

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

Trent M. Molter

The Connecticut Global Fuel Cell Center  
The University of Connecticut  
44 Weaver Rd. Unit 5233  
Storrs, CT 06269  
Phone: (860) 486-2898  
E-mail: [tmolter@engr.uconn.edu](mailto:tmolter@engr.uconn.edu)

DOE Technology Development Manager:  
Nancy Garland

Phone: (202) 586-5673  
E-mail: [Nancy.Garland@ee.doe.gov](mailto:Nancy.Garland@ee.doe.gov)

DOE Project Officer: Reg Tyler

Phone: (303) 275-4929  
E-mail: [Reginald.Tyler@go.doe.gov](mailto:Reginald.Tyler@go.doe.gov)

Technical Advisor: Thomas Benjamin

Phone: (630) 252-1632  
E-mail: [Benjamin@anl.gov](mailto:Benjamin@anl.gov)

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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, 5,000 hours based on a test protocol issued by DOE in 2007.
- By 2015, 5,000 hours based on a test protocol issued by DOE in 2007.

### Accomplishments

Hydrocarbon Testing

- Completed testing of the most critical hydrocarbon species likely to be present in hydrogen fuel streams including: formic acid, formaldehyde, methane, ethane, ethylene and acetaldehyde.
- Developed analytical procedures and mixing protocols for evaluating concentrations of acetaldehyde, formic acid, and formaldehyde in the fuel stream.

Other Impurities

- Evaluated the effects of several likely concentrations of ammonia on polymer electrolyte fuel cells (PEFCs) and characterized its effects on membrane integrity in the ammonium form.
- Characterized the effects of methyl chloride on PEFC performance.



### Introduction

PEFCs 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 causes for this is the introduction of impurities into the fuel stream that impacts the functionality of ion exchange groups within the electrolyte, degrades catalyst activity, and function causing voltage to degrade.

### Objectives

- Identify the specific impurities and impurity families and their concentrations present in the fuel.
- Develop analytical chemistry protocols to detect the fate of contaminating species within fuel cells.
- Determine through controlled laboratory experiments and literature the main drivers for decay.
- Develop 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 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

The technical issues addressed center around 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 and procedures for contaminant testing of PEFCs. 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 PEFCs. Experimental data collected from test protocols will be leveraged to create mathematical models that predict performance of PEFCs exposed to specific impurities. These models will be validated through laboratory experimentation and will be utilized to develop novel technologies for mitigating the effects of impurities on fuel cell performance. The effects of cationic impurities on the fundamental physico-chemical properties of perfluoroionomer membranes are also being evaluated. 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. We have focused our efforts on the evaluation of 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. Studies have focused on the evaluation of gaseous impurities, volatile liquids and less volatile liquids. Testing of many of the less volatile liquids requires the use of a saturator apparatus (Figure 1) that we developed specifically for these experiments.

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. Testing was conducted at 200, 600 and 800 mA/cm<sup>2</sup>

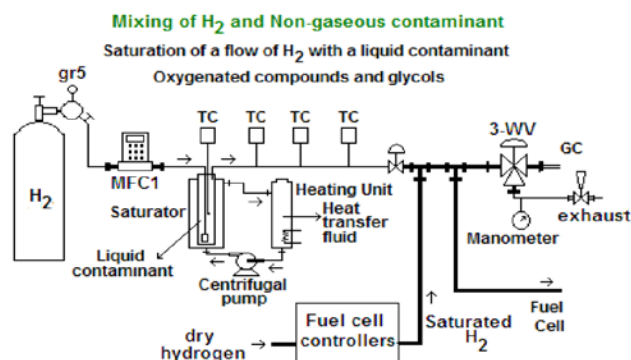


FIGURE 1. Gas Mixing Set-Up for Liquid Hydrocarbons

TABLE 1. Test Cell Definition

| Parameter                              | Early                   | Intermediate            | Recent                   |
|--|-------------------------|-------------------------|--------------------------|
| Membrane                               | Nafion <sup>®</sup> 212 | Nafion <sup>®</sup> 212 | Gore PRIMEA <sup>®</sup> |
| Pt Loading (mg/cm <sup>2</sup> ) (A/C) | 0.4/0.2                 | 0.4/0.4                 | 0.1/0.4                  |
| Anode Type                             | 50% Pt on C             |                         | 50% Pt on C              |
| Cathode Type                           | 50% Pt on C             |                         | 50% Pt on C              |
| MEA Manufacturer                       | Ion Power               | Ion Power               | Gore                     |
| GDL                                    | SGL 10BB                | SGL 10BB                | SGL 25BC                 |
| Cell Active Area (cm <sup>2</sup> )    | 25                      |                         |                          |
| Hardware Manufacturer                  | Fuel Cell Technologies  |                         |                          |

A - anode; C - cathode; GDL - gas diffusion layer

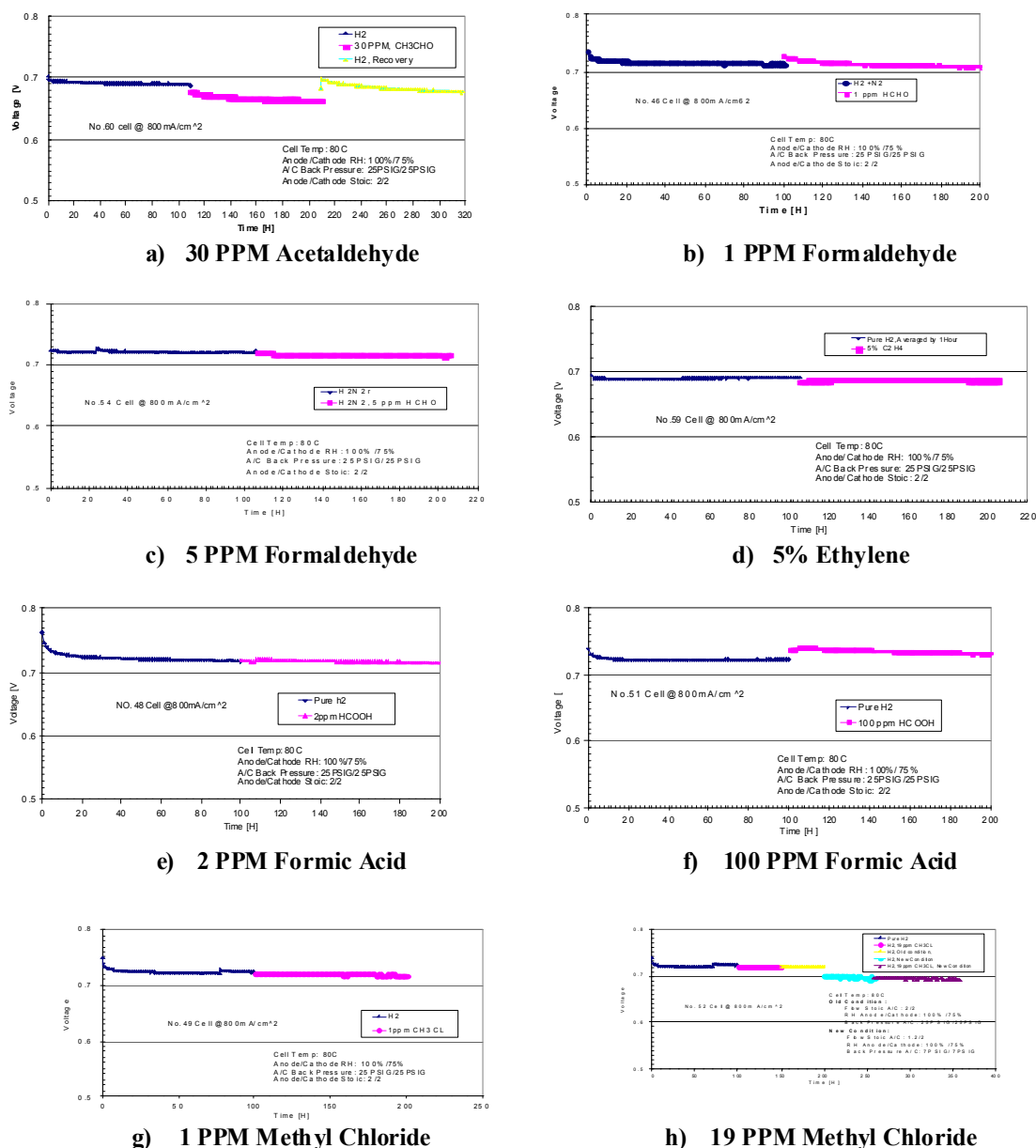
with standard test conditions defined below in Table 2. Conditions were modified as defined to achieve better performance stability during testing.

**Acetaldehyde** - The effect of acetaldehyde (CH<sub>3</sub>CHO) on cell performance was investigated at an impurity concentration of 30 ppm. Cell performance immediately dropped with 30 ppm acetaldehyde in the fuel stream. At the conclusion of the contaminant test, recovery was attempted using pure H<sub>2</sub> as fuel to run the fuel cell, and cell performance was restored to pre-contaminant injection performance. Figure 2a provides these test results. Our conclusion is that a

TABLE 2. Definition of Major Test Parameters

| Parameter                             | i                                 | ii      | iii     | iv      |
|---------------------------------------|-----------------------------------|---------|---------|---------|
| Stoichiometry (A/C)                   | 1.3/2.0                           | 2.0/2.0 | 2.0/2.0 | 1.2/2.0 |
| Back Pressure (A/C <sub>2</sub> psig) | 25/25                             | 25/25   | 25/25   | 7/7     |
| RH (A/C, %)                           | 100/100                           | 100/100 | 100/75  | 75/25   |
| Cell Temperature (°C)                 | 80                                | 80      | 80      | 80      |
| Flow Rate (A/C)                       | Commensurate with current density |         |         |         |

RH - relative humidity



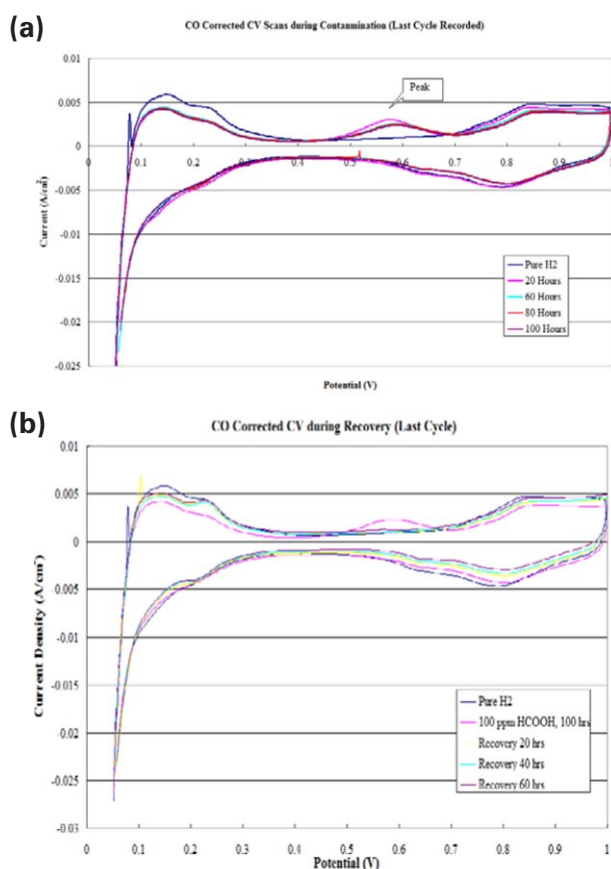
**FIGURE 2.** Results of 100-Hour Performance Tests of PEFCs Using Different Impurities and Concentrations

moderate effect on cell performance was found during this impurity test. Further tests are being conducted to determine the mechanism.

**Formaldehyde** - Testing of the effect of formaldehyde (HCHO) on cell performance was investigated at impurity concentrations of 1 ppm and 5 ppm. No significant influence on cell performance was found during these lower concentration impurity tests (Figures 2b and 2c).

**Ethylene** - Testing of the effect of ethylene (C<sub>2</sub>H<sub>4</sub>) on cell performance was investigated at impurity concentrations of 5%. No significant effect on cell performance was observed (Figure 2d).

**Formic Acid** - Testing of the effect of formic acid (HCOOH) on cell performance was investigated at impurity concentrations of 2 ppm and 100 ppm. No significant effect on cell performance was found during the 5 ppm impurity tests (Figure 2e). Some degradation was found in the 100 ppm formic acid test (Figure 2f). Cyclic voltammetry (CV) scans performed at 20 mV/sec before and after the impurity tests showed that electrochemical area of the cathode decreased, signifying that HCOOH has a negative effect on the cathode catalyst. Similar scans were also performed every 20 hours (Figure 3a) during contamination and recovery periods to provide detail of the mechanism for contamination on the cathode. Pure nitrogen was



**FIGURE 3.** (a) Progressive CV Scans on the Cell, Figure (b) Scans Showing Recovery

fed to the cathode at 250 sccm, while HCOOH/H<sub>2</sub> was fed to the anode at 250 sccm. The CV scans indicate a decrease in H<sub>2</sub> absorption peaks and an oxidation peak at 0.6 V which could be caused by adsorbents on Pt surface. An individual CV scan is shown in Figure 3b. Each scan consists of four cycles. In the first CV cycle, the hydrogen absorption peak nearly disappeared. The Pt surface seems to be covered by adsorbents (peaks at 0.4 V and 0.6 V that are not seen with pure H<sub>2</sub>). Adsorbents are oxidized around 0.4 V and 0.6 V in the 1st cycle. In the next three cycles, recovery of H<sub>2</sub> absorption peak is observed, but evidence of surface coverage still exists. Mechanistic studies to evaluate the specific effect of formic acid on cell components using analytical tools, rotating disk electrodes and hydrogen pump experiments are underway.

**Methyl Chloride** - Testing of the effect of methyl chloride (CH<sub>3</sub>Cl) on cell performance was investigated at impurity concentrations of 1 ppm and 19 ppm. No significant effect on cell performance was found during these impurity tests (Figures 2g and 2h).

Testing is summarized in Table 3. Testing has indicated little effect of simple hydrocarbon species on

fuel cell performance; however, more complex species do seem to affect performance.

**Cationic Impurities** - The effect of ammonia contamination on PEFCs was investigated with pseudo-reversible hydrogen electrodes. It was found that NH<sub>4</sub><sup>+</sup> affects the anode causing an increase in the overpotential in a hydrogen pump cell. Figure 4a shows the overpotential variations of the anode and the cathode respectively during contamination and recovery. 50 ppm NH<sub>3</sub> in H<sub>2</sub> can significantly affect the electrochemical kinetics on the electrodes. The initial drop of the overpotential is due to the poisoning effect of NH<sub>4</sub><sup>+</sup> on pseudo-reversible hydrogen electrodes. In a fuel cell, NH<sub>4</sub><sup>+</sup> was also found to affect the anode, however, the anode performance loss was less than on the cathode (Figure 4b).

## Conclusions and Future Directions

### Conclusions

- Simple hydrocarbons including methane, ethane, ethylene and acetaldehyde, particularly in low concentrations do not significantly affect fuel cell performance.
- Simple halogenates such as methyl chloride in low concentrations do not affect performance
- Acetaldehyde impurities show some effect on performance at higher concentrations.
- Formic acid impurities affect performance at higher concentrations likely due to adsorption on the electrode surface as well as the formation of reaction byproducts such as CO.
- Testing has shown both anode and cathode performance impacts of ammonia.

### Future Directions

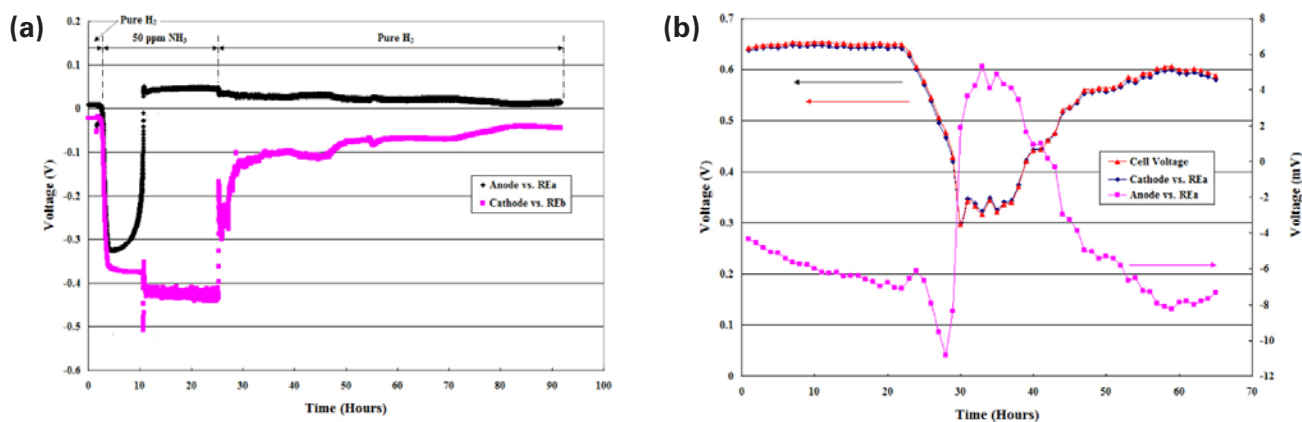
- Mechanistic evaluation of formic acid and acetaldehyde to support International Organization for Standardization standard development.
- Finalizing testing on aromatic hydrocarbons.
- Study the impact of catalyst ageing on sensitivity to hydrocarbon contamination.
- Finalizing modeling of impurity effects.
- Developing mitigation techniques for key impurities that show an impact on cell performance.

## FY 2010 Publications/Presentations

1. Molter, T., "The Effects of Hydrocarbons and Halogenated Compounds on PEFC Performance", Presented to the Joint Hydrogen Fuel Quality Working Group, San Francisco, CA, January 2010.

**TABLE 3.** Compilation of Test Data from Impurity Tests

| #  | Contaminant                             | I mA/cm <sup>2</sup> | RH (%) (A/C) | Pressure (psig) (A/C) | Stoich (A/C) | Results                    |
|----|---|----------------------|--------------|-----------------------|--------------|----------------------------|
| 1  | 100 ppm CH <sub>4</sub>                 | 200                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 2  | 100 ppm CH <sub>4</sub>                 | 600                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 3  | 5% CH <sub>4</sub> or 5% N <sub>2</sub> | 600                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 4  | 100 ppm CH <sub>4</sub>                 | 800                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 6  | 5% C <sub>2</sub> H <sub>6</sub>        | 600                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 7  | 5% C <sub>2</sub> H <sub>4</sub>        | 800                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 11 | 30 ppm CH <sub>3</sub> CHO              | 800                  | 100 / 100    | 25 / 25               | 1.3 / 2.0    | No significant degradation |
| 31 | 100 ppm CH <sub>3</sub> CHO             | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 35 | 100 ppm HCOOH                           | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Significant degradation    |
| 38 | 50 ppm HCOOH                            | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Some degradation           |
| 40 | 2 ppm HCOOH                             | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 41 | 50 ppm HCOOH                            | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Some degradation           |
| 43 | 50 ppm HCOOH                            | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Some degradation           |
| 44 | 2 ppm HCOOH                             | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 45 | 1 ppm HCHO                              | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 46 | 1 ppm HCHO                              | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 48 | 2 ppm HCOOH                             | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 49 | 1 ppm CH <sub>3</sub> Cl                | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 51 | 100 ppm HCOOH                           | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Some degradation           |
| 52 | 19 ppm CH <sub>3</sub> Cl               | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 54 | 5 ppm HCHO                              | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 57 | 5% C <sub>2</sub> H <sub>4</sub>        | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | No significant degradation |
| 60 | 30 ppm CH <sub>3</sub> CHO              | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Degradation at beginning   |
| 64 | 1% C <sub>2</sub> H <sub>6</sub>        | 1000                 | 75 / 25      | 7 / 7                 | 1.2 / 2.0    | No significant degradation |
| 66 | 30 ppm CH <sub>3</sub> CHO              | 800                  | 100 / 75     | 25 / 25               | 2.0 / 2.0    | Degradation at beginning   |



**FIGURE 4.** (a) The Overpotentials Versus Reversible Hydrogen Electrode Measured During NH<sub>3</sub> Contamination and Recovery of a 25 cm<sup>2</sup> MEA; (b) Contamination of 25 cm<sup>2</sup> MEA With 50 ppm NH<sub>3</sub> and Recovery Process (The cell was operated at 400 mA/cm<sup>2</sup> at 60°C with relative humidity at 50% NH<sub>3</sub> flow was introduced at 20 hours and shut down at 36 hours, followed by pure H<sub>2</sub>.)

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, 5539 (2010).
3. Zhang, X\*, Galindo, H.M\*, Garces, H.F\*, Baker, P\*, Wang, X\*, Pasaogullari, U., Suib, S.L., Molter, T., “Influence of formic acid impurity on proton exchange membrane fuel cell performance”, *J Electrochem Soc*, 157, B409 (2010).
4. Zhang, X\*, Galindo, H.M\*, Grace, H.F\*, Baker, P\*, Wang, X\*, Pasaogullari, U., Suib, S.L., and Molter, T., “Impact of Fuel Impurities on PEFCs”, *The 2<sup>nd</sup> International Forum on Multidisciplinary Education and Research for Energy Science*, December 12-16, 2009, Okinawa, Japan.
5. Ozdemir, M.O\*, Serincan, M.F\*, Pasaogullari, U., Molter, T., “Cation Transport and Its Effects in an Operating Polymer Electrolyte Fuel Cell,” *The 2<sup>nd</sup> International Forum on Multidisciplinary Education and Research for Energy Science*, December 12-16, 2009, Okinawa, Japan.
6. Zhang, X\*, Pasaogullari, U., Molter, T., “Influence of ammonia on membrane-electrode assemblies in polymer electrolyte fuel cells”, *Int. J Hydrogen Energy*, 34, 9188 (2009).
7. Zhang, X\*, Galindo, H.M\*, Grace, H.F\*, Baker, P\*, Wang, X\*, Pasaogullari, U., Suib, S.L., and Molter, T., “Influence of formic acid impurity on proton exchange membrane fuel cell performance”, *ECS Transactions*, 1633 (2009).
8. Zhang, X\*, Serincan, M.F\*, Pasaogullari, U., and Molter, T., “Contamination of membrane-electrode assemblies by ammonia in polymer electrolyte fuel cells”, *ECS Transactions*, 1565 (2009).