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

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Project Start Date: July 20, 2009
Project End Date: September 2013

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 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) 2013 Objectives

- Identify impact of operating conditions
- Identify contamination mechanism(s) for system contaminants
- Develop a model for contamination mechanism
- Disseminate project information to the fuel cell community

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 decrease 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 2013 Accomplishments

- Screened seven additional, relevant, commercially available BOP materials, as recommended by Ballard and Nuvera, for fuel cell contamination (62 BOP materials screened total).
- Identified contamination mechanism(s) of organic compounds: adsorption on catalyst, redox reaction, reaction and absorption with ionomer, and membrane poisoning.
- Determined that functional groups of organic compounds are important in understanding system contaminants and that performance loss may contain reversible, recoverable, and non-recoverable contributions. This knowledge can help identify future mitigation strategies for contaminants.

- Performed in-depth parametric studies to determine the impact of various fuel cell operating conditions (cell temperature, contaminant concentration, relative humidity [RH], current density, and catalyst loading) on fuel cell performance for selected extracts and organic compounds.
- Developed a model on the effect of organic compounds on fuel cell performance.
- Disseminated project information to the fuel cell community via the NREL website (www.nrel.gov/hydrogen/contaminants.html), publications, and presentations. The NREL website also includes an interactive material-selection tool that enables viewers to quickly find relevant and revealing information for a specific material relative to other materials in the same family class (www.nrel.gov/hydrogen/system_contaminants_data/).

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INTRODUCTION

Cost and durability issues of polymer electrolyte membrane fuel cell (PEMFC) systems have been challenging for the fuel cell industry. The projected BOP system cost (over $25/kW in 2012 [1]) has risen in importance as projected fuel cell stack cost has decreased (approximately $20/kW in 2012 [1] compared to $65/kW in 2006 [2]). Lowering the cost of PEMFC system components requires understanding of the materials used in these components and the contaminants that are derived from them, which have been shown to affect the performance and durability of fuel cell systems. 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 R&D), 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.

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 [6-9]. Our approach is to perform parametric studies to characterize the effects of system contaminants on fuel cell performance and durability, 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.

Last year, we identified and quantified potential contaminants derived from system component materials and screened the impact of leachants on the fuel cell catalyst, ionomer, and membrane via ex situ and in situ tests. Model compounds capable of replicating the deleterious impact of system-based contaminants were also studied.

The majority of our effort is focused on the liquid-based contaminants derived from structural plastics and assembly aid materials (lubricant, grease, adhesive, and seal). A minor part of our efforts is focused on an in situ durability study of gas-based contaminants (siloxane focus) and an ex situ electrochemical study of the effect of membrane degradation by-products on catalysis. 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.

RESULTS

We completed screening of 62 BOP materials total—from 14 different manufacturers, comprising different chemistries, and used for different functions—using multiple screening methods, totaling more than 740 experiments and over 1,000 h of in situ testing. Because there is a tremendous amount of data and knowledge generated from this project, we developed an NREL website (www.nrel.gov/hydrogen/system_contaminants_data/) to share the data with the public, including the screening results. For this report, we highlight some key accomplishments that emerged from our work, including the contamination mechanisms identified and the effect of fuel cell operating parameters.

We performed fundamental/mechanistic studies on selected organic model compounds and mixtures of compounds to understand their poisoning mechanisms and how they affect voltage loss, in both in situ fuel cell and ex situ electrochemical testing. Figure 1 shows an example data set that includes the performance effect of an extract

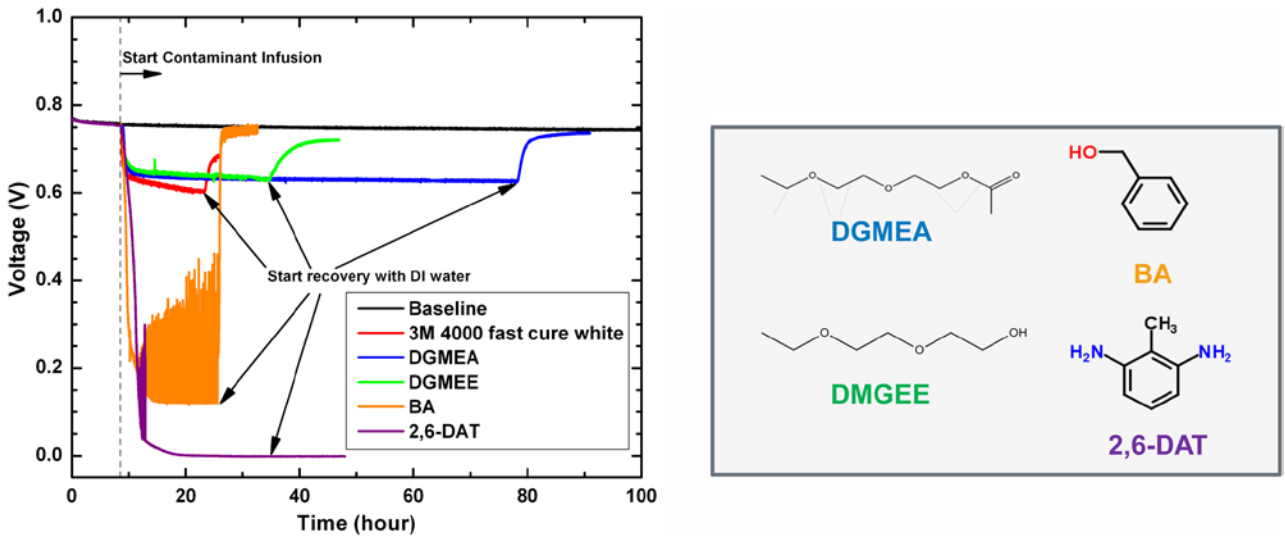
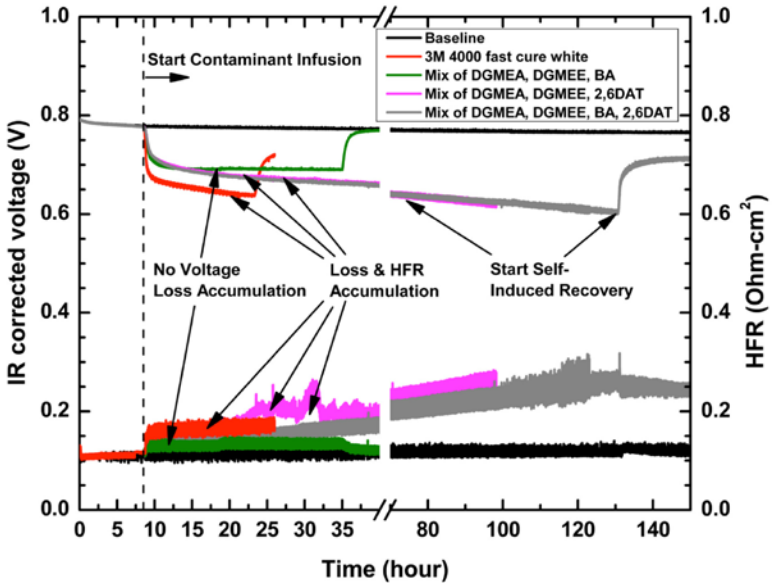


FIGURE 1. Total in situ cell voltage loss due to contamination of the fuel cell cathode by the individual organic model compounds (2-(2-ethoxyethoxy)-ethanol acetate, 2-(2-ethoxyethoxy)-ethanol, benzyl alcohol, and 2,6-DAT; total organic carbon = 1,280 ppm each). The black curve is the baseline curve where no contaminants were infused into the cathode. The red curve is the voltage loss resulting from infusing the 3M™ 4000 Fast Cure white extract (total organic carbon = 1,280 ppm). Standard operating conditions: cell temperature = 80°C, RH = 32%/32%, H_2 and air stoichiometry = 2/2, back pressure = 150/150 kPa, i = 0.2 A/cm^2.

as well as that of individual model compounds that were found in the extract. The extract was created by aging the urethane material 3M™ 4000 Fast Cure white in de-ionized water at elevated temperature. The four individual organic compounds, shown in Figure 1, were model compounds. Note that the experiment was designed such that all compounds or compound mixtures had the same total organic compound value. Voltage losses for the individual aliphatic compounds (2-[2-ethoxyethoxy]-ethanol acetate and 2-[2-ethoxyethoxy]-ethanol) reached steady state while the voltage loss for the extract continued to decrease. Voltage losses for the aliphatic and benzyl alcohol compounds were mostly reversible, indicating that these organic compounds were likely contaminated by reversible processes like physisorption onto the Pt surface and/or absorption into the membrane and ionomer. The voltage loss for 2,6-methyl benzenediamine (2,6-DAT) was irreversible, indicating that it may have chemisorbed and/or reacted with the membrane and ionomer. In summary, model compounds result in different contamination effects (voltage loss, high frequency resistance [HFR], and recoverability) than that observed for the multi-component extract.

Our studies show that mixtures of organic compounds may have different contamination and recovery effects than individual compounds, indicating that compound concentration is very important and further suggesting that interaction between organic compounds may occur. Figure 2 shows that the voltage loss and HFR for mixtures of aliphatics and benzyl alcohol reached steady state and were reversible (green curve), indicating minimal interaction between these three model compounds. Voltage loss and HFR for mixtures containing 2,6-DAT continued to change with time and were not reversible (magenta and grey curves), suggesting that 2,6-DAT dominated the contamination and recovery responses. The resistance data also indicated that organic contaminants can impact kinetic performance by either eliminating proton pathways to catalyst reaction sites or increasing the resistance of the ionomer in the catalyst layer. This process appeared to be slow and was associated with the 2,6-DAT compound. Voltage and HFR responses for 3M™ 4000 Fast Cure white showed the combined effect of the four individual organic compounds. Although the extract contained many components (organics, inorganics, and ions), these studies indicated that organic compounds can dominate the contamination and recovery effects. The table in Figure 2 is an example of the comprehensive quantitative analysis that we will be doing to quantify and understand the contamination effects.

From the 62 BOP materials screened, three structural materials and two assembly aid materials were selected for parametric studies. In situ infusion experiments were carried out on selected extracts and organic compounds to understand the effect of different operating conditions (contaminant concentration, RH, cell temperature, current density, and catalyst loading) on fuel cell performance and recovery. The parameters studied reflect 80% of typical fuel cell operation. Figure 3 shows the effect of concentration and RH on fuel cell performance in the presence of 2,6-DAT contaminant in the feed stream. The data confirmed that concentration was an important driver for cell performance loss. In addition, the data suggested that liquid water content may have impacted performance and recovery effects. This



Material Extract	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 [%]
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.

FIGURE 2. In situ cell voltage loss (internal resistance-corrected) and HFR change due to contamination of the fuel cell cathode by different organic compound mixtures. The total concentration for all mixtures were the same (total organic carbon = 1,280 ppm). Standard operating conditions were used.

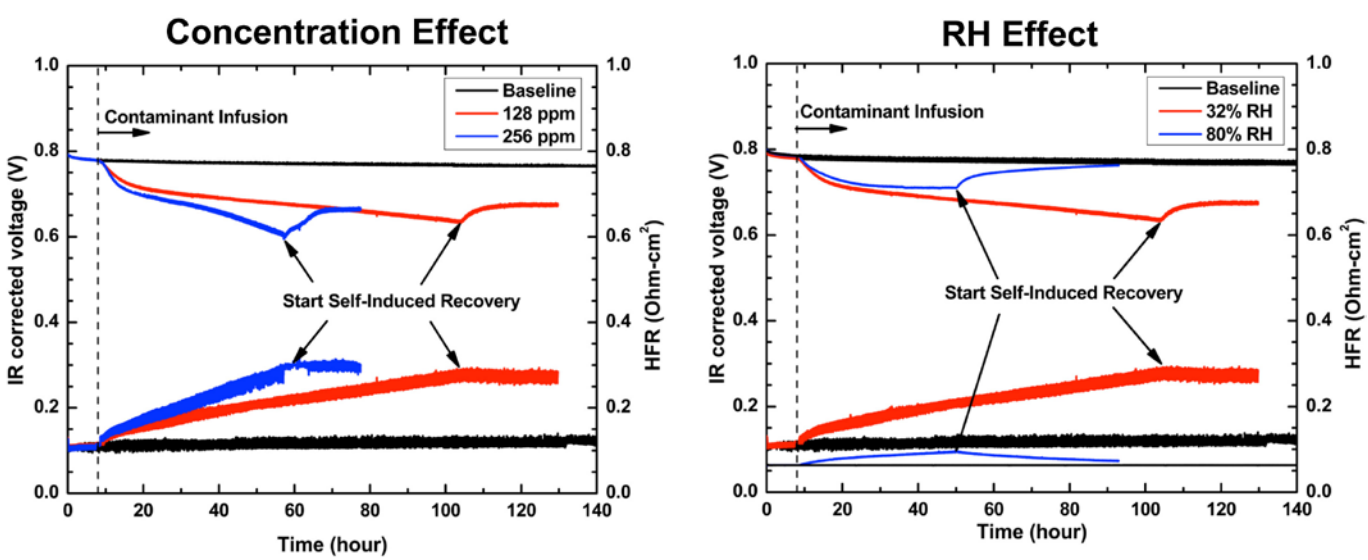
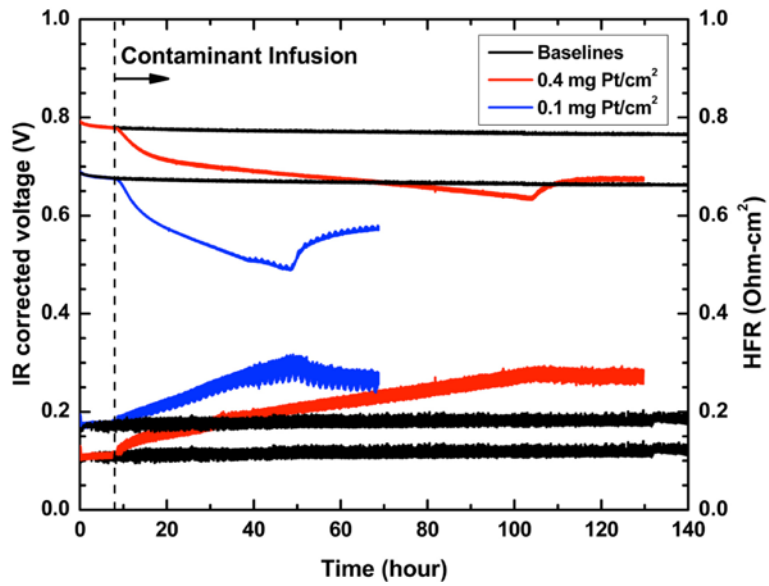


FIGURE 3. Example data from parametric study of organic compound: 2,6-DAT. The left plot shows the effect of contaminant concentration and the right plot shows the RH effect on fuel cell performance and recovery. Standard operating conditions were used.

information may be useful for mitigating the effect of specific contaminants. The plot and table in Figure 4 show that lower catalyst loading resulted in a stronger response to an identical contaminant (2,6-DAT). This response was indicated by a higher immediate performance loss, which was likely due to contaminant adsorption onto the catalyst surface. A larger



Anode/Cathode Catalyst Loading [mg Pt/cm^2]	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 [%]
0.05/0.4	77	11	1	1.7	24	38
0.05/0.1	104	15	4	3.2	45	47

FIGURE 4. The effect of catalyst loading on fuel cell performance and recovery in the presence of 2,6-DAT contaminant. Standard operating conditions were used.

performance loss accumulation was also observed for the lower catalyst loading and this loss may be related to the contaminant reacting with ionomer and membrane.

The experimental work for the project is complete, and in-depth analysis of in situ parametric data will be performed for the remainder of the project. Furthermore, we have developed and are finalizing the isothermal time-dependent two-dimensional model for characterizing the effects of contaminants at various operating conditions and for selected model compounds. The model has been validated with experimental data.

CONCLUSIONS AND FUTURE DIRECTIONS

- We found that functional groups of organic compounds are important in understanding system contaminant effects.
- We found that performance loss may contain reversible, recoverable, and non-recoverable contributions.
- We identified several contamination mechanisms: adsorption on catalyst, redox reaction, and reaction/absorption processes with ionomer and membrane, resulting in ohmic and kinetic loss.
- We found that the feed rate, RH, and current density strongly affected contamination while cell temperature changes (80°C and 50°C) showed some impact on performance loss and recovery. We also found that liquid water content may impact performance and recovery and that lower Pt catalyst loading resulted in higher performance loss.
- We modeled the effects of operating conditions on fuel cell performance for specific contaminating species and model compounds.
- We will continue to perform comprehensive quantitative analysis of in situ parametric data to characterize the contamination effects.
- We will disseminate project information via the NREL website, publications, reports, and presentations.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Macomber, C.S.; Christ, J.; Wang, H.; Pivovar, B.S.; Dinh, H.N. "Characterizing Leachant Contaminants from Fuel Cell Assembly Aids, a Prelude to Effects on Performance." *ECS Transactions* **2012,** *50* (2), 603-618.

2. Opu, M.S.; Ohashi, M.; Cho, H.-S.; Macomber, C.S.; Dinh, H.N.; Van Zee, J.W. "Understanding the Effects of Contaminants from Balance of Plant Assembly Aid Materials on PEMFCs In-Situ Studies." *ECS Transactions* **2012,** *50* (2), 619-634.

3. Wang, H.; Macomber, C.S.; Dinh, H.N. "Evaluation of PEMFC System Contaminants on the Performance of Pt Catalyst via Cyclic Voltammetry." *ECS Transactions*, **2012**, 50(2), 659-669.

4. Christ, J.M.; Neyerlin, K.C.; Wang, H.; Richards, R.; Dinh, H.N. "Impact of Polymer Electrolyte Membrane Degradation Products on the Activity of the Oxygen Reduction Reaction for Platinum Catalysts." *ECS Transactions*, **2012,** *50* (2), 691-700.

5. Dinh, H. "Effect of System Contaminants on PEMFC Performance and Durability." Section V.B.1. *2012 DOE Hydrogen and Fuel Cells Program Annual Progress Report*; pp. V57-V62.

6. H. Cho and J.W. Van Zee, "An isothermal model for predicting performance loss in PEMFCs from BOP leachates", *J. Electrochem. Soc*., submitted (2013).

7. H. Cho, M. Ohashi, and J.W. Van Zee, "Understanding the contamination mechanisms for PEMFCs resulting from aniline leachate", *Electrochim. Acta*, submitted (2013).

8. C.S. Macomber, J. Christ, H. Wang, B. Pivovar, H.N. Dinh. "Characterizing Leachant Contaminants from Fuel Cell Assembly Aids, a Prelude to Effects on Performance." 222nd ECS Meeting, Honolulu, HI, Oct. 7–12, 2012.

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10. Hyun-Seok Cho, Md. S. Opu, Masato Ohashi, J.W. Van Zee. "The Contamination Behavior of Organic Compounds on PEMFC." 222nd ECS Meeting, Honolulu, HI, Oct. 7–12, 2012.

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12. J.M. Christ, K.C. Neyerlin, H. Wang, R. Richards, H.N. Dinh. "Utilizing a Rotating Ring Disk Electrode to Simultaneously Measure Contaminate Species Adsorption Effects on Two Different Catalyst Surfaces." 222nd ECS Meeting, Honolulu, HI, Oct. 7–12, 2012.

13. J.M. Christ, K.C. Neyerlin, H. Wang, R. Richards, H.N. Dinh. "Impact of Polymer Electrolyte Membrane Degradation Products on the Activity of the Oxygen Reduction Reaction for Platinum Catalysts." 222nd ECS Meeting, Honolulu, HI, Oct. 7–12, 2012.

14. H.N. Dinh, M. Das, K.C. Neyerlin, Md. Opu, H. Wang, C.S. Macomber, M. Ohashi, J.W. Van Zee. "Screening Balance of Plant Materials to Understand Their Effect on Fuel Cell Performance." 222nd ECS Meeting, Honolulu, HI, Oct. 7–12, 2012.

15. H.N. Dinh, B. Lakshmanan. "Effect of System Contaminants on PEMFC Performance and Durability." Fuel Cell Tech Team Presentation, Nov. 14, 2012.

16. H.N. Dinh, G. Bender. "Effect of System Contaminants on PEMFC Performance and Durability." DOE Mid-Year Review, Golden, CO, Feb. 21, 2013.

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