

V.C.1 Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

Fernando H. Garzon (Primary Contact),
Tommy Rockward, Rangachary Mukundan,
Brian Kienitz, Jerzy Chlistunoff, Eric L. Brosha
and Jose-Maria Sansiñena
Los Alamos National Laboratory (LANL)
MPA-11, MS. D429
Los Alamos, NM 87545
Phone: (505) 667-6643
E-mail: garzon@lanl.gov

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

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Objectives

- Investigate effects of impurities on catalysts, membranes and other fuel cell components.
- Understand the effect of catalyst loadings on impurity tolerance.
- Investigate the impacts of impurities on catalyst durability.
- Develop methods to mitigate negative effects of impurities.
- Develop models of fuel cell-impurity interactions.
- Determine impurity tolerance limits in view of the technical targets for catalyst loading, performance and durability.
- Provide experimental data to hydrogen suppliers for defining fuel specifications.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost: the cost of fuel cells limits their use:
- Fuel and air impurity removal systems increase cost, weight and complexity.
 - Higher platinum group metal loading required for maintaining performance, in the presence of impurities, increases cost.
- (A) Durability: Durability may decrease in the presence of impurities.

- (C) Performance: Fuel cell performance is degraded by impurity effects.

Technical Targets

The technical targets for catalyst loading are indicated in Table 1. These targets were formulated with the assumption that fuel cell performance will not be degraded by fuel and/or air impurities or contaminants. One of the specific goals of this project is the experimental determination of the limits of impurity tolerance within those technical targets. The results of this project will provide data for defining the fuel cell hydrogen fuel specifications and intake air quality and assess the role of impurities in fuel cell performance degradation.

TABLE 1. Technical Targets: Electrocatalysts for Transportation Applications (Extracted from Table 3.4.12, Technical Plan, April 27, 2007)

Characteristic	Units	2005 Status		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal (PGM) total content (both electrodes)	g/kW (rated)	0.6	1.1	0.3	0.2
PGM total loading	mg PGM/cm ² electrode area	0.45	0.8	0.3	0.2

Accomplishments

- H₂S anode poisoning/durability test completed with current generation membrane electrode assemblies (MEAs) (*milestone*).
- SO₂ long-term testing was completed (*milestone*).
- Long-term NO_x fuel cell poisoning was characterized (*milestone*).
- NH₃ effect on oxygen reduction on Pt/C was studied by rotating disk electrode voltammetry.
- Iridium oxide solid state pH sensors were developed for local proton activity measurements in polymer electrolyte membrane fuel cells.
- Neutron imaging at the National Institute of Standards and Technology (NIST) showed some cationic impurities change local water concentration in fuel cells (*milestone*).



Introduction

Fuel cells efficiently convert flows of chemical fuel and oxygen to electrical power. Fuel cell performance may be severely impacted by contaminants or impurities that decrease the electrochemical catalytic rates, interfere with proton transport across the polymer electrolyte, or impede the flow of reactants to/or reaction products away from the anode or cathode charge transfer interfaces. The impurities may be generated by the fuel synthesis process or be present as ambient air impurities. The platinum metal catalyst surfaces may be deactivated by strongly adsorbing species such as sulfur containing molecules and carbon monoxide. The strongly bound species both block surface sites for catalytic activation and alter the electronic structure of the surface decreasing charge transfer rates. Positively charged contaminant ions often times have much greater chemical affinity to the ion transport sites within the polymer than protons. The foreign cations typically have lower mobilities than protons and reduce ionic conductivity. The presence of impurities may also decrease the operational lifetime of the fuel cell by decreasing performance irreversibly to an unacceptable value or by increasing component failure rate.

Approach

Our approach to understanding impurity interactions with fuel cell components utilizes both experimental and modeling efforts. We carry out fuel cell performance measurements in the presence of known quantities of introduced impurities and then study the impurity interactions with fuel cell components using electrochemical diagnostic methods such as adsorbate stripping voltammetry and alternating current impedance spectroscopy. Sometimes the experiments are performed in neutron imaging systems to visualize the effect of the impurity upon the water content and transport properties of fuel cell components. Post-experimental analysis includes trace level chemical analysis of fuel cell components and effluent water, electron microscopy and X-ray diffraction of the solid materials. We also experimentally determine impurity thermodynamic behavior (ion-exchange, proton and water activity coefficients) and transport properties such as membrane permeability and ionic conductivity.

Theoretical studies include computer models of impurity interactions with anode and cathode electrocatalysis. We also model the effects of foreign cations upon fuel cell performance. The modeling results are validated with experimental measurements such as hydrogen pump experiments and X-ray and electron beam microscopy of impurity distribution.

Results

Sulfur compounds are well known electrode catalysis poisons, however tolerable impurity levels at low Pt catalyst loading have not been yet determined. Last year we completed a long-term drive cycle test with hydrogen spiked with 10 ppb hydrogen sulfide. The degradation rate was the same as the control cell. However, both cells were using experimental membrane electrode assemblies that exhibited a higher performance loss than desirable. We obtained second generation fuel cell membrane assemblies from commercial suppliers and repeated the tests. An anode loading of 0.10 mg Pt/cm², cathode-0.20 mg Pt/cm² cycled in constant voltage mode between 0.85 V-0.6 V. After a pre-exposure run of 100 hours, the test cell received 10 ppb H₂S, for 1,000 hours.

Figures 1a, 1b, and 1c respectively show the baseline fuel cell performance at differing time intervals, the performance of an identical fuel cell with 10 ppb hydrogen sulfide and the electrochemical surface area of the electrodes after ~1,000 hours of operation. There was no significant difference in performance loss or electrochemical surface area loss between the control sample and the fuel cell fed with contaminated hydrogen thus supporting the earlier results.

The most prevalent sulfur containing air species is sulfur dioxide from fossil fuel combustion. The Fuel Cells sub-program targets call for a decrease in anode and cathode Pt loading. We evaluated the response of two 50 cm² fuel cells: a LANL-prepared Nafion[®] 212 fuel cell and a commercial fuel cell membrane with anode/cathode loading: 0.1/0.2 mg Pt/cm², to 100 ppb SO₂ in air (2.0 stoichiometry) injection at the cathode inlet past the humidification system (100% saturation). The fuel cell tests were performed at constant current 1 A/cm² for 500 hr. The fuel cell operating voltages at constant current decreased rapidly with approximately 200 mV of loss for both cells after sulfur dioxide injection was terminated. Unfortunately air concentrations of >100 ppb of sulfur dioxide are still common in industrial areas of the developing world.

Another common class of emission species from fossil fuel combustion systems is oxides of nitrogen. High combustion temperatures and pressures promote the reaction of nitrogen with air to form these acid gases. We studied by cathode injection, the long-term effects of 5 ppm NO₂, into an operating fuel cell similar to the one used for the sulfur dioxide experiments. Figure 2 illustrates the results of an over a 350-hour test. NO₂ reduces the fuel cell voltage by ~150 mV but reaches steady-state after about 50 hours of operation. The NO₂ is probably being reduced by hydrogen to ammonium cations; their concentration may be controlled by the ammonium ion-aqua ammonia equilibrium reaction.

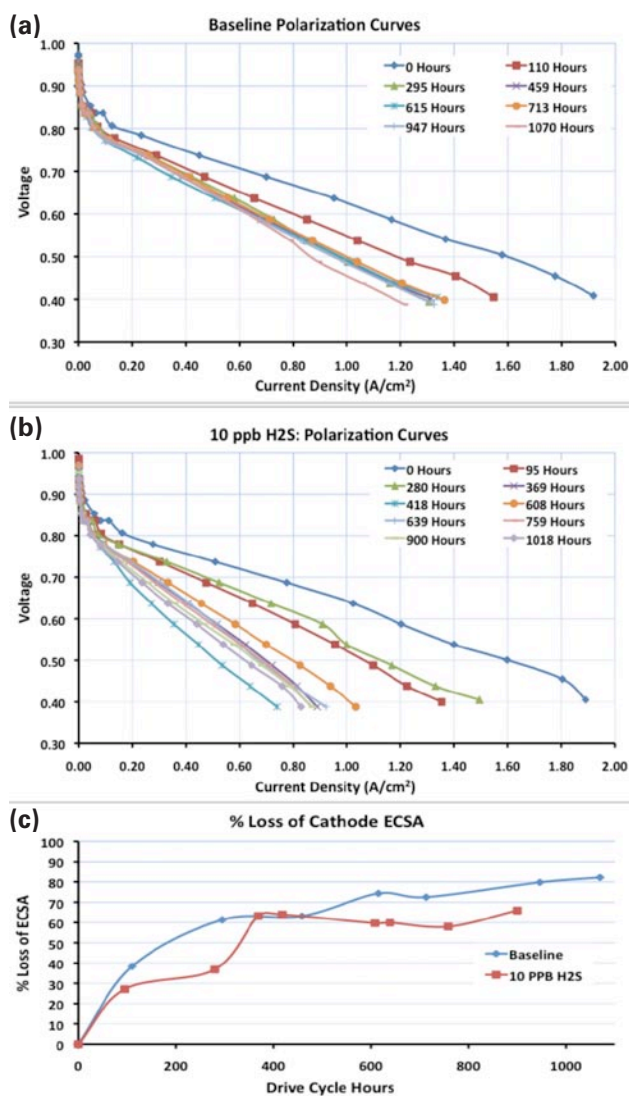


FIGURE 1. (top) baseline fuel cell performance at differing time intervals, (middle) the performance of an identical fuel cell with 10 ppb hydrogen sulfide and (bottom) the electrochemical surface area of the electrodes after ~1,000-hour operation.

Ammonia is also present as an impurity in hydrogen fuel from reforming and as an air impurity from the decomposition of urea and agricultural activities. Ammonia reacts strongly with protons in the perfluorsulfonic acid membrane, forming ammonium cations and increasing the pH of the membrane. A decrease in membrane acidity shifts fuel cell open circuit potential, decreases fuel cell electrocatalytic rates and reduces proton conductivity. We completed a rotating ring disk electrode (RRDE) study of the effect of ammonium ions on oxygen reduction on Pt-C catalysts. The study was carried out by measuring the oxygen reduction reaction (ORR) on carbon-supported platinum in 0.1 mol dm⁻³ HClO₄ solutions containing different quantities of ammonium perchlorate. ORR current losses and increases in hydrogen peroxide generation

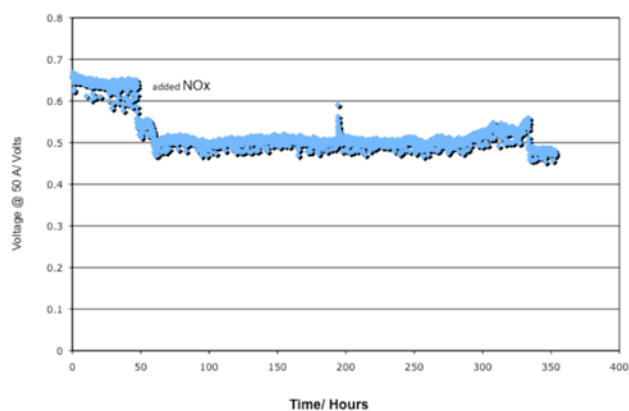


FIGURE 2. Effect of 5 ppm nitrogen dioxide injection into fuel cell cathode air operating at a constant current density of 1 A/cm² and 80°C.

were seen in two distinct potential regions, namely at $E > 0.7$ V vs reference hydrogen electrode (RHE) and at $E < 0.4$ V vs RHE. In order to better understand the observed effects, similar experiments were performed with solutions containing different concentrations of sodium perchlorate. Qualitatively similar, but different in magnitude effects were observed. It appears that the electrochemical oxidation of ammonia is responsible for the more significant effects of ammonium in the range of higher potentials, whereas the losses in the range of less positive potentials are mostly due to the coadsorption of ammonium and ClO₄⁻.

A concentrated solution theory model was previously developed by us to describe the one-dimensional cation impurity profiles as a function of current density. The slow removal rate of foreign cations coupled with lower mobilities than protons was shown to produce non-uniform impurity profiles. The concentration ratio of protons to impurity ions decreases from anode to cathode when current spontaneously flows in the fuel cell. Increasing the current density decreases the proton concentration in the cathode leading to decreased proton transport to the oxygen reduction inhibiting fuel cell performance. However our cation poisoning experiments show impacts to performance in both electrokinetic and mass transport segments of the fuel cell polarization curve. We suspected that foreign cations might also be changing the water concentration in the electrode layer. We verified these results by studying cation contaminated fuel cell membranes at the NIST neutron imaging beam line. Figure 3 shows the presence of cesium ions significantly changes the local water concentration.

The most likely effects of the impurities on the ORR kinetics are associated with changes in pH and water activity, which both depend on the cell operating conditions. Consequently, there is a need for a quantitative evaluation of these effects in situ,

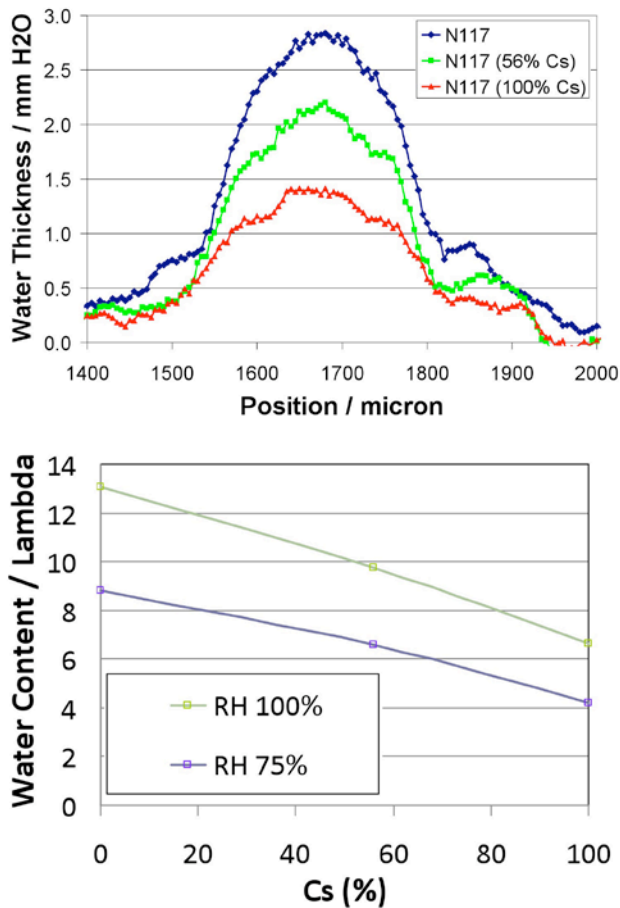


FIGURE 3. Neutron imaging of the Nafion® 117 membrane water profile as a function of the Cs⁺ ion concentration.

i.e., in operating fuel cells or under conditions closely resembling those encountered during fuel cell operation.

Iridium oxide-coated electrodes have been used as pH sensors in various environments due to their chemical inertness and fast response and offer promise for pH measurements and indirect determination of cationic impurities in Nafion®. Iridium oxide (IrO_x) can be deposited on a variety of substrates using three different techniques: electrochemical, sputtering, and high temperature oxidation. Gold and platinum were selected as substrates for the electrochemical deposition of the oxide. Gold was selected because of its inertness in a wide potential range and a common use a substrate for iridium oxide-based pH sensors. On the other hand, platinum was tested to determine the viability of platinum interdigitated array electrodes for use in experiments aimed at monitoring local pH changes during oxygen reduction on Nafion®-coated platinum.

Iridium oxide layers were grown electrochemically employing various electrodes, including standard disk electrodes (1 mm diameter), ultramicroelectrodes (100 μm diameter), interdigitated electrodes (5 μm

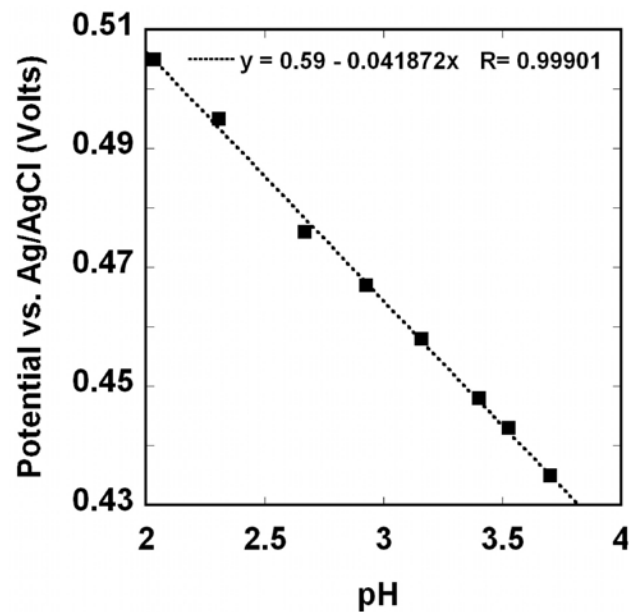


FIGURE 4. The potential vs. pH dependence for an iridium oxide sensor prepared by high-temperature chemical oxidation.

interdigitated bands separated by 5 μm gaps), and wire electrodes (1 mm diameter). The deposition was performed using a solution containing 4 mmol dm⁻³ IrCl₄ and 40 mmol dm⁻³ H₂C₂O₄. The pH of the solution was adjusted to ~10.5 using solid K₂CO₃. The electrode potential was cycled at a rate of 100 mV s⁻¹ between +0.6 V and -0.75 V vs. Ag/AgCl (3 M NaCl) reference electrode. The rate of growth of iridium oxide under such conditions was equivalent to ~3 monolayers per 100 potential cycles.

The films grown electrochemically on platinum exhibited approximately linear potential (E) vs. pH characteristics between pH = 1 and pH = 3.7. The slopes of E vs. pH plots were lower than 60 mV per 1 pH unit and the response time was very short, in a sub-second to a few seconds range. While the fast response of the sensors utilizing electrochemically grown films made them an excellent choice for real time monitoring pH changes during oxygen reduction on platinum interdigitated electrodes, their other characteristics made them unsuitable for this application. Specifically, the films were very permeable which could lead to the participation of platinum in electrochemical equilibrium and, consequently, to a mixed potential. Despite the interference of redox agents with the electrochemical equilibrium of electrochemically grown IrO_x films, iridium oxide sensors offer a great promise for the determination of cationic impurities in polymer electrolyte fuel cells.

In pursuit of ways to mitigate the problem of sensitivity of the sensors to oxygen, we employed chemical oxidation of iridium metal in molten lithium

carbonate. The process produces thick and compact layer of black iridium oxide. The initial response of the sensor prepared this way upon immersion in acidic aqueous medium is relatively slow most likely because the equilibration is associated with a slow penetration of the initially dry film by water. Upon film hydration, the potential of the sensor was found to be virtually insensitive to oxygen and hydrogen in solution. Moreover, the response time of the hydrated film was significantly improved. The potential vs. pH dependence for the hydrated film is described by an excellent linear relationship with a slope of 42 mV as shown in Figure 4. Optimized sensors of this type will be used to monitor changes in pH (and concentration of cationic impurities) inside the membrane of an operating fuel cell.

Conclusions and Future Directions

- Low concentrations 10 ppb hydrogen sulfide do not appear to affect durability of current generation fuel cell MEAs.
- 100 ppb of SO₂ in air substantially decreases fuel cell performance of low-loading thin-ionomer polymer electrolyte fuel cells.
- NO₂ in air decreases fuel cell performance:
 - Fuel cells reach a steady-state equilibrium at constant concentration exposure.
- NH₄⁺ ions hamper oxygen reduction on Pt-C catalysts in acid environments.
- The impurity cation species type is important in determining local water of hydration concentrations.

FY 2010 Publications

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