

## V.B.5 Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

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### Fiscal Year (FY) 2011 Objectives

- Investigate effects of impurities on catalysts, membranes and other fuel cell (FC) 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

- (B) Cost: the cost of fuel cells limits their use:
- Fuel and air impurity removal systems increase cost, weight and complexity.
  - Higher Pt 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 FC 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 FC 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 <sup>2</sup> electrode area	0.45	0.8	0.3	0.2

### FY 2011 Accomplishments

- Effect of 100 ppb SO<sub>2</sub> in air on 0.1 mg/cm<sup>2</sup> Pt loading cathode fuel cell performance testing completed (*milestone*).
- Effect of 100 ppb SO<sub>2</sub> in air on 0.2 mg/cm<sup>2</sup> Pt loading cathode fuel cell long term (500 hr) performance testing completed (*milestone*).
- NO<sub>2</sub> fuel cell poisoning effect was shown to occur via hydrogen reduction of oxides of nitrogen (NO<sub>x</sub>) to ammonia.
- Effect of 5 ppm NO<sub>2</sub> in air on 0.2 mg/cm<sup>2</sup> Pt loading cathode fuel cell long term (500 hr) performance testing completed (*milestone*).
- Iridium oxide solid-state pH sensors were used to determine changes in local proton activity in cation-poisoned, polymer membrane fuel cell electrodes.



### 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

The most prevalent sulfur containing air species is sulfur dioxide from fossil fuel combustion. The DOE future targets call for a decrease in anode and cathode Pt loading. Last year we evaluated the response of two 50 cm<sup>2</sup> fuel cells: a LANL-prepared Nafion<sup>®</sup> 212 fuel cell and a commercial fuel cell membrane with an anode/cathode loading: 0.1/0.2 mg Pt/cm<sup>2</sup>, to 100 ppb SO<sub>2</sub> 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/cm<sup>2</sup> 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. This year we evaluated the effect of lowering the cathode loading to 0.1 mg Pt/cm<sup>2</sup>. A loss of ~200 mV of fuel cell voltage was also observed for the 1 A/cm<sup>2</sup> constant current experiment. Sulfur dioxide tolerance still remains a key issue in the widespread deployment of fuel cells in areas of poor air quality.

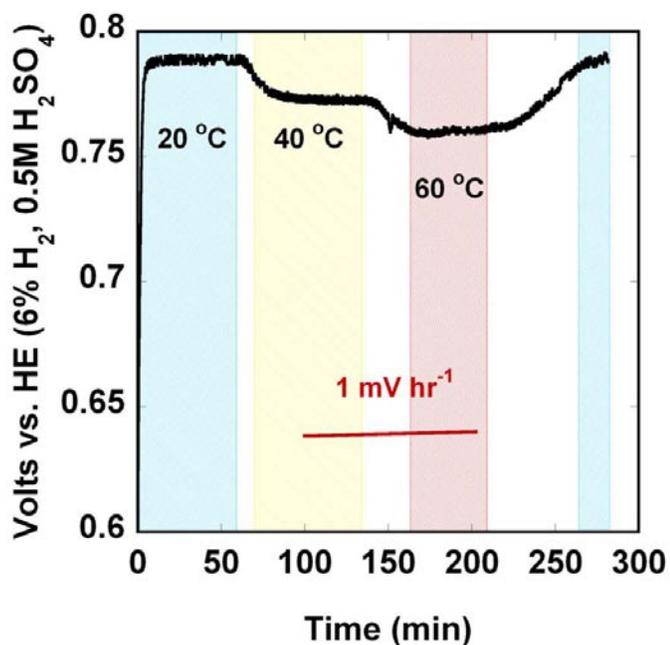
NO<sub>x</sub>, from fossil fuel combustion systems, also pose a potential threat to fuel cell performance. High combustion temperatures and pressures promote the reaction of nitrogen with air to form these acid gases. We have studied, by cathode injection, the long term effects of 5 ppm nitrogen dioxide, into an operating fuel cell similar to the one used for the sulfur dioxide experiments. Our experiments last year indicated that NO<sub>2</sub> reduces the fuel cell voltage by ~150 mV but reaches steady-state after about 50 hours of operation. We previously hypothesized that the NO<sub>2</sub> is probably being reduced by hydrogen to ammonium cations; this year we detected, using infrared spectroscopy, the presence of ammonium ions in nitric oxide contaminated fuel cell assemblies.

We have continued the effort to develop iridium oxide-based pH sensors and test their viability as local probes of the effects of cationic impurities in perfluorosulfonic acid polymers on oxygen reduction. Due to the electroneutrality condition, the impurities stoichiometrically replace hydrated protons (H<sup>+</sup><sub>aq</sub>) in Nafion<sup>®</sup> and the associated pH changes can be used to monitor local concentrations of the impurities.

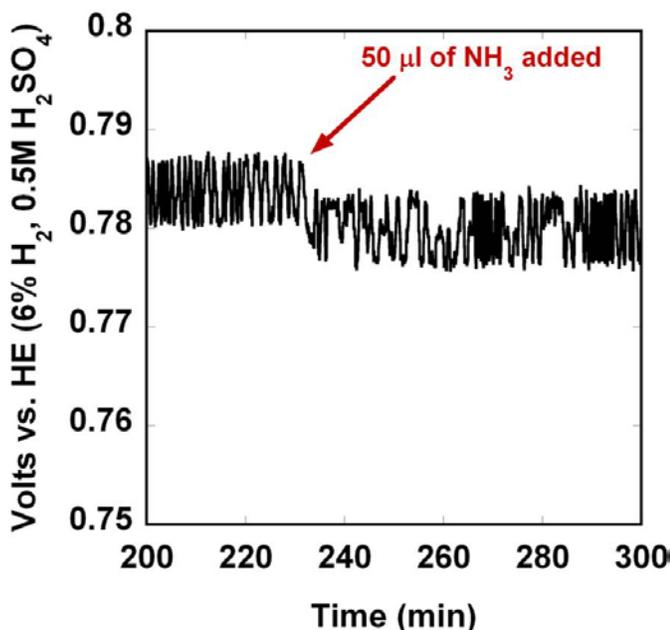
The effort has focused on sensors fabricated by the chemical oxidation of pure iridium metal in molten lithium carbonate at 790°C. Such sensors have better mechanical properties than the sensors obtained by the electrochemical deposition of iridium oxide onto metallic substrates and are also less sensitive to interferences from red-ox agents. We tested the sensors using pure and partially neutralized Nafion<sup>®</sup>, containing 40%, 60%, and 90% of Cs<sup>+</sup>. The testing was performed in pure oxygen atmosphere at three temperatures (20, 40 and 60°C) and 100% relative humidity.

As the time necessary to attain equilibrium in the polymer electrolyte was longer than that in liquid electrolytes and the measured potential was frequently unstable for long periods of time, we tentatively assumed that the potential reached its equilibrium value, when its drift did not exceed 1 mV hr<sup>-1</sup>. The process of equilibration could be accelerated by short time excursions to higher temperatures (60°C), after which the measured potentials were reversible to temperature changes but stable (<1 mV hr<sup>-1</sup>) at a constant temperature (Figure 1). However, the behavior such as that shown in Figure 1 was observed only for pure and 90% Cs-doped Nafion<sup>®</sup>. The potentials of Ir/IrO<sub>x</sub> sensors comprising pure Nafion<sup>®</sup> and equilibrated in the above way were found to be sensitive to gaseous ammonia contamination (Figure 2).

The potentials of Ir/IrO<sub>x</sub> sensors in Nafion<sup>®</sup> partially (40% and 60%) doped with Cs<sup>+</sup> exhibited an erratic



**FIGURE 1.** Measured potential of a Ir/IrO<sub>x</sub> sensor in pure Nafion<sup>®</sup> at 100% relative humidity and different temperatures. Temperature: 20°C (blue), 40°C (yellow), 60°C (red), variable (no color).



**FIGURE 2.** Effect of ammonia on the potential of a Ir/IrO<sub>x</sub> sensor embedded in pure Nafion<sup>®</sup>. The experimental chamber had a volume of ~200 cm<sup>3</sup>. 50 µl of 25% NH<sub>3</sub> solution was added to ~10 cm<sup>3</sup> of deionized water on the bottom of the chamber. Temperature 20°C, relative humidity 100%.

behavior. No stable potentials could be measured at all selected temperatures. Moreover, temperature increase invariably led to a very quick decrease of the measured potential that significantly exceeded ~1 mV/°C decrease observed for pure (Figure 1) or 90% neutralized Nafion<sup>®</sup>. The behavior could not be linked to any sensor failure, such as iridium oxide or Nafion<sup>®</sup> delamination, water condensation, loss of electrical contact, etc., and consequently it is believed to originate from an actual drop in H<sup>+</sup><sub>aq</sub> concentration (pH increase) at the IrO<sub>x</sub>/Nafion<sup>®</sup> boundary. The drop in H<sup>+</sup><sub>aq</sub> concentration may result from either the interface becoming preferentially occupied by the hydrophobic (backbone) component of Nafion<sup>®</sup> [1,2] or by Cs-populated ionic component of Nafion<sup>®</sup> at elevated temperatures. Both options can be linked to temperature induced nanophase transitions in partially doped Nafion<sup>®</sup>. As the transitions are visible only when Nafion<sup>®</sup> is nearly half neutralized (40% and 60%) with Cs, the second option seems more likely, i.e., that weaker hydrated Cs<sup>+</sup> rather than H<sup>+</sup> tend to occupy the interface at elevated temperatures. The conclusion is supported by X-ray radiography, which demonstrates virtually no ion exchange, i.e., persistent phase separation at the boundary between pure Nafion<sup>®</sup> and Nafion<sup>®</sup> ~100% neutralized with Cs. Irrespective of the above interpretation of the data, the results indicate that the unfavorable effect of cationic impurities on the oxidation reduction reaction through the lowering of H<sup>+</sup><sub>aq</sub> concentration and water activity at the fuel cell cathode may be additionally amplified by the unfavorable phase separation phenomena.

## Conclusions and Future Directions

Gas phase and cation impurities were demonstrated to decrease fuel cell performance. The mechanisms include: catalyst poisoning, cation ion exchange and a reduction in the local proton concentration near the electroactive cathode interface.

## FY 2011 Publications

1. Brosha, E.L.; Rockward, T.; Uribe, F.A.; Garzon, F.H., Measurement of H<sub>2</sub>S Crossover Rates in Polymer Fuel Cell Membranes Using an Ion-Probe Technique. *Journal Of The Electrochemical Society* 2010, 157 (1), B180-B186.
2. Kientiz, B.; Pivovar, B.; Zawodzinski, T.; Garzon, F.H., Cationic Contamination Effects On Polymer Electrolyte Membrane Fuel Cell Performance, accepted for publication, the *Journal Of The Electrochemical Society*.
3. Lopes, T.; Sansinena, J.-M.; Chlistunoff, J.; Garzon, F. H., Oxygen Reduction Reaction On A Pt/Carbon Fuel Cell Catalyst In The Presence Of Trace Quantities Of Ammonium Ions, submitted to *Electrochimica Acta*.