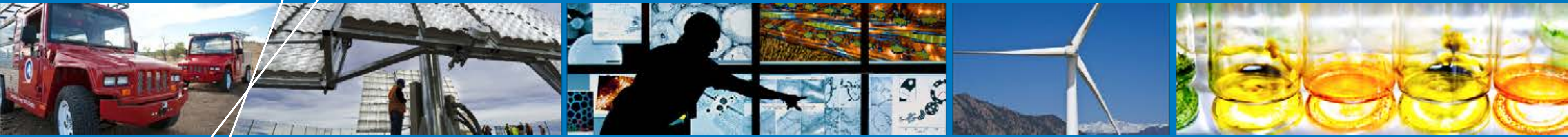
NATIONAL RENEWABLE ENERGY LABORATORY

Effect of System Contaminants on PEMFC Performance and Durability



Huyen Dinh (PI)
National Renewable Energy Laboratory
June 10, 2015

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.

Overview

Timeline and Budget

- Project start date: 10/1/2013
- FY14 DOE funding: $400K
- FY15 planned DOE funding: $150K
- Total DOE funds received to date: $75K
- Estimated GM-NREL CRADA funding: $100K

Barrier	2020 Target
A: Durability	5,000 h for Transportation 60,000 h for Stationary
B: Cost	$30/kW for transportation $1,000–$1,700/kW for stationary (2–10 kW)

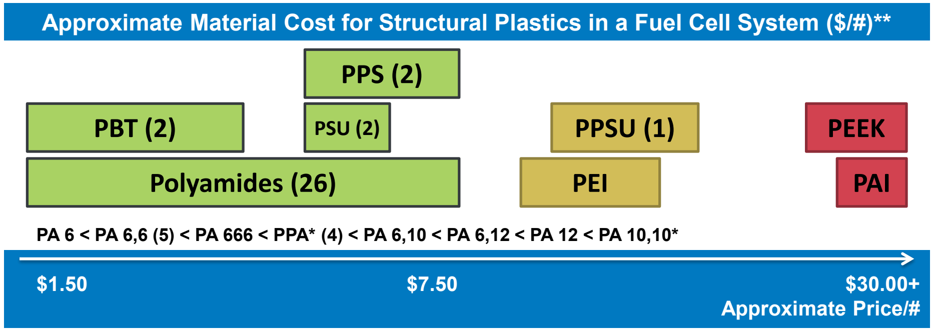
Partners

- General Motors
  - Paul Yu and Balsu Lakshmanan
- Colorado School of Mines
  - Ryan Richards
- NREL (project lead)

*Project leverages the competitively awarded system contaminants project (2009-2013).

Relevance

- **System contaminants have been shown to affect the performance/durability of fuel cell systems.**
- **Balance of plant (BOP) costs have risen in importance with decreasing stack costs.**
- **Commodity plastic materials used in BOPs are not designed for fuel cell applications.**



** 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)

Size of Component

Information provided by GM

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

Objectives:

- Understand the extent of fuel cell performance impact of relevant BOP materials
- Identify and quantify contaminants derived from BOP material
- Understand fundamental contamination mechanisms and recoverability of BOP material components
- Be a resource to fuel cell community

Impact:

- Guide BOP material selection for fuel cell systems
- Guide material design to lower BOP material cost
- Minimize performance loss and enhance durability of fuel cells

Approach

- **Determine the effect of leaching parameters on structural material leaching concentration (NREL and GM)**
  - *Leaching*: different temperature, time, and surface area/volume ratio
  - *Ex-situ characterization*: solution conductivity, pH, total organic carbon (TOC), gas and liquid chromatography mass spectrometry (GCMS, LCMS), inductively coupled plasma (ICP), ion chromatography (IC)
- **Develop GCMS method to identify and quantify organic contaminants (NREL)**
  - *GCMS*: flame ionization detector (FID), total ion count – single ion monitoring (TIC-SIM), thermal conductivity detector (TCD), liquids, solid phase micro-extraction (SPME)
- **Investigate fundamental mechanism of contamination and recoverability using model compounds (NREL)**
  - *Ex-situ electrochemistry*: cyclic voltammetry (CV) on rotating disc electrode (RDE) to obtain electrochemically active surface area (ECA) and adsorption effect, oxygen reduction reaction (ORR) activity using RDE, electrochemical quartz crystal microbalance (EQCM)
  - *In-situ infusion fuel cell testing*: beginning of test (BOT), during infusion, end of life (EOL), and after recovery diagnostics: ECA, polarization curve, H_2/N_2 electrochemical impedance spectroscopy (EIS), H_2/air EIS, H_2/O_2 EIS

Approach – FY 2015 Milestones

FY 2015	**Q1 QPM**	Select two model compounds (organics, anions, or cations) derived from structural materials for electrocatalytic impact studies to isolate the component(s) in the extract that caused the voltage loss observed in the extract infusion results. • **Selected caprolactam (organic) and sulfate (anion)**	12/31/2014	complete
	Q2 QPM	Using standards, develop a GCMS method to quantify the concentration of organics in the extract solution in order to provide a better understanding of concentration effect of organic contaminants on fuel cell performance.	3/31/2015	complete
	Q3 AM	Quantify the contamination effect of two model compounds derived from structural materials on ECA and ORR activity to determine if they result in the 50%–80% loss that has been seen with some organic model compounds derived from assembly aid materials.	6/30/2015	on track
	Q4 QPM	Measure the fuel cell performance loss due to two model compounds derived from structural plastics leading to the generalization of the impact of representative classes of compounds (e.g., based on specific functional groups) on the fuel cell performance.	9/30/2015	on track

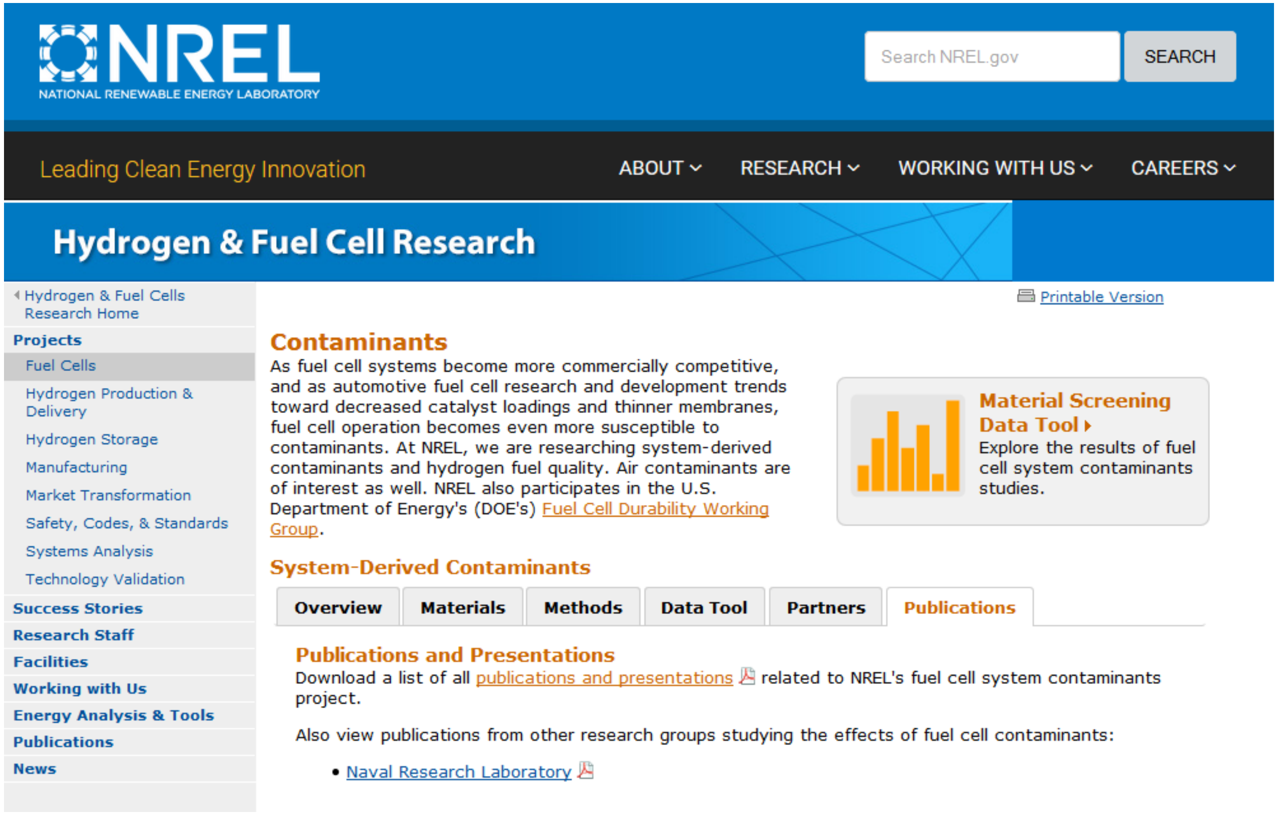
QPM = quarterly progress measure

AM = annual milestone

Accomplishments and Progress – Improved NREL Websites for Project Info Dissemination

NREL contaminants websites and BOP materials database are resources for the fuel cell community

- NREL offers to be a central location for contaminants info
  - Updated website with Naval Research Lab's list of publications on contaminants
- General project information (www.nrel.gov/hydrogen/contaminants.html)
- Interactive material screening data tool (www.nrel.gov/hydrogen/system_contaminants_data/)
- The websites have almost 1,000 pageviews each since the launch in May 2013



Contaminants

As fuel cell systems become more commercially competitive, and as automotive fuel cell research and development trends toward decreased catalyst loadings and thinner membranes, fuel cell operation becomes even more susceptible to contaminants. At NREL, we are researching system-derived contaminants and hydrogen fuel quality. Air contaminants are of interest as well. NREL also participates in the U.S. Department of Energy's (DOE's) Fuel Cell Durability Working Group.

Material Screening Data Tool

Explore the results of fuel cell system contaminants studies.

System-Derived Contaminants

Publications and Presentations

Download a list of all publications and presentations related to NREL's fuel cell system contaminants project.

Also view publications from other research groups studying the effects of fuel cell contaminants:

- Naval Research Laboratory

Accomplishments and Progress – Understand Effect of Leaching Parameters on Contaminant Concentration

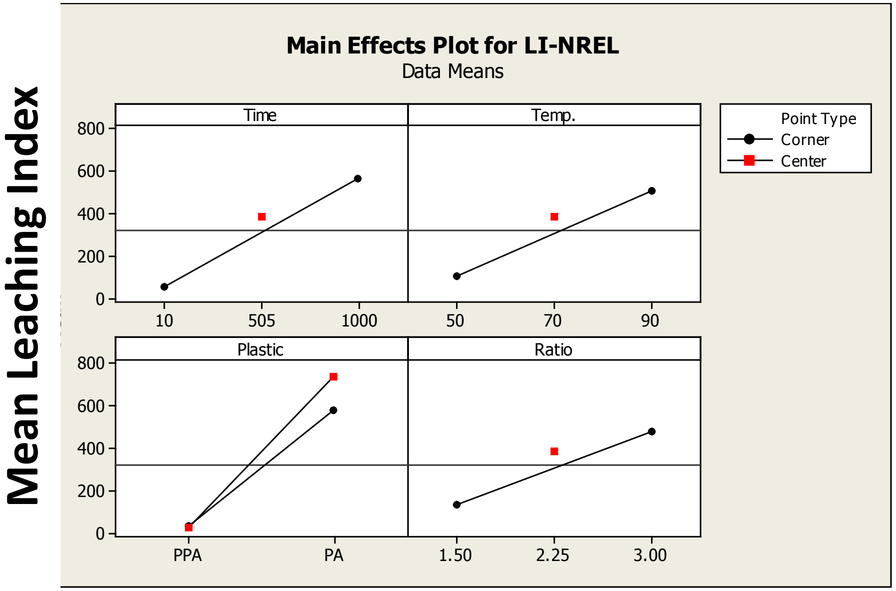
- **Standard leaching conditions are highlighted and discussed in more detail:** 90°C, 1000 h, 1.5 cm^2/ml
- **Expanded the set of leaching conditions: time, temperature, surface area (SA) of material/volume of deionized (DI) water ratio**

	Plastic	Temp. [°C]	Time [h]	SA/Vol Ratio [cm^2/ml]	Sample #	TOC [ppm]	Solution Conductivity [µS/cm]
1	PPA	50	10	1.5	W-81	0.6	3
2	PPA	50	1000	3	W-82	4.7	12
3	PPA	90	10	3	W-83	6.9	7
4	PPA	90	1000	1.5	W-84	47	55
5	PA	50	10	3	W-85	50	19
6	PA	50	1000	1.5	W-86	246	78
7	PA	90	10	1.5	W-87	84	23
8	PA	90	1000	3	W-88	1422	391
9	PA	90	1000	1.5	W-89	983	221
10	PA	70	505	2.3	W-90	585	154
11	PPA	70	505	2.3	W-91	13	18

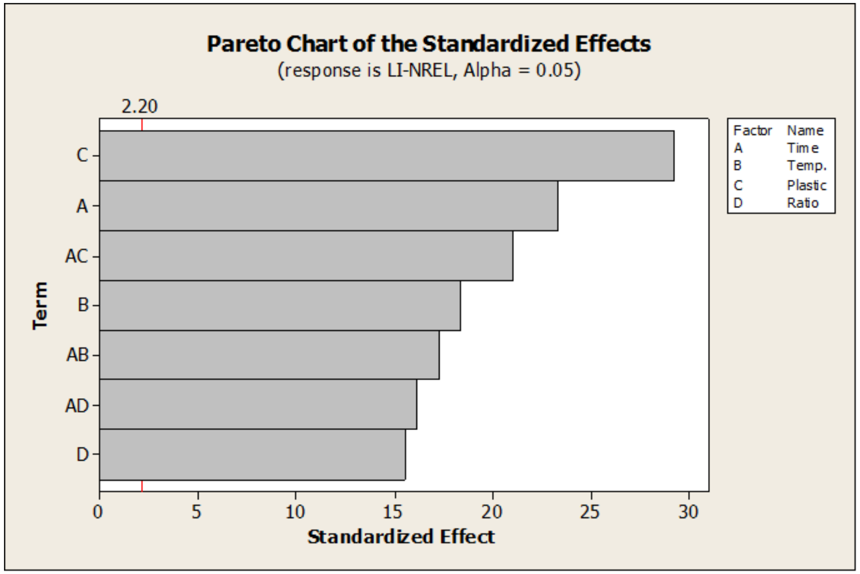
Structural materials: PA = polyamide (BASF Ultramid PA – A3HG6)
PPA = polyphthalamide (Solvay Amodel PPA – HFZ – 1133)

Accomplishments and Progress – Leaching Parameters Effect on Leaching Index (LI)

Main Effects on Leaching Index



Pareto Chart



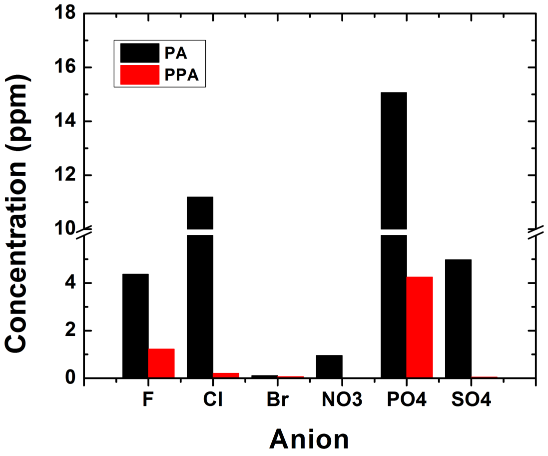
- **Statistical analysis suggest that the main factors and the interactions of each factor are significant.**
- **The three major significant factors are in order of:**

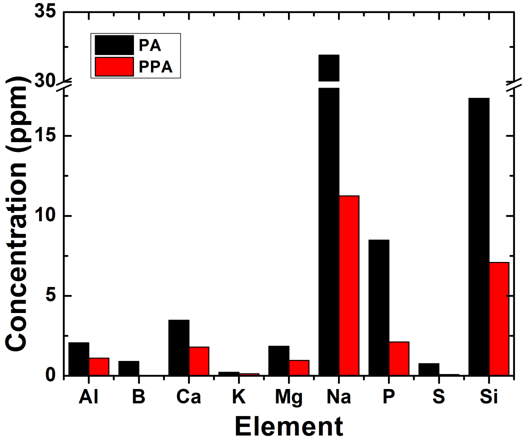
  Plastic material > Time > (Time) x (material)

Leaching index (LI) = solution conductivity + total organic carbon (TOC)

Accomplishments and Progress – Identified Major Species in Structural Material PA and PPA Leachates

Material	TOC (ppm)	Solution Conductivity (µS/cm)
PA	983	221
PPA	47	55



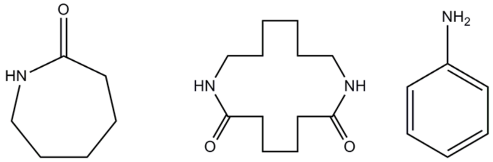


Organics Identified in PA Leachate:

Caprolactam

DCTDD

Aniline



- Leachates contain mixtures of organics and ions
- Less expensive PA material leaches out more contaminants
- Anions: < 15 ppm
  - Anions can adsorb on Pt surface
- Elements: < 35 ppm
  - Some elements can be cations & can affect ionomer conductivity
  - P and S may be in the form of PO_4^{3-} and SO_4^{2-}
- Organics: PPA material is clean
  - Three major organics identified in PA leachates
  - Organics can adsorb on Pt surface and/or affect membrane/catalyst ionomer conductivity

DCTDD : 1,8 Diazacyclotetradecane-2,7-dione

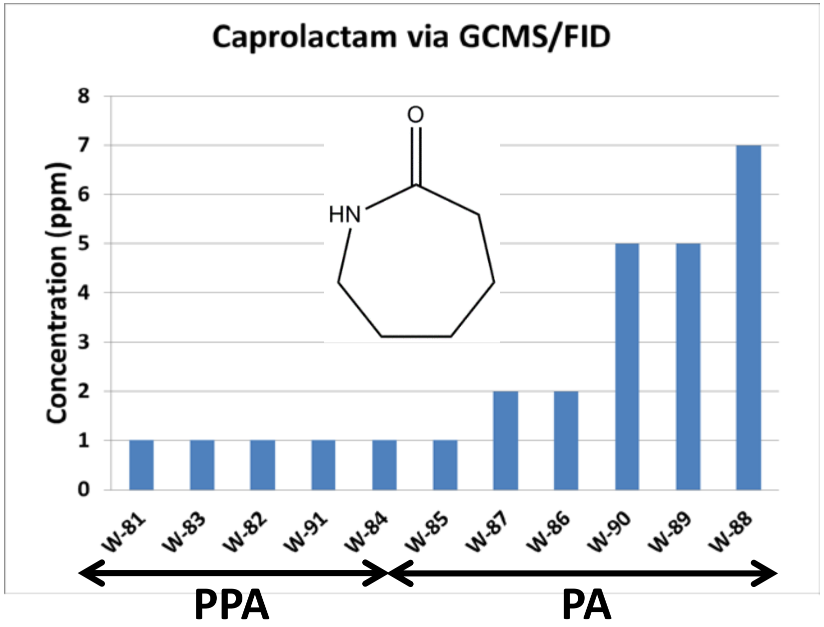
Leachate conditions: 90°C, 1000 h, 1.5 cm^2/ml

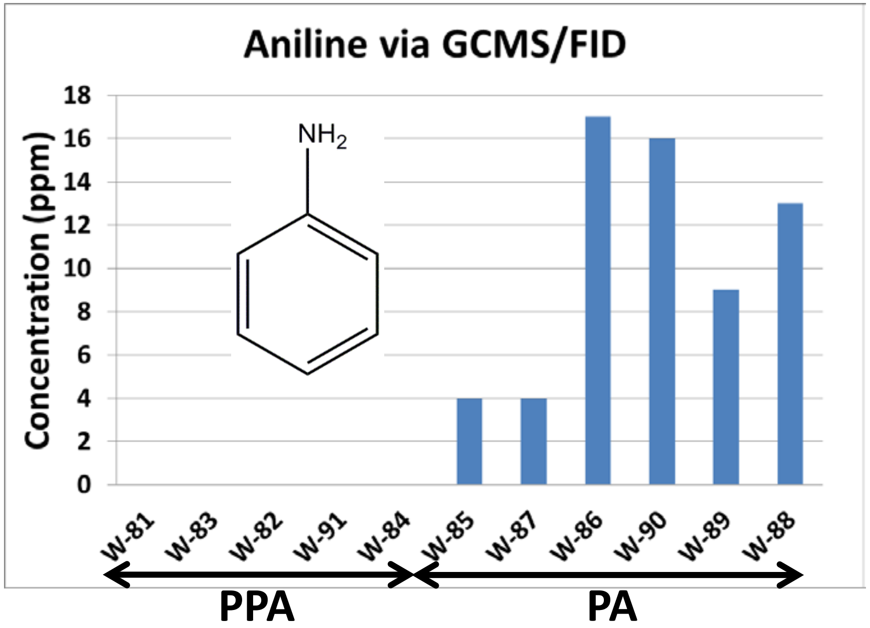
Accomplishments and Progress – Quantified Organic Contaminants in Leachates

Developed GCMS method to quantify concentration of organic contaminants in material leachates

- Three methods were explored to quantify organic concentration (TIC-SIM, TCD, FID)
- GCMS/FID yielded best trade-off between sensitivity and reproducible data
  - PPA materials are relatively clean. For PA, the concentrations of caprolactam were < 10 ppm and concentrations of aniline were < 20 ppm.

The ranges of caprolactam and aniline concentrations found in these structural material leachates provide more realistic dosages to be used in infusion experiments



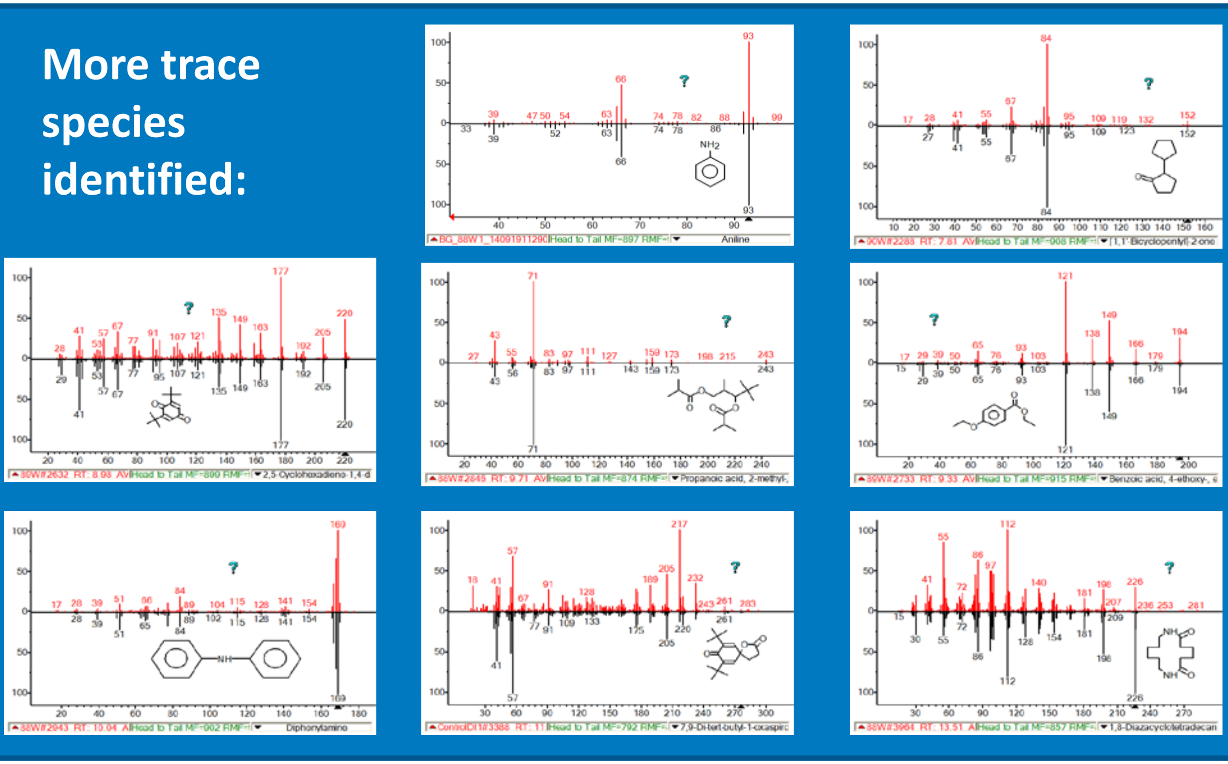


Accomplishments and Progress – More Trace Organic Species Identified via SPME GCMS

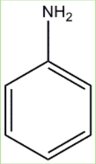
Solid phase micro-extraction (SPME) GCMS identified more species than observed via GCMS liquids method

- Trace species were identifiable due to SPME being a more sensitive technique
- BOP leachates comprise complicated mixtures of organics

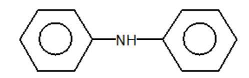
More trace species identified:



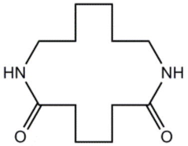
Major species identified:



Aniline



Diphenylamine



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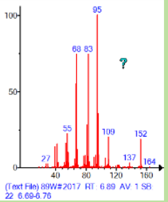
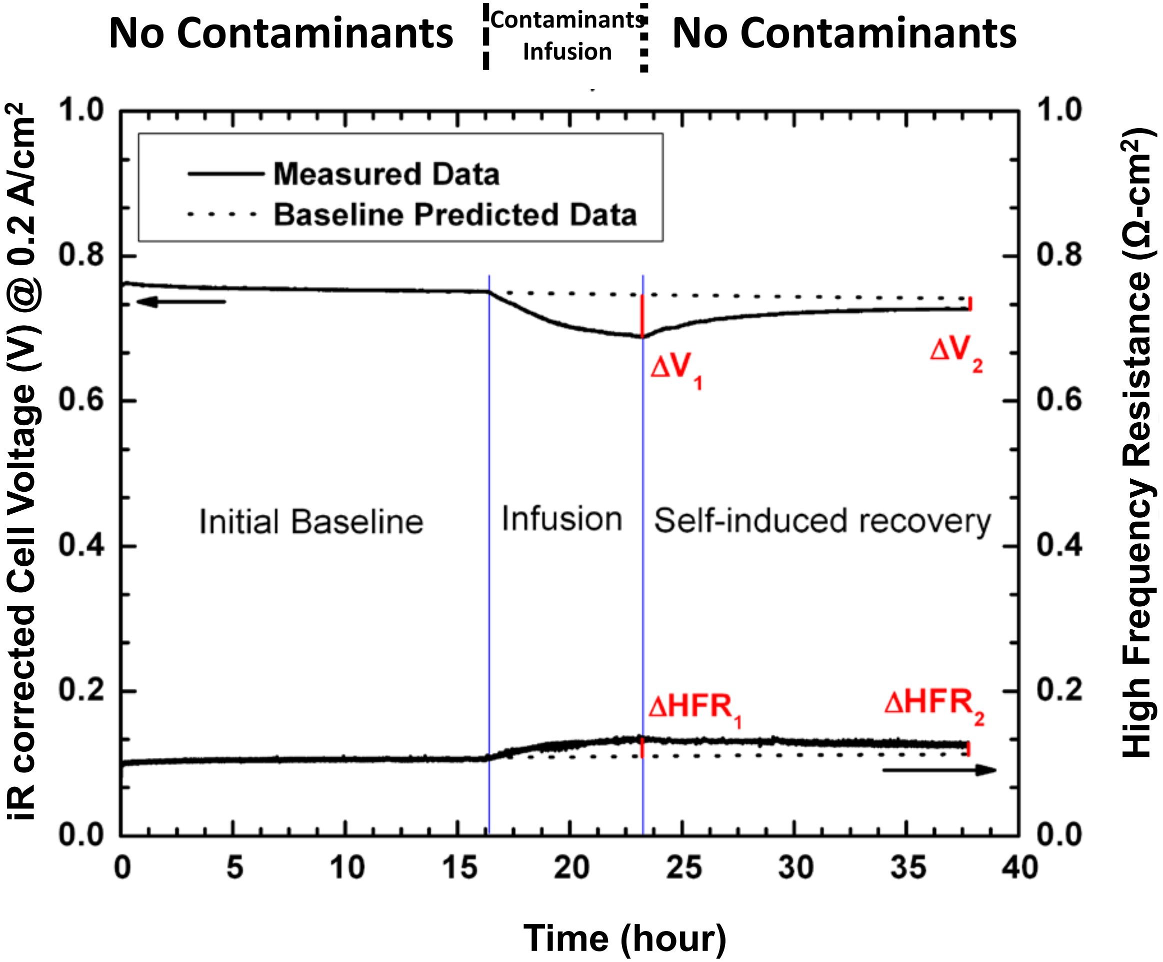


MS1

Accomplishments and Progress – Contaminants Infusion Test Profile



Standard operating conditions (SOC):
Cell temperature = 80°C, back pressure = 150/150 kPa, 0.2 A/cm^2,
32/32% inlet RH, H_2/air stoic = 2/2; cathode Pt loading = 0.4 mg/cm^2

Major results:

→ **voltage loss (ΔV_1) and HFR change (ΔHFR_1) due to contamination**

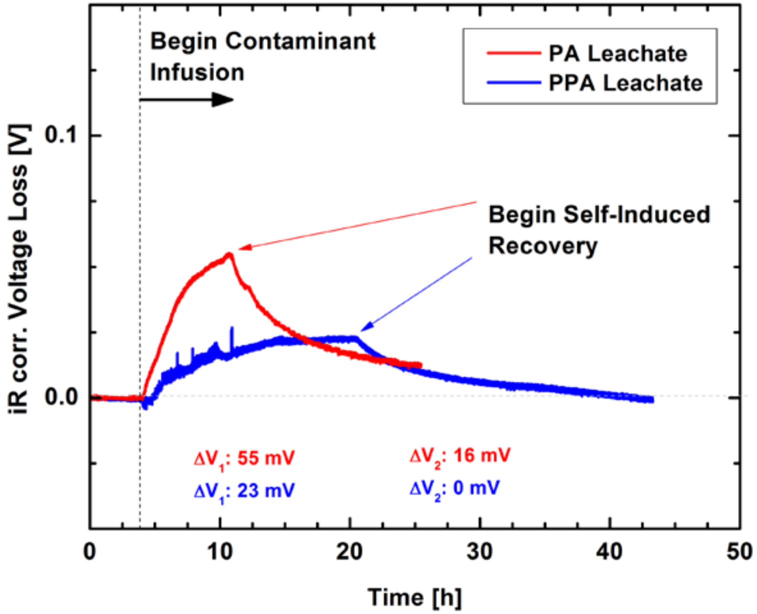
→ **voltage loss (ΔV_2) and HFR change (ΔHFR_2) after self-induced recovery**

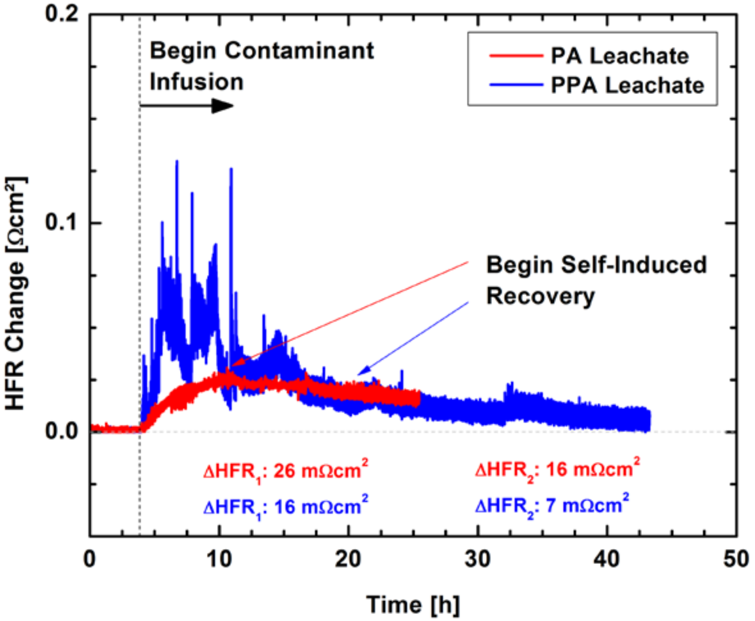
Materials studied:

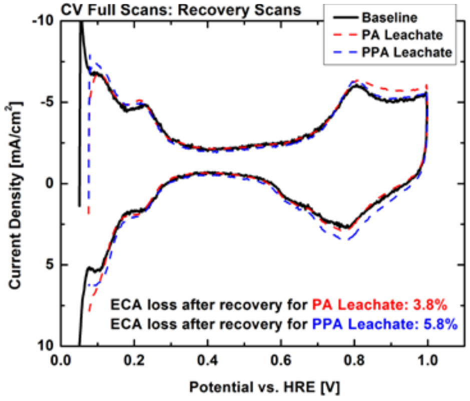
- PA leachate
- PPA leachate
- Caprolactam
- Sulfate
- Mixture

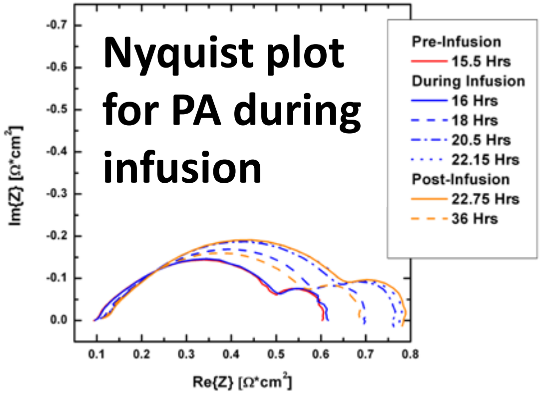
Accomplishments and Progress – Impact of Leachate Solutions on Fuel Cell Performance

- **Both PA and PPA leachate contaminants result in fuel cell performance loss and membrane conductivity change. PA leachate show incomplete self-induced recovery.**
- **Low concentration of contaminants can still have an effect**





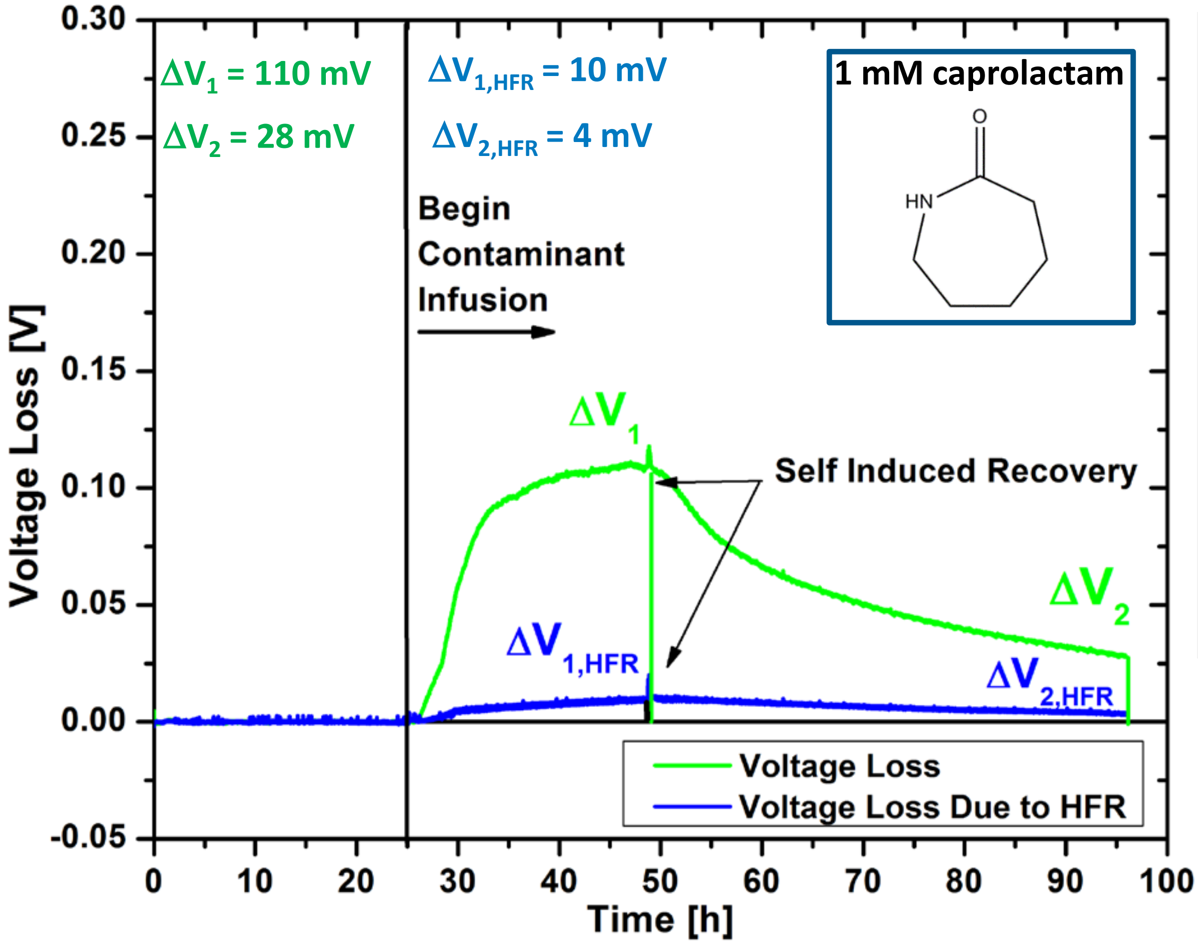




Nyquist plot for PA during infusion

Material	Leachate TOC (ppm)	Leachate Solution Conductivity (µS/cm)	Caprolactam concentration in leachates (ppm)
PA	983	221	5
PPA	47	55	1

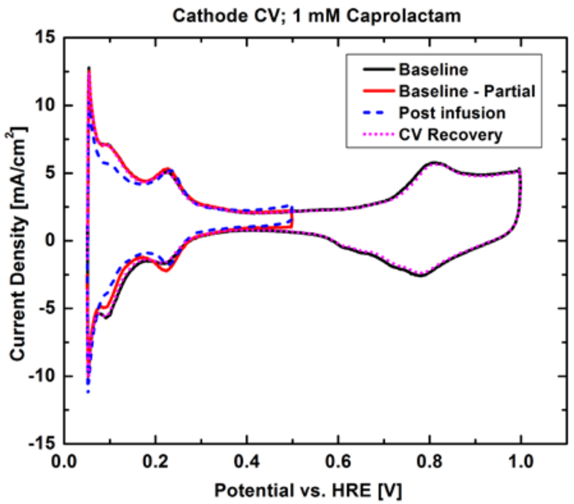
Accomplishments and Progress – Effect of Caprolactam Model Compound on Fuel Cell Performance



Caprolactam results in

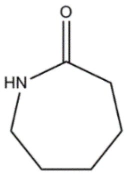
- fuel cell performance loss,
- membrane conductivity change,
- incomplete self-induced recovery

- Voltage loss due to HFR (ΔV_{HFR}) is minimal compared to overall voltage loss (ΔV)
- Ionomer contamination may be a large contributor to overall voltage loss. CVs show minimal poisoning of Pt sites .

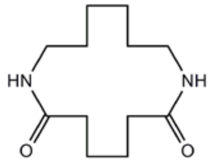


Caprolactam model compound chosen to represent both:

caprolactam



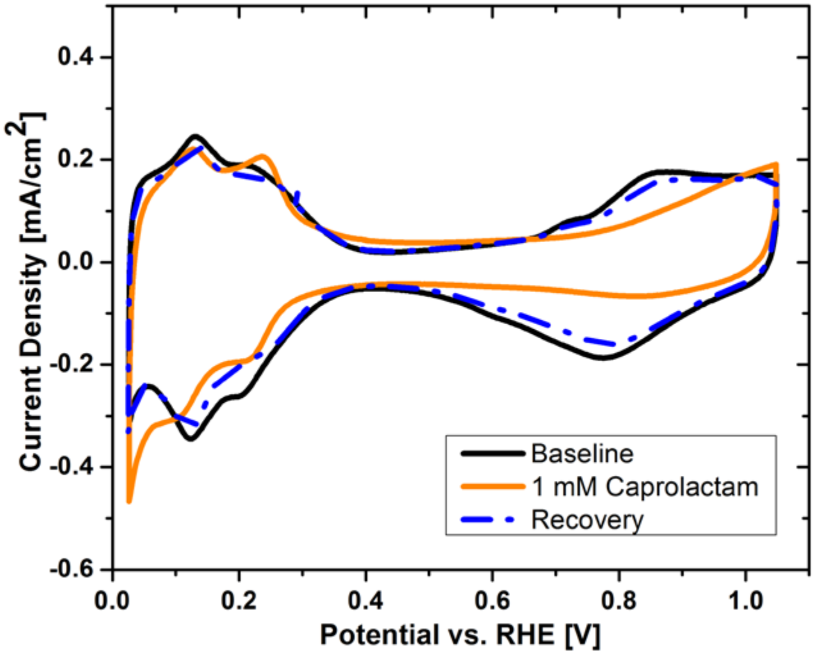
DCTDD

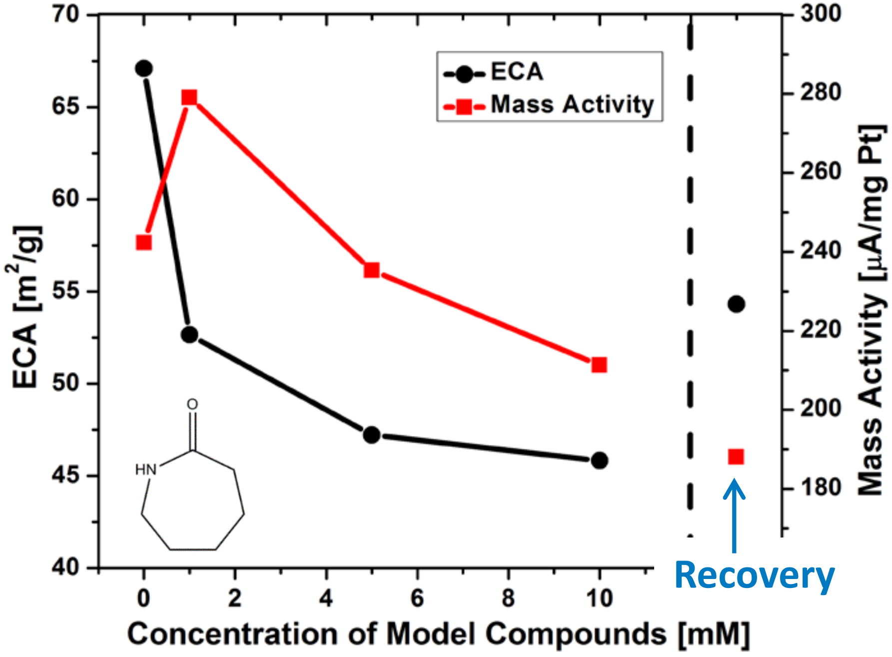


Accomplishments and Progress – Effect of Organic Model Compound on ECA and ORR Activity (Ex-Situ)

Ex-situ rotating disc electrode experiments support that caprolactam has a small impact on ECA and ORR mass activity.

- Decrease in mass activity is due to organic compounds adsorbing onto Pt sites
- The majority of the ECA was recoverable but mass activity continued to decrease.
  - The effect of caprolactam on ORR mass activity is not understood at this time
- Caprolactam impact was less compared to other organic compounds derived from assembly aids materials previously studied



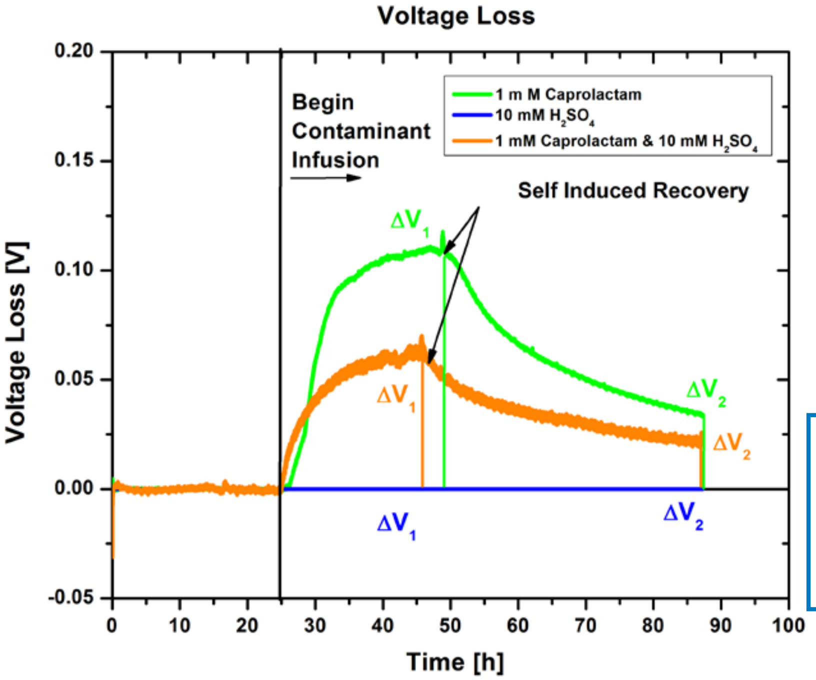


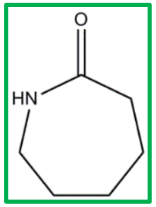
ECA = electrochemical surface area
ORR = oxygen reduction reaction

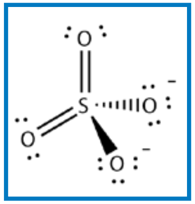
cell temperature = room temperature,
WE = 46wt% Pt/Vulcan, CE = Pt mesh, RE = RHE, 0.1 M $HClO_4$, 20 mV/s
ORR : 1600 rpm, 20 mV/s between -0.01 to 1 V vs. RHE

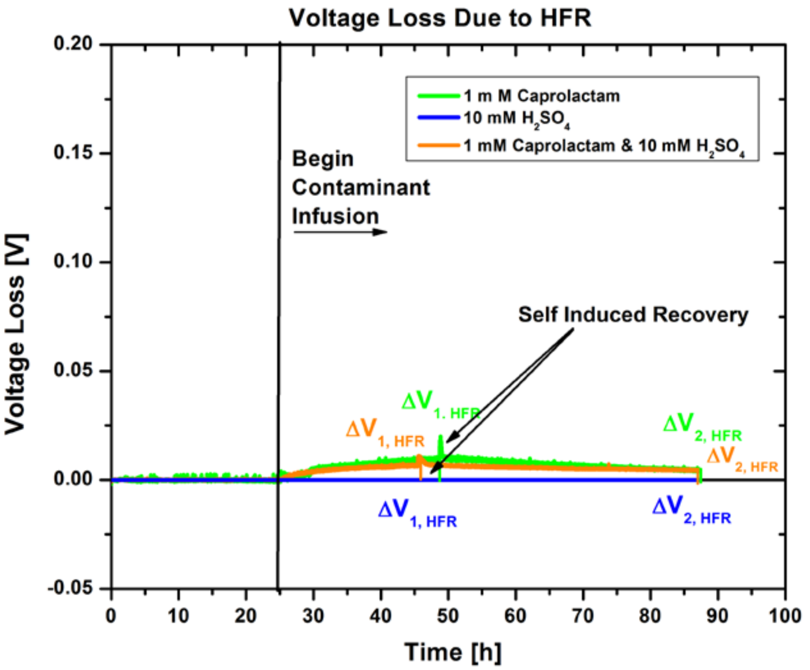
Accomplishments and Progress – Effect of Caprolactam, Sulfate, and Mixtures of Model Compounds on Fuel Cell Performance

- **Interaction between caprolactam and sulfate observed**
  - **The amide group in caprolactam can be protonated and react with the sulfate via acid/base reaction**
- **Sulfate showed no impact on fuel cell performance**
  - **Donnan exclusion effect and/or non-adsorption of sulfate onto Pt oxide?**









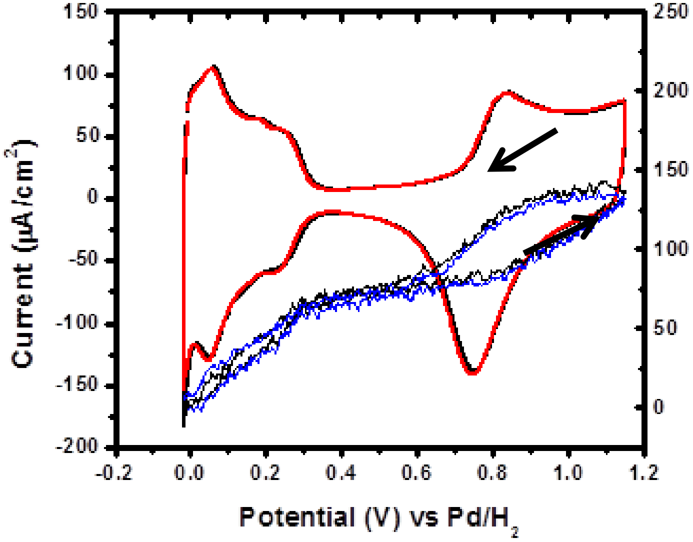
ΔV_1: 110 mV	ΔV_2: 35 mV
ΔV_1: 67 mV	ΔV_2: 22 mV
ΔV_1: 0 mV	ΔV_2: 0 mV

$\Delta V_{1, HFR}$: 20 mV	$\Delta V_{2,HFR}$: 6 mV
$\Delta V_{1, HFR}$: 10 mV	$\Delta V_{2, HFR}$: 4 mV
$\Delta V_{1, HFR}$: 0 mV	$\Delta V_{2, HFR}$: 0 mV

Accomplishments and Progress – Effect of PFSA Membrane Degradation Compounds on Catalyst

Black: Baseline; Red: UFA CV; Blue: UFA EQCM

Christ J. M.; Staub C.; Richards R. M.; Dinh H. N.; *In Preparation,* (2014)

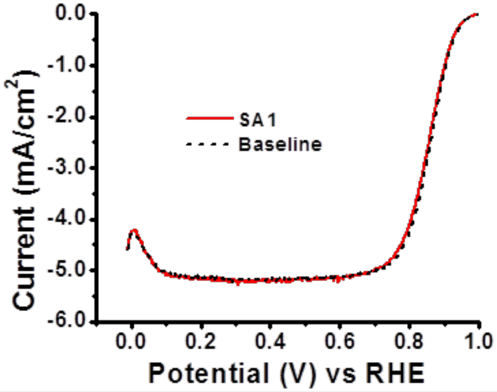


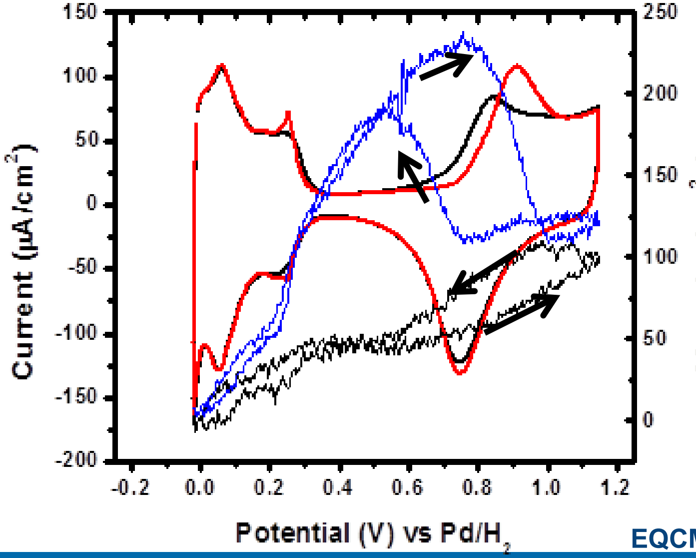
$CF_3—CF_2—CF_2—CF_2—SO_3H$

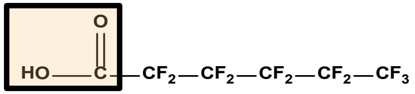
SA1

Electrode surface coverage at 0.9 V < 1%

Perfluorinated <u>sulfonate</u> anion appears to <u>NOT adsorb</u> on poly Pt and has no effect on ORR activity







$HO—C(=O)—CF_2—CF_2—CF_2—CF_2—CF_3$

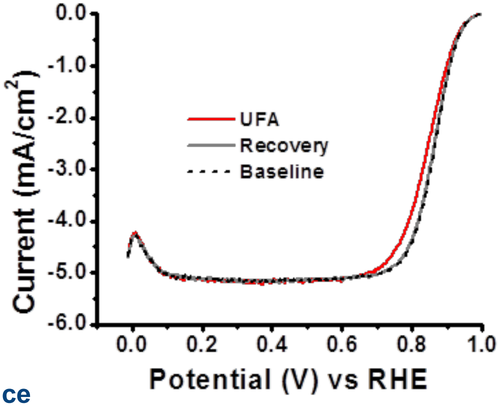
UFA

Electrode surface coverage at 0.9 V: 50%

17% loss in kinetic current

Perfluorinated <u>carboxylate</u> anion

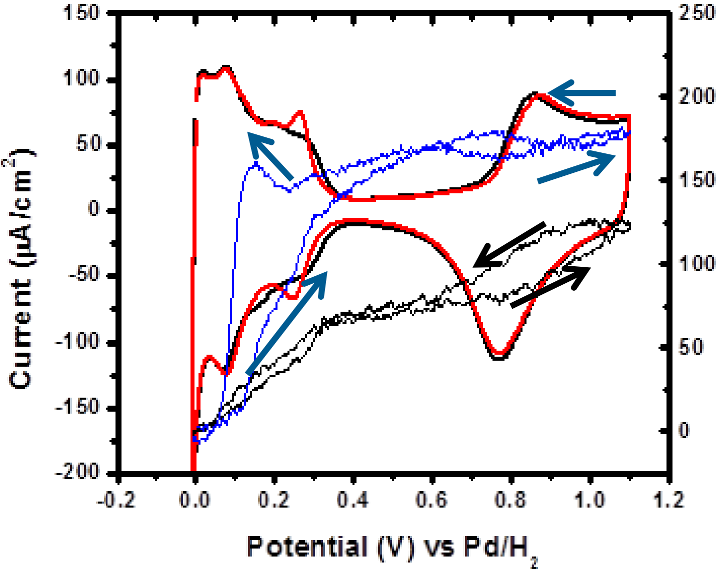
- **adsorbs onto Pt metal,**
- **hinders Pt oxide formation, and**
- **is displaced by Pt oxide**

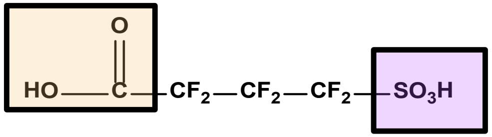


WE = AT-cut quartz crystal coated with Pt/TiO_2 on either side; 6 MHz; CE = Pt mesh
0.1 mM in 0.1 M $HClO_4$; RE = Pd/H_2;
EQCM = 50 mV/s; ORR: 20 mV/s
EQCM = electrochemical quartz crystal microbalance

Accomplishments and Progress – Effect of PFSA Membrane Degradation Compounds on Catalyst

- **Functional group and fluorocarbon chain length play a role in adsorption effect**
- **Perfluorinated di-acids adsorb onto both Pt metal and Pt oxide surfaces**
  - **Di-acids have a different effect on Pt; sulfonate anion appears to play a role**
- **EQCM is a good complementary diagnostic to understand poisoning mechanism of contaminants on catalyst**



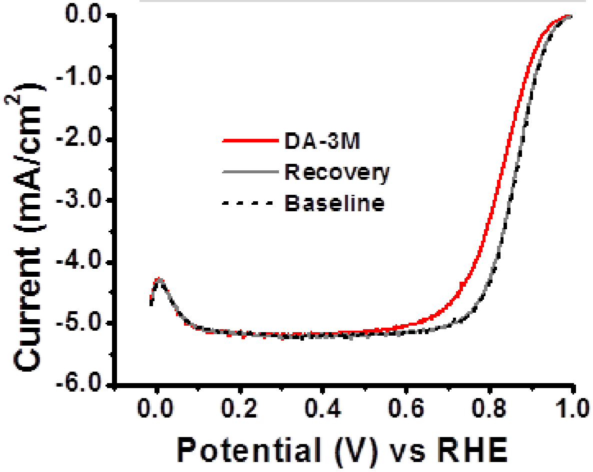

$HO-C(=O)-CF_2-CF_2-CF_2-SO_3H$

(3M™ ionomer degradation product)

DA-3M

Electrode surface coverage at 0.9 V: 43%

47% loss in kinetic current



WE = AT-cut quartz crystal coated with Pt/TiO_2 on either side; 6 MHz; CE = Pt mesh
0.1 mM in 0.1 M $HClO_4$; RE = Pd/H_2;
EQCM = 50 mV/s; ORR: 20 mV/s
EQCM = electrochemical quartz crystal microbalance

Black: Baseline; Red: UFA CV; Blue: UFA EQCM

Christ J. M.; Staub C.; Richards R. M.; Dinh H. N.; *In Preparation* (2014)

Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

- **This project was not reviewed last year.**

Collaborators

Institutions	Role
National Renewable Energy Laboratory (NREL): H. Dinh (PI), G. Bender, C. Macomber, H. Wang, C. Staub, L. McGovern, KC Neyerlin, B. Pivovar	**Lead: analytical characterization; development of characterization methods; fundamental studies of contamination mechanism using model compound**
General Motors LLC (GM): P. Yu, B. Lakshmanan, E.A. Bonn, Q. Li, A. Luong, R. Moses,	**CRADA partner: define material sets, analytical characterization and in-depth analysis of structural materials leachates**
Colorado School of Mines (CSM): R. Richards, J. Christ	**Sub: membrane degradation material study**
3M: S. Hamrock	**In-kind partner: Provide membrane degradation products**

Interactions: Participate in the DOE Durability Working Group

Proposed Future Work

- Perform mechanistic studies on mixtures of model compounds to understand interaction between different species in leachate solutions and their effect on fuel cell performance
- Develop an understanding of the impact of contaminants on catalyst ionomer
- Study the effect of contaminants on low loading catalyst (0.1 mg Pt/cm^2) and advanced catalysts (e.g., Pt alloys/C)
- Study the effect of non-sulfonated perfluorinated membrane degradation products on fuel cell performance
- Identify and quantify volatile species, if any exist, derived from structural materials
- Measure rates of soluble leachates in solution and volatiles in headspace

Summary

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

Approach: Quantify leachate concentrations and determine the effect of leaching parameters on material leaching concentration, determine the fuel cell performance impact of lower leachate concentrations, perform mechanistic studies on organic and ionic model compounds derived from structural plastics to understand the effect of individual and mixtures of compounds on fuel cell performance, and provide guidance on future material selection to enable the fuel cell industry in making cost-benefit analyses of system components.

Accomplishments and Progress: Completed all milestones on time; expanded the set of leaching conditions (time, temperature, surface area/water ratio) and determined that plastic material type and time significantly impacted leachate concentration; determined that low leachate concentrations, caprolactam, and mixtures of caprolactam and sulfate had an impact on fuel cell performance, including Pt adsorption and membrane poisoning; performed multiple techniques (CV, EQCM, ORR) to understand the role of functional groups and fluorocarbon chain length on Pt adsorption and ORR activity; and added Naval Research Lab publications on contaminants to the NREL contaminants project website to provide a central location for fuel cell contaminant information.

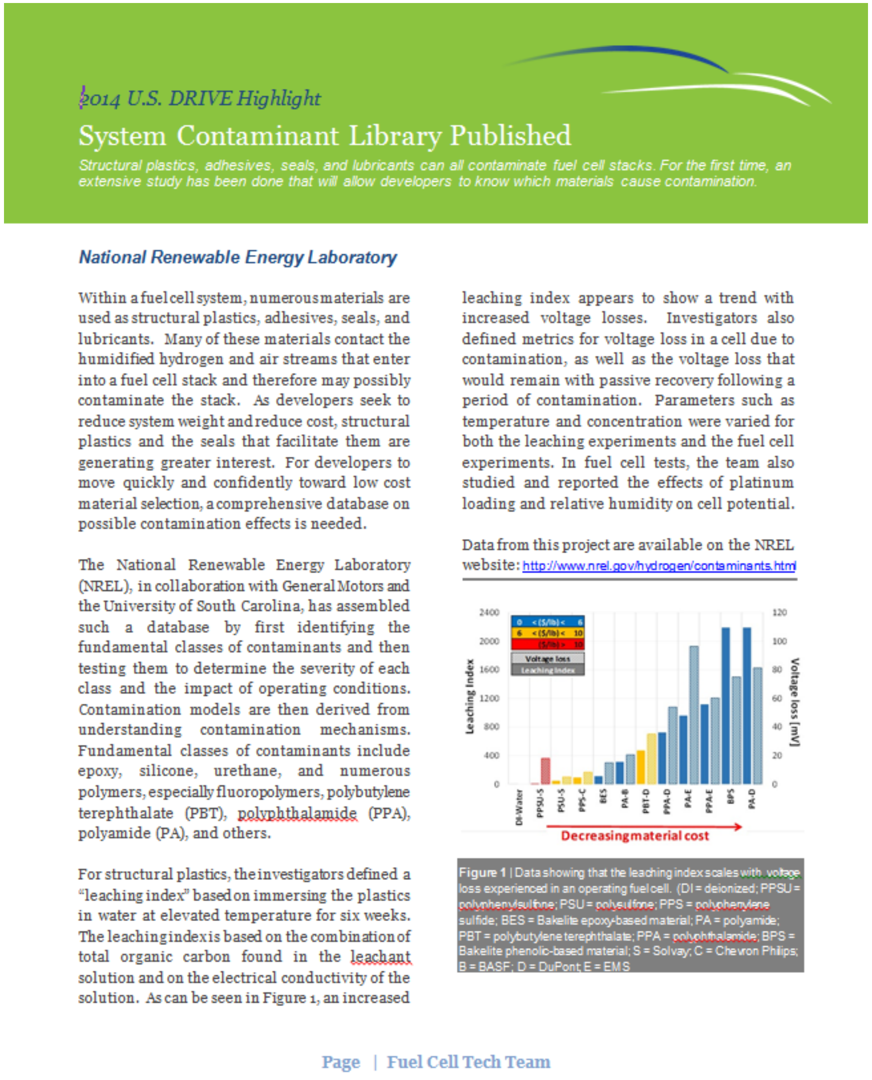
Collaborations: Our team has significant data and relevant experience in contaminants, materials, and fuel cells. We are collaborating with GM via a CRADA, Colorado School of Mines via a subcontract, and partner with 3M for membrane degradation materials.

Proposed Future Work: Study the effect of contaminants on low loading catalyst (0.1 mg Pt/cm^2) and advanced catalysts (e.g., Pt alloys/C); study the effect of non-sulfonated perfluorinated membrane degradation products on fuel cell performance; and identify and quantify volatile species, if any exist, derived from structural materials.

Technical Back-Up Slides

Project Highlights

FCTT Accomplishment Report



2014 U.S. DRIVE Highlight

System Contaminant Library Published

Structural plastics, adhesives, seals, and lubricants can all contaminate fuel cell stacks. For the first time, an extensive study has been done that will allow developers to know which materials cause contamination.

National Renewable Energy Laboratory

Within a fuel cell system, numerous materials are used as structural plastics, adhesives, seals, and lubricants. Many of these materials contact the humidified hydrogen and air streams that enter into a fuel cell stack and therefore may possibly contaminate the stack. As developers seek to reduce system weight and reduce cost, structural plastics and the seals that facilitate them are generating greater interest. For developers to move quickly and confidently toward low cost material selection, a comprehensive database on possible contamination effects is needed.

The National Renewable Energy Laboratory (NREL), in collaboration with General Motors and the University of South Carolina, has assembled such a database by first identifying the fundamental classes of contaminants and then testing them to determine the severity of each class and the impact of operating conditions. Contamination models are then derived from understanding contamination mechanisms. Fundamental classes of contaminants include epoxy, silicone, urethane, and numerous polymers, especially fluoropolymers, polybutylene terephthalate (PBT), polyphthalamide (PPA), polyamide (PA), and others.

For structural plastics, the investigators defined a "leaching index" based on immersing the plastics in water at elevated temperature for six weeks. The leaching index is based on the combination of total organic carbon found in the leachant solution and on the electrical conductivity of the solution. As can be seen in Figure 1, an increased leaching index appears to show a trend with increased voltage losses. Investigators also defined metrics for voltage loss in a cell due to contamination, as well as the voltage loss that would remain with passive recovery following a period of contamination. Parameters such as temperature and concentration were varied for both the leaching experiments and the fuel cell experiments. In fuel cell tests, the team also studied and reported the effects of platinum loading and relative humidity on cell potential.

Data from this project are available on the NREL website: http://www.nrel.gov/hydrogen/contaminants.html

Figure 1 | Data showing that the leaching index scales with voltage loss experienced in an operating fuel cell. (DI = deionized; PPSU = polyphenylsulfone; PSU = polysulfone; PPS = polyphenylene sulfide; BES = Bakelite epoxy-based material; PA = polyamide; PBT = polybutylene terephthalate; PPA = polyphthalamide; BPS = Bakelite phenolic-based material; S = Solvay; C = Chevron Philips; B = BASF; D = DuPont E = EMS

Page | Fuel Cell Tech Team

NREL's R&D Technical Highlight

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Making Fuel Cells Cleaner, Better, and Cheaper

Highlights in Research and Development

NREL helps reduce contaminants in fuel cells, enabling the industry to cut costs and commercialize state-of-the-art technologies.

As fuel cell systems become more commercially competitive, and as automotive fuel cell research and development trend toward decreased catalyst loadings and thinner membranes, fuel cell operation becomes even more susceptible to contaminants. Therefore, the National Renewable Energy Laboratory (NREL) and its partners have performed research on contaminants derived from fuel cell system component materials. Such materials include structural plastics, lubricants, greases, adhesives, sealants, and hoses. Contaminants from all of these components affect the performance and durability of fuel cell systems.

NREL research has shown that less expensive fuel cell materials leach more contaminants and cause more voltage loss. Graph by Huyen Dinh, NREL

Between July 2009 and September 2013, NREL led a team to study the effect of system contaminants on the performance of polymer electrolyte member fuel cells. NREL collaborated with General Motors, the University of South Carolina, and others to screen about 60 balance of plant materials. The materials are from different manufacturers, comprise different chemistries, and are used for different functions.

The team assembled the contaminant database by first identifying classes of contaminants, then testing them to assess the impact of each class on fuel cell performance and the reversibility of the contaminant's impact. Contamination models were then developed from the knowledge gained about the contamination mechanisms. The team determined that the fundamental classes of contaminants included epoxy, silicone, urethane, and numerous polymers, especially fluoropolymers, polybutylene terephthalate (PBT), polyphthalamide (PPA), and polymide (PA), among others.

The fuel cell community can now easily benefit from the study because NREL designed an interactive online tool that both archived the study results and allows users to screen materials according to contaminant characteristics. (The tool is also available to the public.) By knowing the contamination potential of various system components, fuel cell developers can select appropriate fuel cell materials during the design phase, and perform more accurate cost-benefit analyses. Thus, the industry can continue to reduce overall costs, which will enable commercialization of fuel cell technologies.

Technical Contact: Huyen Dinh, *huyen.dinh@nrel.gov*

References: "Hydrogen and Fuel Cell Research: Contaminants" (2014). National Renewable Energy Laboratory. *http://www.nrel.gov/hydrogen/contaminants.html* (See "System-Derived Contaminants," Data Tool tab)

Key Research Results

Achievement

NREL and its partners have completed an extensive study of plastic materials that may be used in fuel cell systems, and published a comprehensive database about possible contamination effects from those materials.

Key Result

NREL designed an interactive online tool to help fuel cell developers and materials suppliers explore the results of the contaminants study.

Potential Impact

By having a better understanding of 1) the degree of contamination caused by different materials and 2) the contaminating species, fuel cell developers will be able to specify materials for their fuel cell systems that minimize contamination. Material suppliers will be better prepared to provide highly desirable (i.e. low-contaminating) materials to their customers. By reducing contamination in fuel cells, overall performance and durability will likely improve and overall costs will likely decrease. Such cost savings could enable and quicken commercialization of fuel cell technologies.

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.

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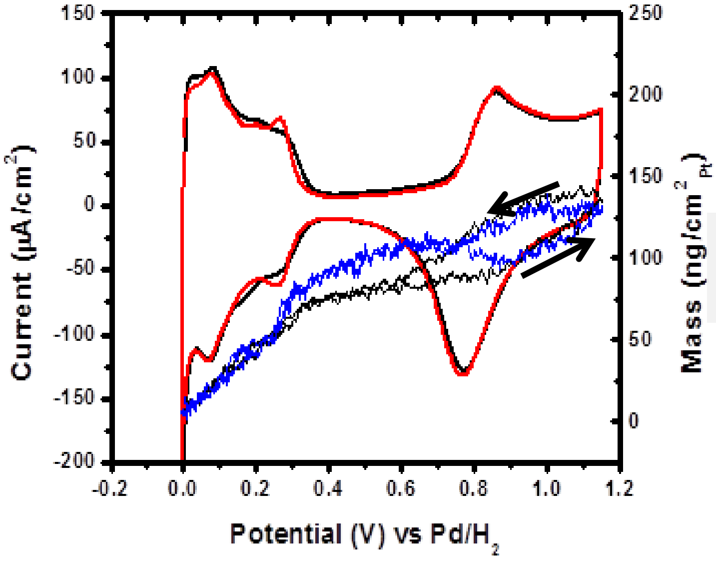
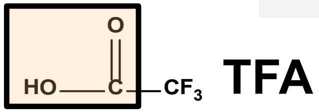
Accomplishments and Progress – Effect of PFSA Membrane Degradation Compounds on Catalyst

Black: Baseline; Red: UFA CV; Blue: UFA EQCM

Christ J. M.; Staub C.; Richards R. M.; Dinh H. N.; *In Preparation,* (2014)

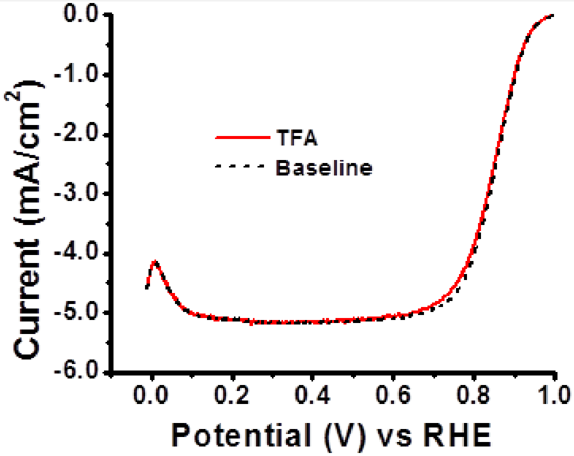
Short chain perfluorinated carboxylate anion, TFA, adsorbs on Pt metal but does NOT adsorb onto Pt oxide and has minimal effect on ORR activity.



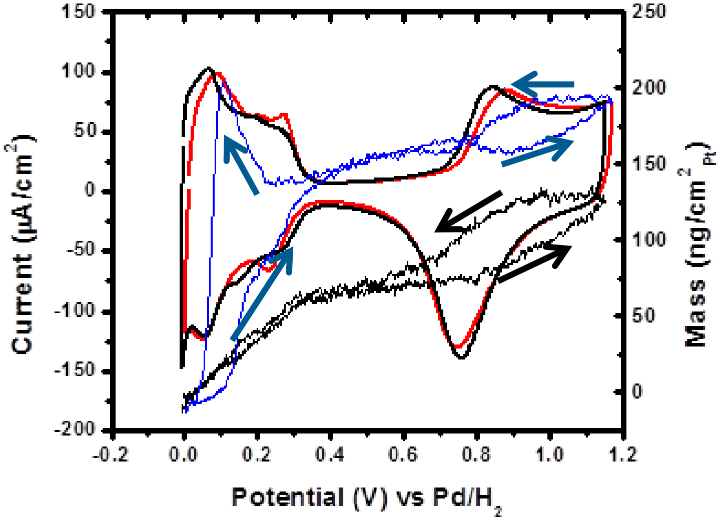


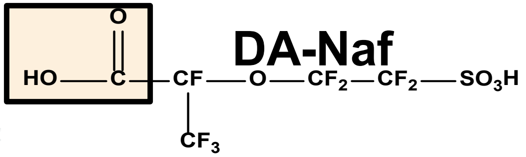
$HO-C(=O)-CF_3$

Electrode surface coverage at 0.9 V < 1%



(Nafion® ionomer degradation product)



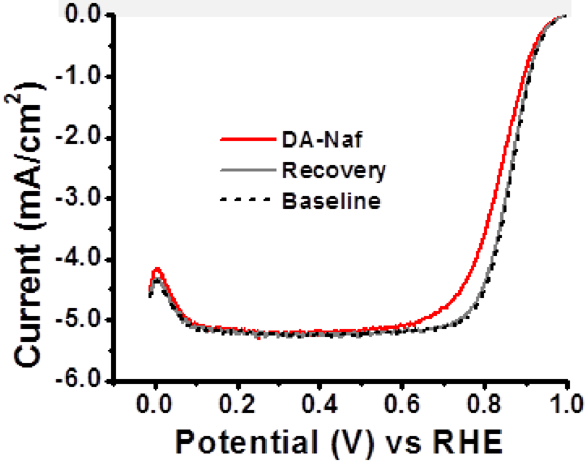


$HO-C(=O)-CF(CF_3)-O-CF_2-CF_2-SO_3H$

Electrode surface coverage at 0.9 V: 25%

DA-Naf adsorbs onto Pt metal and Pt oxide surfaces, and inhibits Pt oxide growth (but not completely)

44% loss in kinetic current



Accomplishments and Progress – Effect of Caprolactam, Sulfate, and Mixtures of Model Compounds on Fuel Cell Performance

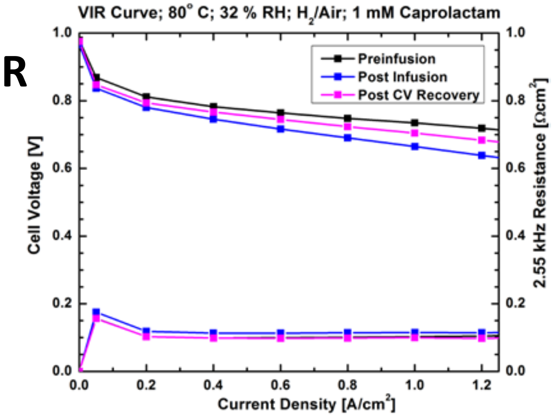
- **VIRs and CVs show that caprolactam and sulfate mixture has an effect on fuel cell performance and ECAs.**
- **Contamination effect of mixtures appear to be recoverable**

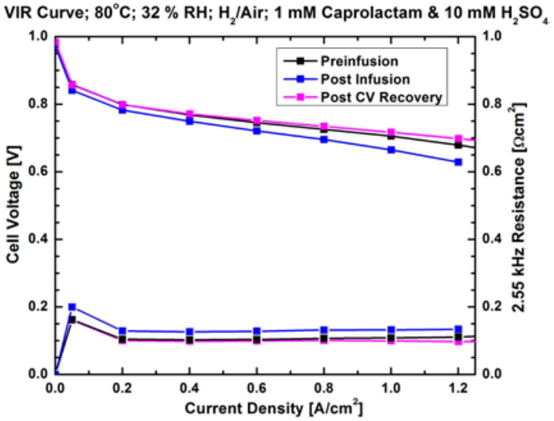
Caprolactam

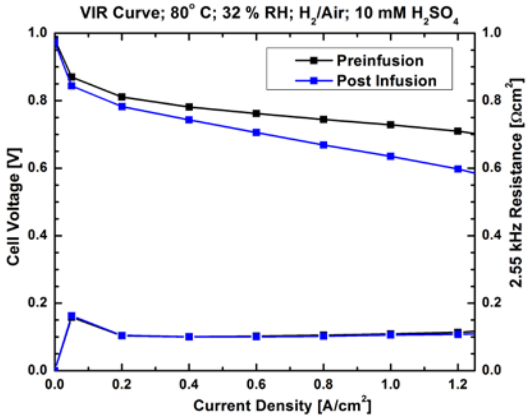
Caprolactam + Sulfate Mixture

Sulfate

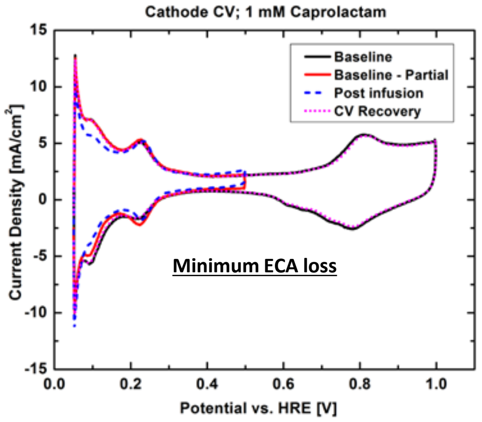
VIR



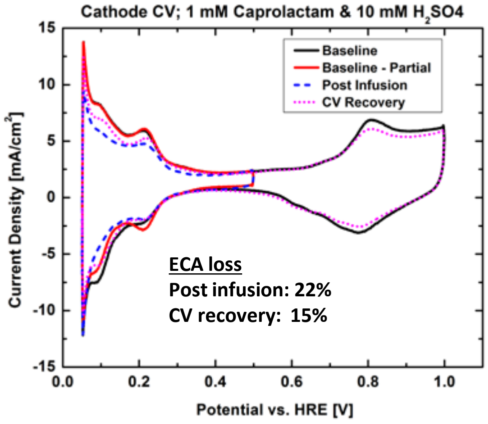




CV



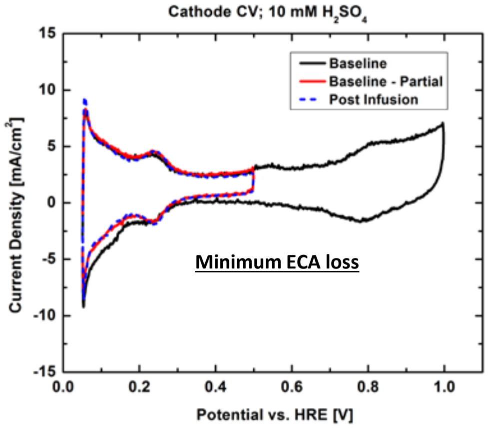
Minimum ECA loss



ECA loss

Post infusion: 22%

CV recovery: 15%



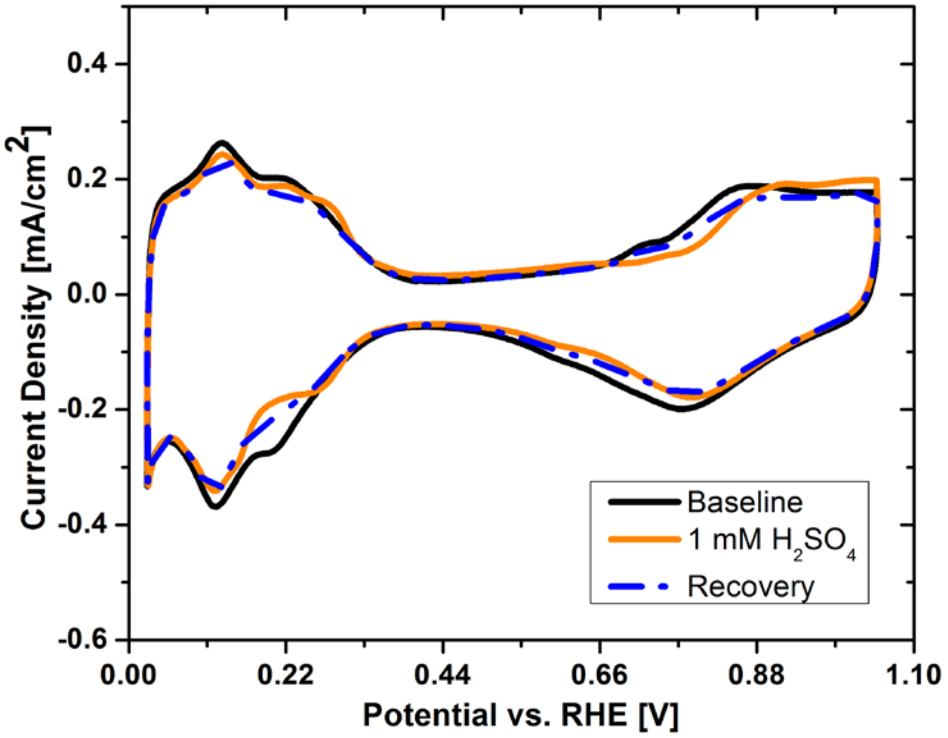
Minimum ECA loss

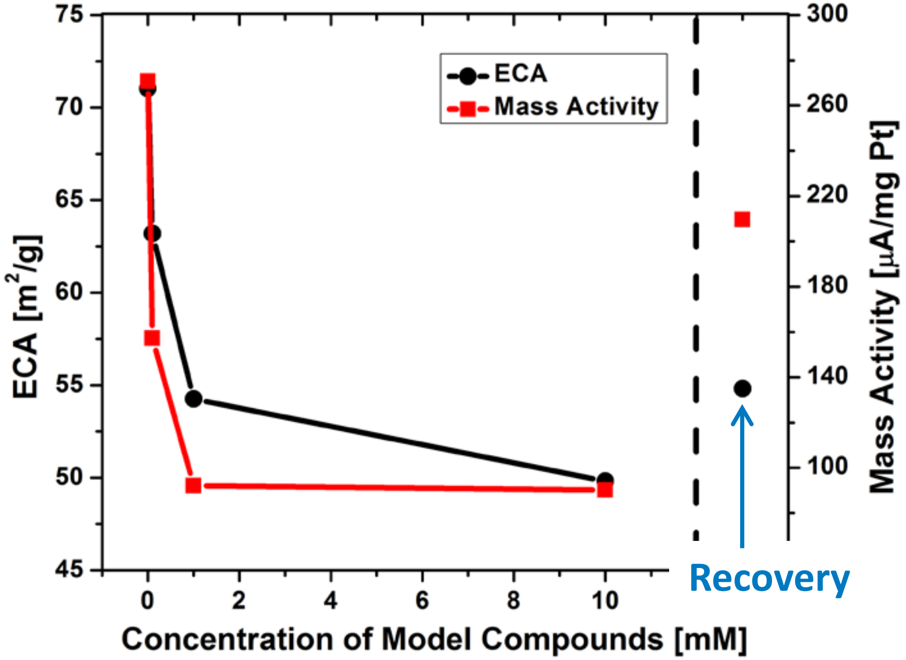
post-CV recovery curve for sulfate was not obtained due to a leak that developed after post infusion CVs

Accomplishments and Progress – Effect of Sulfate Model Compound on ECA and ORR Activity (Ex-Situ)

Sulfate has a larger impact on ORR mass activity than on ECA and the majority of the ECA and mass activity are recoverable.

- Decrease in mass activity is partially due to sulfate anion adsorbing onto Pt sites

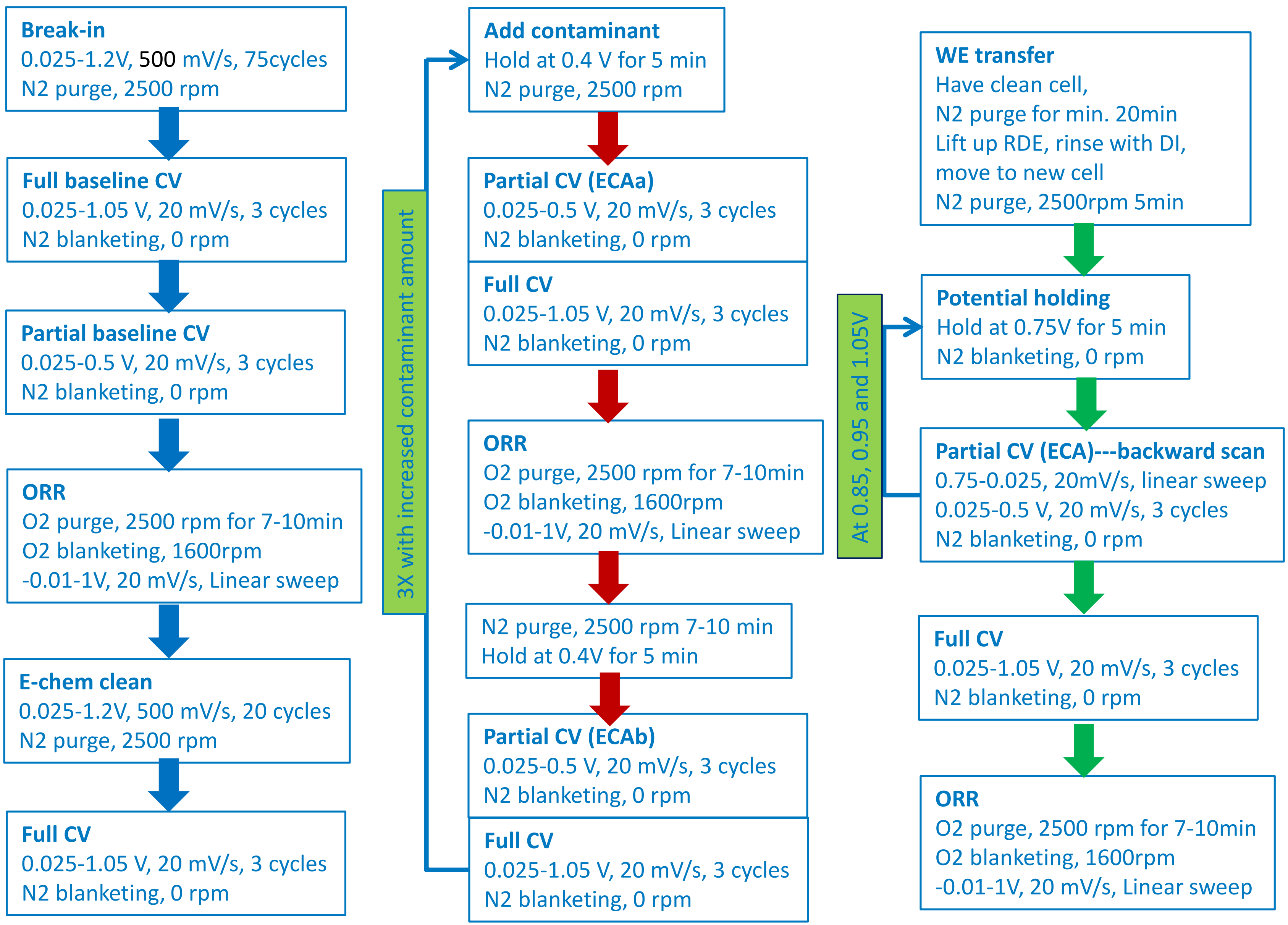




ECA = electrochemical surface area
ORR = oxygen reduction reaction

cell temperature = room temperature,
WE = 46wt% Pt/Vulcan, CE = Pt mesh, RE = RHE, 0.1 M HClO4, 20 mV/s
ORR : 1600 rpm, 20 mV/s between -0.01 to 1 V vs. RHE

RDE Protocol



Baseline

Break-in
0.025-1.2V, 500 mV/s, 75cycles
N2 purge, 2500 rpm

Full baseline CV
0.025-1.05 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Partial baseline CV
0.025-0.5 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

ORR
O2 purge, 2500 rpm for 7-10min
O2 blanketing, 1600rpm
-0.01-1V, 20 mV/s, Linear sweep

E-chem clean
0.025-1.2V, 500 mV/s, 20 cycles
N2 purge, 2500 rpm

Full CV
0.025-1.05 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Contamination

3X with increased contaminant amount

Add contaminant
Hold at 0.4 V for 5 min
N2 purge, 2500 rpm

Partial CV (ECAa)
0.025-0.5 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Full CV
0.025-1.05 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

ORR
O2 purge, 2500 rpm for 7-10min
O2 blanketing, 1600rpm
-0.01-1V, 20 mV/s, Linear sweep

N2 purge, 2500 rpm 7-10 min
Hold at 0.4V for 5 min

Partial CV (ECAb)
0.025-0.5 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Full CV
0.025-1.05 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Recovery

WE transfer
Have clean cell,
N2 purge for min. 20min
Lift up RDE, rinse with DI,
move to new cell
N2 purge, 2500rpm 5min

At 0.85, 0.95 and 1.05V

Potential holding
Hold at 0.75V for 5 min
N2 blanketing, 0 rpm

Partial CV (ECA)---backward scan
0.75-0.025, 20mV/s, linear sweep
0.025-0.5 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

Full CV
0.025-1.05 V, 20 mV/s, 3 cycles
N2 blanketing, 0 rpm

ORR
O2 purge, 2500 rpm for 7-10min
O2 blanketing, 1600rpm
-0.01-1V, 20 mV/s, Linear sweep