IX.5 Hydrogen Fuel Quality

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Objectives

- Develop and test new analytical methods for detecting parts-per-billion (ppb) levels of contaminants.
- Employ, modify and/or create novel techniques that allow reproducible measurements of trace level contaminants.
- Test the effects of critical constituents (NH_3, CO, and H_2S) on fuel cell performance and provide data sets to fuel cell modelers to establish predictive mechanistic models.
- Provide guidance to other test facilities to expedite International Organization for Standardization (ISO) TC197 Working Group 12's experimental results.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Codes and Standards section (3.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(I) Conflicts between Domestic and International Standards

(N) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestone from the Codes and Standards sub-program section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 26** - Revised (Society of Automotive Engineers/ISO) hydrogen quality guidelines adopted. (4Q, 2010)

Accomplishments

- Developed new analytical technique for detecting sulfur and verified using environmental scanning electron microscopy.
- Implemented a gravimetric technique to measure electrochemical active surface area of the catalyst.
- Initiated development of an analytical technique for NH_3 analysis.
- Tested critical constituents (NH_3, CO, and H_2S).
- Developed baseline test procedures for commercial membrane electrode assemblies (MEAs).
- Continued providing data sets to and interacting with fuel cell modelers.

Introduction

LANL scientists have continued their support of the DOE/Energy Efficiency and Renewable Energy Office of Hydrogen, Fuel Cells & Infrastructure Technologies' Safety, Codes and Standards sub-program through their expertise in the various disciplines such as materials physics and applications, chemistry, and modeling. They have maintained a lead role in the collaborative development and implementation of international performance-based codes, standards and regulations based on actual fuel cell performance.

Approach

Our focus on the hydrogen quality emerged from a fuel specification in which the level of the constituents present was based on detection limits. This brings about our two major focus areas: analytical methods development and critical constituent (the most deleterious: NH_3, CO and H_2S) testing.

We employed commercially available ion selective electrodes to verify the levels of sulfur present in a fuel stream. This proved to be a difficult task considering sulfur has a tendency to stick to most surfaces. In addition, the commercial probes also lacked sensitivity for sulfide ion concentrations below 10^{-5} mole/L (M). However, trace quantities of H_2S may be measured by concentrating the sulfide ion in a solution of sulfide

anti-oxidant buffer if the gas flow time and flow rate are known, together with precise knowledge of the titrant concentration, titrant volume, and volume of sample, provided that isothermal conditions are maintained. Commercial sulfide ion probes may be used as an endpoint indicator for titrations. This method is also being investigated for NH_3 concentration in a solution. However, because of its solubility multiple traps were set-up to enhance this technique. Figures 1 and 2 illustrate the experimental set-up for S and NH_3.

LANL has continued testing the critical constituents both independently and combined in order to best describe the fuel cell's response as function of the various constituents and the operating condition. Our tests were conducted with 0.1 and 0.2 mg Pt/cm^2 for the anode and cathode catalyst, respectively. These loadings are consistent with DOE's 2010 technical targets. More recently, the working group members from North America agreed to also test commercial MEAs at 0.1 and 0.4 mg Pt/cm^2. LANL has developed a set of initial baseline tests to be performed by the WG-12 members before testing with fuel specification.

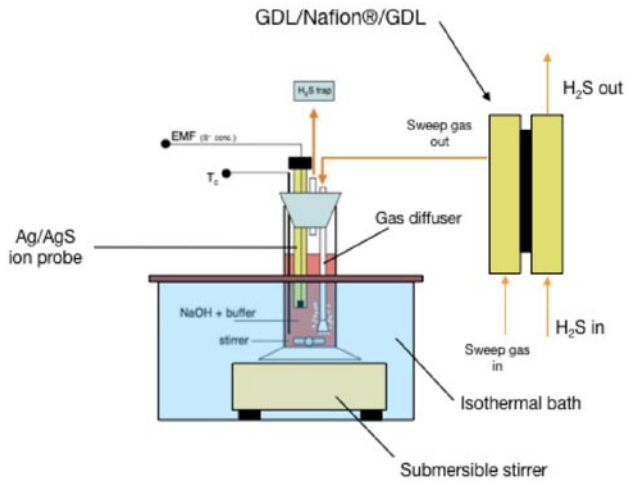

FIGURE 1. Schematic of S trap using an ISE

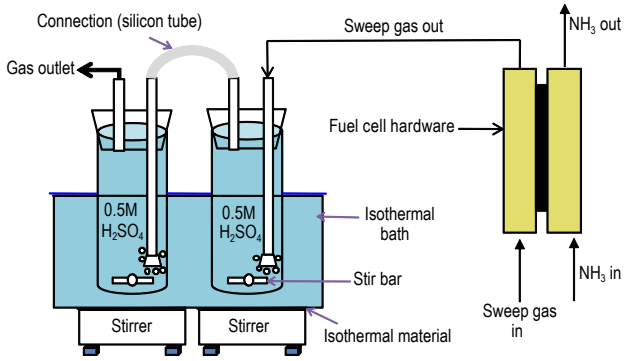

FIGURE 2. Experimental Set-Up for NH_3 Trap using Sequential Trapping

Results

We probed the active surface area on several different catalysts using thermal gravimetric analysis (TGA). Two TGA runs were required for analyses: the first was used to clean the surface of the sample and to prepare it for CO adsorption and in the second run, a 1.1% CO in argon mixture was applied to sample and the mass change recorded. Finally, we verified the CO concentration on the sample by gas chromatography analysis. The catalyst samples examined in the first series of experiments were Pt Black (Alfa HiSpec 1000), Pt/Al_2O_3 (Alfa 5 wt% Pt on gamma alumina), and Pt/XC-72 (ETEK 20 wt% Pt on carbon XC-72). The results are shown in Figure 3 highlight Pt/XC-72 results in which the sample gain approximately 4% after the introduction of CO.

We continued to test NH_3, CO, and H_2S as isolated contaminants, in addition to testing combinations of these contaminants. Our fuel cell tests were conducted with 0.1 and 0.2 mg Pt/cm^2 at the anode and cathode electrodes, respectively. We used 50 cm^2 hardware with Nafion® (NRE212) as the membrane and our catalyst was 20% Pt/C (ETEK). In each result shown we operated the cell in constant current mode, 0.8 A/cm^2, at 80°C with 83% utilization for the hydrogen and 50% for the air. In Figure 4, the fuel cell was exposed to 100 ppb H_2S in the anode feedstream while operating at 100% relative humidity. After approximately 100 hrs of exposure, the voltage dropped by ~70 mV. We noticed a 40 mV increase in voltage 24 hours after returning to pure hydrogen. The voltammogram indicated the presence of S on the electrode surface. In a separate experiment, we tested 1 ppm NH_3 under identical conditions to those mention in the previous experiment. At the end of 100 hrs, the voltage loss was about 40 mV

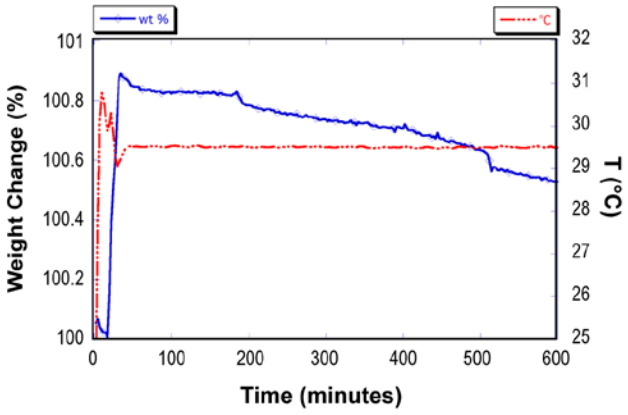

FIGURE 3. Weight Change of a Pt/XC-72 Sample after Exposing it to 1.1% CO in Argon

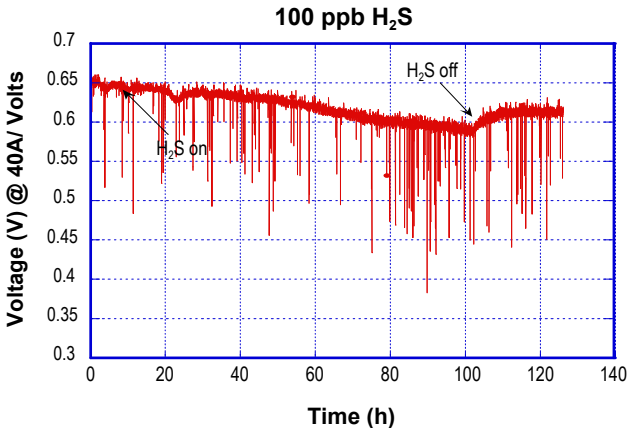

FIGURE 4. Voltage Response to 100 ppb H_2S at 100% Relative Humidity for a Proton Exchange Membrane Fuel Cell with 0.1 and 0.2 mg Pt/cm^2 Operating at 40 A.

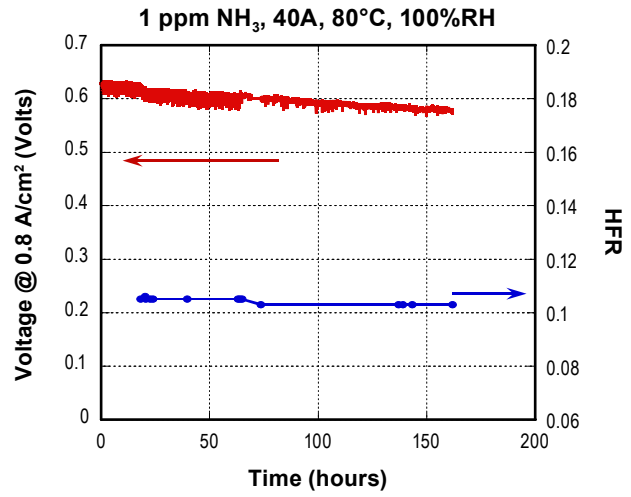

FIGURE 5. Voltage and Resistance as a Function of Time after Introducing 1 ppm NH_3 into the Anode Feedstream of a Fuel Cell

as shown in Figure 5. The actual fuel specification call contain multiple contaminants, however through our previous fuel cell testing experience we have identified NH_3, CO, and H_2S as the constituents having the most impact on fuel cell performance. This is shown in Figure 6, where after less than 70 hours of exposure to 100 ppb CO, 4 ppb H_2S, and 1 ppm NH_3 the voltage loss was 52 mV.

Future Directions

Our technical objectives for Fiscal Year 2009 were achieved. We have agreed to aggressively begin testing commercial MEAs in an attempt to meet the upcoming ISO TC197 deadline. We will also focus on populating the data sheets with high-quality data using

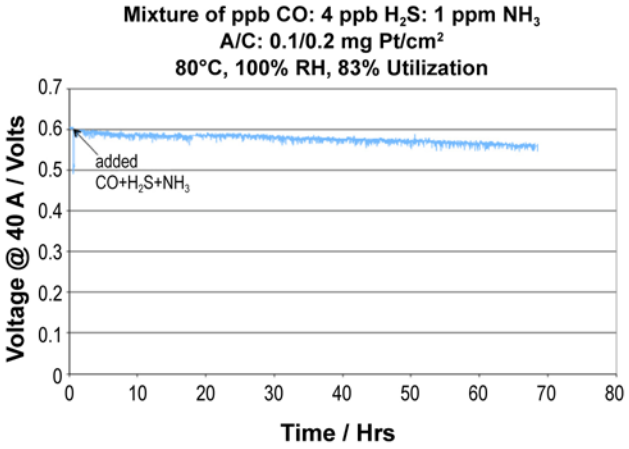

FIGURE 6. Voltage as a Function of Time after Introducing 100 ppb CO, 4 ppb H_2S, and 1 ppm NH_3 into the Anode Feedstream of a Fuel Cell

these commercial MEAs, and further the development of analytical methods for determination of very low concentrations of other contaminants. Next year's objectives:

- Report on results of commercial MEAs at next ISO TC197/WG-12 meeting.
- Optimization of the previously discussed analytical method and its modification for other critical constituents.
- Improve gravimetric capabilities.
- Continue testing the critical constituents (NH_3, CO, and H_2S) and populating the test matrix.
- Continue providing data sets and interacting with fuel cell modelers.

FY 2009 Publications/Presentations

1. E.L. Brosha, T. Rockward, F.A. Uribe, and F. Garzon, "Measurement of H_2S Crossover Rates in Fuel Cell Nafion® Membranes Using Ion-probe Techniques." To be submitted: J. Electrochem. Soc. Spring 2009.

2. Eric L. Brosha, Tommy Rockward, Francisco A. Uribe, and Fernando H. Garzon, "Development of Analytical Techniques to Study H_2S Poisoning of PEMFCs and Components", ECS Transactions for 2008 Fuel Cell Seminar and Exposition, Phoenix, AZ, October 2008.

3. C.M. Johnston, H. Xu, E.L. Brosha, J. Chlistunoff, K. More, E. Orler, M. Hawley, and B. Pivovar, "Measurement and Understanding of Catalyst Utilization in Fuel Cells", ECS Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.

4. T. Rockward, I. Urdampilleta, F. Uribe, E.L. Brosha, and F.H. Garzon, "Co-Adsorption Studies of CO and H_2S on Pt Electrodes", ESC Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.

5. Eric L. Brosha, Tommy Rockward, Francisco A. Uribe, and Fernando H. Garzon, "Qualitative Determination of H_2S Crossover Rates in Nafion® Membranes Using Ion-Probe Techniques", ECS Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.

6. Eric L. Brosha, Rangachary Mukundan, Roger Lujan, and Fernando H. Garzon, "Development of a Zirconia-Based Electrochemical Sensor for the Detection of Hydrogen in Air", ECS Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.

7. Eric L. Brosha, Rangachary Mukundan, and Fernando H. Garzon, "YSZ-Based Electrochemical Gas Sensors for the Detection of Explosives", ESC Letters 11 (12) J92, 2008.