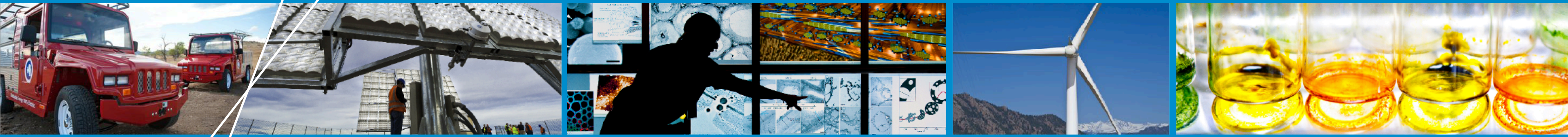
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Effect of System Contaminants on PEMFC Performance and Durability



Venue: 2013 DOE Hydrogen and Fuel Cells Program Review

Presenter: Huyen Dinh (PI)

National Renewable Energy Laboratory

Date: May 14, 2013

FC048

Project Overview

Timeline

Start: July 2009
End: September 2013
% complete: ~90%

Budget

Total project funding:

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

Funding received in FY12:
$1475K*
Planned Funding for FY13:
$1690K*

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

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*
University of South Carolina*
University of Hawaii*
Colorado School of Mines*
Los Alamos National Laboratory
3M (in-kind partner)
Ballard Power Systems (***new*** in-kind partner)
Nuvera (***new*** in-kind partner)

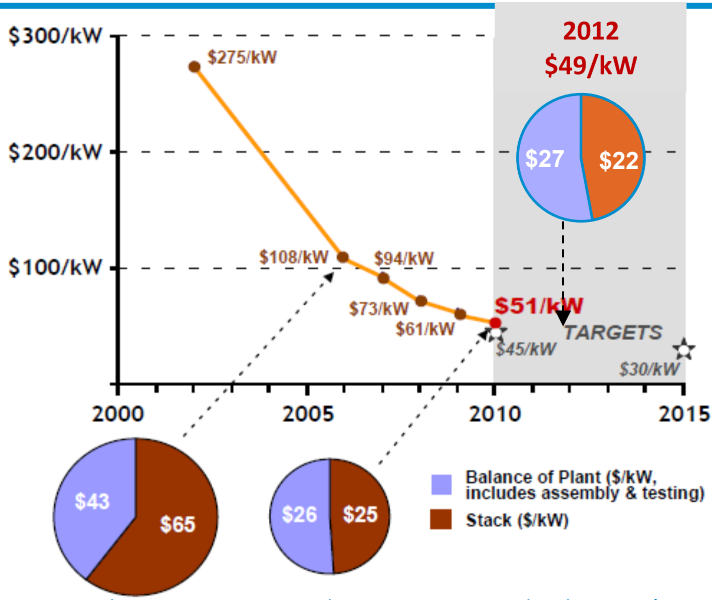
* denotes subcontractor

Relevance

- **System contaminants have been shown to affect the performance/ durability of fuel cell systems (GM).**
- **Balance of plant (BOP) costs have risen in importance with decreasing stack costs.**

Impact

- **Increase performance and durability by limiting contamination related losses**
- **Decrease overall fuel cell system costs by lowering BOP material costs.**



DOE Hydrogen Program Record # 10004, 2010R and Rick Farmer's presentation on Fuel Cell Technologies: FY2011 Budget Request Briefing, Feb. 12, 2010

Examples of common additives in automotive thermoplastics:

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

Approach

Status	Core Project Objectives	
Complete	1. Identify fundamental classes of contamination	
Complete	2. Develop and validate test methods	2010-2011
Complete	3. Identify severity of contaminants	2010-2011
In progress	4. Identify impact of operating conditions	2012-2013
In progress	5. Identify poisoning mechanisms	2012-2013
In progress	6. Develop models/predictive capability	2012-2013
Future work	7. Provide guidance on future material selection	End of FY2013

Dissemination of information on NREL Website:
http://www.nrel.gov/hydrogen/contaminants.html

Approach – FY12-FY13 Milestones

FY 1 2	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	100%
	2	Down-select 20% of all materials and model compounds for in-depth parametric studies	07/2012	100%
	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	100%
FY 1 3	1	Study the effect of three model compounds on ORR activity, quantifying performance loss and recovery in ex-situ experiments.	01/2013	100%
	2	Quantify the extent of in-situ voltage losses due to specific contamination mechanisms (ion exchange effects in membranes and poisoning of catalysts) for two model compounds	06/2013	80%
	3	Identify the impact of fuel cell operating conditions (e.g., RH, temperature, and contaminant concentration) on voltage loss and recovery for two system contaminant extracts	8/2013	70%

Technical Accomplishments

Previous Major Technical Accomplishments :

1. **Screened <u>55</u> 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 origin of leached species**
5. **Selected model compounds and extracts for parametric studies**

Major Technical Accomplishments Since Last Year:

1. **Performed in-depth parametric studies on**
    a. **extracts**
    b. **organic model compounds and mixtures**
2. **Identified contamination mechanism**
    a. **Individual organic model compounds**
    b. **Mixtures of organic model compounds**
    c. **In-situ & ex-situ experiments**
3. **Developed model for contamination mechanism**

Technical Progress – In-depth Study of Selected Material Extract & Contaminants

Screened 62 materials using 6 different ex-situ and in-situ techniques, totaling > 740 experiments and > 1000 h of in-situ testing

Function Description	Material Family	Total Grades
Structural Plastic	PA (Nylon)	26
Structural Plastic	PPS	4
Structural Plastic	PSU	2
Structural Plastic	PPSU	1
Structural Plastic	PBT	2
Structural Plastic	Epoxy	1
Structural Plastic	Phenolic	1
Lubricant/Grease	Perfluoroalkylether/ polytetrafluoroethylene (PFAE/PTFE)	4
Adhesive/Seal	Urethane	6
Adhesive/Seal	Silicone	2
Adhesive	Epoxy	3
Adhesive	Acrylic Acrylate	1
Thread Lock/Seal	Polyglycol Dimethacrylate (PGDA)	4
Hose	Silicone	3
Conformal Coating	Acrylic	1
Ion Exchange Resin	Polystyrene	1
	Total	**62**

Assembly Aids (Lubricant/Grease through Thread Lock/Seal)

Set of Parametric Studies

⇒ **EMS 4**

EMS 7

EMS 10

⇒ **3M® 4000 fast cure white**

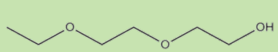
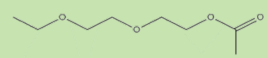
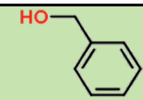
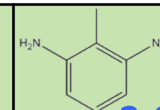
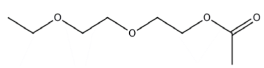
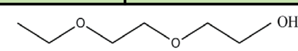
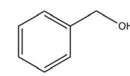
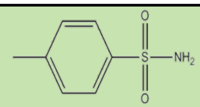
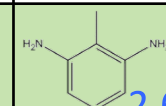
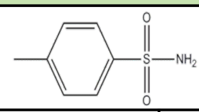
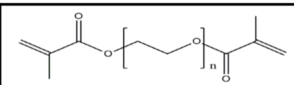
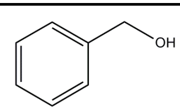
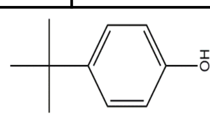
⇒ **Henkel Loctite® #567**

Note: materials highlighted in yellow are new materials for this study, as suggested by Ballard Power Systems and Nuvera Inc.

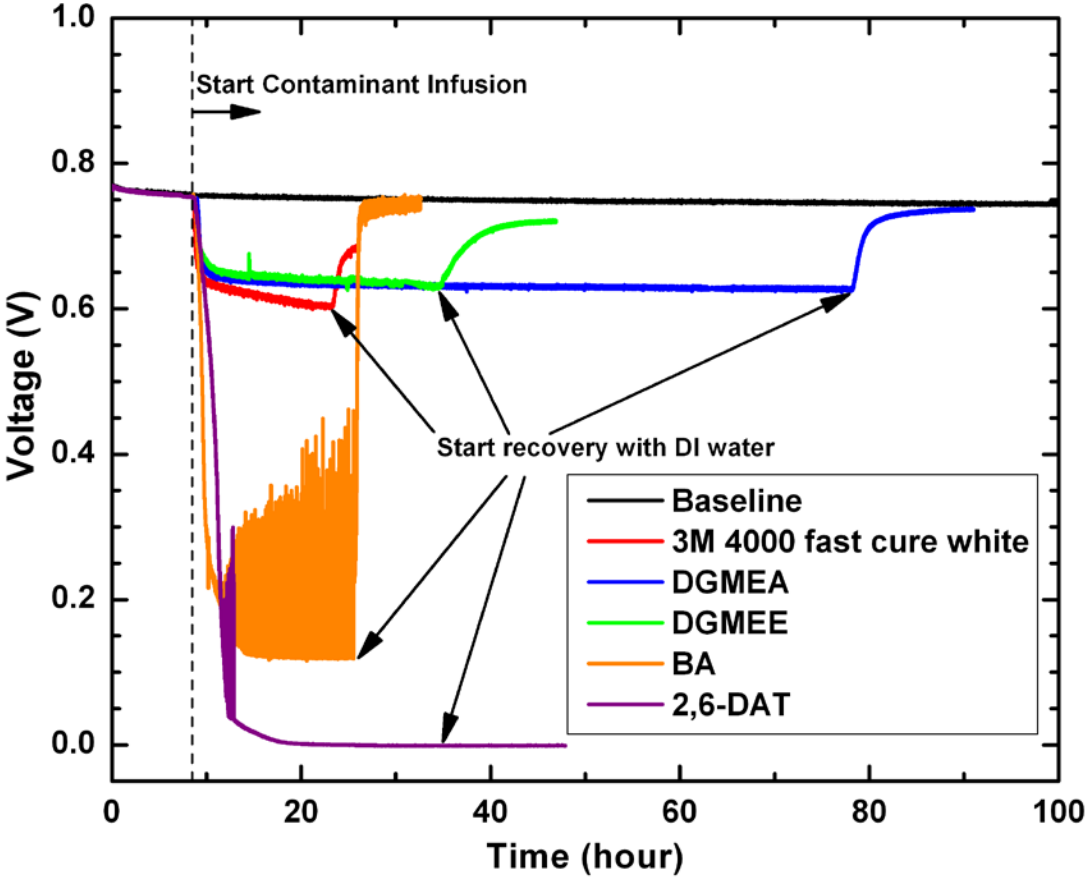
Technical Progress – Aligned Parametric and Model Compound Studies of Select Assembly Aids Materials

Materials selected contain a large variety of selected model compounds

- **Green => 2 Leachants selected for in-situ parametric study**
- **Blue => 7 Compounds selected for model compound studies**
- **3 M® 4000 fcw has 4 main model compounds**

Chemical Description	Trade Name	Liquid GCMS	In-situ voltage drop (mV)	TOC (ppm)
Urethane	**3M® 4000 fast cure white**	 DGMEE;  DGMEA;  BA;  2,6-DAT	**146**	**1280**
Silicone	3M® #8664 black	 DGMEA;  DGMEE;  BA	64	197
Urethane	Loctite® 39916	 4-MBSA; Butyric acid N'-m-tolyl-hydrazide;  2,6-DAT	110	266
Urethane	Bostik® 920 Fast	 4-MBSA	87	109
Polyglycol dimethacrylate	Loctite® # 567	2-methyl-2-hydroxyethyl ester, 2-propenoic acid; 2,2'-[oxybis(2,1-ethanediyloxy)]bis-ethanol;  PEG	84	750
Epoxy	Reltek® Bond-IT® B45	 BA;  PTBP; Benzaldehyde	555	1695
PFAE/PTFE	Krytox® XHT-SX	None Detected	12	10

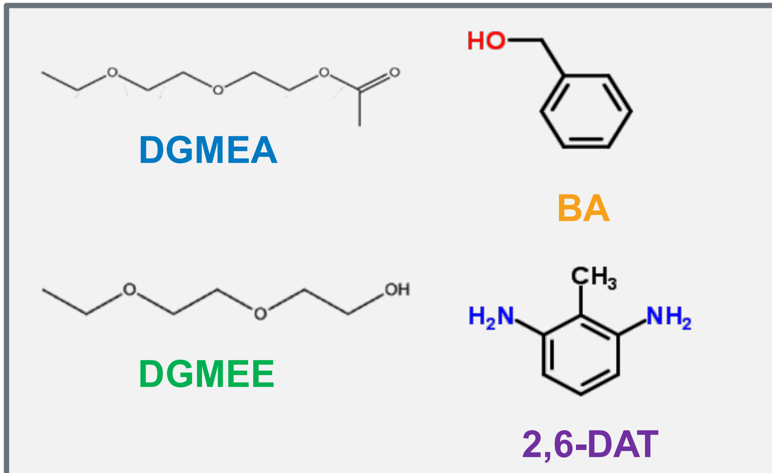
Technical Progress – In-situ Studies of Individual Organic Model Compounds



3M 4000 fast cure is a registered trademark of 3M Corporation

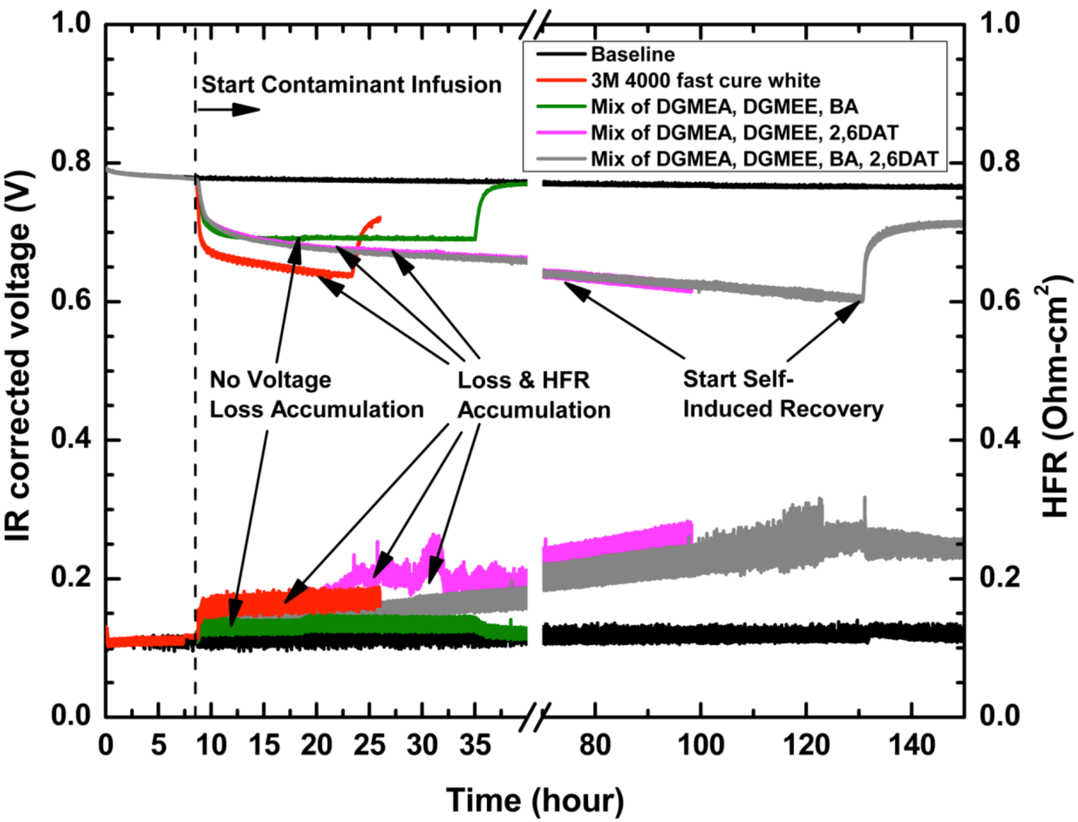
Model compounds result in different contamination effects

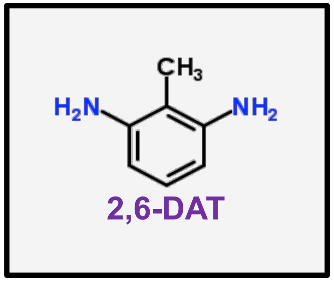
- **Voltage loss,**
- **HFR effects**
- **Recoverability**



Standard Operation Conditions (SOC) = T_{cell}=80 °C , RH%=32/32, Stoich.=2/2, Back pressure=150/150 kPa, i = 0.2 A/cm^2

Technical Progress – In-situ Studies of Organic Model Compound Mixtures

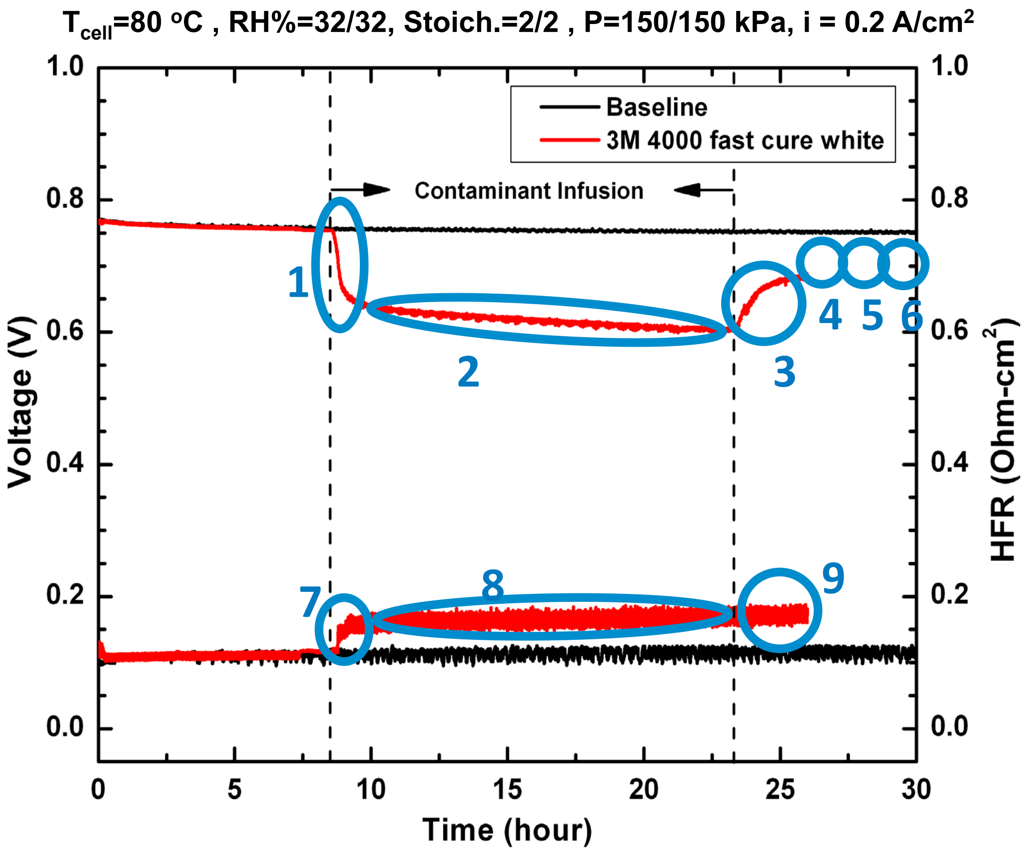




- **Individual vs. multi-component effects**
  - Mixtures may have different contamination and recovery effects than individual compounds
  - Interaction between model compounds can occur
- **Resistance change can impact the kinetic performance**
- **Leachant shows the combined effect of the individual compounds**
- **Organic contaminants can dominate the effects**

SOC = T_{cell}=80 °C , RH%=32/32, Stoich.=2/2, Back pressure=150/150 kPa, i = 0.2 A/cm²

Technical Progress – Quantitative Characterization of Performance Effects



1. Immediate Performance Effect?
2. Performance Effect Accumulation?
3. Reversible Contamination?
4. ECA Loss
5. Recoverable ECA Loss?
6. Residual Contaminants?
7. Immediate Resistance Effect?
8. Resistance Effect Accumulation?
9. Reversible Resistance Effect?

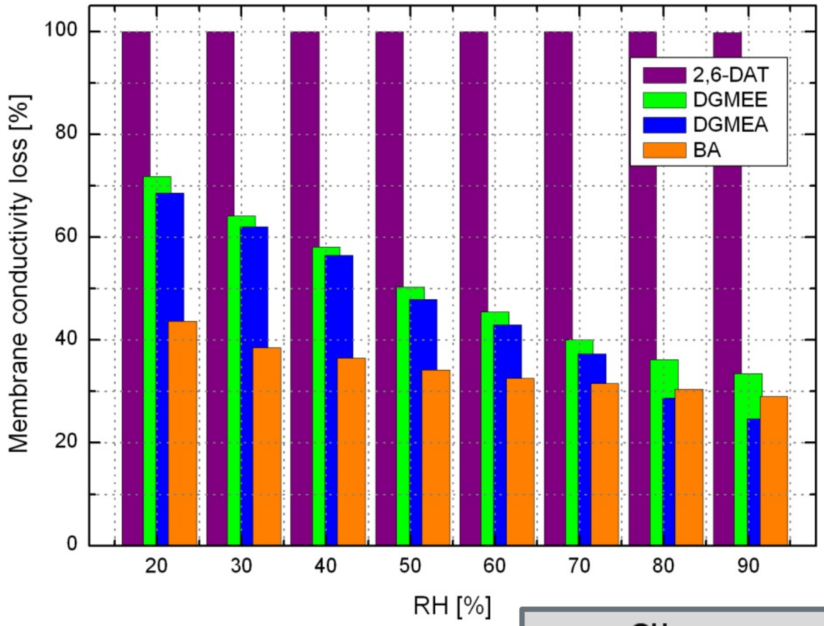
Material Extract	Immediate Voltage Loss [mV]	Immediate Voltage Degradation Rate [mV/h]	Voltage Loss Accumulation Rate [mV/h]	HFR Accumulation Rate [mΩcm^2/h]	Reversible Performance Loss [%]	ECA Loss after self-induced Recovery [%]
3M® 4000 fast cure white	121	251	2.3	1.02	56	36

Example data (fraction)from comprehensive quantitative analysis for characterization of performance effect.

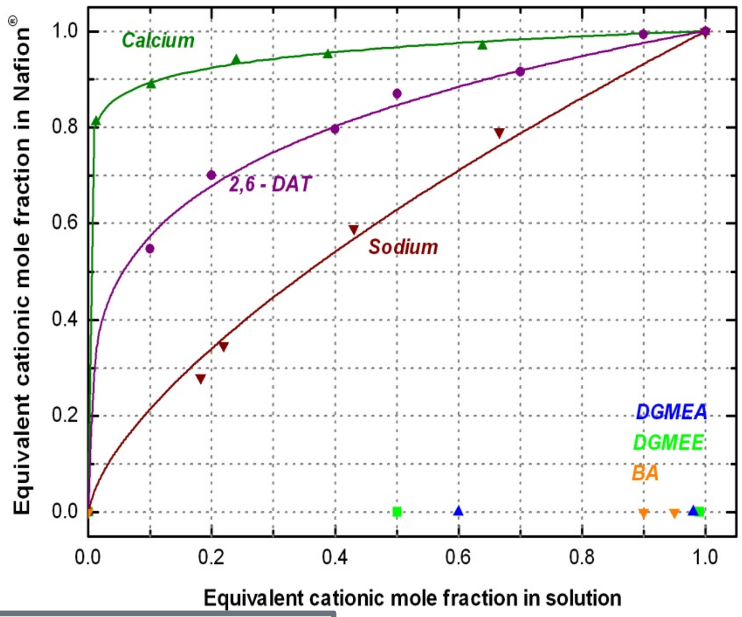
Technical Progress – Membrane Conductivity Loss Mechanisms

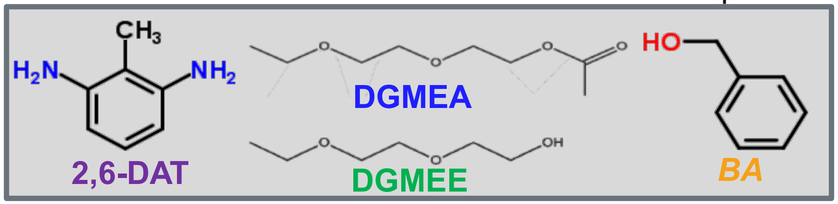
- **Ion-exchange and absorption are two mechanisms that lead to membrane conductivity loss**
  - Amine functional group ion-exchanges and expels water.
  - Alcohol and acetate functional groups absorb into the membrane and expel water.
- **Ion-exchange mechanism has stronger impact**

Membrane Conductivity Loss



Ion-exchange

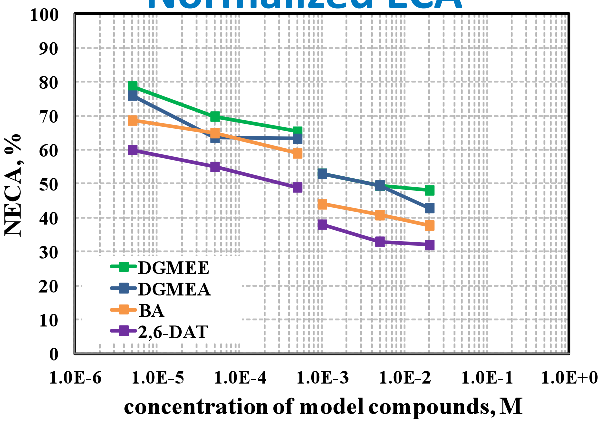




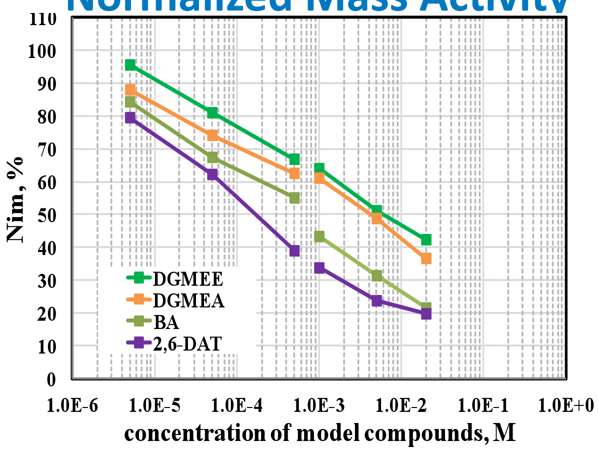
Technical Progress – Effect of Organic Model Compounds on ECA and ORR Activity

- Decrease in mass activity is due to organic compounds adsorbing onto Pt sites
- Organic compounds may alter ORR mechanism to H_2O_2 formation
- The degree of contamination appear to be higher for polymers and aromatics compared to aliphatics

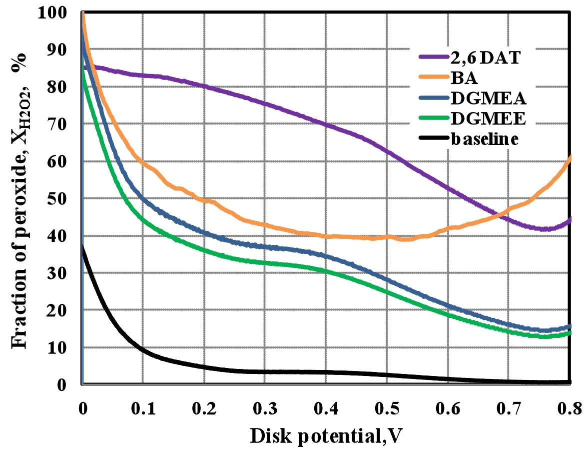
Normalized ECA



Normalized Mass Activity



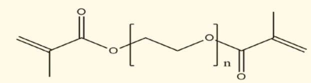
Peroxide Formation



ECA = Electrochemical surface area
ORR = oxygen reduction reaction
Nim = normalized mass activity (normalized to mass activity without contaminants)

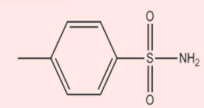
Polymeric

(PEG)

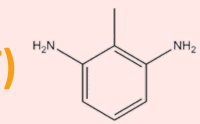


Aromatic

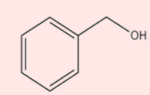
(4-MBSA)



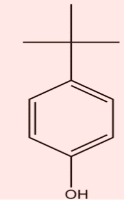
(2,6-DAT)



(BA)

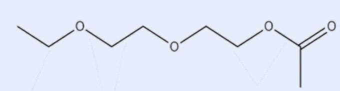


(PTBP)

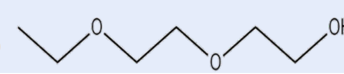


Aliphatic

(DGMEA)



(DGMEE)

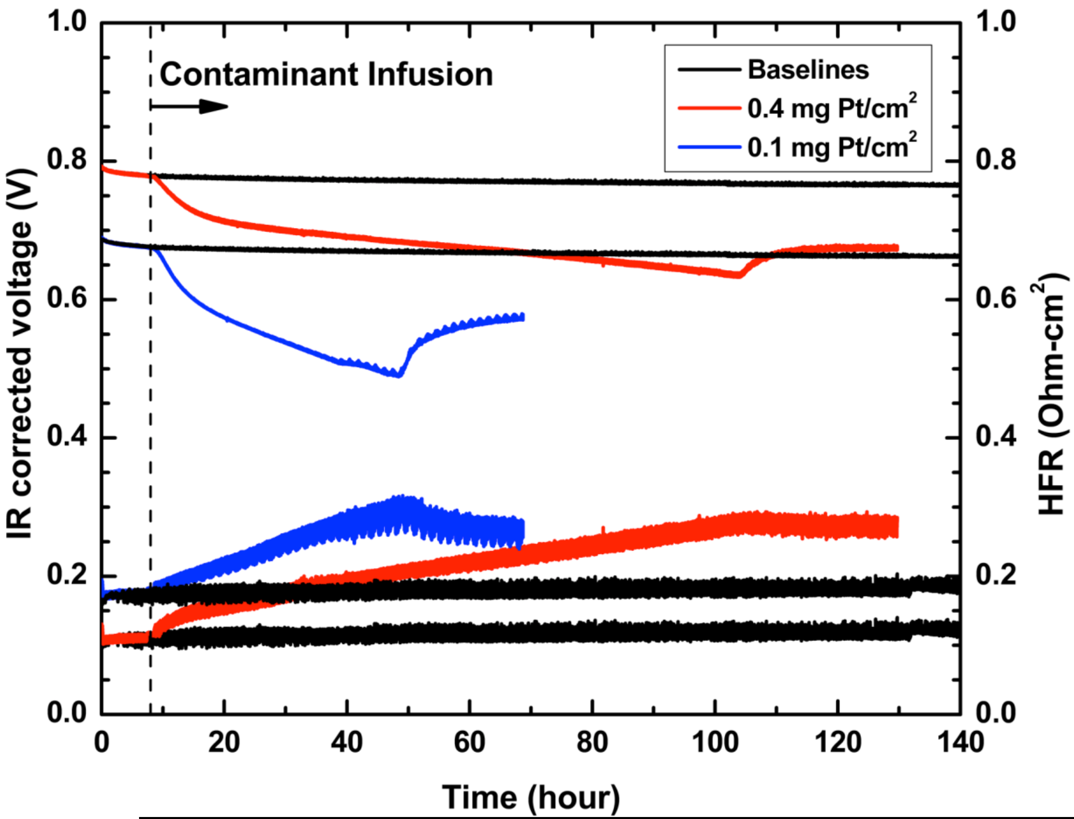


Coverage by contaminant

ORR mass activity follows the same trend as ECA loss

Technical Progress – Effect of Catalyst Loading on Performance with 2,6 DAT

T_{cell}=80°C, RH%=32/32, Stoich.= 2/2, Back pressure=150/150 kPa, i = 0.2 A/cm²



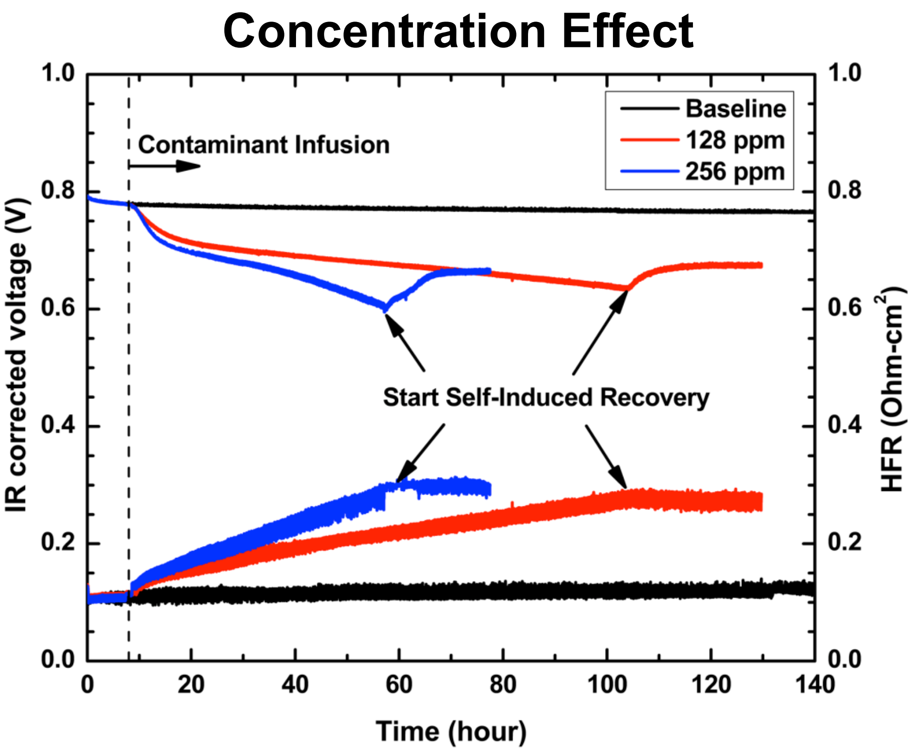
Lower catalyst loading results in:

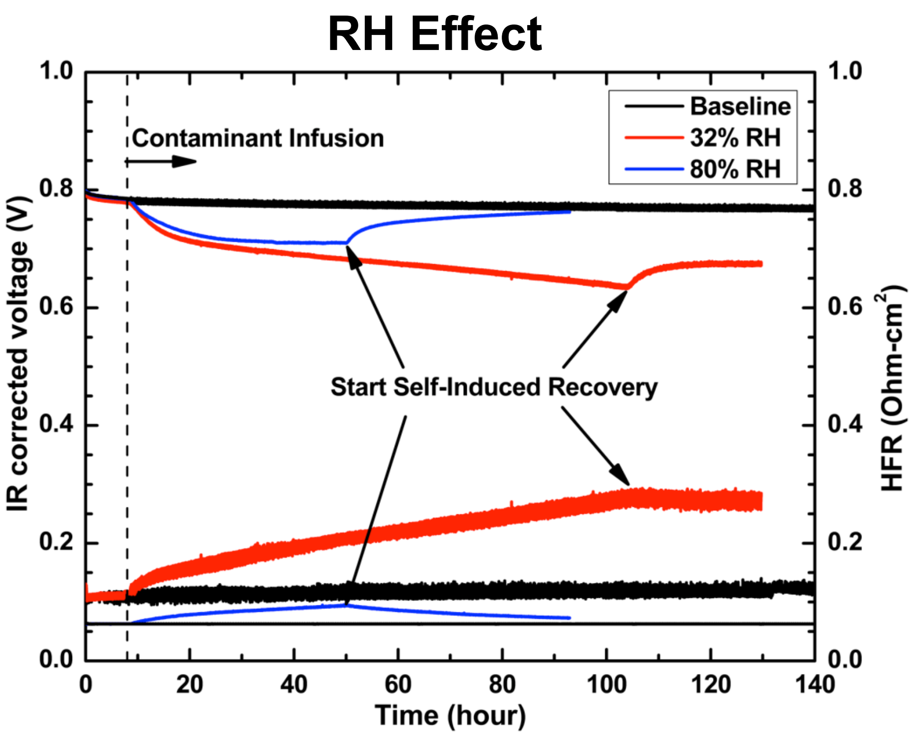
- **Stronger response to contaminants**
- **Higher immediate performance loss, likely due to adsorption**
- **Larger performance loss accumulation, likely due to ion exchange**

Anode/Cathode Catalyst Loading [mg Pt/cm²]	Immediate Voltage Loss [mV]	Immediate Voltage Degradation Rate [mV/h]	Voltage Loss Accumulation Rate [mV/h]	HFR Accumulation Rate [mΩcm²/h]	Reversible Performance Loss [%]	ECA Loss after self-induced Recovery [%]
0.05/0.4	77	11	1	1.7	24	38
0.05/0.1	104	15	4	3.2	45	47

Technical Progress – Example data from parametric study of organic model compound (2,6, DAT)

- Concentration is an important driver for cell performance loss
- Liquid water may be a game changer
- Liquid water may be useful for mitigating the effects of specific contaminants





T_{cell}=80°C , RH%=32/32, Stoich.=2/2, Back pressure=150/150 kPa, i=0.2 A/cm^2, 2,6-DAT

Technical Progress – Summary of Assembly Aids and Model Compound Parametric & Mechanism Studies

Parameter study

- Ranges reflect 80% of typical fuel cell vehicle operation
- Feed rate, RH, and current density strongly affect contamination
- Liquid water content may impact performance & recovery effect
- Cell temperature changes (80°C & 50°C) show some impact on performance loss and recovery
- Lower Pt catalyst loading results in higher performance loss
- Additional parametric studies are being performed with structural materials (see back up slide)

Mechanism study

- Functional groups of organic compounds are important in understanding system contaminants
- Performance loss may contain reversible, recoverable, and non-recoverable contributions
- Identified contamination mechanisms:
  - Adsorption on catalyst
  - Redox reaction (see back up slide)
  - Ion-exchange/absorption processes with ionomer
- Developed a model on the effect of organic compounds on fuel cell performance (see back up slide)

Dissemination via NREL Website: http://www.nrel.gov/hydrogen/contaminants.html

Proposed Future Work

Future Work:

- **Perform in-depth analysis of in-situ parametric data**
- **Finalize modeling the effects of contaminants at various operating conditions**
- **Disseminate project information**
  - website, publications & presentations

Future Research Needs:

- **Study additional low cost BOP materials**
- **Estimate real system contamination rates**
- **Develop durability test protocol for contaminants studies**
  - Real time & Accelerated Stress Test
- **Develop mitigation strategies**
- **Further develop model to include compound mixtures**
- **Stack, system, and/or vehicle studies**
- **Contamination studies on state of the art materials**

Collaborators

Institutions	Role
National Renewable Energy Laboratory (NREL): H. Dinh (PI), G. Bender, C. Macomber, H. Wang, KC Neyerlin, K. O'Neill, B. Pivovar	**Prime, Oversees the project, broad screening and analytical characterization; membrane degradation material study**
General Motors LLC (GM): K. O'Leary, P. Yu, B. Lakshmanan, E.A. Bonn, J. Sergi, 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, J. Weidner, 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)**
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**
Ballard Power Systems and Nuvera Inc. on material selection and testing protocols

Summary

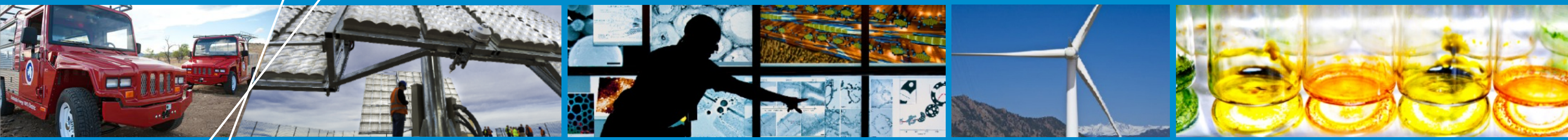
Relevance: Focus on overcoming the cost and durability barriers for fuel cell systems.

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: Completed all milestones on time. Performed parametric in-situ studies and identified key operating conditions that impact fuel cell performance; identified contamination mechanisms; quantified the impact of model compounds on fuel cell performance and relate it to extract results; modeled the contamination effect of specific organic compounds; performed long term testing of selected contaminant; screened additional BOP materials suggested by Ballard and Nuvera; developed a website for dissemination of project information.

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: Perform in-depth analysis of parametric in-situ studies; finalize modeling the effects of contaminants at various operating conditions; disseminate project information via website, publications and presentations.



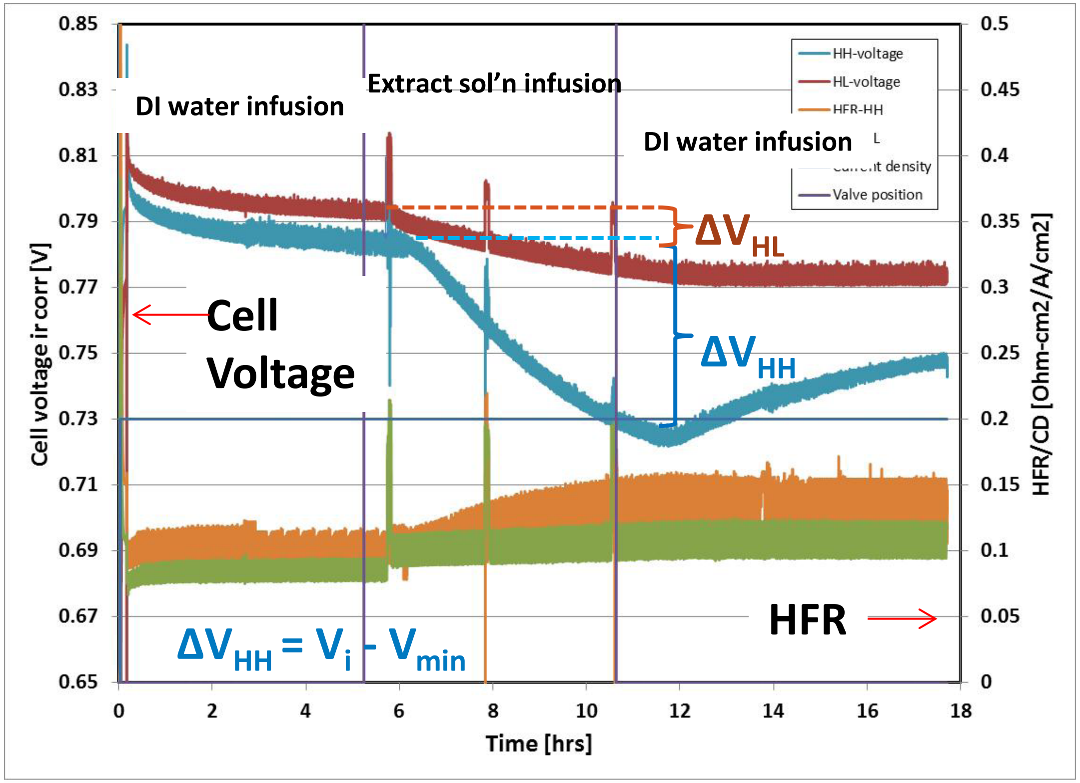
Technical Back-up Slides

Technical Progress – Parametric Studies of Structural Materials (in process)

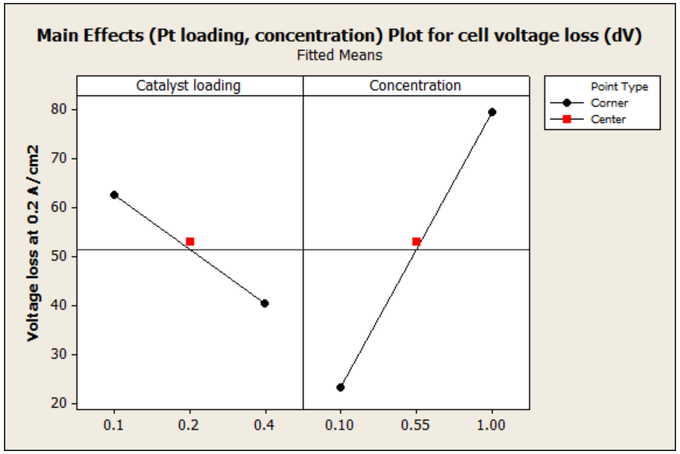
Cell voltage loss (ΔV)

Factors	Pt loading [mg/cm²]	Extraction sol'n concentration	RH [%]	Temp. [°C]	Current density [A/cm²]
Hi	**0.4**	**1X (HH)**	65	**80**	**0.2**
Lo	**0.1**	**0.1X (HL)**	**32**	40	0.06

Cell voltage profile during infusion



Results for EMS-4

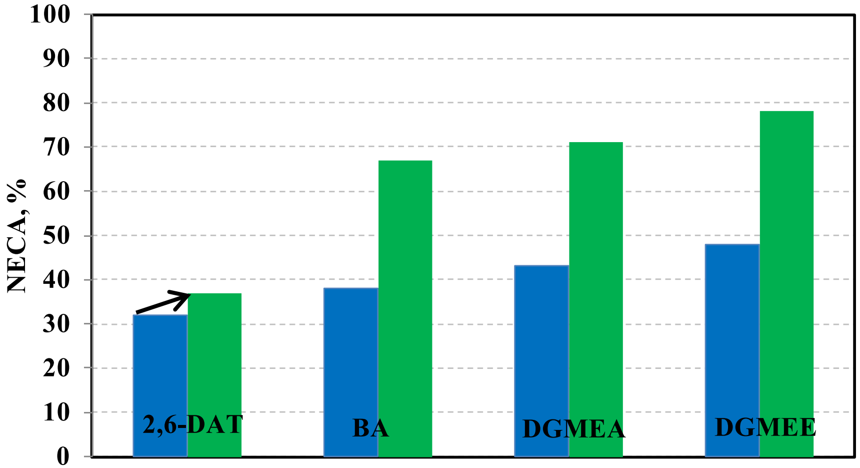


- **A partial factorial [2^2 + 1] test is complete.**
- **ΔV is influenced by Pt loading and extract solution concentration.**
- **High Pt loading, low concentration would relieve voltage degradation.**
- **Voltage loss can be partially recovered via water infusion.**

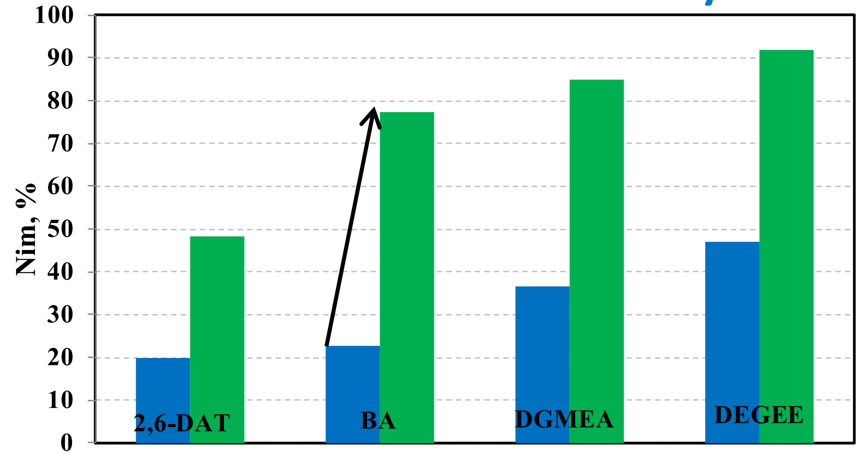
Technical Progress – Recoverability of Organic Model Compounds (ex-situ cyclic voltammetry)

- Physisorbed aliphatic organic compounds are recoverable
- Aromatics with amine group are more difficult to recover
- Some organics can under go redox reactions and their products can have a different effects
- Ex-situ data supports in-situ data

Normalized ECA

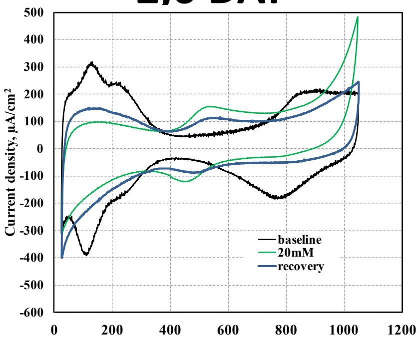


Normalized Mass Activity

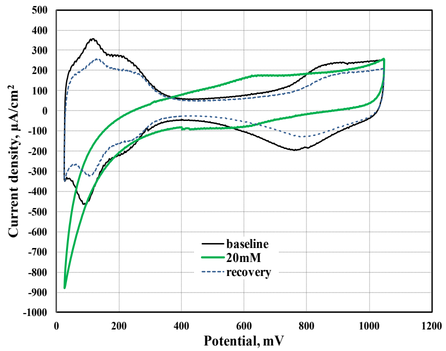


blue = Contamination at 20 mM; green = recovery

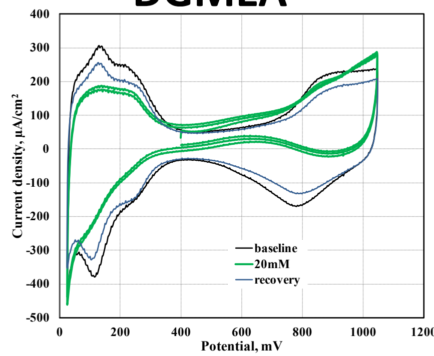
2,6 DAT



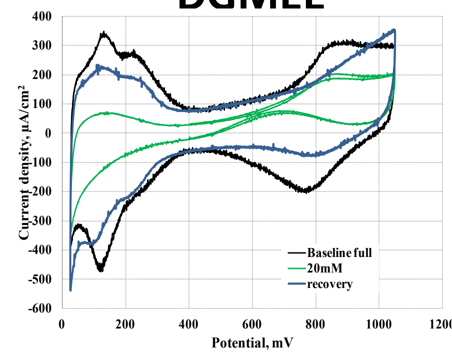
BA



DGMEA

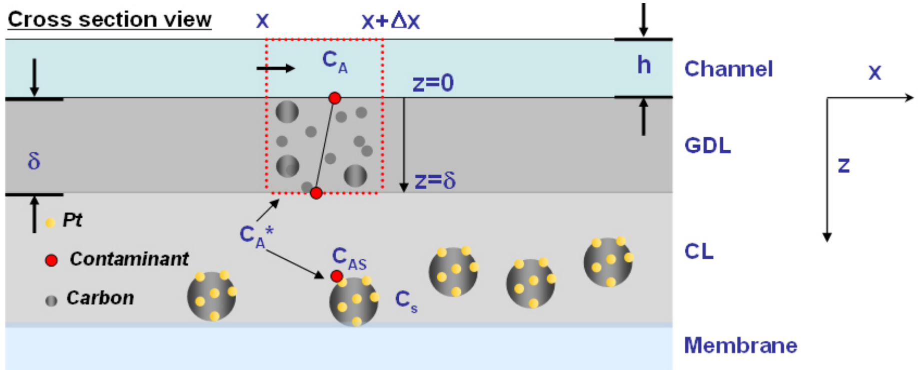


DGMEE



Technical Progress – Develop a model for contamination mechanisms

A. Schematic of channel and adsorption on Pt



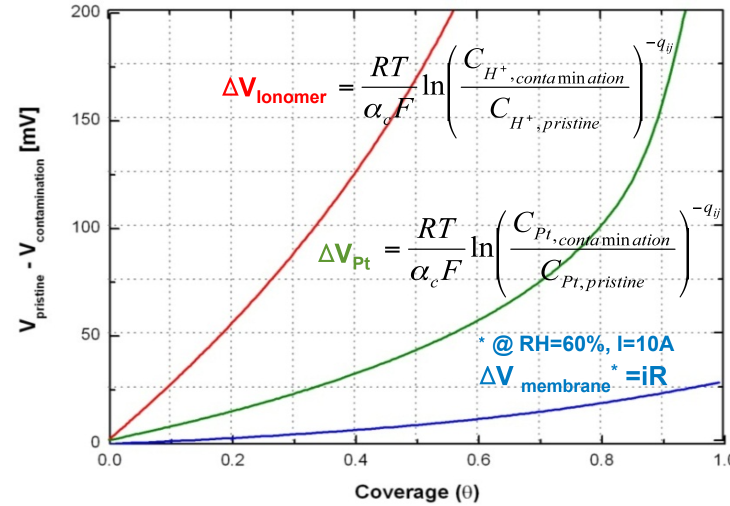
B. Model development & outcome

1. 2-D (x, z) and time (t)
   (i.e., channel length, GDL/CL thickness, time)
2. The model equations included:
   a. Material balance for contaminant
   b. Partition coefficients for surface and membrane species
   c. Stoichiometry for air and water

C. Outcome

- Predict ΔV (loss) and distributions for Pt coverage, ionomer and membrane adsorption/absorption mechanisms
- Model relates *ex-situ* and *in-situ* measurement

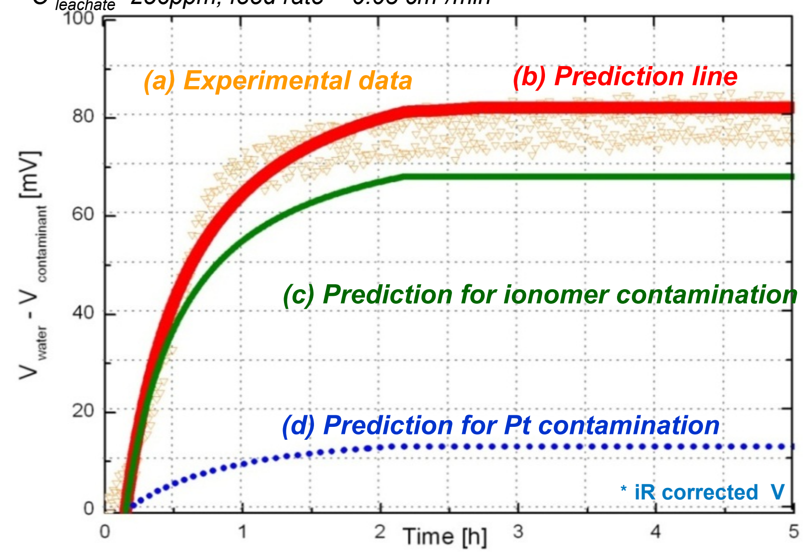
D. Predicting △ V with Butler-Volmer & Conductivity



E. Compare model with DEGEE infusion data

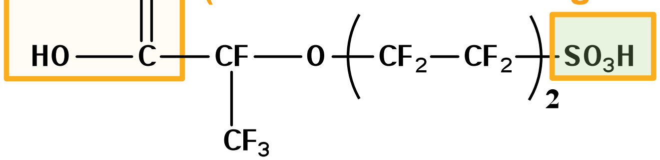
T_{cell}= 80℃, stoich.=2.0/2.0 P=150/150 kPa i=0.2 A/cm², RH=32/32%

$C_{leachate}$=256ppm, feed rate = 0.03 cm³/min



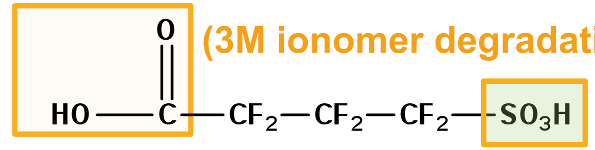
Technical Progress: Impact of PEM degradation products on Pt electrode

(Nafion® ionomer degradation product)

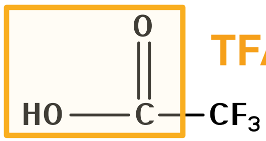


MC2

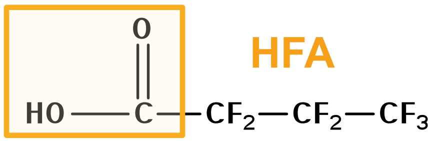
(3M ionomer degradation product)



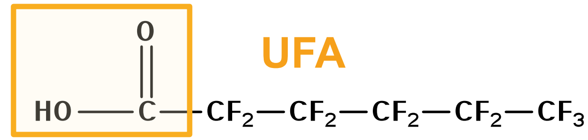
MC3



TFA

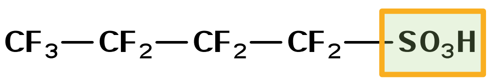


HFA

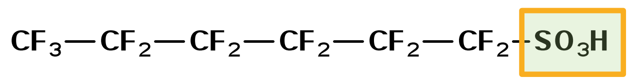


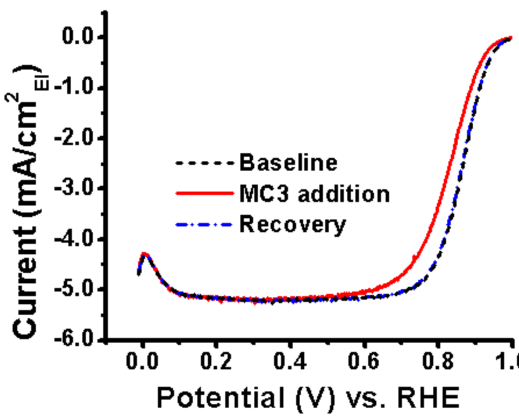
UFA

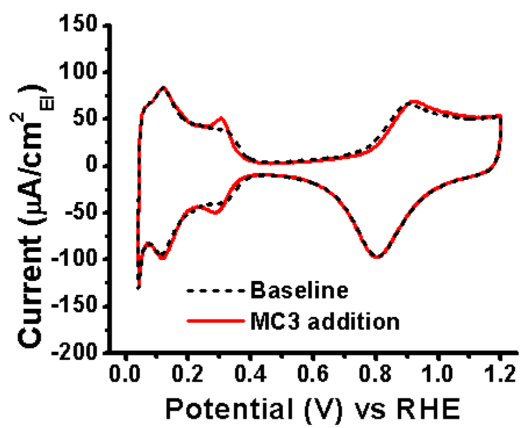
MC5

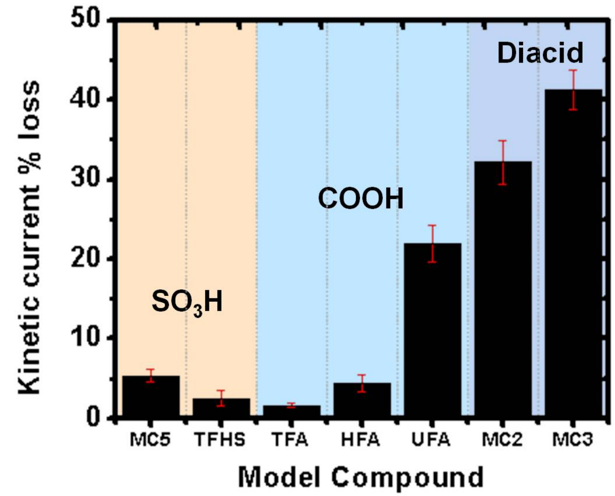


TFHS









- Model compounds were found to adsorb on Pt electrode surfaces with the carboxylic acids showing stronger impact than sulfonic acids, and diacids (MC2, MC3) showing strongest impact
- Performance impact due to an increase in fluorocarbon chain length was observed for carboxylic acids
- ORR performance was recoverable after gentle DI water rinse for all compounds

Approach – Material Selection & Focus

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

1. Balance of Plant Materials (BoP)	**Focus**
– **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