

V.F.1 Effect of System Contaminants on PEMFC Performance and Durability

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Project Start Date: July 20, 2009

Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

Our overall objective is to decrease the cost associated with system components without compromising function, fuel cell performance, or durability. Our specific project objectives are to:

- Identify and quantify system-derived contaminants.
- Develop ex situ and in situ test methods to study contaminants derived from system components.
- Identify severity of system contaminants and impact of operating conditions.
- Identify contamination mechanisms.
- Develop models/predictive capability.
- Guide system developers on future material selection.
- Disseminate knowledge gained to the community.

Fiscal Year (FY) 2014 Objectives

- Identify impact of operating conditions.
- Develop a mechanistic model for contamination.
- Disseminate project information to the fuel cell community.
- Develop understanding of leaching conditions' impact on contaminant concentration.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Office 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 balance-of-plant (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

FY 2014 Accomplishments

- Developed the leaching index as a quick material screening method.
- Identified impact of various fuel cell operating conditions (contaminant concentration, relative humidity, cell temperature, current density, and catalyst loading) on fuel cell performance and recovery for selected structural material extracts. This knowledge can help identify future mitigation strategies for contaminants.
- Developed a model for contamination mechanism based on experiments with model organic compounds.
- Improved NREL website (www.nrel.gov/hydrogen/contaminants.html) and interactive material data tool (www.nrel.gov/hydrogen/system_contaminants_data/) by adding more data (60 system component materials)

total) and project information and improving user experience.

- Presented DOE webinar on “An Overview of NREL’s Online Data Tool for Fuel Cell System-Derived Contaminants” [1].



INTRODUCTION

Cost and durability issues of polymer electrolyte membrane fuel cell (PEMFC) systems have been challenging for the fuel cell industry. The current status of fuel cell system costs is \$55/kW, much lower than \$124/kW in 2006, but still higher than the ultimate target of \$30/kW [2]. As fuel cell systems become more commercially competitive, the impact of contaminants derived from fuel cell system component materials has risen in importance. Contaminants derived from fuel cell system component materials—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 and the contaminants that are derived from them. Unfortunately, there are many possible contamination sources from system components [3-5]. 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 needs to be lowered without sacrificing performance and durability. Fuel cell durability requirements limit the performance loss attributable to contaminants to at most a few mV over 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), operation of fuel cells 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 results will also identify the impact of different operating conditions and possible mitigation strategies for contaminants.

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 [6-8]. Our approach is to perform parametric studies to characterize the effects of system contaminants on fuel cell performance, as well as to identify the severity of contamination, identify contamination mechanisms, develop a model, and disseminate information about material contamination potential that would benefit the fuel cell industry in making cost-benefit analyses for system components. The BOP materials selected for this study are commercially available commodity materials and are generally developed for other applications for which common additives/processing aids may not be a concern, but they may present problems for fuel cells. We studied leachates as well as model compounds that are capable of replicating the deleterious impact of system-based contaminants.

RESULTS

One of this year’s accomplishments was expanding the BOP material data base and project information as well as improving the user experience on the NREL website. The screening results for 60 commercially available BOP materials (structural, hoses, assembly aids such as seals, gaskets, and adhesives), using multiple screening methods to identify and quantify system-derived contaminants, are archived and made publicly accessible on the NREL website. The NREL material screening data tool was designed to be interactive, easy to use and informative to the fuel cell community. Furthermore, a DOE webinar was presented by Dinh to give an overview of NREL’s online data tool and provide a tutorial on how to use the Web-based tool to access project results [1].

General Motors (GM) screened and categorized 34 structural plastic materials into groups based on their basic polymer resin (e.g., polyamide or PA) and manufacturers. They found that the leaching index (LI), which is the sum of the solution conductivity and total organic carbon (TOC), is a quick way to screen plastic materials. The leaching index is an indicator of the amount of contaminants (organics, inorganics, and ions) leaching from the material. Figure 1 shows that higher leaching index generally results in higher cell voltage loss and is correlated with lower material cost. The implication is that fuel cell developers can do a quick screening of the BOP material candidates by carrying out the leaching experiment and measure the TOC and solution conductivity of the extract solution. These measurements are quick and easy to do. If some good material candidates are found, then further testing, such as electrochemistry, membrane conductivity, advanced analytical characterization, and in situ infusion experiments can be carried out to better understand what contaminant species are present and how they impact fuel cell performance.

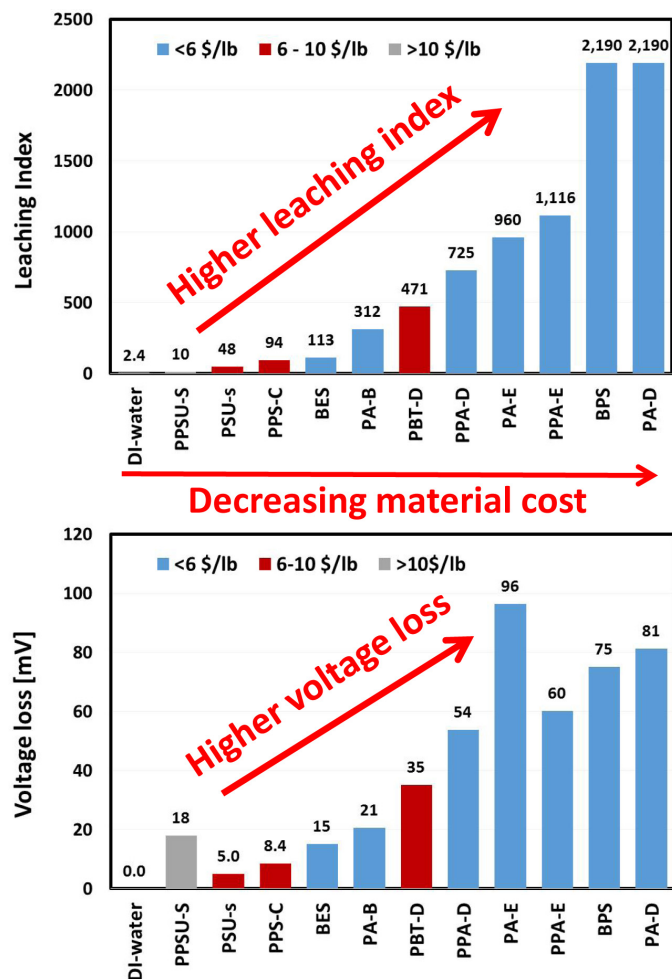


FIGURE 1. Higher leaching index (conductivity + total organic carbon) is generally correlated with higher fuel cell performance loss and lower material cost. BES = Bakelite epoxy-based material – Sumitomo; BPS = Bakelite phenolic-based material – Sumitomo; S = Solvay; C = Chevron Philips; B = BASF; D = DuPont; E = EMS; Information provided by GM.

From 34 structural plastic materials screened, three were selected for in situ infusion parametric studies to understand the effect of the polymer resin (PA and PPA or polyphthalamide), additive (e.g., percent of glass fiber added for plastic structural integrity), and different operating conditions (contaminant concentration, relative humidity (RH), cell temperature, current density (CD), and catalyst loading) on fuel cell performance and recovery. The parameters studied reflect 80% of typical fuel cell operating conditions. Figure 2 shows that the PA material (EMS-4), which has the highest LI, resulted in higher voltage loss than PPA materials. Furthermore, the PPA material that has the lower glass fiber (GF) content (30% GF for EMS-10 vs. 50% GF for EMS-7) resulted in a lower LI and lower fuel cell performance loss. These results imply that the polymer resin type and additives are important contaminant source considerations. In addition, Figure 2 shows that the in situ

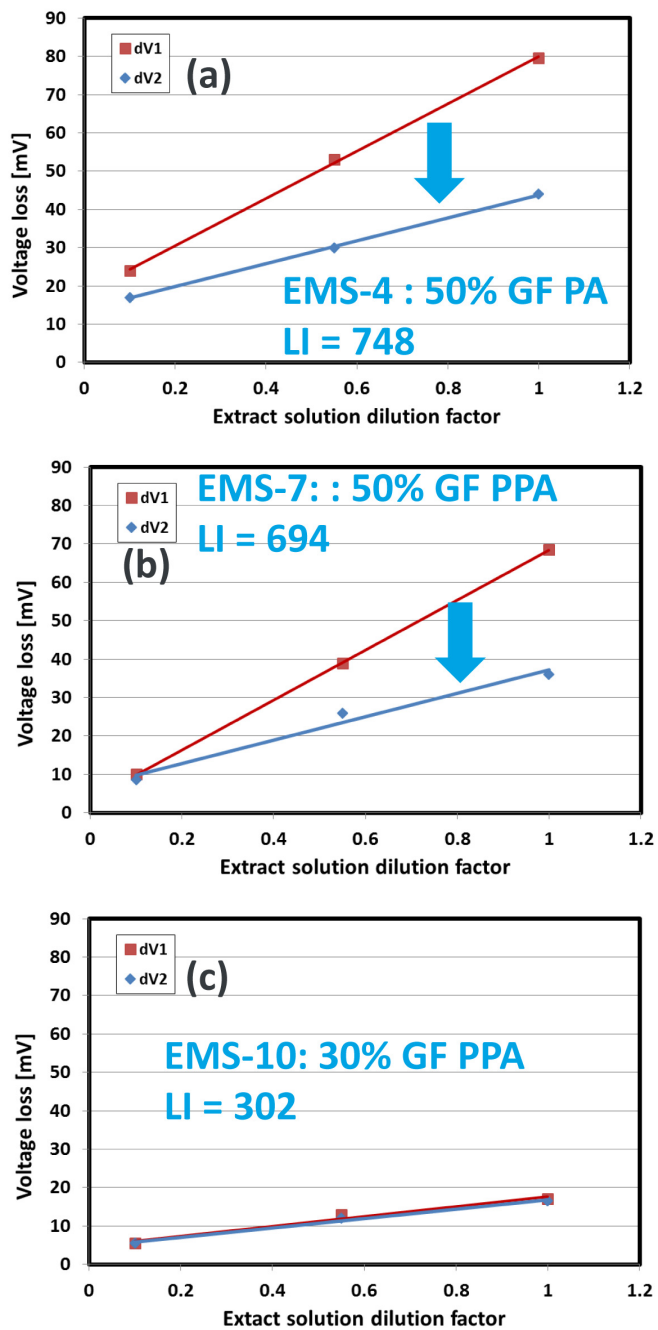


FIGURE 2. In situ fuel cell voltage loss due to contaminants (dV1) increases linearly as a function of structural material leachate concentration due to contamination of the fuel cell cathode: (a) EMS-4 50% glass fiber PA, (b) EMS-7 50% glass fiber PPA, and (c) EMS-10 30% glass fiber PPA. The voltage loss after passive recovery (dV2) is also shown. The plots also show that polymer resin type and additives in plastic materials matter. The LI for the different materials is also shown for comparison. Standard operating conditions (SOC): 80°C, 32/32% inlet RH, 0.2 A/cm², H₂/air stoichiometry = 2/2; 150/150 kPa; Information provided by GM.

fuel cell voltage loss due to contaminants (dV1) increases linearly as a function of leachate concentration (red line) and the contamination effect can be partially reversed in the absence of contaminants (blue line). A similar trend was observed for all three structural materials studied.

Figure 3 summarizes the main effect of different operating conditions (concentration, RH, CD, and catalyst loading) on fuel cell performance loss due to contamination (dV1) and recovery (dV2) in the absence of contaminants (also known as passive recovery). As expected, fuel cells with low Pt loading are more sensitive to BOP plastic leached contaminants and result in higher cell voltage loss, regardless of the material studied. Figure 3a shows that the voltage loss increases with increasing current density while RH appears to have a minimum effect on voltage loss. RH is a complicated factor since it controls the mole fraction of both water and contaminant into the fuel cell. As RH increases, more water vapor enters the fuel cell and can help flush out the contaminants. However, more water vapor also means more contaminants are brought into the fuel cell and results in higher voltage loss. These two phenomena may counter each other and lead to insensitivity of RH to fuel cell performance loss. Figure 3b shows that these four parameters have similar effect on the voltage loss after passive recovery (dV2), but the magnitude of the voltage loss is lower compared to dV1. These voltage losses were obtained during infusion at relatively low current density (0.2 A/cm²). Analysis of the polarization curves before contamination (beginning of life) and after passive recovery showed that the trend on fuel cell voltage loss due to these operating parameters is similar at low and high current densities (e.g., 1.2 A/cm²).

Statistical analysis of the parametric results showed that CD and/or dosage are/is the most significant factor(s) affecting cell performance, followed by leachate

concentration, interaction of RH and Pt loading, Pt loading, and interaction of RH and concentration. It is important to note that interaction between different operating conditions should be considered with respect to contamination effect. For example, trends toward lower catalyst loadings may mean that fuel cells need to operate at higher RH since these two parameters interact with one another.

From the parametric study, we have identified several mitigation strategies to minimize the leachate concentration (leaching index). These strategies include minimizing the contact time and contact ratio of the plastic materials with water in the fuel cell, minimizing exposure of plastic material to high temperature, increasing the RH or increasing the RH and potential cycling (ex situ recovery), choosing clean BOP materials (usually more expensive, e.g., resin type and additive), and working with material suppliers to minimize contaminants (i.e., removing additives that are not applicable to fuel cells and using less or alternative additives that do not leach out contaminants). These strategies can minimize fuel cell performance loss due to system-derived contaminants.

CONCLUSIONS AND FUTURE DIRECTIONS

- We improved the NREL project website and interactive data tool by expanding the material database, enhancing user experience, archiving the results, and making them publicly accessible.
- We developed the leaching index as a good, quick screening method for potential system components. This data is also included on the NREL website.
- We found that cost, polymer resin type and additives need to be considered when selecting BOP plastic materials for fuel cell systems because the choice can have different degrees of contamination impact.

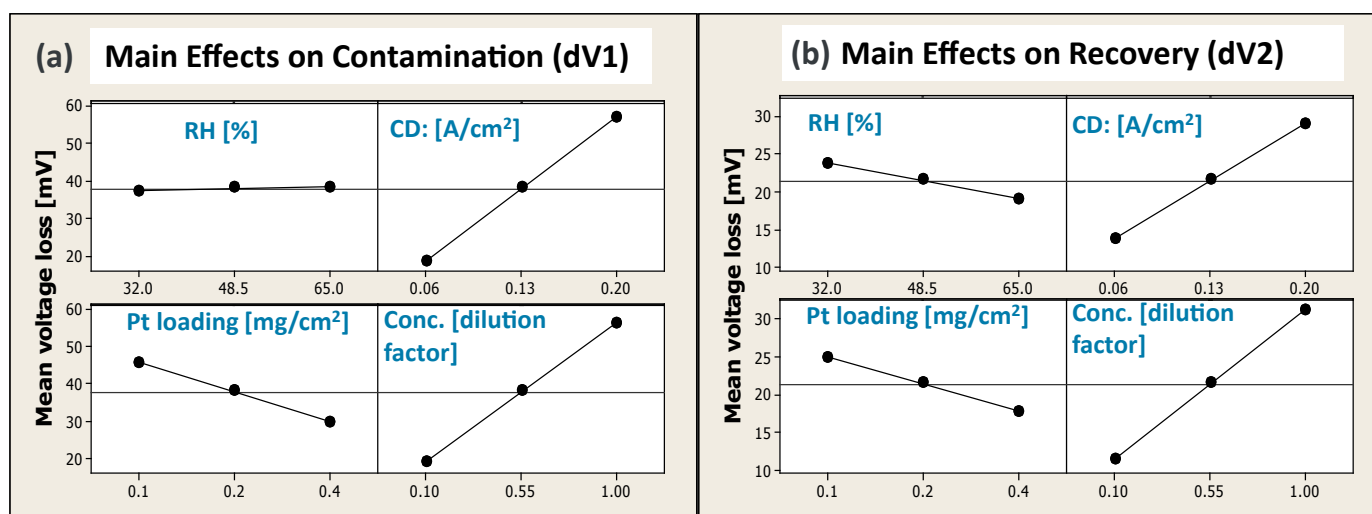


FIGURE 3. Summary of the effects of different operating conditions on fuel cell performance loss (dV1) and passive recovery (dV2). SOC were used.

- We found that contamination impact depends on fuel cell operating conditions (CD, concentration, Pt loading, RH interaction with Pt loading and concentration, temperature) and that interactions between different operating conditions need to be considered.
- We found that operating conditions (e.g., time, temperature) that cause more liquid/plastic contact need to be considered in developing a fuel cell system because they can lead to higher contaminant concentration (higher leaching index).
- We have identified several mitigation strategies to minimize the leaching index and hence minimize the performance loss.
- We will determine the fuel cell performance impact of lower leachate concentrations.
- We will develop analytical methods to measure soluble leachates in solution and volatiles in headspace.
- We will 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.
- We will disseminate project information via the NREL website, publications, reports, and presentations.

FY 2014 PUBLICATIONS/PRESENTATIONS

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6. Christ, J.M. "Adsorption Characteristics of Polymer Electrolyte Membrane Chemical Degradation Products and their Impact on Oxygen Reduction Reaction Activity for Platinum Catalysts." Colorado School of Mines Chemistry Departmental Seminar, Golden, CO, April 2014.
7. Christ, J.M.; Neyerlin, K.C.; Richards, R.; Dinh, H.N. Presentation at the Electrochemistry Gordon Research Conference, Ventura, CA, January 2014.
8. Dinh, H.N.; Yu, P.T.; Weidner, J. "Effect of System Contaminants on PEMFC Performance and Durability." Presentation to the DOE Fuel Cell Tech Team, Southfield, MI, Jan. 15, 2014.

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