V.B.2 Effects of Impurities on Fuel Cell Performance and Durability

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Contract Number: DE-FG36-07GO17020

Subcontractors:
- FuelCell Energy, Inc., Danbury, CT
- United Technologies Corporation – Hamilton Sundstrand, Windsor Locks, CT

Project Start Date: March 1, 2007
Project End Date: August 31, 2011

Fiscal Year (FY) 2011 Objectives

- Identify the specific impurities and impurity 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 impurity analytical models and computer simulations that explain and predict these effects.
- Validate impurity 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 Fuel Cell 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 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.

FY 2011 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 polymer electrolyte fuel cells (PEFCs).
- Mixtures
  - Demonstrated fuel cell tolerance to a hydrogen fuel stream having a composition similar to that of

the International Organization for Standardization (ISO) fuel quality standard.

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Introduction

Polymer electrolyte membrane (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 impurity 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 impurities 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.

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 (eg. 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 conducted 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, ethylene, acetaldehyde, and formic acid as the primary fuel stream impurity and later extended to include a mixture of benzene, toluene and CO. Testing has been established as a series of 100-hour test runs using up to 5% of the impurity in the fuel stream with the cell construction as defined in Table 1.

Testing was conducted at 200, 600, 800 and 1,000 mA/cm^2 with standard test conditions defined in Table 2. Conditions were modified as defined to achieve better performance stability during testing.

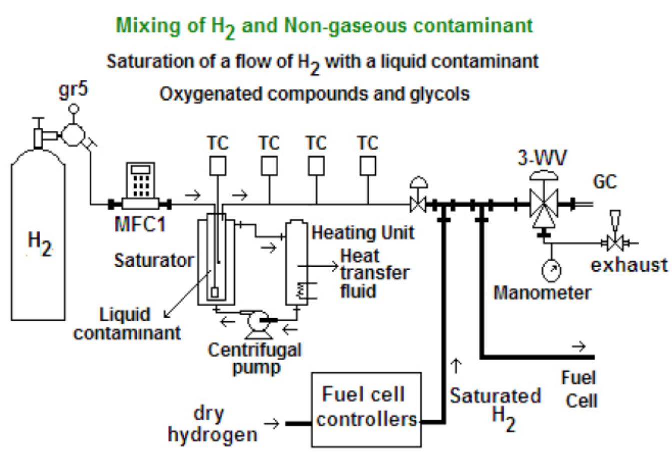


FIGURE 1. Gas Mixing Set-Up for Liquid Hydrocarbons

TABLE 1. Test Cell Definition

Parameter	Early	Intermediate	Recent
Membrane	Nafion®	Nafion® 212	PRIMEA
Loading	0.4/0.2	0.4/0.4	0.1/0.4
MEA OEM	Ion	Ion Power	Gore
GDL	SGL 10	SGL 10 BB	SGL 25
Active Area	25	25	25

OEM - original equipment manufacturer

TABLE 2. Definition of Major Test Parameters

Parameter	Early	Intermediate	Recent
Temperature (°C) (A/Cell/C)	80 / 80 / 80	80 / 80 / 73	80 / 73 / 49
Humidity (%) (A/C)	100 / 100	100 / 75	75 / 25
Stoichiometry (A/C)	1.3 / 2.0	2.0 / 2.0	1.2 / 2.0
Flow Rate (A/C)	Commensurate with current density		
Pressure (psig) (A/C)	25 / 25	25 / 25	7 / 7

A - anode; C - cathode

Ethylene

Testing of the effect of ethylene (C_2H_4) on cell performance was reinvestigated at concentrations of 1% and 5%. These tests were performed to validate previous data obtained with earlier MEAs. No significant effect on cell performance was found during these tests.

Acetaldehyde

Testing of the effect of acetaldehyde (CH_3CHO) on cell performance was investigated at a concentration of 30 ppm. An immediate, but small drop of 20 mV at 800 mA/cm^2 and 50 mV at 1,000 mA/cm^2 was observed with addition of the impurity.

Benzene, Toluene, CO Mixture

The effect of benzene (C_6H_6), toluene (C_7H_8) and CO on fuel cell performance was investigated at an impurity concentration of 10 ppm, 10 ppm and 1 ppm, respectively. Testing showed no significant effect of cell performance during the 100 hour durability test shown in Figure 2.

Hydrogen Pump Studies

NH_3 contamination on PEFCs was investigated with pseudo reversible hydrogen electrodes (pseudo-RHEs). It was found that NH_4^+ can affect the anode causing an increase of the overpotential in a hydrogen pump test. Figure 3 shows the overpotential variations of the anode and the cathode respectively during contamination and recovery. It is seen that 50 ppm NH_3 in H_2 can significantly affect the electrochemical kinetics on the electrodes. The initial drop of the overpotentials is due to the poisoning effect of NH_4^+ on pseudo-RHEs.

Raman Spectroscopy and Gas Chromatograph-Mass Spectroscopy Studies

An investigation of gas diffusion layers (GDLs) revealed minor organic impurities left over from the manufacturing process were still present on the microporous layer of the GDLs. It was found that baking the GDLs would volatize these compounds and clean the surface of organic impurities without damage to the GDLs.

Rotating Disk Electrode

Testing was conducted to further understand the mechanism of formic acid contamination of cell performance. It was found that the concentration of formic acid and presence of hydrogen impacted the oxidation of formic acid as seen in Figure 4. Testing to date has indicated little effect of simple hydrocarbon species on fuel cell performance; however, more complex species do show some performance effects.

Evaluation of Fuel Quality Standards

A model solution of the proposed hydrogen fuel quality ISO standard was evaluated in an operating cell. Results shown in Figure 5 indicate that 100-hour performance was similar to that obtained using pure hydrogen. However, tests run at a contaminant concentration of five times the proposed ISO standard showed significantly higher performance loss over time.

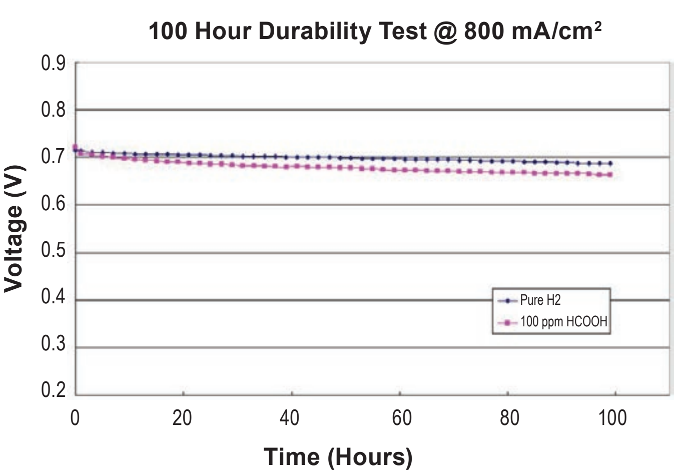
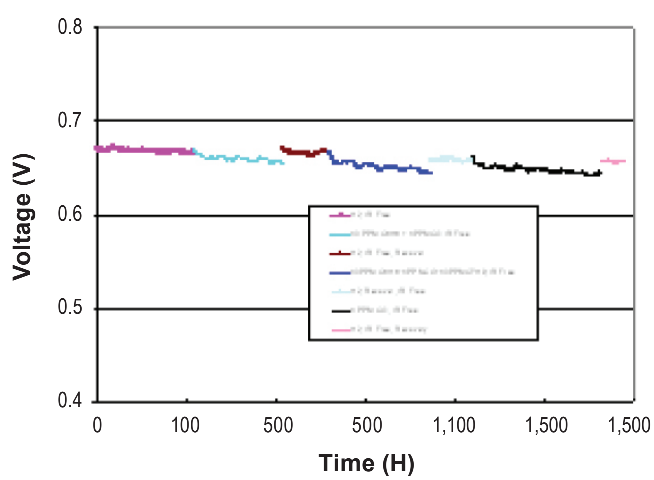


FIGURE 2. Durability Test Using 100 ppm Formic Acid



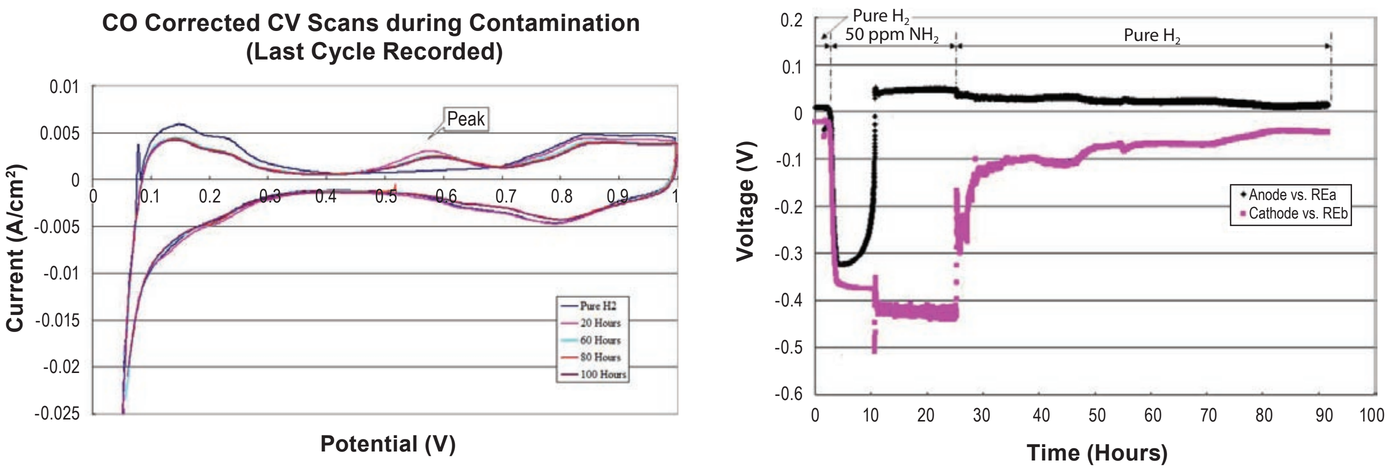


FIGURE 3. The Overpotentials versus RHEs Measured during NH_3 Contamination and Recovery of a 25 cm^2 MEA

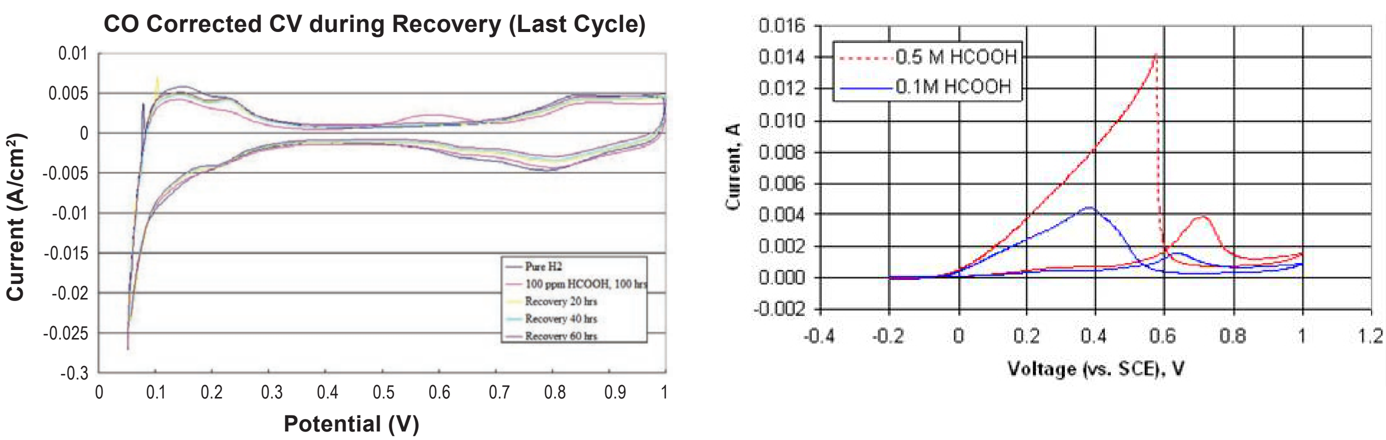


FIGURE 4. Cyclic Voltammetry of 0.1 M and 0.5 M Formic Acid in 0.2 M Sulfuric Acid, No Hydrogen Bubbling

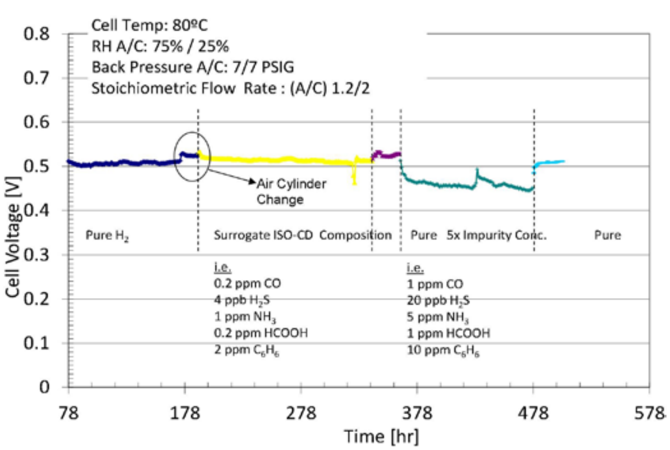


FIGURE 5. Fuel Cell Performance Comparing Pure Hydrogen Feed to Mixtures Emulating the Proposed ISO Fuel Quality Standard, and Contaminant Levels of Five Times the Standard

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 affect 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.
- Testing with a model hydrogen mixture having chemistry similar to the hydrogen quality standard did not result in significant performance degradation.

Future Directions

- Comprehensive evaluation of formic acid and formaldehyde to support ISO standard development:
  - Continued testing using standard test protocols, MEAs.
  - Target low catalyst loadings (reduction from 0.4 mg/cm^2 to 0.1 mg/cm^2).
  - 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.

FY 2011 Publications/Presentations

1. X. Zhang, H. Galindo, H. Garces, P. Baker, X. Wang, U. Pasaogullari, S. Suib, T. Molter, "Influence of Formic Acid Impurity on Proton Exchange Membrane Fuel Cell Performance", J. of Electrochem. Soc. 157 B409 (2010).

2. Serincan, M.F., Pasaogullari, U., Molter, T., "Modeling the cation transport in an operating polymer electrolyte fuel cell (PEFC)," *Int. J. Hydrogen Energy,* 35(11), 5539 (2010).