

V.B.4 Fundamental Effects of Impurities on Fuel Cell Performance and Durability

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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

FY 2011 Accomplishments

The following were the significant accomplishments during this project year:

- The degradation of Nafion[®] by radical products of H₂O₂ formed during fuel cell operation was investigated.
- The effect of Nafion[®] on Pt/C was studied and the siting of the Nafion[®] relative to the Pt identified.
- The effect of perchloroethylene on fuel cell and catalyst performance was determined using both PEM fuel cell and fundamental measurements.
- Diborane was established to be a reversible poison for fuel cell performance.



Fiscal Year (FY) 2011 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

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 International Organization for Standardization Technical Committee 197: Hydrogen Fuel – Product Specification: Proton exchange membrane (PEM) fuel cell application for road vehicles.

Results

During PEM fuel cell operation, formation of H_2O_2 and material corrosion occurs, generating trace amounts of metal cations (i.e., Fe^{2+} , Pt^{2+}) and subsequently initiating the deterioration of cell components and, in particular, PFSA membranes (e.g., Nafion[®]). In a study at Clemson, a quantitative examination of properties and conductivities of degraded Nafion[®] membranes at conditions relevant to fuel cell environments (30-100 % relative humidity [RH] and 80°C) was performed. The degradation degree (defined as: loss of ion-exchange capacity, weight, and fluoride content), water uptake, and conductivity of H_2O_2 -exposed membranes were found to strongly depend on Fe content and H_2O_2 treatment time (see Figure 1). Fourier transform infrared (FT-IR) analysis revealed that Nafion[®] degradation preferentially proceeds at the sulfonic end group and at the ether linkage located in the pendant side chain and that the H-bonding of water is weakened after prolonged H_2O_2 exposure.

Results from an investigation at Clemson established a more fundamental understanding of the effect of humidity on CO poisoning of Pt/C at typical fuel cell conditions (80°C, 2 atm). The presence of water vapor decreased the rate of CO adsorption on Pt, but had very little effect on the resulting CO surface coverage on Pt_s (θ_{CO}) at steady-state. The steady-state θ_{CO} 's at 80°C for Pt exposed to H_2 ($P_{\text{H}_2} = 1$ atm) and a mixture of $\text{H}_2/\text{H}_2\text{O}$ (1 atm H_2 , 10%RH) were 0.70 and 0.66 ML, respectively. Furthermore, total strongly-bound surface hydrogen measured after exposure to $\text{H}_2/\text{H}_2\text{O}$ was, surprisingly, the sum of the exchangeable surface hydrogen contributed by each component, even in the presence of CO.

An exploration of the effect and siting (location) of Nafion[®] on Pt/C as exists in a PEM fuel cell catalyst layer was carried out.

Surprisingly, the presence of 30 wt% Nafion[®] appears to have only a minimal effect on the adsorption capability of either hydrogen or CO on Pt. Experimental and modeling results of cyclopropane hydrogenolysis in an idealized pore suggest that partial blockage of only the pore openings by the Nafion[®] for the meso-macropores is sufficient to induce diffusion limitations on the reaction. The facts suggest that most of the Pt particles are in the meso-macropores of the C support, whereas Nafion[®] is present primarily on the external surface of the C where it blocks the micropores but only partially the pore mouths of the meso-macropores.

PCE was chosen as a model compound for chlorinated cleaning and degreasing agents that may be introduced into a fuel cell as contaminants at a fueling station and/or during vehicle maintenance. During this year SRNL completed fuel cell studies using PCE. Figure 2a shows the results of the PCE concentration detected by Fourier transform infrared at different points in the fuel cell. The spectrum of gaseous PCE has three main peaks in the region between 700 and 1,000 cm^{-1} . From this spectrum, the strong peak at 915 cm^{-1} (see insert of Figure 2a) was used to monitor the PCE. Accordingly, a concentration of 164 ppm of PCE was injected at the anode inlet. However, a substantial reduction

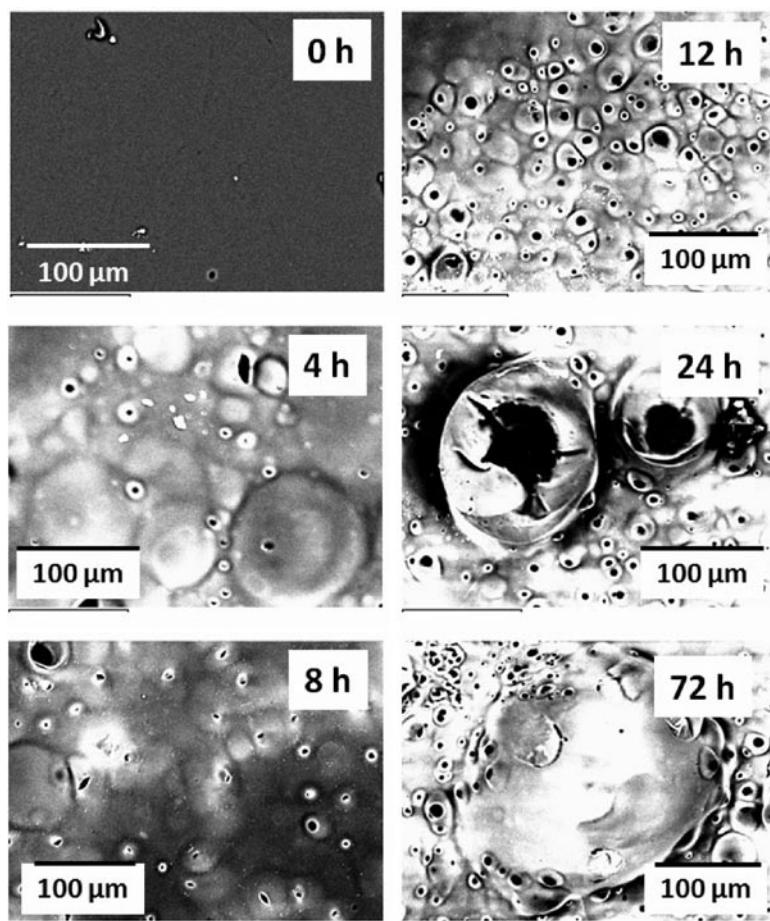
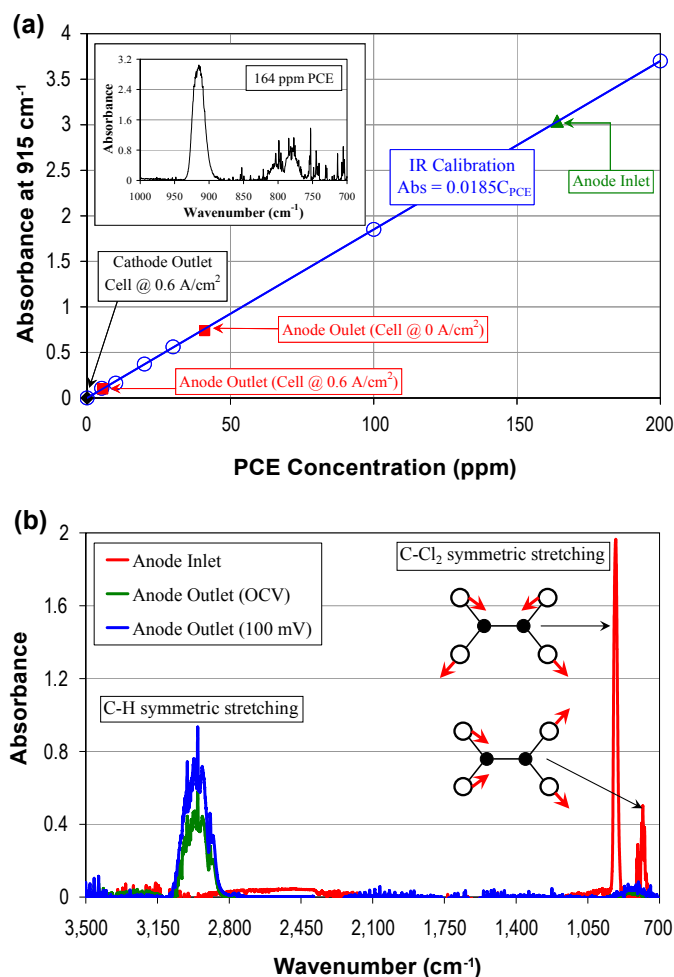


FIGURE 1. Scanning electron microscope images of the surface of a M90 membrane (10% of the H^+ in Nafion replaced by Fe^{2+}) after various times of H_2O_2 treatment.



OCV - open circuit voltage

FIGURE 2. (a) FT-IR calibration and concentration detected during fuel cell operation for PCE using the absorbance band at 915 cm^{-1} of the PCE gas phase spectrum (figure insert). (b) FT-IR absorbance spectra of the decomposition products during fuel cell operation with PCE poisoning.

to 41 ppm was detected at the anode outlet during open circuit. Moreover, after a current of 0.6 A/cm^2 was applied to the cell, the PCE concentration was further reduced to 5.4 ppm. No PCE was detected at the cathode outlet during any of the tests. Figure 2b shows peak transformation from when the spectra were measured at the inlet of the fuel cell and at the outlet with and without a voltage applied. At the exit after the PCE-containing stream had flowed through the catalyst layer, the C-Cl_2 spectrum disappeared and a carbon-hydrogen symmetric stretching was observed. This result indicates the de-chlorination of PCE.

At Clemson, the poisoning effect of PCE on the activity of a Pt fuel cell catalyst for the adsorption and activation of H_2 was investigated at 60°C and 2 atm using hydrogen surface concentration measurements. In the presence of only H_2 , introduction of up to 540 ppm PCE in H_2 to Pt/C resulted in a reduction of available Pt surface atoms (measured by H_2 uptake) by ca. 30% but not enough

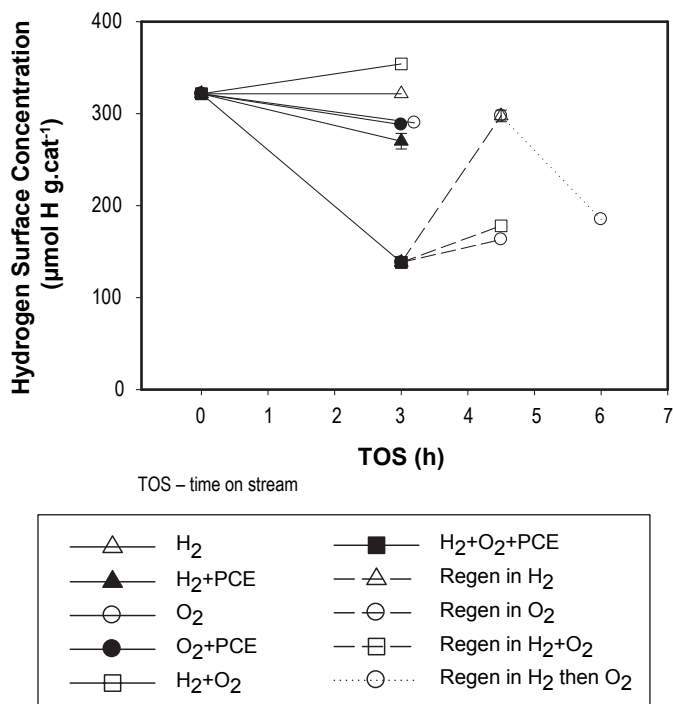


FIGURE 3. Comparison of exposure and poisoning by 150 ppm PCE of Pt/C in different gases (H_2 , O_2 , and $\text{H}_2 + \text{O}_2$) (solid and dotted lines). Effect of different regeneration gases (dashed lines).

to shift the H_2 - D_2 exchange reaction away from being equilibrium limited. Exposure of Pt/C to PCE in a mixed redox environment (hydrogen+oxygen), similar to that at the cathode of a fuel cell, resulted in a much more significant loss of Pt surface atom availability, suggesting a role of oxygen in PCE decomposition and/or Cl poisoning (see Figure 3). Regeneration of the catalyst activity of poisoned Pt/C showed the highest level of recovery when regeneration was carried out in only H_2 , with much less recovery in $\text{H}_2 + \text{O}_2$ or O_2 . The results from this study are in good agreement with those found in the fuel cell study at SRNL.

Diborane (DB) was studied as a model molecule representative of hydrogen storage boron compounds. While no effects were observed on the ionic conductivity and during cyclic voltammetry, a large effect on fuel cell performance was observed as indicated in the potentiostatic curve for a Gore MEA in Figure 4a. There was a drop in performance of about 39% for a concentration of 50 ppm of DB. While the effects seem to be severe, the cell recovers as soon as the DB is removed from the stream. Figure 4b shows the polarization before, during and after recovery from the DB poisoning. The figure indicates that the loss in performance arises mostly from the kinetic limited section (voltage drop in the low current area). However, no indication of catalyst poisoning is observed during cyclic voltammetry. After the DB poisoning is discontinued, the fuel cell performance recovers to approximately 100%.

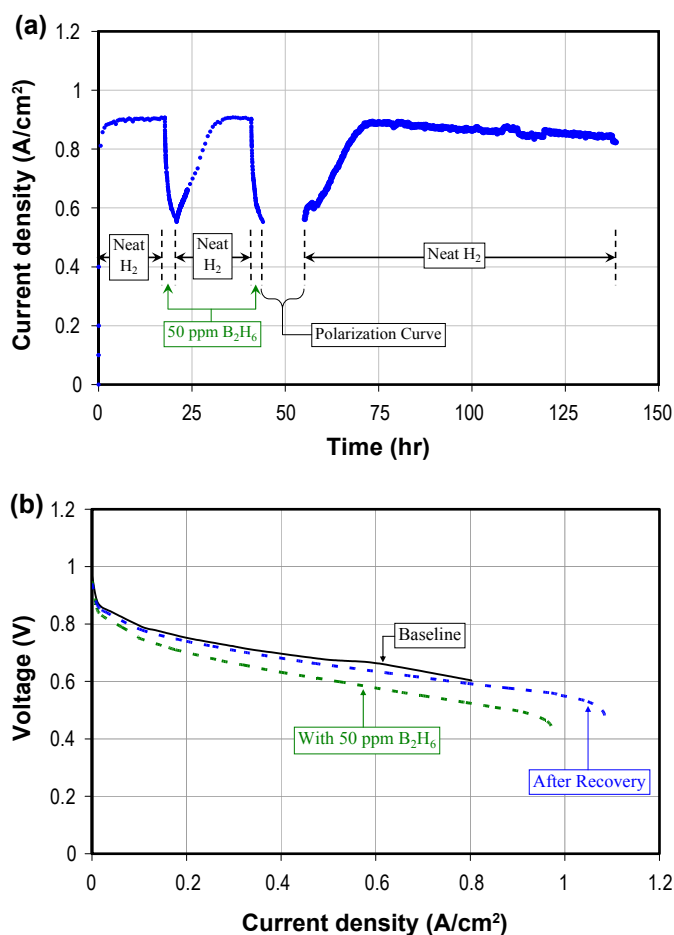


FIGURE 4. (a) Potentiostatic (0.6 V vs. DHE) and (b) polarization scan before, during exposure to 50 ppm of diborane in the hydrogen stream, and after recovery of a fuel cell with a 50 cm² Gore MEA having an anode Pt loading of 0.1 mg/cm² and operated at 60°C and 50% RH.

Conclusions and Mitigation Strategies

- The presence of trace amounts of Fe₂₊ was found to cause significant-severe degradation of Nafion[®] by H₂O₂ formed during fuel cell operation, with degradation preferentially proceeding at the sulfonic end group and at the ether linkage located in the pendant side chain of the Nafion[®].
 - An investigation of Nafion[®] on Pt/C determined that Nafion[®] has little/no effect on the Pt catalyst in the catalyst layer, even though it comprises 30 wt% of that layer. Experimental results and modeling suggest that most of the Pt particles are in the meso-macropores of the C support, whereas Nafion[®] is present primarily on the external surface of the C where it blocks significantly the micropores but only partially blocks the pore mouths of the meso-macropores.
 - The presence of water vapor was found to decrease the rate of CO adsorption on Pt, but had very little effect on the resulting CO surface coverage of PtS (qCO) at steady-state (0.66 vs. 0.70 ML in absence of water vapor).
 - PEM fuel cell studies of the effects of perchloroethylene (PCE) found that the loss in performance arises from the dechlorination of PCE and affects most likely the cathode electrode.
 - Exposure of Pt/C to 150 ppm PCE in a mixed redox environment (hydrogen+oxygen), similar to that at the cathode of a fuel cell, resulted in a much more significant loss of Pt surface atom availability (57% loss) than in hydrogen (15%) or oxygen (11%) alone, suggesting a role of oxygen in PCE poisoning of Pt.
 - Regeneration of catalyst activity of PCE poisoned Pt/C showed the highest level of recovery when regeneration used only H₂, with much less recovery in H₂+O₂ or O₂.
 - Diborane (B₂H₆, DB), a model impurity from hydrogen storage boron compounds, was found to cause a 39% loss in fuel cell performance. However, full recovery was attainable once diborane was removed from the fuel stream.
- Based on the results from this year, the following impurity mitigation strategies can be proposed:
- It is critical to minimize contamination of Nafion[®] with transition metal ions since they (and especially Fe²⁺) catalyze the degradation of Nafion[®] by radical products of H₂O₂ formed during fuel cell operation.
 - Higher humidity lessens the degree of degradation of Nafion[®] conductivity by radical products of H₂O₂.
 - Water vapor does not appear to affect CO poisoning of Pt. Therefore, use of higher or lower humidity would appear not to be a factor in improving resistance to CO poisoning.
 - Chlorinated compounds should be minimized as contaminants in either the oxygen or hydrogen streams, even though poisoning of the Pt requires the presence of oxygen and takes place apparently at the cathode. Poisoning Cl species can be transported from the anode to the cathode.
 - Pt catalysts poisoned by Cl appear to be able to be regenerated by H₂. However, re-exposure of the catalyst to any oxygen even in the absence of PCE in the gas streams results in renewed poisoning of the catalyst.
 - DB should be minimized in the hydrogen fuel stream as ppm levels result in significant poisoning of the fuel cell. However, this effect appears to be totally reversible once the DB is removed from the fuel stream.

FY 2011 Publications/Presentations

Publications

1. "Effect of Cations (Na⁺, Ca²⁺, Fe³⁺) on the Conductivity of a Nafion Membrane," *Journal of Power Sources* 195 (2010) 7213-7220 (Kitiya Hongsirakarn, James G. Goodwin, Jr., Scott Greenway, and Stephen Creager).
2. "Effect of Ammonium Ion Distribution on Nafion[®] Conductivity," *Journal of Power Sources* 196 (2011)

644-651 (Kitiya Hongsirikarn, Thirapong Napapruekchart, Xunhua Mo, and James G. Goodwin, Jr.).

3. "Effect of H₂O₂ on Nafion[®] Properties and Conductivity at Fuel Cell Conditions," *Journal of Power Sources* 196 (2011) 3060-3072 (Kitiya Hongsirikarn, Xunhua Mo, James G. Goodwin, Jr., and Stephen Creager).
4. "Structure Sensitivity of Cyclopropane Hydrogenolysis on Carbon-Supported Platinum," *Journal of Catalysis* 280 (2011) 89-95 (Jack Z. Zhang, Yu-Tung Tsai, Khunya Leng Sangkaewwattana, and James G. Goodwin, Jr.).
5. "The Effect of Low Concentrations of CO on H₂ Adsorption and Activation on Pt/C: Part 2 – in the Presence of H₂O Vapor," *Journal of Power Sources* 196 (2011) 6186-6195 (Jack Z. Zhang, Kitiya Hongsirikarn, James G. Goodwin, Jr.).
6. "The effect of Low Concentrations of Tetrachloroethylene on the Performance of PEM Fuel Cells," *Journal of The Electrochemical Society*, 158 (2011) B698-B702 (M.J. Martínez-Rodríguez, E.B. Fox, W.D. Rhodes, C.S. McWhorter, S.D. Greenway, H. Colón-Mercado).
7. "Effect and Siting of Nafion[®] in a Pt/C PEM Fuel Cell Catalyst," *Journal of Power Sources*, in press (2011) (Jack Z. Zhang, Kitiya Hongsirikarn, and James G. Goodwin, Jr.).
8. "The Effect of Low Concentrations of Tetrachloroethylene on H₂ Adsorption and Activation on a Pt Fuel Cell Catalyst," *Journal of Power Sources*, in preparation (2011) (Jack Z. Zhang, Hector Colon-Mercado, and James G. Goodwin, Jr.).
9. "The Effect of Low Concentrations of Ammonia on the Performance of PEM Fuel Cells," in preparation (2011) (M.J. Martínez-Rodríguez, E.B. Fox, W.D. Rhodes, C.S. McWhorter, S.D. Greenway, H. Colón-Mercado).

Presentations

1. "Prediction of the Conductivity of Nafion[®] Components in a PEMFC Using an Acid-Catalyzed Reaction", oral presentation, Southeastern Catalysis Society 9th Annual Fall Symposium, Asheville, NC, Sept. 26–27, 2010 (Kitiya Hongsirikarn, Xunhua Mo, Zhiming Liu, and James G. Goodwin, Jr.).
2. "Interaction of Nafion[®] with Pt in a PEM Fuel Cell Catalyst", oral presentation, Southeastern Catalysis Society 9th Annual Fall Symposium, Asheville, NC, Sept. 26–27, 2010 (Jack Z. Zhang, Kitiya Hongsirikarn, and James G. Goodwin, Jr.).
3. "Fundamental Effects of Impurities on Fuel Cell Performance and Durability," Fuel Cell Tech Team Meeting, Southfield, Michigan, December 9, 2010 (J.G. Goodwin, Jr., Jack Zhang, K. Hongsirikarn, Xunhua Mo, Hector Colon-Mercado, Michael Martinez and Scott Greenway).
4. "Effect of NH₃ and chlorinated hydrocarbons on the performance of PEM Fuel Cells", ACS National Meeting, Anaheim, Ca., March 2011 (M.J. Martínez-Rodríguez, E.B. Fox, C.S. McWhorter, S.D. Greenway, H. Colón-Mercado).
5. "Effects of Impurities on Fuel Cell Performance and Durability," poster presentation, 2011 U.S. DOE Hydrogen Program Annual Merit Review and Peer Evaluation, Washington, DC, May 9, 2011 (James G. Goodwin, Jr., Jack Zhang, Kitiya Hongsirikarn, Hector Colon-Mercado, Scott Greenway, Michael Martinez, and Peter Finamoore).