Fuel Quality Assurance Research and Development and Impurity Testing in Support of Codes and Standards

Tommy Rockward (Primary Contact), Eric Brosha, Chris Romero, and Rangachary Mukundan
Los Alamos National Laboratory (LANL)
P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 667-9587
Email: trock@lanl.gov

DOE Manager: Laura Hill
Phone: (202) 586-8384
Email: Laura.Hill@ee.doe.gov

Project Start Date: October 1, 2006
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop a low-cost, fast-response device (analyzer) to measure impurities in a dry hydrogen fuel stream at or above the SAE J2719 levels.
- Test the analyzer in real-world environments.
- Develop a better understanding of the analyzer's workings to identify best materials and device configurations for improved analyzer performance.

Fiscal Year (FY) 2018 Objectives

- Develop an external humidification system and evaluate membrane hydration state as a function of membrane thickness, gas diffusion layer composition, and gas flow rate.
- Investigate the role of ionomer in the electrode in order to optimize conditioning time and improve the analyzer's signal to noise.
- Evaluate adsorption/desorption characteristics of carbon monoxide (CO) in order to implement a clean-up strategy for resetting the analyzer.
- Identify location for field trials and plan the system installation.
- Install the analyzer at a hydrogen station and demonstrate a viable operating mode.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan[1]:

(G) Insufficient Technical Data to Revise Standards

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

Contribution to Achievement of DOE Hydrogen Safety, Codes and Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office MYRDD Plan. The MYRDD milestones that align with LANL's work are 2.2, 2.6, 2.15, 2.17, and 3.2.

- Investigate the causes of drift in the baseline current of the analyzer in order to identify the mechanism of current degradation and develop strategies to stabilize the baseline. (1Q, FY 2018)

FY 2018 Accomplishments

- Developed a method to create a strategy to externally humidify the analyzer and produce a stable baseline in order to implement our technology at hydrogen refueling stations where no water is available.
- Enhanced the electrode performance by reducing ionomer content by a factor of 10, which inherently increased access to platinum (Pt) sites and lowered its resistance by an order

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

of magnitude and increased the overall performance from 5 mA to well above 25 mA.

- Tested a novel operating mode that incorporated a clean-up strategy and implemented that in the field.
- Demonstrated analyzer response time of <5 min using 100 and 200 sccm flow rates with 500 ppb and 50 ppm CO/H_2 concentrations. Analyzer's response time is less than the time required to refuel two fuel cell vehicles.
- Successfully conducted testing with 200 ppb CO/H_2 (SAE International level) and met the goal of obtaining a response within 2.5 min by adjusting the alarm trigger level.
- Completed the planning and installation of analyzer in the field (H2Frontier) and conducted on-site baseline measurements while adding wireless capabilities for remote testing.

INTRODUCTION

In 2012 two hydrogen fuel specifications (SAE J2719 and ISO 14687-2) were developed. These specifications outlined the allowable non-hydrogen constituents' levels for hydrogen fuel to be used for fuel cell road vehicles. Research indicates that several of these non-hydrogen constituents can be harmful to fuel cell performance in trace amounts and recommends avoiding them. And, as hydrogen refueling stations are being built, there is an immediate need to implement fuel quality assurance measures to prevent damage to fuel cell vehicles or fleets. While the hydrogen grade at these filling stations would be certified periodically, having a low-cost, fast-responding hydrogen contaminant detector to measure impurities at or above the levels in the fuel specification would be invaluable to vehicle owners, station owners, and fuel suppliers. In FY 2015, LANL scientists demonstrated proof-of-concept for a fuel quality analyzer and are now (FY 2018) in the planning and development stages for field trial testing their device. The results of the field trials testing guide the research on the fundamental understanding of the working mechanism of the analyzer to enable advances in this technology.

APPROACH

Research on fuel impurities conducted over the years at LANL indicates fuel cells with membrane electrode assemblies (MEAs) made of low-surface-area Pt-type electrodes as being the best sensors for detecting surface-adsorbing contaminants such as CO and hydrogen sulfide (H_2S). Both of these contaminants can chemisorb onto active Pt sites and reduce activity for hydrogen dissociation and inherently the overall fuel cell performance. Our findings demonstrated that the overall performance was impacted more as the contaminant concentration increased. In order to mitigate or minimize performance losses due to these species, the Pt loading was increased or Pt-alloys were introduced. Our work here proposes a device that uses an asymmetric MEA that has ultra-low-loaded Pt as the working electrode to detect minuscule amounts of adsorbates and a relatively higher amount of Pt or PtRu (platinum;ruthenium) at the reference electrode to alleviate impacts of impurities and maintain stability. We operated the device as an electrochemical hydrogen pump because there is no continuous source of oxygen or water at the hydrogen refueling station, and this method does not require oxygen. However, it does require proper membrane and electrode hydration. To overcome this challenge, we developed a wicking scheme to provide the necessary hydration.

RESULTS

LANL scientists have continued to make progress on the development and deployment of a hydrogen contaminant detector. Several fundamental improvements and hardware modifications were made to enhance the analyzer's performance while also incorporating the appropriate measures for field trials. Fundamental improvements such as optimizing the ionomer content improved Pt access, allowing larger baseline currents to be obtained while simultaneously reducing the conditioning time. The implementation of periodically applying 1.5 V was proven effective as a clean-up strategy for desorbing surface contaminants. These findings (shown in Figures 1, 2, and 3) made it possible to demonstrate an operating mode for the analyzer to be used during the field test trials.

Figure 1 shows the response of the analyzer when exposed to 100 sccm flow rate of ultra-high-purity hydrogen followed by the addition of two different CO concentrations (500 ppb and 50 ppm) with 1.5 V applied for 30 seconds every 15 minutes. The analyzer operated at 30°C and ambient pressure with a dry hydrogen stream. By applying the external voltage using a Gamry potentiostat, we were able to maintain performance within an operating window and establish an alarm trigger level. We set the alarm trigger level to 30 mA and monitored the time required for the performance to drop below it during CO exposure. Our desired response time was set for less than 5 minutes. During the challenge with 500 ppb CO in hydrogen, our analyzer responded in 2.79 minutes while the 50 ppm CO challenge yielded a response time of 33 seconds; both times met our desired response time goal.

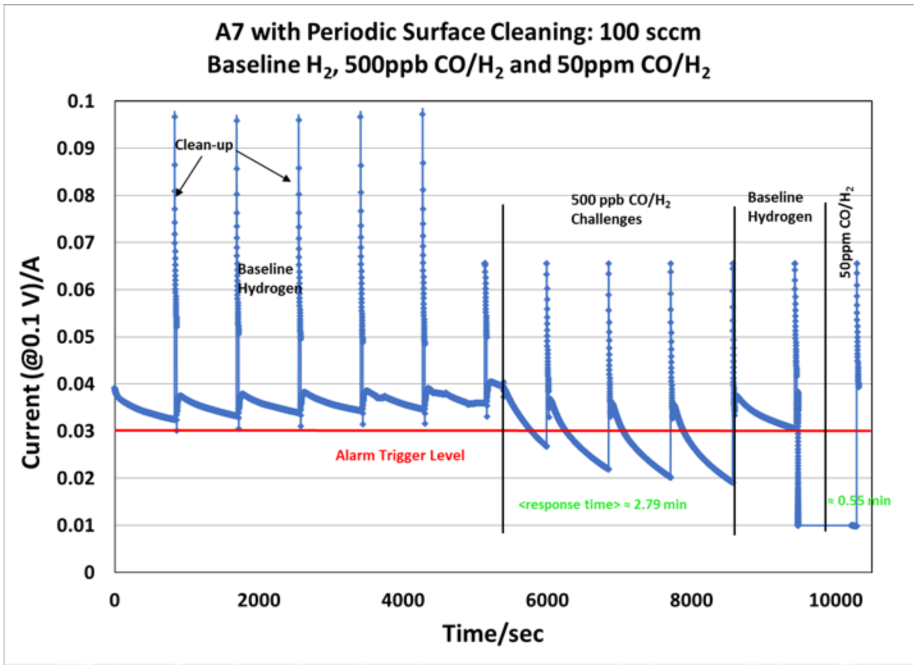

Figure 1. Analyzer exposed to 500 ppb and 50 ppm CO/H_2 using 100 sccm flow rate with periodic 1.5 V clean-up steps

Figure 2 shows the impact of flow rate on the analyzer response time using identical conditions and operating parameters as mentioned above. We increased the flow rate to 200 sccm. These results unexpectedly showed a lower baseline current while operating on the ultra-high-purity hydrogen; this is possibly due to membrane drying. We observed that the response times at both concentrations met our goal but had increased from the times measured using 100 sccm as the flow rate. The response times were 3.48 and 1.5 minutes for 500 ppb and 50 ppm CO concentrations, respectively.

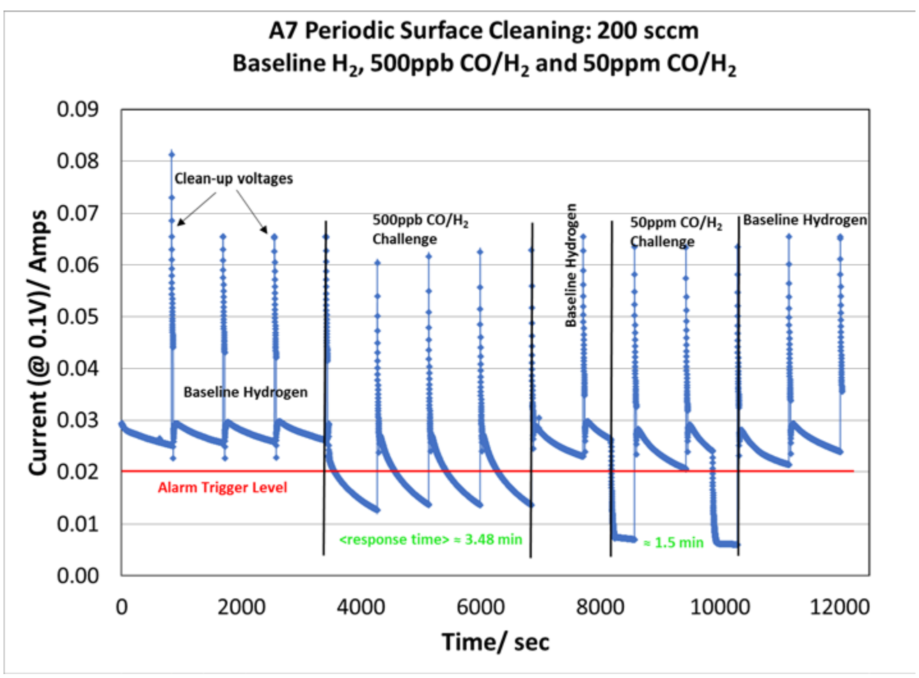

Figure 2. Analyzer exposed to 500 ppb and 50 ppm CO/H_2 using 200 sccm flow rate with periodic 1.5 V clean-up steps

Results shown in Figures 1 and 2 were useful in helping to determine an operating mode for our field trials; however, the CO concentrations used were above the SAE level. In Figure 3, we challenged the analyzer using 200 ppb CO in hydrogen. Using identical conditions as previously stated, we observed the analyzer performance began to slowly decay, which is indicative of its sensitivity to 200 ppb CO. We also found the current drop did not fall below the initial trigger alarm level within the desired response time goal of 5 minutes. The average response time to surpass the alarm trigger level was measured at 6.9 minutes. In order to achieve our response time target we were able to adjust the trigger level, which reduced the average response time to 2.5 minutes.

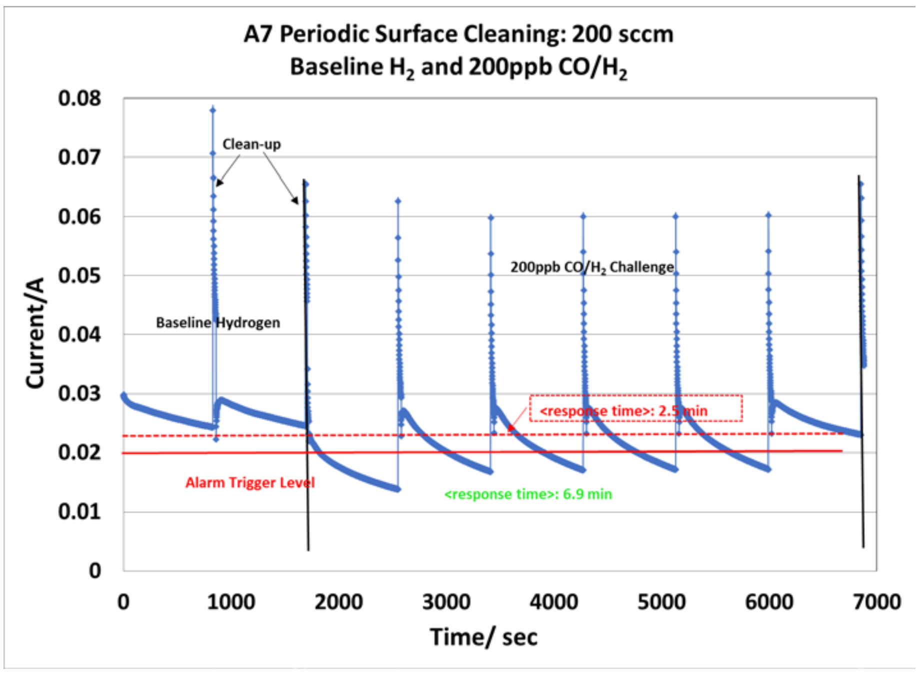

Figure 3. Analyzer exposed to 200 ppb CO/H_2 using 200 sccm flow rate with periodic 1.5 V clean-up steps

During FY 2018, LANL was successful in identifying a partner to allow field testing for the analyzer. H2Frontier, Inc. in Burbank, California, a long-time collaborator of LANL's sensor team, agreed to provide fuel sampling to our device. In preparation for the field trials, several phases were established to ensure safety and compliance as well as a functional system. In July 2017, LANL staff visited the H2Frontier site to discuss the installation and planning phase. The team identified several potential constraints in the field such as temperature control of the enclosure, gas access ports, system location, remote monitoring and testing, etc., and established timely solutions to each in order to successfully install and the test the device in March 2018. The analyzer in the field is currently equipped with remote monitoring and control with experiments being designed and controlled from LANL.

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2018, we successively made improvements to the analyzer prototype. We modified components to stabilize the membrane hydration (i.e., high-frequency resistance), varied the ionomer content to stabilize the baseline as well as improve conditioning, and implemented a clean-up strategy to reset the device after exposure to contaminants. In doing so, we were able to demonstrate sensitivity to 200 ppb CO in dry H_2 in less than the 5 minutes. Our efforts also included identifying a location in the field for the analyzer to be tested and its successful installation and testing. Furthermore, our staff also installed remote access software and a valve control system to operate experiments from Los Alamos.

We have decoupled our upcoming activities into two sections—field experiments and R&D.

1. In the field experiments conducted at H2Frontier, we will:

- Validate baseline stability and identify factors affecting stability
- Test analyzer periodically with challenges of CO and during reformer startup to assess response stability
- Develop Gen 2 analyzer and electronics design
- Look for industrial partners to transition this work to.

2. Our R&D will consist of the following:

- Eliminate the humidification system by using advanced membranes
- Improve our understanding of analyzer working mechanisms (based on field trials feedback)
- Extend analyzer work to include H_2S and ammonia (NH_3)
- Incorporate impedance spectroscopy into analyzer
- Design analyzer for operation under pressure.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. 2017 R&D 100 winner for hydrogen safety sensor work.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. R. Mukundan, et al. “Electrochemical Approaches to Hydrogen Contaminant Detection.” International Hydrogen Infrastructure Workshop, Boston, MA, September 2018.