V.E.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

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

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 assessing the role of impurities in fuel cell performance degradation.

Accomplishments

- Measurement of increased degradation of fuel cell performance by H_2S with increasing temperature.
- Measurement of H_2S membrane crossover for wet and dry membranes.
- CO and H_2S co-adsorption kinetic studies show fast adsorption kinetics for CO but eventually displaced by H_2S.
- H_2S anode poisoning studied by H_2 pump cells. High anode overpotentials result from small amounts of H_2S.
- Model development and measurement of alkali cation contaminant behavior in perfluorosulfonic acid membranes.
- Experimental measurement of fuel cell losses due to alkali cation contamination - good agreement with model.

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Introduction

The best fuel cell performance occurs when the fuel cell is supplied with ultrapure hydrogen and air. The reason for this behavior is that the electrochemical charge transfer processes require electrode surface mediated catalytic activation of the hydrogen fuel and the oxygen oxidant. Some impurities such as common sulfur compounds adsorb very strongly to the electrode surfaces blocking surface sites for catalytic splitting of diatomic hydrogen on the anode and diatomic oxygen on the cathode. The adsorption of some impurities is so strong that part per million impurity levels can substantially degrade fuel cell performance. Unfortunately, the cost of removing these common impurities rises rapidly with increasing purity requirements.

Another class of impurities is cationic impurities primarily arising from salt aerosols from natural and anthropogenic sources. These impurities such as sodium, magnesium and calcium form ions in the presence of water and ion exchange for mobile protons in the ionomer membrane. These foreign positively charged ions are more strongly bound to the membrane than protons and impede the proton transport and negatively affect the electrochemical charge transfer reactions.

Approach

The approach we use to understand impurity effects in fuel cells is threefold. The first method is direct measurements of fuel cell performance subjected to controlled amounts of impurities directly introduced into the fuel cells. These measurements include the direct injection of sulfur compounds, carbon monoxide, nitrogen oxides, ammonia and salts into working fuel cells. After performance measurements are completed, the fuel cell materials are subsequently analyzed for trace quantities of impurities by various methods. The second method is the use of carefully designed experiments to measure the interactions of impurities on fuel cell components. An example of this is impurity permeation studies of hydrogen sulfide to measure gas crossover rates in the ionomer. These are important as fuel cell cathodes may be poisoned by anode fuel impurities crossing over the membrane into the cathode compartment. The third method we use is the theoretical first principles modeling of impurity effects on the important physiochemical reactions required for fuel cell operation. An example of this approach is the modeling of the effect of a slowly diffusing cation impurity on fuel cell performance.

Results

Numerous results were achieved this fiscal year. One type of fuel cell measurement accomplished was the determination of the temperature dependence of hydrogen sulfide poisoning on fuel cell performance. Fuel cells subjected to 2 parts per million of hydrogen sulfide injected into the anode hydrogen stream show greater performance losses at higher temperatures (80-90°C) than lower temperatures (40-70°C) as illustrated in Figure 1.

Two common hydrogen fuel impurities that often coexist are carbon monoxide and hydrogen sulfide. While the behavior of the individual species has been characterized, the combined effects in fuel cells have not until recently. Fuel cells were exposed to the gases one species at a time sequentially and then the performance and adsorbate behavior was characterized by electrochemical methods. Hydrogen sulfide pre-adsorbed on the Pt anode surface prevented the adsorption of carbon monoxide. If carbon monoxide was first adsorbed, it was gradually replaced by sulfur deposited by the dissociative adsorption of hydrogen sulfide. Simultaneous injection of both species yielded strong initial adsorption of carbon monoxide but longer exposures showed the gradual displacement of reaction of the carbon monoxide species, illustrated in Figure 2.

Past fuel cell experiments determined that hydrogen sulfide exposure lowered the fuel cell operation voltage for constant current operation. We performed hydrogen pump experiments to help determine the anode polarization losses for hydrogen sulfide exposure (0.5 ppm, 1 hr) at a given current density. Our results show that significant anode overpotentials ~75 mV at 1 A/cm^2 occur after short term hydrogen sulfide
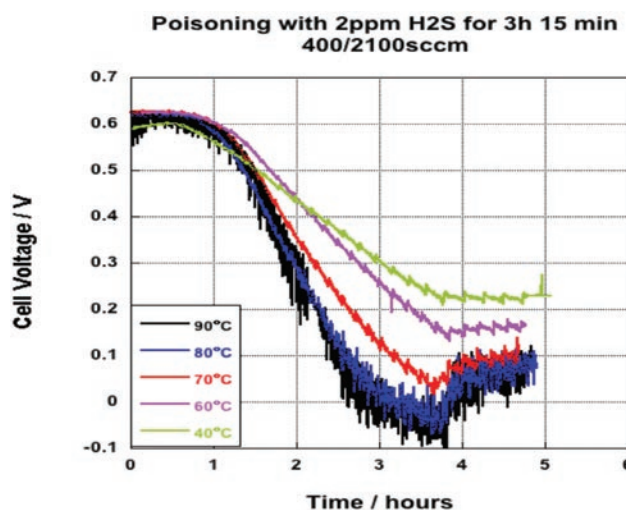

FIGURE 1. Fuel cell voltage changes at 0.6 A/cm^2 for various operational temperatures after the introduction of 2 ppm H$_2$S saturated humidification.
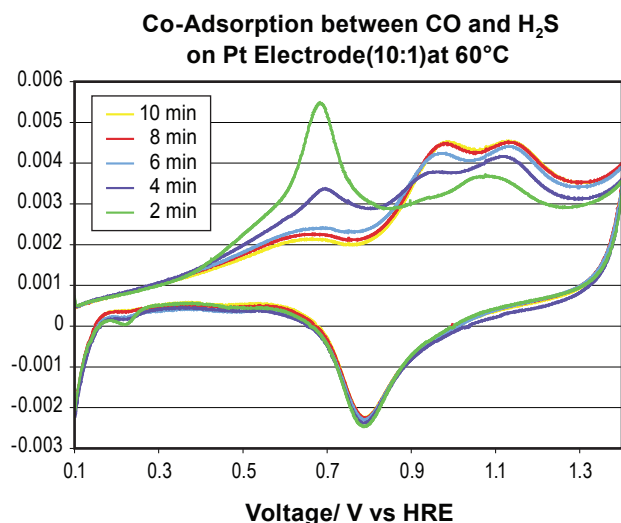
FIGURE 2. Cyclic voltammetry of a fuel cell subjected to CO-H_2S 500/50 parts per million ratio; note decreasing CO peak at 0.6 V with increasing exposure time.

FIGURE 3. Hydrogen sulfide permeation fluxes across ionomer membranes of differing thickness (N117 - 175 μm, N212 - 51 μm) and 0 and 100% water vapor saturation of hydrogen at 25°C.

exposure. These anode overpotentials do not normally occur in standard fuel cell operation and result in fuel cell performance losses.

Our previous work has demonstrated that very small amounts of hydrogen sulfide can also affect the kinetically slower oxygen reduction reaction on Pt surfaces. The possibility of hydrogen sulfide crossover cannot be neglected as it is a polar molecule with a very high solubility in water. As the membranes are highly permeable to water, hydrogen sulfide permeation is a possibility. Three types of transport mechanisms may occur; dry membrane permeation, copermeation with water, and electro-osmotic drag with the proton flux. We successfully measured the hydrogen sulfide crossover rate at differing relative humidities and membrane thicknesses. The permeation rate across wet membranes was many times greater than for dry membranes as illustrated in Figure 3.

Cation impurity behavior was successfully studied using fuel cell measurements, novel combined electrochemical/X-ray fluorescence spectroscopy cells and by electrochemical modeling. Cesium was chosen as a model alkali cation as it is very easily measured nondestructively in situ by X-ray fluorescence spectroscopy. Perfluorosulfonic acid membranes were partially ion exchanged with Cs and then subjected to a flux of protons. The concentration profile measured was in excellent agreement with the ion impurity model developed by our partners, Case Western Reserve University. The build-up of foreign cations at the cathode, Figure 4, effectively blocks access of protons to Pt cathode sites, limiting the reaction current density. This affects fuel cell performance far more than the loss in overall proton conductivity as measured by high frequency impedance analysis.
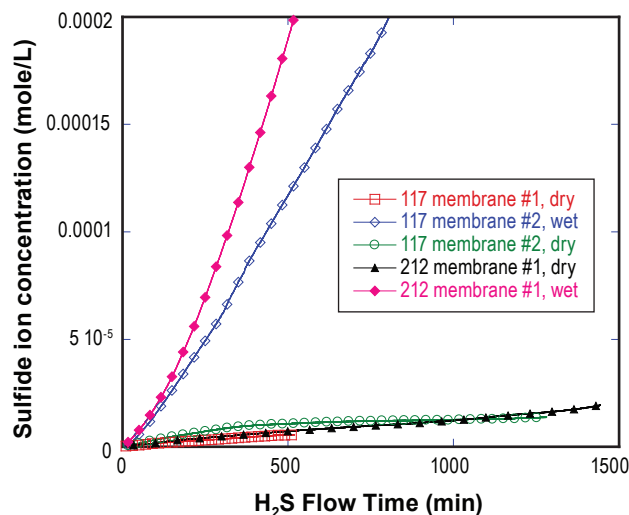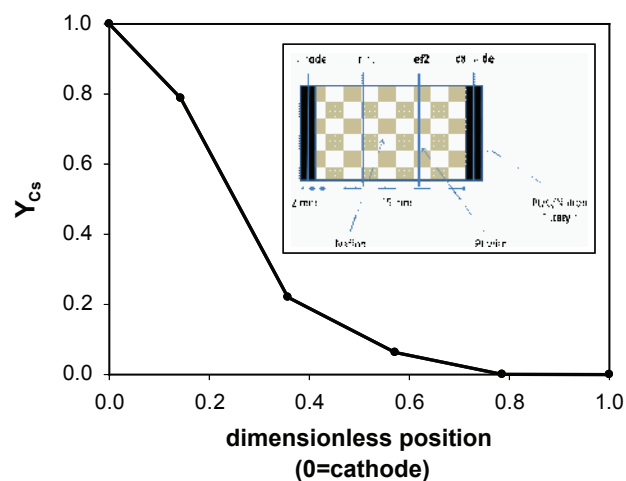
FIGURE 4. Cesium impurity ion concentration profile measured across hydrogen pump strip cell illustrated in inset schematic.

Conclusions and Future Directions

- Continued contaminant crossover studies: proton drag of H_2S.
- Lower cathode loading impurity studies.
- Impurity effects on durability studies using new commercial membrane electrode assemblies with 2010 loadings.
- Refinement and validation of electrode impurity modeling efforts.
- Studies of the effect of divalent cations on fuel cell performance.

FY 2008 Publications/Presentations

1. "PEMFC Poisoning with H_2S: Dependence on Operating Conditions" I. Urdampilleta, F. Uribe, T. Rockward, E.L. Brosha, B. Pivovar, and F.H. Garzon, ECS Trans. 11, 831 (2007).

2. "The Effects of Multiple Contaminants on Polymer Electrolyte Fuel Cells" T. Rockward, I. Urdampilleta, F. Uribe, E.L. Brosha, B. Pivovar, and F.H. Garzon, ECS Trans. 11, 821 (2007).

3. "Micro And Nano X-Ray Tomography Of PEM Fuel Cell Membranes After Transient Operation " F.H. Garzon, S.H. Lau, J.R. Davey, and R. Borup, ECS Trans. 11, 1139 (2007).

4. "A Half Cell Model to Study Performance Degradation of a PEMFC due to Cationic Contamination", B. Kienitz, B. Harihara, T. Zawodzinski, and B. Pivovar, ECS Transactions 11, 777 (2007).