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

Huyen N. Dinh (Primary Contact), Clay Macomber, Heli Wang, Guido Bender, Kevin O'Neill, Bryan Pivovar
National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401-3305
Phone: (303) 275-3605
Email: Huyen.Dinh@nrel.gov

DOE Manager
HQ: Kathi Epping Martin
Phone: (202) 586-7425
Email: Kathi.Epping@ee.doe.gov

Subcontractors:
- Kelly O'Leary, Balsu Lakshmanan, Rob Reid, General Motors LLC (GM), Honeoye Falls, NY
- John Van Zee and Masato Ohashi, University of South Carolina (USC), Columbia, SC
- Tommy Rockward, Los Alamos National Laboratory (LANL), Los Alamos, NM
- Jean St-Pierre, University of Hawaii, Honolulu, HI
- Ryan Richards and Jason Christ, Colorado School of Mines (CSM), Golden CO
- Steve Hamrock (in kind partner), 3M, St. Paul, MN

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Fiscal Year (FY) 2012 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 contamination mechanisms.
- Develop models/predictive capability.
- 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 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 2012 Accomplishments

- Screened 55 relevant BOP materials for fuel cell contamination.
- Completed preliminary assessment of studied BOP materials on fuel cell performance.
- Identified leached species for all structural materials and assembly aids.
- Determined that leached species come from the hydrolysis and degradation of the polymer resins and additives.
- Selected model organic compounds and leachant extracts for in-depth parametric studies.
- Performed initial ex situ and in situ studies on selected model compounds.

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 system ($49/kW in 2012 [1]) has risen in importance as fuel cell stack cost has decreased ($22/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 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 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 close to 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 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 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 help provide guidance in the implementation and, where necessary, 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 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 predictive modeling, and disseminate information about material contamination potential that would benefit the fuel cell industry in making cost-benefit analyses of system components. We are identifying and quantifying potential contaminants derived from stack or component fabrication materials and quickly screening the impact of the leachants on the 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. The majority of our effort is focused on the liquid-based contaminants derived from structural plastics and assembly aid materials (lubricant, grease, adhesive, 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.

Our prioritization and selection of system materials is based on properties such as exposed surface area, total mass or volume in a system, fluid contact, function, cost, and performance implications. Material selection is also based on the materials' physical properties (i.e., stable in fuel cell operating conditions: 0% – 100% relative humidity, -40° – 90°C), cost, commercial availability, and input from original equipment manufacturers and fuel cell system manufacturers. These commercially available commodity materials 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 55 BOP materials (Table 1)—from 10 different manufacturers, comprising different chemistries, and used for different functions—using multiple screening methods, totaling more than 660 experiments. The screening techniques included leaching tests to extract water-based contaminants, solution conductivity, pH, total organic carbon (TOC), cyclic voltammetry, membrane conductivity, in situ 50 cm^2 fuel cell test, and advanced analytical characterization (gas and liquid chromatography mass spectrometry [GCMS, LCMS], inductively coupled plasma – optical emission spectroscopy [ICP-OES], ion chromatography, and Fourier transform infrared spectroscopy).

A wide range of TOC and solution conductivity values were measured for the 55 BOP materials screened. The low-cost Nylon™ family (polyamide and polyphthalamide) showed the greatest variety with grades, as expected by design. Higher-cost, non-commodity materials (perfluoroalkylether/polytetrafluoroethylene [PFAE/PTFE], polyphenylene sulfide, polybutylene terephthalate, polysulfone, polyphenylsulfone) were cleaner, leaching out less ionic and organic contaminants. Elemental analyses were performed by ICP-OES to identify and quantify the species present in the leachant solutions. The elements with the highest concentrations, via ICP screening of the six-week leached structural material extracts and the one-week leached urethane material extracts, are identified in Figure 1. Based on knowledge of the plastic type, common additives in these types of plastics, and information from material datasheets, the identified elements were linked to fillers and additives. For example, Al, B, Si, and Ca are commonly found in glass fiber reinforcement additives (alumino-borosilicates and soda lime) for structural automotive thermoplastics. Common additives in urethane adhesive/seal materials include fillers and flame retardants (alumina trihydrate, talc, dolomite), hence Al, Ca, Mg, and Si were found in the urethane extracts. If it is found that these species adversely affect the fuel cell performance and that the additive is not needed for a material's function in fuel cell applications, then perhaps the manufacturers can remove the additive. If an additive is required for function, then perhaps a different, non-contaminating additive can be used. This type of information is valuable for properly selecting BOP materials and can help DOE meet its durability and cost targets.

TABLE 1. Summary table of the 55 BOP materials studied (structural materials, adhesives, sealants, greases), grouped by chemical description

Function Description	Chemical Description	Manufacturer	Trade Name	Total Grades
Structural Plastic	Polyamide (PA), polyphthalamide (PPA) (Nylon™)	DuPont, EMS, BASF, Solvay,	Zytel®, Grivory®, Grilon®, Grilamid® Ultramid®, Amodel®	26
Structural Plastic	Polyphenylene sulfide (PPS)	Chevron Phillips	Ryton®	4
Structural Plastic	Polysulfone (PSU)	Solvay	UDEL®	2
Structural Plastic	Polyphenylsulfone (PPSU)	Solvay	RADEL®	1
Structural Plastic	Polybutylene terephthalate (PBT)	DuPont	Crastin®	2
Lubricant/Grease	Perfluoroalkylether/ polytetrafluoroethylene (PFAE/PTFE)	DuPont	Krytox®	4
Adhesive/Seal	Urethane	3M, Bostik, Henkel	Marine®, Loctite®	6
Adhesive/Seal	Silicone	3M	Super silicone	2
Adhesive	Epoxy	3M, Reltek®	Scotch Weld®, Bond-IT®	3
Adhesive	Acrylic acrylate	LORD®	LORD®	1
Thread Lock/Seal	Polyglycol dimethacrylate (PGDMA)	Henkel	Loctite®	4
	Total			**55**

Assembly Aids ↓

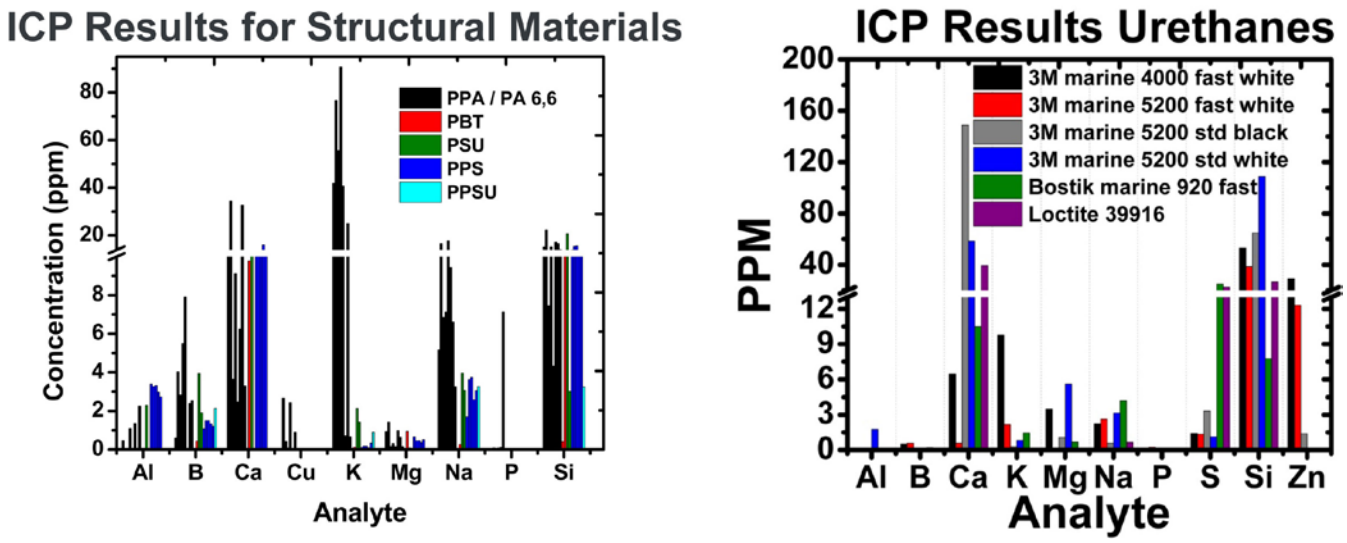

FIGURE 1. Elements with the highest concentrations identified by ICP-OES for all structural materials (left) and urethane materials (right)

Liquid GCMS analysis identified a large number of organic species in the material extracts. Using the same approach as described above, we determined that the organic compounds come from the hydrolysis and degradation of the polymer resins, additives (water scavenger, cross-linking agent, solvent), and by-products of incomplete polymerization. A few organic model compounds from structural materials and assembly aids were selected for further fundamental/mechanistic studies. Their chemical structures are shown in Figure 2. The identified organic compounds consist of aromatics and aliphatics with a variety of functional groups. These compounds have not been studied before in in situ, parametric, or recoverability experiments and are part of our future work. Identifying and quantifying specific model compounds and/or functional groups that adversely affect fuel cell performance can provide valuable understanding of the impact of organic compounds and can help determine the "bad actor" in the leachant extract mixture.

In situ infusion screening of the BOP materials showed that system contaminants can have an adverse effect on fuel cell performance, but the effect is complex. Figure 3 shows the in situ infusion results for three groups of assembly

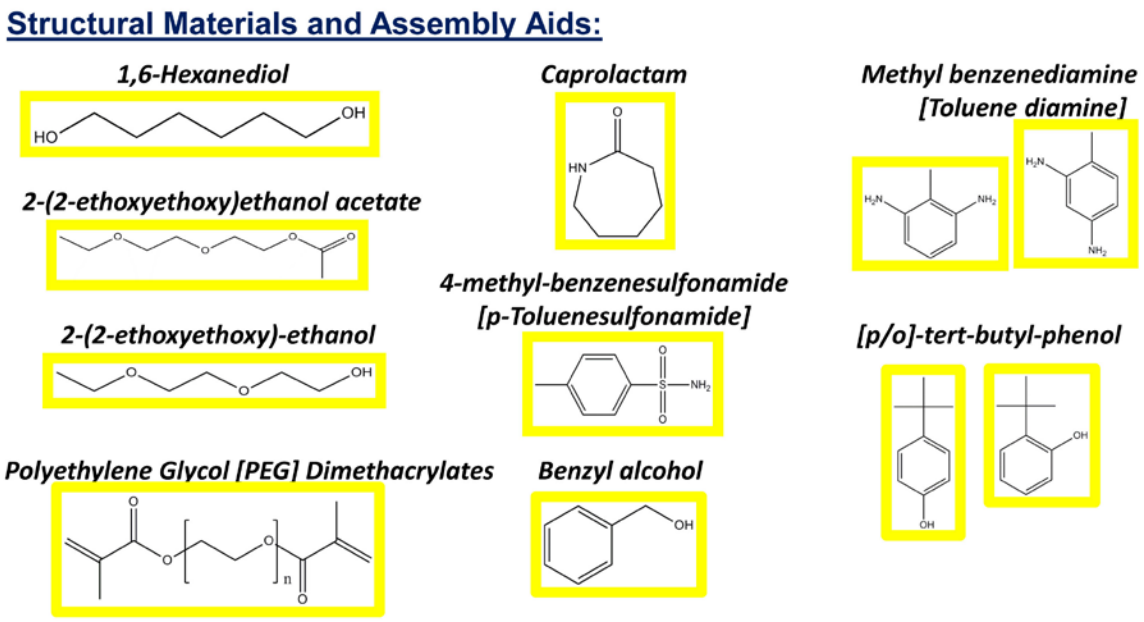

FIGURE 2. Chemical structure of organic model compounds selected for further in-depth studies. The organic species were identified by liquid GCMS and came from structural materials and assembly aids.

aids material. These examples were selected to show the different types of effects system contaminants have on fuel cell performance. The more expensive PFAE/PTFE materials (different grades of Krytox®) showed essentially no effect on the fuel cell performance (voltage response at 0.2 A/cm^2 is similar to the deionized (DI) water baseline) and were classified as "clean". The two urethane Marine® adhesive/seal materials showed a voltage drop of 100–150 mV and the effect was partially reversed when DI water was infused instead of the leachant solutions. These materials were classified as "contaminating but partially recovers". The two epoxy materials (different grades of Bond-It®) showed a very large voltage drop (ca. 550 mV) and the effect was not reversible with DI water infusion. These materials were classified as "contaminating and does not recover". The high frequency resistances were essentially constant for all materials over the 15–20 h of contaminant infusion, indicating that membrane conductivity was not affected during this short duration of infusion. Concentration, species, and operating condition effects will be studied further to understand the mechanism of contamination.

Conclusions and Future Directions

- We determined that structural materials and assembly aids can leach contaminants that adversely impact fuel cell performance.
- We identified and quantified the elements, anions, and organic species in the leached solutions for all of the structural materials and assembly aids.
- We selected organic species and extracts for further studies.
- We determined that leached species come from the hydrolysis and degradation of the polymer resins, additives, and by-products of incomplete polymerization.
- We will establish statistical relationships and capabilities for correlating ex situ characteristics to in situ performance loss.
- We will perform parametric in situ studies on selected leachate solutions.
- We will perform fundamental/mechanistic studies on selected model compounds.
- We will model the effects of operating conditions on fuel cell performance for specific contaminating species and model compounds.
- We will perform durability testing of selected contaminants.

FY 2012 Publications/Presentations

1. H.-S. Cho, M. Ohashi, and J. W. Van Zee, "The Effect on PEMFC Contamination of Functional Groups of Some Organic Contaminants," *ECS Trans.*, Vol. 41(1), Polymer Electrolyte Fuel Cells 11- Diagnostics and Phenomena: Porous Transport Layers, The Electrochemical Society, pp. 1487-1499 (2011).

2. J. St-Pierre, "PEMFC contaminant tolerance limit - Foreign cations in ionomers," *Int. J. Hydrogen Energy*, Vol. 36, pp. 5527-5535 (2011).

3. J. St-Pierre, "PEMFC contamination model: Foreign cation exchange with ionomer protons," *J. Power Sources*, Vol. 196, pp. 6274-6283 (2011).

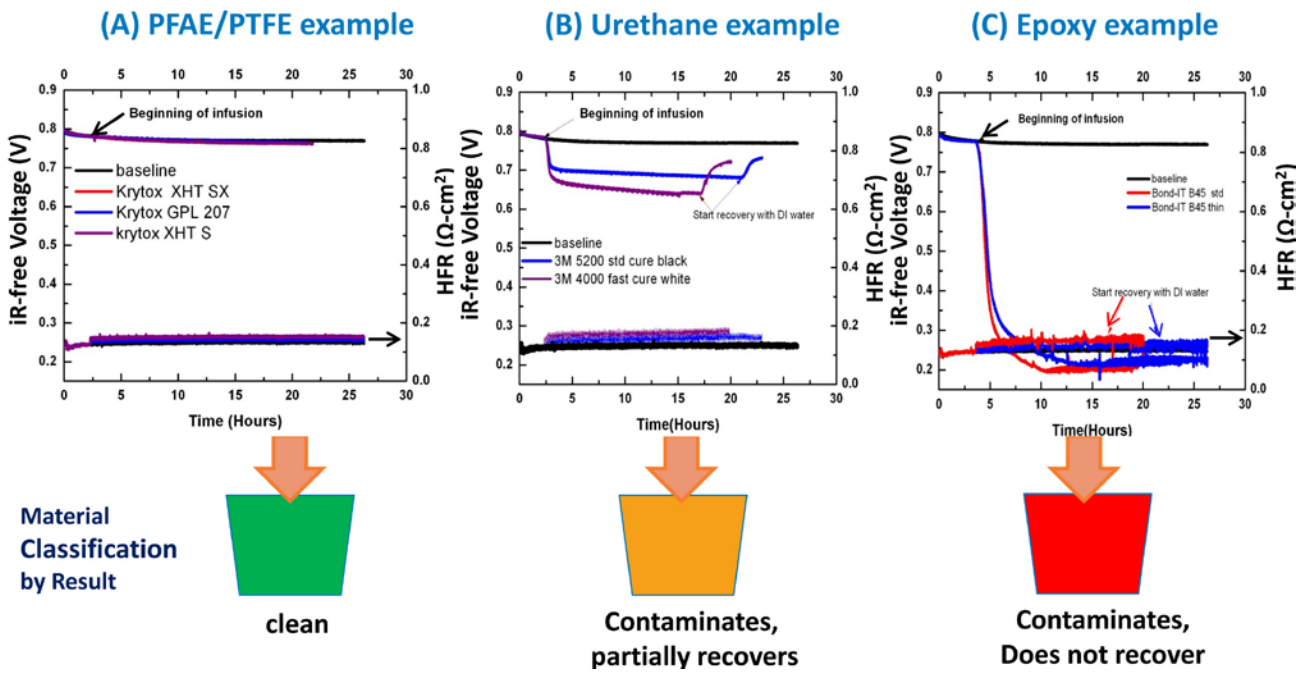

FIGURE 3. Voltage and high frequency resistance responses at 0.2 A/cm^2 during the infusion of DI water (black, baseline) and leachant solutions from different assembly aids materials. (A) three PFAE/PTFE materials (6 week soak): Krytox® XHT SX (red), Krytox® GPL 207 (blue), Krytox® XHT S (purple); (B) two urethane materials (1 week soak): 3M 5200 standard cure black (blue), 3M 4000 fast cure white (purple); (C) two epoxy materials (1 week soak): Bond-IT® B45 (blue), Bond-IT® B45TH (red). (cell temperature = 80°C, relative humidity = 32%/32%, H_2 and air stoich = 2/2, back pressure = 150 kPa)

4. K.A. O'Leary, R. Reid, and B. Lakshmanan, "A Systematic Comparison of Screening Techniques to Evaluate Fuel Cell System Contamination," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

5. M.S. Opu, M. Ohashi, K.A. O'Leary, B. Lakshmanan, R. Reid, C.S. Macomber, H. Wang, H. Dinh, and J. Van Zee, "In Situ Experiments for Understanding the Effects of Contaminants from Balance of Plant Materials on PEMFCs," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

6. M. Das, M. Ohashi, C.S. Macomber, H. Wang, H. Dinh, K.A. O'Leary, R. Reid, B. Lakshmanan, and J. Van Zee, "Ex Situ Experiments for Understanding the Effect of Contaminants from Balance of Plant Materials on PEMFCs," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

7. C.S. Macomber, H. Wang, K. O'Neill, J. Christ, M. Das, J.W. Van Zee, K.A. O'Leary, and H.N. Dinh, "Leachant Contaminants and Degradation Schemes of PEM Fuel Cell System Components," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

8. J. Christ, H. Wang, G. Bender, R. Richards, and H.N. Dinh, "Impact of Proton Exchange Membrane Degradation Products on the Activity of the Oxygen Reduction Reaction in PEM Fuel Cells," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

9. H. Cho, M. Ohashi, C.S. Macomber, H. Wang, H. Dinh, and J.W. Van Zee, "The Effect on PEMFC Contamination of Functional Groups of Some Organic Contaminants," 220th Meeting of the Electrochemical Society, Boston, MA, October 9–14, 2011.

10. C.S. Macomber, H. Wang, K. O'Neill, J. Christ, G. Bender, B. Pivovar, H.N. Dinh, "Identifying leachant contaminants and degradation schemes of PEM fuel cell system components, leading to effects on performance," 2011 Fall ACS Meeting, Denver, CO, August 28–September 1, 2011.

11. H. Wang, C.S. Macomber, K. O'Neill, G. Bender, B. Pivovar, R. Reid, B. Lakshmanan, K. O'Leary, M. Das, M. Ohashi, J.W. Van Zee, H.N. Dinh, "Effect of PEMFC system contaminants on the performance of catalyst," 2011 Fall ACS Meeting, Denver, CO, August 28–September 1, 2011.

12. H.N. Dinh and K. O'Leary, "Effect of System Contaminants on PEMFC Performance and Durability," Fuel Cell Tech Team Meeting, Southfield, MI, December 14, 2011.

13. H.N. Dinh, C.S. Macomber, H. Wang, J. Christ, "Effect of System and Air Contaminants on PEMFC Performance and Durability," DOE Mid-Year Review, Denver, CO, February 7, 2012.

14. J. Christ, K.C. Neyerlin, H. Wang, R. Richards, H.N. Dinh, "Impact of Proton Exchange Membrane Degradation Products on Platinum Catalyst Performance," Western States Catalysis Club Conference, Boulder, CO, March 9, 2012.

15. H. Wang, J. Christ, C.S. Macomber, K. O'Neill, K.C. Neyerlin, K.A. O'Leary, R. Reid, B. Lakshmanan, M. Das, M. Ohashi, J.W. Van Zee, and H.N. Dinh, "Effect of fuel cell system contaminants on the Pt catalyst," 243rd ACS Meeting in San Diego, CA, March 25–29, 2012.

16. H.N. Dinh, "Effect of System Contaminants on PEMFC Performance and Durability," DOE Fuel Cell Technologies Program Annual Merit Review, Washington, D.C., May 14–18, 2012.

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6. Q. Guo, R. Pollard, J. Ruby, T. Bendon, P. Graney, and J. Elter, *ECS Trans*., Vol. 5(1), p. 187 (2007).

7. G.A. James, et. al., "Prevention of membrane contamination in electrochemical fuel cells," U.S. 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.