

V.C.3 Effects of Impurities on Fuel Cell Performance and Durability

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- United Technologies – Hamilton Sundstrand, Windsor Locks, CT

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Objectives

- Identify the specific contaminants and contaminant families and their concentrations present in the fuel stream.
- Develop analytical chemistry protocols and tools to detect the nature and fate of contaminating species within fuel cells.
- Determine through controlled laboratory experimentation and literature study the main drivers for voltage decay.
- Develop contaminant analytical models and computer simulations that explain and predict these effects.
- Validate contaminant models through single cell experimentation using standardized test protocols.
- Develop and validate novel technologies for mitigating the effects of contamination on fuel cell performance.
- Disseminate results through outreach activities.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

This project is conducting fundamental research into the effects of impurities on fuel cell performance and durability. This activity broadly supports the following technical targets established by DOE:

- By 2010, develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of \$45/kW; by 2015, a cost of \$30/kW.
- By 2011, develop a distributed generation polymer electrolyte membrane (PEM) fuel cell system operating on natural gas or liquefied petroleum gas that achieves 40% electrical efficiency and 40,000 hours durability at \$750/kW.

Accomplishments

Hydrocarbon Testing

- Completed testing of acetaldehyde and formic acid up to a concentration of 100 ppm showing little effect of acetaldehyde on fuel cell performance but a significant effect of formic acid on fuel cell performance.
- Developed a better understanding of membrane electrode assembly (MEA) variability and the effects of this factor on impurities testing.
- Developed analytical procedures for evaluating concentrations of acetaldehyde, formic acid, and formaldehyde in the fuel stream.
- Developed mixing protocols for injecting specific concentrations of acetaldehyde, formic acid and formaldehyde into the fuel stream.

Other Impurities

- Evaluated effects of pertinent cations on the physio-chemical properties of Nafion[®].
- Completed testing of cells with various concentrations of ammonia in the fuel stream.
- Developed a multi-dimensional model predicting the effects of cationic contaminants on PEM fuel cells.



Introduction

PEM fuel cells show significant promise in providing efficient, clean power for stationary and transportation applications. The technology has shown limitations relative to long-term durability goals, particularly with regard to the operational lifetime of MEAs. One of the key causes for this is the introduction of impurities into the fuel stream that impacts the functionality of ion exchange groups within the electrolyte, degrade catalyst activity, and function as diluents causing the cell voltage to degrade.

The initial technical issues being addressed concern the identification of contaminant species located in the fuel stream that may have an effect on overall fuel cell performance, and evaluation of these effects against standard test protocols. The U.S. Fuel Cell Council in conjunction with Japanese Automobile Research Institute and others have been developing hydrogen quality standards as well as procedures for contaminant testing of PEM fuel cells. These studies provide the background and basis for the initiation of our research.

Approach

This project is mainly focused on the experimental determination of the effects of key contaminants on the performance of PEM fuel cells. Experimental data collected from formalized test protocols will be leveraged to create mathematical models that predict the performance of PEM fuel cells that are exposed to specific contaminant streams. These models will be validated through laboratory experimentation and will be utilized to develop novel technologies for mitigating the effects of contamination on fuel cell performance. Results will be publicly disseminated through papers, conference presentations, and other means.

In addition, the effects of cationic impurities on the fundamental physio-chemical properties of perfluoroionomer membranes are being evaluated. Membrane samples are processed and exposed to fixed concentrations of cation salts. These samples are then evaluated with regard to gas/water crossover, ionic resistance, water content, and mechanical properties.

Results

Hydrocarbon Impurities – Based on input from working groups and industry, our team has focused our efforts on the evaluation of hydrocarbons and halogenated compounds using very specific test protocols developed as part of a multi-laboratory collaborative effort. Our strategy is to evaluate molecules that may be present in a candidate hydrogen fuel stream in order to

evaluate the effects of functionality and molecular size (e.g., number of carbon atoms).

In support of this, our team has developed techniques to prepare accurate mixtures of impurities in hydrogen and to determine the level of impurities entering the fuel cell through the hydrogen stream. A gas chromatograph has been utilized to characterize both the mixtures entering the fuel cell and those exiting the fuel cell in an effort to assess accumulation and reaction of impurity species within the fuel cell reactor. While previous studies by our group have focused on the evaluation of either gaseous or volatile liquids, recent studies have centered around the development of methods for mixing and analyzing less volatile liquids such as acetaldehyde, formic acid and formaldehyde. Figure 1 shows a saturator apparatus that we have developed to accomplish this task.

Previous testing had been completed using methane, ethane, and ethylene as the primary fuel stream impurity and later extended to include acetaldehyde. Testing has been established as a series of 100-hour test runs using up to 5% of the contaminant in the fuel stream with the cell construction as defined in Table 1.

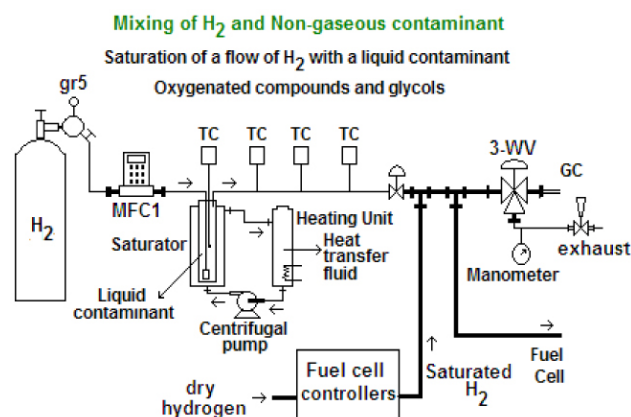


FIGURE 1. Gas Mixing Set-Up for Liquid Hydrocarbons

TABLE 1. Test Cell Definition

Parameter	Value (Early)	Value (Recent)
Membrane	Nafion® 212	Nafion® 212
Anode Loading	0.4 mg/cm ²	0.4 mg/cm ²
Anode Type	50% Pt on C	50% Pt on C
Cathode Loading	0.2 mg/cm ²	0.2 mg/cm ²
Cathode Type	50% Pt on C	50% Pt on C
MEA OEM	Ion Power	Ion Power
Cell Area	25 cm ²	25 cm ²
OEM	Fuel Cell Technologies	Fuel Cell Technologies

OEM - original equipment manufacturer

Testing was conducted at 200, 600 and 800 mA/cm² with standard test conditions defined below in Table 2. Conditions were modified as defined to achieve better performance stability during testing.

TABLE 2. Definition of Major Test Parameters

Parameter	Value (Early)	Value (Recent)
Anode Temperature	80°C	80°C
Cathode Temperature	80°C	73°C
Cell Temperature	80°C	80°C
Anode Humidity	100%	100%
Cathode Humidity	100%	75%
Anode Stoich	1.3	2.0
Cathode Stoich	2.0	2.0
Anode Flow	Commensurate with Current Density	
Cathode Flow	Commensurate with Current Density	
Anode Pressure	25 psig	25 psig
Cathode Pressure	25 psig	25 psig

Acetaldehyde

Testing of the effect of acetaldehyde (CH₃CHO) on cell performance was investigated at two impurity concentrations, 100 ppm and 30 ppm. No significant effect on cell performance was found during these impurity tests.

Formic Acid

The effect of formic acid (HCOOH) on fuel cell performance was investigated at two impurity concentrations, 100 ppm and 50 ppm. Testing showed moderate degradation of the cell performance during the 100-hour durability test shown in Figure 2.

Cyclic voltammetry (CV) scans performed at a rate of 20 mV/sec before and after the impurity test show that the electrochemical area of the cathode decreased, signifying that HCOOH has a negative effect on the cathode catalyst layer. Similar scans were also performed periodically (every 20 hours – Figure 3) during contamination and recovery period to provide more details of the mechanism for contamination on the cathode. In the CV scans, the cell temperature, the dew points, and the pressures remained unchanged. Pure nitrogen was fed to the cathode at 250 sccm, while HCOOH/H₂ was fed to the anode at 250 sccm. The CV scans indicate a decrease in H₂ adsorption peaks and an oxidation peak at 0.6 V which could be caused by the presence of adsorbents on Pt surface.

100 Hour Durability Test @ 800 mA/cm²

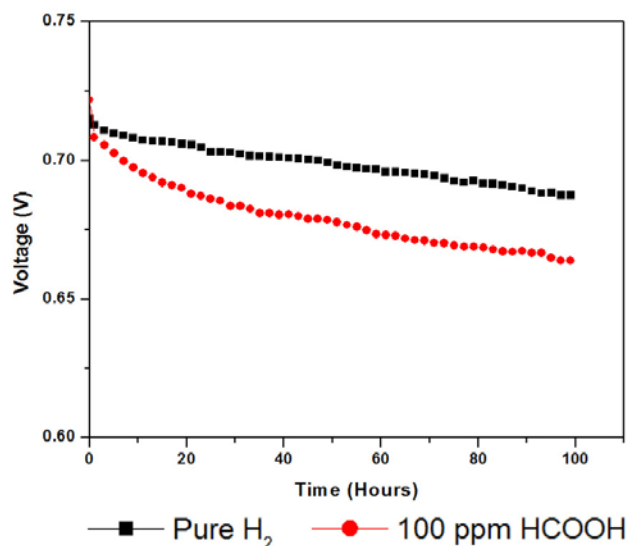


FIGURE 2. Durability Test using 100 ppm Formic Acid

CO Corrected CV Scans during Contamination (Last Cycle Recorded)

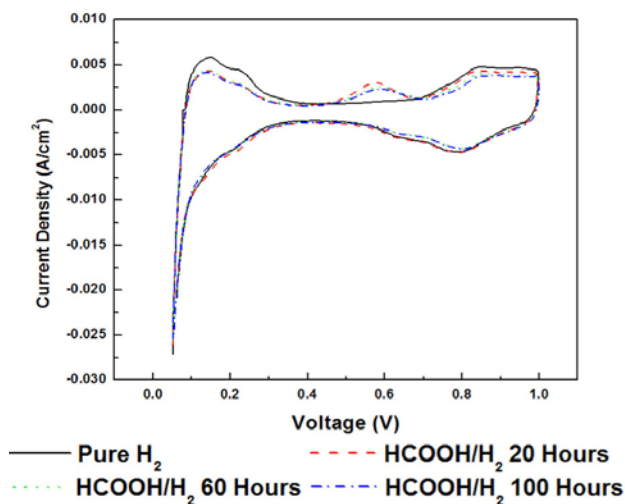


FIGURE 3. Progressive CV Scans on the Cell

An example of an individual CV scan is shown in Figure 4. Each scan consists of four cycles. In the first CV cycle, the hydrogen adsorption peak nearly disappeared. The Pt surface appears rather than seems to be covered by adsorbents (evident by peaks at 0.4 V and 0.6 V that are not seen with pure H₂). The adsorbents are oxidized around 0.4 V and 0.6 V (e.g. CO) in the 1st cycle. In the next three cycles, recovery of H₂ adsorption peak is observed, but evidence of surface coverage still exists.

CO Corrected CV during Recovery (Last Cycle)

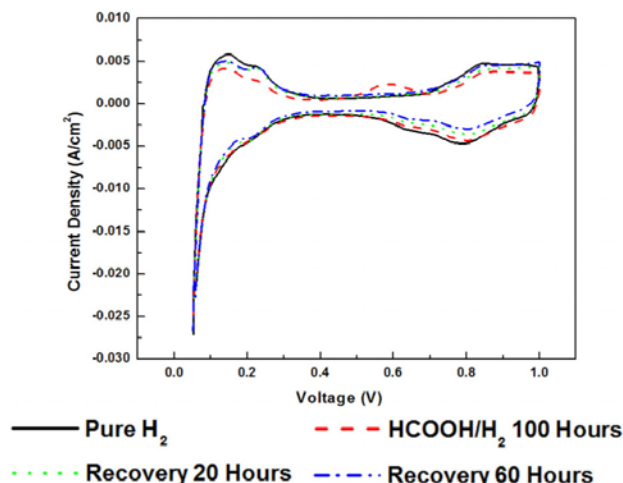


FIGURE 4. CV Scans Showing Recovery

Testing to date is summarized in the matrix shown in Table 3. Testing has indicated little effect of simple hydrocarbon species on fuel cell performance; however, more complex species do appear rather than seem to affect performance.

Cationic Contaminants - The effects of cationic impurities on membrane properties have been investigated. In this regard, fully hydrated Nafion[®] membrane samples have been doped with concentrations of various metal cations, including Li, Na, K, Cs, Ca, Mg, Ni, Fe, Al, Cu, and Cr in an effort to study the effects of contaminant mass and valence on critical membrane properties. Studies have focused on a balance between constituents that would normally be present in the materials of construction of the fuel cell, those that might be ingested in the fuel cell from hydrogen, and those that would provide important information for contaminant modeling activities.

Membrane physio-chemical properties, including permeability of common gases such as nitrogen, hydrogen, and oxygen have been measured at very low ionic loadings.

This year we initiated collaboration with Oak Ridge National Laboratory to gain further insight into the characterization of MEAs of PEM fuel cells. The emphasis was placed on fine tuning analytical procedures and sample preparation for MEAs. We continued this work at UConn's Institute for Materials Science in preparing samples and conducting elemental mapping analysis on cation-doped MEAs to identify the ion distribution within the MEAs. These Nafion[®] membrane samples had been exchanged with cations in an aqueous bath having concentrations of cations ranging from 1 M to about 0.00001 M. Samples were analyzed by taking an energy dispersive X-ray spectrum of the sample in the scanning electron microscope (JEOL JSM 6335F). Some elemental mapping was done to confirm the constituents of the membrane.

Impurity Model Development - We have developed a multi-dimensional model predicting the effects of cationic contaminants on PEM fuel cells. The model is based on a previously developed multi-physics PEM fuel cell model that solves for electrochemistry coupled transport phenomena, namely mass, momentum, species, energy and charge conservation. The first step of cationic contamination implementation is the development of the submodel for the cation transport across the polymer electrolyte. To make the model as generic as possible, a multi-component cationic transport model for polymer electrolyte is developed and validated against Sodaye's (2008) experimental data. The transport model is based on the Nernst-Planck equation and combines the migration and diffusive transport of charged ions across the polymer electrolyte. The multi-component model results in $n+1$ coupled equations (n is the number of cationic impurity) solved simultaneously, as opposed to decoupled equations that can be solved separately in dilute approximation. As seen from

TABLE 3. Summary of Fuel Cell Testing Using Organic Impurities

Cell #	Impurity	Current Density	RH (A/C)	Cell Temp	Flow Rates A/C	Description
1	100 ppm CH ₄	200 mA/cm ²	100%/100%	80°C	58.5/214 sccm	No significant degradation
2	100 ppm CH ₄	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
3	5% CH ₄ or 5% N ₂	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
4	100 ppm CH ₄	1800 mA/cm ²	100%/100%	80°C	234/857 sccm	No significant degradation
6	5% C ₂ H ₆	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
7	5% C ₂ H ₄	800 mA/cm ²	100%/100%	80°C	234/857 sccm	No significant degradation
11	30 ppm CH ₃ CHO	800 mA/cm ²	100%/100%	80°C	181/664 sccm	No significant degradation
31	30 ppm CH ₃ CHO	800 mA/cm ²	100%/75%	80°C	181/664 sccm	No significant degradation
35	100 ppm HCOOH	800 mA/cm ²	100%/75%	80°C	181/664 sccm	Significant degradation

RH - relative humidity

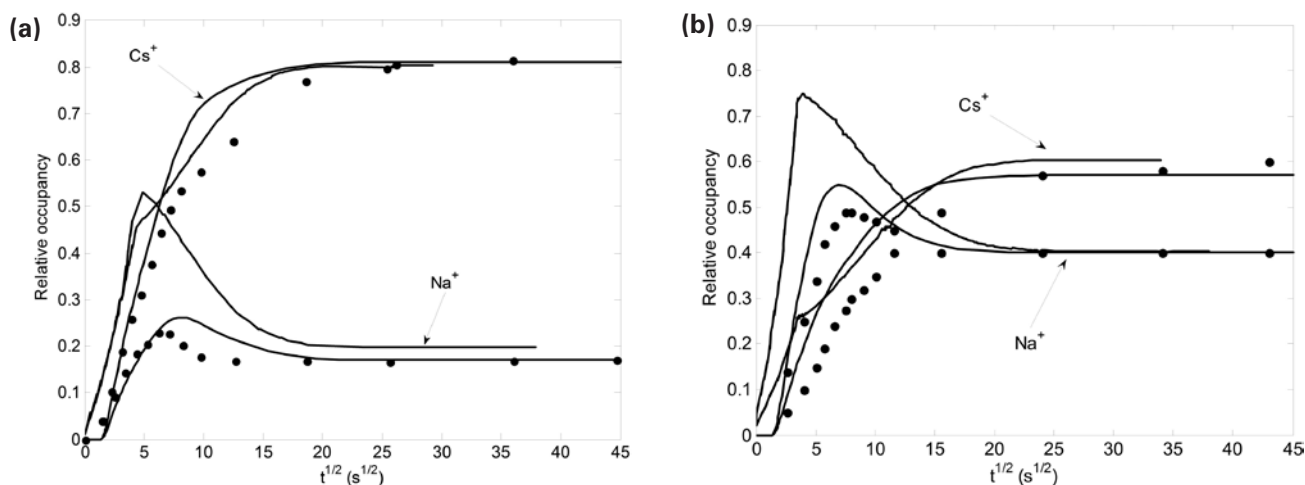


FIGURE 5. Competitive absorption of sodium (Na^+) and cesium (Cs^+) ions into a Nafion[®] 117 electrolyte: (a) Relative occupancy when the membrane is equilibrated in a solution of NaCl and CsCl having a ratio of 1:1; (b) Relative occupancy when the membrane is equilibrated in a solution of NaCl and CsCl having a ratio of 5:1. The symbols represent Sodaye's (2008) experimental data, the solid lines represent our model predictions, the dashed lines represent Sodaye's (2008) model predictions.

Figure 5, the multi-component transport model is able to better capture the competitive exchange of proton sites with cationic species. As seen, the Na^+ ions are faster to diffuse into membrane, so initially Na^+ concentration is higher, however due to their higher selectivity, Cs^+ ions are able to displace the Na^+ ions in addition to H^+ ions.

This submodel is incorporated into the above described multi-physics PEM fuel cell model. The effects of cation contamination are included into the properties of the polymer electrolyte, and it is currently assumed that cationic impurities neither affect the electrochemical kinetics of fuel cell reactions, nor adsorb on the catalyst surface. Figure 6 shows the concentration of Na^+ ions in the membrane electrode assembly, where NaCl is introduced into the cathode of a PEM fuel cell. As seen, the migration and diffusion are counter-acting (i.e. migration is from anode to cathode, diffusion is from cathode to anode) therefore the cationic impurity (i.e. Na^+) is not able to penetrate into the membrane, but

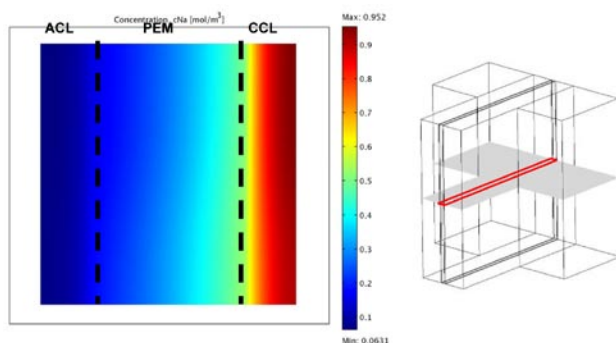


FIGURE 6. Fraction of Na^+ across the MEA

rather concentrates in the cathode catalyst layer. As a result of the Na^+ contamination, the average current density at a cell voltage of 0.7 V and 50% relative humidity at the inlet of both anode and cathode drops from 0.42 A/cm^2 to 0.29 A/cm^2 .

The model is currently being updated and improved to incorporate the effects of cationic impurities that can be introduced from anode (e.g. NH_4^+), the potential effect of cationic impurities on the electrochemical reactions, as well as the effect on mechanical properties, and mechanical stress distributions in polymer electrolytes of operating polymer electrolyte fuel cells, based on the data we have generated previously.

Conclusions and Future Directions

Conclusions

- Simple hydrocarbons including methane, ethane, ethylene and acetaldehyde do not significantly affect fuel cell performance.
- Formic acid impurities do show an appreciable effect on performance possibly due to adsorption on the electrode surface as well as the formation of reaction byproducts such as CO.
- A multi-component cationic transport model has been created and validated against experimental data.

Future Directions

- Comprehensive evaluation of formic acid and formaldehyde to support International Organization for Standardization standard development:

- Continued testing using standard test protocols, MEAs.
 - Target low catalyst loadings (reduction from 0.4 mg/cm² to 0.1 mg/cm²).
 - Develop an understanding of mechanism for performance impact.
 - Modeling of effects/sharing of data.
 - Extension to simple halogenated compounds.
 - Continued study of effects of cations on membrane properties:
 - Application-relevant contamination types/levels.
 - Commercially relevant membranes.
 - Modeling of effects/sharing of data.
3. “Evaluation of the Effects of Impurities on Fuel Cell Performance and Integrity”, NRC – Canada, February, 2009.
 4. M.F. Serincan, U. Pasaogullari, T. Molter “Effect of cathode side cationic contamination on the performance of an operating PEFC” to appear in *Proceedings of 7th ASME International Fuel Cell Science, Engineering & Technology Conference*, 8–10 June, 2009 Newport Beach, CA.
 5. X. Zhang, U. Pasaogullari, T. Molter, J. Preston, “Influence of Ammonia on Membrane-Electrode Assemblies in Polymer Electrolyte Fuel Cells” to appear in *Proceedings of 7th ASME International Fuel Cell Science, Engineering & Technology Conference*, 8–10 June, 2009 Newport Beach, CA.
 6. M.F. Serincan, “Multiphysics Modeling of Fuel Cells”, Ph.D. Defense, June, 2009.

FY 2009 Publications/Presentations

1. “Effects of Impurities on Fuel Cell Performance and Durability”, Modeling Workshop, Denver, CO, November, 2008.
2. “Fuel Cells and Transportation”, School of Engineering Seminar Series, The University of Vermont, December, 2008.