

V.C.4 Effect of System and Air Contaminants on PEMFC Performance and Durability

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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 catalogues based on system contaminant potential to guide system developers on future material selection.
- Disseminate knowledge gained to 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 determining the effect of system components on fuel cell performance and durability. Insights gained from these studies will be applied toward the development of a catalogue of system component materials that help meet the following DOE 2010 targets:

- Cost: \$30/kW for transportation, \$750/kW for stationary
- Lifetime: 5,000 hours for transportation, 40,000 hours for stationary

Accomplishments

- Established a standard set of experimental protocols for analysis, including leaching, cyclic voltammetry, and analytical characterization protocol(s).
- Performed leachant experiments on 10 polymeric material sets.
- Evaluated and applied multiple techniques for analyzing leachants (e.g., gas chromatograph mass spectroscopy [GCMS], Fourier transform infrared-attenuated total reflectance [FTIR-ATR], inductively coupled plasma [ICP], pH, conductivity, total organic content [TOC], contact angle).
- Identified leachants via GCMS for the ten polymeric materials studied.
- Performed electrochemical tests on leachants to determine effect on electrocatalysts and recovery after exposure.



Introduction

Cost and durability issues of proton exchange membrane fuel cell (PEMFC) systems have been challenging in the fuel cell industry. The cost of the balance of plant (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 the understanding of the materials used in the system components and the contaminants that derive 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 not limited to low-cost 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, fuel cells become even more susceptible to contaminant effects. 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 of the effects of system contaminants on fuel cell performance and durability to identify poisoning mechanisms, recommend mitigation strategies, develop predictive modeling, and disseminate material catalogues that benefit the fuel cell industry in making cost-benefit analyses of system components. We will identify and quantify potential contaminants derived from stack/component fabrication materials and quickly screen 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 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 will be validated with in situ testing.

Our system materials selection is based on properties such as exposed surface area, total mass/volume, fluid contact, function, cost, and performance implications. Current material prioritization to study is based on perceived impact of potential system contaminants (based on GM internal knowledge): structural materials, coolants, elastomers for seals and (sub)gaskets, assembly aids (adhesives, lubricants), hoses, membrane degradation products, bipolar/end plates, ions from catalyst alloys. Our project has a strong polymer focus, as much of the system is polymer-based. Furthermore, our approach is to study 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 investigated 10 commercially available polymers (see Table 1) for their potential impact as system contaminants in fuel cell systems. These 10 polymeric materials underwent leaching protocols for two months to derive potential contaminants from the parent materials into solution. The leaching protocols were provided to the group by GM prior to the kick-off of the project. We tested three different leaching conditions (deionized water, 0.1 M H₂SO₄, and 0.1 M H₂SO₄+3% H₂O₂ at 80°C) and found that soaking in deionized water was the best leaching condition as it reflected the most realistic fuel cell condition. Acid solutions were eliminated as test conditions as they were found to be excessively aggressive compared to a fuel cell environment.

We evaluated various techniques for analyzing leachants. These include GCMS, FTIR-ATR, ICP pH, conductivity, TOC, contact angle, and electrochemistry. The results of the GCMS and electrochemistry are summarized below.

The leachant solutions derived from soaking the ten polymeric materials were analyzed via FTIR-ATR for functional groups and by GCMS to determine the identity of the leachants in solution for each polymer. TOC was measured in the final solutions at the end of the trials to determine quantitatively the total amount of leachant from the solid that made it into solution. Table 1 summarizes the starting materials, the TOC values in parts per million (ppm), and the predominant leachants identified for each sample. Due to the number of materials tested, discussion will be limited to styrene-butadiene-rubber (SBR). SBR was chosen because it was a good example to illustrate the type and number of contaminants that leached from the material as well as the effect of contaminants on catalysis.

SBR is synthetic polymer, derived from styrene and butadiene and an alkyl mercaptan chain transfer agent,

TABLE 1. Identified Leachants and TOC Values for Ten Commercially Available Polymers Tested and Deionized Water Control

Material	TOC (ppm)	Predominant Leachants Identified via GCMS
Deionized Water Control	N/A	Hexamethylcyclotrisiloxane-column bleed
Acrylic Buna-N Blended Rubber	304.7 ± 0.3	N,N Dibutyl formamide
Aramid/Buna-N Gasket, Green	238.4 ± 0.3	Aniline
Abrasion-Resistant SBR Rubber, Red	314.7 ± 0.3	Aniline
Weather-Resistant EPDM Rubber, Black	N/A	2-Methoxythiobenzamide
FDA-Compliant Silicone Rubber, Black	86.9 ± 0.8	Dimethylsilanediol
Corrosion-Resistant Viton® Fluoroelastomer	722.6 ± 0.9	Triphenylphosphine oxide
Amber Polyurethane Sheet	653.0 ± 1.4	1,2-Ethanediol
M-Strength Neoprene Rubber, Black	1,347 ± 0	4,4-Methylenebis-benzenamine
Silicone Gasket	294.6 ± 0.3	dimethylsilanediol
Teflon®-coated fiberglass, Furon®	6.92 ± 0.9	x

EPDM = ethylene propylene diene monomer

and is widely used in car tires. Identified contaminants, aniline and other thiol-based aromatics, seem reasonable given the chemical structure of the polymer and possible additives. TOC values for SBR rubber show final amounts of carbon at levels of 314.7 ± 0.3 ppm. Aniline was the major leachant identified, and was present at levels nearly an order of magnitude higher than other identified constituents. Calculated areas show that it comprised 80% of the total leachant.

Cyclic voltammetry (CV) is extremely useful to quickly screen changes in electrochemical response of Pt catalysts in the presence of leachants. Two types of experiments were used: a quick screen, and a recovery screen (protocols provided by GM). Figure 1 shows a baseline polycrystalline Pt CV in leachant-free electrolyte solution compared to the response of this electrode with increasing amounts of SBR rubber leachant added to the solution. The CV shows that SBR rubber leachant decreases the active surface area, and is oxidized at high potential. The presence of the

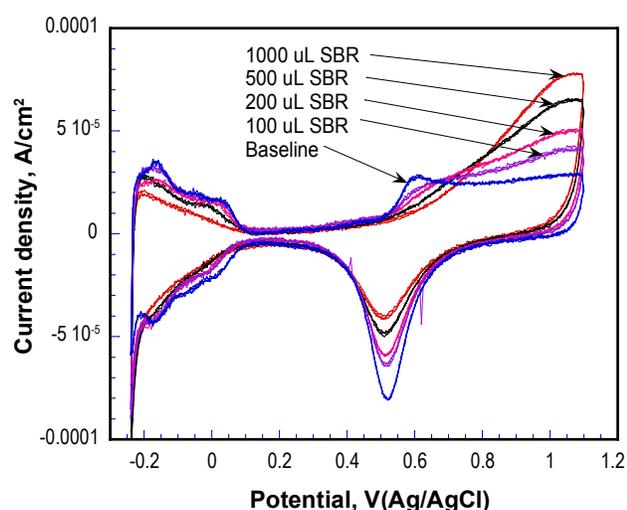


FIGURE 1. Effect of SBR rubber leachant amount on Pt catalysis in 0.1 M HClO₄ solution. Cell volume was 150 ml. Scanning rate was 20 mV/s.

leachant reduces the extent of Pt oxidation as witnessed by the decreased charge associated with oxide reduction. After removing the electrode from the leachant containing solution and testing again in leachant-free electrolyte, it was observed that the leachants impact on electrochemical response was not permanent (Figure 2).

Conclusions and Future Directions

- Leaching experiments should be performed in deionized water for most BOP materials. Acid solutions are not representative of the state-of-the-art fuel cell system and are too aggressive for many materials.
- Ten polymeric sealant materials were characterized with GCMS, FTIR-ATR, pH, conductivity, and TOC. Most of the materials analyzed leached out a number of organic compounds common in the

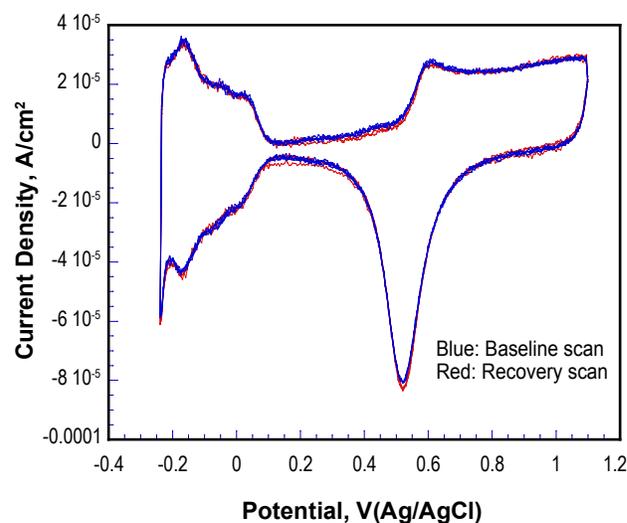


FIGURE 2. Comparing the baseline Pt CV in 0.1 M HClO₄, Ar purged, 20 mV/s with the CV obtained after a contaminated Pt electrode was rinsed with water and immersed in fresh electrolyte solution. The Pt electrode was contaminated with SBR rubber leachant.

synthesis and processing of the materials, as was expected.

- Based on CV results, extracted molecules from SBR rubber are a potential source of performance loss in fuel cells when operated at low potentials. At high potentials when the exposure to the contaminant was removed, changes in the electrochemical response were found to be recoverable.
- We have selected to focus our studies on polymeric structural materials because they have the highest perceived impact of potential system contaminants.
- We will continue establishing standard ex situ and in situ testing protocols to evaluate system contaminant materials.
- We will benchmark equipment and testing methods among all project partners.
- We will establish correlations between analytical screening of extract solutions, CV results, and fuel cell performance loss.

FY 2010 Publications/Presentations

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