V.E.3 Effect of System Contaminants on PEMFC Performance and Durability

Huyen N. Dinh (Primary Contact), Guido Bender, Clay Macomber, Heli Wang

National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401-3305
Phone: (303) 275-3605
Email: Huyen.Dinh@nrel.gov

DOE Manager

David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

Partners

- CRADA: Paul T. Yu and Balsu Lakshmanan, General Motors LLC (GM), Honeoye Falls, NY
- John Weidner, University of South Carolina, Columbia, SC
- Ryan Richards and Jason Christ, Colorado School of Mines, Golden, CO

Project Start Date: October 1, 2013
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

Our overall objective is to decrease the cost associated with balance of plant (BOP) materials in polymer electrolyte membrane fuel cell (PEMFC) systems without compromising function, fuel cell performance, or durability.

Our specific project objectives are to:

- Understand the severity of relevant BOP materials on fuel cell performance.
- Identify and quantify contaminants derived from BOP materials.
- Understand fundamental contamination mechanisms and recoverability of BOP materials.
- Guide system developers on future material selection.
- Be a resource to the fuel cell community.

Fiscal Year (FY) 2015 Objectives

- Determine the effect of leaching conditions on contaminant concentration
- Develop gas chromatography mass spectrometry (GCMS) method to identify and quantify organic contaminants
- Investigate fundamental mechanisms of contamination and recoverability using organic and anion model compounds

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Office's Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

Technical Targets

This project focuses on quantifying the impact of system contaminants on fuel cell performance and durability. Insights gained from these studies will increase performance and durability by limiting contamination-related losses and decreasing overall fuel cell system costs by lowering BOP material costs. Proper selection of BOP materials will help meet the following DOE 2020 targets:

- Cost: $30/kW for transportation; $1,000–1,700/kW for stationary
- Lifetime: 5,000 hours for transportation; 60,000 hours for stationary (2–10 kW)

FY 2015 Accomplishments

- We expanded the set of leaching conditions (time, temperature, surface area/water ratio) and determined that plastic material type and time significantly impacted leachate concentration. Hence, BOP material selection and the material's exposure time to water are important considerations for fuel cell systems and operations.
- Three methods to quantify organic concentrations in leachates were explored. GCMS-flame ionization detector (FID) yielded the best trade-off between sensitivity and reproducible data. The ranges of caprolactam (<10 ppm) and aniline (<20 ppm) concentrations found in polyamide material leachates provided important guidance on selecting concentrations to be used in infusion experiments.
- More trace organic species were identified via solid phase micro-extraction GCMS, suggesting

BOP leachates comprise complicated mixtures of organics.

- We determined that low BOP leachate concentrations, caprolactam, and mixtures of caprolactam and sulfate had an impact on fuel cell performance, including Pt adsorption and membrane and catalyst ionomer poisoning.
- Multiple techniques (cyclic voltammetry, electrochemical quartz crystal microbalance, and oxygen reduction reaction [ORR]) were performed to understand the role of functional groups and fluorocarbon chain length on Pt adsorption and ORR activity.
- The NREL website (www.nrel.gov/hydrogen/contaminants.html) and interactive material data tool (www.nrel.gov/hydrogen/system_contaminants_data) were enhanced by updating the list of NREL publications and presentations and adding contaminants-related publications from the Naval Research Lab. This website serves as a resource for the fuel cell community.

INTRODUCTION

Cost and durability issues of PEMFC systems are challenging for the fuel cell industry. The current status of fuel cell system cost is $55/kW, much lower than $124/kW in 2006, but still higher than the ultimate target of $40/kW [1]. As fuel cell systems become more commercially competitive, the impact of contaminants derived from fuel cell system component materials becomes more important. Such contaminants—from structural materials, lubricants, greases, adhesives, sealants, and hoses—have been shown to affect the performance and durability of fuel cell systems. Lowering the cost of PEMFC system components requires understanding of the materials used in these components as well as the contaminants derived from them. Unfortunately, there are many possible contamination sources from system components [2-12]. Currently deployed, high-cost, limited-production systems use expensive materials for system components. In order to make fuel cell systems commercially competitive, the cost of BOP components must be lowered without sacrificing performance and durability. Fuel cell durability requirements limit the performance loss attributable to contaminants to at most a few millivolts over the required lifetimes (thousands of hours), which means system contaminants must have a near-zero impact.

As catalyst loadings decrease and membranes are made thinner (both are current trends in automotive fuel cell research and development), fuel cell operation becomes even more susceptible to contaminants. In consumer automotive markets, low-cost materials are usually required, but lower cost typically implies higher contamination potential. The results of this project will provide the information necessary to help the fuel cell industry make informed decisions regarding the cost of specific materials versus the potential contaminant impact on fuel cell performance and durability. The project will also identify the impact of different operating conditions on contaminant concentrations, quantify and identify the contaminants in leachate solutions, and enhance understanding of the impact of selected model compounds on fuel cell performance.

APPROACH

Our goal is to provide an increased understanding of fuel cell system contaminants and to help guide the implementation and, where necessary, development of system materials to support fuel cell commercialization. While much attention has been paid to air and fuel contaminants, system contaminants have received limited public attention and very little research has been publicly reported [2-9]. Our approach aims to 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 compounds and mixtures of compounds on fuel cell performance, and disseminate information about material contamination potential that would benefit the fuel cell industry in making cost-benefit analyses for system components. To date, fuel cell system BOP materials are based upon existing automotive material sets. These materials often contain additives and processing aids that may be detrimental to fuel cell performance and durability. The BOP materials selected for this study were generally developed for other applications. Leachate solutions were created from BOP materials to identify compounds that leach out of them. The leachates, individual compounds and compound combinations were studied to understand the effect of BOP materials and specific functional groups on the fuel cell.

RESULTS

One of this year's accomplishments was updating NREL's contaminants website with related publications and presentations from NREL as well as the Naval Research Lab. This publicly accessible website serves as a resource for the fuel cell community—it has a material database of about 60 commercially available BOP materials (structural components, hoses, and assembly aids such as seals, gaskets, and adhesives) and their contamination potential and impact on fuel cell performance. The NREL material screening data tool was designed to be interactive, easy to use, and informative to the fuel cell community [2].

In addition, we expanded the conditions for extracting contaminants from plastics: time (10–1,000 h), temperature (50–90°C), and plastic surface area/water ratio (SA/vol = 1.5–3 cm^2/mL), as outlined in Table 1. The effects of these leaching conditions and the plastic material type on the leaching index (LI), which is the sum of the total organic carbon (TOC, ppm) and solution conductivity (µS/cm), are shown in Figure 1. As expected, the less expensive polyamide (PA) material leached out more contaminants (higher LI) than the polyphthalamide (PPA) material. Furthermore, longer time, higher temperature, and higher SA/vol ratio resulted in more contaminants extracted. Statistical analysis showed that the three major leaching parameters affecting contaminant concentration are: plastic material type, time, and the interaction between time and material type. Hence, BOP material selection and the material's exposure time to liquid water are very important considerations for fuel cell systems design and operations.

One focus this year was to develop a GCMS method to quantify the concentration of organic contaminants in material leachates. To accomplish this, we explored three GCMS methods: total ion count-single ion monitoring, thermal conductivity detector, and FID. GCMS-FID yielded the best trade-off between sensitivity and reproducibility. The results for the eleven leachate solutions (Table 1) are summarized in Figure 2. The caprolactam and aniline concentrations in the PA leachates were below 10 ppm and 20 ppm, respectively. In contrast, the PPA leachate solutions were relatively clean with caprolactam and aniline concentrations of 1 ppm or below the detection limit of the GCMS method. The quantification of caprolactam and aniline, two major organic species identified in structural plastic leachates, provided important guidance on selecting concentrations for fuel cell infusion experiments.

Leachates typically contain a variety of contaminants, including organics, inorganics, anions, and cations. These species can adsorb onto Pt catalyst surface and/or affect membrane/catalyst ionomer conductivity. We studied the impact of mixtures, as produced from the leaching of PA and PPA materials (Figure 3a), as well as the impact of individual model compounds (caprolactam and sulfate anion, Figure 3b). Both caprolactam and sulfate anion were found in the leachate solutions, and hence they were chosen for the model compound study.

Figure 3a shows that the PA leachate, which has more organic and ionic contaminants (Table 1), resulted in a higher fuel cell performance loss (ΔV_1) than the cleaner PPA leachate. Also, the PA leachate showed incomplete self-induced recovery (ΔV_2) while full recovery was observed

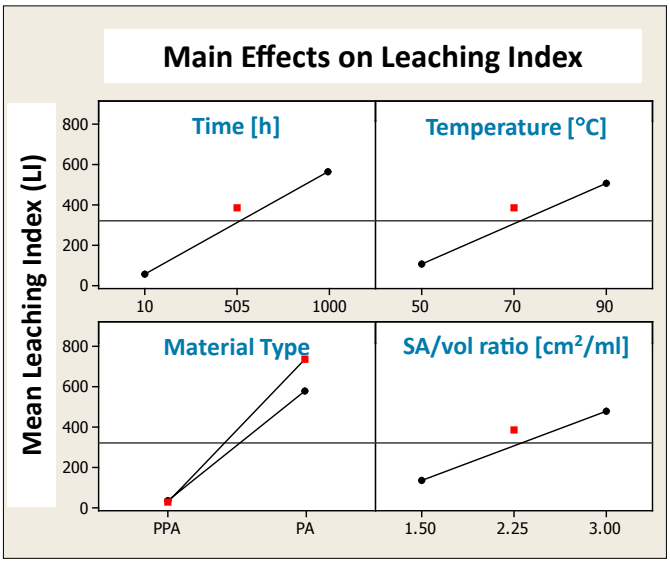


FIGURE 1. Effects of material type and leaching conditions (time, temperature, and surface area to volume ratio) on the solution LI (conductivity + total organic carbon). Leachates and analysis provided by GM.

TABLE 1. Different Leaching Conditions Used to Extract Contaminants from the PPA and PA Material, as well as the Sample Number and the Measured TOC and Solution Conductivity of These Leachate Solutions

	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)

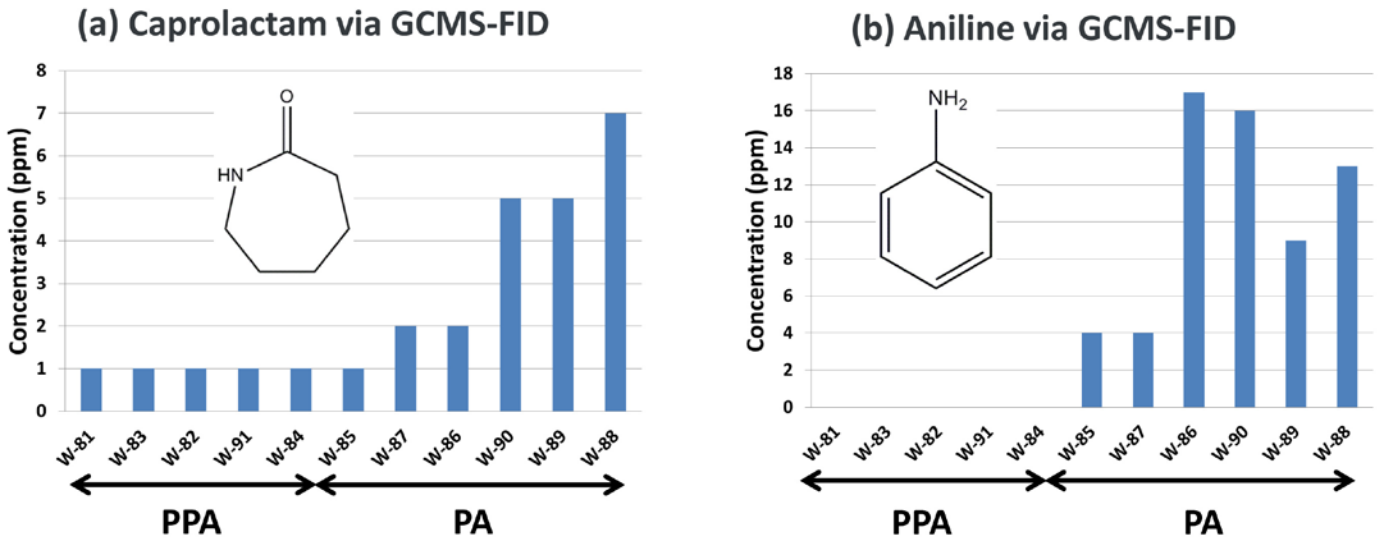
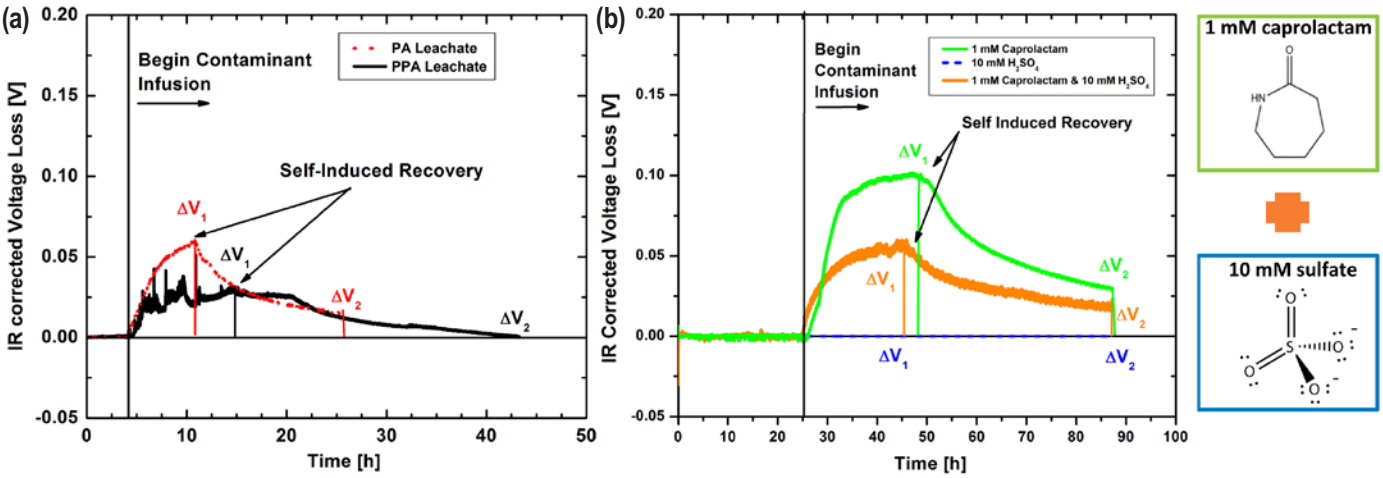


FIGURE 2. Concentration of caprolactam and aniline in the different PPA and PA leachates, as quantified by GCMS-FID method developed at NREL. PPA material leachates are relatively clean compared to PA material leachates.

for the PPA leachate. When 1 mM caprolactam was infused into the fuel cell cathode (Figure 3b, green curve), a relatively high fuel cell performance loss (ΔV_1 = 100 mV) and incomplete self-induced recovery (ΔV_2 = 30 mV) were observed. Surprisingly, no fuel cell performance loss was measured for the infusion of 10 mM sulfate anion at 0.2 A/cm^2 (Figure 3b, blue curve). This may be due to the Donnan exclusion effect and/or non-adsorption of sulfate onto Pt oxide. When a mixture of 1 mM caprolactam and 10 mM sulfate was infused into the fuel cell cathode (Figure 3b,



PA	ΔV_1 = 55 mV	ΔV_2 = 16 mV
PPA	ΔV_1 = 23 mV	ΔV_2 = 0 mV

1 mM caprolactam	ΔV_1 = 100 mV	ΔV_2 = 30 mV
1 mM caprolactam & 10 mM sulfate mixture	ΔV_1 = 60 mV	ΔV_2 = 17 mV
10 mM sulfate	ΔV_1 = 0 mV	ΔV_2 = 0 mV

FIGURE 3. (a) In situ fuel cell voltage loss due to contaminants (ΔV_1) derived from the PPA (black) and PA (red) materials. (b) The effect of individual model compounds: caprolactam (green), sulfate anion (blue), and mixtures of caprolactam and sulfate anion on the in situ fuel cell voltage loss due to contaminants (ΔV_1) and self-induced recovery (ΔV_2). Standard operating conditions (SOC): 80°C, 32/32% inlet relative humidity, 0.2 A/cm^2, H_2/air stoic = 2/2; 150/150 kPa, cathode Pt loading = 0.4 mg/cm^2.

orange curve), a lower fuel cell voltage loss was measured (ΔV_1 = 60 mV) compared to the caprolactam alone. This indicates that there is an interaction between caprolactam and sulfate, which is currently being investigated. Incomplete self-induced recovery was also observed for this mixture. Other supporting data (not shown) indicates that caprolactam had an impact on membrane conductivity, poisoned Pt sites to some extent, blocked Pt oxide formation, and decreased oxygen reduction reaction mass activity.

Model compound studies are important because they provide a more in-depth understanding of the contamination and recovery mechanisms of specific contaminants, identify the contaminant(s) that may have contributed to the overall fuel cell performance loss, and provide insights about the potential interaction(s) of different contaminants. Furthermore, results from the model compound studies contribute to the general understanding of compound-specific contaminants, based on their chemical structure, rather than specific plastic materials. This helps with BOP material selection and design for fuel cell systems.

CONCLUSIONS AND FUTURE DIRECTIONS

- We updated the list of NREL publications and presentations and added contaminants-related publications from the Naval Research Lab on the NREL project website.
- We determined that plastic material type and leaching time significantly impacted leachate concentration. Hence, BOP material selection and the material's exposure time to water are important considerations for fuel cell systems and operations.
- We developed a method to quantify organic concentrations in leachates. GCMS-FID yielded the best trade-off between sensitivity and reproducible data. The ranges of caprolactam (<10 ppm) and aniline (<20 ppm) concentrations found in polyamide material leachates provided important guidance on selecting concentration to be used in infusion experiments.
- We determined that low BOP leachate concentrations, caprolactam, and mixtures of caprolactam and sulfate had an impact on fuel cell performance, including Pt adsorption and membrane and catalyst ionomer poisoning.
- We will perform ex situ mechanistic studies on individual and mixtures of model compounds to understand interaction between different species in leachate solutions and their effect on fuel cell performance.
- We will develop analytical methods to identify and quantify volatile species, if any exist, derived from structural materials.
- We will study the effect of contaminants on low loading Pt/C catalyst (0.1 mg Pt/cm^2) and advanced catalysts (e.g., Pt alloys/C).
- We will develop an understanding of the impact of contaminants on catalyst ionomers.
- We will study the effect of non-sulfonated perfluorinated membrane degradation products on fuel cell performance.
- We will disseminate project information via the NREL website, publications, reports, and presentations.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Jason M. Christ, K.C. Neyerlin, Ryan Richards, and Huyen N. Dinh, "Concentration Effects of Polymer Electrolyte Membrane Degradation Products on Oxygen Reduction Activity for Three Platinum Catalysts," *J. Electrochem. Soc.* **161** (14) F1360–F1365 (2014).

2. Jason M. Christ, K.C. Neyerlin, Heli Wang, Ryan Richards, and Huyen N. Dinh, "Impact of Polymer Electrolyte Membrane Degradation Products on Oxygen Reduction Activity for Platinum Electrocatalysts," *J. Electrochem. Soc.* **161** (14) F1481–F1488 (2014).

3. James Waldecker, "System Contaminant Library Published," Fuel Cell Tech Team Accomplishment Report, 2014 U.S. DRIVE Highlight.

4. Huyen N. Dinh, "Making Fuel Cells Cleaner, Better, and Cheaper," NREL R&D Technical Highlight (2015).

5. Hyun-Seok Cho, Mayukhee Das, Heli Wang, Huyen N. Dinh, and J.W. Van Zee, "The Contamination Mechanism and Behavior of Amide Bond Containing Organic Contaminant on PEMFC," *J. Electrochem. Soc.* **162** (4) F427–F435 (2015).

6. Huyen N. Dinh, "Effect of System Contaminants on PEMFC Performance and Durability," Section V.B.1. *2014 DOE Hydrogen and Fuel Cells Program Annual Progress Report*, pp. V128–V132.

7. Jason M. Christ, K.C. Neyerlin, Ryan Richards, and Huyen N. Dinh, "Adsorption Characteristics of Polymer Electrolyte Membrane Chemical Degradation Products and Their Impact on Oxygen Reduction Reaction Activity for Platinum Catalysts," American Chemical Society Meeting, San Francisco, CA, August 2014.

8. Huyen N. Dinh, Jason M. Christ, Clay Macomber, Charles Staub, Guido Bender, and Heli Wang, "Effect of System Contaminants on PEMFC Performance and Durability," Project update to DOE, NREL, Golden, CO, September 24, 2014.

9. Jason Christ, Charles Staub, K.C. Neyerlin, Ryan Richards, and Huyen N. Dinh, "Effect of Organic Model Compound Contaminants on Platinum Catalysts," 226th Electrochemical Society Meeting, Cancun, Mexico, October 9, 2014.

10. Huyen N. Dinh, Jason Christ, Clay Macomber, Guido Bender, Charles Staub, and Paul Yu, "Effect of System Contaminants on PEMFC Performance and Durability," Fuel Cell Tech Team Meeting, Southfield, MI, February 11, 2015.

11. Charles Staub, Jason Christ, Guido Bender, Clay Macomber, Heli Wang, and Huyen N. Dinh, "Multiple Advance Diagnostics to Probe the Effect of Balance of Plant Materials on Fuel Cell Performance," Abstract #1599, 227th Electrochemical Society Meeting, Chicago, IL, May 2015.

12. Huyen N. Dinh, "Effect of System Contaminants on PEMFC Performance and Durability," DOE Fuel Cell Technologies Office Annual Merit Review, Washington, DC, June 2015.

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3. Huyen N. Dinh, "Effect of System Contaminants on PEMFC Performance and Durability," Section V.E.1. *2013 DOE Hydrogen and Fuel Cells Program Annual Progress Report*, pp. V129–V134.

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5. Huyen N. Dinh, "Effect of System Contaminants on PEMFC Performance and Durability," Section V.B.1. *2011 DOE Hydrogen and Fuel Cells Program Annual Progress Report*, pp. 640–643.

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