VIII.3 Hydrogen Fuel Quality

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Collaborators/Partners

- Japan Automotive Research Institute
- National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee
- ASTM International
- SAE International
- Smart Chemistry
- Commissariat à l’énergie atomique et aux énergies alternatives (CEA), Liten, France
- VTT, Helsinki, Finland
- International Electrotechnical Commission Technical Committee 105 Working Group 11 (IEC/TC 105/WG 11)

Project Start Date: October 2006
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

To support the Hydrogen Safety, Codes and Standards sub-program through:

- Participation in working groups.
- Providing leadership to hydrogen fuel quality efforts.
- Performing the R&D needed to develop science-based codes and standards.
- Developing tools that can remove safety and hydrogen fuel quality barriers to the commercialization of fuel cells.

Fiscal Year 2016 Objectives

- Evaluate fuel quality impacts on membrane electrode assemblies (MEAs) with DOE 2015 loadings and disseminate data to inform the revision of fuel quality standards.
- Build a prototype fuel quality analyzer based on the proof of concept demonstrated in FY 2015.
- Collaborate with international institutions to harmonize testing protocols to aid istandards development.
- Serve as subcommittee chair for ASTM D03.14: Gaseous Fuels and participate in ASTM interlaboratory studies.
- Provide technical support to IEC/TC 105/WG 11.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes, and Standards section of the Fuel Technologies Program Multi-Year Research, Development, and Demonstration Plan.

(F) Enabling National and International Markets Requires Consistent RCS (regulations, codes and standards)

(G) Insufficient Technical Data to Revise Standards

(H) Insufficient Synchronization of National Codes and Standards

(K) No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

FY 2016 Accomplishments

- Demonstrated hydration scheme that allows for constant baseline measurements in the prototype fuel quality analyzer, which subsequently allowed for a provisional patent application to be initiated with LANL Richard P. Feynman Center for Innovation.
- Obtained a response to 50 ppm CO (limited only be the lag time of the system) in hydrogen after switching from neat hydrogen. To date, this was the fastest response time ($t < 1$ min) obtained even though the CO concentration was much higher than the SAE International Organization for Standardization (ISO) limit.
- Several ASTM test methods have been published. “Standard Test Method for Determination of Trace Carbon Dioxide, Argon, Nitrogen, Oxygen, and Water in Hydrogen Fuel by Jet Pulse Injection and Gas Chromatography/Mass Spectrometer Analysis (D7649),” “Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In Stream Filter (D7650),” and “Standard Test Method for Gravimetric Measurement of Particulate Concentration of Hydrogen Fuel (D7651)” were reviewed (five years after initial publication), approved by ballot, and resubmitted.

- Chaired two semi-annual ASTM meetings whose outcome led to the development of a database which helped identify interested test-sites with existing capabilities for conducting interlaboratory studies according to ASTM guidelines. These meetings were held in Austin, Texas, in December 2015, and Bellevue, Washington, in June 2016.
- Fuel quality work performed with several international partners (CEA, VTT, Joint Research Centre)
- LANL and Japan Automotive Research Institute baseline tests demonstrated fuel cell performance to be within 5% of each other, using either institutions protocol, hardware, and facilities.
- Hydrogen impurity testing is ongoing and will continue (collaboration with Hydrogen Contaminant Risk Assessment [HyCoRA] project that was extended). LANL initiated a parametric study to determine CO tolerance with lower loaded MEAs varying the relative humidity (RH) and pressure. Their test matrix probes three different RHs and three pressures, along with various CO concentrations. To date, we have completed testing at two different RHs and two different pressures.
- Extensive impurity testing performed using a fuel re-circulation system (VTT collaboration). These tests allow comparisons between single-pass mode and recirculation of CO, H_2S and CO/H_2S fuel mixtures. We have completed 100 hours of fuel cell testing with CO and H_2S, at the SAE limits, as single impurities in hydrogen.

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INTRODUCTION

LANL scientists' interactions with the fuel cell community through the DOE's Safety, Codes and Standards program continues to provide expertise in the area of hydrogen fuel quality testing in support of developing international fuel quality standards, guidance and leadership for ASTM standards development, as well as the development of an in-line fuel quality analyzer.

In the hydrogen fuel quality efforts, LANL has continued its investigation on the impact of fuel impurities at the levels listed in the "Hydrogen Fuel Quality for Fuel Cell Vehicles" SAE J2719 [1], and ISO 14687-2:2012 [2]. This ongoing effort has continued to focus on the "critical constituents: carbon monoxide, hydrogen sulfide, and ammonia" as fuel contaminants for fuel cells operated with low platinum loaded electrodes (anode: 0.05 mg/cm^2 and cathode: 0.1 mg/cm^2).

LANL has also made advances in the development of a prototype in-line fuel quality analyzer. Previous years' work has progressed to finalizing the design and testing of a novel hydration scheme. The most recent results of the analyzer indicate that the prototype is getting closer to field testing. Our goal is to accomplish this in FY 2017.

APPROACH

R&D for Fuel Quality Standards

LANL carried out parametric studies to help determine the tolerance to fuel impurities as a function of fuel cell operating conditions. Also, the newly installed re-circulating system was used to compare the impact of CO and H_2S in single pass mode versus recirculating the fuel. LANL continues to interact with several International collaborations to harmonize impurity testing. Finally, LANL scientists will host IEC/TC 105/WG 11 to finalize the development of an international document entitled, "Single Cell Test Methods for Polymer Electrolyte Fuel Cell (PEFC)."

In-line Fuel Quality Analyzer

LANL built and tested their new prototype design and hydration scheme for the fuel quality analyzer in FY 2016. A series of tests were conducted to determine the best conditions for maintaining membrane hydration. LANL scientists determined the various operating parameters that optimize sensitivity, response time, and stability.

RESULTS AND DISCUSSIONS

R&D for Fuel Quality Standards

In previous studies, LANL scientists determined CO tolerance using a common MEA tested at fixed fuel cell conditions, i.e., 1 A/cm^2, 100% RH, 83% fuel utilization, 25 psig. The tests used a constant dosage of CO. The voltage loss versus CO concentration was measured and the CO tolerance value was extrapolated to determine CO tolerance level. Our approach has expanded to include a similar parametric study to determine CO tolerance with lower loaded MEAs varying the relative humidity and pressures. Our test matrix probes three different RHs and three pressures. To date, we have completed testing at two different RHs and two different pressures. These preliminary fuel cell results indicate as the RH increases, the losses due to CO are enhanced, while the losses decreased as the pressure was increased.

In FY 2015, fuel cell performance in single-pass operation versus hydrogen recirculation with 200 ppb CO/H_2 was compared at 80°C in constant current mode at 1 A/cm^2 with 80°C with the back pressure set to 150 kPa. After 100 h of operation, the single-pass results showed a 38 mV voltage loss, while the recirculation system loss 50 mV. Similar studies were conducted with H_2S in FY 2016, and the findings also show an increase in voltage loss when the fuel is recirculated. This result also was anticipated considering the interactions between CO and platinum surfaces are similar to that of sulfur, which has an even stronger interaction. In preparation for additional comparison tests, LANL has completed single-mode tests with ammonia, carbon monoxide, and hydrogen sulfide present simultaneously at the SAE J2719 levels. The tests conditions used were identical to when individual CO and H_2S contaminants were used. We included a subsequent test varying the RH from 100% to 50%. The results showed (Figure 1) an increase in voltage loss when the RH was lowered. At 100% RH, the voltage loss was 60 mV and it increased to 67 mV when the RH was reduced to 50%.

In-line Analyzer

LANL scientists have systematically studied materials for electrodes that are best suited for a hydrogen fuel quality analyzer and have strategically incorporated them into a newly developed prototype. Maintaining membrane hydration is essential in order to ensure the analyzer's viability. This particular task was challenging considering the hydrogen gas being monitored will be dry and that water is considered an impurity and will not be available. Using a unique water-wicking scheme, LANL tested the stability of the analyzer at various flow rates with two different membrane thicknesses, 2 mil (N112) and 7 mil (N117). High frequency resistance measurements of the membranes indicated that the thicker membranes maintained hydration longer at identical flow rates. The membrane resistance was measured and it was concluded that flow rates play an important role in the operation of the analyzer. Tests of the prototype analyzer with the thicker membrane and specially designed flow fields and gas diffusion layers resulted in a stable high frequency resistance and stable analyzer baseline in dry hydrogen. Figure 2 shows a stable current from the analyzer operated at 1.15 mA for up to 2 h before the introductions of CO. Figure 2 also illustrates the sensitivity of the analyzer to CO. Further studies are underway to optimize this analyzer for improved sensitivity to the SAE J2719 levels and response time to within 5 min. Finally, the analyzer was exposed to neat hydrogen to obtain a baseline response followed by exposure to 50 ppm CO in hydrogen and we observed an instant response. Figure 2 highlights the response.

Hydrogen Fuel Quality: International Collaborations

LANL scientists have completed their efforts within IEC/TC 105/WG 11 to advance the "Single Cell Test Methods–PEFC" document. In FY 2016, LANL and DOE

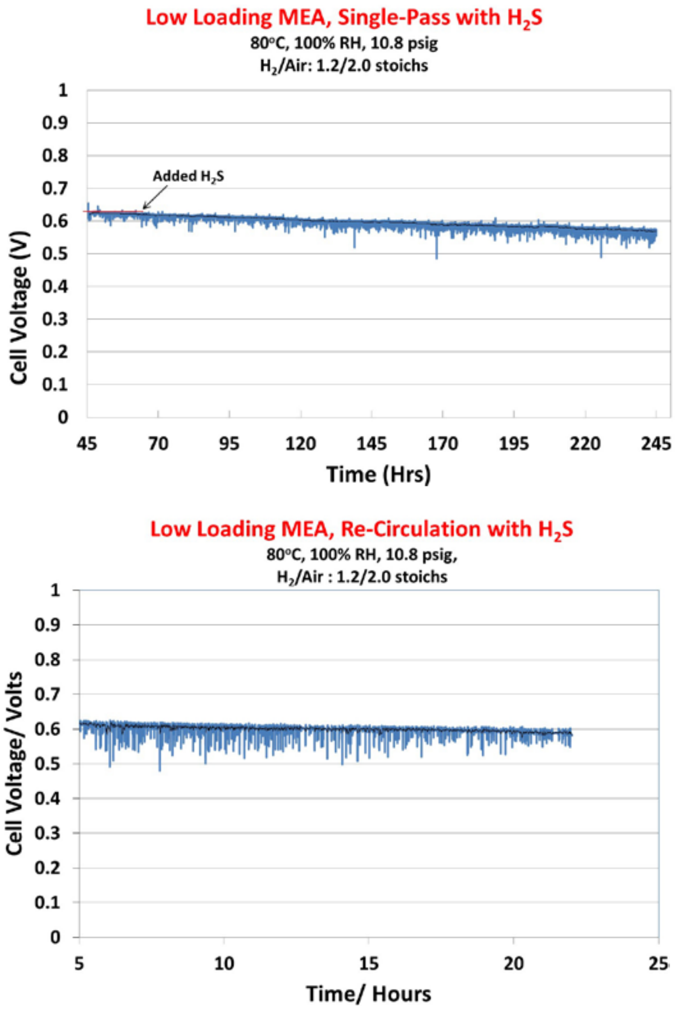

FIGURE 1. Comparison of fuel cell results using single-pass vs. recirculated fuel: 200 ppb H_2S

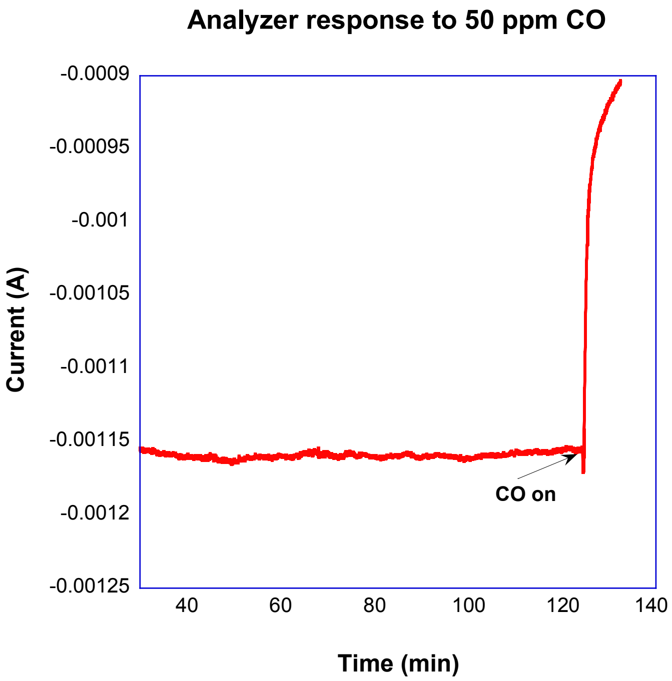

FIGURE 2. Analyzer results: 50 ppm CO response

hosted the members of WG 11 in Washington, D.C., where the document was finalized for submission. LANL has also continued fuel quality testing initiatives with CEA and VTT-Finland. LANL completed fuel cell tests with 25 cm^2 MEAs using LANL hardware at CEA's testing facility. These results (Figure 3) measured by LANL scientists investigated the impact of CO after pre-dosing the fuel cell with H_2S. The rationale behind this approach was to probe the fuel cell performance in the presence of CO in the hydrogen fuel stream after unexpected exposure to H_2S. Two days of fuel cell experiments were completed at the CEA fuel cell testing facility. The tests were carried out at 80°C and 50% RH. We used 20 ppm H_2S as the unexpected exposure concentration in the fuel stream. Afterward, we injected CO to investigate its impact on a partially poisoned fuel cell. During the first day of testing, the fuel cell was exposed to 20 ppm H_2S for 1 h and subsequently exposed to 1 ppm CO for another hour. The results of CO, for the given exposure time, showed minimal voltage losses (i.e., voltage loss < 10 mV). The next day we exposed the fuel cell to the same dosage of hydrogen sulfide and varied the CO concentration during the 1 h of exposure. We perform this test sequence three times and recorded the voltage response. Unlike the experiments results from Day 1, after subsequent exposures to CO, we observed a gradual decay in the cell voltage that became more pronounced over time.

In our collaboration with VTT-Finland, we probed the impact of internal air bleeding on CO by assessing the carbon balance using an operating fuel cell. We tested this impact using 25 cm^2 hardware with a low loading MEA, describe above. The fuel cell was run on neat hydrogen for 2.5 h before introducing 1.86 ppm CO into the anode stream with the current fixed at 0.4 A/cm^2. Using gas chromatography connected before and after the anode feed, the carbon monoxide and carbon dioxide concentrations were measured before, during and after CO exposure in the fuel cell. At the onset, the gas chromatography did not show any evidence of CO, however it did show high CO_2 concentrations that eventually reduced to a fixed amount. Afterwards, during the CO poisoning, we observed the CO_2 concentration increased. This CO_2 was due to the oxidation of CO to CO_2 from the internal air bleed of oxygen crossing the membrane. The window of opportunity for the CO_2 measurement existed only at the introduction of CO as its concentration returned to the same value as before CO poisoning. The source of the pre-existing CO_2 was from either the fuel or oxidant. The amount of pre-existing CO_2 was overwhelmingly large and made it challenging to obtain an accurate carbon balance.

Contributions to ASTM Standards Development

The ASTM hydrogen and fuel cells committee (D03.14) held its two semi-annual meetings in FY 2016, which LANL chaired. The first meeting was held in June in Austin, Texas, and the subsequent meeting in December in Bellevue, Washington. A highlight of this year was the addition of an excel spreadsheet that helped identify test sites and test facilities with capabilities and interests in participating in interlaboratory studies. While momentum was gained with the development of this database of test facilities, the committee also unveiled the lack of funding for testing labs as a critical barrier.

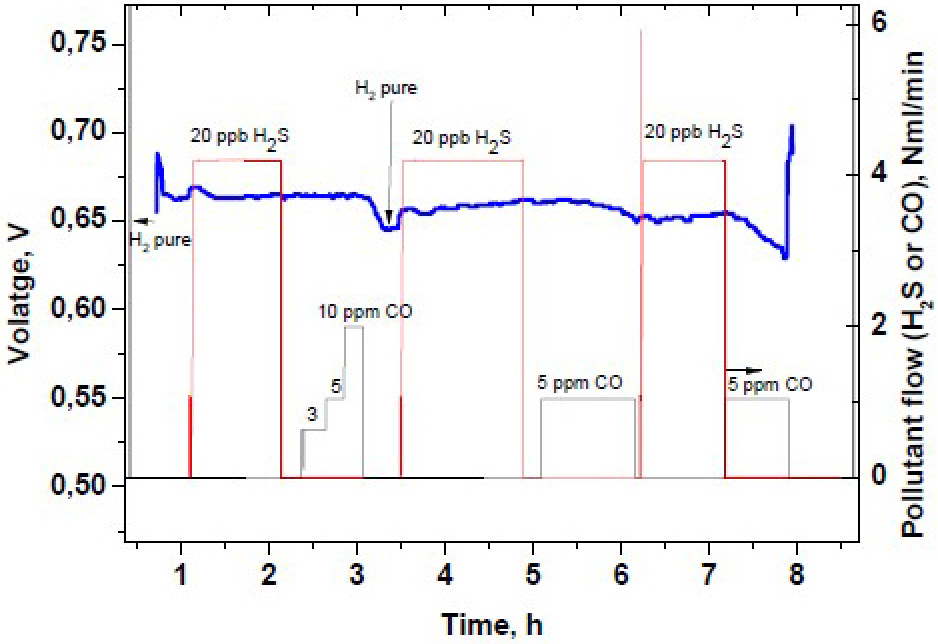

FIGURE 3. CEA-LANL pre-dosing experiments

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2016, LANL's hydrogen fuel quality efforts continued to investigate CO tolerance in order to assess the concentrations in existing fuel specifications. A test matrix was developed to compile findings into a format that will be made available to the fuel cell community. Also, using the fuel recirculation system, comparisons between recirculation vs. single-pass mode were completed using CO and H_2S.

The international collaborations with CEA and VTT through HyCoRA expanded to include impurity testing with CO and H_2S and these interactions should continue into FY 2017. Some of the work expected includes the completion of an international round robin and impurity testing using fuel cell stack systems. The work with IEC/TC 105/WG 11 concluded with the development and submission of the final draft technical specification for a polymer electrolyte membrane fuel cell testing protocol document.

In FY 2017, LANL will transition from their leadership in ASTM to focus more on the fuel quality, international collaborations, and the deployment of an in-line fuel quality analyzer.

REFERENCES

1. SAE J2719: Hydrogen Fuel Quality for Fuel Cell Vehicles, www.sae.org

2. Organization, I.S., *Hydrogen fuel — Product specification — Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles*, in *ISO TC 197*2012, ISO copyright office: Case postale 56 • CH-1211 Geneva 20.