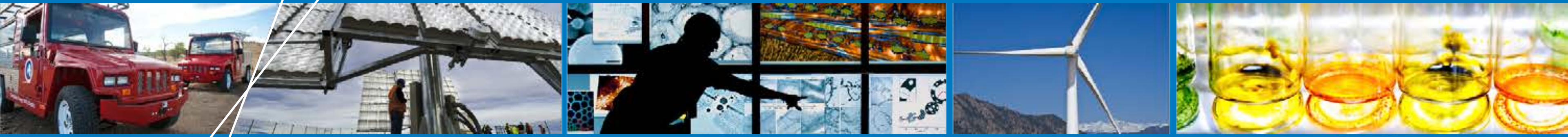
NATIONAL RENEWABLE ENERGY LABORATORY

Effect of System Contaminants on PEMFC Performance and Durability



Venue: 2012 DOE Hydrogen and Fuel Cells Program Review

Presenter: Huyen Dinh (PI)

National Renewable Energy Laboratory

Date: May 16, 2012

FC048

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Project Overview

Timeline

Start: July 2009
End: September 2013
% complete: ~65%

Budget

Total project funding:
- **DOE share: $6,000,000***
- **Cost share: $788,850**

Funding received in FY11:
$1050K*
Planned Funding for FY12:
$1475K*

***Includes $400K to LANL (sub)**

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

Barriers

Barrier	2020 Target
A: Durability	**5,000 h for Transportation** **60,000 h for Stationary**
B: Cost	**$30/kW for transportation** **$1000-1700/kW for Stationary (2-10 kW)**

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) (in-kind partner)
Colorado School of Mines* (Ryan Richards)

* denotes subcontractor

Collaborators

Institutions	Role
National Renewable Energy Laboratory (NREL): H. Dinh (PI), B. Pivovar, G. Bender, H. Wang, C. Macomber, KC Neyerlin, K. O'Neill	**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 of structural materials**
University of South Carolina (USC): J. Van Zee, M. Ohashi, M. Opu, M. Das, H. Seok Cho	**Sub; Broad screening and deep probe study of assembly aids materials; modeling**
Los Alamos National Laboratory (LANL): T. Rockward	**Minor partner; Durability testing of liquid phase contaminant**
University of Hawaii (UH): J. St.-Pierre , Keith Bethune	**Minor sub; Durability testing of gas phase contaminant (silicone material)**
3M: S. Hamrock	**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*
Ballard Power Systems and Nuvera Inc. on material selection and testing protocols

Relevance

Status	Core Project Objectives	
Complete	1. Identify fundamental classes of contamination	
Complete	2. Develop and validate test methods	2010-2011 focus
Complete	3. Identify severity of contaminants	
In progress	4. Identify impact of operating conditions	2012-2013 focus
In progress	5. Identify poisoning mechanisms	
In progress	6. Develop models/predictive capability	
Future work	7. Provide guidance on future material selection	2013 objective

Impact

1. Increase performance and durability by limiting contamination related losses
2. Decrease overall fuel cell system costs by lowering balance of plant (BoP) material costs.

Project Milestones and Timeline

Previous Major Technical Accomplishments at Previous AMR:

1. **Compiled list of plausible polymer families and grades for fuel cell use**
2. **Developed ex-situ and in-situ experiments for screening leachable contaminants**
   - **Quantified impact of 4 contaminants on fuel cell performance**
   - **Isolated electrochemically inhibiting compounds from 4 materials**
3. **Benchmarked screening experiments among the laboratories**

Major Technical Accomplishments Since Last Year:

1. **Screened 55 materials for fuel cell contamination**
2. **Preliminary assessment of studied BoP materials on fuel performance**
3. **Identified leached species for all structural materials and assembly aids**
4. **Determined that leached species come from the hydrolysis and degradation of the polymer resins and additives**
5. **Selected model organic compounds and leachant extracts for in-depth parametric studies**
   - **Performed initial studies on model compounds**

Ongoing Objectives:

1. **Establish approach for quantitatively/statistically comparing and correlating screening data**
2. **Perform parametric in-situ studies on several grades of materials**
   - **Study the effects of relative humidity, current, electrode loading, reactant inlet, and concentration on voltage loss.**
3. **Quantify the impact of model compounds on fuel cell performance and relate information back to leachant extract results**
4. **Model the effects of operating condition on fuel cell performance**

Approach – FY11 – FY12 Milestones

FY11	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	100% complete

FY12	1	Perform parametric in-situ studies on three variety of PPA plastic to understand the mechanism of performance loss (> 50 mV loss) and recovery during fuel cell operation.	05/2012	50%
	2	Down-select 20% of all materials and model compounds for in-depth parametric studies	07/2012	60%
	3	Quantify the impact of two model compounds (with different functional groups) on fuel cell performance via ion exchange effects in membranes and adsorption on electrodes.	09/2012	

Approach – Material Selection

Materials chosen based on:

1. **Physical properties**
   - **Operating conditions (0-100% RH, -40-90˚C)**
2. **Commercial availability**
3. **Cost**
4. **Input from OEMs and fuel cell system manufacturers**
   - **GM (active project collaborator)**
   - **Ballard Power Systems**
   - **Nuvera**

Material Selection Prioritization:
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. Fuel Impurities
9. Ions from catalyst alloys

	Focus
1.Balance of Plant Materials (BoP)	
– Liquid path	**90%**
• Structural plastics	
• Adhesives	
• Lubricants	
– Gas path	5%
• General silicone material	
2.By-products of membrane degradation	5%

Note: materials highlighted in red were chosen for this study

Technical Progress – Screening Complete

Screened 55 materials using 6 different techniques, totaling > 660 experiments

‘Quick’ Screen
Multi-component solutions
Objective < 1 day/ experiment

1. **Leaching test to capture water based contaminants**
2. **Electrical conductivity, pH, and Total organic carbon (TOC) measurement**
3. **Cyclic voltammetry (CV)**

Advanced Screening Approach
Objective = 2-3 day/ experiment

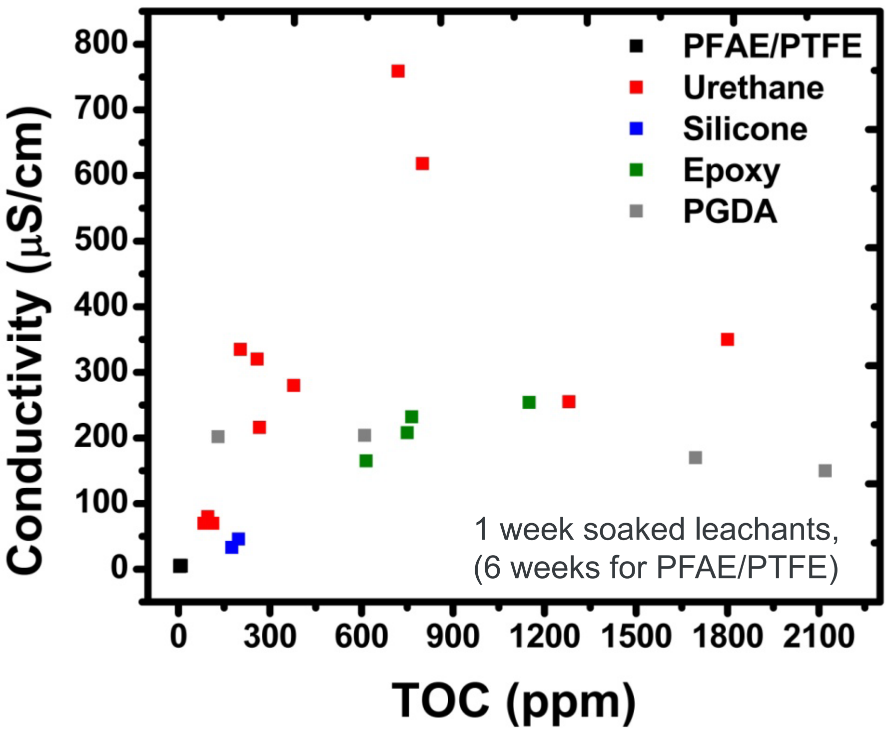
4. **Membrane Conductivity**
5. **In situ 50cm^2 fuel cell test**
6. **Advanced analytical analysis (FTIR, ICP, IC, GCMS, LCMS)**

Function Description	Material Family	Total Grades	% Complete Screening
Structural Plastic	PA (Nylon)	26	100
Structural Plastic	PPS	4	100
Structural Plastic	PSU	2	100
Structural Plastic	PPSU	1	100
Structural Plastic	PBT	2	100
Lubricant/Grease	Perfluoroalkylether/ polytetrafluoroethylene (PFAE/PTFE)	4	100
Adhesive/Seal	Urethane	6	100
Adhesive/Seal	Silicone	2	100
Adhesive	Epoxy	3	100
Adhesive	Acrylic Acrylate	1	100
Thread Lock/Seal	Polyglycol Dimethacrylate (PGDA)	4	100
	Total	**55**	**100**

Assembly Aids

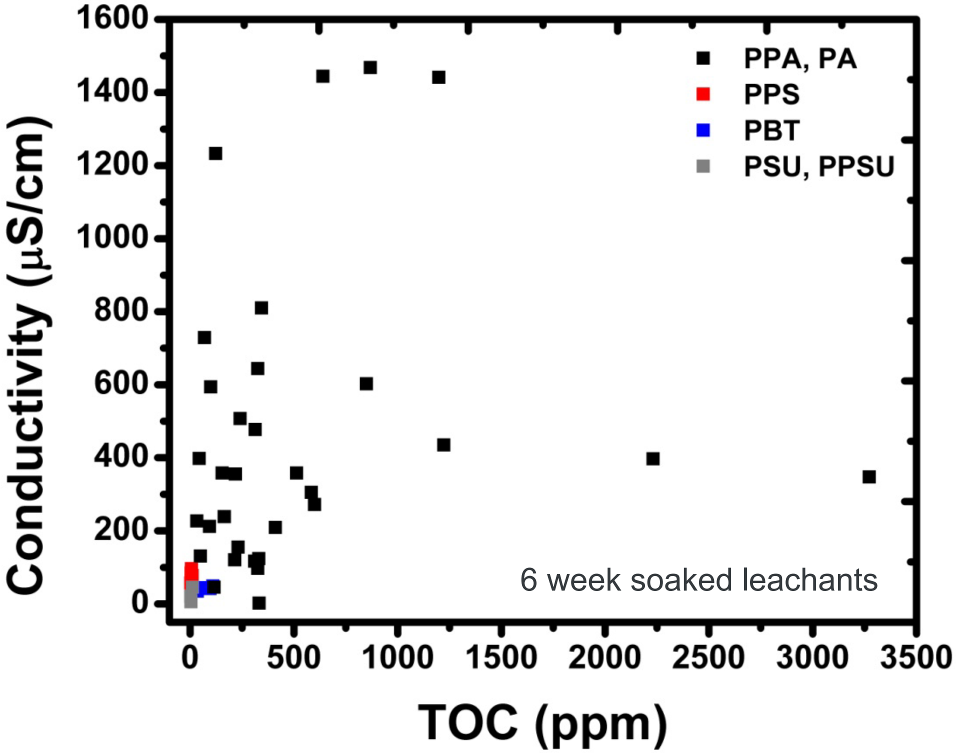
Technical Progress – TOC and Conductivity Screening of Extract Solutions

Assembly Aids Materials



1 week soaked leachants, (6 weeks for PFAE/PTFE)

Structural Materials



6 week soaked leachants

- **Solution conductivity and TOC provide a quick screening of the materials for potential contaminants.**
- **Likely target BoP materials: low TOC and low solution conductivity**
- **Higher cost, non-commodity materials (PFAE/PTFE, PPS, PBT, PSU, PPSU) leached out less ionic and organic contaminants.**
- **Nylons (PA & PPA) show the greatest variety with grade as expected (by design).**

Technical Progress – Elemental speciation by ICP screening of extract solutions

Elemental analysis identify leached species, which were linked to fillers and additives, base on knowledge of the type of plastic, common additives and information from datasheets.

Common structural automotive thermoplastic additives:

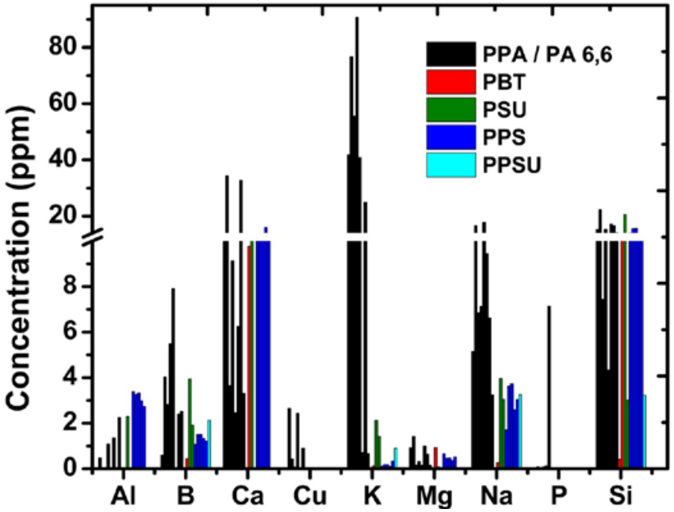
- Glass fiber reinforcement
  - Alumino-borosilicates (Al, B, Si)
  - Soda lime (Ca)
- Antioxidant/Heat stabilizers
  - Calcium stearate (Ca),
  - Phenolic antioxidants with phosphites (PO_3^{3-})
- UV Stabilizer
  - Nickel (Ni) and Benzoates

Common additives in urethanes[1,2]:

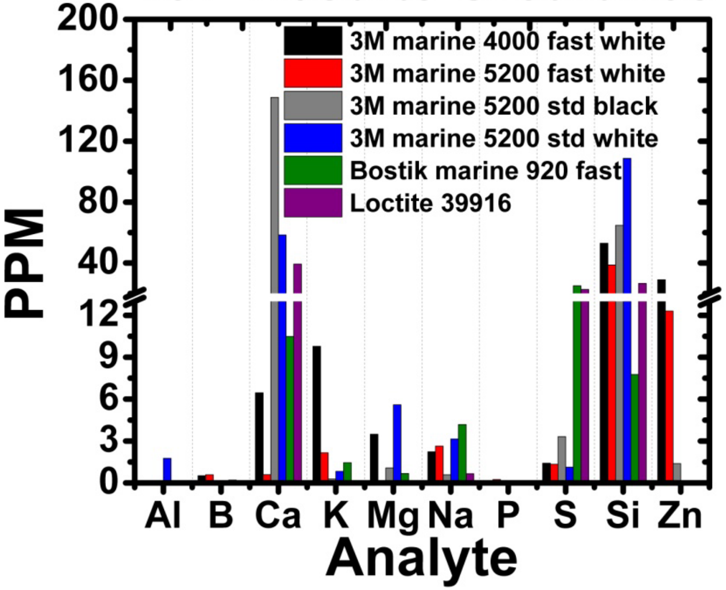
- Flame retardant
  - Alumina trihydrate (hydroxide) [Al], K
- Fillers and flame retardants
  - Limestone, dolomite, talc (Ca,Mg, Si)
- Catalysts
  - K, Zn

ICP = inductively coupled plasma

ICP Results for Structural Materials



ICP Results Urethanes



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1. Manufacturer's MSDS; 2. Lindholm, J., et al., J. Appl. Polym. Sci. 123(3): p. 1793-1800 (2011).

Technical Progress – Organic compounds identified via GCMS

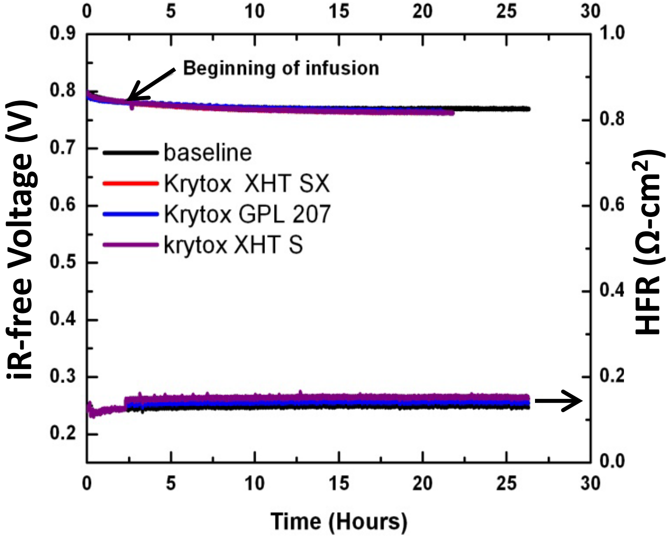
Material function	Chemical description	Major organic compounds identified	Source of species
Structural Plastic	**PA (Nylon), PPA**	1, 8- diazocyclotetradecane 2,7 dione	hydrolysis of base resin or waste product from synthesis
		Caprolactam	Trapped residual monomer
		1,6 Hexanediol	Residual chain linker or cross-linking agent
Structual Plastic	**PBT**	Butanediol	
		1, 8- diazocyclotetradecane 2,7 dione	hydrolysis of base resin or waste product from synthesis
Struct. Plastic	**PPS**	Relatively clean with trace p, m, or o-chloroaniline	
Struct. Plastic	**PSU**	None	
Struct. Plastic	**PPSU**	None	
Lubricant/ Grease	**PFAE/PTFE**	None	
Adhesive/Seal	**Urethane**	methyl benzenediamine	hydrolysis product of residual monomer
		4- methyl benzenesulfoneamide	hydrolysis product of a cyano water scavenger
		2-(2-ethoxyethoxy)-ethanol acetate	Residual solvent (added for material flowability)
		2-(2-ethoxyethoxy)-ethanol	
Adhesive/Seal	**Silicone**	benzyl alcohol	
		2-(2-ethoxyethoxy)-ethanol acetate	
		2-(2-ethoxyethoxy)-ethanol	
Adhesive/Seal	**Epoxy**	benzyl alcohol	
		[p/o]-tert-butyl-phenol	
Adhesive/Seal	**Acrylic Acrylate**	2-methyl-2-hydroxyethyl ester, 2-propenoic acid	
Thread Lock /Seal	**PGDA**	polyethylene glycol dimethacrylate	Lower molecular weight molecule derived from original polymer

PA = polyamide (nylon); PPA = polyphthalamide; PSU = polysulfone ; PPS = polyphenylene sulfide; PPSU = polyphenylsulfone; PBT = polybutylene terephthalate; PFAE/PTFE = Perfluoroalkylether/ polytetrafluoroethylene; PGDA = Polyglycol Dimethacrylate

- **Organic compounds come from polymer resins, additives, and by-products of incomplete polymerization.**
- **The more expensive materials such as PPS, PSU, PPSU and PFAE/PTFE are clean (no organics detected).**

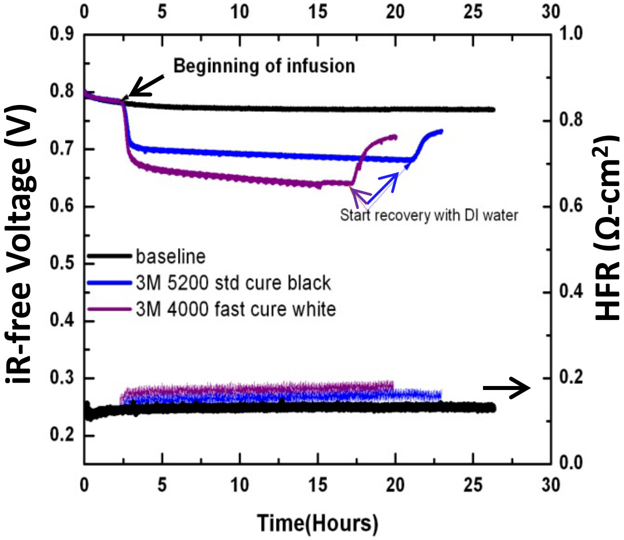
Technical Progress – In-situ infusion screening: Assembly aids material example

PFAE/PTFE example

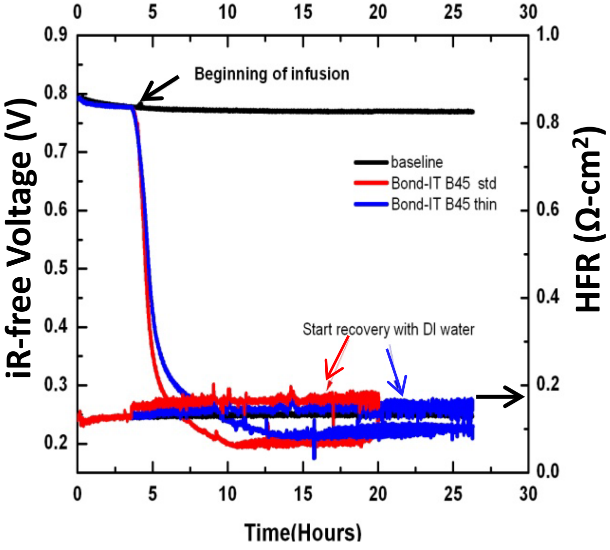


Krytox is a registered trademark of E.I. du Pont de Nemours and Company

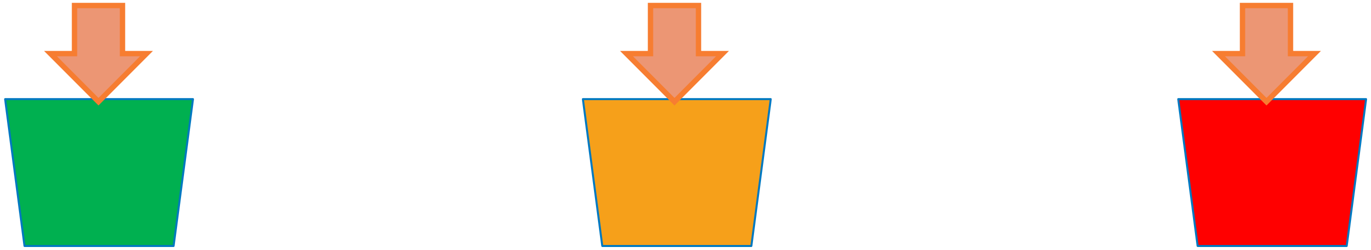
Urethane example



Epoxy example



Material Classification by Result



clean

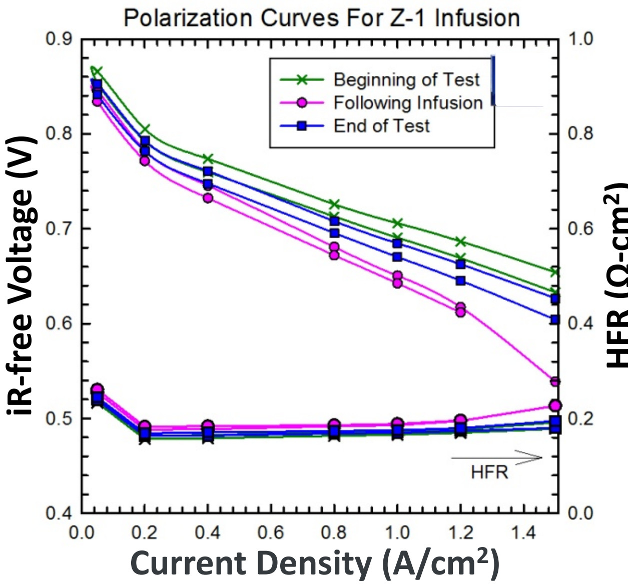
Contaminates, partially recovers

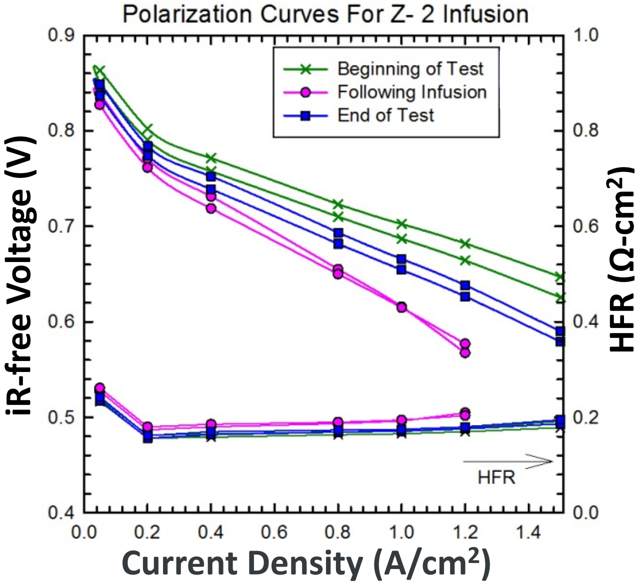
Contaminates, Does not recover

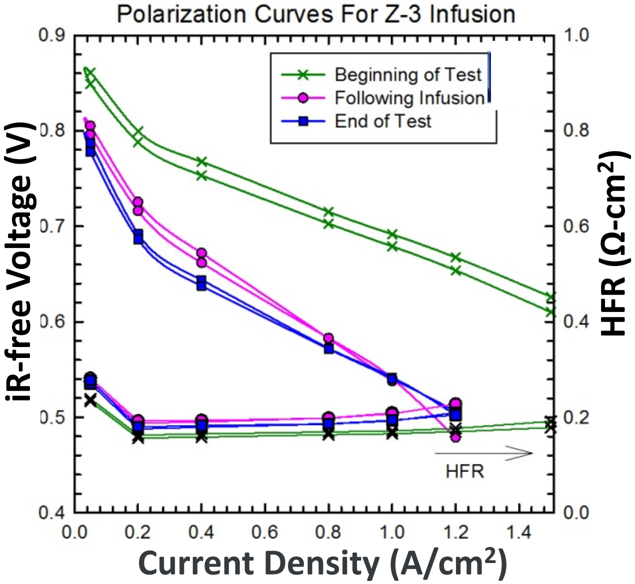
System contaminants can have an adverse effect on fuel cell performance, but the effect is complex.

- Concentration, species, and operating condition effects will be studied further to understand the mechanism of contamination

Technical Progress – In situ performance loss and recovery screening: Structural material example







Material Classification by Result

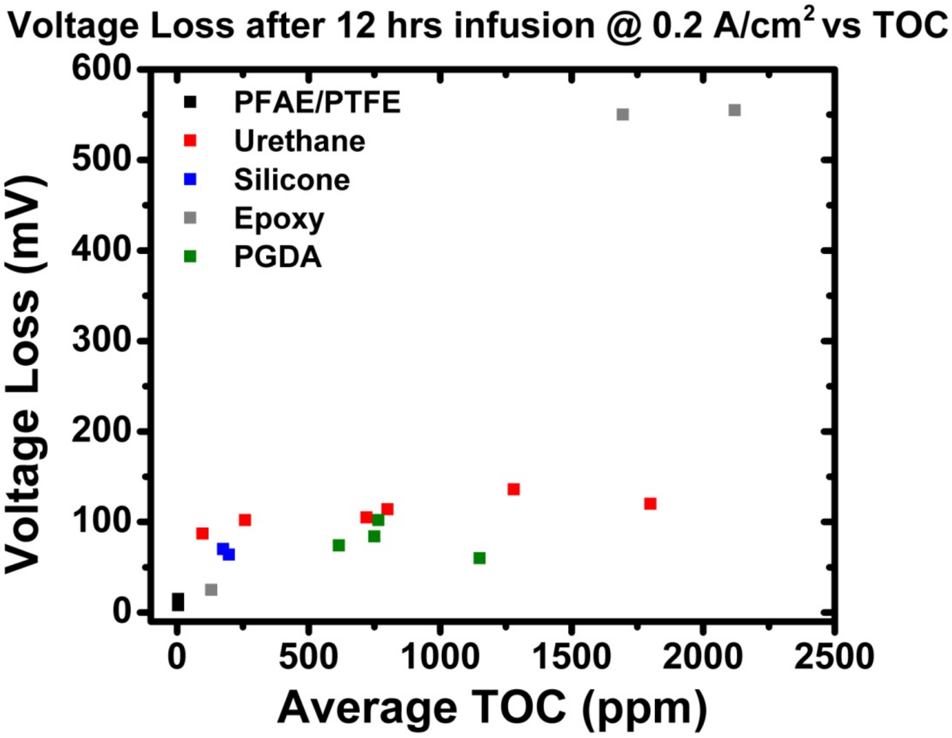
Contaminates, recovers

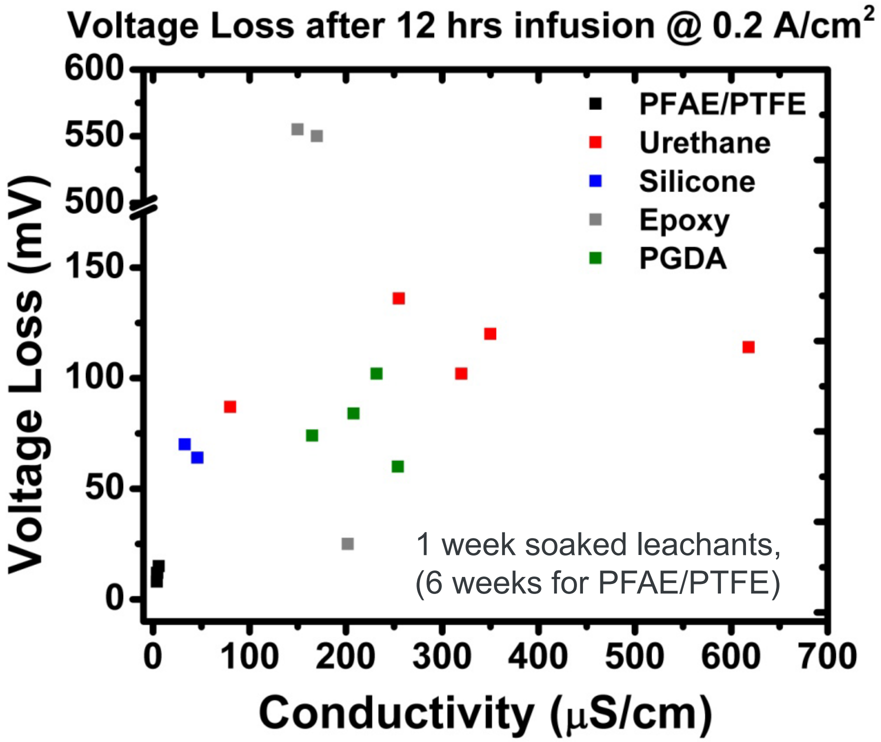
Contaminates, partially recovers

Contaminates, Does not recover

- **System contaminants can adversely affect fuel cell catalyst**
  - voltage loss observed across all current densities (minimum change in HFR)
- **Some contamination are recoverable (Z1 & Z2) while others are not (Z3)**

Technical Progress –
High level correlation between *ex-situ* & *in-situ* data


Voltage Loss after 12 hrs infusion @ 0.2 A/cm² vs TOC


Voltage Loss after 12 hrs infusion @ 0.2 A/cm²

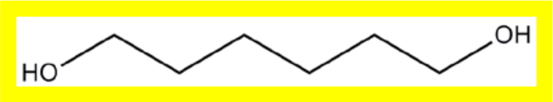
1 week soaked leachants,
(6 weeks for PFAE/PTFE)

- **General trends are observed**
  - **In-situ fuel cell voltage loss increases with increasing TOC and solution conductivity: Materials that test 'high' generally prove harmful to fuel cell performance.**
- **A higher level of analysis is needed.**
  - **Difficult to draw conclusions on correlation because in-situ screening experiments are too short and contaminant concentration and speciation varied with material**

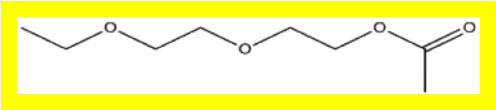
Technical Accomplishments – Model compounds identified & selected for further study

Structural Materials and Assembly Aids:

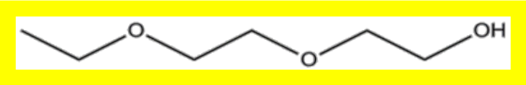
1,6-Hexanediol



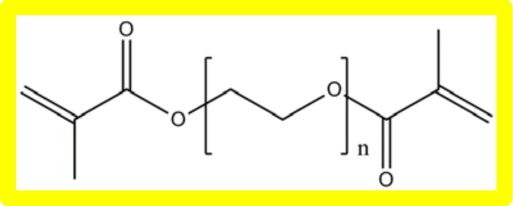
2-(2-ethoxyethoxy)ethanol acetate



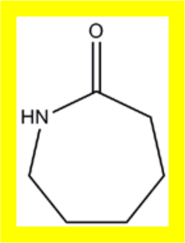
2-(2-ethoxyethoxy)-ethanol



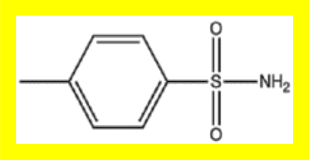
Polyethylene Glycol [PEG] Dimethacrylates



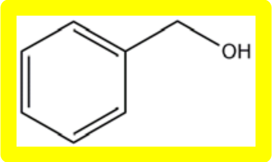
Caprolactam



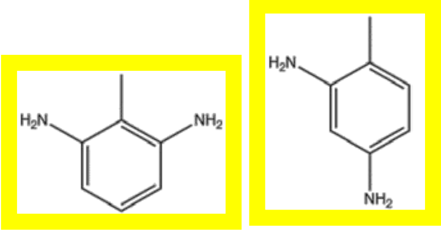
4-methyl-benzenesulfonamide [p-Toluenesulfonamide]



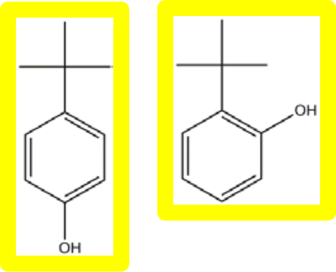
Benzyl alcohol



Methyl benzenediamine [Toluene diamine]



[p/o]-tert-butyl-phenol

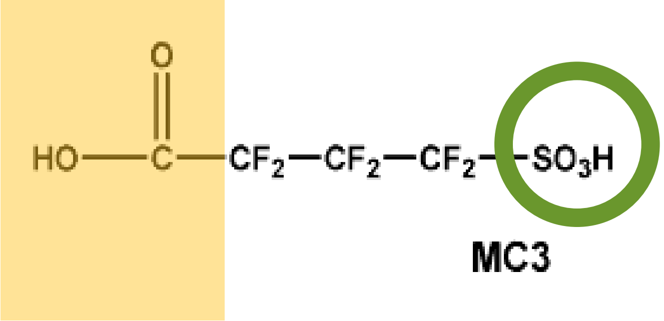


Model compounds selected for further fundamental/mechanistic studies.
Model compounds consist of aromatics and aliphatics with a variety of functional groups.

Technical Progress – Mechanistic understanding and evaluation of model compounds – Membrane degradation by-product example

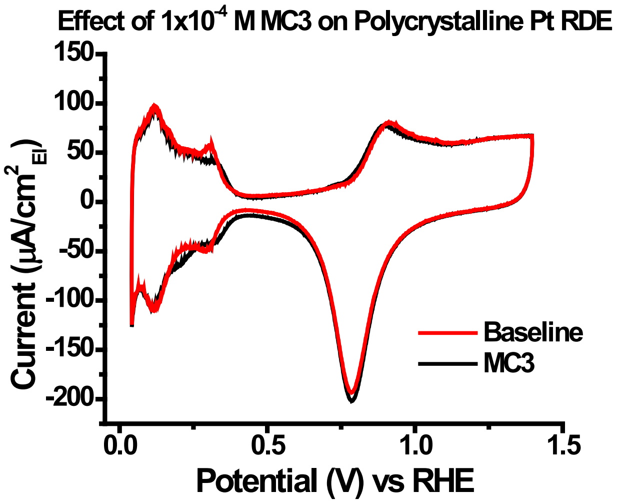
- Membrane degradation by-products are potential electrochemical contaminants of fuel cells.
- Goal of ex-situ CV is to understand the effects of model compounds on the change of Pt CV and oxygen reduction reaction (ORR)
  - Effect on Pt CV (effect on Pt surface coverage) may not indicate an effect on ORR
- General model organic compound study: Further work is underway to understand the mechanism of contamination and quantify impact in fuel cell systems.

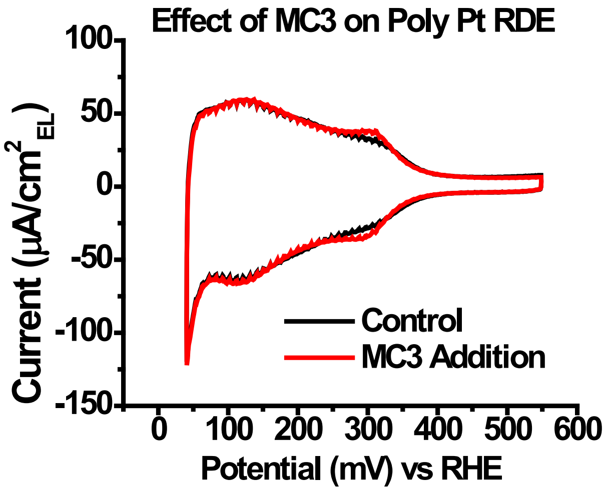
Change in CV / Change in ORR

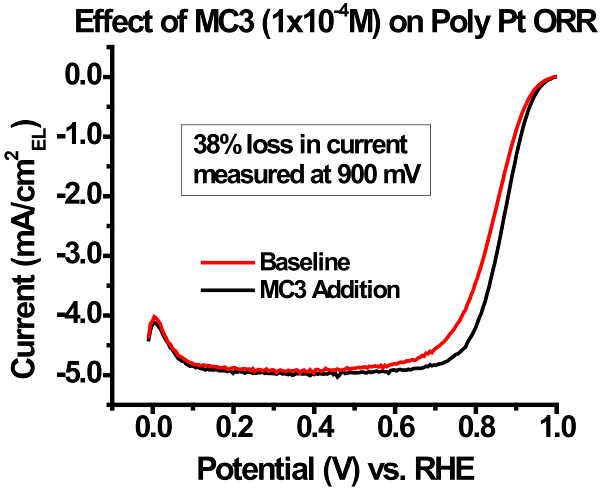


$HO-C(=O)-CF_2-CF_2-CF_2-SO_3H$

MC3


Effect of 1x10^{-4} M MC3 on Polycrystalline Pt RDE


Effect of MC3 on Poly Pt RDE


Effect of MC3 (1x10^{-4}M) on Poly Pt ORR

Proposed Future Work

- Establish approach for quantitatively/statistically comparing and correlating screening data
- Establish correlations between ex-situ characteristics to in-situ performance loss
- Perform parametric in-situ studies on selected leachant solutions
  - Study the effects of relative humidity, current, electrode loading, reactant inlet, and concentration on voltage loss.
- Fundamental/mechanistic studies on selected model compounds.
  - Quantify the impact of model compounds on fuel cell performance and relate information back to leachant extract results
- Develop predictive models for specific contaminating species and model compounds.
  - Model the effects of operating condition on fuel cell performance
- Durability and longer term testing of selected contaminants.
- Screen BoP material suggested by Ballard and Nuvera

Summary

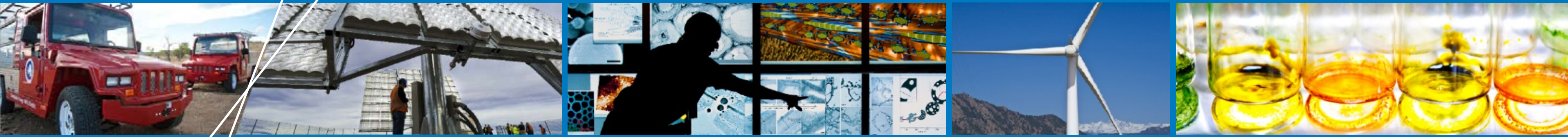
Relevance: Focus on overcoming the cost and durability barriers for fuel cell systems.

Approach: Screen BoP materials and select leachants and model compounds; 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 provide guidance on future material selection to enable the fuel cell industry in making cost-benefit analyses of system components.

Technical Accomplishments and Progress: 55 prospective BoP fuel cell materials were thoroughly screened. Qualitative relationships were developed between ex-situ and in-situ screening results. Leachant species were identified for all structural and assembly aids materials. Model compounds for further fundamental/mechanistic experiments were selected. A series of extract solutions were selected for further parametric studies evaluating the impact of in-situ operating conditions. The identified organic compounds have not been studied before (in-situ, parametric, recoverability) and do not overlap with the air contaminants project. Intiated in-situ durability study of gas-based contaminants (siloxanes). Initiated set up for durability study of liquid-based contaminants. Contacted Ballard Power Systems and Nuvera re. providing input on BoP materials for screening. 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 4 industry partners.

Proposed Future Research: Establish statistical relationships and capabilities for correlating ex-situ characteristics to in-situ performance loss. Fundamental/mechanistic studies on selected model compounds and extract solutions. Develop predictive models for specific contaminating species and model compounds. Durability and longer term testing of selected contaminant compounds.



Technical Back-up Slides

Technical Progress: Develop In-situ durability method for studying liquid-based contaminants

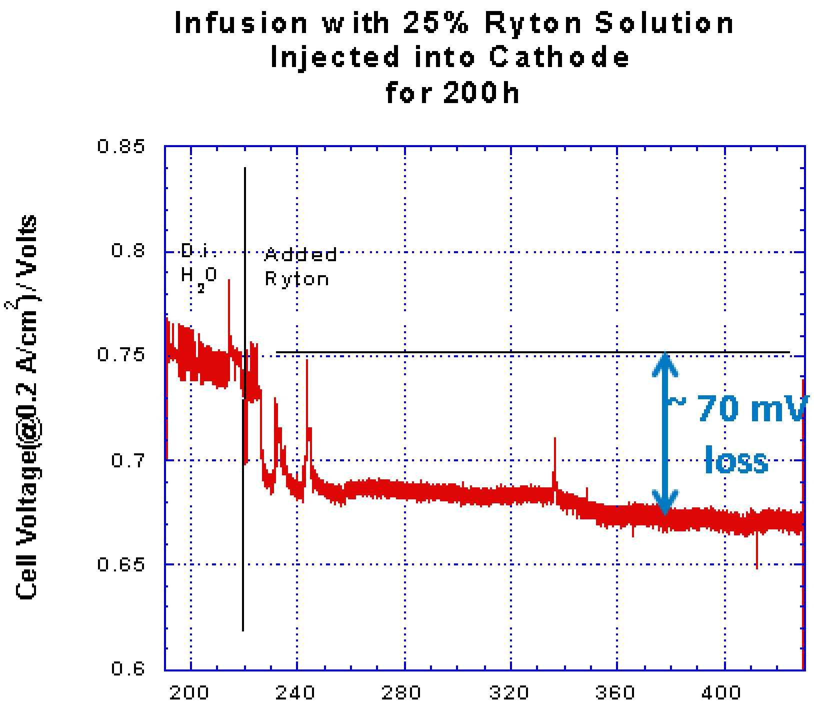
MEA exposure to Ryton® R4 220BL material resulted in a significant fuel cell performance loss.

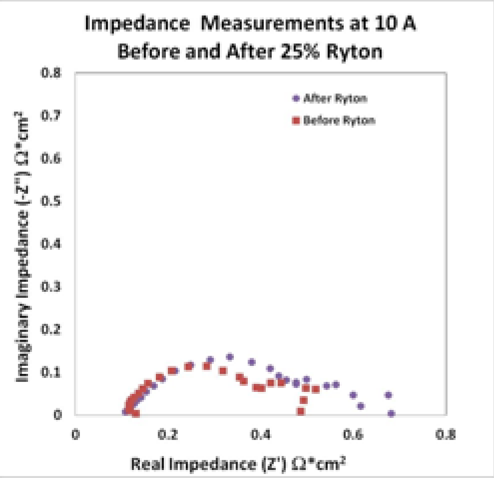
Durability testing at 0.2 A/cm² over 200 h resulted in:

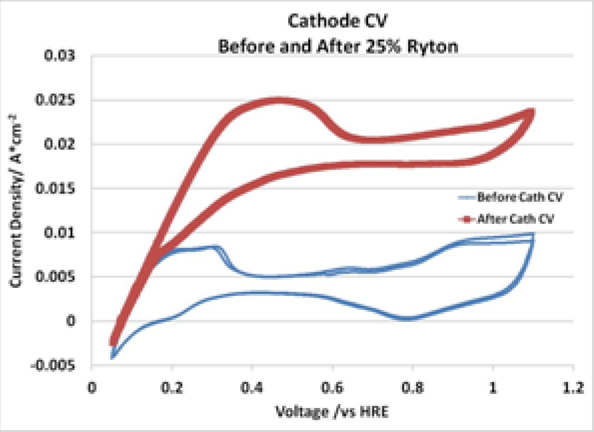
- Voltage loss of ca. 70 mV
- Increased hydrogen cross-over
- Development of an electrical short
- Impact on both cathode and anode cyclic voltammograms
- Change in ac impedance response
- Discoloration of the MEAs and flow fields

Future work:

- Cause and effect will be investigated
- Durability test of higher contaminant concentration
- Durability test of another contaminant
- Investigate the application of DOE accelerated stress test for liquid-based contaminants







Technical Progress: In-Situ Durability Study of Gas-based Contaminants (Siloxane focus)

MEAs exposed to Loctite® 5039™ material resulted in a significant loss in electrode performance.

- Durability testing (DOE OCV accelerated stress test) of MEAs in the presence of siloxane emissions was carried out for 300 hours.

- After 300 hours, both the baseline and contaminated part failed from chemical degradation of the membrane rather than mechanical failure (brittle membrane) from contaminant.

- Losses in electrochemical surface area and fuel cell performance were observed in the contaminated case.

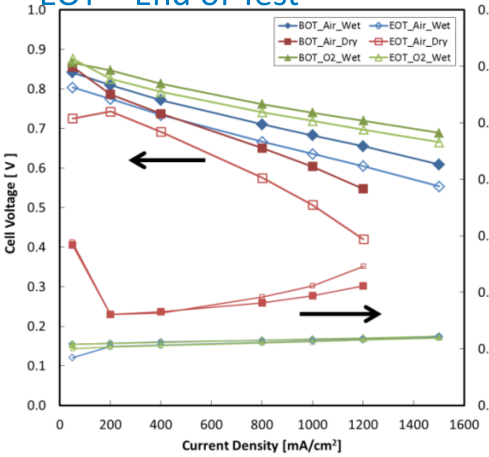
- Future work will use different GM-made MEAs and durability test will be conducted with RH cycling with load rather than OCV testing.
  - RH cycling with load designated ideal test for failure mode, but not current AST

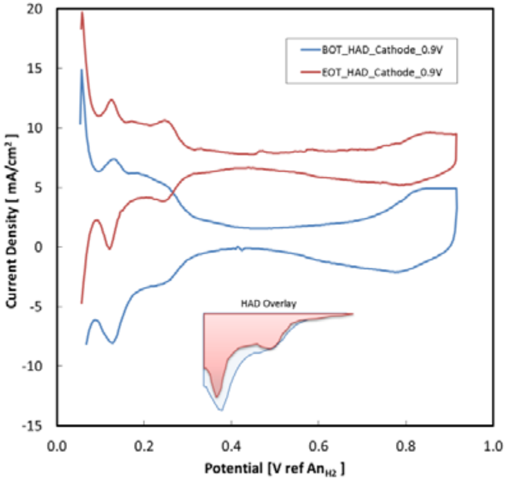
BOT = Beginning of Test

EOT = End of Test

Baseline Results

GORE™ MEA used

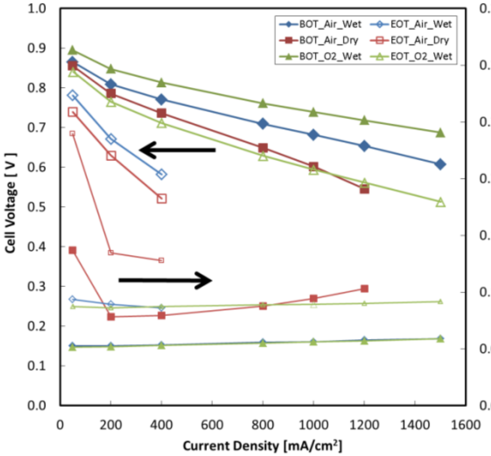


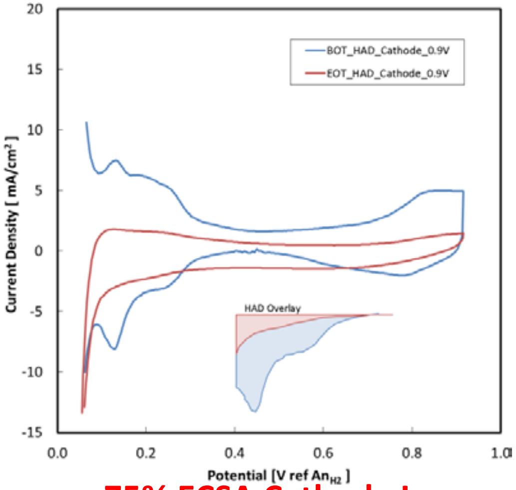


25% ECSA Cathode Loss

(49% ECSA Anode Loss)

Loctite 5039 Results





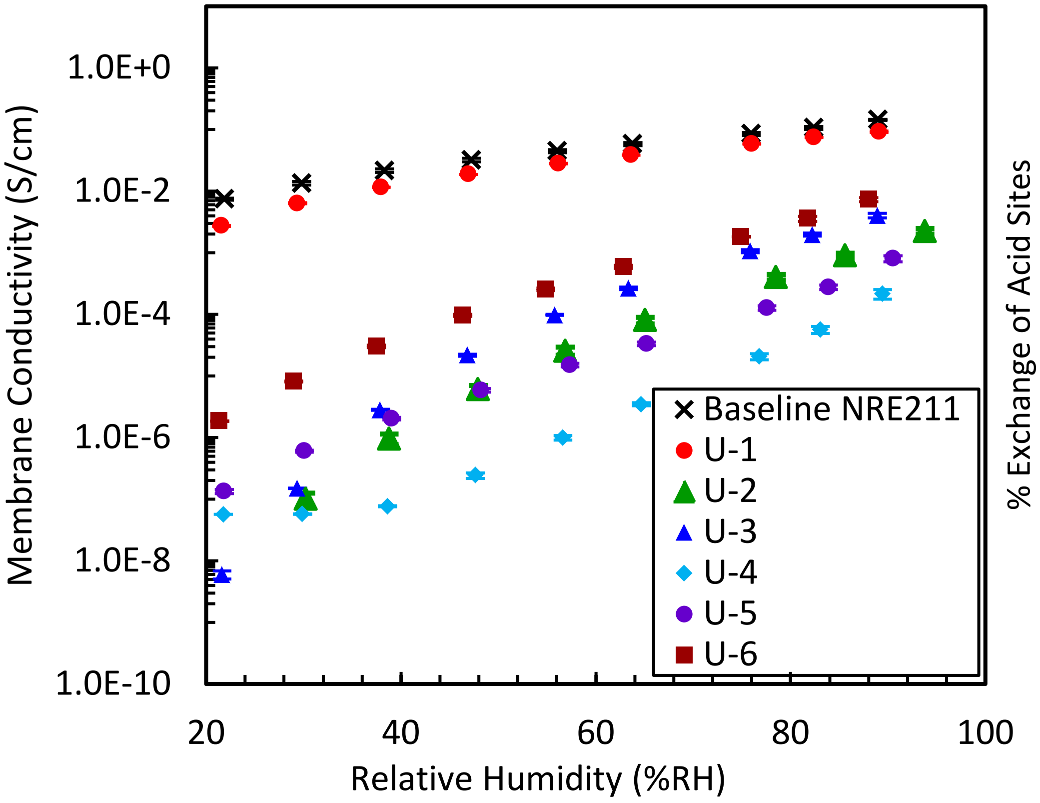
75% ECSA Cathode Loss

(53% ECSA Anode loss)

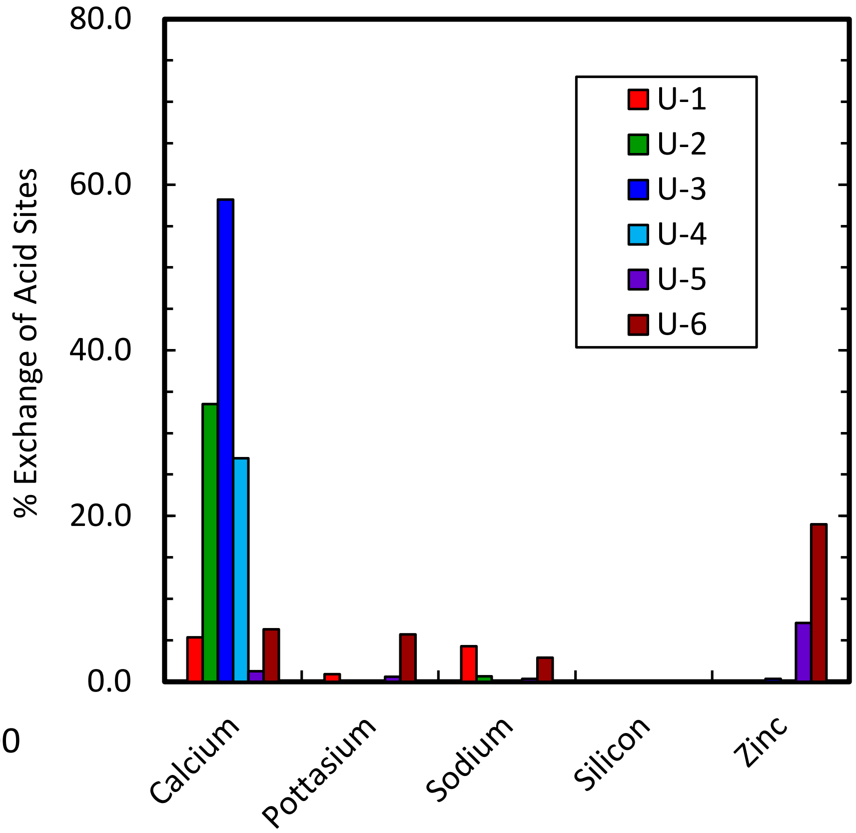
Technical Progress – Effects of Urethane Extract Solutions on Membrane Conductivity

- Urethane extracts adversely affected the membrane conductivity
- Metal ions from the extracts absorbed into the membrane and remained there.

Influence of Urethane Type Extracts on Membrane Conductivity



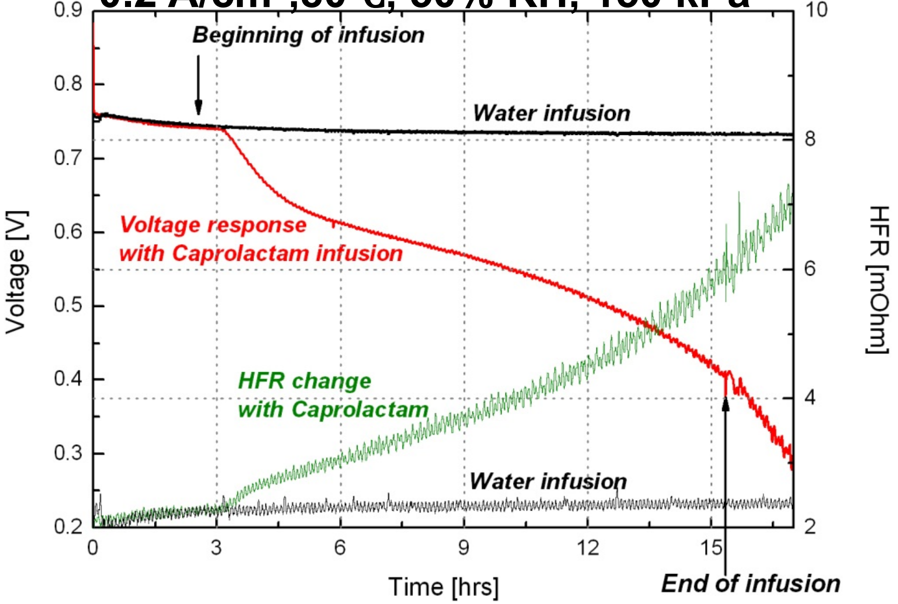
ICP results of digested membrane (NRE 211) following exposure to urethane extract solutions

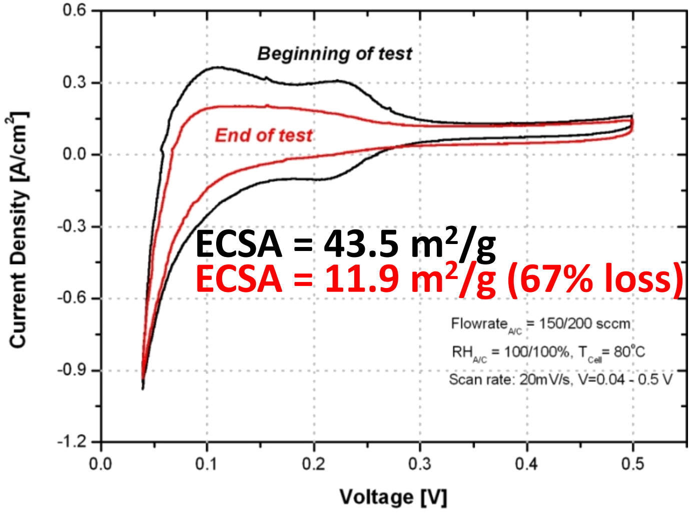


Technical progress – Caprolactam model compound *In-situ* PEMFCs response

- Infusion of caprolactam on the cathode resulted in loss of performance and ECSA and higher HFR.
- Caprolactam appears to poison the catalyst and ion-exchange with the proton in the membrane. The effects do not seem to be recoverable.

Caprolactam solution infusion: 11μmol/h
0.2 A/cm^2,80℃, 50% RH, 150 kPa





ECSA = 43.5 m^2/g

ECSA = 11.9 m^2/g (67% loss)

Flowrate$_{A/C}$ = 150/200 sccm
RH$_{A/C}$ = 100/100%, T$_{Cell}$ = 80°C
Scan rate: 20mV/s, V=0.04 - 0.5 V

Approach – Material Selection

Examples of common additives in automotive thermoplastics and assembly aids to provide specific physical properties:

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

Experiment Objective: To study effects of various ingredients used to manufacture plastics on fuel cell performance

Systematic approach to materials selection example:

1 manufacturer,
5 different resin grades,
3 glass fill levels,
2 additive types

Structural Material Abbreviation	Resin	Glass Fill (%)	Additive
E1	PA A	0	halide stabilizer
E2	PA B	0	none
E3	PA B	30	halide stabilizer
E4	PA B	50	halide stabilizer
E5	PA A	50	organic stabilizer
E6	PPA C	30	halide stabilizer
E7	PPA C	50	halide stabilizer
E8	PPA D	30	halide stabilizer
E9	PPA D	50	halide stabilizer
E10	PPA E	30	halide stabilizer

A systematic approach was used to select different grades of BoP materials

- to study the effects of polymer resins and additives on fuel cells.