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

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

Fiscal Year (FY) 2011 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:

- 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 poisoning mechanisms and investigate mitigation strategies.
- Develop models/predictive capability.
- Develop material/component catalogs based on system contaminant potential to guide system developers on future material selection.
- Disseminate knowledge gained to the community.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program'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 be applied toward the development of a catalog of system component materials that help meet the following DOE 2010 targets:

- Cost: $30/kW for transportation, $750/kW for stationary
- Lifetime: 5000 hours for transportation, 40,000 hours for stationary

Accomplishments

- Selected 50 relevant balance-of-plant (BOP) materials based on physical properties, functionality in a fuel cell environment, and cost.
- Established a standard set of experimental protocols for analysis, including leaching, cyclic voltammetry, analytical characterization and in situ fuel cell protocol(s).
- Benchmarked testing protocols and equipment among the different labs.
- Preliminary ex situ screening of 19 polymeric structural plastics.
- Identified leachants via gas chromatography-mass spectroscopy (GC-MS) and selected a few model species for further study.
- Developed a clear long-term project plan with gates and strategies for selecting materials for in-depth fuel cell studies, model species studies, durability testing, and modeling.

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Introduction

Cost and durability issues of polymer electrolyte membrane fuel cell (PEMFC) systems have been challenging in the fuel cell industry. The cost of the BOP ($51/kW in 2010 [1]) system has risen in importance with decreasing fuel cell stack cost ($25/kW in 2010 [1] compared to $65/kW in 2006 [2]). Lowering the cost of PEMFC system components requires understanding of the materials used in the system 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 are using expensive materials for system components. In order to make fuel cell systems commercially competitive, the cost of the BOP components needs to be reduced without sacrificing performance and durability. Fuel cell durability requirements limit the performance loss due to contaminants to at most a few mV over required lifetimes (thousands of hours), which means close to zero impact for system contaminants.

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 typically 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 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 help provide guidance in the implementation, and where necessary, the development of system materials that will help enable fuel cell commercialization. While much attention has been paid to air and fuel contaminants, system contaminants have received very limited attention publicly and very little 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 poisoning mechanisms, recommend mitigation strategies, develop predictive modeling, and disseminate material catalogs that benefit the fuel cell industry in making cost-benefit analyses of system components. We are identifying and quantifying potential contaminants derived from stack/component fabrication materials and quickly screening the impact of the leachants on fuel cell catalyst and membrane via ex situ tests. Model compounds capable of replicating the deleterious impact of system-based contaminants are also being studied. Developing standard test protocols to evaluate materials is important as this approach will allow for broader studies to be performed. Furthermore, information obtained from ex situ methods is being validated with in situ testing.

Our system materials selection is based on properties such as exposed surface area, total mass or volume in a system, fluid contact, function, cost, and performance implications. Current material prioritization and selection to study is based on perceived impact of potential system contaminants (based on GM internal knowledge): structural materials, elastomers for seals and (sub)gaskets, assembly aids (adhesives, lubricants), membrane degradation products, bipolar/end plates, and ions from catalyst alloys. Our project has a strong polymer focus, as much of the system is polymer based. Furthermore, we are studying commercially available, commodity materials. These materials are generally developed for other applications, where common additives/processing aids may not be a concern, but may present problems for fuel cells.

Results

We completed benchmarking of solution conductivity and total organic content (TOC) techniques, using the leachant solutions generated at GM for two polyphthalamide (PPA) structural materials (Dupont Zytel HTN51G35 HSLR® and Zytel HTN52G35 HSL®). As shown in Figure 1, reproducibility among the different labs for these techniques is consistent. Similar benchmarking was carried out at NREL and GM for GC-MS and inductively coupled plasma – optical emission spectroscopy; consistent reproducibility was found.

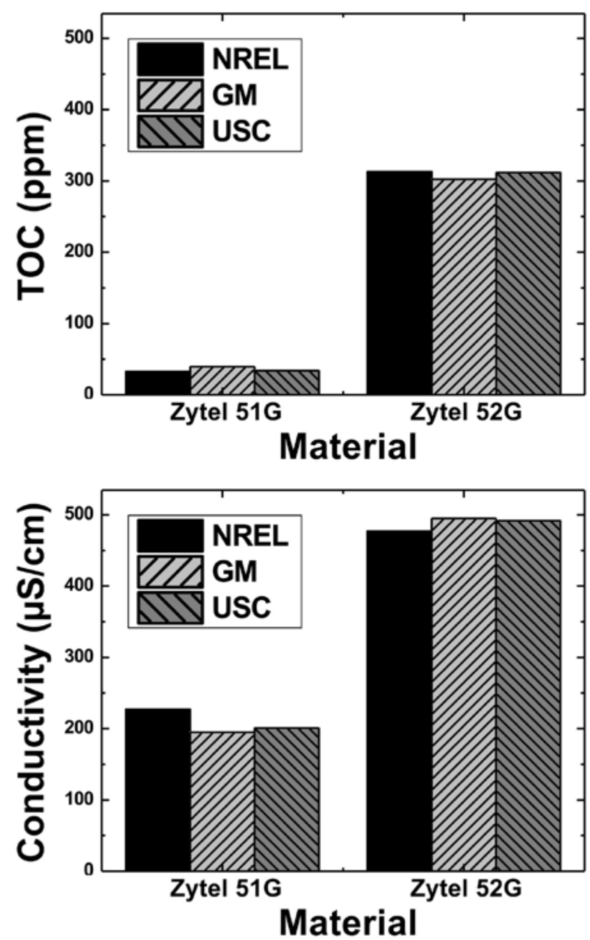

FIGURE 1. The TOC (upper) and solution conductivity (lower) measurements were carried out at NREL, GM, and USC. Reproducibility was consistent among the three labs.

We are screening 19 commercially available structural materials for their potential impact as system contaminants in fuel cell system. They are from the low cost Nylon™ family (polyamide and PPA) and the relatively more expensive polysulfones (PSU), polyphenylenesulfides (PPS) and polyphenylsulfones (PPSU) families. These structural materials underwent leaching protocols (soaked in de-ionized water at 90°C) for six weeks to extract potential contaminants from the parent materials into solution. Figure 2 summarizes the TOC and solution conductivity of these structural materials. As shown, the materials that have high levels of organic leachants do not necessarily have high ionic content. Preferred materials would have low TOC and conductivity values, as highlighted by the circle on the figure.

Initial screening of the leachants after one week of soaking shows that the PPS, PSU and PPSU families are relatively clean materials, with low TOCs and solution conductivities. Also, the liquid GC-MS method did not detect any organic leachants for these materials.

For the polyamide family (PA6, PA6,6, PPA), three common organic species were identified by liquid injection GC-MS: 1,8-diazacyclotetradecane-2,7-dione [DCTDD], caprolactam, and 1,6-hexandiol. The chemical structures of these species are shown in Figure 3. These species will be used as model compounds for further study. It is likely that DCTDD is a Nylon™ decomposition product and/or trapped waste product from the synthetic condensation reaction of adipic acid and hexamethylenediamine. Caprolactam is likely a residual monomer from a ring opening polymerization to synthesize PA6. Knowing the chemistry of the parent polymer and the polymer synthesis, it is understandable where these organic compounds originate from.

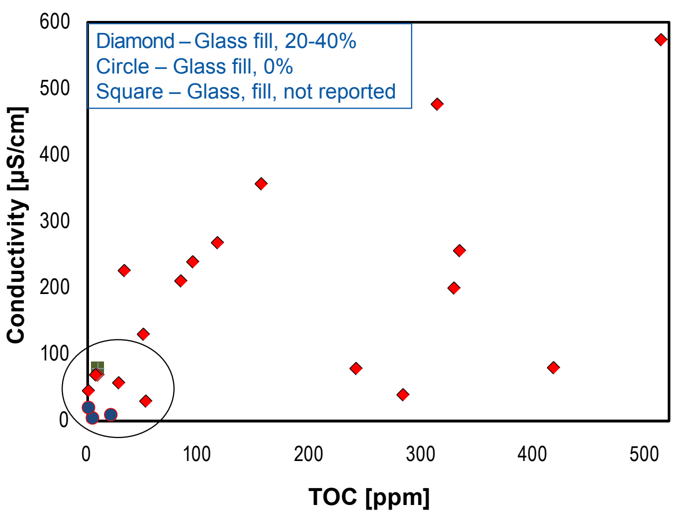

FIGURE 2. Solution conductivity vs. TOC plot for all the structural materials screened to-date. Each point represents a different material tested. Target materials appear at the bottom left corner: low TOC and low solution conductivity.

Conclusions and Future Directions

- We selected a complete set of relevant BOP materials for system contaminant studies based on the level of perceived impact (physical property, function and cost).
- We developed and benchmarked ex situ characterization methods and protocols for screening potential system contaminants.
- We benchmarked fuel cell hardware, test equipment and protocol between the different team members.
- We screened 19 structural materials and identified and quantified the organic and ionic contaminants present.
- We will establish correlations between analytical screening of extract solutions, cyclic voltammatry results, and fuel cell performance loss.
- We will screen the other selected structural materials, assembly aids (adhesives, lubricants), and elastomers for seals and gaskets.
- We will continue to identify and initiate screening of model compounds.
- We will initiate gas-phase durability testing and membrane degradation by-products study.

FY 2011 Publications/Presentations

1. H. Wang, S. Coombs, C. Macomber, K. O'Neill, G. Bender, B. Pivovar, and H.N. Dinh, "Evaluating Polymeric Materials as Potential Sources of PEMFC System Contaminants," ECS Transactions, 33(1) 1617-1625 (2010).

2. H. Cho, M. Jung, J. Navarro, M. Ohashi, and J.W. Van Zee "Aniline as Cationic and Aromatic Contaminants in PEMFC," ECS Transactions, 33(1) 1627-1635 (2010).

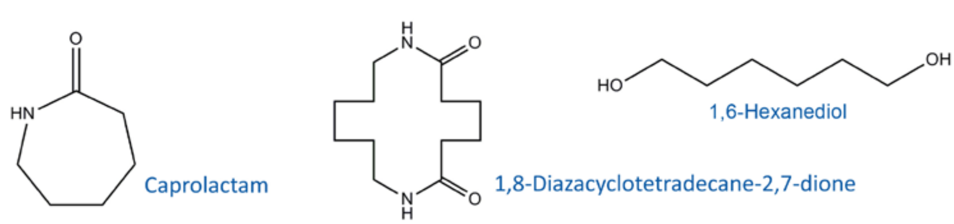

FIGURE 3. Chemical structure of the organic species identified in polyamide family of polymers by liquid GC-MS.

3. C. Macomber, H. Wang, K. O'Neill, S. Coombs, G. Bender, B. Pivovar, and H.N. Dinh, "Characterizing Polymeric Leachants for Potential System Contaminants of Fuel Cells", ECS Transactions, 33(1) 1637-1643 (2010).

4. J. St-Pierre, 'PEMFC contaminant tolerance limit - Foreign cations in ionomers', *Int. J. Hydrogen Energy*, in press, Department of Interior:10.1016/j.ijhydene.2011.01.143.

5. J. St-Pierre, 'PEMFC contamination model: Foreign cation exchange with ionomer protons', *J. Power Sources*, submitted.

6. H. Wang, S. Coombs, C. Macomber, K. O'Neill, G. Bender, B. Pivovar, and H.N. Dinh, "Developing Ex Situ Testing Methods to Evaluate PEMFC System Contaminants," 218th ECS Meeting, Las Vegas, NV, Oct. 2010.

7. H. Cho, M. Jung, J. Navarro, M. Ohashi, and J. W. Van Zee "Aniline as Cationic and Aromatic Contaminants in PEMFC," 218th ECS Meeting, Las Vegas, NV, Oct. 2010.

8. C. Macomber, H. Wang, K. O'Neill, S. Coombs, G. Bender, B. Pivovar, and H.N. Dinh, "Identifying Leachant Contaminants of Fuel Cell System Components and Their Effect on Performance" 218th ECS Meeting, Las Vegas, NV, Oct. 2010.

9. K.A. O'Leary and B. Lakshmanan, "Methodologies for Screening Balance of Plant Materials for Fuel Cell Contamination," 218th ECS Meeting, Las Vegas, NV, Oct. 2010.

10. S. Kocha, Project participation in Durability Working Group Meeting, Las Vegas, NV, Oct. 2010.

11. H.N. Dinh and K. O'Leary, "Effect of System and Air Contaminants on PEMFC Performance and Durability," Fuel Cell Tech Team Meeting, Southfield, MI, Oct . 28, 2010.

12. H.N. Dinh , "Effect of System and Air Contaminants on PEMFC Performance and Durability," DOE Mid-Year Review, Denver, CO, Jan. 19, 2011.

13. J. St-Pierre, 'PEMFC contaminant tolerance limit - Foreign cations in ionomers,' 219th ECS Meeting, Montreal, CA, May 2011.

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3. D. Gerard, "Powertrain Plastic Materials." SAE Mid Michigan Conference, February 11, 2008.

4. D. Gerard, "Materials and Materials Challenges for Advanced Automotive Technologies being Developed to Reduce Global Petroleum Consumption" (Invited). 2007 Materials Science and Technology, September 16–20, 2007, Detroit, MI.

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7. G.A. James, et. al., "Prevention of membrane contamination in electrochemical fuel cells,",US Patent Application US2005089746A.

8. R. Moses, "Materials Effects on Fuel Cell Performance," National Research Council Canada Institute for Fuel Cell Innovation, International Fuel Cell Testing Workshop, September 20–21 (2006).

9. K. O'Leary, B. Lakshmanan, and M. Budinski, "Methodologies for Evaluating Automotive PEM Fuel Cell System Contaminants." 2009 Canada-USA PEM Network Research Workshop, February 16, 2009.