VIII.4 Hydrogen Fuel Quality

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Collaborators/Partners
Japan Automobile Research Institute
European Union
WG-11
ASTM International
Air Liquide
California Fuel Cell Partnership
CONSCI

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 research and development (R&D) needed to develop science-based codes and standards
- Develop tools that can remove safety and hydrogen fuel quality barriers to the commercialization of fuel cells

Fiscal Year 2015 Objectives

- To carry out the duties of ASTM sub-committee chair for D03.14 gaseous hydrogen fuel efforts
- To install and validate a hydrogen recirculation system at LANL and evaluate its impact on the carbon monoxide (CO) poisoning of a low platinum loaded membrane electrode assembly (MEA)
- To demonstrate sensitivity of electrochemical analyzer to hydrogen sulfide
- To demonstrate an electrochemical analyzer capable of detecting 4 ppb hydrogen sulfide (H_2S) and 200 ppb CO in hydrogen with a response time <5 min
- Report findings/results to the DOE

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section (3.7.5) of the Fuel Cell Technologies Office 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 2015 Accomplishments

- Testing completed and results coordinated for Interlaboratory Study Program (ILS) 751- *Test Method for Determination of Trace* CO_2*, Ar,* N_2*,* O_2 *and* H_20 *in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis*
- Established ILS for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer
- Chaired two semiannual ASTM meetings for D03.14 Gaseous Hydrogen Fuel in December 2014 and June 2015
- Improved response time of analyzer to 200 ppb CO to less than 5 minutes
- Tested simultaneous poisoning with CO and H_2S: results indicate short-term exposure favors CO adsorption and poisoning effects are not additive
- Finalized the initial design of the prototype fuel quality analyzer
- Continued international collaborations with the Japan Automobile Research Institute (JARI), CEA, and VTT
- Completed baseline tests with new 25 cm^2 MEAs with results showing excellent agreement with JARI MEAs (membrane: DuPont XL100®, anode: 0.05 mg Pt/cm^2, and cathode: 0.1 mg Pt/cm^2)
- Sent new MEAs to CEA and received first set of data for direct comparison with the LANL-JARI results

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INTRODUCTION

The work performed in this project has been partitioned into three tasks: (1) R&D for fuel quality standards including international interactions, (2) in-line fuel quality analyzer development, and (3) contributions to ASTM standards development.

While steam reforming natural gas will make hydrogen affordable and available, it will produce trace amounts of CO and H_2S. The international team (International Organization for Standardization [ISO] TC197 WG-12) for "development of a hydrogen fuel product specifications for use in proton exchange membrane fuel cell applications for road vehicles;" (ISO 14687-2:2012) [1] and SAE J2719 [2] indicate acceptance levels of several contaminants. Although these contaminants are at sub-ppm levels, their effect on fuel cell performance is uncertain, especially since the total platinum content in the fuel cell MEA has been continuously lowered. Previously conducted fuel cell tests with the fuel specification indicated that ammonia, carbon monoxide, and hydrogen sulfide were the critical constituents most harmful to proton exchange membrane fuel cell performance and/or its durability. In FY 2015 LANL conducted fuel quality testing to evaluate the impact of these critical constituents on current fuel cell MEAs and has continued to engage the international community to incorporate the research results into future updates to these standards.

Although science-based standards for fuel quality have been established [1,2], there is still a need to provide the tools necessary to implement this standard. For example, the ISO and SAE standards have a maximum allowance of 0.2 ppm for CO and 4 ppb for H_2S [1,2]. LANL is helping this effort by providing leadership to ASTM in developing methods to determine the impurity content in the fuel that can be used to certify the hydrogen. Although the hydrogen grade would be certified periodically using these methods, it would be invaluable to have in-line analyzers to protect expensive fuel cell systems and components from these contaminants. LANL demonstrated proof-of-concept for an in-line fuel quality analyzer using various concentrations of CO at or below the levels in the aforementioned standard. In FY 2015 we optimized the MEA to reduce our response time to <5 min and have finalized a design for a prototype in-line fuel quality analyzer. Our goal is to provide a quick and cheap method of detection at various points in the supply chain. The successful commercialization of this product will have a positive impact on the safety of filling stations and the reliability of fuel cell vehicles. This work directly addresses the targets set in Table 3.7.6 of the Safety, Codes and Standards technical plan.

APPROACH

R&D for Fuel Quality Standards

LANL installed a recirculating system on the H_2 side in order to evaluate the impact of impurities while increasing H_2 utilization. This recirculation system was developed under collaboration with VTT (Finland) and represents a significant upgrade in the infrastructure available at LANL for fuel quality testing. In this report we present the first results obtained at LANL using this recirculation system. This system will be used extensively in all our upcoming international collaborations. LANL will continue to engage in collaborations with JARI, CEA (France) and VTT (Finland) to harmonize impurity testing with a view to updating the current fuel quality standards. Finally, LANL scientists were recently invited to participate along with several other countries in the development of an international document entitled, *Single Cell Test Methods –PEFC*.

In-line Fuel Quality Analyzer

The interaction of either H_2S or carbon monoxide in a hydrogen stream over a platinum surface results in inhibition of hydrogen dissociation, and inherently lower current output from an MEA operated at a constant voltage in a H_2 pump mode. The fuel quality analyzer is composed of an active area MEA $\leq$5 cm^2 with platinum-based electrodes. In FY 2015 the electrodes were optimized in order to improve the analyzer's response time. More specifically, by lowering the Pt loading and increasing the Pt particle size we were able to improve the analyzer's response time from a few hours (FY 2014) to <5 min (FY 2015).

RESULTS AND DISCUSSIONS

In-line Analyzer

LANL has continued tests for the development of an in-line hydrogen fuel quality analyzer and has successively made progress towards improving the sensitivity and response time. Our previous results (not shown) using a working electrode loaded with 0.067 mg-Pt/cm^2 and a reference electrode with 0.2 mg-Pt-Ru/cm^2 adhered to a 7-mil thick Nafion® membrane (N117) showed response to CO and H_2S at the SAE J2719 levels only after exposure for >1 h. Using new working electrodes containing 0.04 mg-Pt/cm^2, we tested the response of the analyzer to both CO and also H_2S at the SAE J2719 concentration levels, individually and simultaneously for different time periods. Figure 1 illustrates that this analyzer responds to these low concentration levels of CO and H_2S within minutes. This >100-fold increase in the response time is very encouraging. This analyzer also demonstrated a clear response within minutes after exposure to both CO and H_2S. At short exposure times, the poisoning closely followed the CO only poisoning data while at the

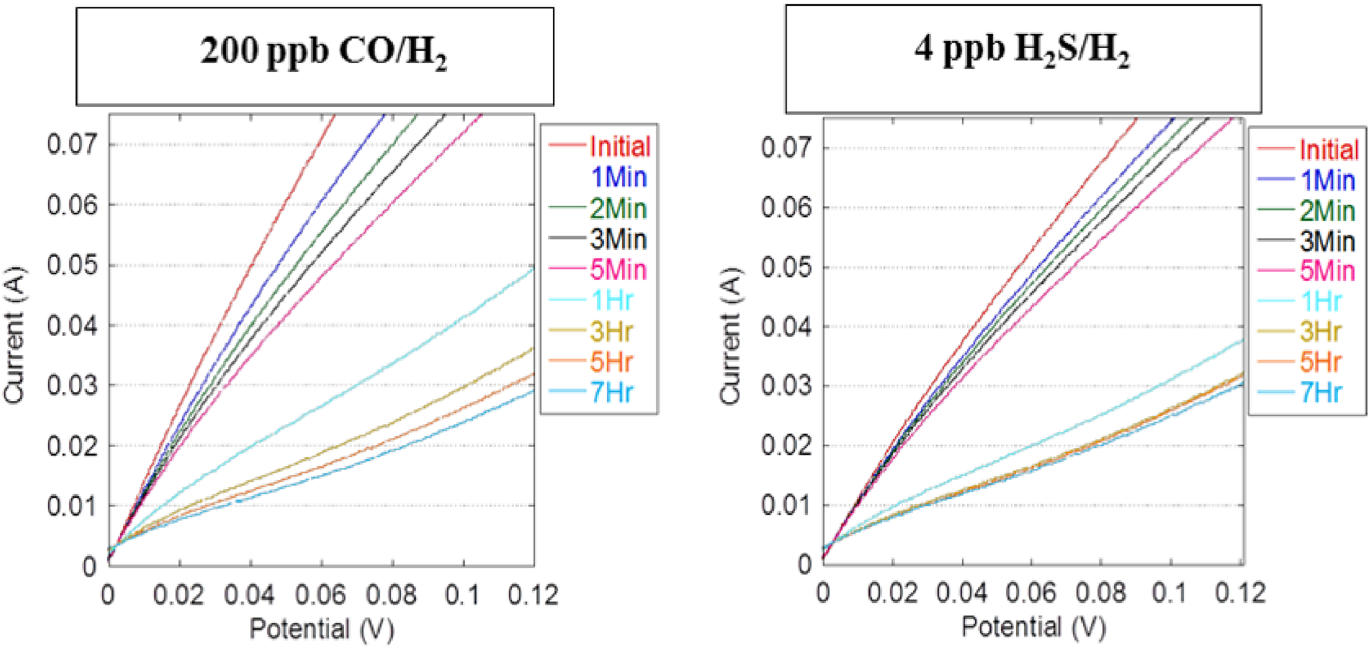


FIGURE 1. Analyzer (0.04 mg-Pt/cm2) response to 200 ppb CO (left) and 4 ppb H_2S (right) at various time intervals

longer exposure times the data is more representative of H_2S poisoning. These tests clearly demonstrate that our analyzer is capable of detecting multiple contaminants at the SAE J2719 levels, simultaneously within the time required for one fill in a station.

We also examined the long-term shelf life of one of our analyzer MEAs. We originally reported in 2014 the response during 7 h of exposure to 200 ppb CO (100 sccm flow rate) from an analyzer with a 0.1 mg-Pt/cm^2 working electrode. After over one year, we retested the same sample under similar conditions. The graphs (Figure 2) show the comparison of the analyzer performance. The baseline data of the analyzer before and after the one year storage is identical (red line) indicating that the membrane shows no sign of degradation and its humidification is identical in both the tests. However the data also indicate some ageing in the electrode resulting in slightly different poisoning effects in these two tests. This could potentially be due to contaminants adsorbed on the electrode during storage. This problem can be alleviated with a clean-up step. This phenomenon will be further examined in the lower loaded (0.04 mg-Pt/cm^2) MEAs in the future to determine analyzer durability.

Hydrogen Fuel Quality: International Collaborations*:*

LANL scientists have continued their efforts within Working Group 11 to advance the *Single Cell Test Methods –PEFC* document in successive stages to be presented as Committee Draft in September 2015 and projected to become a technical specification by November 2016. The document's scope is to provide guidance using performance-based tests to describe fuel cell materials and components. In addition, an internationally accepted document will allow uniform fuel cell testing and provide a basis for comparing test results from around the world. This document also details a standardized way to report test results.

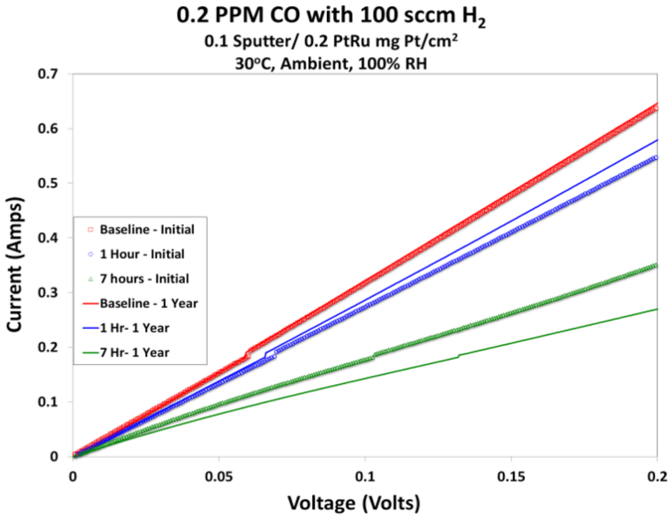


FIGURE 2. Comparison of analyzer response at baseline, and after exposure to 200 ppm for 1 h and 7 h. The data is shown for the initial analyzer response and the response after 1 year of storage of the analyzer MEA.

LANL completed baseline fuel cell tests with 25 cm^2 MEAs using both JARI and LANL hardware. These results agree well with those measured by LANL scientists at JARI's testing facility. These tests (graphs shown in Figure 3) confirmed and verified that the MEA performance from different manufacturers was similar regardless of hardware or test facilities. Figure 3a represents the break-in and polarization data with JARI hardware and LANL MEAs while Figure 3c represents the same data obtained with the newly developed LANL MEA and LANL hardware (blue curve is voltage and red is current density). A comparison of Figures 3a and 3c clearly shows little to no effect of varying hardware with the LANL MEA. Figure 3b shows the current data during the conditioning portion of the break in (first 2 hours of graphs in in Figures 3a and 3c) of the JARI MEA (in blue) and old LANL MEA (yellow). This illustrates that the new LANL MEA (Figures 3a and 3c) performs identical to the JARI MEA irrespective of hardware. The low performance of the old MEA (yellow in Figure 3b) was due to the use of an unoptimized ionomer and has been corrected to obtain these consistent results. This baseline testing is crucial in providing confidence that all future tests at the various tests sites can be directly compared with one another without the need for any extraneous calibration or data manipulation. LANL has now extended these studies to involve CEA and all three organizations will perform impurity testing to harmonize international standards.

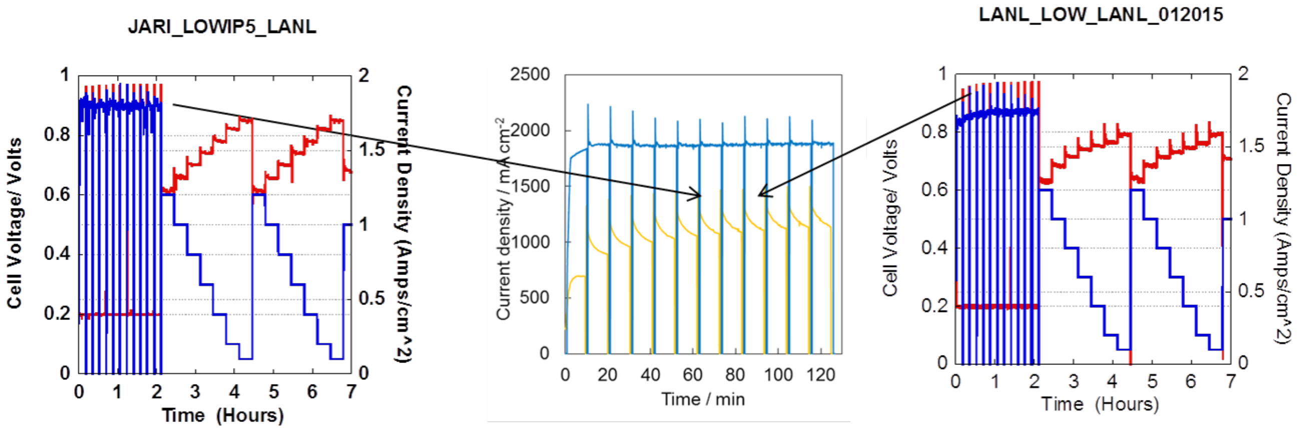
In this FY 2015, we installed a hydrogen recirculation system similar to the one developed by VTT (Finland) in their HyCoRA (Hydrogen Contaminant Risk Assessment) project. Here, we report life-test results of a 25 cm^2 polymer electrolyte fuel cell with an anode and cathode of 0.05 and 0.1 mg Pt/cm^2, respectively. The cell was operated at 80°C, 100% relative humidity and 150 kPa in the presence of 200 ppb CO. The hydrogen fuel utilization was initially run at 50% with approximately 90% of the unused H_2 returning into the fuel stream. Under these conditions we observed a 50 mV voltage loss over 100 hours of operation at 1 A/cm^2 (see Figure 4a, left). Under identical test conditions but with no recirculation we observed only a 38 mV voltage loss over the same time period (Figure 4b, right). This demonstrates the effect of recirculation in increasing the impact of impurities on the fuel cell performance. In the single pass system any of the 200 ppb CO that does not adsorb on the Pt is vented while in the recirculation system, this CO is once again sent into the inlet of the fuel stream thus leading to the greater (almost 30%) voltage degradation rate. More systematic studies are planned where we will evaluate the effect of varying the H_2 stoichiometry and recirculation rate on this degradation. Finally we will combine these results with simulated drive cycle operations of fuel cells, to provide better guidance on fuel quality standards.

Contributions to ASTM Standards Development

LANL scientist serves as subcommittee chair for D03.14 Gaseous Fuels. Hydrogen and fuel cells held two semiannual meetings in FY 2015. The ILS 775, ASTM D7649 - *Test Method for Determination of Trace CO_2, Ar, N_2, O_2 and H_20 in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis* was completed and the experimental results were discussed by the participating test labs. The results differed between the test sites and it was concluded that unique testing apparatus should not be incorporated into a standardized test methods. Based upon these discussions of the data, a revision of the test method was called for and the new test method will incorporate the findings of the ILS. There is also an additional ILS that is planned to evaluate cavity ring-down spectroscopy which will be initiated as soon as adequate test sites are identified.

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2015, the analyzer electrode was optimized to improve the response time to 200 ppb CO/4 ppb H_2S from >1 hour to <5 minutes. LANL also installed an H_2 recirculation system and initial results observed a 30% increase in the voltage degradation due to CO poisoning.



(a) JARI Hardware with IP#5 (b) JARI Hardware and MEA (c) LANL Hardware with IP#5

FIGURE 3. Baseline testing shows great agreement (i) MEAs (a) vs. (b); (ii) hardware (a) vs. (c); and (iii) facilities (b) and (c)

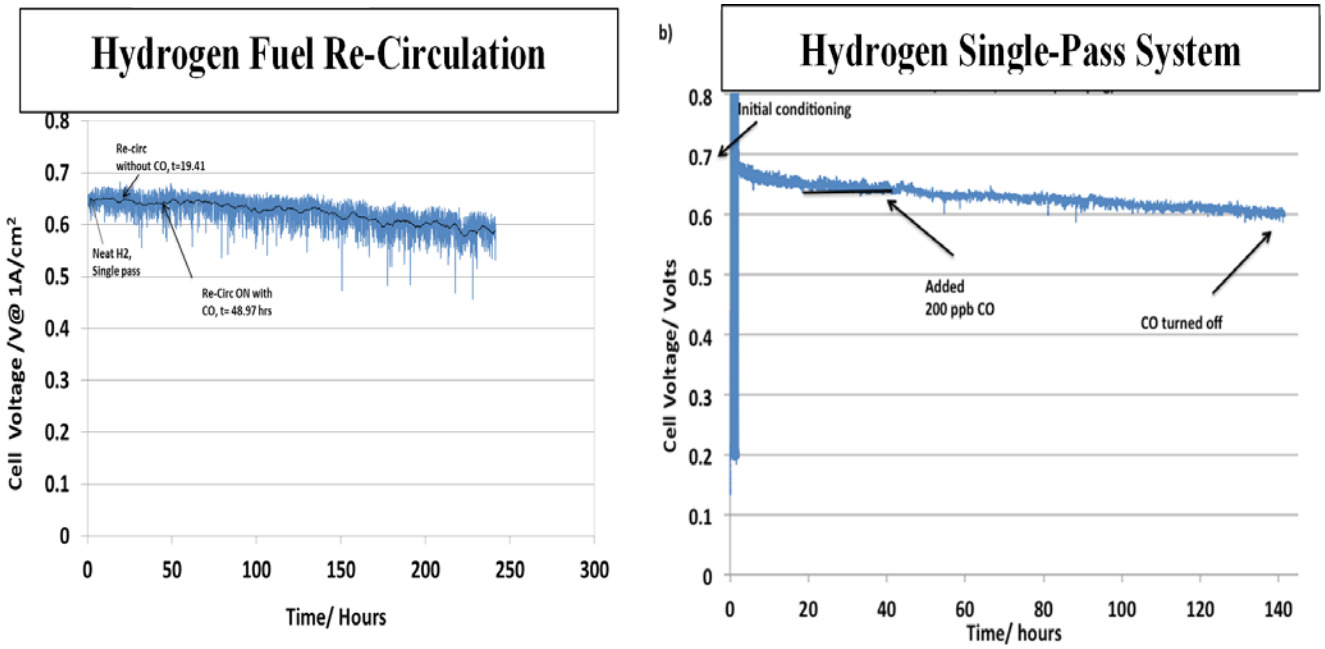


FIGURE 4. Fuel cell voltage at a current of 1 A/cm^2 when operating under H_2 + 200 ppb CO with H_2 recirculation (left) and H_2 single-pass (right)

LANL also completed baseline fuel cell performance testing as part of an international collaboration with JARI and CEA. Finally, in FY 2015 LANL continued to provide leadership to the ASTM subcommittee D03.14 on hydrogen and fuel cells. LANL will work on the following tasks in FY 2015.

- Continue with new standards development – ILS coordination
- Coordinate a workshop on in-line fuel quality, December 2015 ASTM meeting
- Optimize operating conditions of analyzer to further improve sensitivity
- Work with hydrogen fuel suppliers to better understand S-upsets
- Study impact of humidity
- Evaluate long-term durability
- Design and build prototype analyzer by end of FY 2016 to be evaluated at an independent test site
- Continue working with international collaborators
- Initiate an international round robin for impurity testing
- Compare performance degradation with and without **recirculation system** and quantify effect of anode recirculation on CO poisoning of proton exchange membrane fuel cells at different utilizations

REFERENCES

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