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

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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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

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 total content (both electrodes)	g/kW (rated)	0.6	1.1	0.3	0.2
Platinum group metal (PGM) total loading	mg PGM/cm^2 electrode area	0.45	0.8	0.3	0.2

Accomplishments

- Demonstrated common hydrocarbons, methane, ethane and propane, at PPM concentrations, do not impact fuel cell performance.
- Established that 5 ppm SO_2 in air decreases fuel cell performance of low-loading thin-ionomer proton exchange membrane fuel cells (PEMFCs).
- Confirmed that 5 ppm NO_2 in air decreases fuel cell performance however fuel cells recover quickly after exposure.
- Demonstrated ammonia reacts with membranes to form NH_4^+.
  – Measured very low electrochemical oxidation rate in acidic conditions.
  – Demonstrated removal is via ammonium ion–aqua ammonia equilibrium.
- Validated cation impurity models they explain why low levels of ionic contaminants can cause significant performance losses.

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Introduction

Fuel cells efficiently convert flows of chemical energy to electrical power. Fuel cell performance can 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 platinum metal catalyst surfaces may

be deactivated by strongly adsorbing species such as sulfur containing molecules and carbon monoxide. The strongly adsorbing 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 perform fuel cell performance measurements in the presence of introduced impurities and follow the measurements with electro-analytical diagnostic methods such as adsorbate stripping voltammetry and alternating current (AC) impedance spectroscopy. Post-experimental analysis includes trace level chemical analysis of fuel cell components and effluent water, electron microscopy and X-ray diffraction. We also experimentally determine impurity thermodynamic behavior (ion-exchange 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. The most prevalent sulfur-containing air species is sulfur dioxide from fossil fuel combustion. The Department of Energy future targets call for a decrease in anode and cathode Pt loading. We evaluated the response of a 50 cm^2 fuel cell (Nafion® NRE212) to 5 ppm SO$_2$ in air (2.0 stoichiometry) injection at the cathode inlet past the humidification system (100% saturation). Figure 1 illustrates the results of a fuel cell test run at constant current 0.8 A/cm^2 (H$_2$ at 1.2 stoichiometry). The fuel cell operating voltage at constant current decreased rapidly with approximately 50% recovery after sulfur dioxide injection was terminated. The sensitivity of the oxygen reduction reaction to sulfur is evident from this experiment. Stripping voltammetry indicates a Pt-S
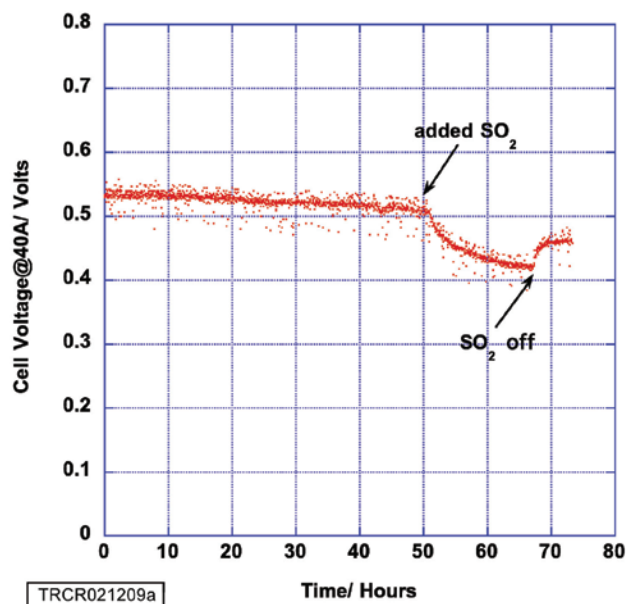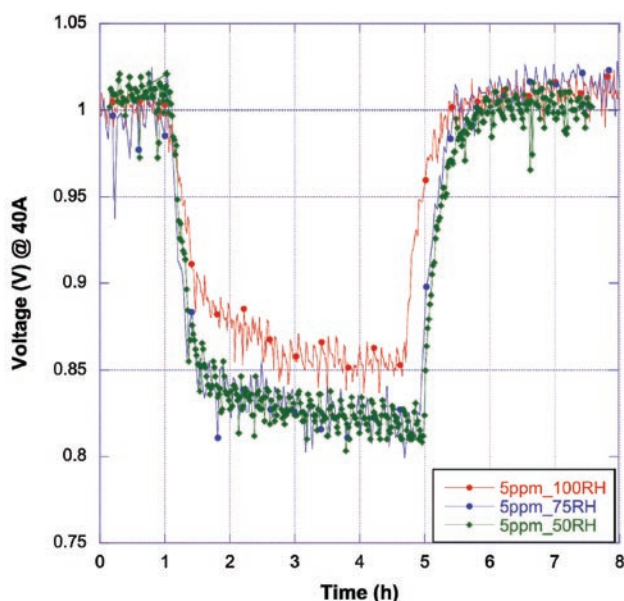

FIGURE 1. Effect of 5 ppm Sulfur Dioxide Injection to Fuel Cell Cathode Air Stream (80°C, 100% relative humidity)

species similar in redox behavior to species formed by introduction of hydrogen sulfide or sulfide ions. High ambient air concentrations of sulfur dioxide will continue to be a barrier for the introduction of fuel cells in the industrialized urban areas of highly polluted developing countries such as China.

Another common class of emission species from fossil fuel combustion systems are 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 effects of 5 ppm nitrogen dioxide, into an operating fuel cell similar to the one used for the sulfur dioxide experiments. The relatively humidity was also varied to assess the effects of the water vapor partial pressure on the poisoning reaction. Figure 2 illustrates the loss of cell voltage at constant current operation. The cells recover quickly from the introduction of nitrogen dioxide. Nitrogen dioxide may be reduced to nitrogen oxide on the cathode; the nitrogen oxide may be further reduced to ammonia on the anode. An alternate mechanism is the nitrogen dioxide may be rapidly reacting with water to form highly soluble nitrate ions. At high relatively humidity, free water is available to carry nitrate ions or ammonia away from the fuel cell interfaces. The fuel cells are poisoned less and recover faster when saturated humidification conditions are used as seen in Figure 2.

Ammonia is 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.
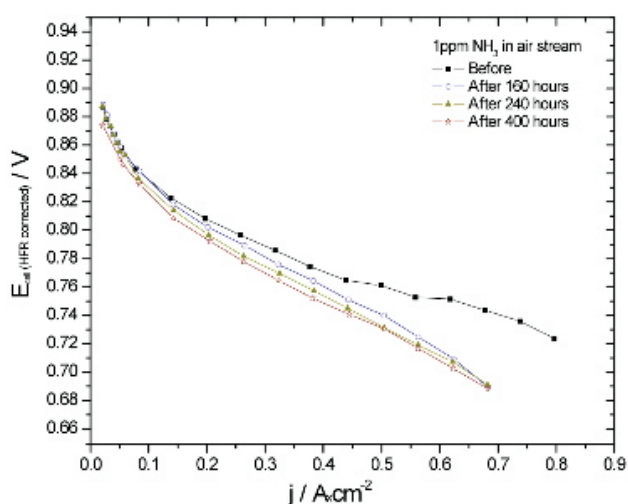
FIGURE 2. Effect of 5 ppm Nitrogen Dioxide Injection into Fuel Cell Cathode Air at Varying Relative Humidity: 100, 75, and 50% @ 80°C

FIGURE 3. Effect of 1 ppm Ammonia Injection to the Cathode for Varying Times (100% relative humidigy, 80°C)

A decrease in membrane acidity shift fuel cell open circuit potential, decreases fuel cell electrocatalytic rates and reduces proton conductivity.

It is therefore expected that ammonia introduced from either the fuel or air side, will severely impact polymer fuel cell performance. Figure 3 displays the effect of 1 ppm ammonia introduction into a PEMFC for varying time periods. The impact on the polarization curve is substantial; the kinetic, ohmic and mass transport portions of the polarization curves are negatively impacted by the presence of ammonia.

Ammonium oxidation and/or dissolution into product water are two possible removal/recovery mechanisms. Ammonium oxidation was studied by introduction of a 0.1M $NH_4(SO_4)$ solution into a 5 cm^2 Nafion® 117 PEMFC anode compartment. A small ammonia oxidation current, $<10^{-3}$ A/cm^2 above 0.6 V was detected by sweep voltammetry. The oxidation current was very low, probably too small to account for fuel cell recovery. The aqua-ammonia water reaction equilibrium is the more significant mechanism of ammonia removal.

Electrochemical modeling continues to clarify why relatively small quantities of foreign cations produce a large negative effect on fuel cell performance. A model was developed by Kienitz using concentrated solution theory to describe the one-dimensional ammonia 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 deceases the proton concentration in the cathode leading to decreased proton transport to the oxygen reduction inhibiting fuel cell performance. However our ammonia poisoning experiments show impacts to performance in both electrokinetic and mass transport segments of the fuel cell polarization curve. We suspect that foreign cations are also changing the water concentration in the electrode layer. Reducing the water content of the ionomer at the reaction interface will decrease the oxygen reduction kinetics and will decrease the proton conductivity of the ionomer (catalyst layer sheet resistance). We will probe water and ion profiles simultaneously within the electrodes in future model refinements.

Conclusions and Future Directions

Experimental measurements and theoretical modeling has increased our understanding of impurity effects in low temperature fuel cells. We now possess a much better understanding of how impurities fundamentally interact with fuel cells, particularly ions that substitute for protons within the electrolyte. We need to further understand the impurity removal processes and kinetics. Our future work will:

- Improve understanding of SO_2 interaction with Pt using cyclic voltammetry coupled with gas chromatography and mass spectroscopy.

- Improve understanding of membrane N speciation via spectroscopy and determine tolerance as a function of cathode loadings at various conditions.

- Membrane transport studies, water equilibrium studies and fuel cell testing of loss rates.

- Model water activity effects upon electrode kinetics.

- Extend model to analyze slowly diffusing divalent metal cations.
- Perform neutron imaging at the National Institute of Standards and Technology to determine cation-impurity effects on water transport.
- Future in situ imaging of impurities in operating fuel cells by X-ray tomography.

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