

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

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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, N₂, Ar), CO₂, 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

- Determined that there is significant H spillover from Pt to the carbon support at fuel cell conditions (\approx H coverage of Pt).
- Measured the degree that CO poisoning in the range of 10-70 ppm decreases H₂ activation, hydrogen chemisorption, and H spillover on Pt/C.
- Calculated surface coverage of CO indirectly from hydrogen surface concentration measurements and directly from temperature-programmed desorption (TPD) results in the range of 70-500 ppm on Pt/C, which indicated a maximum CO coverage of approximately 42%.
- NH₃ and inert gases (N₂, Ar, and He) were determined not to have an effect on H₂ activation on Pt/C.
- It was found that CO, CO₂, perchloroethylene (PCE), acetaldehyde, tetrahydrofuran (THF), and ethylene did not affect the conductivity of Nafion[®] membrane and the proton availability of Nafion[®] components (membrane and Nafion[®] supported on Pt/C).
- However, 1 ppm PCE in the H₂ fuel was found to decrease fuel cell current by 90% at 0.6 V in less than 15 hours. This appears to be a result of Pt poisoning. Even at 50 ppb, the current International Organization for Standardization (ISO) limit, PCE was found to be detrimental to fuel cell performance.

- The effect of NH_3 on the conductivity of Nafion[®] was measured to be a strong function of relative humidity (RH), with a reduction in conductivity of 3.4X at 100% RH, but 50X at 30% RH. Poisoning also occurs at a slower rate at higher %RH.
- NH_3 poisoning at 80°C was found to cause significantly less decrease in fuel cell performance than at 60°C, but poisoning kinetics were faster.
- NH_3 was shown to cause a significant decrease in fuel cell performance at 2 ppm. Testing will be conducted to determine effects at 0.1 ppm at 60°C and 80°C per a request by DOE - Bryan Pivovar at the National Renewable Energy Laboratory together with Jim Ohi and Gerald Voecks (DOE consultants for fuel quality efforts) who are charged with defining testing priorities for all the national laboratories for the October 2009 ISO meeting. The priority for SRNL is to test the effect of NH_3 at low concentration.
- Foreign cations (Na^+ , Ca^{2+} , and Fe^{3+}) were found to have a more detrimental effect on the conductivity of Nafion[®] membrane than ammonia. At 80°C, the conductance declined by a factor of 6 and 125 at 100% RH and 30% RH, respectively.
- Esterification was validated to be a simple and convenient technique to quantitatively determine the proton availability of Nafion[®] components under fuel cell operation conditions.
- PCE has been shown to be detrimental to fuel cell performance even at the 50 ppb, the current ISO limit.
- SRNL has developed a permeation tube impurity generator to facilitate testing at DOE ISO hydrogen quality standard limits.



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. The fuel cell team at SRNL is integrated into the U.S. Fuel Cell Council Joint Hydrogen Quality Task Force (JHQTFF), presently engaged to address the ISO TC 197: Hydrogen Fuel – Product Specification: Proton exchange membrane (PEM) fuel cell application for road vehicles.

Results

Phenomenological and fuel cell investigations at Clemson University and SRNL have expanded our knowledge of the MEA materials and the interactions between them and CO , NH_3 , CO_2 , PCE, acetaldehyde, THF, ethylene, N_2 , Ar, He, Na^+ , Ca^{2+} , and Fe^{3+} . CO , CO_2 , PCE, acetaldehyde, THF, and ethylene were found to have minimal effect on Nafion[®] conductivity. NH_3 and inert gases N_2 , Ar, and He have been found to have a minimal effect on H_2 activation on Pt/C other than as diluents. CO_2 has been shown to minimally affect fuel cell performance other than as a diluent.

Direct measurement of the hydrogen surface concentration on Pt/C has been able to be made with a variation on H_2 - D_2 reaction. It was found that, in the absence of CO , the surface concentration of hydrogen was approximately double that of total Pt sites available, most likely due to hydrogen spillover. However, introduction of even 10 ppm CO decreased the hydrogen surface concentration by approximately 64%. Due to the reversibility of CO adsorption and, especially, its low concentration, the time for equilibrium/steady-state CO surface coverage on Pt/C scaled proportionally to CO concentration (Figure 1).

Using TPD to study the amount of CO on the poisoned Pt/C, it was found that the total amount of CO plus hydrogen on the surface equaled that of only the total number of Pt sites available. This appears to suggest that, in the presence of CO , hydrogen spillover is severely limited.

Measurements of hydrogen surface concentration were made on Pt/C samples with different average particle sizes (Pt/C-3 [3 nm] and Pt/C-4 [4 nm]). Due to a decrease of approximately 36% in metal dispersion and 30% in metal surface area, the amount of hydrogen on Pt/C-4 was approximately half that of Pt/C-3. However, reduction in hydrogen surface concentration, in the presence of CO , was found to be similar for both catalysts (Table 1).

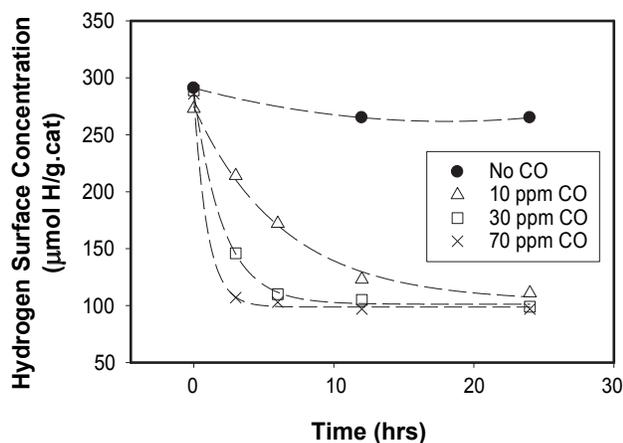


FIGURE 1. Surface concentration of hydrogen measurements on 100 mg Pt/C-4 as a function of time and CO concentration at 80°C and 2 atm.

The time-on-stream conductivities of Nafion[®] membranes (NRE-211s) in the presence of ppm NH₃ concentrations at various humidities and 80°C were determined using electrochemical impedance spectroscopy (EIS). The ionic conductivity of Nafion[®] is affected by the operating conditions (temperature and humidity), ammonium composition, and ammonium distribution in the membrane. The conductivity linearly decreases with time-on-stream (figure not shown) and reaches the same plateau regardless of the partial pressure of ammonia under similar conditions. The final conductivity is a strong function of humidity (see Figure 2). For the same ammonium content, uniformly poisoned membranes yield lower conductivities than non-uniformly contaminated membranes.

The real time conductivity of the Nafion[®] membrane during impurity exposure under practical fuel cell

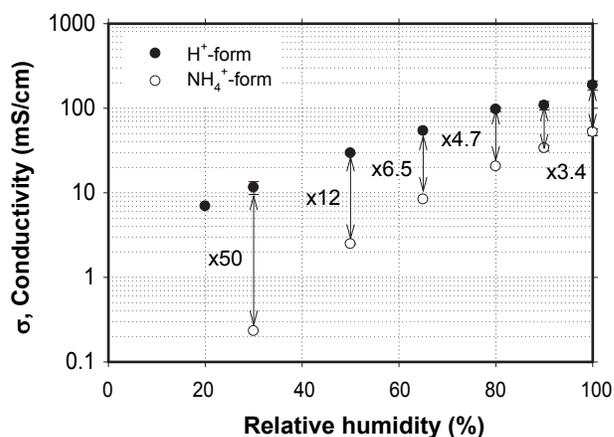


FIGURE 2. Conductivity of N-211 in the protonic and ammonium forms at different humidities and 80°C.

conditions was investigated. It was found that the time-on-stream conductivity after exposures to 5% CO, 5% CO₂, 5% ethylene, 500 ppm PCE, 500 ppm acetaldehyde, or 500 ppm THF was constant over 24 h.

The conductivities of Nafion[®] membranes pre-contaminated with known amounts of cations (Na⁺, Ca²⁺, and Fe³⁺) at various humidities were examined. The results show that the conductivities of Nafion[®] containing different cation ions are similar at the same cationic composition and same conditions. The effect of cations on the Nafion[®] conductivity appears to be more dramatic than that of ammonia. The conductance in the protonic form is 6X higher than that in the cationic form at 100 % RH, and 125X higher at 30 % RH.

SRNL has been involved in ongoing discussions with Bryan Pivovar, Chad Blake, and the Hydrogen Quality working group to determine the testing schedule,

TABLE 1. Time on stream results of hydrogen surface concentration of Pt/C-3 and Pt/C-4 in the absence and presence of CO at 80°C and 2 atm.

Sample	CO Conc. (ppm)	Hydrogen Surface Concentration (μmol H/g cat)					Total Percent Decrease in Surface H Conc.*
		0 hrs	3 hrs	6 hrs	12 hrs	24 hrs	
Pt/C-3	No CO	588	-	-	-	532	-
	70	585	-	-	-	215	63.3%
	500	636	-	-	-	226	64.5%
Pt/C-4	No CO	291	-	-	265	265	-
	10	273	214	172	123	111	59.3%
	30	289	146	110	105	99	65.7%
	70	286	107	103	97	97	66.1%

*Calculated by:
$$\frac{(\text{Surface H})_{\text{No CO}} - (\text{Surface H})_{x \text{ ppm CO}}}{(\text{Surface H})_{\text{No CO}}}$$

conditions, and MEAs to get the data needed for hydrogen fuel quality work. For this work, SRNL will be focusing on NH_3 poisoning experiments at the ISO limits at various temperature and humidity conditions. Clemson will be investigating the thermodynamic equilibrium of NH_3 with Nafion[®] at concentrations of ammonia approaching the ISO limits at different temperatures and relative humidities. Fuel cell tests are underway to measure a baseline (1,000 h) and the effect of 0.1 ppm poisoning at 60°C and 50/50 % RH with an Ion Power MEA to determine the impact of NH_3 at the ISO limit.

Impurity fuel cell tests have been performed at SRNL with PCE to characterize the performance effects that chlorinated cleaning agents (PCE concentrations of 30 ppm, 1 ppm, and 0.05 ppm) can have on fuel cell performance for anode/cathode relative humidities of 100%/50% RH (see Figure 3). The 50 ppb concentration is the ISO total limit for halogenated compounds in the hydrogen stream.

After poisoning with PCE, polarization curves were performed in the hydrogen stream to understand how PCE affected the system at different potentials. As seen in previous experiments, the cell did not recover from poisoning during operation in neat hydrogen. However, the cell did recover after cyclic voltammetry on the anode. After recovery in hydrogen was attempted, the cell was purged and cyclic voltammetry was performed on the anode. Figure 4 shows the first and second cycles of cyclic voltammogram (CV) experiments after the PCE poisoning at 1 ppm. The initial CV showed a notable oxidation peak for PCE at 0.8 V not present in baseline scans. EIS experiments on the cell showed that the membrane resistance was unchanged from the value before poisoning. This preliminary analysis suggests that PCE poisons the catalyst and not the membrane surface.

Thus, fuel cell results have shown that halogenated hydrocarbons can cause rapid degradation of fuel cell

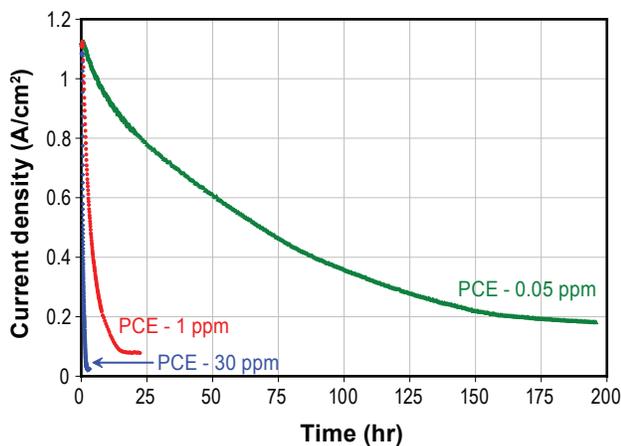


FIGURE 3. Effect of perchloroethylene concentration on PEM fuel cell performance at 60°C.

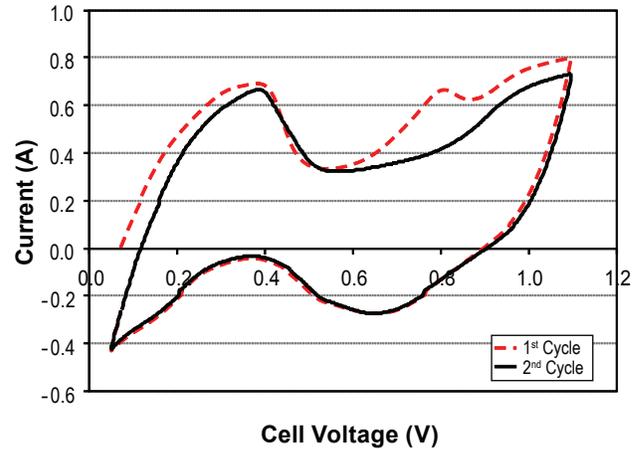


FIGURE 4. Cyclic Voltammograms of the fuel cell anode after poisoning with 1 ppm of PCE.

performance even at the ISO standard concentration of 0.05 ppm PCE. SRNL will be working with hydrogen producers to identify other halogenated compounds such as heat transfer fluids that should be studied as part of the evaluation of halogenated compounds for the ISO standard. It is recommended that the ISO standard be amended to exclude halogenated hydrocarbons such as PCE or place a more stringent limit on the concentration of this class of compounds. It is likely that other chlorinated alkenes such as trichloroethylene, dichloroethylene, and chloroethylene would also need to have a reduced fuel quality limit.

Conclusions

Overall results to date can be summarized as shown in Table 2.

TABLE 2. Summary of Impurities Investigated

MEA Component	Poisons	No Effect
Pt	CO, PCE	NH_3 , CO_2 , N_2 , He, Ar
Nafion [®] Membrane	NH_3 , Na^+ , Ca^{2+} , and Fe^{3+}	CO, CO_2 , PCE, acetaldehyde, THF, and ethylene

At 80°C, there is a significant spillover of hydrogen onto the carbon support for Pt/C equivalent in amount to that chemisorbed on the Pt. The presence of CO, even at concentrations as low as 10 ppm, appears to prevent this. Approximately 42% of the Pt surface is covered by CO for 30 ppm concentrations and higher and this appears to be the saturation coverage in the presence of large quantities of hydrogen.

The presence of low concentrations of ammonia reduces the conductivity of the Nafion[®] membrane by a factor of 3.4-50 depending on the % RH with

the greatest reduction at lower humidities. Results for ammonia poisoning measured in liquid phase can be significantly different from results measured in the gas phase. Also, distribution of the NH_4^+ ions in the membrane can affect conductivity. Thus, even for the same amount of NH_4^+ ions overall, a uniform distribution manifests a different conductivity than a non-uniform distribution.

The presence of the metal ion impurities Na^+ , Ca^{2+} , and Fe^{3+} poison the Nafion[®] membrane even more than ammonia. The poisoning effect is also a strong function of RH.

Fuel cell results for 0.05-30 ppm of PCE have shown that halogenated hydrocarbons such as PCE are detrimental to fuel cell performance even at the ISO limit of 0.05 ppm. The effect seems to be mainly on the Pt catalyst.

Fuel cell tests are underway at SRNL to determine long term fuel cell behavior at the ammonia limit of 0.1 ppm. Fundamental measurements of ammonia uptake at this concentration are also planned at Clemson.

Over the coming year, measurements of the effects of ppm levels of ethylene, PCE, and CO on hydrogen surface coverage of Pt/C as a function of % RH will be carried out. The impact of Nafion[®] on the catalyst on these effects will also be ascertained.

FY 2009 Publications/Presentations

1. "Esterification as a Diagnostic Tool to Investigate the Proton Activity of the Nafion Components of a PEMFC," poster presentation, Southeastern Catalysis Society 7th Annual Fall Symposium, Asheville, NC, September 28-29, 2008 (Kitiya Hongsirikarn, Jack Zhang, James G. Goodwin, Jr., and Scott Greenway).
2. "The Effect of Low Concentration CO on H₂ Activation on Pt/C," poster presentation, Southeastern Catalysis Society 7th Annual Fall Symposium, Asheville, NC, September 28-29, 2008 (Jack Zhang and James G. Goodwin, Jr.).
3. "Effects of Impurities on Fuel Cell Performance and Durability," oral presentation, 2009 Annual Dept. of Energy Hydrogen Program Review Meeting, Washington, D.C., May, 2009 (James G. Goodwin, Jr., Jack Zhang, Kitiya Hongsirikarn, Hector Colon-Mercado, Scott Greenway, and Peter Finamoore).
4. "The Effect of Low Concentrations of CO on H₂ Activation on Pt/C," poster presentation, 21th North American Meeting of the North American Catalysis Society, San Francisco, CA, June 5-10, 2009 (Jack Zhang, Kitiya Hongsirikarn, and James G. Goodwin, Jr.).
5. "Influence of Ammonia on the Conductivity of Nafion Membranes," *Journal of Power Sources*, 195 (2010) 30-38 (Kitiya Hongsirikarn, Jack Zhang, James G. Goodwin, Jr., Scott Greenway, and Stephen Creager).