VIII.9 Hydrogen Fuel Quality Research and Development

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Fiscal Year (FY) 2011 Objectives

- Provide data and analysis to the international effort to determine the levels of non-hydrogen constituents in support of the development of an international standard for H_2 fuel quality.
- Test the critical constituents (NH_3, CO, and H_2S).
- Isolated and combined at various conditions.
- Present data and have open discussions at International Organization for Standardization (ISO) TC197/Working Group 12 Meetings.
- Solicit guidance from leading industrial experts.

Technical Barriers

This project is directed to ameliorate many of the technical barriers from the Codes and Standards section (3.7) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan, however it is focused on the following primary barriers:

(I) Conflicts between Domestic and International Standards

(N) Insufficient Technical Data to Revise Standards

Technical Targets

Technical targets in Table 3.4.4 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan are addressed in this project. Specifically, select tasks that apply to the technical targets in this project are listed in the following, while their status is listed in the Accomplishments section.

- Provide testing results from Common membrane electrode assembly (MEA) in the presence of critical constituents.
- Measure the fuel cell tolerance to carbon monoxide using Common MEAs.
- Identify MEA manufacturer to provide Common MEA DOE 2015 target loadings.
- Perform baseline test with lower anode loading MEAs.
- Participation in domestic and international working groups and review meetings.

Approach

We approached our 2011 technical targets by conducting multiple fuel cell tests mimicking conditions that a fuel cell may be subjected to in vehicular applications. Initially, we employed 'Common MEAs' to perform these tests with 0.1 and 0.4 mg Pt/cm^2 loadings on the anode and cathode, respectively. Although, theses loadings are not identical to the DOE targets (0.05 and 0.15 mg Pt/cm^2), the results provide a means for comparing different testers and facilities. These results were presented and discussed at several forums throughout the year. In addition, commercial suppliers of the DOE 2015 technical target loadings were being identified and, the preliminary testing steps were put in place to qualify their materials.

FY 2011 Accomplishments

- Completed multiple tests under various conditions using calibrated quantities of the critical constituents.
- Measured CO tolerance level of Common MEA.
- Interacted with multiple industrial, university, or laboratory partners, as well as international collaborators.
- Identified Ion Power as the Common MEA supplier for DOE 2015 platinum loadings.
- Performed initial baseline tests to qualify lower loaded MEAs.

Results and Discussions

The development of international hydrogen fuel specifications has been discussed for several years. In particular, the focus has been on determining the acceptable level of non-hydrogen constituents. LANL researchers have continued fuel cell testing at the agreed upon contaminant levels using a Common MEA loaded at 0.1 and 0.4 mg Pt/cm^2 under various operating conditions. Although the loadings mentioned are slightly higher than DOE

targets, the results are useful. Previous tests results with contaminant mixtures showed that the fuel cell performance losses were due to hydrogen sulfide (H_2S), ammonia (NH_3), and carbon monoxide (CO). These are referred to as 'critical constituents'. Our fuel cell test results include investigating the critical constituents both isolated and combined.

H_2S has a strong affinity for platinum surfaces and blocks the dissociative chemisorption of hydrogen on the electrode surface. This platinum-sulfur interaction inhibits the hydrogen electrooxidation process, which consequently reduces fuel cell performance. In separate experiments, we exposed the anode of operating fuel cells to both 4 and 8 ppb for 50 hours each. The fuel cells operated in constant current mode (1 A/cm^2) at 80°C, 100% relative humidity (RH) and 25 psig backpressure. We performed polarization experiments before and after sulfide exposure. After 50 hours of exposure, the fuel cell did not show performance loss in the presence of 4 ppb, however the performance is progressively depressed when the concentration of H_2S was increased. This effect is demonstrated in Figure 1. As expected, we did not observe any change in the alternating current (AC) high frequency resistance. However, in the low frequency charge transfer region, the semi-circle grew as the H_2S concentration increased. This implies the sulfur coverage on the platinum surface also increased with concentration. Cyclic voltammetry (CV) also confirmed this finding. Also, in the mass transport region, we observed unexpected losses for 4 PPB H_2S. This result is being further investigated.

In order to study the effect of CO concentration upon fuel cell performance, we exposed a fuel cell with an anode loading of either 0.05 or 0.1 mg Pt/cm^2 to several different concentrations at 80°C. We kept the dosage in each experiment constant (20 ppm-hr CO) by varying both concentration and exposure times. CVs were used to clean the platinum surface after CO exposure following each experiment. The CVs were performed, with ultra-high purity (UHP) N_2 flowing through the anode and UHP H_2 flowing through the cathode after pre-purging the cathode for 20 minutes with UHP N_2. The scan rate was 20 mV/s and the applied voltage ranged between 0.06 V and 1.1 V for 4 cycles. The cleaning procedure allowed us to use the same cell in subsequent experiments. Figure 2 shows the experimental results for a Pt loading of 0.1 mg Pt/cm^2 for the differing concentrations of CO. We also measured the voltage loss for each test and plotted it as a function of CO concentration. This allowed us to extrapolate the point at which the voltage loss approaches zero; the concentration under these tested conditions, that the fuel cell is tolerant to CO. Figure 2 highlights these results. Similar experiments were performed at 60°C and 45°C.

Ammonia is yet another important impurity constituent deemed critical in this effort. It typically reacts with proton in the ionomer forming ammonium cations and affects the ionomer throughout the MEA by lowering its conductivity. Figure 3 illustrates the impact of a variety of ammonia concentrations and RH. Tests were carried out at 50 A

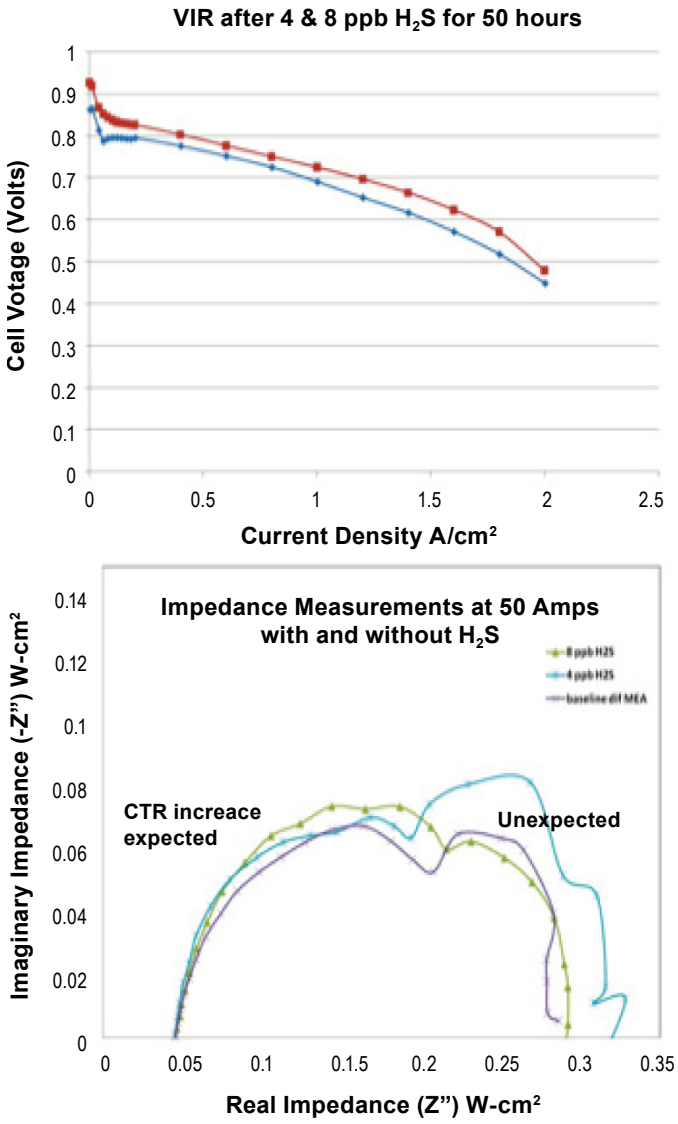

FIGURE 1. Voltage-current-resistance tests and AC Impedance measured using the Common MEA after being exposed to 4 and 8 ppb of hydrogen sulfide for 50 hours.

(constant current mode) using 25 psig backpressure. We used three different concentrations: 100, 200, and 500 ppb. The RH ranged from 25 to 100%. The entire data set is not included in this report, but the findings indicate that the performance decreases as the concentration of ammonia is increased. Because ammonia is water soluble, as the RH increased for identical concentrations, the performance losses decreased from 24 mV at 25% RH to 8 mV at 50% RH (see Figure 3).

The previously mentioned results were obtained from Common MEAs with Pt loading greater than the DOE targets. This year, we identified Ion Power as a commercial supplier to provide MEAs at DOE targeted loadings. We ran preliminary test to investigate the durability of the new materials. Figure 4 shows VIR tests competed 150 hours

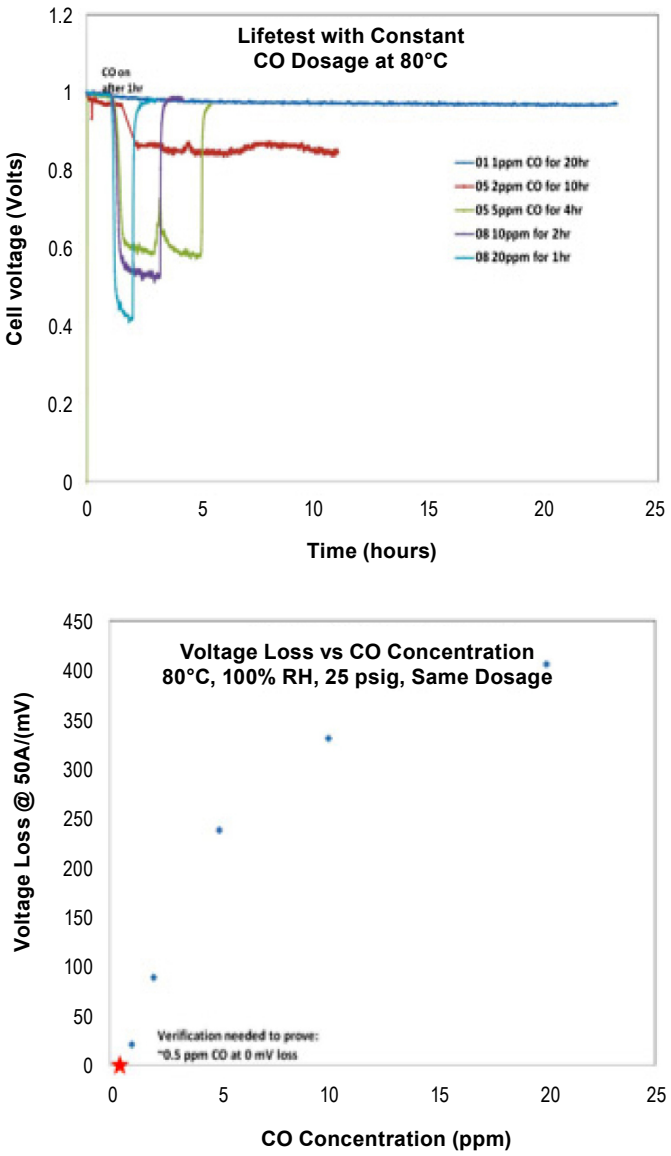

FIGURE 2. Results show the impact of CO on an operating fuel cell using identical doses. The adjacent graph allows the CO tolerance level to be extrapolated.

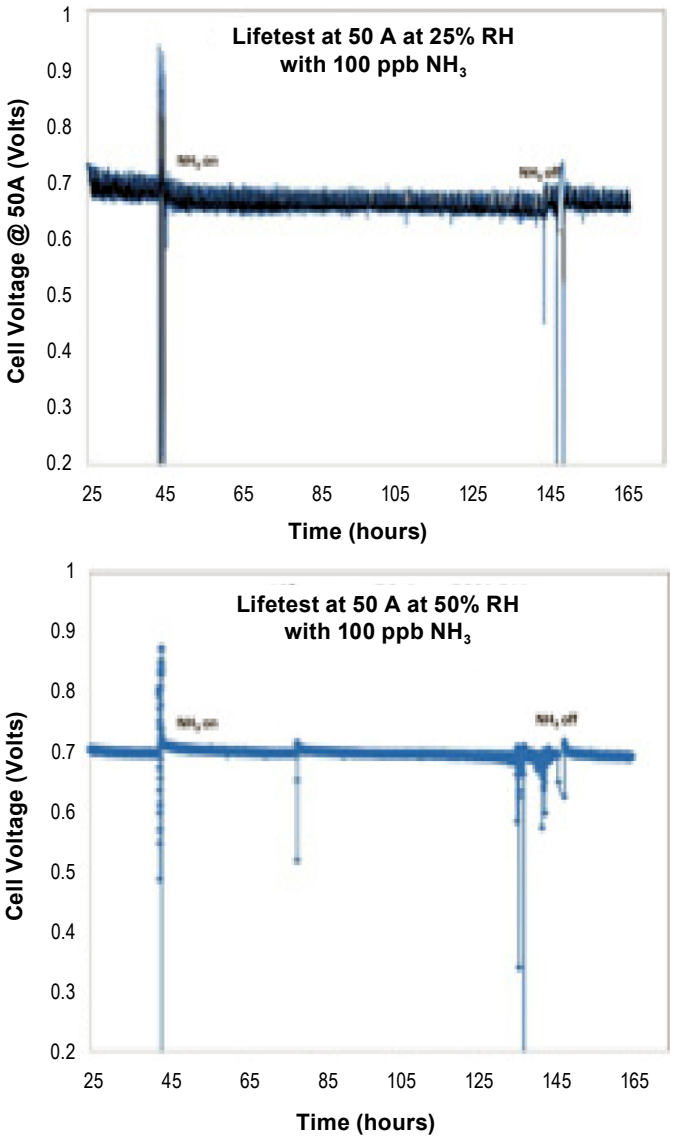

FIGURE 3. Cell voltage monitored before, during and after 100 ppb ammonia exposure at two different RHs for a fuel cell operating at 1 A/cm^2.

apart. The performance improved during that period. This indicates the MEA was fully broken in at 150 hours. However, more importantly, this result demonstrated membrane durability. We also performed other preliminary tests such as AC impedance (shown in Figure 4 on the right) and CV.

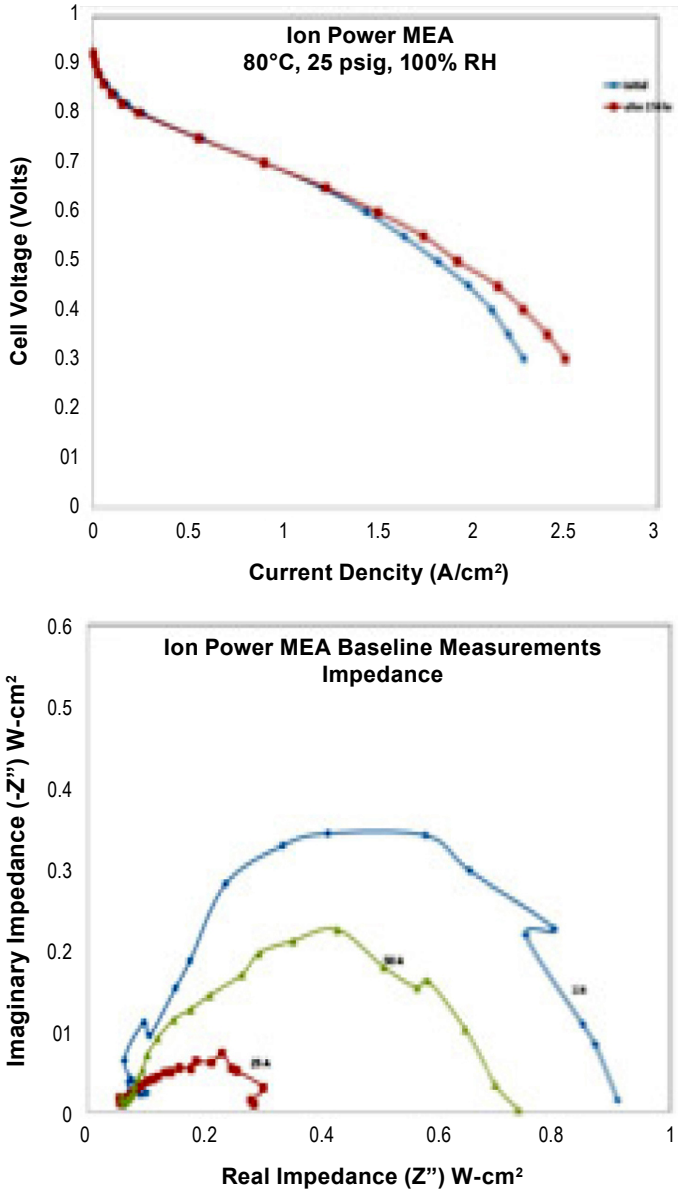

FIGURE 4. Initial tests results of Ion Power MEA (i.e. low loading) to probe durability concerns/issues.