

## V.G.10 Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

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### Objectives

- Evaluate the effects of fuel and air impurities on fuel cell performance.
- Evaluate catalyst durability under the effects of impurities.
- Investigate the effect of impurities on fuel cell components other than the membrane electrode assembly.
- Find ways to mitigate negative effects of impurities.
- Demonstrate a method for cleaning sulfur-poisoned Pt catalysts.
- Quantify threshold levels of impurities.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Electrode Performance

### Technical Targets

- 5,000 hrs durability
- \$30/kW by 2010
- 55% energy conversion efficiency
- 0.3 g/kW Pt loading

Fuel cells will need to meet the technical targets with hydrogen fuel that will contain trace impurities such as those shown in Table 1. The impact of these impurities on durability, efficiency and Pt loading (cost) needs to be determined. The following table lists a first draft specification of hydrogen quality required as input into the fuel cell system. (Technical Plan-Fuel Cells, p. 8)

TABLE 1. FreedomCAR Fuel Specification

Component	Level	LANL Test
Hydrogen	>99.9	95-99*
Sulfur (as H <sub>2</sub> S)	10 ppb	10 ppb
CO	0.1 ppm	0.1 ppm
CO <sub>2</sub>	5 ppm	5 ppm
NH <sub>3</sub>	1 ppm	1 ppm

\* Includes dilution due to inert gas in stock mixtures

### Approach

- Study the effects of fuel impurity mixtures (e.g., H<sub>2</sub>S, CO, NH<sub>3</sub>) on fuel cell performance.
- Determine minimum harmful threshold levels of fuel impurities on fuel cell performance.
- Investigate effect of impurities on catalysts and other fuel cell components.
- Identify materials or methods to mitigate negative effects of impurities.
- Develop analytical methods for trace measurements.
- Develop models of fuel cell-impurity interactions.
- Continue collaborations with the U.S. Fuel Cell Council, the FreedomCAR and Fuel Partnership Fuel Cell Technical Team, industry and other national laboratories to foster a better understanding of impurity effects.

### Accomplishments

- Demonstrated that 10 ppb of H<sub>2</sub>S in fuel test mixture is primarily responsible for 20% fuel cell performance loss at 0.8 A/cm<sup>2</sup> after 1,000 hrs.
- Observed little effect from 0.1 ppm CO in mixture.
- Developed new analytical method for ppb-level H<sub>2</sub>S gas trace analysis.
- Measured 0.2 wt% H<sub>2</sub>S adsorption on XC-72 and higher amounts on other carbons.
- Determined that ammonia at 1 ppm levels is ion exchanging for protons and causes conductivity losses.

- Demonstrated that an SO<sub>2</sub>-poisoned cathode can be partially cleaned by open circuit voltage (OCV) cycling.
- Correlated fuel cell operating voltage (0.3 V to OCV) to extent of anode H<sub>2</sub>S poisoning.
- On shut-down, OCV appears to be an important factor for cleaning an H<sub>2</sub>S-poisoned anode.
- Demonstrated that air purging H<sub>2</sub>S-contaminated anodes results in partial performance recovery.
- Developed Dual H oxidation pathway and poisoning model.
- Evaluated fuel cell performance with the fuel mixture specified in Table 1.
- Determined that conductivity changes in ionomer from ion exchange is the primary effect of NaCl contamination.

## Introduction

Proton exchange membranes fuel cells (PEMFCs) are devices that generate electrical power from two complementary electrochemical reactions. Hydrogen is oxidized at the anode, and oxygen (from air) is reduced at the cathode. Therefore, efficient fuel cell operation relies on the availability of both high-purity fuel and air. The important electrochemical reactions take place on the surface of highly dispersed Pt catalysts that are embedded in a proton-conducting ionomer within the catalyst layer. It has been shown that the catalytic activity of the Pt surface and the proton conductivity of the ionomeric component are very sensitive to the presence of certain impurities.

In hydrogen fuel, impurities can be present in the primary source of fuel or can be generated during the reforming process. For instance, reformation of hydrocarbon fuels such as methane or gasoline, besides H<sub>2</sub>, may produce various impurities at levels that can be detrimental to fuel cell operation. Typical fuel impurities are carbon monoxide (CO), ammonia (NH<sub>3</sub>) and hydrogen sulfide (H<sub>2</sub>S) [1-3]. On the cathode side, ambient air contains pollutants (e.g., NO<sub>x</sub> and SO<sub>2</sub>), mostly coming from fossil fuel combustion, which also degrade fuel cell performance [4-6]. In general, this project focuses on assessing the severity of the impurity effects and finding ways of mitigating their negative effects on performance.

## Approach

We have focused our efforts on studying the effects of H<sub>2</sub>S, NH<sub>3</sub>, CO and hydrocarbon mixtures on fuel cell performance. The tests included a range of impurities and impurity mixtures at various operating conditions such as cell voltage and times of exposure.

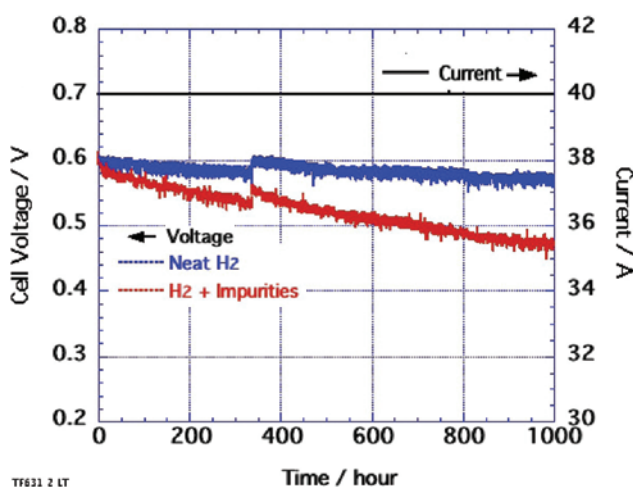
Analytical methods included fuel cell polarization experiments, cyclic voltammetry, and effluent water and gas analysis using specific ion sensor probes. The sulfur-compound impurities severely degrade fuel cell performance; however, the behavior of impurity mixtures had not been determined. We have conducted tests aiming to establish these behaviors. This information is particularly useful in defining future fuel quality standards in industrial production of H<sub>2</sub> for fuel cells. H<sub>2</sub>S and SO<sub>2</sub> exposure severely degrades fuel cell performance. The effects are irreversible during normal fuel cell operation due to strong Pt-catalyst adsorption. The most frequently recommended approach for mitigating these effects is gas filtration [5]. Inevitably, the fuel cells will be exposed to these common contaminants from the air or fuel gases. We have studied methods to remove these impurities such as voltage and current transient techniques and air purging.

Reaction pathway modeling was used to provide insight into the sulfur poisoning mechanism. Ion exchange modeling was used to determine conductivity changes in NaCl-contaminated fuel cells and the resulting performance degradation.

## Results

### Fuel Cell Testing and Modeling

Recently, the FreedomCAR Technical Team proposed that Los Alamos National Laboratory (LANL) conduct preliminary fuel cell tests using the fuel mixture specified in Table 1. The fuel cells were 50 cm<sup>2</sup> devices with 0.2 mg/cm<sup>2</sup> of catalyst (20 wt% Pt on XC-72 carbon) on both the cathode and anode. The operating temperature was 80°C. The results of a 1,000 hour life test at constant current are presented in Figure 1.



**FIGURE 1.** Voltage losses of two 50 cm<sup>2</sup> equivalent cells run at 0.8 A/cm<sup>2</sup> for 1,000 hours on neat hydrogen and on the mixture of Table 1. Loadings: 0.2 mg Pt at each electrode. Nafion membrane N112. Temperature: 80°C.; psig: 30/30.

A reference cell operating on neat  $H_2$  was also tested in parallel. At the end of the test, the performance losses attributed to impurities in the hydrogen supply amounted to 100 mV. This significant degradation is excessive for commercial applications and validates concerns over even trace levels of impurities. We were able to ascribe the losses to the presence of  $NH_3$  and  $H_2S$ , with the other components ( $CO$  and  $CO_2$ ) apparently playing no role in performance loss. The high-frequency resistance (HFR) of the cell increased during the operation as shown in Figure 2.

$NH_3$  gas probably reacts with  $H^+$  in the ionomer and generates  $NH_4^+$ . This exchange lowers the proton conductivity and results in performance loss. The loss in proton conductivity is not necessarily represented by the HFR, as this value takes into account the mobility of the ammonium ion, which likely doesn't contribute to proton conduction. The electrochemical performance of the anode is also decreased. Figure 3 shows a cyclic voltammetry (CV) diagram of the exposed anode after 1,000 hours of operation. The CV indicates that the Pt catalyst surface was partially poisoned. The features of this CV are very similar to others we have acquired for sulfur poisoning. The characteristic signature of sulfur adsorption is observed without corresponding lower potential peaks of CO adsorption, showing that at the levels of impurity investigated here, only sulfur species are important. Similar experiments with just 10 ppb of  $H_2S$  in  $H_2$  produce similar cyclic voltammetry results. In contrast, experiments performed with 0.1 ppm CO show characteristic peaks for CO adsorption. The lack of CO adsorption from the multi-component test may be due to competitive adsorption effects. Correlating Figure 3 with saturated surfaces of the same loading, after 1,000 hours, about 40% of the Pt surface was covered with adsorbed  $H_2S$ , resulting in a meaningful performance loss. This

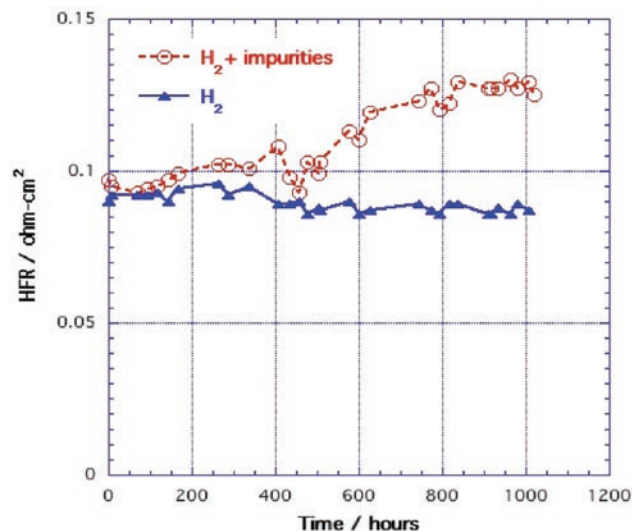


FIGURE 2. HFR Changes During Test Described in Figure 1

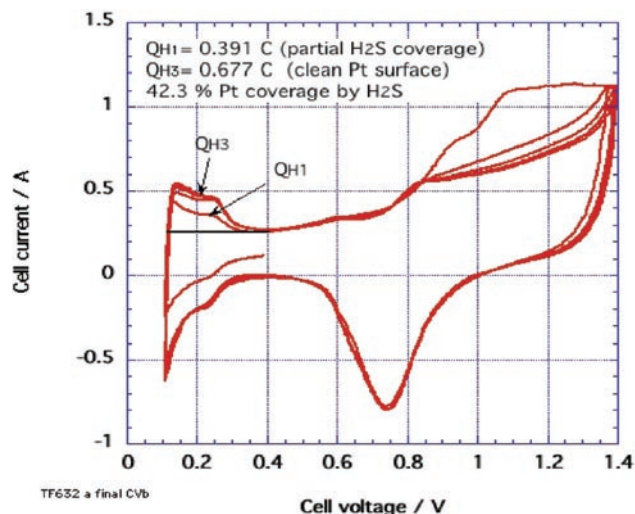


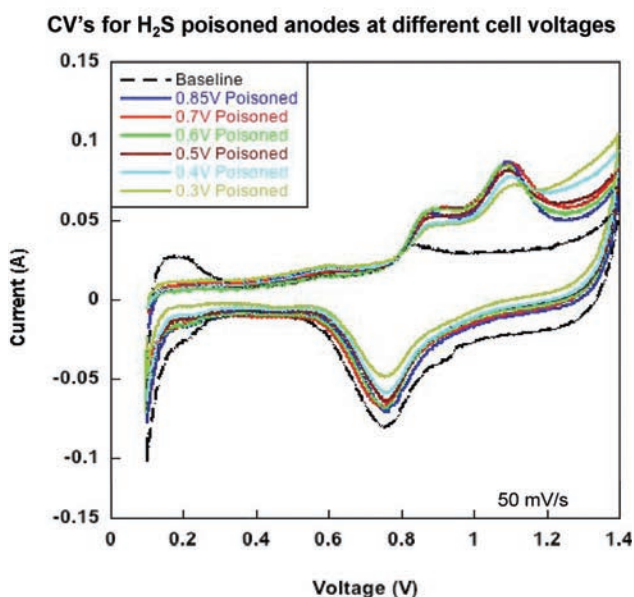
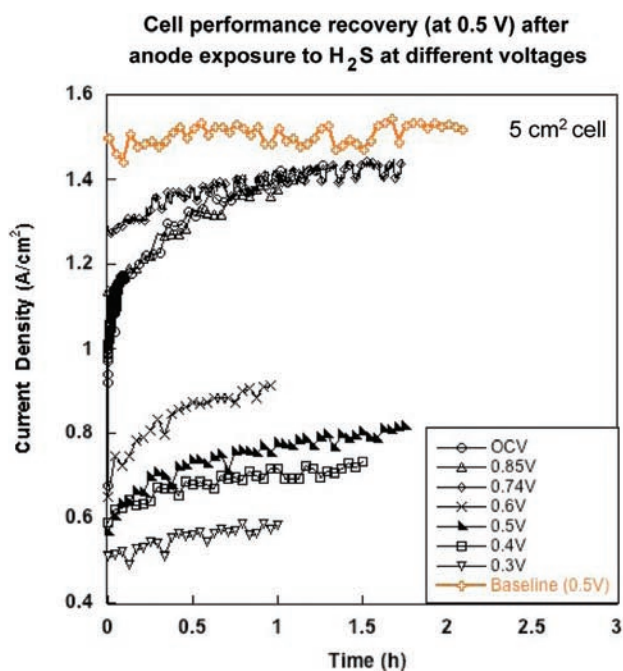
FIGURE 3. CV after Anode Exposure to 10 ppb  $H_2S$  for 1,000 hours (Cell and test described in Figure 1)

experiment indicates that the presence of ammonia and hydrogen sulfide impurities, even at very low levels (10 ppb  $H_2S$ ), will negatively impact cell operation, and DOE targets for lifetime and performance will not be met. Thus, these impurities will be a primary future focus.

$H_2S$  poisoning was also studied as a function of cell operating voltage. Constant time (50 minutes) poisoning experiments at 2 ppm  $H_2S$  were conducted at fuel cell voltages from 0.3 V to OCV. The cell performance was measured at 0.5 V. A clear trend was evident in the fuel cell response, as shown in Figure 4, top; the lower the cell operating voltage, the greater was the effect of the poisoning. Subsequent cyclic voltammetry experiments shown in Figure 4, bottom demonstrated that the sulfur species were more strongly bound (stripped at higher voltages) when the  $H_2S$  was adsorbed at lower fuel cell operating voltages.

Mitigation of  $H_2S$  and  $SO_2$  poisoning by current interruption (cycling to OCV) and air purging for up to 24 hours was investigated. Both of these methods were partially effective at removing the chemisorbed sulfur species. They were not as effective as voltage pulsing or cycling to 1.4 V using an external power source.

The Dual Tafel-Heyrovsky Pathway Hydrogen Oxidation Model was applied to  $H_2S$  irreversible poisoning. The presence of a site-blocking impurity strongly changes the polarization behavior of the anode. This is primarily due to changes in the reaction pathways created by the adsorbate. The Tafel reaction requires adjacent Pt sites for  $H_2$  dissociation, while the Heyrovsky pathway directly transfers charge to the  $H_2$  molecule. The Dual Pathway Model predicts the observed inflection in the polarization behavior of a fuel cell that is poisoned by a site-blocking adsorbate.

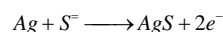


**FIGURE 4.** (top) Fuel Cell Performance at 0.5 V after Poisoning by 2 ppm H<sub>2</sub>S for 1 Hour at Differing Operating Voltages (bottom) CVs after Anode Exposure to H<sub>2</sub>S at Differing Operating Voltages

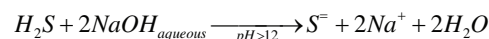
#### Trace Impurity Analysis and Materials Characterization

Ultra-low (ppb) levels of impurities in hydrogen testing requires the development of specialized analytical methods to accurately measure the gas concentrations. We have developed an Ag/Ag<sub>2</sub>S specific ion probe method to sense H<sub>2</sub>S at the ppb level. The Ag/Ag<sub>2</sub>S, in

conjunction with a reference electrode, measures the total sulfide ion concentration:



The H<sub>2</sub>S gas is bubbled through a gas washing cylinder that contains the Ag/Ag<sub>2</sub>S specific ion probe and a basic solution that causes the hydrogen sulfide gas to disproportionate to sulfide ions and water:



The sulfide ion concentration is then measured by the Nernstian response of the specific ion probe. The analysis system was successfully used to calibrate the H<sub>2</sub>S impurity levels and was combined with a temperature programmed adsorption/desorption system to measure H<sub>2</sub>S adsorption onto carbon supports and 20% Pt on XC-72 carbon. Almost no adsorption of H<sub>2</sub>S occurred on Vulcan XC-72 carbon, but 2 wt% adsorption occurred on 20% Pt supported on XC-72 carbon.

#### Conclusions and Future Directions

The effect of sulfur-containing gases on fuel cell performance is complex. Cell operating voltage must be taken into consideration along with concentration and exposure time. Air purging and OCV operation can result in some partial recovery. Our studies demonstrate the need to control sulfur levels in fuel gases and air intake systems. The effects of sulfur compounds greatly overwhelm the effects of other impurities at commonly found levels. We will continue sulfur species studies to determine the maximum tolerable impurity concentrations for optimal fuel cell performance. We will measure adsorption of impurity gases on fuel cell components in an aqueous environment. We will conduct fundamental voltammetry and surface science studies to determine sulfur speciation on Pt surfaces. The effects of common divalent cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>) on fuel cell performance will also be tested. We will further refine our impurity models based on the fundamental data. The impact of fuel impurities on fuel cell durability will also be assessed.

#### FY 2006 Publications/Presentations

1. M. Mikkola, T. Rockward, F. Uribe and B. Pivovar, "The Effect of NaCl in Cathode Air Stream on PEMFC Performance," Submitted to Fuel Cells - From Fundamentals to Applications (2006).
2. F. Uribe and T. Rockward, "Cleaning PEMFC Electrodes with Adsorbed S-species," 208<sup>th</sup> ECS Meeting, Los Angeles, CA, October (2005).
3. F. Uribe et al, "Electrode Structures and Effects of Fuel Cell Impurities," Invited talk, INRS, Quebec, Canada, (2006).

## Special Recognitions & Awards/Patents Issued

1. F. Uribe and T. Rockward, "Cleaning (de-poisoning) PEMFC electrodes from strongly adsorbed species on the catalyst surface," 104229 Non-Provisional patent application (2006).

## References

1. F. A. Uribe, S. Gottesfeld, and T. A. Zawodzinski Jr., *J. Electrochem. Soc.* 149, A293 (2002).
2. F. Uribe and T. Zawodzinski, Jr., 200<sup>th</sup> Meeting of The Electrochemistry Society, San Francisco, CA, September 2001. Abstract 339.
3. (a) H. Soto, W. Lee, J. Van Zee, and M. Murthy, *Electrochemical and Solid-State Letters*; July 2003; vol. 6, no. 7, p. A133-5. (b) R. Mohtadi, W. K. Lee, S. Cowan, J. W. Van Zee, and M. Murthy, *Electrochemical and Solid-State Letters*; Dec. 2003; vol. 6, no. 12, p. A272.

4. J. M. Moore, P. L. Adcock, J. B. Lakeman and G. O. Mepsted, *J. Power Sources*, **85** (2000) 254.

5. (a) F. Uribe, J. Valerio, T. Rockward and E. Stenersen, 205<sup>th</sup> Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 332. (b) M. Mikkola, T. Rockward, E. Stenersen and F. Uribe, 205<sup>th</sup> Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 331.

6. R. Mohtadi, W. Lee, and J. Van Zee, *Journal of Power Sources*, 2004, **138**, no. 1-2, p. 216-225.