NATIONAL RENEWABLE ENERGY LABORATORY

Effect of System Contaminants on PEMFC Performance and Durability

Venue: 2014 DOE Hydrogen and Fuel Cells Program Review

Presenter: Huyen Dinh (PI)

National Renewable Energy Laboratory

Date: June 18, 2014

FC048

Project Overview

Timeline

Project Start Date: July 2009
Project End Date: September 2014

Budget

FY13 DOE funding: $1690K
Planned FY14 DOE funding: $400K
Total project value: $7,188,850*
(includes cost share)
Cost share: 20%

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

Barriers

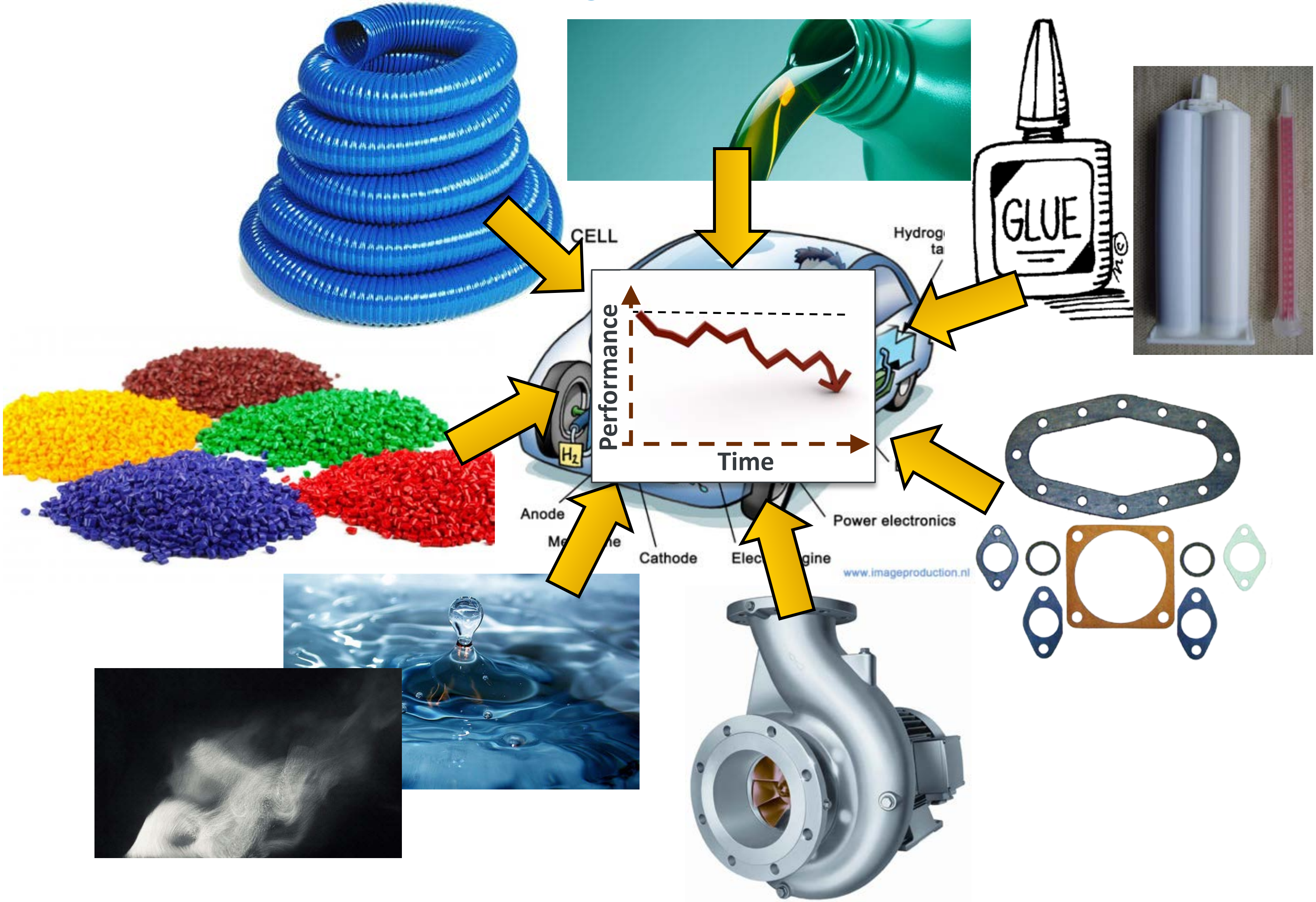
Barrier	2020 Target
A: Durability	5,000 h for Transportation 60,000 h for Stationary
B: Cost	$30/kW for transportation $1000-1700/kW for Stationary (2-10 kW)

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 (in-kind partner)
Nuvera (in-kind partner)

* denotes subcontractor

Relevance: System Contaminants Originate From the System Itself

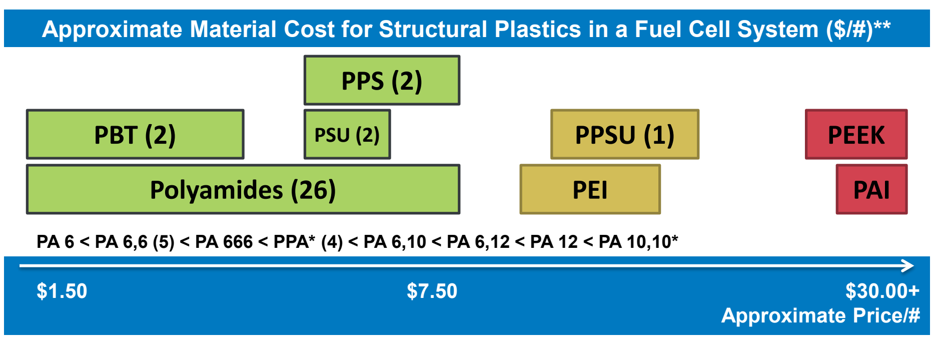


Relevance

- **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.**

Impact

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



** 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

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
Ongoing	4. Identify impact of operating conditions	2012-2014
Complete	5. Identify poisoning mechanisms	2012-2014
Ongoing	6. Develop models/predictive capability	2012-2014
Ongoing	7. Provide guidance on future material selection	2013-2014

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

Additional Scope for FY2014:
Develop understanding of leaching conditions' impact on contaminant concentration (NREL & GM)

Approach – FY2014 Milestones

FY 1 4	**Q1**	GM defines two structural plastics to be studied based on commercial relevance to automotive application, cost and physical properties required under typical fuel cell operating conditions (0-100% RH, -40-90˚C). 1. BASF **PA**- A3HG6 2. Solvay Amodel – **PPA** – HFZ – 1133 Chose relatively low cost materials with lowest voltage loss	12/2013	Complete
	Q2	Design the experiment and set up for estimating real system contamination rates that simulate surface exposure of BOP materials in automotive fuel cell application. Deliver the range of operating conditions for this set up (e.g. temperature, time).	03/2014	Complete
	Q3	Report on quantification of leachant concentrations from two fuel cell structural plastics (concentrations are expected to be 100x diluted compared to the previously studied plastics).	06/2014	On Track
	Q4	Report on fuel cell performance impact (net voltage loss at 0.2 A/cm^2 and 32% RH at the end of contaminant infusion) for two structural plastic extracts or extract compounds.	09/2014	On Track

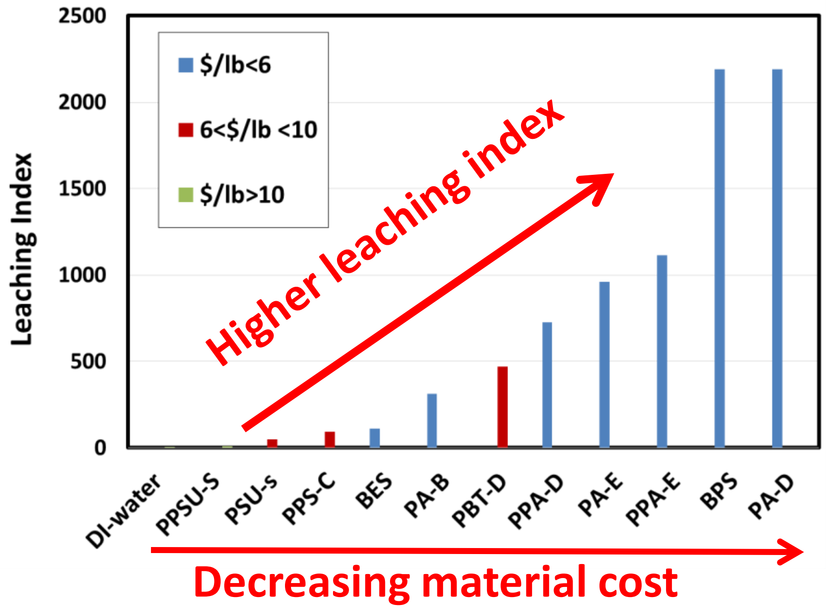
Major Technical Accomplishments Since FY2013 AMR:

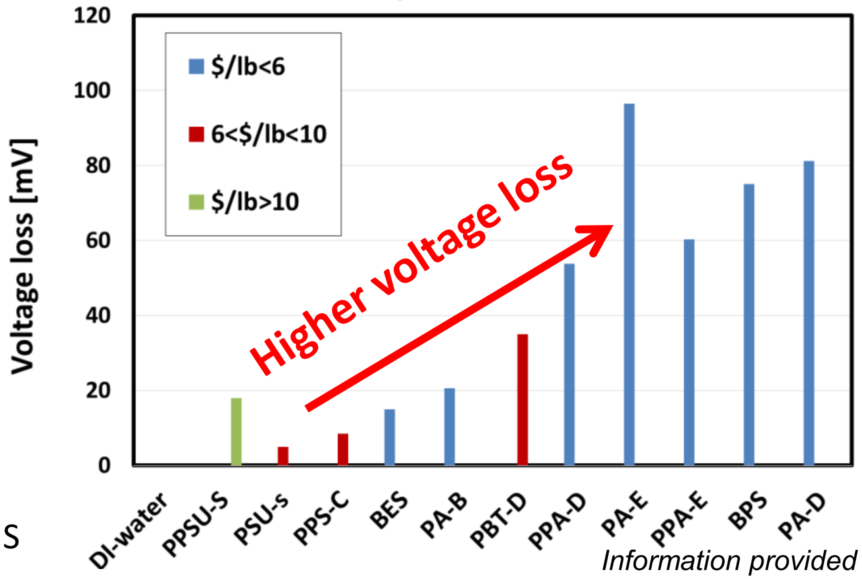
1. Developed the leaching index as a quick material screening method (GM)
2. Improved website and interactive material data tool (NREL)
   a. added more data & project info
   b. improved user-experience
3. Designed experiment to understand effect of leaching parameters on contaminant concentration (NREL & GM)
4. Identified impact of fuel cell operating conditions on voltage loss and recovery
   a. extracts (3 structural plastics: GM)
   b. organic model compounds (2,6 DAT: USC)
5. Developed model for contamination mechanism (USC)
   a. based on experiments with organic model compound

Technical Accomplishments –
Leaching Index as a Quick Material Screening Method

GM screened and categorized 34 plastic materials into groups based on their basic polymer resin and brands

- Leaching index (conductivity + total organic carbon) is a quick way to screen plastic materials
- Leaching index shows trends with voltage loss and material cost; In general, the higher the leaching index,
  - Higher cell voltage loss
  - Lower material cost





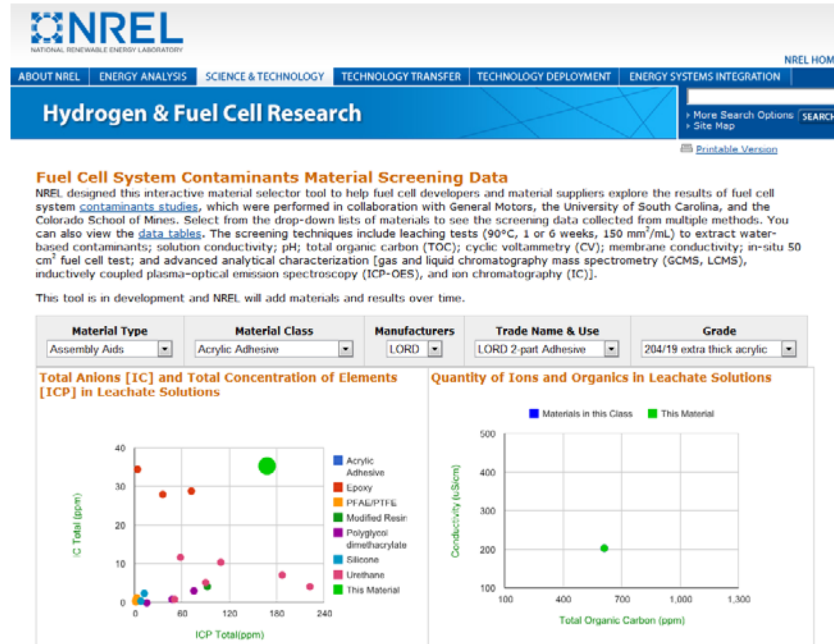
BES = Bakelite epoxy-based material – Sumitomo;
BPS = Bakelite phenolic-based material – Sumitomo;
S = Solvay; C = Chevron Philips; B = BASF; D = Dupont; E = EMS

Information provided by GM

Technical Accomplishments – Improved NREL Website for Project Info Dissemination

General Project information:
http://www.nrel.gov/hydrogen/contaminants.html

Interactive material screening data tool:
http://www.nrel.gov/hydrogen/system_contaminants_data.html



- Graphically compares contaminants derived from 60 system component materials and their effect on fuel cell performance
  - Added data for 34 structural, 3 hose, and 3 assembly aids materials;
  - Added leaching index plots; ICP plots;
  - Improved user-experience: tabs for easier navigation of different project info; freeze material selection row at the top of the page for better viewing of all available data
- Presented DOE webinar on 5/27/2014, "An Overview of NREL's Online Data Tool for Fuel Cell System-Derived Contaminants"

Technical Progress – Understand Effect of Leaching Parameters on Contaminant Concentration

- **Previous leaching experiments were fixed at one condition**

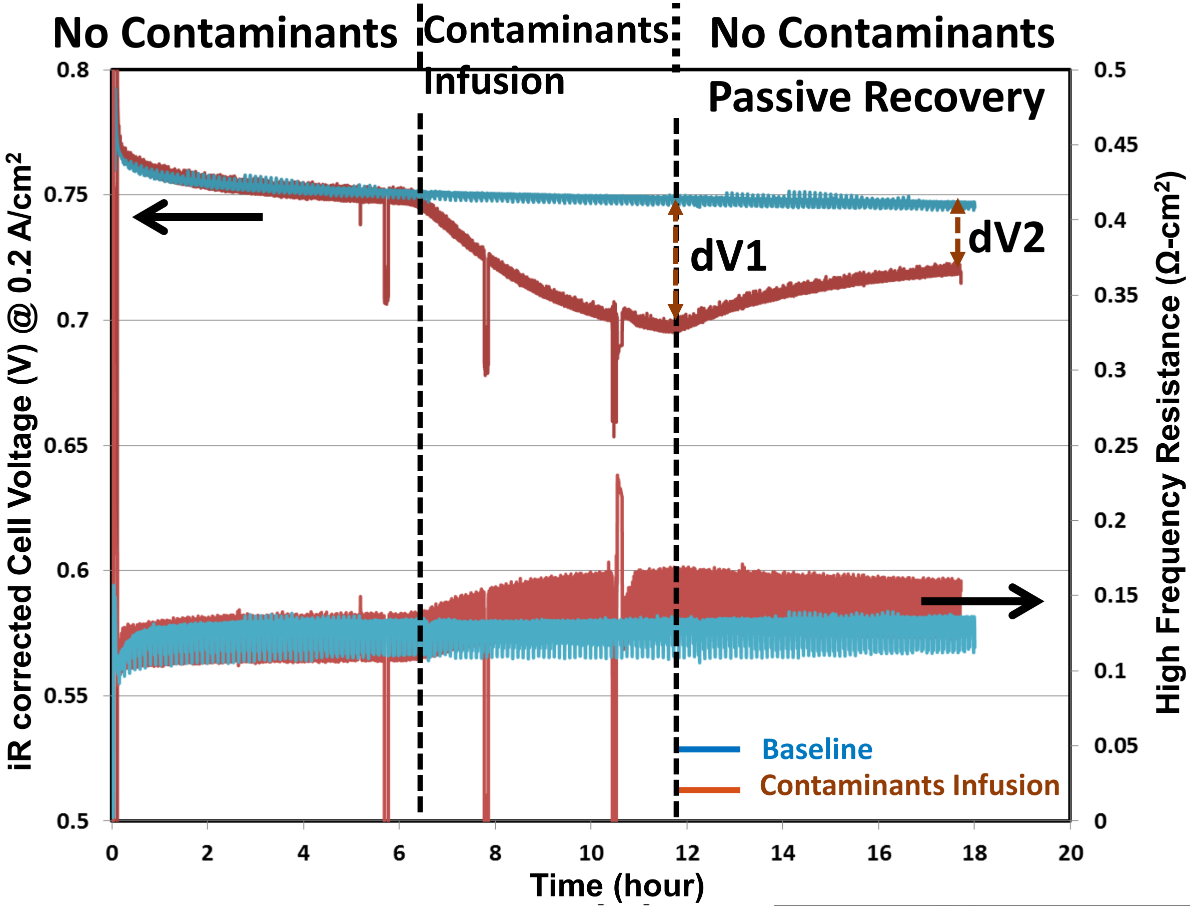
  90°C, 1000 h, 1.5 cm^2/ml

- **Expanded the set of leaching conditions**

	Plastic	Temp. [°C]	Time (h)	SA/vol ratio [cm^2/ml]
1	PPA	50	10	1.5
2	PPA	50	1000	3
3	PPA	90	10	3
4	PPA	90	1000	1.5
5	PA	50	10	3
6	PA	50	1000	1.5
7	PA	90	10	1.5
8	PA	90	1000	3
9	PA	90	1000	1.5
10	PA	70	505	2.3
11	PPA	70	505	2.3

- **Goal of current experiments**
  a. Determine effect of leaching parameters on contaminant concentration
  b. Estimate a range of system contaminant concentration
  c. Determine acceleration factor with previous screening leaching results

Technical Accomplishments – Contaminants Infusion Test Profile



Major results:
→ **voltage loss due to contamination (dV1)**

→ **voltage loss after passive recovery (dV2)**

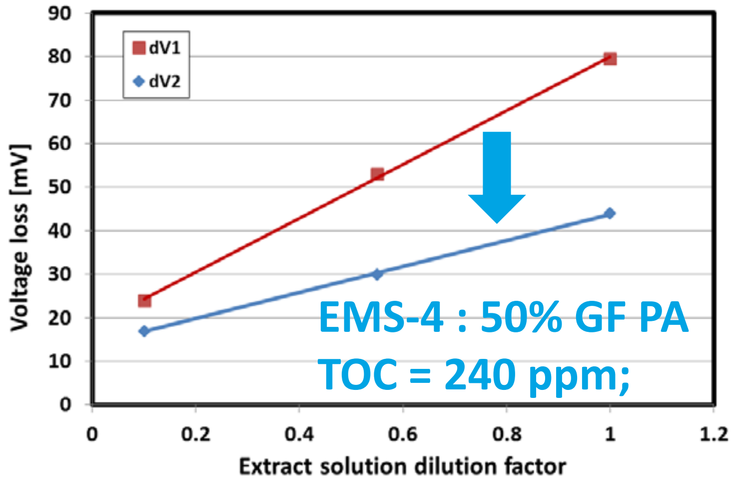
Test conditions: 80°C, 150/150 kPa, 0.2 A/cm^2, 32/32 % inlet RH, H_2/air stoic = 2/2; Pt loading = 0.4 mg/cm^2

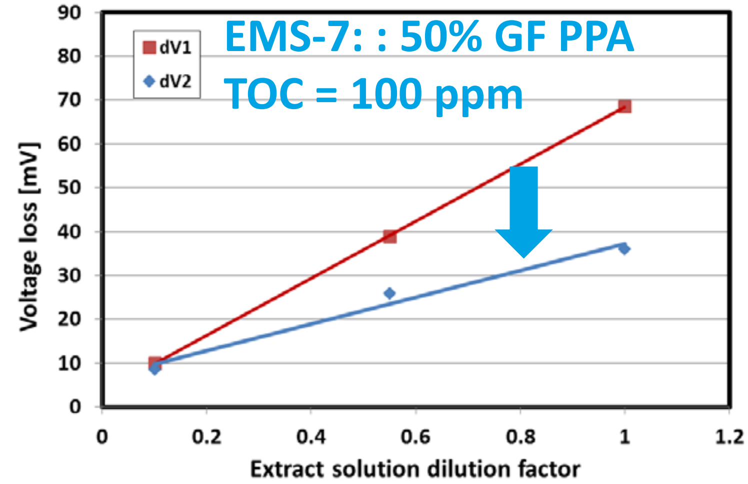
Material	Plastic and glass filler	Description
EMS-4	50% GF PA	Halogenide based heat stablization
EMS-7	50% GF PPA	Halogenide based heat stablization
EMS-10	30% GF PPA	Halogenide based heat stablization

PA = polyamide; PPA = polyphthalamide; GF = glass fiber

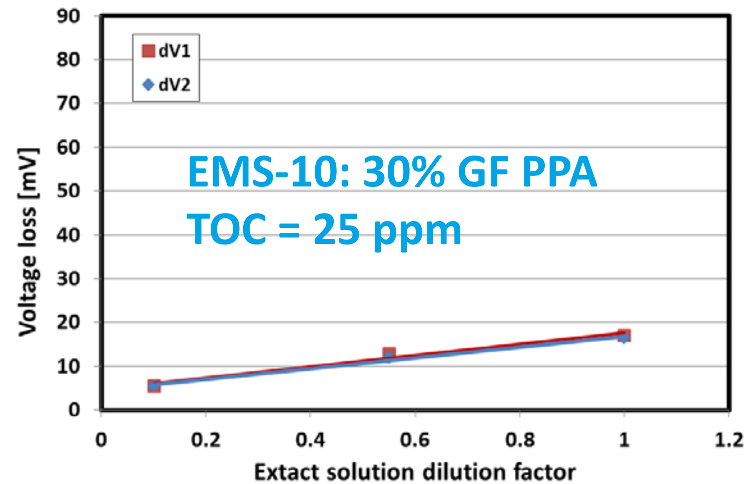
Information provided by GM

Technical Accomplishments –
Effect of Extract Solution Concentration





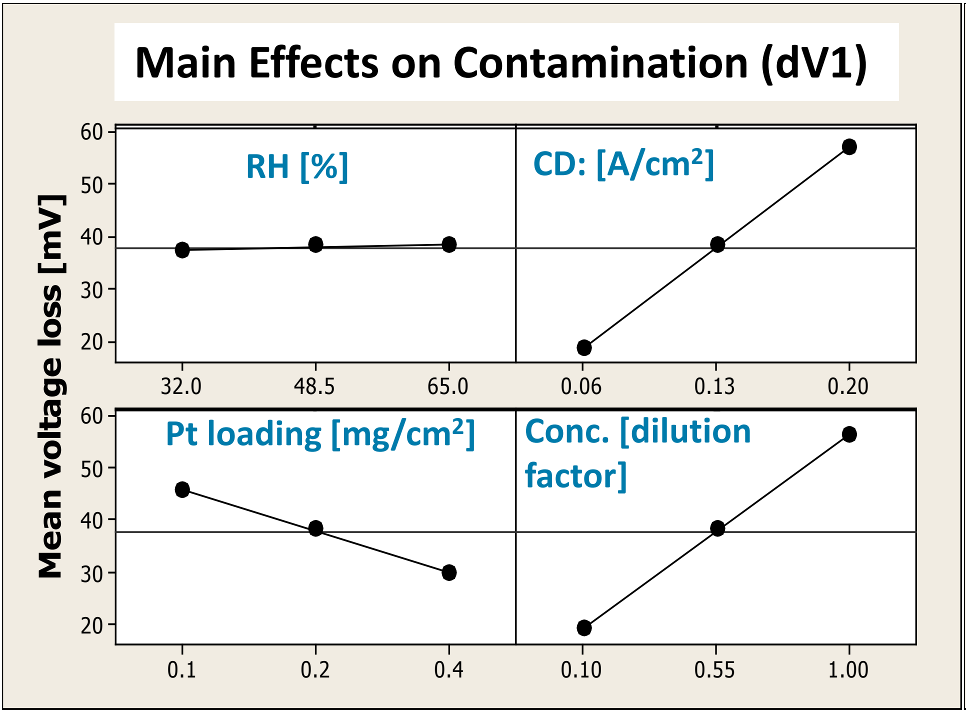
- Contamination effect can be partially reversed in the absence of contaminants
- **Polymer resin type matters**
  - PA materials result in more leached contaminants and higher cell voltage loss than PPA materials
- **Additives in plastic materials matters**
  - Glass fiber (GF) filler is found in leached solutions & can degrade fuel cell performance (EMS-10 has lower %GF than EMS-7)
- Other compounds (e.g., anions, cations) in addition to organics also affect voltage loss

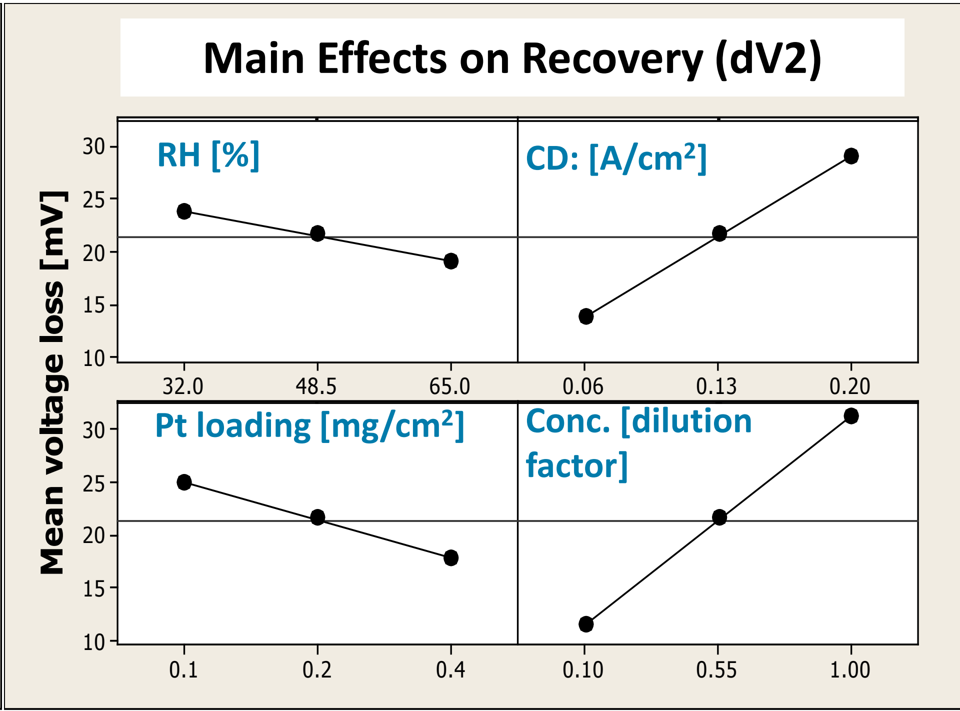


Test conditions: 80°C, 32/32 % inlet RH, 0.2 A/cm^2, H_2/air stoic = 2/2; 150/150 kPa

Information provided by GM

Technical Progress – Significant Operating Factor(s) Affecting Fuel Cell Contamination and Recovery



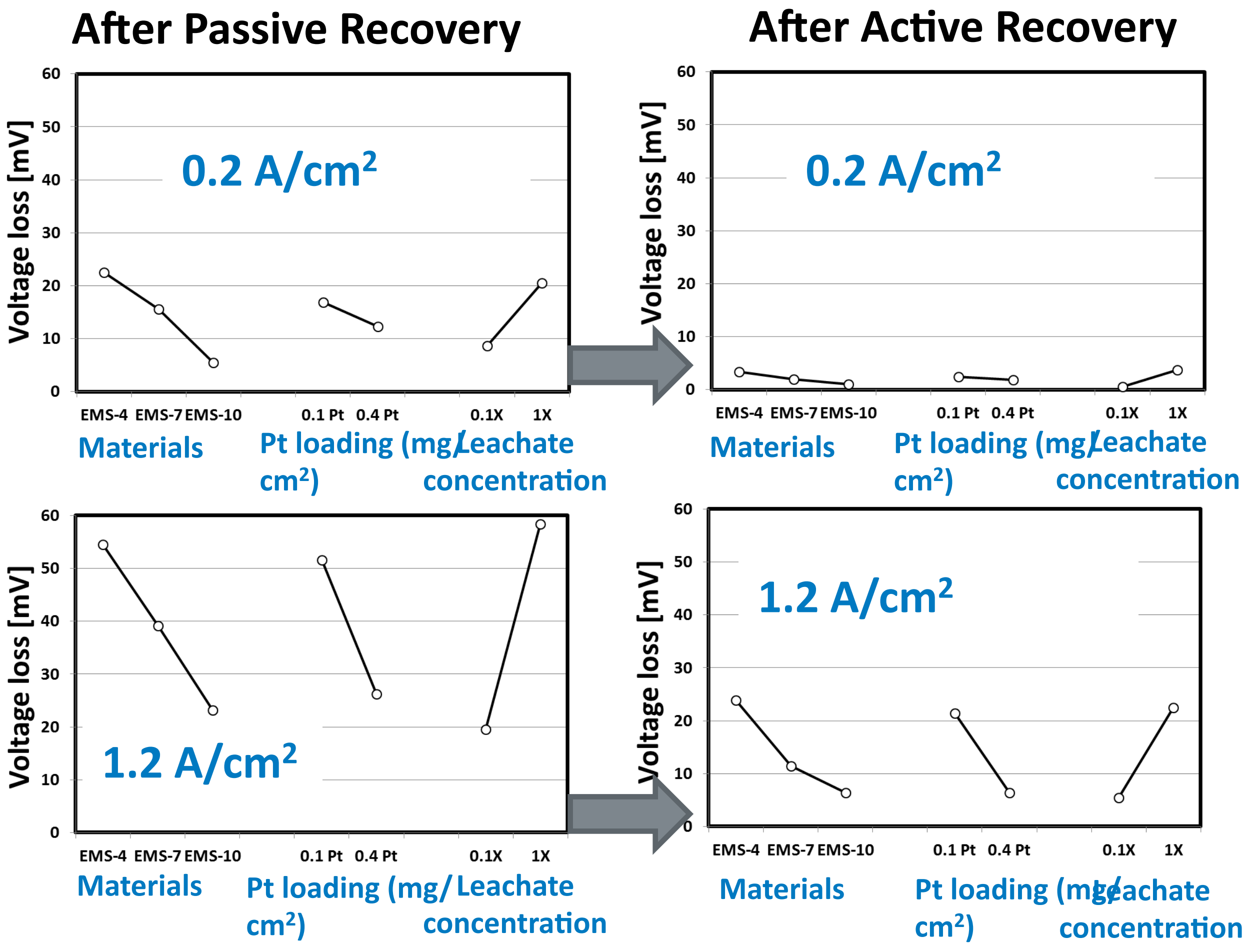


- Current density (CD) and/or dosage are/is the most significant factor(s) affecting cell performance (based on statistical analysis) followed by
- Concentration > interaction of relative humidity (RH) and Pt loading > Pt loading > interaction of RH and concentration
- Interaction between different parameters should be considered
- Similar trends are observed for dV2 compared to dV1

Information provided by GM

Technical Accomplishments – Impact of Operating Factors Analyzed at Different Current Densities

- **The trend on fuel cell voltage loss due to operating parameters is similar at low & high current densities.**
- **At high current density, higher voltage loss was observed.**
- **Active recovery procedures can reverse contamination effects.**



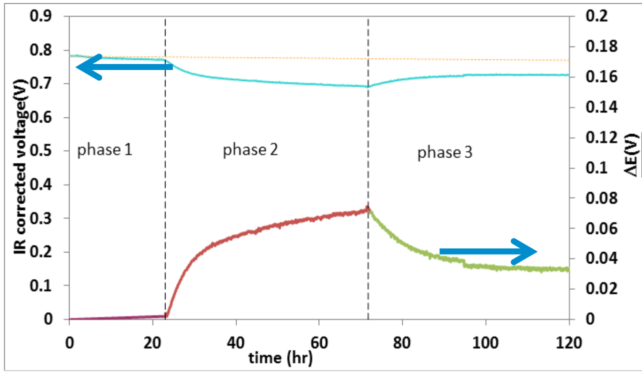
- **Data were analyzed from pol. curve data;**
- **Voltage loss determined by subtracting the voltage from BOT pol. curve; all voltage data were iR corrected.**
- **Active recovery = GM proprietary voltage procedure**

Test conditions: 80°C, 32/32% inlet RH, H_2/air stoic = 2/2; 150/150 kPa;

Information provided by GM

Technical Progress – Zero-Dimensional Mechanistic Model to Understand Poisoning & Recovery Mechanisms

Experimental Infusion Data



Model & Fit

$$V_{cell} = E_{eq} - \mathrm{IR_m} - \eta_a - \eta_c - IR_i$$

Open circuit potential; Ohmic loss across membrane; Activation overpotentials at anode & cathode; Overpotential arising from ionomer resistance in electrode

Contamination (phase 2)

$$\Delta E = -\frac{1}{\beta}\ln\left[1-\theta_1\left(1-e^{-\frac{(t-t_1)}{\tau_1}}\right)\right] + I\Delta R_i$$

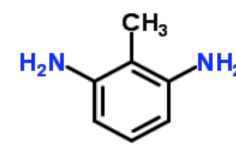
Recovery (phase 3)

$$\Delta E = -\frac{1}{\beta}\ln\left[(1-\theta_1)+(\theta_1-\theta_2)\left(1-e^{-\frac{(t-t_2)}{\tau_2}}\right)\right] + I\Delta R_i$$

Output

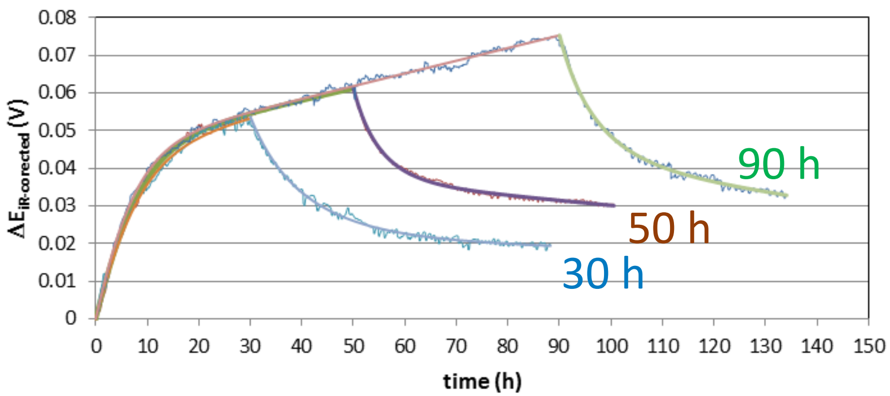
- Coverage of catalyst sites (θ)
- Time constant (τ)
- Rate of ionomer contamination (**a**) & recovery (**b**)
- Predictive

Parametric studies were carried out with a model organic compound,



2,6-DAT

Effect of infusion time (64 ppm 2,6-DAT)



- **Model fits experimental data well**
- **Model provides info (e.g., θ_1, τ_1) that cannot be measured experimentally**
- **Have not verified the model fully**

Light blue line is experimental data
Dark blue, red & green lines are fits to contamination & recovery data, respectively

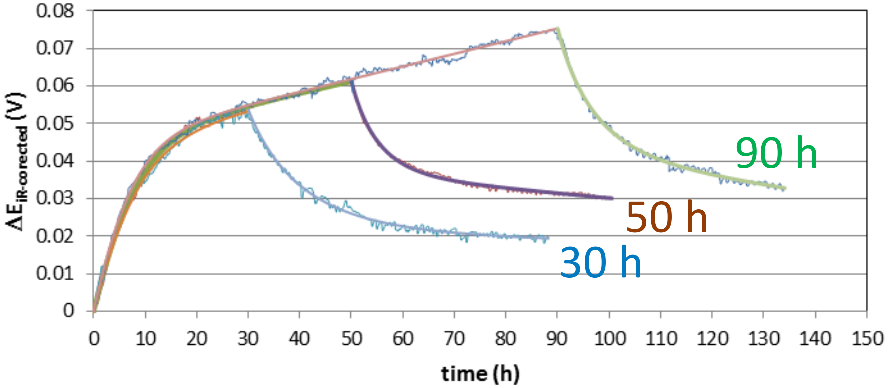
Cell T = 80°C, RH = 32/32%RH, Back pressure = 150/150kPa, Current density = 0.2A/cm^2, Cathode catalyst = 0.4 mg/cm^2

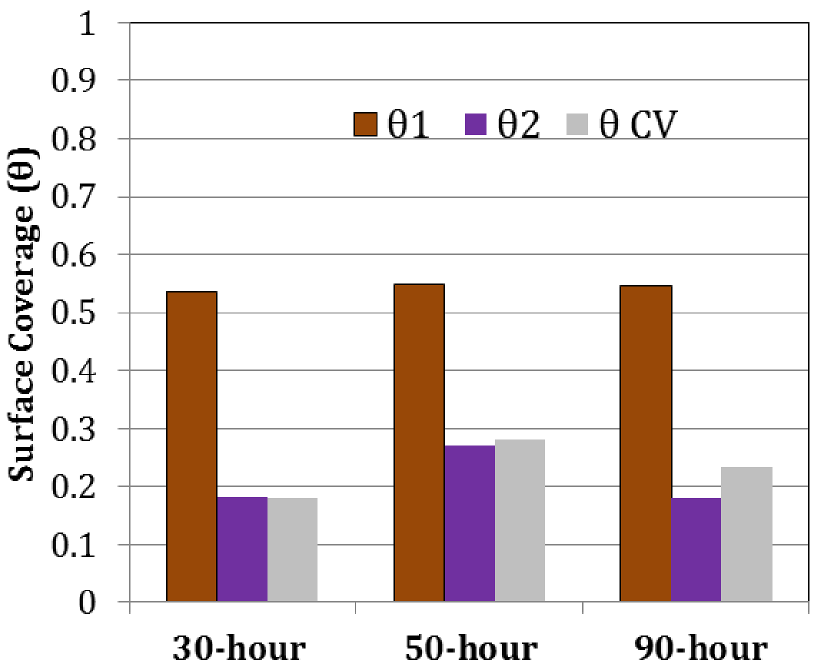
Information provided by USC

Technical Progress – Effect of Infusion Time on Fuel Cell Contamination & Passive Recovery

- **Longer infusion time resulted in greater performance loss**
- **Infusion time has minimum impact on Pt sites poisoned (θ_1)**
- **Model can predict catalyst site coverage well**
  - **θ_2 and θ_{CV} agree**

Effect of infusion time (64 ppm 2,6-DAT)





θ_1 = Pt surface coverage after steady-state contamination, determined from modeling

θ_2 = Pt surface coverage after steady-state passive recovery, determined from modeling

θ_{CV} = Pt surface coverage after passive recovery, independently measured via cyclic voltammetry

Information provided by USC

Technical Accomplishments – Summary of Structural Materials Parametric and Modeling Studies

Parametric study

- Contamination impact depends on operating conditions (CD, concentration, Pt loading, RH interaction with Pt loading & concentration, temperature).
- Operating conditions (e.g., time, temperature) that cause more liquid/plastic contact need to be considered in developing a fuel cell system
- Cost, resin type & additives need to be considered when selecting BOP plastic materials

Suggested mitigation strategies:

- Minimize extract solution concentration (low leaching index)
    - Minimize contact time of the plastic materials with water in the fuel cell system
    - Minimize exposure of plastic material to high temperature
    - Increase RH (water flush) or increase RH and potential cycling (ex-situ recovery)
    - Choose clean BOP materials (usually more expensive, resin type)
    - Modify commercial plastic materials to minimize contaminants (i.e., coating, less or alternative additives)

Model

- Model can predict catalyst site coverage and voltage loss due to contamination and recovery well
- Model still need to be validated over a wider range of operating conditions (extract concentration, infusion time, current density, RH, & temperature)

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

Technical Accomplishments – Responses to Previous Year Reviewers' Comments

- **The lack of developer input on contaminants outside of GM is a weakness. The premise of the project could lead to results that are particular for one developer or group of developers.**

  Response: Ballard Power Systems, Nuvera, and Proton Onsite provided input on BOP materials studied and shared insight on test procedures and poisoning mechanisms.

- **A project that seeks to address contamination from within the system is relevant to development. What compromises the probability that the end results of this project will be relevant to any individual developer is the low probability that an individual contaminant studied will be the same that actually affects a developer**.

  Response: This project's objective is to determine what leaches out from the BOP materials, quantify the impact of these multi-component leachates on fuel cell performance and then study the effect of the individual components and the effect of their interactions. The study of model compounds with specific functional groups will allow us to generalize what compounds will have an adverse effect on fuel cell performance. Furthermore, understanding whether these compounds come from the parent material or additives will help material suppliers design more appropriate materials for fuel cell application and fuel cell developers can pick "clean" materials for their system. We feel that this approach provides information that will be widely applicable, rather than relevant to a specific fuel cell developer.

  One of our objectives was to increase the awareness of contamination as an issue for fuel cell performance and durability as well as initiate similar research in the fuel cell community. The ultimate objective is to understand fundamental mechanisms of fuel cell contamination which will assist suppliers make cleaner, cheaper materials, and aid in the commercialization of automotive fuel cells.

- **Only one addition is suggested: reproduction of small-scale results with a larger cell or stack. It would be interesting to see if the results can be reproduced at that level.**

  Response: There are no current plans to reproduce this work with a larger cell or stack because the cost of stack testing is high. Furthermore, the amount of plastic material available is limited and hence, the extract amount available for testing is limited. With limited time and resources, we choose to focus on understanding the effects system contaminants have on fuel cell performance. In general, the fuel cell developers have observed that the effect on a 20-cell stack is always worse than a single 50 cm^2 cell. We chose cell size that's accepted in the fuel cell community & scalable.

Proposed Future Work

- Quantify leachate concentrations and determine the effect of leaching parameters on material leaching concentration
- Determine the fuel cell performance impact of lower leachate concentrations
- Measure rates of soluble leachates in solution and volatiles in headspace
- Perform mechanistic studies on organic and ionic model compound derived from structural plastics to understand the effect of individual and mixtures of compounds on fuel cell performance
- Validate mechanistic model against different contaminants, mixture of contaminants and a wider range of operating conditions

Collaborators

Institutions	Role
National Renewable Energy Laboratory (NREL): H. Dinh (PI), G. Bender, C. Macomber, H. Wang, KC Neyerlin, B. Pivovar	**Prime, Oversees the project, broad screening and analytical characterization; membrane degradation material study**
General Motors LLC (GM): P. Yu, K. O'Leary, B. Lakshmanan, E.A. Bonn, Q. Li, A. Luong, R. Reid, J. Sergi, 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. Weidner, B. Tavakoli, J. Van Zee, M. Ohashi, M. Opu, M. Das, H. Cho	**Sub; Broad screening and deep probe study of assembly aids materials; modeling**
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.

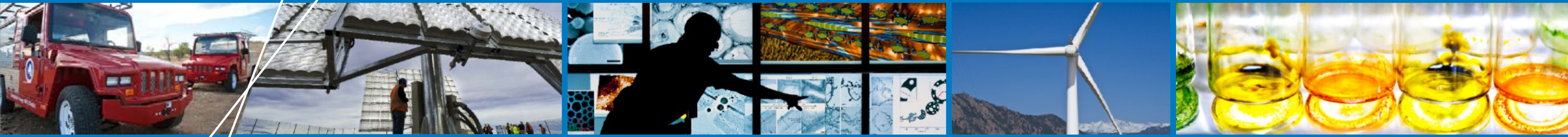
Approach: Screen BOP materials and select leachants and model compounds; perform parametric studies of the effect of system contaminants on fuel cell performance and durability; identify poisoning mechanisms and recommend mitigation strategies; develop predictive modeling and provide guidance on future 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. Completed parametric in-situ studies of structural materials and identified key operating conditions and interactions of parameters that impact fuel cell performance; developed a simple model to predict the voltage loss and recovery as a function of time due to contamination by an organic compound; parametric study and model provided better understanding of the impact of BOP contaminants and operating conditions on contamination and recovery mechanisms (Pt adsorption, absorption into catalyst ionomer, and ion-exchange with membrane); suggested mitigation strategies related to minimizing extract solution concentration; add more screening data to the NREL contaminants project website to disseminate 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 national labs, universities, and industry partners.

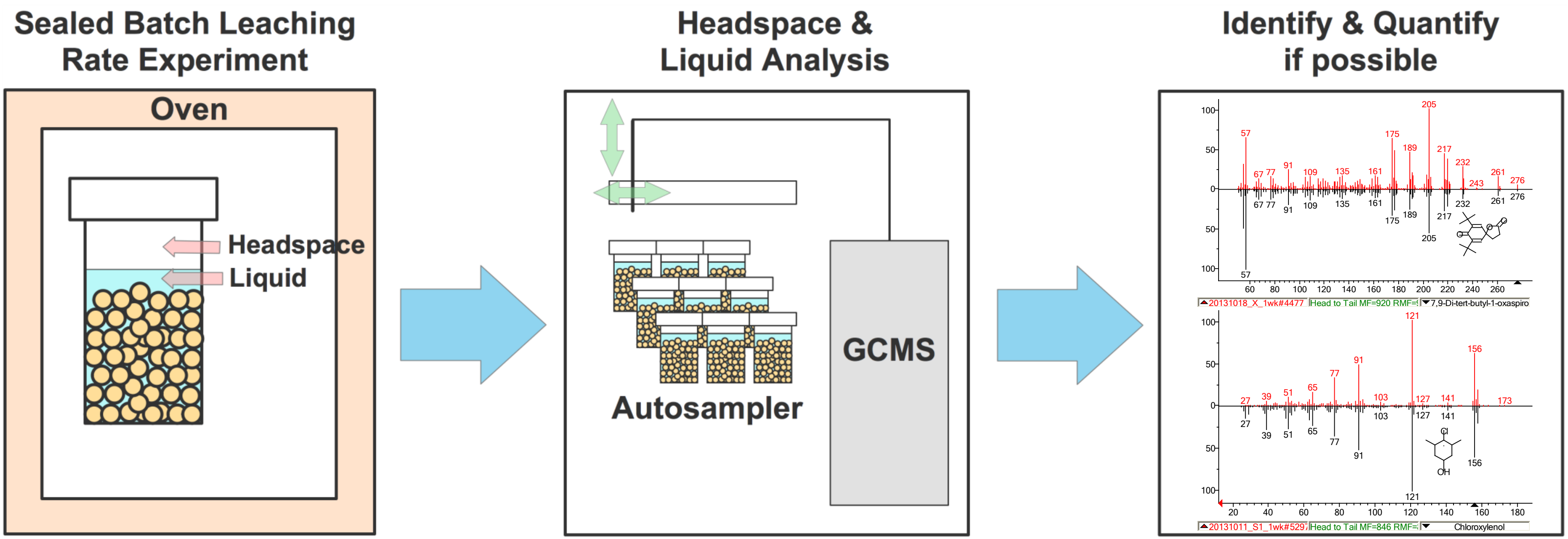
Proposed Future Research: Quantify leachate concentrations and determine the effect of leaching parameters on leachate concentration; Determine the fuel cell performance impact from the lower concentration of leachates; Measure rates of soluble leachates in solution and volatiles in headspace.

NREL
NATIONAL RENEWABLE ENERGY LABORATORY



Technical Back-up Slides

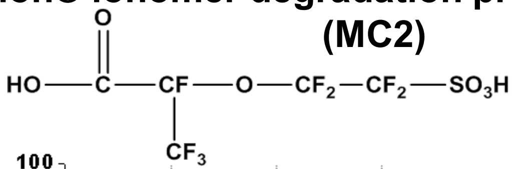
Technical Progress – Improve Characterization of Contaminants

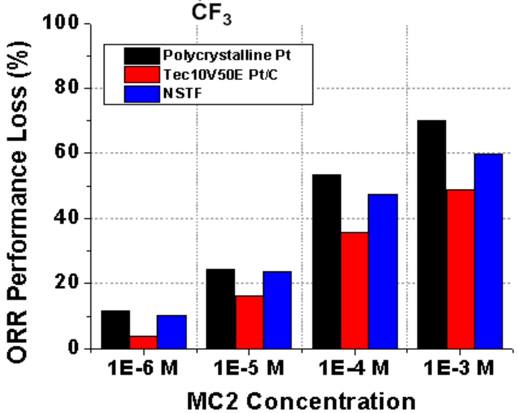


- **Use new GCMS tool to quantify organic leachates**
- **Design experiment and set up to determine leaching rates**
- **Explore volatile contaminants in headspace**
  - Goal is to measure rates of soluble leachates in solution and volatiles in headspace

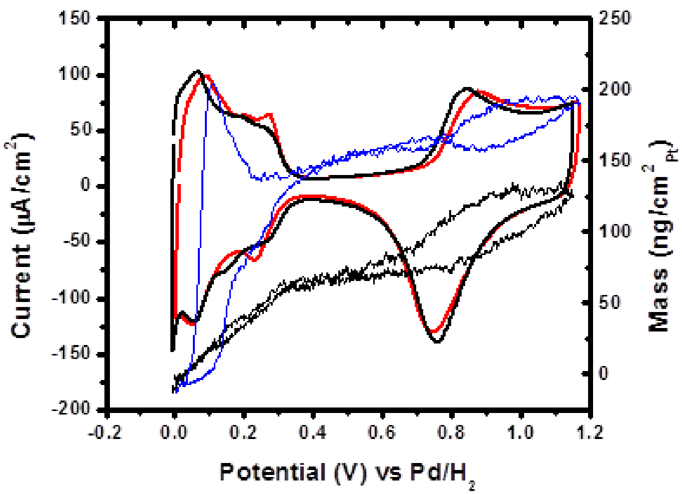
Technical Progress: Impact of PEM degradation products on Pt electrode

Nafion® ionomer degradation product (MC2)

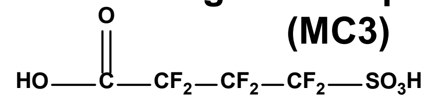


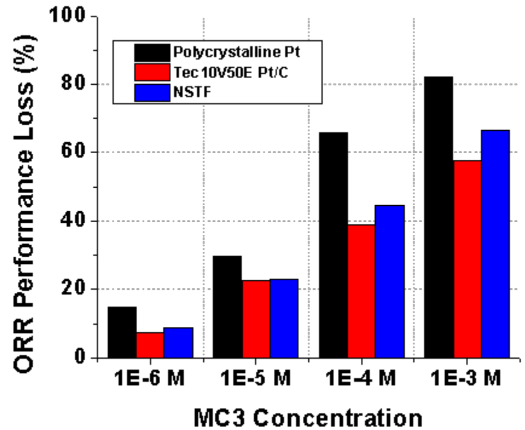


Electrode surface coverage at 0.9 V = 21%
34% loss in kinetic current

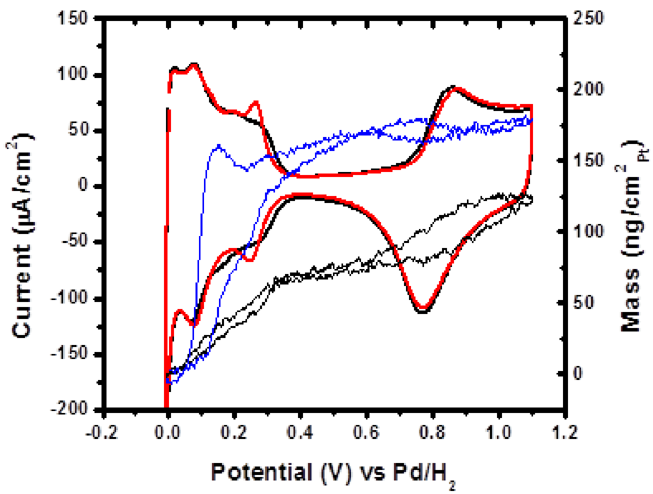


3M™ ionomer degradation product (MC3)





Electrode surface coverage at 0.9 V = 26%
42% loss in kinetic current

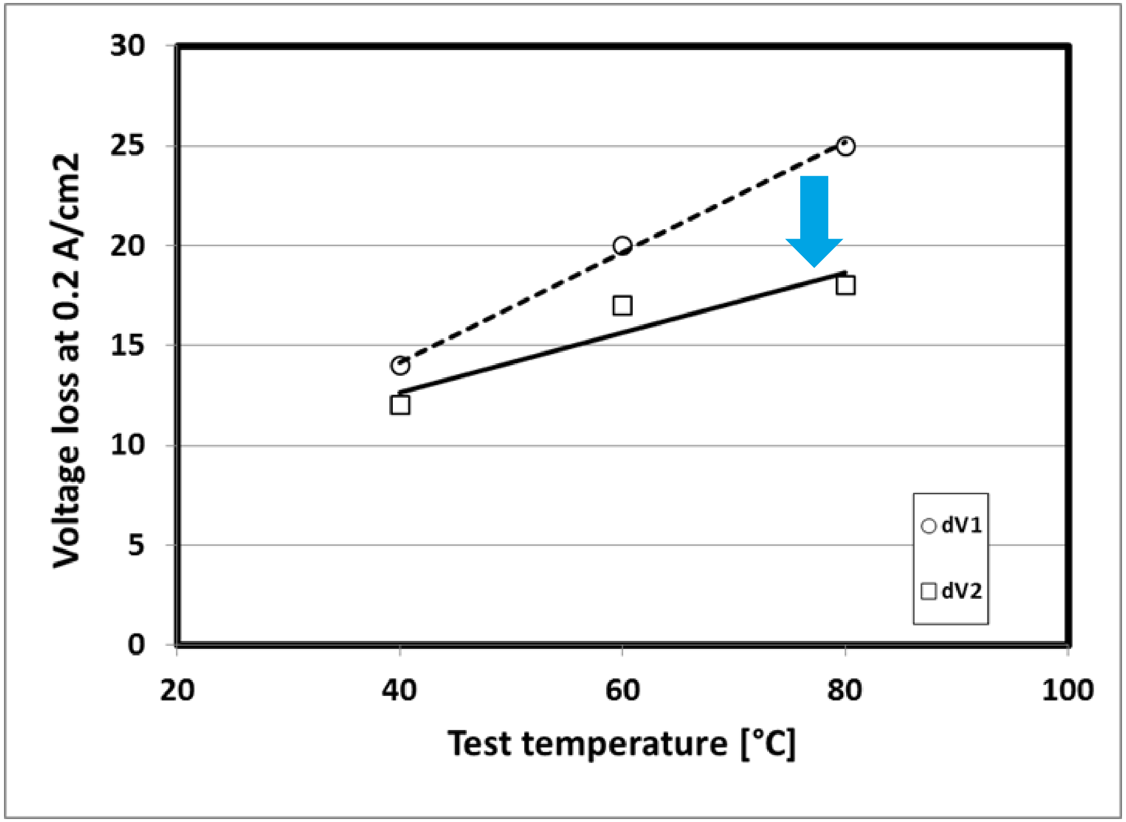


Pt EQCM: scan rate 50 mV/s; initial potential -0.01 V; 1×10^{-4} M

- Concentration effect on ORR performance is similar for polycrystalline Pt, high surface area Pt/C and 3M™ NSTF catalyst
- Electrochemical quartz crystal microbalance (EQCM) capability has a been developed to better understand the effect of contaminants on catalyst
  - Measure mass change simultaneously with current as a function of potential

Information provided by CSM & NREL

Technical Progress – Effect of Operating Temperature (EMS-4)

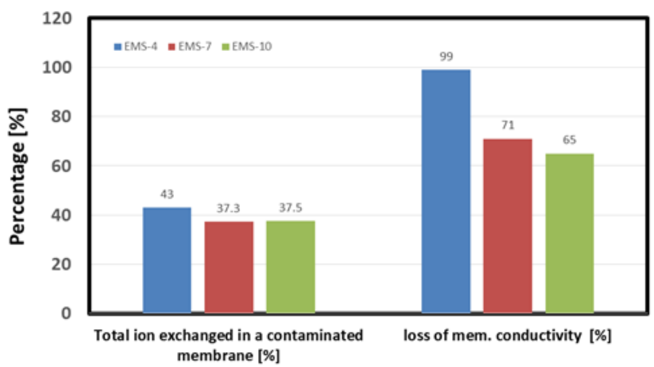


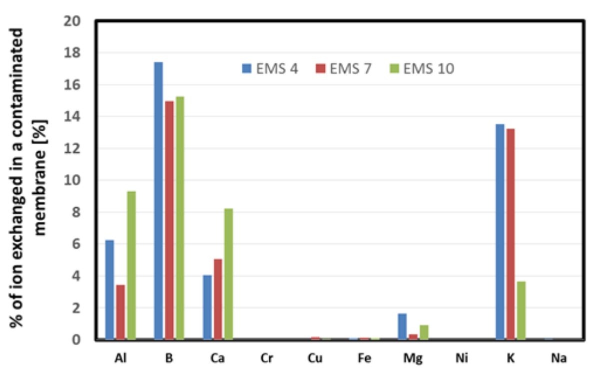
- Cell voltage loss, dV1, increases linearly with increased temperature
  - Trend may be due to mixtures of contaminants present
- More recovery observed at 80°C than at 40°C
  - May be due to higher water mole fraction in gas phase at 80°C, flushing away contaminants

Information provided by GM

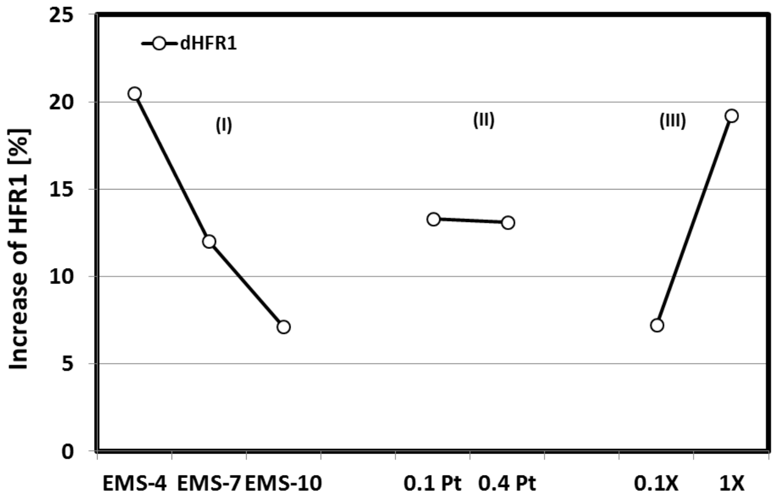
Technical Progress – Contaminants Impact on High Frequency Resistance (HFR)

- HFR increases with higher extract solution concentration,
  - Species in extract solution (e.g., Ca^{2+}, K^{+}) react with membrane sulfonic group, resulting in loss of membrane conductivity;
  - consistent with membrane ex-situ test results
- HFR is not significantly impacted by Pt loading
- Contamination of membrane is partially reversible (ΔHFR2 < ΔHFR1)

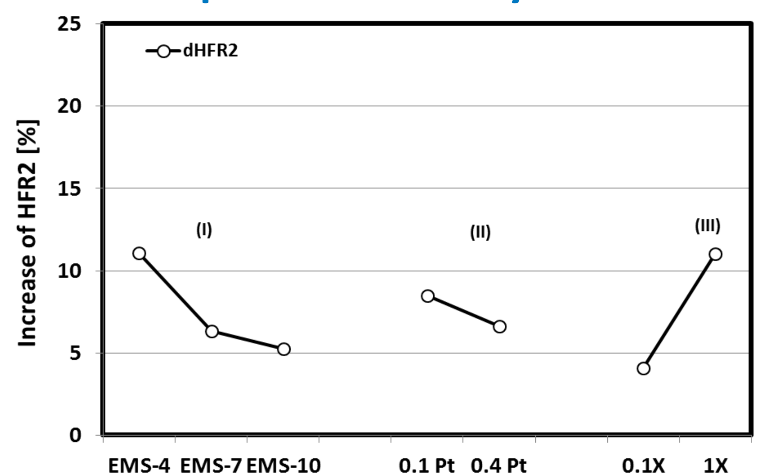




ΔHFR1 after contaminant infusion



ΔHFR2 after 7-hour of passive recovery



Information provided by GM

Remaining Challenges and Barriers

- **Batched leaching method does not adequately represent the real fuel cell systems, but it is a good method to concentrate the contaminants.**
- **One of the biggest challenges to determining realistic contamination rates is that extremely low concentrations are obtained and they may be below the detection limit of the instruments used to quantify the contaminants.**
- **Low contaminants concentrations may not affect fuel cell performance**
- **Extracts contain multiple components (organics, inorganics, cations, anions) and it is difficult to determine contamination mechanisms**
- **Volatile contaminants may also be present and have an effect on fuel cell performance. Previous work focused on aqueous soluble contaminants.**
- **Determining realistic dosages for in-situ fuel cell test**