Fuel Quality Assurance R&D and Impurity Testing in Support of Codes and Standards

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

Fiscal Year (FY) 2019 Objectives

- Evaluate the performance of the LANL HCD in a hydrogen refueling station (HRS).
- Improve the design of the humidification system in the current HCD to decrease maintenance requirements.
- Develop an alternative membrane for the HCD that has the potential to work without external humidification.
- Demonstrate stable baseline pumping current with alternative HCD design.

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 Plan[1]:

- Insufficient Technical Data to Revise Standards
- No Consistent Codification Plan and Process for Synchronization of R&D and Code Development.

Contribution to Achievement of DOE Milestones

This project will contribute to achievement of the following DOE milestones from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone: Down-select membrane electrode assemblies based on performance of polybenzimidazole (PBI) or tin pyrophosphate (TPP) membranes.
- Milestone: Quantify baseline response of membrane electrode assembly (MEA).

FY 2019 Accomplishments

- Demonstrated successful field operation of LANL's HCD technology with an external humidification system.
- Identified a commercialization partner for this technology through a successful Technology Commercialization Fund (TCF) proposal.
- Down-selected a PBI-based membrane to eliminate external humidification from the LANL HCD design.
- New HCD design demonstrated a stable baseline current response in clean hydrogen even when the flowrate was varied.

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

INTRODUCTION

In 2012 two hydrogen fuel specifications (SAE J2719 and ISO 14687-2) were developed. These specifications outlined the allowable levels of non-hydrogen constituents in the 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. With the rollout of HRSs, especially in California, 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 the HRSs would be certified periodically, having a low-cost, fast-responding HCD to measure impurities at or above the levels in the fuel specification would be invaluable to vehicle owners, station operators, and fuel suppliers. In FY 2015, LANL scientists demonstrated proof-of-concept for a fuel quality analyzer and successfully field tested this device in FY 2019. The current LANL HCD technology uses a Nafion membrane and utilizes an external humidification system to maintain its conductivity and is ready for commercialization. While this design has been extremely successful at detecting contaminants in the fuel stream, the elimination of the humidification system will have profound implications on the flexibility of this device and its widespread deployment. Therefore, LANL has initiated a multi-year program to develop novel electrolytes, electrodes, and operating strategies required to successfully design an HCD that can operate in dry hydrogen at higher pressures without the need for a humidification system.

APPROACH

Research on fuel impurities conducted over the years at LANL indicates that fuel cell MEAs made with low-surface-area Pt-type electrodes are the best for detecting surface-adsorbing contaminants such as CO and 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 dosage increased and active Pt surface area decreased. In order to mitigate or minimize performance losses due to these species, the Pt loading was increased or Pt alloys like Pt-Ru for CO tolerance were introduced. Our work here proposes a device that uses an asymmetric MEA that uses ultra-low-loaded Pt as the sensing electrode to detect minuscule amounts of adsorbates and a relatively higher amount of Pt or PtRu at the counter electrode to alleviate impacts of impurities and serve as a pseudo-reference electrode. The operation of the device as an electrochemical hydrogen pump instead of a fuel cell greatly simplifies the design and eliminates the need for air/oxygen. However, it does require proper membrane and electrode hydration. To overcome this challenge, we developed and patented a wicking scheme to provide the necessary hydration and demonstrated this scheme in a HRS. The current research effort is targeted at alternate membrane development in order to eliminate this external humidification system while maintaining HCD baseline stability and target gas sensitivity.

RESULTS

In FY 2018 several fundamental improvements to the HCD design were made to enhance its performance while also rendering it suitable for deployment in the field. Improvements such as optimizing the ionomer content improved Pt accessibility, allowing larger baseline currents to be obtained while simultaneously reducing the conditioning time. The implementation of a 1.5 V pulse applied periodically to the HCD was proven effective as a clean-up strategy for desorbing surface contaminants. Temperature control, flow control, and communications were incorporated into the HCD allowing its successful installation at the H2Frontier HRS in Burbank, California.

The loss in pumping current at 0.1 V of LANL HCD-1 under exposure to various concentrations of CO measured in operando at the H2Frontier filling station is illustrated in Figure 1. This calibration curve shows a logarithmic dependence of hydrogen pumping current on the CO concentration in the H_2 stream despite the data being collected in the field and not under highly controlled laboratory conditions. This response is ideal for commercial detector applications where both high detector sensitivity for low contaminant concentrations and a wide detection range are required. For example, a 40% loss in pumping current was observed for 200 ppb of CO (SAE J2719 permissible level), while the loss at 1 ppm CO was 60% and reached over 75% in the presence of 10 ppm CO. The percentage loss in current is measured at the end of each 0.1 V hold step just before the application of the 1.5 V clean-up pulse. This calibration curve can be used to quantify the amount of CO present in the station’s product gas in real time and could be used to build a low-cost commercial product that provides real-time digital display of CO levels in the hydrogen being dispensed at the station. This is contingent upon a stable calibration curve and how well the HCD maintains calibration over time.

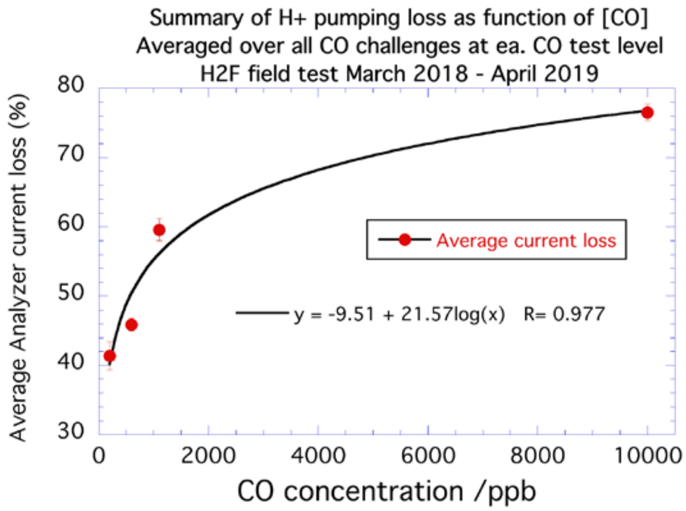

Figure 1. Plot of percent (%) hydrogen pumping current loss versus CO concentration in first in operando calibration performed at H2Frontier in Burbank, California.

The field test data collected to date suggest that the HCD design exhibits minimal drift in either sensitivity or calibration. Figure 2a is a plot showing the complete HCD-1 CO challenge history collected in the field from the initial installation in March 2018 until its decommissioning in September 2019. Although CO challenge data for 579 and 200 ppb are limited, the percentage current loss for all the 1 ppm challenges over the 9-month period is very reproducible. The current loss measured in March 2019 (59.1%) falls within the average values recorded from June 2018 to November 2018 despite the HCD being placed in a standby mode for 4 months. The average current loss for 1 ppm CO over 13 challenges is 59.6 ± 1.4% error (1 standard deviation). The HCD response to 579 ppb CO measured before and after a 161-day standby period was also identical. Figure 2b illustrates a similar response from a second detector (HCD -2) that was installed in September 2019. This HCD has interdigitated (instead of straight channel) flow fields and a larger water reservoir requiring less frequent maintenance. This HCD-2 also shows similar stability and sensitivity to CO in the H_2 stream, confirming good detector-to-detector reproducibility. Currently LANL is working with Skyre, Inc. as part of a TCF award to develop low-cost packaging for this analyzer that will be important for commercialization.

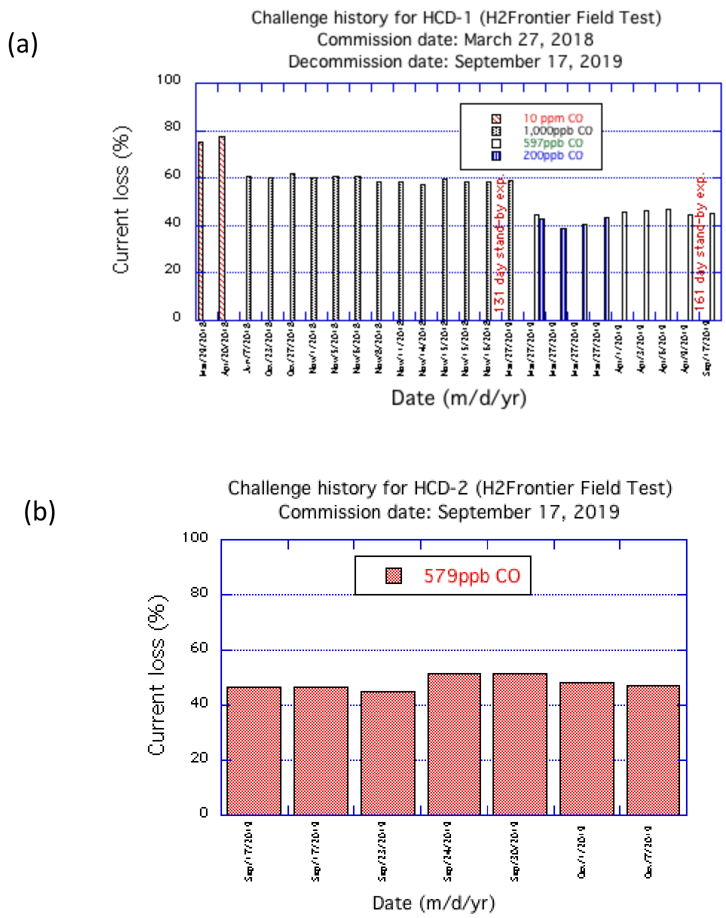

Figure 2. Plot of all CO challenges performed on LANL HCDs since the start of field trial experiments at H2Frontier: (a) HCD-1 from March 2018 to September 2019 and (b) HCD-2 from September 2019 to present.

In FY 2019, LANL initiated an effort to replace the Nafion membrane with an advanced membrane capable of operation without a humidification system. Three different TPP membranes were developed for this project. The proton conductivity of the TPP material (SnP_2O_7) is controlled by the P/M ratio where P is the phosphorus content and M is the tin content. High proton conductivities are obtained when the P/M ratio is greater than 2 with the conductivity increasing with increasing P/M ratio. However, the higher P/M ratios also make this material hygroscopic with less than desirable mechanical properties. Therefore, the casting of the TPP material with a Nafion binder is required in order to make dense mechanically stable membranes for practical use. The strength and conductivity of these composite membranes is controlled by the TPP/Nafion ratio with the 90:10 membrane providing higher conductivity and the 80:20 membrane providing better mechanical stability. Three different HCDs were built with these three membranes and were labelled ATPP16, ATPP17, and ATPP18. The electrochemical impedance spectroscopy (EIS) data from the three analyzers is illustrated in Figure 3a. The HCD labeled ATPP18 with a P/M ratio of 9.3 and an 80/20 TPP/Nafion ratio showed the highest conductivity and least resistance. This HCD also demonstrated the least electrode resistance, while HCD ATTP17 showed the highest resistance (both high and low frequency) with an 80/20 TPP/Nafion ratio and P/M of 4.6. It should also be noted that ATTP18 had a higher loading (1.5 mg_{Pt}/cm^2) at the working electrode, which is responsible for the lowest electrode conductivity (low frequency resistance). These results indicate that high P/M ratios can be beneficial to both lower membrane and electrode conductivities while higher TPP/Nafion ratios are beneficial to the membrane conductivity.

A series of PBI membranes were also prepared with varying concentrations of phosphoric acid (H_3PO_4) content, and the effects of acid loading on membrane conductivity were studied. Figure 3b shows the results of EIS measurements made on a series of membranes fabricated in-house as the H_3PO_4 concentration is varied from 5 M to 10 M to 15 M. For these experiments, commercial high Pt-loaded gas diffusion electrodes (without ionomer) were utilized. Figure 3b illustrates that both high frequency resistance (ionic conductivity) and low frequency resistance (electrode resistance) are a function of acid loading, and the combined effect is to greatly impact hydrogen pumping current through the HCD. It should be noted that the pumping current was significantly increased (up to 100 mA) by decreasing the low frequency resistance from >15 Ohms (APBI 13) to <1 Ohm for the 15 M phosphoric acid doped PBI analyzer with high Pt loading (APBI14).

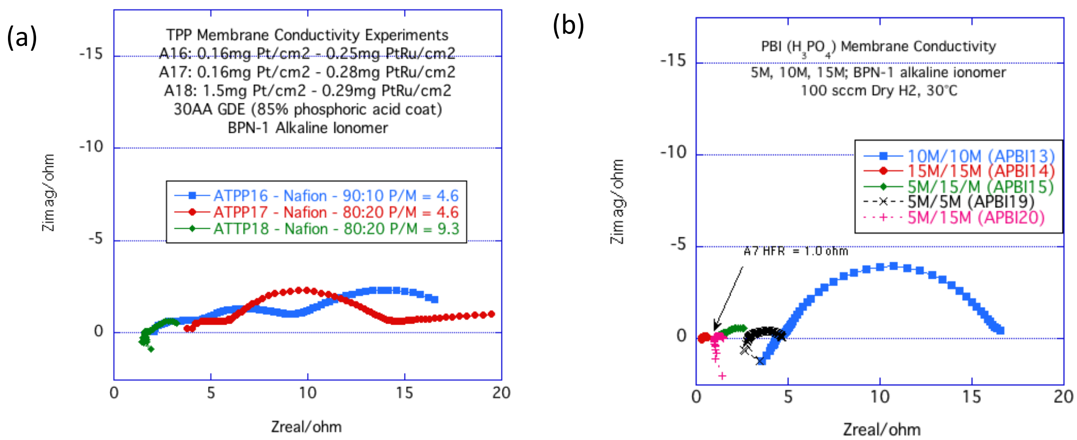

Figure 3. EIS spectra of three different (a) TPP and (b) PBI membranes incorporated into analyzers

Figure 4a illustrates the strong water dependence of the LANL HCD technology when a Nafion membrane is used. The internal electrode/electrolyte humidification using the water wicking scheme that permits the operation of the HCD in a hydrogen pumping mode even when sampling dry hydrogen streams results in a flow rate dependence. This is because higher flow rates cause faster evaporation and a change in the balance of water uptake from the reservoir and water loss from evaporation resulting in decreased membrane conductivity and lower pumping current. As the dry H_2 flow rate is increased from 50 sccm to 100 sccm, the baseline current at 0.1 V applied voltage drops from 42.5 mA to 40 mA. This is not a problem so long as the internal reservoir is replenished with water and the flow rate of the hydrogen sample gas is fixed (typically at 100 sccm). Figure 4b shows one of the first PBI-based HCD devices tested at LANL. Because the proton conductivity of this membrane is not dependent on external humidification, the pumping current is independent of hydrogen flow rate. However, comparison of Figure 4b to the pumping currents of the Nafion HCD cell in Figure 4a shows a much lower hydrogen pumping current of 4.5 mA for the PBI-based device compared to 40 mA for the Nafion-based device. However, the baseline current for the PBI device is independent of flow rate. Having successfully demonstrating a stable baseline, future work will be focused on PBI membrane optimization and electrode design for improved HCD sensitivity.

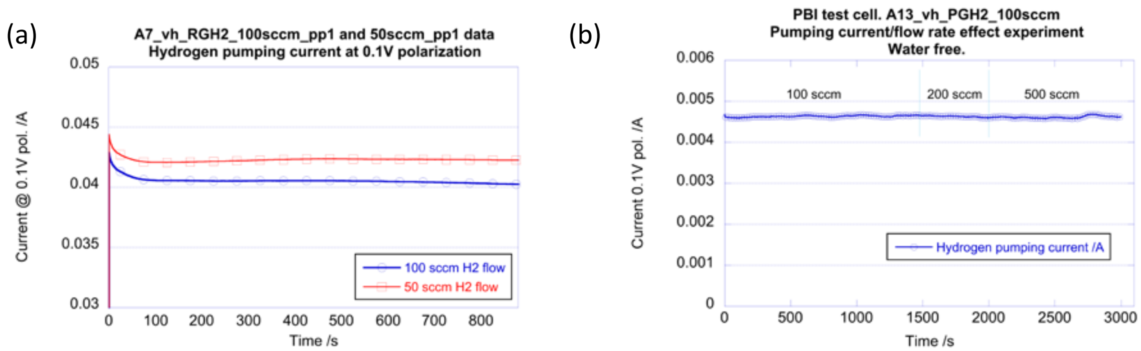

Figure 4. The baseline hydrogen pumping current at different flow rates on (a) Nafion-based HCD with external humidification and (b) PBI-based HCD without any external humidification, showing hydrogen pumping current independent of water and flow rate in PBI-based HCD

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2019, we successively field tested a LANL HCD at the H2Frontier Station in Burbank, California. This HCD maintained excellent baseline stability and sensitivity to CO over the course of this field test. Calibration curves obtained in the field confirm the ability of this HCD to quantitatively track CO concentration at or below the SAE J2719 level of 200 ppb in the hydrogen fuel. LANL is currently working with Skyre, Inc. as part of a TCF to further advance this technology. LANL also evaluated two alternate membrane technologies that have the ability to operate under dry conditions, thus eliminating the need for an external humidification system. The PBI-based membrane was down-selected for this task and demonstrated stable baseline under varying flow rates of dry H_2. The following tasks will be performed in the coming years.

- Improve our understanding of the effect of impurities on hydrogen pumping current, especially with novel membranes operating without humidification.
- Develop sensing electrodes for non-humidified HCD with sufficient sensitivity to CO.
- Extend HCD work to include H_2S and NH_3.
- Incorporate EIS into HCD for potential operation in environments with varying temperature and pressure conditions.
- Design HCD for operation under high pressure.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

Technology Commercialization Fund (TCF) award from DOE to work with Skyre, Inc. to commercialize the field tested LANL HCD technology.

FY 2019 PUBLICATIONS/PRESENTATIONS

A report and presentation were provided to the National Renewable Energy Laboratory along with an operation LANL HCD for testing and evaluation.