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

James G. Goodwin, Jr. (Primary Contact),
Hector Colon Mercado (SRNL),
Scott Greenway (SRNL), Xunhua Mo,
Kitiya Hongsirikarn, and Jack Zhang
Department of Chemical & Biomolecular Engineering
Clemson University
Clemson, SC 29634-0909
Phone: (864) 656-6614
E-mail: jgoodwi@clemson.edu

DOE Technology Development Manager:
Nancy Garland
Phone: (202) 586-5673
E-mail: Nancy.Garland@ee.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Walt Podolski
Phone: (630) 252-7558
E-mail: podolski@anl.gov

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Objectives

- Investigate the effect of impurities in the hydrogen fuel streams on the operation and durability of fuel cells. These impurities include water, hydrocarbons (including formaldehyde, formic acid), oxygen, inert gases (He, N_2, Ar), CO_2, CO, sulfur-containing gases, ammonia, halogenated compounds and particulates.
- Propose mechanisms for how impurities in the hydrogen fuel stream affect the components of the fuel cell catalyst and polymer membrane.
- Determine strategies to reduce the poisoning effect of these impurities.
- Disseminate findings so that they are available to other members of the DOE Hydrogen Quality team and to FreedomCAR technical teams.

Technical Barriers

This project addresses the following technical barrier 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 addressing fundamental research into effects and mechanisms of impurities on the performance and durability of polymer electrolyte membrane (PEM) fuel cell systems. The activity broadly supports the following technical targets established by DOE:

- Transportation Fuel Cells
    - Durability with cycling: 5,000 h by 2015

- Stationary PEM Fuel Cell Power Systems:
    - Durability @ <10% rated power degradation: 40,000 h by 2011

Accomplishments

- It was confirmed that the effects of CO_2, C_2-C_7 paraffins, HCOOH and N_2 on Nafion® conductivity and on Pt for H_2 activation are insignificant.
- A simple acid catalyzed reaction (esterification) was used to quantitatively predict conductivity of a contaminated membrane and/or catalyst layer under typical fuel cell conditions and the predicted values agree well with experimental data.
- The effects of ammonium distribution on the conductivity of Nafion® membrane in the liquid and gas phase were studied. In the gas phase, the conductivities of uniformly poisoned membranes considerably differed from those of non-uniformly poisoned membranes having equivalent ammonium concentrations.
- The surface concentration of hydrogen on Nfn-Pt/C (Nafion®-loaded Pt/C) under fuel cell operation conditions was obtained using H_2/D_2 switching and it was found that:
    - Hydrogen activation occurred only on Pt.
    - Transport of protons between the sulfonic sites of Nafion® and the Pt particles was extremely fast.
- Humidity has been determined to have a minimal effect on the apparent activation energy of H_2 activation on Pt/C under typical fuel cell conditions. However, the humidity significantly influences the degree of CO poisoning on Nfn-Pt/C and the final rate of H_2 activation.

- PEM fuel cell studies on the effects of 18 ppm tetrahydrofuran (THF) found ~40% loss in performance and full recovery once THF was removed from the fuel stream.

- Investigation of long-term NH_3 poisoning at 0.1 ppm (maximum International Organization for Standardization [ISO] specified level) found no appreciable degradation at 60°C and 80°C.

- CO poisoning experiments were performed to study the performance decay at ISO limits. Even a small concentration of CO (0.2 ppm) led to 10% performance decay in a few hours, but this could be recovered by electrochemical oxidation.

- CO poisoning experiments were also performed to correlate and compare results from PEM fuel cell tests at SRNL to the results from H_2 activation on Nfn-Pt/C experiments at Clemson. The results match well.

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Introduction

PEM fuel cells show significant potential to enable efficient, clean power for stationary and transportation applications; however, the present-day technology falls short of meeting the necessary product performance and durability requirement standards. An important limitation in the operational life of PEM fuel cells is caused by the presence of hydrogen-feed stream contaminants (e.g., ammonia, carbon monoxide, etc.). These contaminants degrade the functionality of ion exchange groups within the electrolyte, degrade catalyst activity, and result in a degradation of the overall fuel cell efficiency and operational performance.

Approach

This project is a unique combination of phenomenological studies (at Clemson University) and fuel cell membrane electrode assembly (MEA) durability testing at SRNL, with MEAs tested at SRNL composed of the same/similar materials as being investigated at Clemson. By determining the effect of impurities on the component parts of an MEA as well as overall fuel cell performance, a comprehensive mechanism of poisoning can be proposed which should suggest means to diminish that effect. Development of an integrative model is also being undertaken by Argonne National Laboratory using the fundamental measurement results obtained by Clemson and SRNL. The fuel cell team at SRNL is integrated into the U.S. Fuel Cell Council Joint Hydrogen Quality Task Force, presently engaged to address the ISO TC 197: Hydrogen Fuel – Product Specification: Proton exchange membrane (PEM) fuel cell application for road vehicles.

Results

The investigation of the effects of H_2O on the surface hydrogen coverage and dissociation on Pt/C under fuel cell operation conditions suggests that: 1) in the absence of a poison like CO, equilibrium is still reached for H_2 activation on Nfn-Pt/C at 80°C in the presence of water vapor; 2) humidity has minimal effect on E_a for H_2 activation on Nfn-Pt/C in 10 ppm of CO at typical fuel cell conditions; 3) however, the humidity significantly influences the degree of poisoning by CO of Nfn-Pt/C and the final rate of H_2 activation.

Esterification was used as a diagnostic tool to investigate the proton availability of Nafion® components of a PEM fuel cell. It was found that a simple acid catalyzed reaction (esterification) can be used to quantitatively investigate the number of proton sites in a Nafion® membrane and can be further used to predict conductivity of a contaminated membrane under typical fuel cell conditions, as shown in Figure 1. In addition, this methodology can be used to determine the effects of impurities on the number of proton sites in a catalyst layer of a PEM fuel cell, which can be further used to predict the conductivity of the catalyst layer.

With respect to the effects of impurities on the ionic conductivities of Nafion® membranes, the effects of NH_4^+ distribution in the liquid and gas phase were studied using physically assembled membranes with known ammonium compositions. Under typical fuel cell operations, the conductivities of non-uniformly poisoned membranes were ca. 1.07–1.86 times larger than those of uniformly poisoned membranes, depending on humidity, contamination level, and ammonium ion distribution.

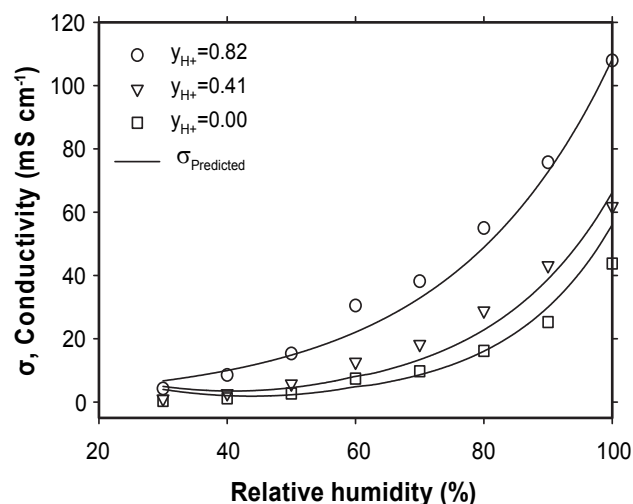The effect of Nafion® on H_2 activation on Pt was studied. It was found that while the impregnation of

**FIGURE 1.** Experimental and predicted ionic conductivities of N-211 in the H^+/Na^+-form at 80°C.

30 wt% Nafion® on Pt/C has dramatic effects on the physical characteristics of Pt/C, such as a reduction in Brunauer-Emmett-Teller surface area from 170 m^2 (g.cat)$^{-1}$ to 37 m^2 (g.cat)$^{-1}$, the overall effect of the Nafion® on the adsorption capability of hydrogen and CO by Pt is small. However, a clear blocking of cyclopropane from reacting during cyclopropane hydrogenolysis, a structure sensitive reaction, on a large portion of surface Pt sites by the Nafion® can be observed. This inhibition of cyclopropane by Nafion® appears to be due, mainly, to steric hindrance rather than the direct blocking of significant numbers of surface Pt atoms.

The DOE provided conditions for desired experiments at low levels of NH$_3$ and wanted 1,000-hour tests to be completed as soon as possible. SRNL worked on the required ammonia tests with the provided GORE membrane electrode assemblies. A baseline and 0.1 ppm poisoning at 60°C or 80°C and 50/50 percent relative humidity (RH) with an Ion Power MEA to determine the impact of NH$_3$ at the ISO limit were performed. As shown in Figure 2, no appreciable degradation from the introduction of NH$_3$ at the ISO specified level was observed over 800 hr.

THF was used to characterize the performance effects that hydrocarbons can have on fuel cell performance since THF is a popular solvent used in many chemical synthesis which include hydrogen storage materials. Approximately 40% loss in performance was observed within 1 h after 18 ppm THF was injected to the feed as indicated in Figure 3. It also can be seen that full recovery was observed as soon as THF was removed from the fuel stream.

SRNL is finishing the runs with CO poisoning experiments at the ISO limits and suggested new lower limits. It was found that even a small concentration of CO (0.2 ppm) led to 10% performance decay in a few hours (Figure 4a). Electrochemical oxidation after CO poisoning was able to successfully remove all traces of CO and the MEA performance was recovered (Figure 4b).

CO poisoning experiments were also performed under similar conditions at SRNL and Clemson to correlate and compare results from PEM fuel cell tests at SRNL to the results from H$_2$ activation on Nfn-Pt/C experiments at Clemson. The cyclic voltammetry data before and after PEM poisoning runs with CO were analyzed to characterize the number of electrocatalyst active sites poisoned. It was found that the electroactive surface areas of Pt obtained with the CO desorption peak matches closely with those obtained with the hydrogen desorption peaks. Also, the electroactive surface area of Pt was reduced with CO poisoning at 60°C and 80°C. However, after the cell was left at open circuit and 25°C with 8 ppm CO the electroactive area was recovered.
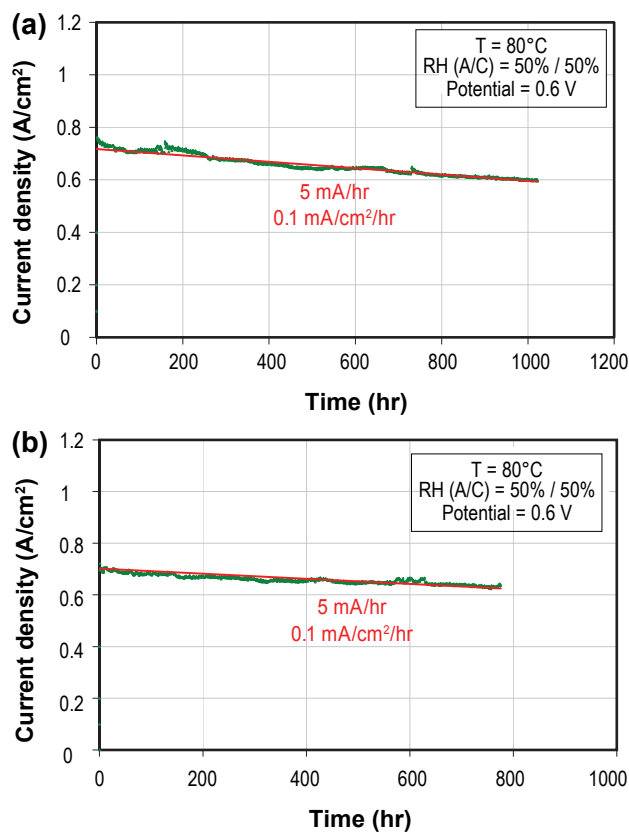

FIGURE 2. H$_2$/Air potentiostatic polarization baseline (a) without NH$_3$ and (b) in the presence of 0.1 ppm NH$_3$ for a GORE MEA with 0.1/0.4 mg/cm^2 catalyst loadings at 80°C and 50%/50% RH.

Conclusions and Mitigation Strategies

Major conclusions are covered in the Accomplishments section.

To date, the following preliminary impurity mitigation strategies can be proposed based on the findings of this project:

- Fuel cells can tolerate up to 0.1 ppm of NH$_3$ (maximum ISO specified level) for long periods of time.
- Use of higher percent RH results in a smaller decrease in conductivity with NH$_3$ poisoning. Thus, a higher percent RH is recommended for fuel cell operation to increase the performance and lifetime when trace amounts of NH$_3$ are present in the fuel.
- Since during CO poisoning, CO does not fully cover all the Pt sites regardless of CO concentration, in order to maintain better fuel cell performance, the use of higher loadings of Pt is recommended if better CO-resistant catalysts are not available.
- Preliminary data suggest that in the presence of CO, lower humidity appears to decrease the effect
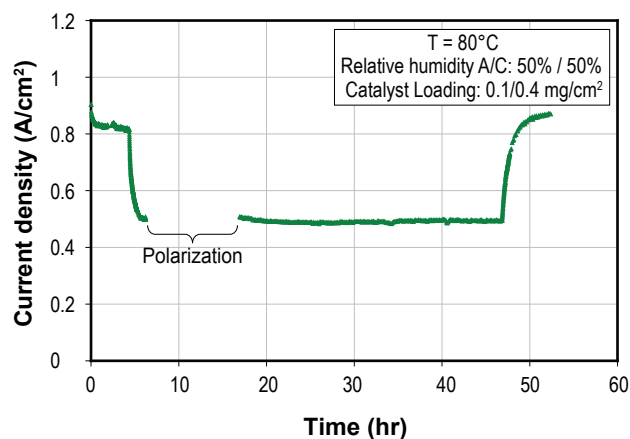
FIGURE 3. Current decay and recovery during 18 ppm THF poisoning of a 50 cm^2 GORE MEA with an anode Pt loading of 0.1 mg/cm^2 at 80°C.
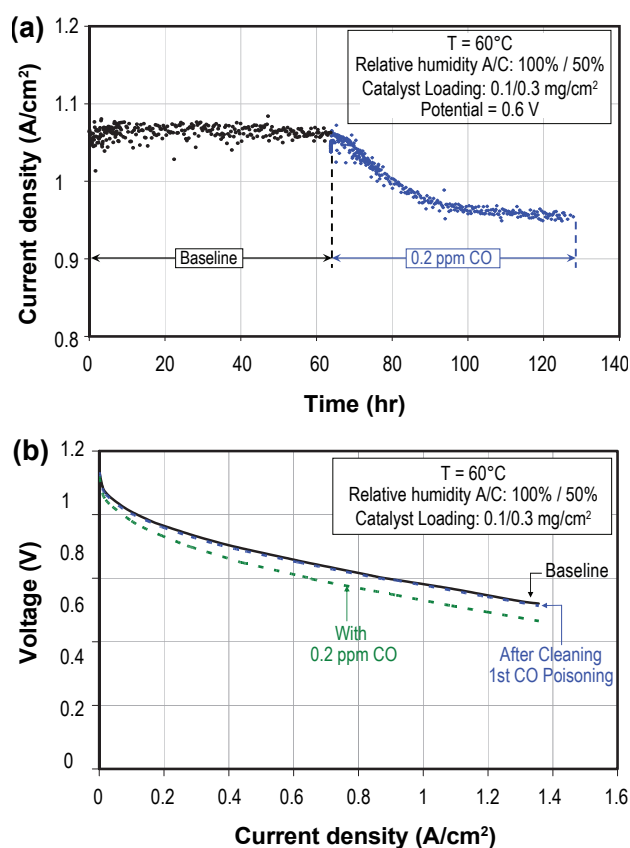
FIGURE 4. (a) Current decay during 0.2 ppm CO poisoning of a 50 cm^2 Ion Power MEA with an anode Pt loading of 0.1 mg/cm^2 at 60°C; (b) Polarization scan before, during and after electrochemical cleaning of the cell during the 0.2 ppm CO poisoning test of a 50 cm^2 Ion Power MEA with an anode Pt loading of 0.1 mg/cm^2 at 60°C.

of CO poisoning on Pt. Thus, lower humidity is recommended in order to minimize CO poisoning on Pt.

Obviously, the actual materials and operational conditions chosen for use in a fuel cell must be determined by an optimization of material properties, operation conditions, possible mitigation strategies to minimize the effect of impurities, and desired fuel cell performance.

The project is on track for completion of the major objectives of this research in 2011.

FY 2010 Publications/Presentations

Publications

1. "The Effect of Low Concentrations of CO on H$_2$ Adsorption and Activation on Pt/C," *Journal of Power Sources* 195 (2010) 3060-3068 (Jack Z. Zhang, Zhiming Liu, and James G. Goodwin, Jr.).

2. "Esterification as a Diagnostic Tool to Predict Proton Conductivity Affected by Impurities on Nafion Components for PEMFCs," *Journal of Power Sources* 195 (2010) 3416-3424 (Kitiya Hongsirikarn, Xunhua Mo, and James G. Goodwin, Jr.).

3. "Prediction of the Effective Conductivity of Catalyst Layer in a PEMFC using Esterification and the Agglomerate Model ," *Journal of Power Sources*, 195 (2010) 5493-5500 (Kitiya Hongsirikarn, Xunhua Mo, and James G. Goodwin, Jr.)

4. "Effect of Cations (Na$^+$, Ca^{2+}, Fe^{3+}) on the Conductivity of a Nafion Membrane," *Journal of Power Sources* 195 (2010) 7213-7220 (Kitiya Hongsirikarn, James G. Goodwin, Jr., Scott Greenway, and Stephen Creager).

5. "Effect of Ammonium Ion Distribution on Nafion® Conductivity," *Journal of Power Sources*, in press (2010) (Kitiya Hongsirikarn, Thirapong Napapruekchart, Xunhua Mo, and James G. Goodwin, Jr.).

6. "Pt Alloy Electrocatalysts for Proton Exchange Membrane Fuel Cells: A Review," in preparation (Zhiming Liu, Lingling Ma, Jack Zhang, Kitiya Hongsirikarn, James G. Goodwin, Jr.).

Presentations

1. "Influence of Ammonia on the Conductivity of Nafion Membranes," oral presentation, ACS National Meeting, Washington, D.C., August 2009 (Kitiya Hongsirikarn, James G. Goodwin, Jr., and Scott Greenway).

2. "Hydrogen Surface Coverage of Pt/C in Presence of CO," Southeastern Catalysis Society Annual Symposium, oral presentation, Asheville, NC, Sept. 27–28, 2009 (Jack Z. Zhang, Zhiming Liu, James G. Goodwin, Jr.).

3. "Effects of Impurities on Fuel Cell Performance and Durability," invited oral presentation, 2010 Annual Dept. of Energy Hydrogen Program Review Meeting, Washington, DC, June 7-11, 2010 (James G. Goodwin, Jr., Jack Zhang, Kitiya Hongsirikarn, Xunhua Mo, Hector Colon-Mercado, Scott Greenway, Michael Martinez, and Peter Finamoore).