Effect of System and Air Contaminants on PEMFC Performance and Durability

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National Renewable Energy Laboratory

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2011 DOE Hydrogen and Fuel Cells Program Review

FC048

Project Overview

Timeline

Start: July 2009
End: September 2013
% complete: ~30%

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
$6,000,000	$788,850	$6,788,850*

	DOE Budget ($K)
FY 2009	1035
FY 2010	700
FY 2011	1100
FY 2012	1476
FY 2013	1689

* Final award amounts are subject to appropriations and award negotiations.

Barriers

Barrier	2015 Target
A: Durability	5,000 h for Transportation 40,000 h for Stationary
B: Cost	$30/kW for transportation $750/kW for Stationary

Partners (PI)

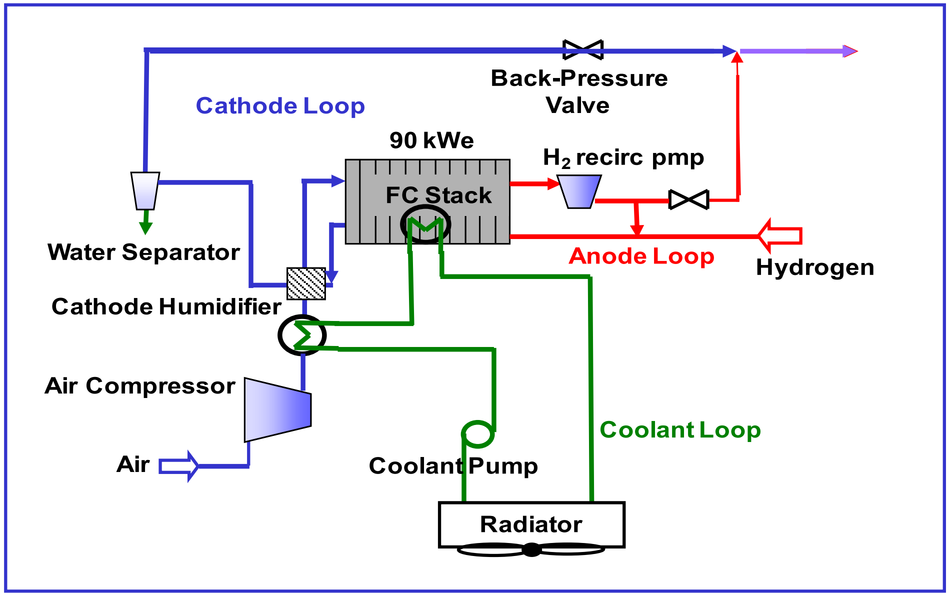
General Motors* (Kelly O'Leary)
University of South Carolina* (John Van Zee)
Los Alamos National Laboratory (Tommy Rockward)
University of Hawaii* (Jean St. Pierre)
3M (Steve Hamrock)
Colorado School of Mines* (Ryan Richards)

* denotes subcontractor

Relevance – Importance of System Contamination

- Balance of plant (BOP) costs have risen in importance with decreasing stack costs.
  - BOP materials comprise > 50% fuel cell system costs (large volume projections)
  - Cost of BOP materials need to come down to reduce overall cost of system
- Contaminants from system components (GM) have been shown to affect the performance/durability of fuel cell systems.
  - Higher cost stack materials may be required to avoid voltage loss from BOP contamination
- Durability requirements limit performance loss due to contaminants to at most a few mV over required lifetimes (1000s of hours). ~Zero impact for system contaminants.

Commercially relevant, system-derived contaminants have many potential sources



D.A. Masten, A.B. Bosco Handbook of Fuel Cells (eds: W. Vielstich, A. Lamm, H.A. Gasteiger), Wiley (2003): vol. 4, chap ter 53, p. 714.

Examples of common additives in automotive thermoplastics:

- Glass fiber
- Antioxidant
- UV Stabilizer
- Flame retardant
- Processing aids
- Biocides
- Catalysts
- Residual polymer
- Residual solvents

Relevance – Project Objectives (FY10-11)

To assist the DOE Fuel Cell Technologies (FCT) Program in meeting cost, durability, and performance targets in the areas of fuel cell systems. The effort is focused on system-derived contaminants.

- Select relevant BOP materials based on physical properties and functionality
- Develop *ex-situ* and *in-situ* test methods to study system components
- Benchmark testing protocols and equipment among the different institutions
- Screen BOP materials: identify and quantify system-derived contaminants and determine their effect on membrane conductivity and catalyst performance
- Identify and select model species for further study
- Develop gates and strategies for selecting materials for in-depth analysis and durability testing

Approach – Overall Project Plan

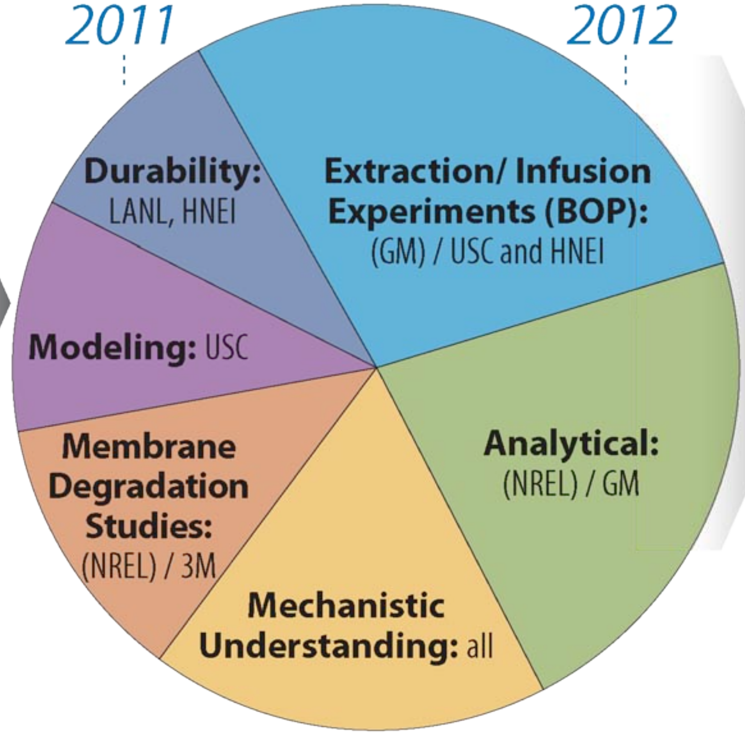
2010 | 2011 | 2012 | 2013

Protocol Development/ Benchmarking: all

Preliminary Screening: all

Material Selection: GM
Prioritization was based on wetted surface area, total mass/volume, proximity to MEAs, function, cost, and performance implications.

1. **Structural materials**
2. Coolants
3. Elastomers for seals
4. Elastomers for (sub)gaskets
5. **Assembly aids (adhesives, lubricants)**
6. Hoses
7. **Membrane degradation products**
8. Bipolar/end plates
9. Fuel impurities
10. Ions from catalyst alloys



Performance testing with materials approaching DOE targets: all

Durability Testing: LANL, HNEI

Identify Functional Groups/ ionic species (Bad actors/ benign actors): all

Project Goals:
- Make recommendations for cleaner materials
- Develop mechanistic understanding
- Identify functional groups for future tolerance studies

By 2013: Quantify potential impact of system contaminants, screen a number of materials, and establish framework and foundation for further studies with tolerance limits.

Approach – 2010-2011 Milestones

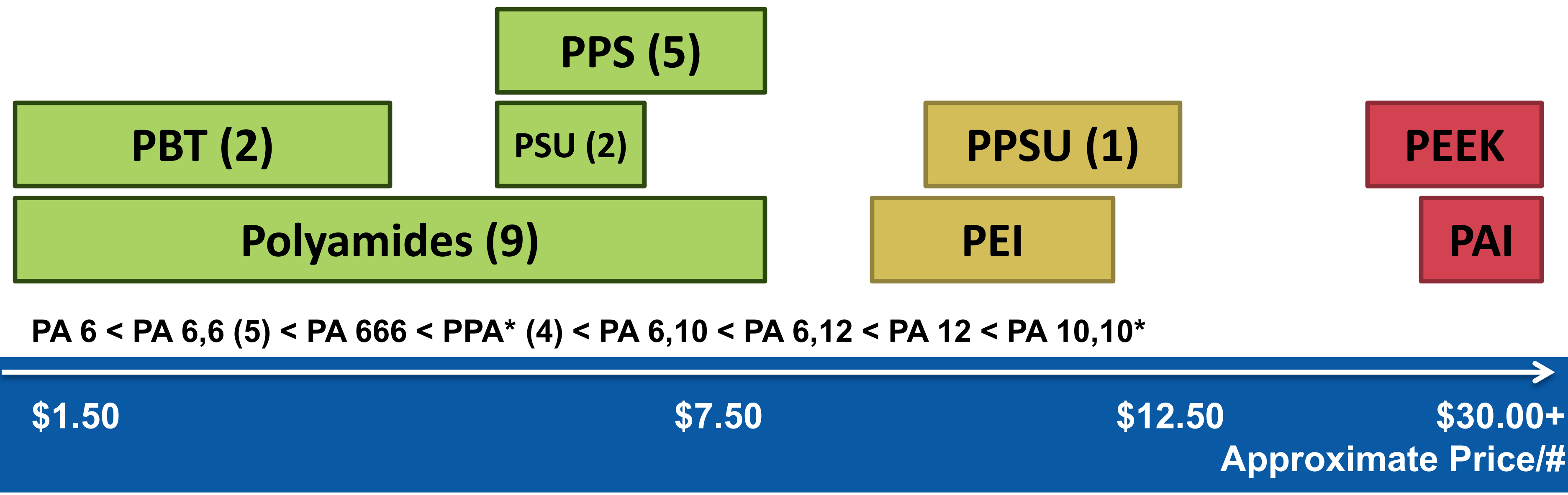
2010	1	Compile comprehensive list of identified, plausible polymer families for fuel cell systems.	07/2010	100% complete
	2	Quantify the impact of identified leachant mixtures (at least 4) on fuel cell performance and durability.	09/2010	100% complete
	3	Isolate electrochemically inhibiting compounds from (at least 4) polymeric leachants.	09/2010	100% complete

2011	1	Establish 4 standard ex-situ and in-situ test protocols to evaluate system contaminant materials	12/2010	100% complete
	2	Provide a summary list of all materials selected for study and reasoning behind selection.	3/2011	100% complete
	3	Establish correlations among analytical screening of extract solutions, cyclic voltammetry results, and fuel cell performance loss for one polymer family.	9/2011	15% complete

Technical Accomplishments & Progress
Material Selection – Structural Plastics

Completed 2010 Milestone 1: **Establish a list of 'structural' polymer families for fuel cell BOP use based on physical property and cost.**

Approximate Material Cost for Structural Plastics in a Fuel Cell System ($/#)**



** Prices are approximations based on 5/2010 dollars, they are dependent on market and specific material. Figure should be used as a general guideline only. Scale is non-linear.

PA = polyamide (nylon); PPA = polyphthalamide; PSU = polysulfone; PPS = polyphenylene sulfide; PPSU = polyphenylsulfone; PEI = polyethylene imine; PEEK = polyether ether ketone; PAI = polyamide imide; PBT = polybutylene terephthalate

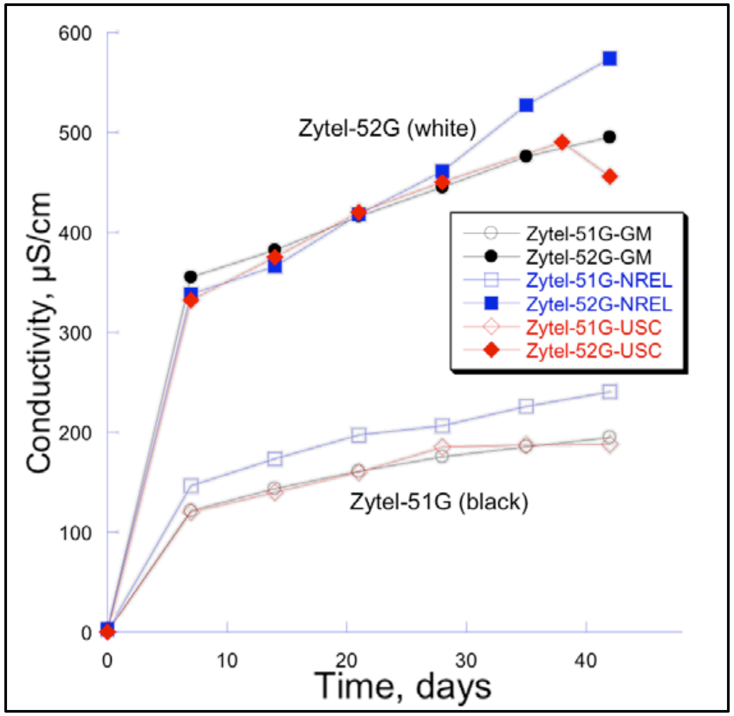
(Number of materials studied to-date**)**

Information provided by GM

Technical Accomplishments & Progress
Benchmark analytical techniques

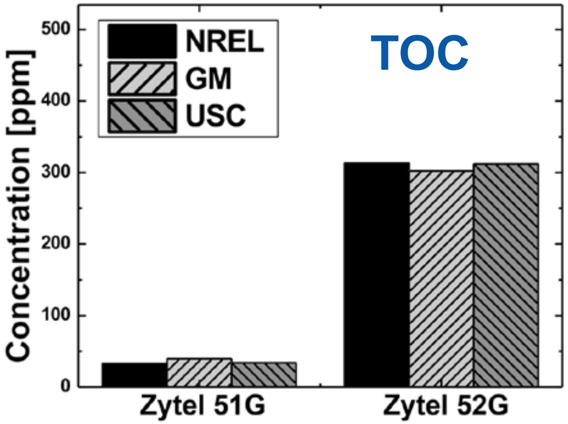
Zytel HTN51G35 HSLR® & Zytel HTN52G35 HSLR®

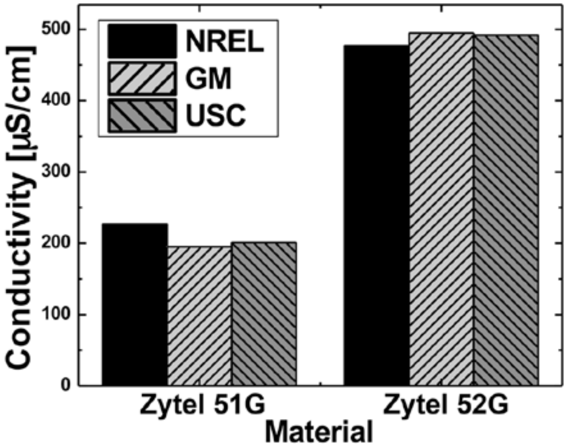
- GM, USC and NREL completed benchmarking leaching, solution conductivity and total organic content (TOC) techniques.
- The objective is to determine the offset from lab-to-lab.



Reproducibility among the different labs for these techniques are good.

The leaching and solution conductivity measurement was carried out at NREL, GM, and USC. All reported similar trends for conductivity.



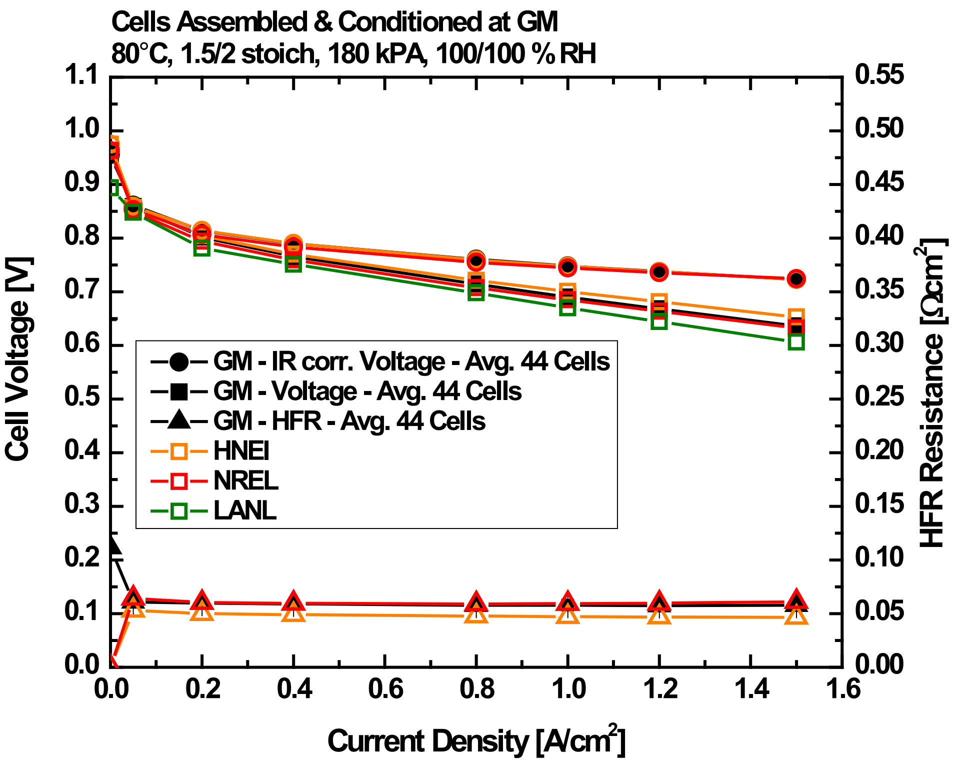


Information provided by NREL, GM, USC

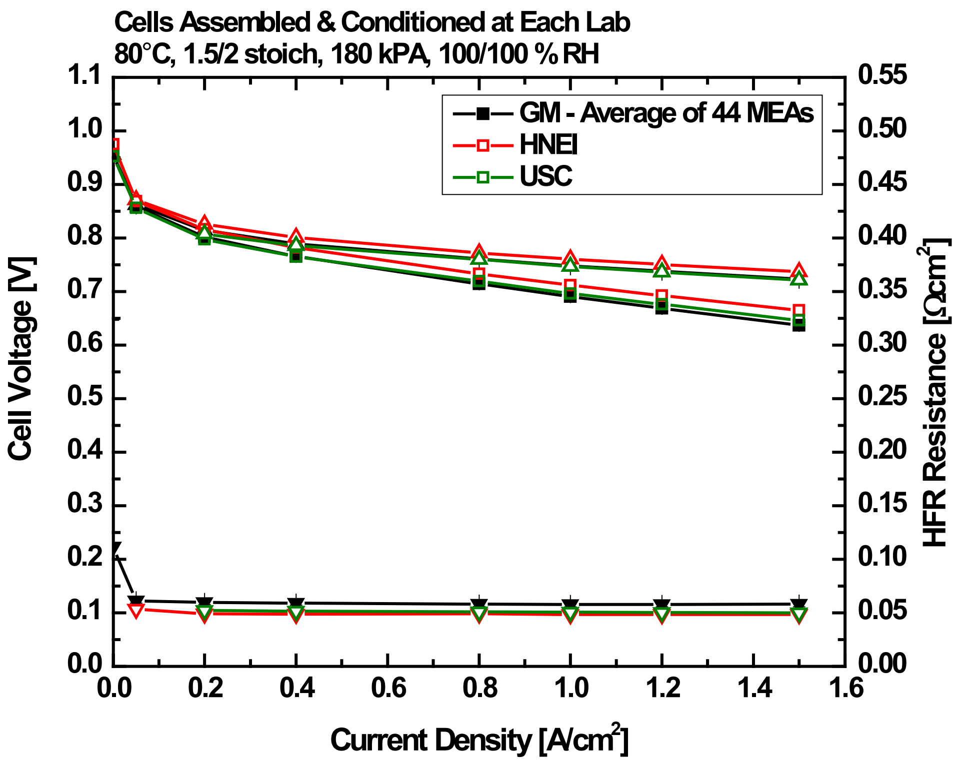
Technical Accomplishments & Progress
Benchmark Fuel Cell Hardware, Test Station, Protocol

MEAs Assembled and Conditioned

At GM



At different labs

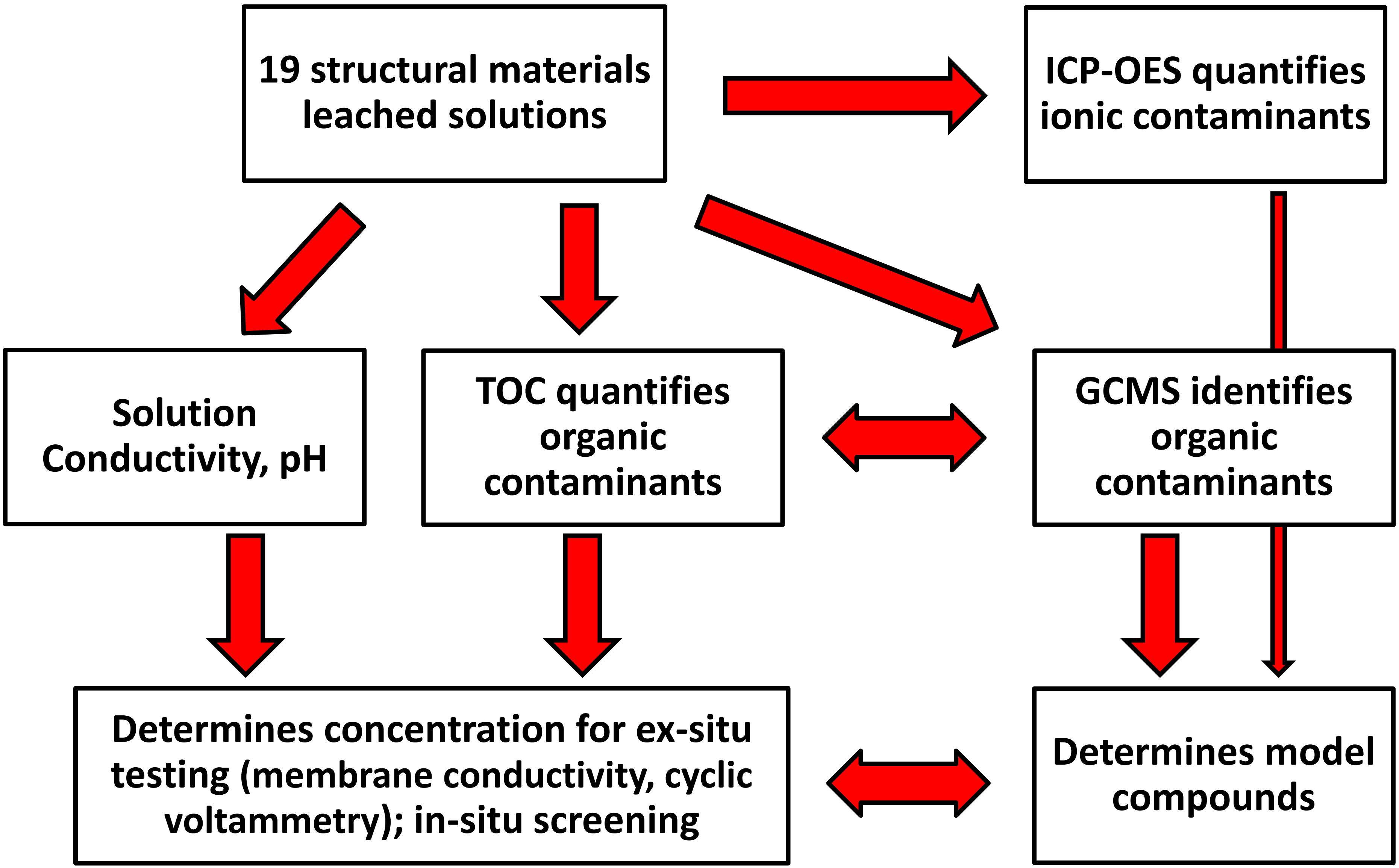


The standard deviation is minimal among **44 MEAs tested at GM** in **3 flow fields** and **3 test stands**.
Good reproducibility from different labs using different test stands.

Good reproducibility from different labs in cell assembly and conditioning protocol

Information provided by GM, NREL, USC, LANL

Technical Accomplishments & Progress Work Flow – Leachants



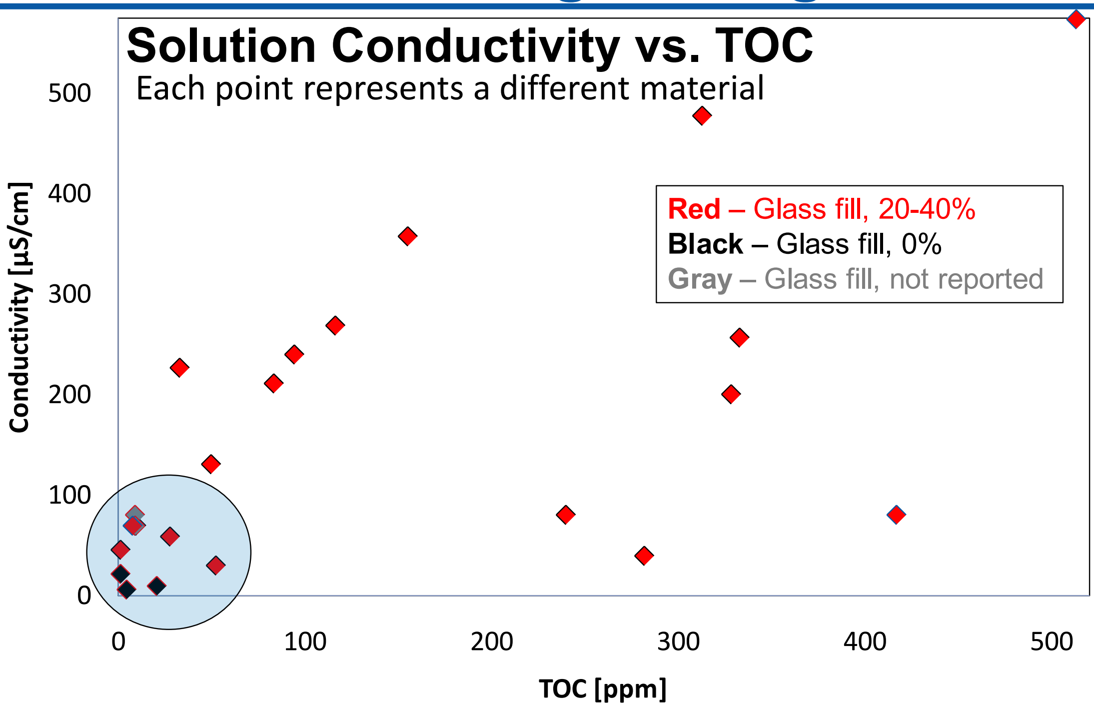
Technical Accomplishments & Progress
Liquids GCMS/TOC Quickly Identify and Quantify Organic Contaminants

Structural Material	TOC [ppm]	Conductivity [µS/cm]	% Glass Fill	Liquids GCMS[1]: Peak #1 Peak #2 – Area %
Zytel® HTN52G35 HSL (PPA)	513	574	35	DCTDD – 90.9%, Hex - 8.6%
Zytel® HTN51G35 HSL (PPA)	94.3	240.2	35	Cap - 60.8%, Hex - 39.2%
Amodel® A1933 HSL BK328 (PPA)	83.3	211.7	33	Ace - 100%
Amodel® AS-1933 HS BK324 (PPA)	155	358.0	33	DCTDD– 100%
Ultramid ®A3HG6 (PA 6,6)	240	80	30	DCTDD– 100%
Zytel® 70G30HSLR NC010 (PA 6,6)	417	80.5	30	DCTDD– 100%
Zytel®101 NC010 (PA 6,6)	333	257.3	-	DCTDD– 100%
Ultramid® A3WG7 (PA 6,6)	328	200	35	DCTDD– 100%
EMS Grivory (PA 6,6 + PA6)	282	40	35	DCTDD– 99.4%, Cap - 0.6%
DuPont Crastin® HR533 (PBT)	51.9	30	30	-
Dupont Crastin® 6130 (PBT)	20.7	10	0	-
Ryton® R4-220NA (PPS)	9.3	70	40	-
Ryton® R7-120BL (PPS)	9.2	80	-	-
Ryton® R4-200BL (PPS)	9	70	40	-
Ryton® R7-220BL (PPS)	8.7	70	-	-
Ryton® R4-220BL (PPS)	7.3	70	40	-
Radel R-5000NT (PPSU)	4.5	5.9	0	-
Udel P-1700NTII (PSU)	3.9	21.0	0	-
Udel GF-120 BK937 (PSU)	12.1	45.6	20	-

[1] - Compound abbreviations and structures appear later.

Information provided by NREL, USC

Technical Accomplishments & Progress
Quick screening for Organic and Ionic Contaminants

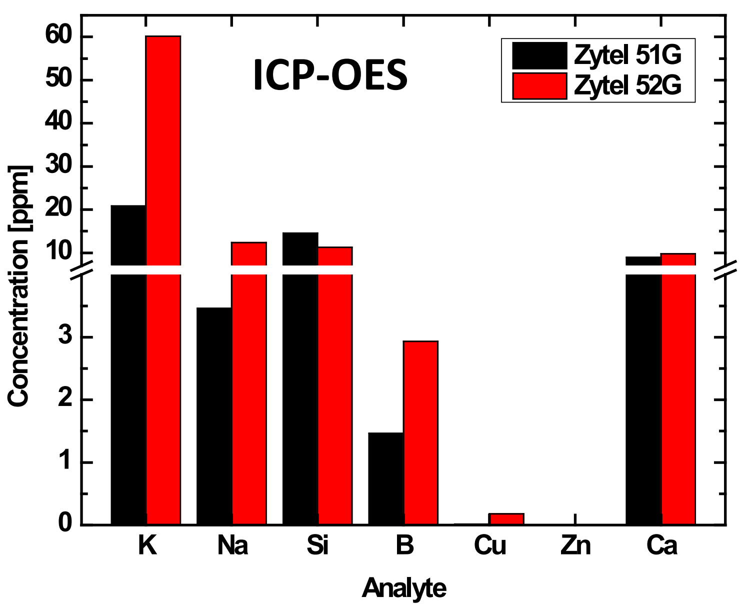


Solution conductivity and TOC provide a quick screening of the materials for potential contaminants. **Materials that test 'high' generally prove harmful to fuel cell performance.** Target materials appear in the bottom left corner: low TOC and low solution conductivity .

Materials with no glass fill have low TOC and conductivity, but glass fill may be necessary for the physical property of the polymer.

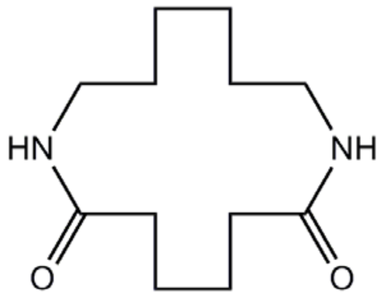
ICP-OES identifies and quantifies cationic contaminants.

Major components for two commercially available PPA structural materials (Zytel 51G & Zytel 52G) are K, Si, Na and Ca.

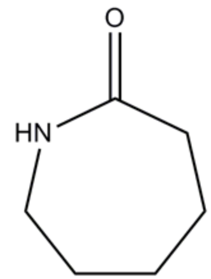


Information provided by NREL, USC

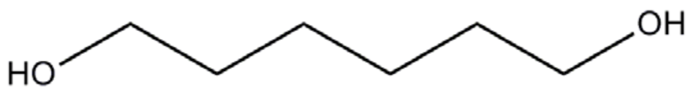
Technical Accomplishments & Progress “Model” Species Identified



1,8-Diazacyclotetradecane-2,7-dione [DCTDD]



Caprolactam [Cap]



1,6-Hexandiol [Hex]

Relationship between model compound and polymer:

<u>1,8-Diazacyclotetradecane-2,7-dione [DCTDD]:</u>

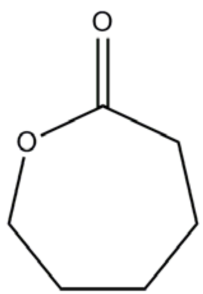
Nylon decomposition product and/or trapped waste product from the synthetic condensation reaction of adipic acid and hexamethylene diamine

<u>Caprolactam: [Cap]</u>

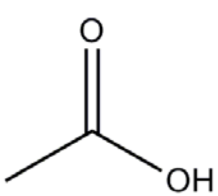
Monomer that undergoes a ring opening polymerization to synthesis Nylon 6

<u>Acetic Acid [Ace]:</u>

- All nylons susceptible to hydrolysis, especially in strong acids
- Essentially the reverse of the synthesis condensation reaction



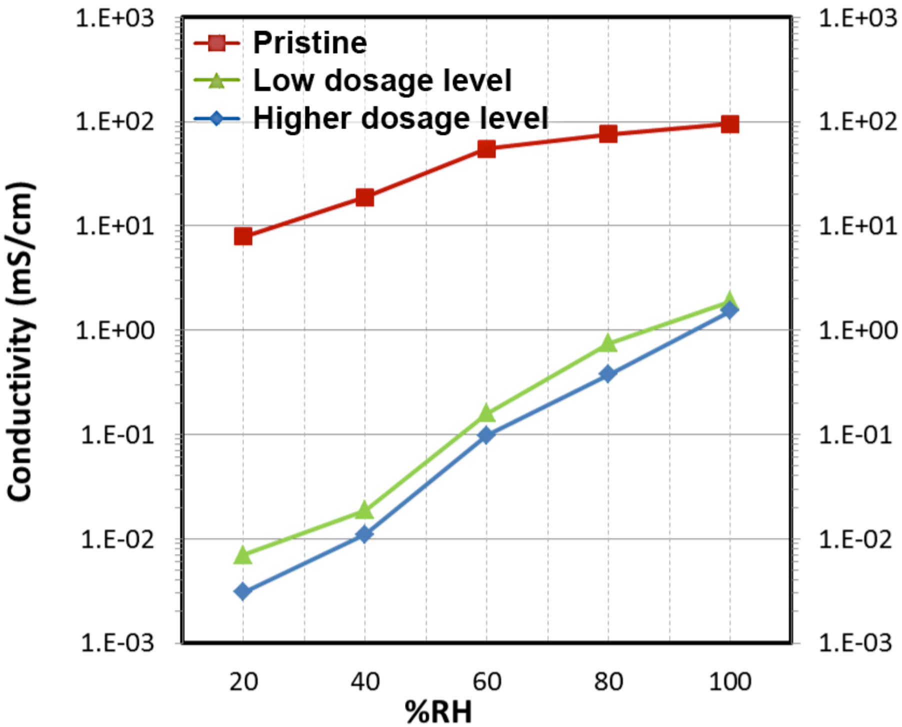
2-Oxepanone [Oxe]



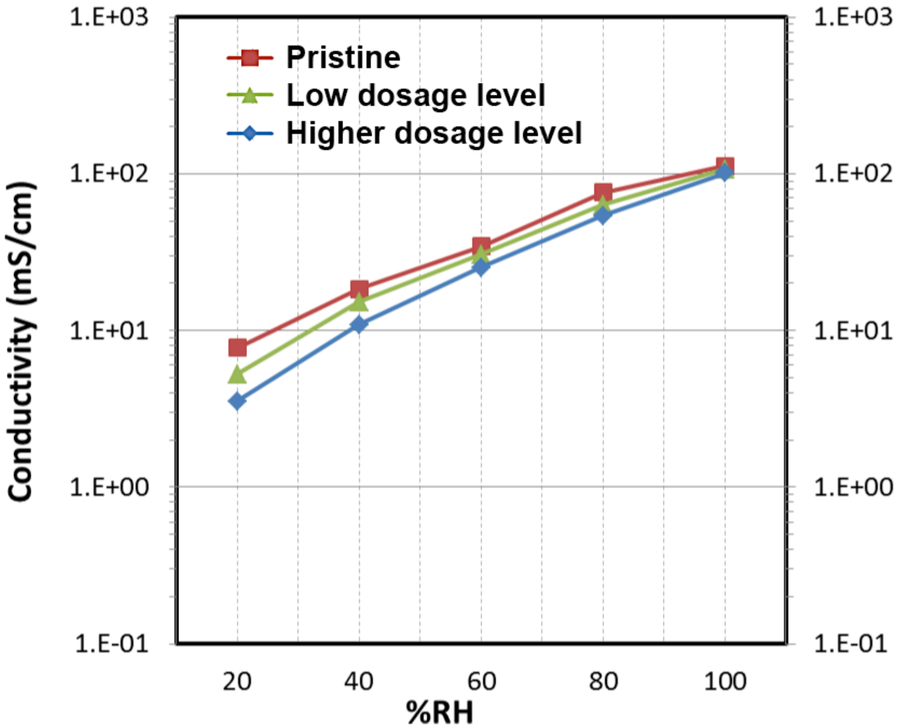
Acetic Acid [Ace]

Technical Accomplishments & Progress
Developing Membrane Conductivity Protocol

Zytel HTN52G35 HSLR®



Zytel HTN51G35 HSLR®



Zytel 52G material is "dirtier" than Zytel 51G, as indicated by the high TOC and solution conductivity values, resulting in a bigger effect on membrane conductivity.

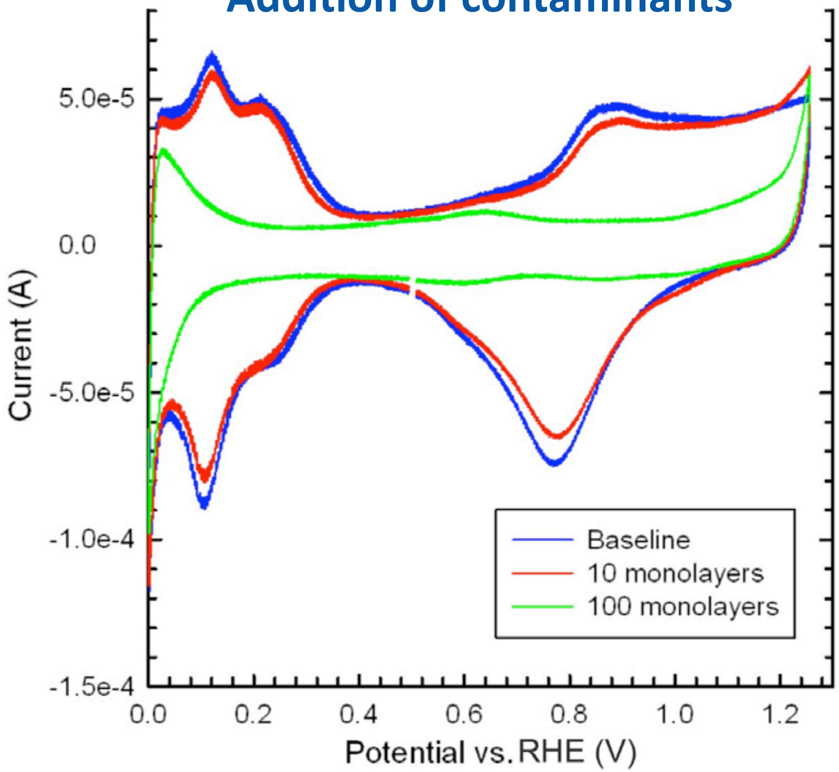
Further protocol development is needed to determine the appropriate leachant solution dosage to study the effect of contaminants on membrane conductivity.

Information provided by USC

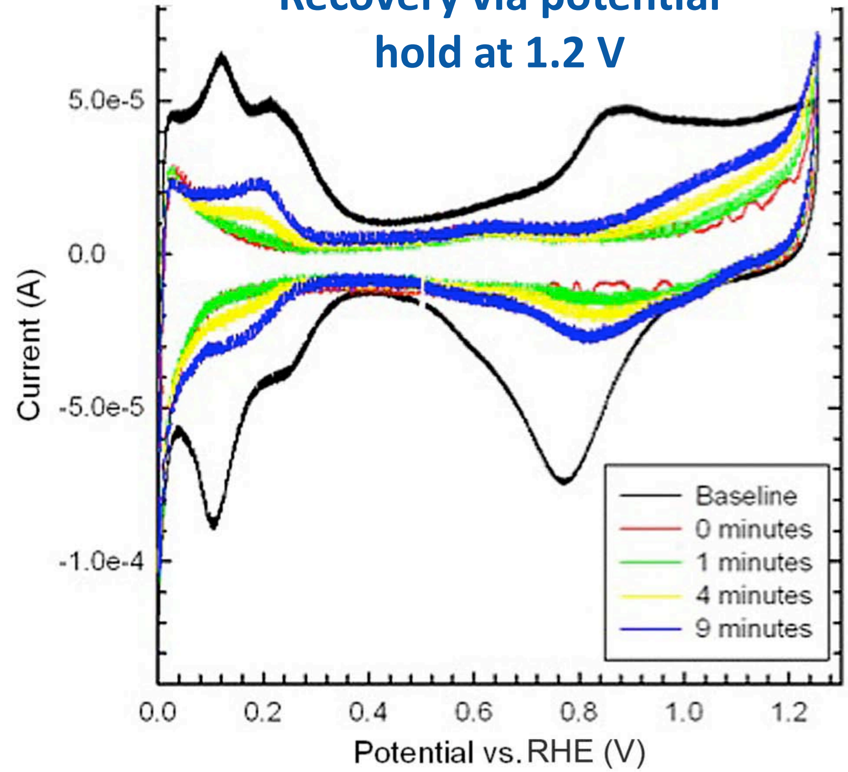
Technical Accomplishments & Progress
CV Results – Study Effect of Contaminants on Catalyst

Zytel HTN52G35 HSLR®

Addition of contaminants



Recovery via potential hold at 1.2 V



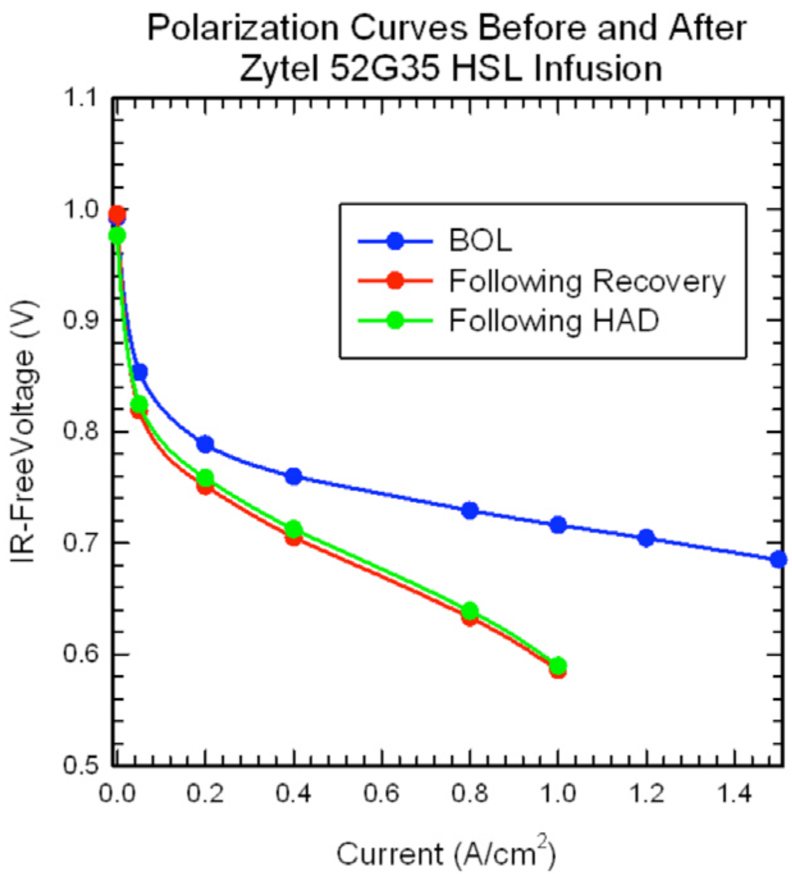
High concentration of Zytel 52G® leachant resulted in blocking of Pt sites, preventing hydrogen adsorption and Pt oxide formation and reduction.

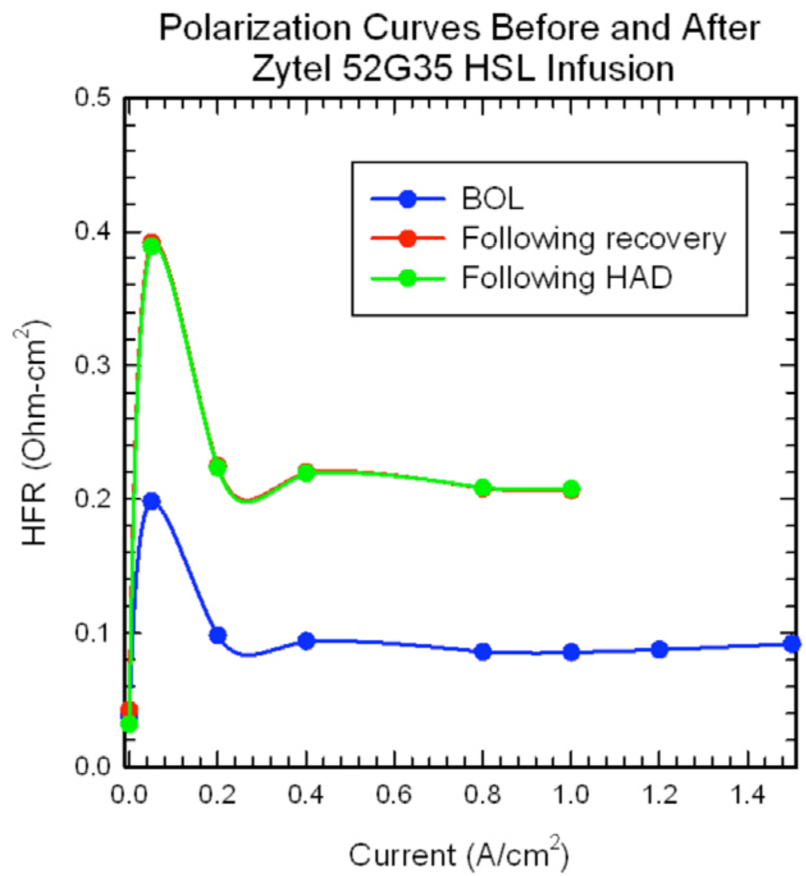
The Pt/C electrode was not fully recoverable, even at some times of holding at 1.2 V.
The contaminant was oxidized, but only at potentials above the fuel cell operating range.
The material is considered "dirty".

Information provided by GM

Technical Accomplishments & Progress
Effect of System Contaminants on Fuel Cell Performance

Pol curve conditions: 1.5/ 2 stoichs, 80°C, 32% RH anode/ cathode inlet, 150 kPa





Following infusion of the leachants and then DI water infusion, a series of diagnostics were performed in the following order: standard polarization curve, anode ECA, cathode ECA, standard polarization curve. No recovery was observed: the voltage loss associated with the infusion is the same after recovery step at 0.4 A/cm^2.

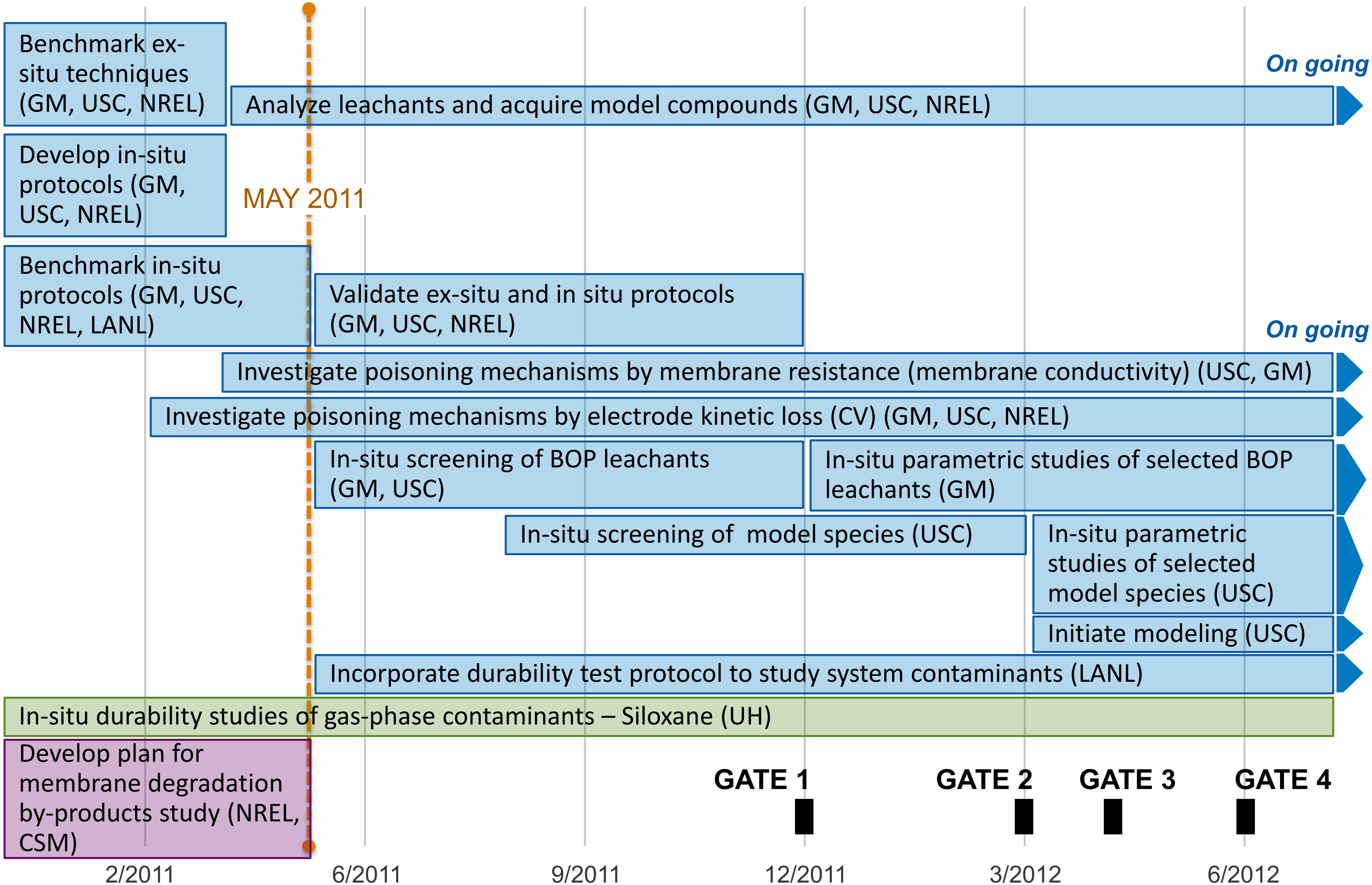
Information provided by GM

Collaborators

Institutions	Role
National Renewable Energy Laboratory (NREL): H. Dinh (PI), B. Pivovar, G. Bender, H. Wang, C. Macomber, K. O'Neill, S. Kocha	Prime, Oversees the project, broad screening and analytical characterization; membrane degradation material study
General Motors LLC (GM): K. O'Leary, B. Lakshmanan, R. Reid, R. Moses, S. Bhargava, and T.Jackson	Sub; Define material sets, broad screening, analytical characterization and in-depth analysis
University of South Carolina (USC): J. Van Zee, M. Ohashi, O. MD, M. Das, H. Seok Cho	Sub; Broad screening and deep probe study, modeling
Los Alamos National Laboratory (LANL): T. Rockward	Partner; Durability testing
University of Hawaii (UH): J. St.-Pierre , S. Dorn	Sub; Durability testing of silicone material
3M: S. Hammrock	In-kind partner; Provide membrane degradation products;
Colorado School of Mines (CSM): R. Richards, J. Christ	Sub; membrane degradation material study

Interactions: Participate in the DOE Durability working group and Fuel Cell and Hydrogen Energy Association Contaminants working group

Proposed Future Work
Timeline and Project Path Forward



Summary

Relevance: Focus on overcoming the cost and durability barriers for fuel cell systems.

Approach: Perform parametric studies of the effect of system contaminants on fuel cell performance and durability, identify poisoning mechanisms and recommend mitigation strategies, develop predictive modeling and disseminate material catalogues that benefit the fuel cell industry in making cost-benefit analyses of system components.

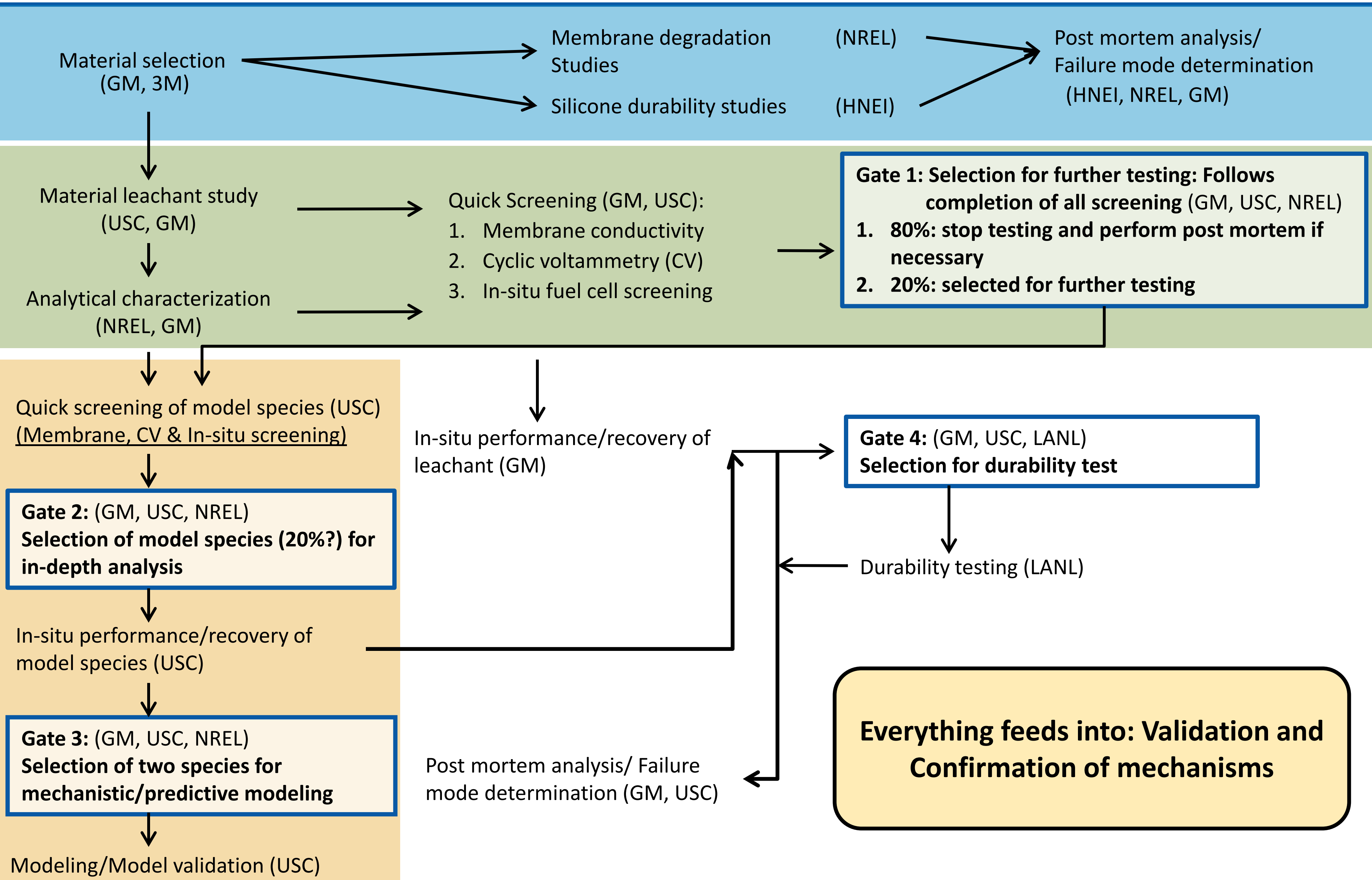
Technical Accomplishments and Progress: Selected relevant material sets for system contaminant studies based on level of perceived impact; Developed ex-situ and in-situ characterization methods and protocols for screening potential system contaminants (Leaching, pH, Conductivity, TOC, ICP-OES, GC-MS, FTIR-ATR, CV, Membrane Conductivity, In-situ Infusion and Fuel Cell tests); Benchmarked test equipment and protocols between the different team members; Analytical screening of 19 structural materials; Developed a clear long term project plan with gates and strategies for selection of materials for in-depth fuel cell studies, model species studies, durability testing and modeling; Developed a test plan and initiated test station set up for in-situ durability study of gas-based contaminants (siloxanes); Completed all milestones on time.

Collaborations: Our team has significant background data and relevant experience in contaminants, materials and fuel cells. It consists of a diverse team of researchers from several institutions including 2 national labs, 3 universities, and 2 industry partners.

Proposed Future Research: Screen the selected structural materials and assembly aids to identify and quantify the system-derived contaminants and their effect on performance. Identify and initiate screening of model compounds. Validate ex-situ and in-situ protocols. Continue gas-phase durability testing and develop a plan for membrane degradation by-products study.

Technical Back-Up Slides

Approach: Work Flow and Gates for project



Technical Accomplishments & Progress
Establish Experimental Protocols & Benchmarking

Leaching: Designed to leach water soluble species from materials for analytical characterization, cyclic voltammetry (CV), membrane conductivity, and fuel cell tests. (control the surface area to volume ratio, soaked in DI water at 90°C for 6 weeks)

Analytical Screening Methods:

Electrical conductivity and pH
Measured 1x/week

Total Organic Carbon (TOC)
Measured after end of soak

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)
Measures trace metal concentration
Measured after end of soak

Gas Chromatography-Mass Spectroscopy
Identify the leachant species

Other Screening Methods:

Cyclic Voltammetry
Screen the effect of different amount of system contaminants on catalysis and whether the poisoning effect can be recovered

Membrane Conductivity
Screen the effect of system contaminants on the ionic conductivity of the membrane

In-Situ Fuel Cell Testing
Screen effect of system contaminants on fuel cell performance

Conductivity, pH, TOC and ICP-OES are the four quickest analytical techniques to screen materials for potential contaminants. Materials that test 'high' generally prove harmful to fuel cell performance. Completed 2011 Milestone 1

Silicone Exposure Durability Experiments:

Background: Siloxane species from Silicone based materials are known to react with and embrittle PFSA materials under load. Siloxanes are very 'slippery' and mobile compounds that migrate readily in air or gasses.

Migration of low molecular weight cyclic siloxanes to the membrane electrode interface → Siloxanes get chemically oxidized to form silicon dioxide derivatives → This contamination can turn the membrane brittle (glassy) → Cause internal fractures/pinholes during humidity cycling → Premature failure

Silicone adhesives/sealants are attractive materials for fuel cell use due to their physical properties:

- Thermal stablility (-100 to 250C)
- Hydrophobic/non-sticky nature
- Excellent chemical resistance
- Low water absorption

Objective:

1. Determine the concentration of Siloxane species required for MEA failure.
2. Investigate different Siloxane species for effects.
3. Correlate accelerated durability testing to non-accelerated life.

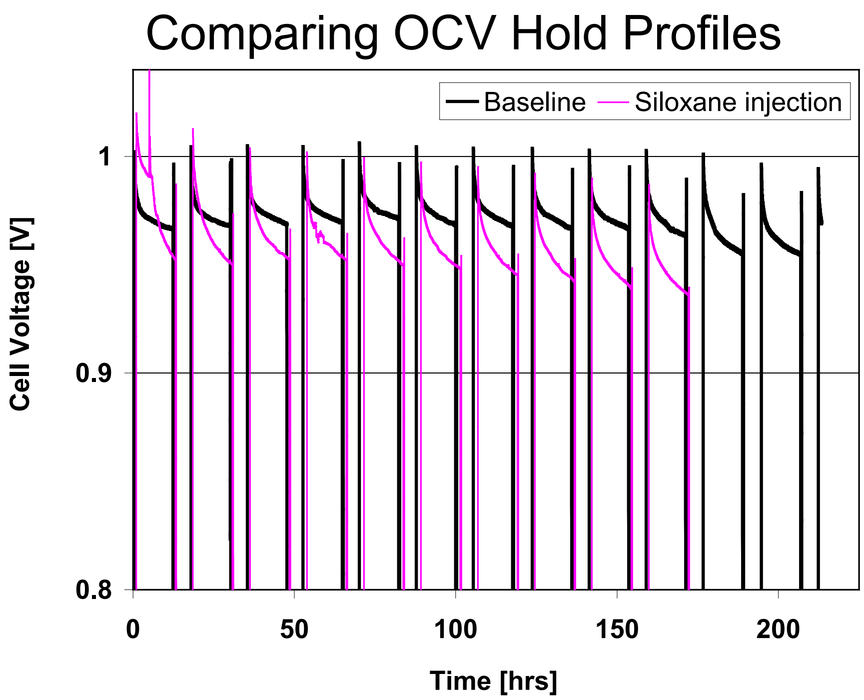
Information provided by GM

Technical Accomplishments & Progress

Gas-based contaminants in-situ durability method development, combining AST DOE protocol with system contaminants infusion, is underway (UH)

AST DOE protocol for MEA chemical stability

1. **BOL (Beginning of Life) diagnostics** to test for pinholes and shorts
2. **Conditioning** of cell
3. **BOT (Beginning Of Test)** diagnostics
4. **Dry Infusion Protocol** (according to DOE protocol table #3)
   - OCV Hold at 90C, H2/Air, 30%30% RH
   - Shorting diagnostics every 12hrs at 90C,
   - H2XO diagnostics every 12hrs at 90C,
   - HFR (at 1kHz) every 24 hrs at 0.2 A/cm2, 90C,
5. **EOT (End of Test) Diagnostics**



Information provided by UH

Experimental Protocols – 50 cm² Infusion

1. MEA and Lab Calibration:

MEA Recipe: GM MEAs

Component	Material
Membrane	NRE 211
Anode Electrode	0.05 μg/cm² Pt-V loading
Cathode Electrode	0.4 μg/cm² Pt-V loading
Ionomer in Ink	D2020
Diffusion Media	MRC105 from 3M

Calibration

A calibration study is being performed to:

1. Benchmark MEAs
2. Benchmark lab-to-lab variability
3. Benchmark stand-to-stand variability

2. Infusion Procedure Benchmarking

Protocol Development

Significant work went into developing an infusion protocol

1. GM spent 2 years working with single component infusion
2. Compromises were made to insure both quick screening capabilities and thorough analysis
3. Method is still being properly developed

Infusion Experiments

1. Infusion experiments have been performed on 4 varieties of PPA to date.
   - **Completed 2010 Milestone 2**

Information provided by GM