VIII.3 Hydrogen Fuel Quality

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- Smart Chemistry, Sacramento, CA
- CEA-Liten, Grenoble, France
- VTT, Helsinki, Finland
- International Organization for Standardization (ISO)/ Technical Committee (TC) 197/Working Groups (WG) 27 and 28

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

Overall Objectives

- Support the Hydrogen Safety, Codes and Standards subprogram through:
  - Providing leadership to hydrogen fuel quality efforts.
  - Performing the research and development (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.
  - Participation in working groups.

Fiscal Year 2017 Objectives

- Evaluate the effect of critical fuel impurities on the performance of membrane electrode assemblies (MEAs) with low loadings (A/C: 0.05/0.10 mg Pt/cm^2).
  - Test MEAs in two modes (hydrogen single pass and re-circulation).
  - Test the impact of fuel contaminants at the SAE J2719/ISO 14687-2 levels.
  - Disseminate results.
- Demonstrate a prototype fuel quality analyzer capable of detecting fuel impurities in dry hydrogen at the SAE J2719 specification levels.
  - Test the prototype for a fuel quality analyzer.
  - Optimize sensitivity to CO.
  - Operate analyzer under dry conditions.
  - Investigate clean-up strategies.

Technical Barriers

This project addresses the following technical barriers from Section 3.7.5 Hydrogen Safety, Codes & Standards of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(F) Enabling National and International Markets Requires Consistent RCS

(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 2017 Accomplishments

- Performed R&D to demonstrate that low-loaded MEAs are not tolerant to SAE J2719 level of impurities (both CO and H_2S), especially when operated in re-circulation mode.
- Continued a parametric study of impurities to quantify CO and H_2S tolerance levels of low-loaded MEAs to establish data sets to assist in the advancement of developing predicative mechanistic models. This study is critical in determining the impurity tolerance levels of low-loaded MEAs under various operating conditions.
- Developed an in-line fuel quality analyzer and demonstrated its capability of detecting low CO concentrations in dry hydrogen. Additional performance capabilities include:
  - Demonstrated CO sensitivity of <200 ppm.
  - Demonstrated response time <10 min.

- Demonstrated sustained operation under dry H_2 for >1 mo.
- Developed prototype (patent application filed).
- Demonstrated the ability to reset analyzer after poisoning.

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INTRODUCTION

The FY 2017 work performed in this project has two distinct tasks: (1) R&D for fuel quality standards including international interactions and (2) in-line fuel quality analyzer 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 (ISO TC197 WG-12) for "development of hydrogen fuel product specifications for use in proton exchange membrane fuel cell applications for road vehicles" (developed standards ISO 14687-2:2012) [1] and SAE J2719 [2], which 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. 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, 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 has 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. We optimized the MEA response time to <10 min (approximate time for two fuel refills) 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

In our fuel impurity testing, we are continuing to use MEAs produced by Ion Power. Here we report fuel cell results for fuel impurity studies that were conducted on 25 cm^2 cells. In this report we summarize the results obtained with both high (0.4 mg Pt/cm^2) and low (0.15 mg Pt/cm^2) platinum loaded MEAs. Our overall objective was to test MEAs with total platinum loadings equivalent to the 2015 DOE target loading, 0.15 mg Pt/cm^2 total. X-ray fluorescence results of the original set of MEAs provided by the manufacturer indicated a total platinum loading range from 0.4 mg Pt/cm^2 to–0.44 mg Pt/cm^2 for the high-loading MEAs. LANL obtained the lower-loading MEAs during the third quarter of FY 2017, and the X-ray fluoresence results showed the total platinum loadings were near the DOE targets (approximately 0.143 mg Pt/cm^2 total). These two results will be used to evaluate the effect of Pt loading using the SAE J2719 fuel specification for contaminant levels: hydrogen sulfide, carbon monoxide, and ammonia.

In-line Fuel Quality Analyzer

Over the past two years, we focused on electrode materials optimization utilizing a relatively thick membrane. LANL has experimentally shown using the ISO 14687-2/ SAE J2719 contaminant levels of 200 ppb CO and 4 ppb H_2S in hydrogen gas that it is possible to obtain responses within minutes using ultra-low-loaded electrodes made by sputtering relatively larger particle-size platinum directly on a gas diffusion media. This working electrode is coupled with a platinum-ruthenium reference electrode on a 7 mil thick membrane. Tests on these materials were performed with humidified hydrogen fuel at both electrodes in hydrogen pump mode using a standard 5 cm^2 fuel cell hardware made by Fuel Cell Technologies (Albuquerque, New Mexico). In the last fiscal year, we demonstrated a humidification scheme that would keep the membrane wet when exposed to dry H_2. In this fiscal year, we built a prototype analyzer using this humidification scheme and designed flow fields and MEAs to maximize response to CO impurity in hydrogen fuel.

RESULTS

Hydrogen Fuel Quality

Table 1 provides a summary of the decay in fuel cell voltage under various conditions over a 100 h test. It is seen that at 32% relative humidity, the high-loaded MEAs are tolerant to all the CO concentrations at all the pressures tested. However, at the higher relative humidity, the MEA is tolerant to 200 ppb CO (which is the SAE J2719 level) only at the higher pressures. Since fuel cell systems are expected to operate at pressures greater than 150 kPa, the

TABLE 1. Voltage Loss Measured at 1 A/cm^2 Under Various Impurity Testing Conditions

T: 80°C		Tolerance of [CO] in PEM Fuel Cells								
Pressure (kPa)		80	150		80	150		80	150	
[CO] (ppm)		1	1		0.5	0.5		0.2	0.2	
RH (%)	32	0	0		0	0		0	0	
	50	51 mV	42 mV		25 mV	9 mV		2 mV	0	
	100	51 mV	51 mV		29 mV	10 mV		13 mV	0	

MEA can be deemed tolerant to CO at the SAE J2719 levels. Currently this matrix is being populated with data obtained from a 0.05 mg Pt/cm^2 loaded anode. This data will be used as input to models that can predict the CO tolerance of these lower-loaded MEAs under various operating conditions. Furthermore, a drive cycle test will be performed in addition to these constant current holds to understand the effect of potential cycling on improving CO tolerance. Fuel cell test results for 0.143 mg Pt/cm^2 (total Pt loading) in the presence of 200 ppb CO showed 30 mV losses after 100 h of exposure, while the losses due to 4 ppb H_2S were approximately 19 mV for the same exposure time.

LANL has been conducting tests using a recirculating system over the past year, and this has been shown previously to enhance impurity losses compared to a single pass system. During this fiscal year, we continued this testing to evaluate the effect of the simultaneous presence of CO and H_2S. In one experiment, the MEA was pre-dosed with either 4 ppb or 10 ppb of H_2S for 5 min. During this pre-dosing step, there was no loss in performance. However, when 200 ppb of CO was then subsequently added, the losses were amplified significantly for the higher sulfur pre-dosed sample (red line versus green line in Figure 1). This data is consistent with the fact that the H_2S pre-dosing does poison some of the Pt surface sites in proportion to the total dosage of H_2S. Although this dosage is not sufficiently high to result in performance loss, these poisoned Pt sites remain poisoned during the CO portion of the test and result in the enhanced losses that are seen. These tests are indicative of the additive effects of impurities and show that small upsets in H_2 impurity concentration can accumulate over time and result in fuel cell losses.

In-line Analyzer

In FY 2017 we were able to design a prototype analyzer capable of detecting impurities in dry H_2. LANL has applied for a patent for this novel analyzer design. We also demonstrated a way to reproducibly return the analyzer to its baseline, and to improve the response characteristics in the presence of CO. We demonstrated that a 0.75 V, 10 min clean-up step resulted in almost complete recovery of the baseline current. However, the analyzer did require a long break-in period, which was thought to be the result of excessive ionomer content. Varying the ionomer content of the working electrode resulted in an improved analyzer response.

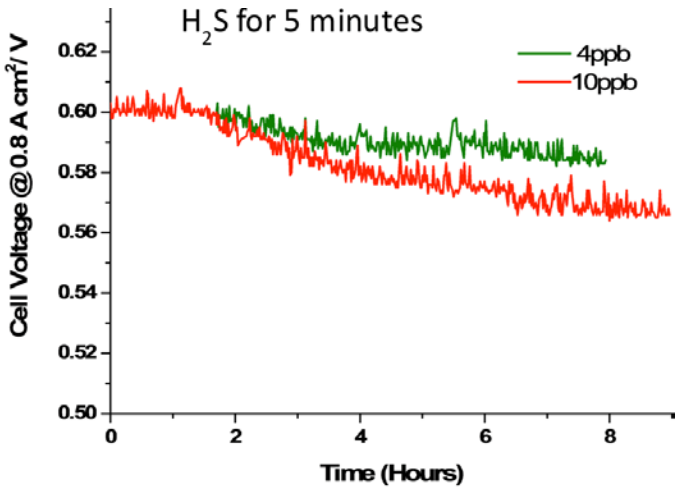

FIGURE 1. Effect of 200 ppb CO on fuel cells pre-dosed with either 4 ppb or 10 ppb H_2S for 5 min

The analyzer had an electrode with 0.035 mg Pt/cm^2 sputtered onto a 30 AA gas diffusion layer with 2.3 mg of ionomer painted on top. While this dramatically increased the active area of Pt and helped improve the baseline current signal (3x improvement in baseline current over previous design without ionomer), the sensor was sluggish and the break-in time excessive (>1 wk). This is illustrated in Figure 2. We reduced the ionomer loading from 2.3 mg to 0.2 mg, an order of magnitude decrease, and kept the Pt loading nearly constant at 0.041 mg Pt/cm^2. This analyzer exhibited a very short break-in time; essentially on the order of a couple of hours were required to stabilize temperature and test with CO. The new analyzer with the lower ionomer content showed a stable baseline during the very first run, before any conditioning, and the exposure to high concentration of CO was the only conditioning performed. From the very second run, the analyzer showed sensitivity to even trace contaminants in base H_2. Longer-term tests are needed to quantify this baseline and develop a calibration curve that would quantify the dosage of CO that has gone through the analyzer. We also showed that the analyzer does not saturate even at 50 ppm CO and can be easily cleaned up with the application of 0.75 V. This is illustrated in Figure 3, where the impedance responses after clean-up are identical for all three CO exposures. The increase in the electrode resistance (the arc in the impedance data) is attributable to the CO poisoning and is proportional to the CO dosage.

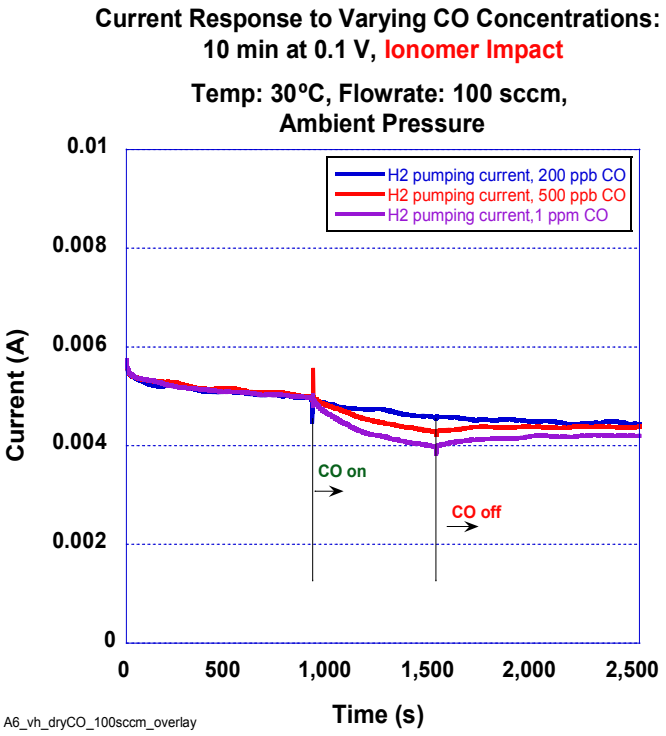

FIGURE 2. Current response to varying CO concentrations using analyzer (with membrane wicking system) in a dry gas stream

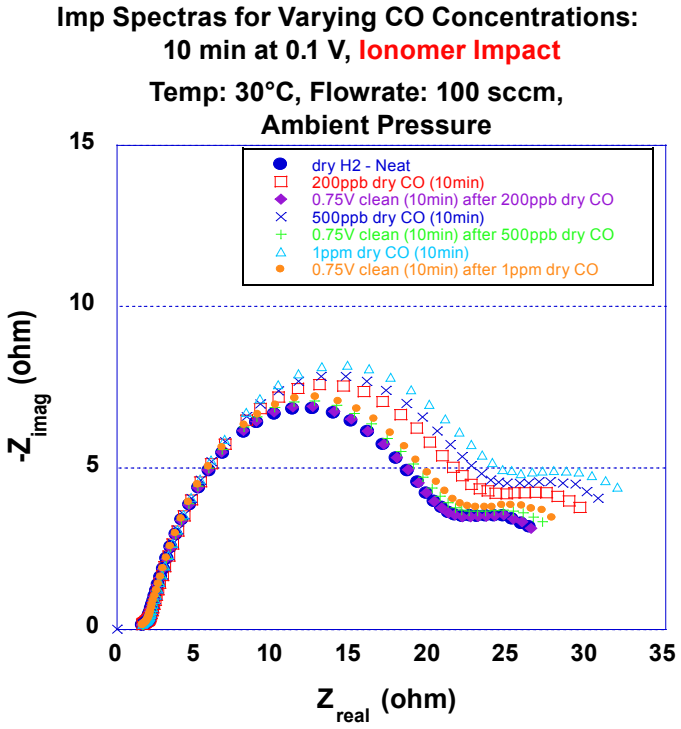

FIGURE 3. Impedance spectra for varying CO concentrations before and after applying 0.75 V for clean-up

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2017, LANL has made significant progress in both focus areas: fuel quality and analyzer development. MEAs with the DOE 2015 target loadings (0.15 mg Pt/cm^2) were evaluated at various conditions in the presence of impurities at the SAE J2719 levels. Unlike the higher-loaded MEAs, the low-loaded MEAs are not tolerant to these levels of impurities and show performance losses. The exact amount of performance loss is dependent on the operating conditions and can vary from a few millivolts to hundreds of millivolts. A new fuel quality analyzer prototype was designed, constructed, and built. The analyzer was sensitive to approximately <200 ppb of CO and responded in <10 min. The analyzer baseline was reset by the application of 0.75 V, even after exposure to 250 times the allowable CO limit. LANL will evaluate this analyzer in the field in FY 2018 and use the learning to modify key components and parameters to advance the analyzer design to improve sensitivity, response time, and stability.

REFERENCES

1. 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.

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