V.E.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 present in both fuel and oxidant streams.
- Develop analytical chemistry protocols and tools to detect the nature and fate of contaminating species within fuel cells.
- Determine both 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 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 proton exchange 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 calibration of test equipment using test protocols jointly developed amongst participating laboratories.
  - Completed testing of methane, ethane and ethylene; showed no effect of these impurities on fuel cell performance at levels of up to 5% in the hydrogen stream.
- Cation Testing:
  - Examined the effects of cationic contaminants on the physio-chemical properties of perfluoroionomer membranes. Specifically examined the effects of these species on ion exchange capacity, water content, mechanical properties, gas crossover, and ionic resistance.
  - Ion charge density appears to govern membrane water content with small ions demonstrating the highest water content.
  - Permeability studies showed transport in accordance with Fick's law in the following order: $H_2 > O_2 > N_2 > H_2O$. Cations negatively affect gas and water transport, with charge density affecting transport rates. Unique diffusion coefficients were calculated for each contaminating species suggesting that the

contaminant is an integral participant in the transport process.

- Alternating current (AC) resistance measurements showed that size of the ion charge carrier is an important factor in the conduction mechanism and that membrane area specific resistance correlates well with water content.
- Increases in membrane yield strength and the modulus of elasticity were demonstrated with increased contamination. Tensile tests showed that cation size plays an important role in determining the magnitude of this increase, indicating that larger ions interfere more with strain than smaller ones.
- Contaminants reduced strain to break with smaller ions showing the greatest effect. Ultimate tensile strength increased slightly with all contaminants except lithium, which effected a reduction in this property, reflecting a relationship with contaminant physical size.

- Modeling Activity:
  - Initiated modeling activity targeted at explaining and predicting the performance impact of various impurities on fuel cell performance.

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 membrane electrode assemblies (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 a diluent 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 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 contaminants 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 Testing – This major project activity initially involved identifying which contaminants the fuel cell will be exposed to during normal operation for both stationary and transportation applications. This has been done by deriving input from ongoing DOE development activities and historical data relative to operational demonstrations. Through technical interchange activities and coordination with other laboratories investigating the effects of contaminants on fuel cell performance, our team has been focused on the evaluation of hydrocarbons and halogenated compounds using very specific test protocols developed as part of a multi-laboratory collaborative effort. These test protocols are based on the utilization of similar cell hardware, test systems, and operating conditions at multiple laboratories.

Our initial efforts were focused on the evaluation of the effect of methane on cell performance. In this regard, cells were initially evaluated on pure hydrogen for a 100-hour period, then switched over to hydrogen with fixed concentrations of methane gas and operated for another 100-hour period. In carrying out this testing, it was necessary to develop a gas mixing apparatus that permitted dilution of known concentrations of methane in hydrogen, as well as facilitated the analytical validation of the concentrations of methane in the hydrogen stream. This apparatus is shown in Figure 1.

MEAs for the cell were supplied by Ion Power and the test cell was supplied by Fuel Cell Technologies per the definition outlined in Table 1.

Testing was conducted at 200, 600 and 800 mA/cm^2 with standard test conditions established as defined in Table 2.

Figure 2 shows the results of fuel cell testing using 100 ppm methane at a current density of 600 mA/cm^2. Cell operating conditions were consistent with those

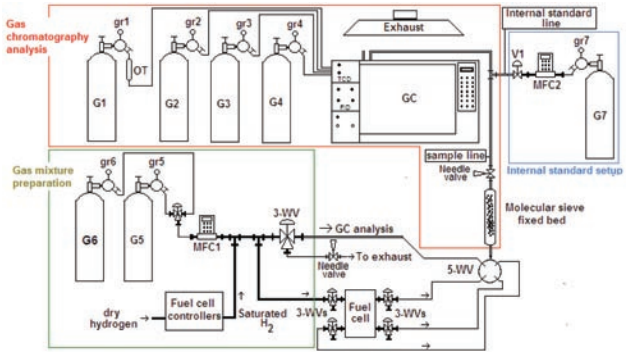

FIGURE 1. Impurity Dilution and Analysis Test Set-Up

TABLE 1. Test Cell Definition for Hydrocarbon Testing

Parameter	Value
Membrane	Nafion 112
Anode Loading	0.4 mg/cm2
Anode Type	50% Pt on C
Cathode Loading	0.2 mg/cm2
Cathode Type	50% Pt on C
Cell Area	25 cm2
OEM	Fuel Cell Technologies

identified in Table 2. Tests conducted at 200, 600 and 800 mA/cm^2 have been completed at various concentrations up to 5%. To date we have not identified any significant performance effect for methane.

Similar tests were performed with ethane and ethylene up to a concentration of 5% in the fuel stream. Example data for ethane are shown in Figure 3 at a concentration of 5% and a current density of 600 mA/cm^2. Future activities will focus on organic acids and aldehydes.

Cation Testing - Our team has further focused our activities on the evaluation of the effects of different metallic cation contaminants on the fundamental properties of perfluoroionomer membranes (gas/water permeability, ionic conductivity, mechanical properties, etc.). Our efforts have focused on investigating group IA ions with the goal of establishing whether contaminant atomic mass substantially affects membrane properties. Further studies have focused on common multivalent metal cations including Ca, Mg, Ni, Fe, Al, Cu, and Cr. These are constituents of common automotive alloys including carbon steels, low and intermediate alloy steels, stainless steels, copper and copper alloys, nickel and nickel alloys, and aluminum alloys.

The data collected as part of this effort were focused on commercially available Nafion® 117 membrane having the following processing history:

- 1 hour boil in de-ionized H_2O

TABLE 2. Definition of Major Test Parameters

Parameter	Value
Anode Temperature	80C
Cathode Temperature	80C
Cell Temperature	80C
Anode Humidity	100%
Cathode Humidity	100%
Anode Stoich	1.3
Cathode Stoich	2.0
Anode Flow	Commensurate With Current Density
Cathode Flow	Commensurate With Current Density
Anode Pressure	25 psig
Cathode Pressure	25 psig

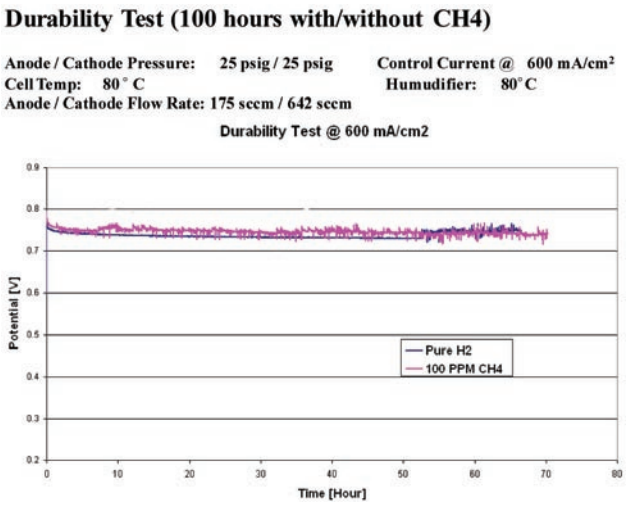

FIGURE 2. Durability Testing With 100 ppm Methane 600 mA/cm^2

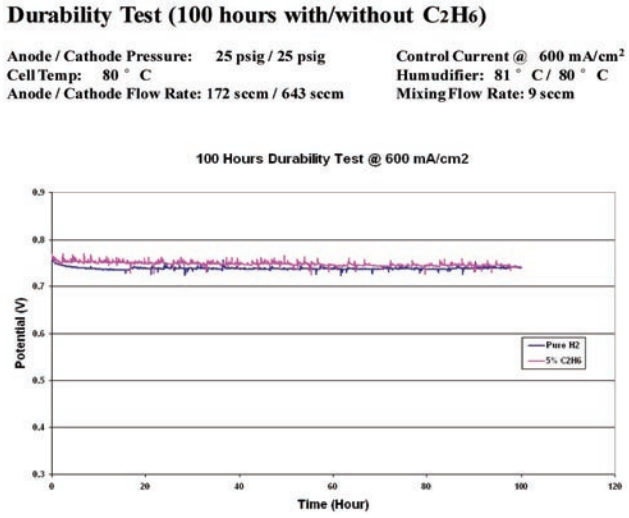

FIGURE 3. Durability Testing With 5% Ethane 600 mA/cm^2

- 1 hour soak in one of the following cation salts
  - 1 M
  - 0.1 M
  - 0.01 M

Several critical findings and relationships were gleaned from this work. Laboratory tests demonstrated that cations rapidly transport into the membrane and disperse readily throughout the membrane structure achieving high equilibrium concentrations. Studies showed that ion charge density governs membrane water content with small ions having a large water shell demonstrating the highest water content and larger ions having a small water shell demonstrating the lowest water content. Gas and hydrodynamic permeability studies showed transport in accordance with Fick's law in the following rank order: $H_2 > O_2 > N_2 > H_2O$. Data showed that cation contaminants negatively affect gas transport, with charge density appearing to be a factor in transport rate determination. Figure 4 shows crossover data using nitrogen, as an example. Unique diffusion coefficients were calculated for each contaminating species suggesting that the contaminant is an integral participant in the transport process. Cation contaminants were found to enhance water transport with ion size being a key factor in determining the transport rate.

Alternating current resistance measurements showed that size of the ion charge carrier itself and not the hydrated ion is an important factor in the conduction mechanism. Studies showed that membrane area specific resistance correlates well with water content.

Increases in membrane yield strength and the modulus of elasticity were demonstrated with contamination. Studies showed that cation size plays an important role in determining the magnitude of this increase, indicating that larger ions interfere more with strain (elastic and plastic) than smaller ones (Figure 5).

Cation contaminants were found to reduce strain to break with smaller ions having the largest water shell showing the greatest effect (Figure 6). Ultimate tensile strength was found to increase slightly with all contaminants with the exception of lithium, which effected a reduction in this key property, again reflecting a relationship with contaminant size.

Impurities Modeling – Modeling efforts have been initiated to:

- Interpret existing experimental data
- Develop a predictive tool to analyze effects of a given fuel mixture

This modeling is being conducted at several different levels as follows:

- Systems level
- Macroscopic fuel cell modeling
  - Kinetics
  - Transport
  - Durability

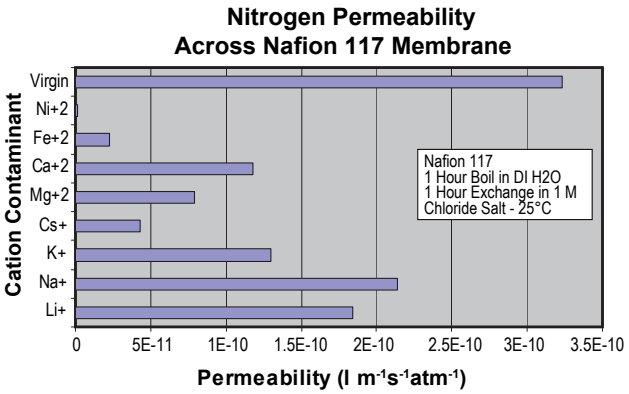

FIGURE 4. Nitrogen Permeability Across Cation Contaminated Nafion® 117

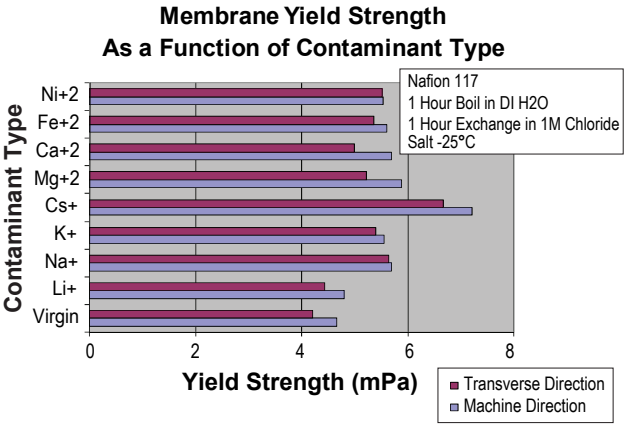

FIGURE 5. Yield Strength of Cation Contaminated Nafion® 117

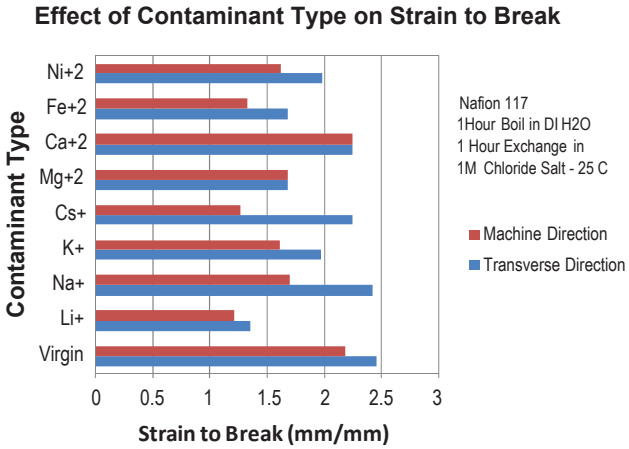

FIGURE 6. Strain to Break of Cation Contaminated Nafion® 117

- Microscale modeling

The development of these system models will be followed up through a series of validation tests.

Conclusions and Future Directions

The following bullets describe the conclusions of the research performed to date:

- Methane, ethane and ethylene impurities do not significantly affect fuel cell performance even at concentrations as high as 5%:
  - Because testing is very time consuming, it was determined that initiating tests at high concentrations of impurity was preferred (5%). It is assumed that if a 5% concentration of impurity does not significantly affect fuel cell performance, then lower concentrations likely will not.
  - Lower concentrations of impurities were able to be developed through dilution of more concentrated standards.
  - Analytical methods using gas chromatography were developed for each contaminating species.
- Cationic contaminants rapidly transport into the membrane upon exposure and tend to distribute uniformly throughout the structure. Specific physio-chemical effects include:
  - All contaminants tested were shown to inhibit transport of H_2, O_2, N_2, and H_2O. Li^+ and Ni^{2+} showed the greatest effect on transport.
  - Membrane area specific resistance correlates with water content for contaminated membrane.
  - Mechanical property testing showed increases in yield strength and modulus of elasticity with contamination, largely governed by the size of the ion. Strain to break was reduced for all contaminants with anisotropy enhanced. Ultimate tensile strength was found to moderately increase for all contaminants except lithium which negatively affected ultimate tensile strength.
  - Empirical constants were determined to support future multi-physics modeling efforts.

The following bullets describe future developments:

- Complete testing of critical hydrocarbon species as defined by industry and the US Fuel Cell Council Joint Hydrogen Quality Task Force.
- Initiate testing on halogenated hydrocarbons as defined by industry and the US Fuel Cell Council Joint Hydrogen Quality Task Force.
- Finish generating data relative to the effects of cations on the physio-chemical properties of perfluoroionomer membranes.
- Characterize membrane for ammonia and H_2S effects including crossover.
- Complete initial empirical models, begin multi-physics modeling efforts, begin model validation.

FY 2008 Publications/Presentations

1. "Effects of Impurities on Fuel Cell Performance and Durability", Workshop Held by National Research Council, Canada, March, 2008.

2. "Effects of Impurities on Fuel Cell Performance and Durability", Presentation to the Fuel Quality Working Group, March/April, 2008.

3. "The Effects of Cationic Contamination on the Physio-Chemical Properties of PerfluoroionomerMembranes", Ph. D. Dissertation Defense by T. Molter, April, 2008.

4. "The Effects of Cationic Contamination on the Physio-Chemical Properties of PerfluoroionomerMembranes", Ph. D. Dissertation by T. Molter, May, 2008.