional change → stress cycling

<u>Motivation</u>:

RH cycling critical to UTC cell design

No established ex-situ methodology exist for evaluating advanced membrane or operation conditions

No established ex-situ methodology exist for evaluating degraded membranes

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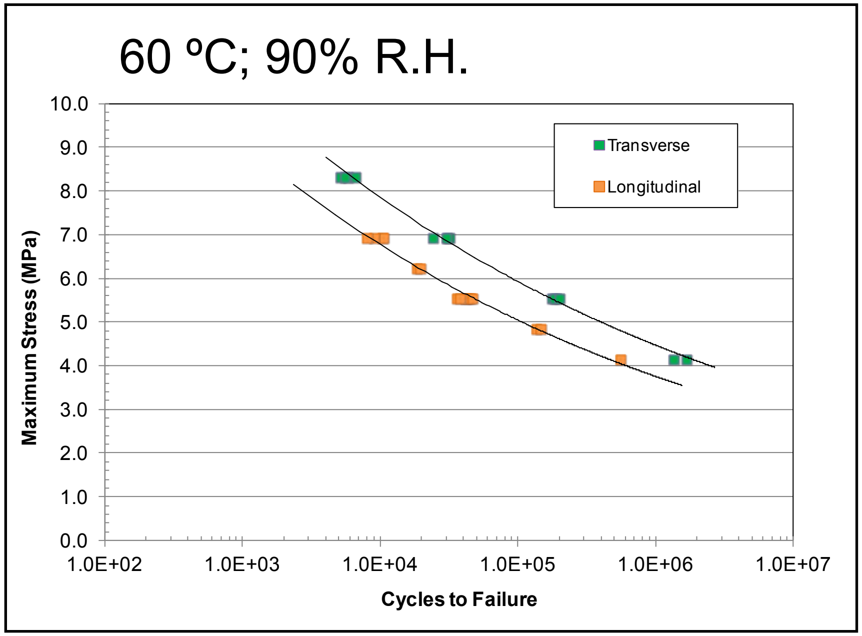
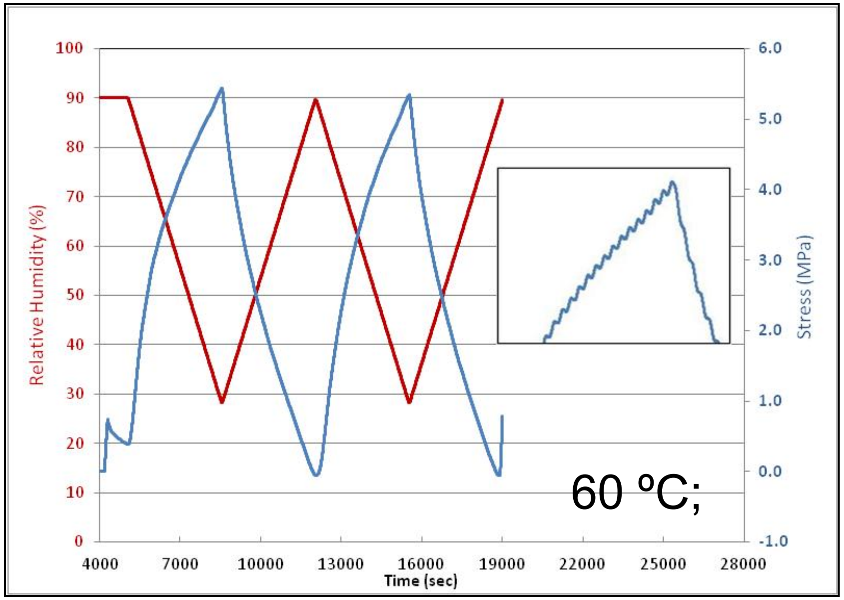
Technical Accomplishments

Using DMA as rapid membrane screening tool

S-N Curves of MEA

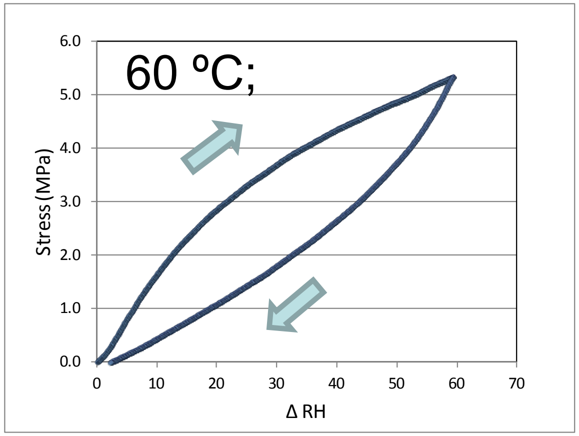


Fixed Strain RH Cycling



Anisotropy in MEA

Fatigue resistance (cycles-to-failure) in the air-in direction(transverse)
higher than that in the fuel-in (longitudinal) direction (~4X)



Correlation of ΔRH with stress
Stress response isotropic

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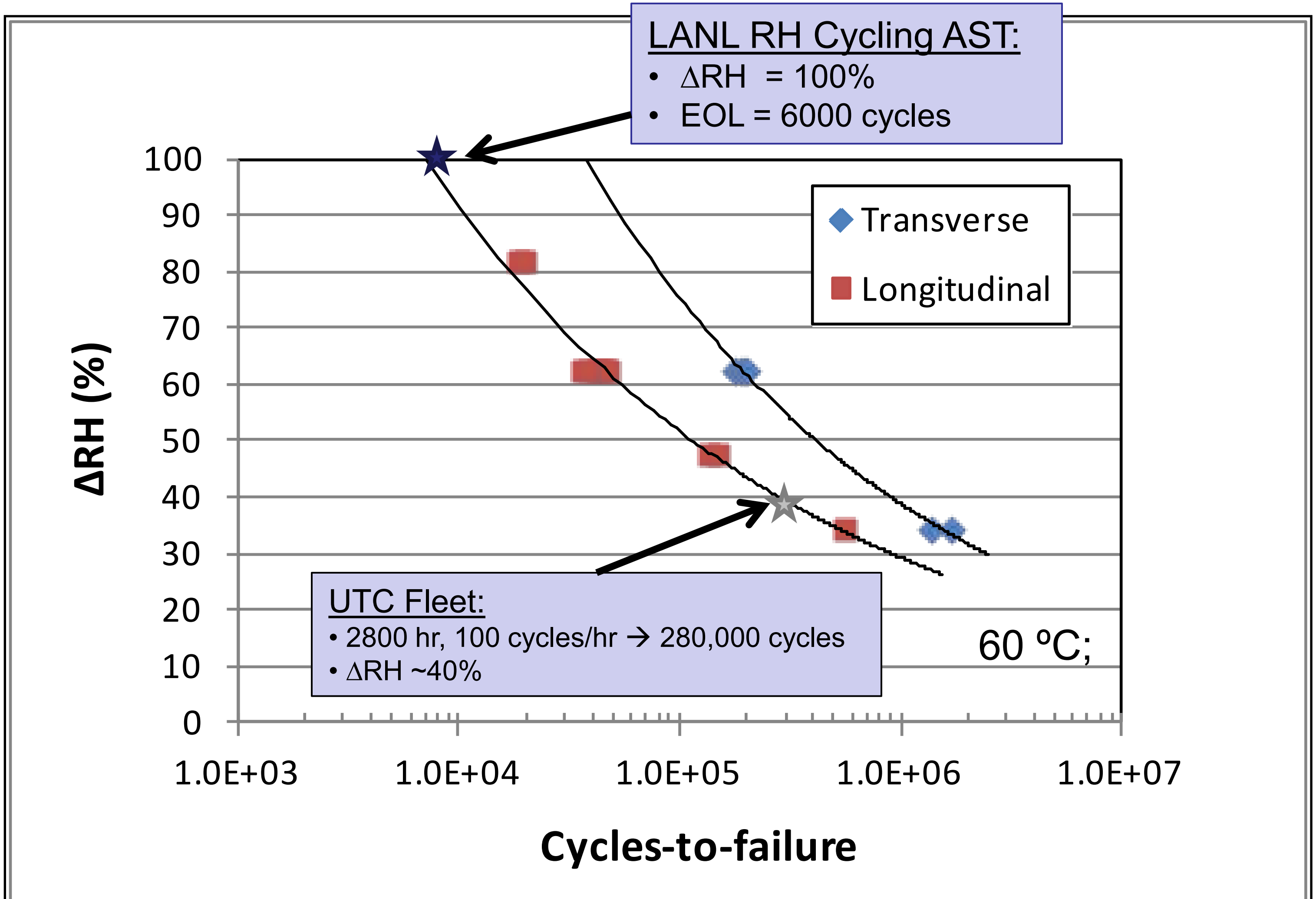
Using DMA as rapid membrane screening tool



S-N curves → ΔRH-N curves → Lifetime Estimate

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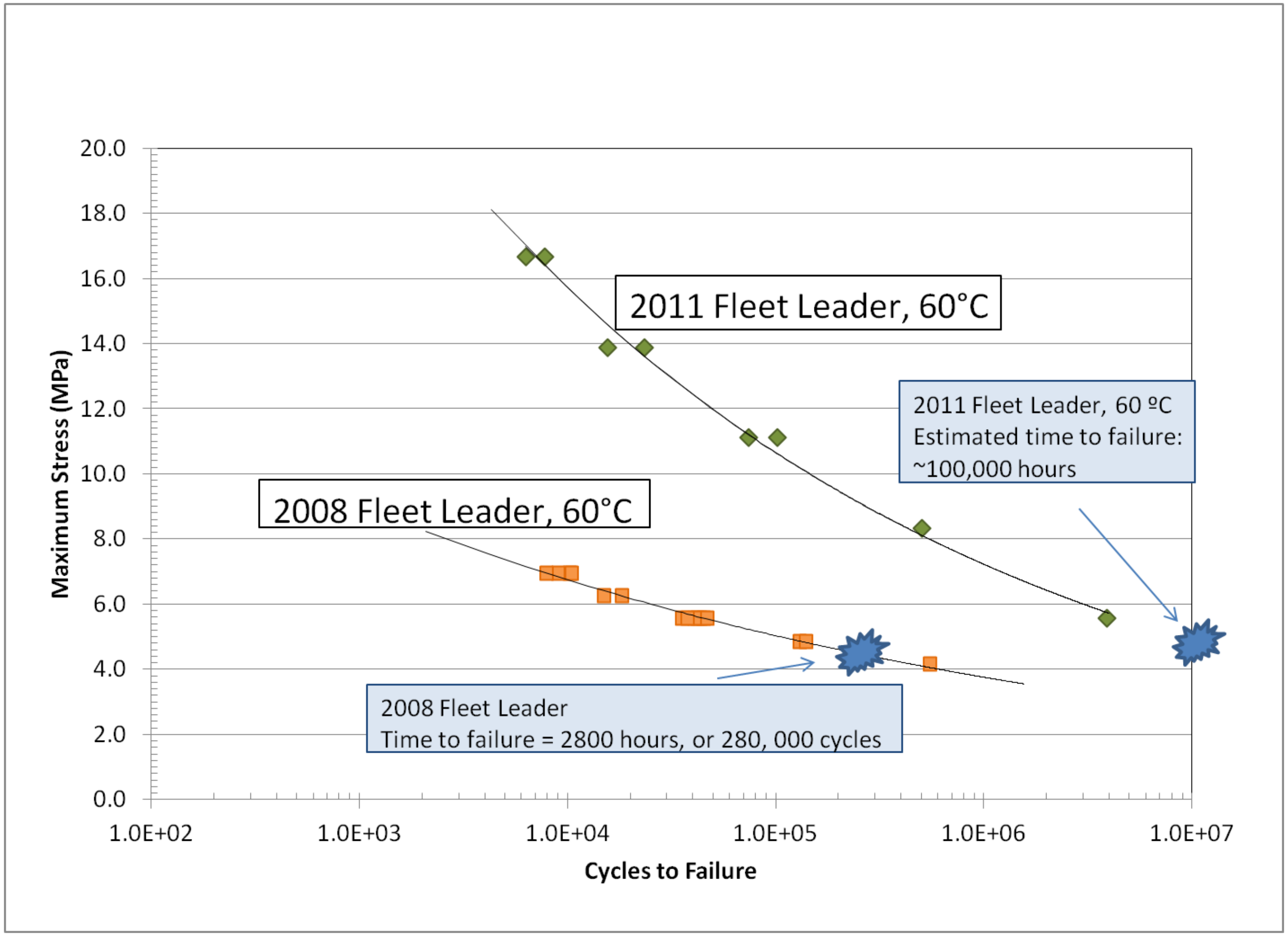
Technical Accomplishments

Using DMA as rapid membrane screening tool

Membrane in 2011 Fleet Leader was 30X better than 2008 Fleet Leader in DMA testing

2011 Fleet Leader expected to last ~100,000 hours in absence of chemical degradation

Good screening tool for membrane reinforcement, but cannot replace accelerated testing since it doesn't address chemical degradation



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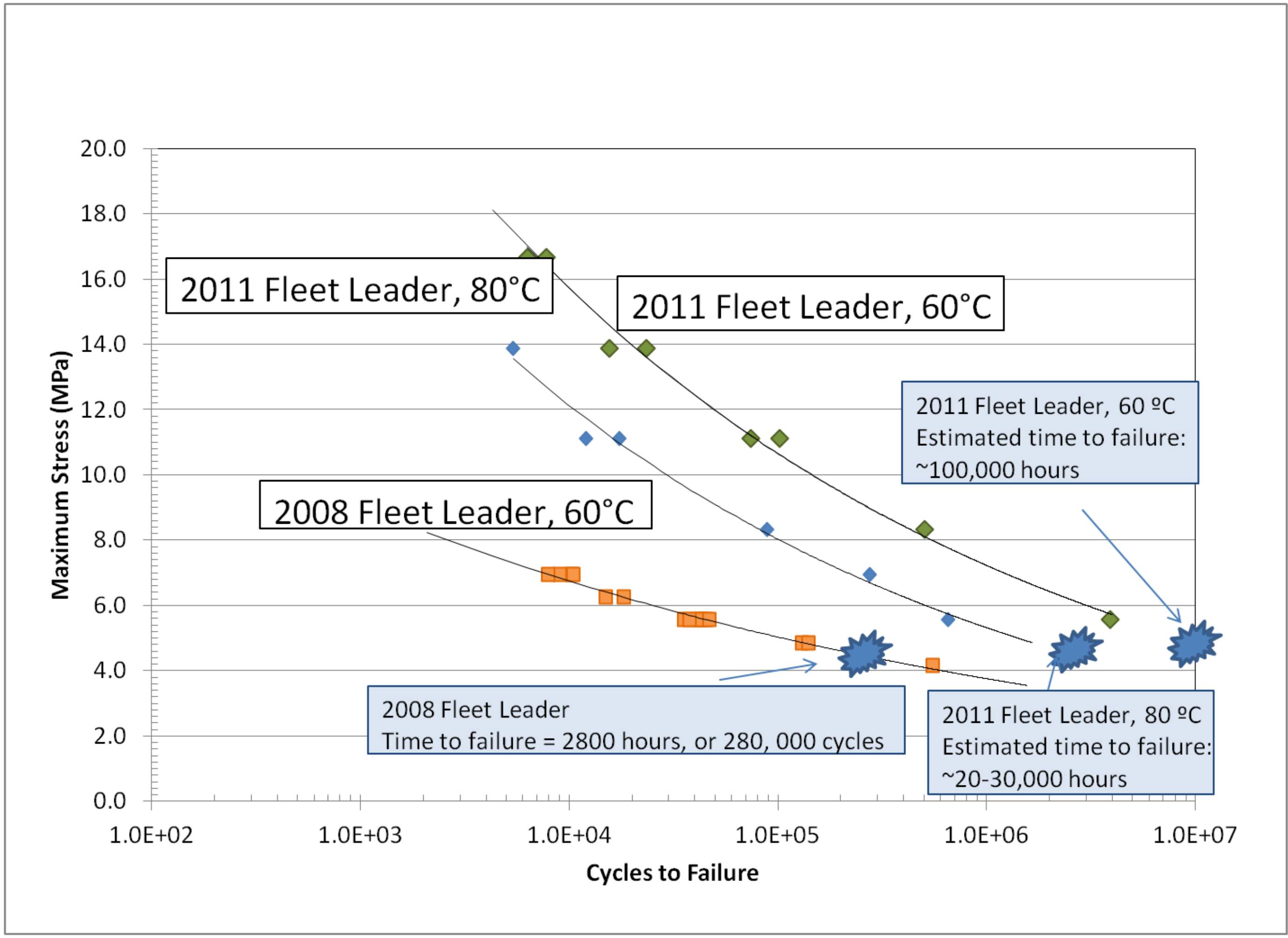
Technical Accomplishments

Using DMA as rapid membrane screening tool

At 80ºC operating temperature, lifetime is expected to be reduced to 20-30,000 hours in absence of chemical degradation



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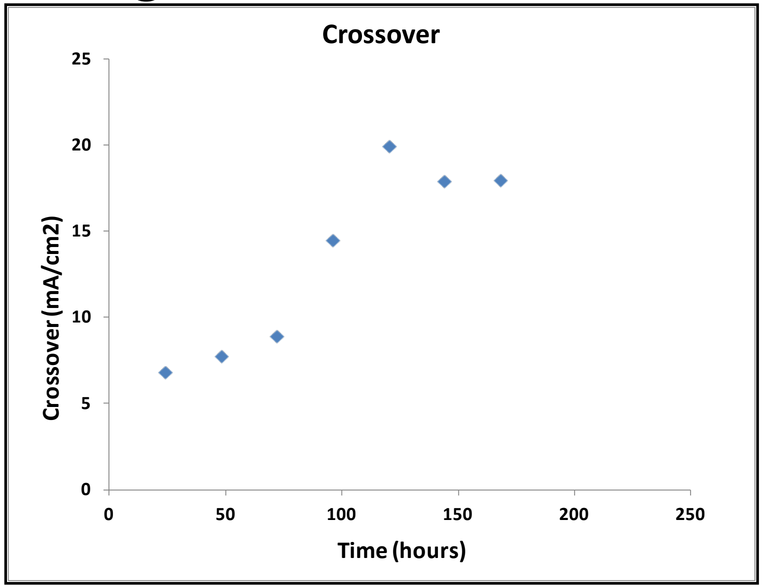
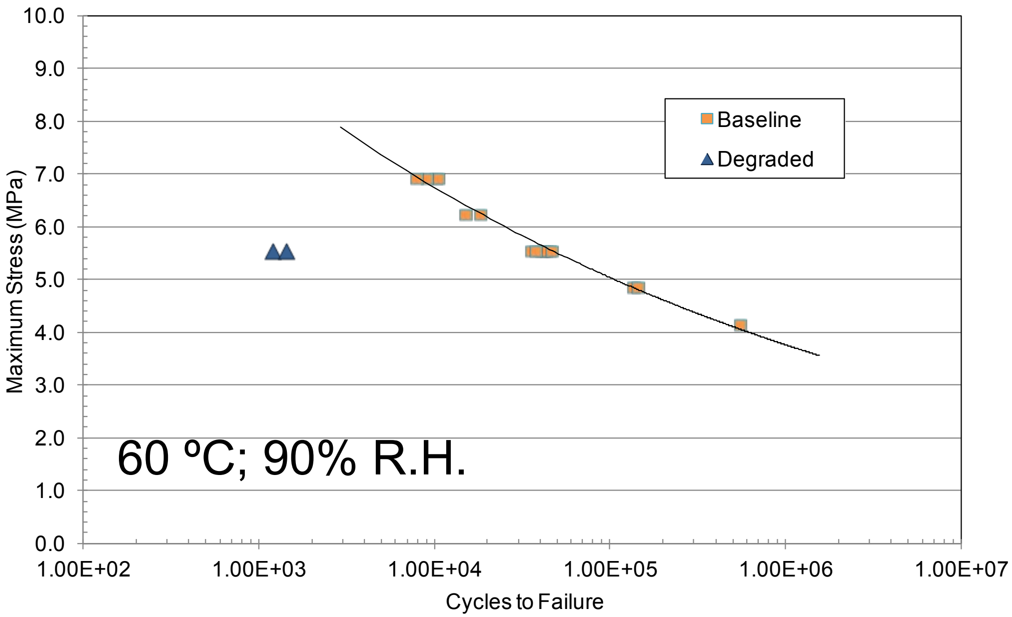
Technical Accomplishments

Using DMA to estimate remaining life

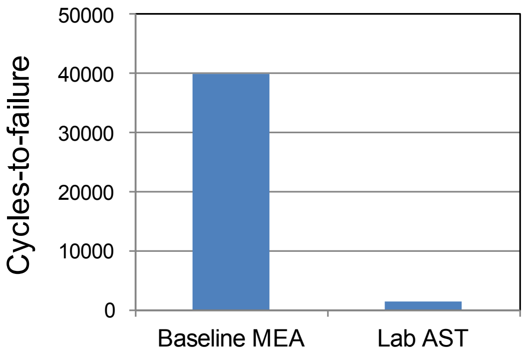




MEA subjected to accelerated stress test for membrane chemical degradation (i.e. OCV) shows severe crossover after ~150h.

DMA testing on AST tested (~150h OCV) MEA shows severe reduction in structural Estimated life remaining <5%

DMA testing (cycles-to-failure) used as post-mortem analysis



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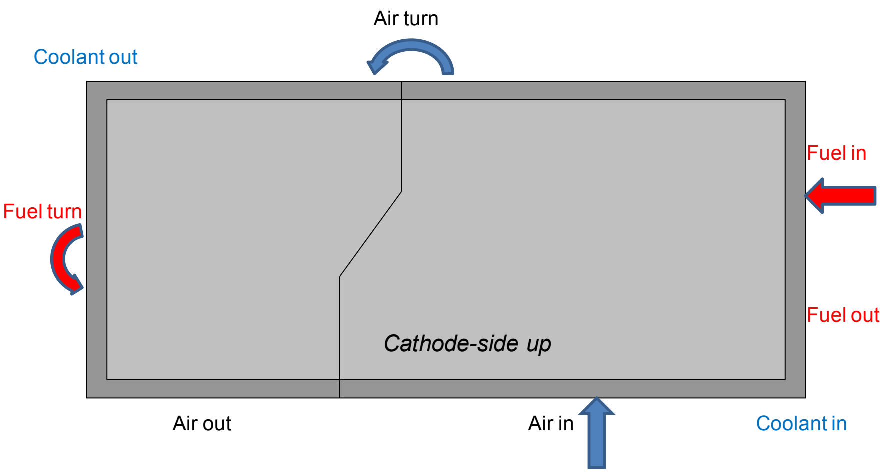
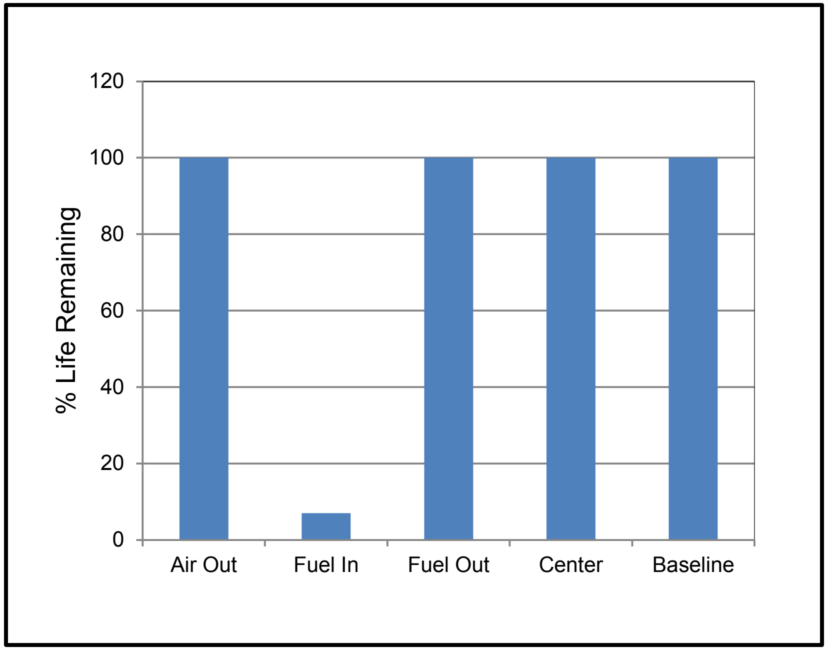
Using DMA to estimate remaining life





DMA results obtained from various areas in the planform

Cycles-to-failure can be used to estimate 'remaining life'

DMA data can be used to estimate remaining life of MEAs

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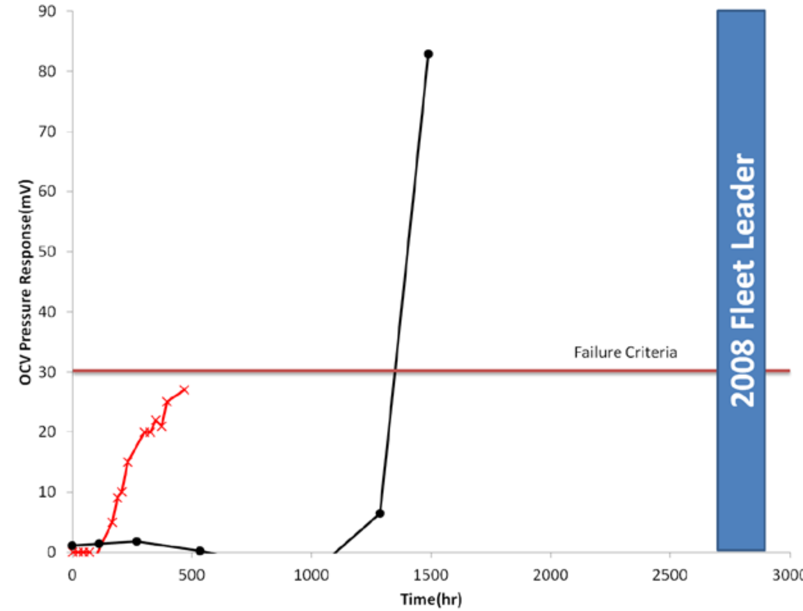
Technical Accomplishments

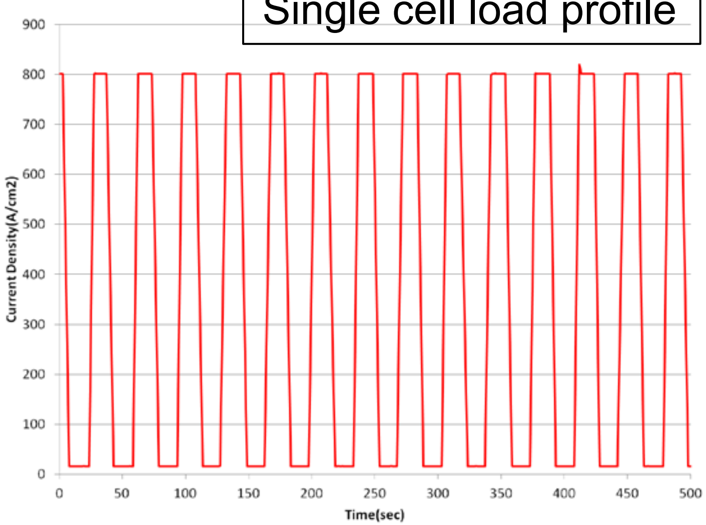
Accelerated Life Test (ALT) rig

ALT failed after approximately 1200 hours, or 2X faster than fleet

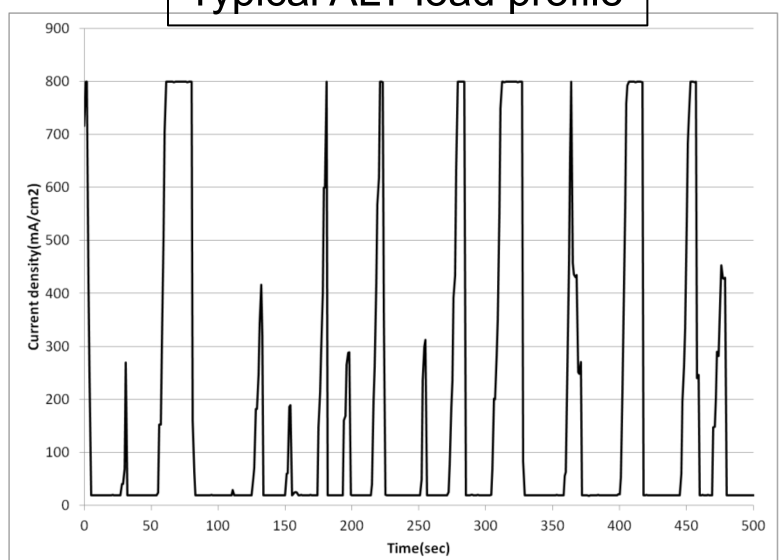
At same temperature(70 ºC), cell running membrane AST protocol failed in 20% of time of ALT, which is running a similar load profile to the fleet; ALT load cycle protocol, based on fleet protocols, has fewer prolonged high current density holds than single cell AST



Single cell load profile



Typical ALT load profile



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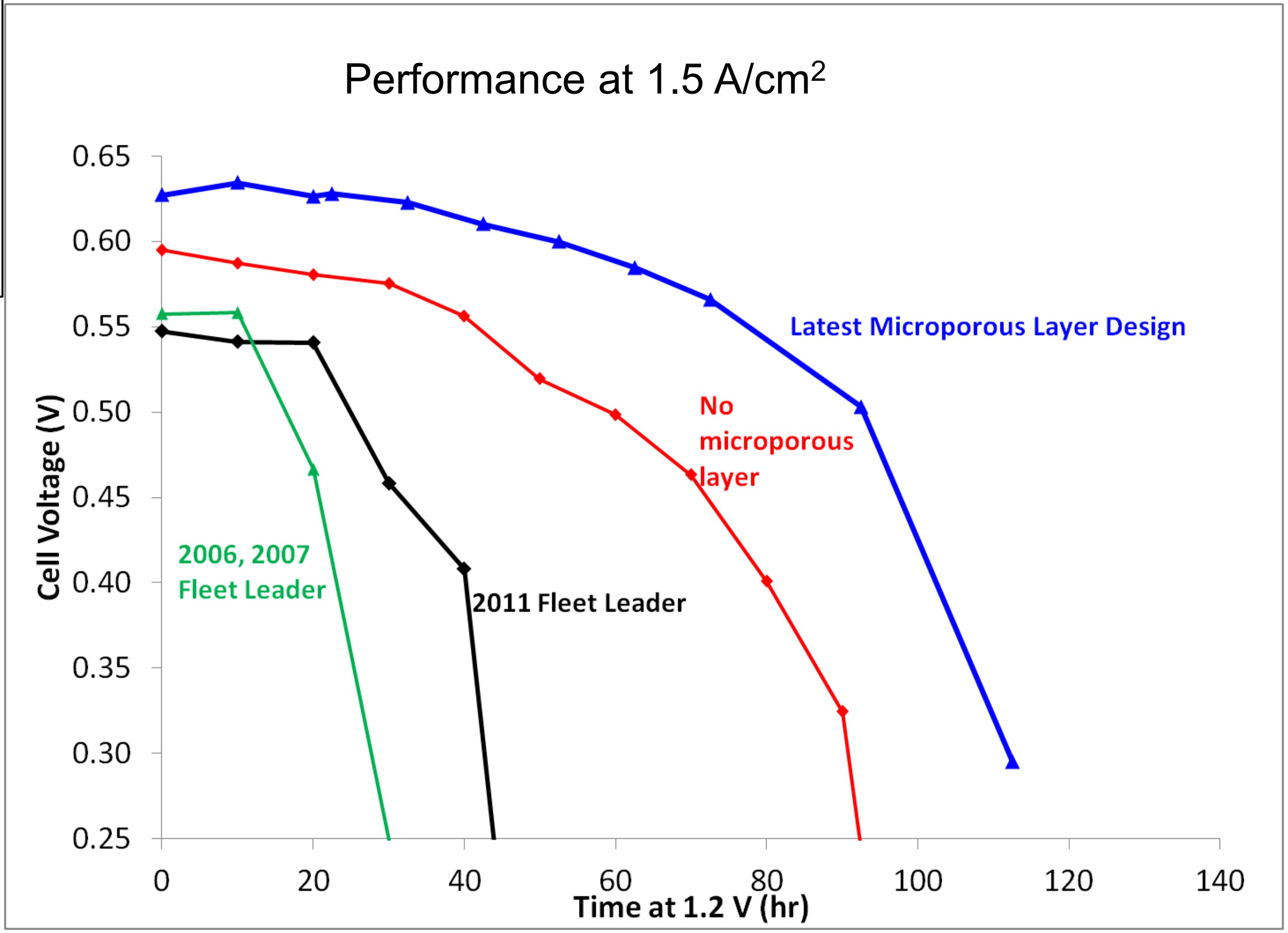
Technical Accomplishments

Carbon corrosion AST(1.2 V hold @ 80ºC)

Coolant inlet temperature (ºC)	80 ºC
Anode Reactant	4% H_2 in N_2
Cathode Reactant	N_2
Applied Voltage	1.151 V vs Ref(1.2 V vs H_2)

Cell in development in laboratory shows 2X improvement over 2011 fleet leader; Similar to cell run without microporous layer



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Technical Accomplishments

Summary of real world to AST comparisons

Mechanism	AST	Comparison	AST (hrs)		Fleet Failure Time(hrs)		AST Improvement Factor	Fleet Improvement Factor	Acceleration Factor
			Baseline	Improved	Baseline	Improved			
GDL carbon corrosion	Air-air cycling	2006 vs. 2008 Fleet Leader	150	550	1250	9800	>3.6X	>8 X	8X
Catalyst layer carbon corrosion	DOE Carbon Corrosion AST	2006,2007 vs 2008, 2011 Fleet Leader	10	20	1500	>11,000	2X	>7X	>150-500X
Membrane chemical/ mechanical failure	80 ºC flow/load cycling	2008 vs. 2011 Fleet Leader	140	>2100	2800	9800	>15X	>3.6	20X
Platinum loss	PGM AST	N/A	7 mV in 200 hours	-	15 mV in 2800 hours	-	N/A	N/A	6.5X

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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 ASTs 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 ASTs;

-Correlated membrane and GDL AST results to all field failures

-Completed accelerated life test of breadboard unit (ALT)

-DMA used to estimate lifetime, effect of temperature, and estimate remaining life of tested samples

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

Proposed Future Research: Develop validated ex-situ GDL oxidation test; Validate use of DMA as lifetime prediction tool; Run second ALT rig at higher temperature using latest material set

This work is funded under DOE Project # DE-PS36-08GO98009