
VIII.5 Hydrogen Fuel Quality

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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 e.g., Working Group 12
 - 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 (FY) 2013 Objectives

- To carry out the duties of ASTM International (ASTM) sub-committee chair for D03.14 gaseous hydrogen fuel efforts.
- To help determine levels of impurity constituents for the development of an international standard for hydrogen fuel quality—International Organization for Standardization Technical Committee (ISO TC) 197 WG12.
- Investigate the impact of fuel impurities on polymer electrolyte fuel cell performance using state-of-the-art membrane electrode assemblies (MEAs).
- To demonstrate proof-of-concept of an electrochemical analyzer to detect low levels of impurities in hydrogen fuel.
- 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 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

Technical Targets

Most Hydrogen Safety, Codes and Standards activities do not have quantifiable technical targets.

FY 2013 Accomplishments

- Contributions to ASTM
 - Sub-committee Chair D03.14
 - Multiple standards developed and/or under development
 - Chaired two separate ASTM national meetings
- Inline Fuel Quality Analyzer
 - Proof of concept demonstrated for CO analyzer using sputtered platinum electrode
 - Improved sensitivity
 - Improved durability
 - CO dosage monitoring possible—analyzer under construction
- Impurity testing expanded to state-of-the-art MEAs
 - Hydrogen fuel standard developed based on common MEA
 - Lower loading results in significantly higher performance loss
 - State-of-the-art nano-structured thin-film (NSTF) MEAs also exhibit significantly higher losses than the common MEA
- U.S. DOE/Japanese Automotive Research Institute Meeting on Fuel Quality and Durability
 - Potential collaborations identified: drive cycle testing, exchange of MEAs and protocols



INTRODUCTION

The work performed is divided into three tasks:

a) contributions to ASTM standards development, b) inline fuel quality analyzer development, and c) R&D for fuel quality standards development.

Recently, an international team (ISO TC197 WG-12) developed hydrogen fuel product specifications for use in proton exchange membrane fuel cell (PEMFC) applications for road vehicles (ISO 14687-2:2012). Fuel cells tested with the fuel specification indicated that ammonia, carbon monoxide and hydrogen sulfide were the critical contaminants; i.e. the impurities that were the most harmful to PEMFC performance and/or its durability. While the fuel specification was based on actual PEMFC data from MEAs using conventional dispersed Pt/C catalysts; the DOE target loading for platinum has been continuously lowered and is currently based on novel materials that were unavailable during the development of the ISO standard. The current status of PEMFC technology as monitored by the DOE Fuel Cell Program is based on NSTF materials. MEAs based on these novel materials show great promise for reduced cost (better performance at lower precious metal loadings) and greater durability over conventional Pt/C electrodes [1]. However, their thin electrode structure may face water management challenges, especially during low temperature operations [2]. In addition, LANL scientists showed that an increase in local water can enhance performance with certain impurities [3]. Therefore, there is still uncertainty in whether or not the fuel standards may need revising to accommodate these novel catalyst layers and low loadings. In FY 2013 we evaluated PEMFC performance utilizing these novel materials in the presence of surface adsorbing contaminants.

Once science-based defensible standards are established, there is still a need to provide the tools necessary to implement this standard. LANL is helping this effort by providing leadership to ASTM to develop methods to determine the impurity content in the fuel. Finally LANL is also developing an inline fuel quality analyzer capable of quick and cheap detection of the key impurities in the H₂ fuel at various points in the supply chain. For example, carbon monoxide and hydrogen sulfide are impurities in hydrogen reformed from fossil fuels, or bio gas. While steam reforming natural gas will make hydrogen affordable and available, it will produce trace amounts of CO and H₂S. The ISO has set a fuel standard of 99.97% H₂ as applicable to PEMFC vehicles with a maximum allowance of 0.2 ppm for CO and 4 ppb for H₂S [4]. In addition to the hydrogen grade being certified, it would be prudent to have inline analyzers to protect expensive fuel cell components from these contaminants. Previous publications have demonstrated that Nafion[®]-based sensors using platinum electrodes respond to CO [5]. This

response can be used to quantitatively analyze the amount of CO present in the hydrogen fuel stream. In FY 2013 LANL demonstrated a proof of concept CO dose monitor that has that the potential to be incorporated into an inline analyzer.

APPROACH

R&D for Fuel Quality Standards

Tests were conducted on 50-cm² MEAs using a total platinum loading of 0.15 mg/cm². The NSTF anode was 0.03 mg Pt/cm², the NSTF cathode was 0.125 mg Pt/cm² (Pt₃Ni₇, de-alloyed and annealed), and the electrode was a 24-μm 3M 850 equivalent weight electrolyte-PEM. The gas diffusion layers (GDLs) used were also provided by 3M—2979 GDL at both the cathode and anode. The MEAs were subjected to 50 hours of exposure to either 4 ppb H₂S or 100 ppm CO in the anode feed stream of a fuel cell operating at 50A constant current held at 80°C.

Inline Fuel Quality Analyzer

Carbon monoxide chemisorbs on platinum surfaces preventing hydrogen dissociation from occurring, and inherently reducing the current output that can be measured as increasing resistance of the system. The fuel quality analyzer is a 5-cm² MEA with platinum electrodes. One electrode is low surface area Pt sputtered on carbon cloth with 0.1 mg Pt/cm² loading. The opposing electrode is a BASF Pt-Vulcan higher surface area 0.2 mg Pt/cm². Both were hot-pressed onto a Nafion[®] 117 membrane. The higher surface area electrode is positioned as the counter/reference electrode and exposed to ultra-high purity hydrogen only, while CO/H₂ is introduced at the sputtered electrode. Stripping voltammetry is used to verify the presence of CO, its amount, and to oxidize CO off the electrode's surface, which inherently regenerates the analyzer for subsequent uses.

RESULTS

Contributions to ASTM Standards Development

Sub-Committee Chair: Officer Duties: The sub-committee chair is responsible for preparing items for Sub- and Main-Committee ballots, resolving negative votes on the website, hosting meetings and recording minutes. Furthermore, the duties include registration of a work items, organizing collaboration areas, submitting items for ballot, scheduling virtual meetings, and handling negatives and comments and organizing inter-laboratory studies (ILS).

On-Going Standards Development: The D03 Subcommittee D03.14 on Hydrogen and Fuel Cells is responsible for developing standards, specifications, practices, and guidelines relating to hydrogen used in

energy generation or as feed gas to low-, medium- and high-temperature fuel cells. Table 1 lists the on-going standards being developed under ASTM D03.14.

Inter-Laboratory Studies [6]: The ultimate goal of ILS is to enhance the quality of ASTM standard test methods by assisting technical committees as they develop precision statements backed by high quality laboratory data for their test method, so as to incorporate at least a repeatability statement.

Inline Analyzer Development

The analyzer is designed to be operated as a hydrogen pump, with H₂ flowing on both sides. A potentiostat is used to probe the electrode with a voltage and to measure the

current response from hydrogen oxidizing on one side and protons reducing on the other. The inverse of the slope of the resulting line gives the resistance of the cell that is strongly affected by any poisoning of the Pt electrode. Figure 1 demonstrates resistance increases over time of a standard Pt electrode (0.2 mg-Pt/cm²) in the presence of 0.5 ppm CO for two hours. While the standard Pt electrode does get poisoned over time, decreasing the Pt loading and/or the Pt surface area can dramatically improve sensitivity. This is demonstrated in Figure 2a illustrating the performance of a sputtered Pt electrode operated under the same conditions as the conventional Pt/C electrode. The decrease in loading and surface area of the sputtered electrode resulted in a >100% improvement in the CO sensitivity. Figure 2b illustrates the performance of this same device exposed to 0.1 ppm CO for

TABLE 1. On-Going Standards being Developed under ASTM D03.14

Work Item	Title	Constituents (Detection Limit)	Update
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	CO ₂ (0.5 ppm), nitrogen (5 ppm), argon (1 ppm), oxygen (2 ppm), and water (1 ppm)	Published official item: D7649-10 Awaiting test samples
Published	Standard Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases	Gaseous sampling	Published official item: D7606-11
Published	Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography	Formic Acid (low ppb to ppm)	Published official item: D7550-09
Published	Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In Stream Filter	Particulate sampling	Published official item: D7650-10 Addressed
Published	Standard Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy	Ammonia, CO ₂ , CO, formaldehyde, formic acid, and water (defined by EPA 40 CFR part 136 Appendix A "meet detection limits of SAE TIR J2719")	Published official item: D7653-10 ILS complete, collecting data on going
21162	Standard Test Method for the Characterization of Particles from Hydrogen Fuel Streams by Scanning Electron Microscope	Particulates	N/A
Published	Standard Test Method for Visualizing Particulate Sizes and Morphology of Particles Contained in Hydrogen Fuel by Microscopy	Particulates	Published official item: D7634-10
Published	Standard Test Method for Gravimetric Measurement of Particulate Concentration of Hydrogen Fuel	Particulates	Published official item: D7651-10
Published	Standard Test Method for Test Method for the Determination of Total Hydrocarbons in Hydrogen by FID Based Total Hydrocarbon (THC) Analyzer	Total hydrocarbons (0.1 ppm)	Published official item: D7675-11 Editorial changes
23815	Determination of Total Halocarbons contained in Hydrogen and other gaseous fuels	Total halogenated compounds ("halocarbon determination requirements contained in SAE J2719" 0.1 ppb)	Editorial changes address, negatives need resolution (D.Bartel)
Published	Standard Test Method for Determination of Trace Hydrogen Sulfide, Carbonyl Sulfide, Methyl Mercaptan, Carbon Disulfide and Total Sulfur in Hydrogen Fuel by Gas Chromatography and Sulfur Chemiluminescence Detection	Total sulfur (0.02 ppb)	Published official item: D7652-11
34574	Standard Test Method for Determination of Trace Hydrogen Bromide, Hydrogen Chloride, Chlorine and organic halides in Hydrogen Fuel by Gas Chromatography with Electrolytic Conductivity Detector and Mass Spectrometer	Trace hydrogen bromide, hydrogen chloride, chlorine and organic halides	Ballot closed Dec 12, New Standard

EPA – Environmental Protection Agency

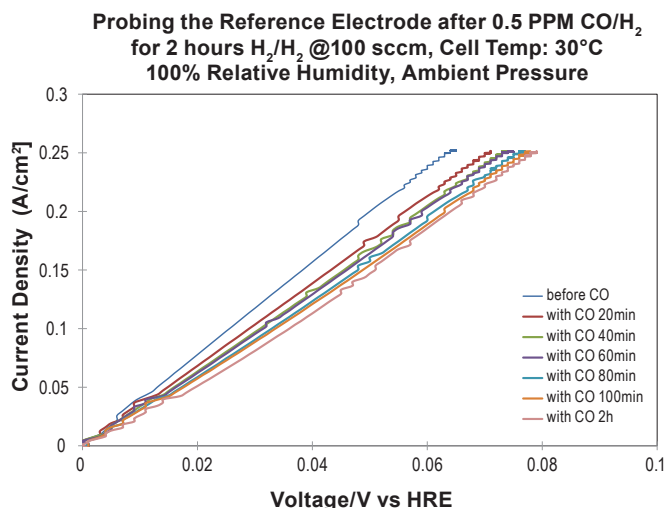


FIGURE 1. Resistance increase of the reference electrode (0.2 mg-Pt/cm²) in the presence of 0.5 ppm CO over 2 hours

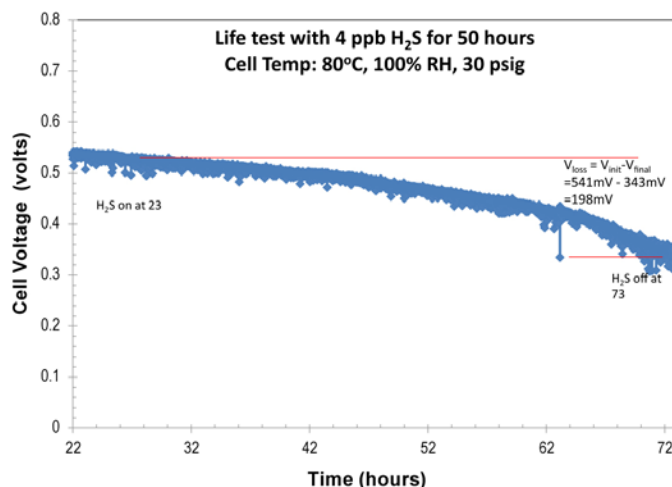


FIGURE 3. Voltage loss during 50 hours of exposure to 4 ppb H₂S at an operating current of 1 A/cm² (total losses observed ≈198 mV)

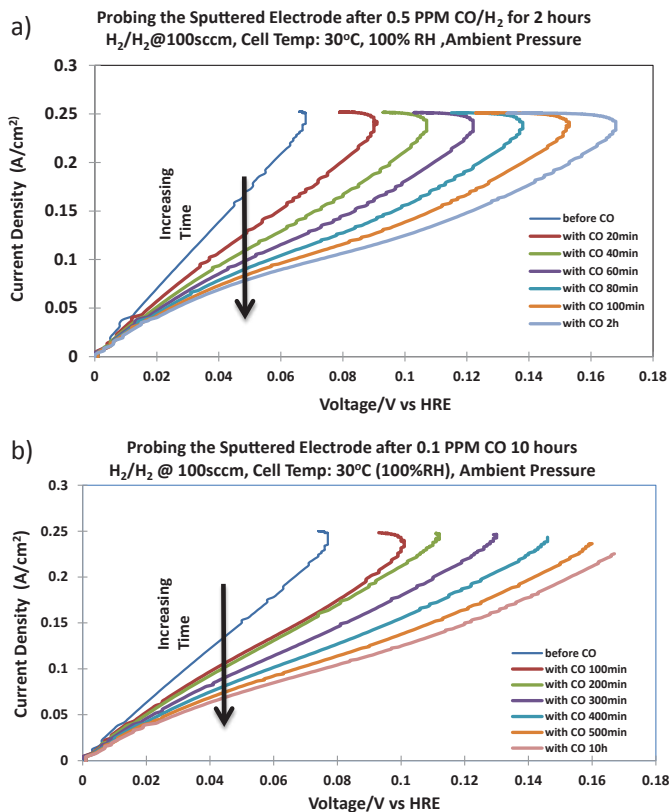


FIGURE 2. Resistance increase of the sputtered platinum sensing electrode in the presence of a) 0.5 ppm CO over 2 hours and b) 0.1 ppm over 10 hours

10 hours. Extensive studies on this device suggest that this sputtered electrode could serve as the sensing electrode of a CO dosage monitor. Operating conditions were varied in an effort to find optimal conditions for increased sensitivity of

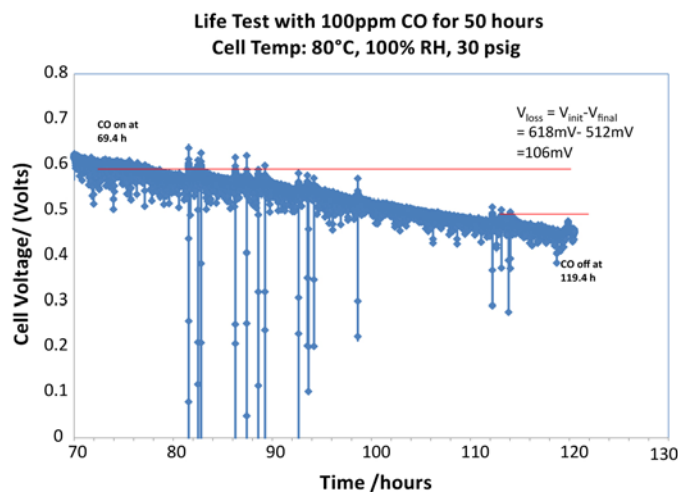


FIGURE 4. Voltage loss during 50 hours of exposure to 100 ppm CO at an operating current of 1 A/cm² (total losses observed ≈106 mV)

CO. The operating conditions tested were 30°C and 60°C and an applied voltage bias of 0.0 V and 0.2 V. The sensitivity of the device was lower at 0.2 V than at 0.0 V and the use of a voltage >0.6 V resulted in complete CO clean up. Therefore the device could be used as a dosage monitor for CO that can be reset by the use of high potentials.

R&D for Fuel Quality Standards

Figures 3 and 4 highlight the voltage response over time of fuel cells operated at 100% relative humidity (RH) and 30 psig back pressure with CO and H₂S concentrations at or below the current fuel quality standards limit. The hydrogen sulfide caused approximately 198 mV drop (at 1 A/cm²) in the fuel cell performance, while an approximate 106 mV drop (at 1 A/cm²) was observed when the fuel cell

was exposed to carbon monoxide. The fuel quality standards were determined using a common MEA with a 0.1 mg-Pt/cm² loading. The lower-loaded anodes (0.03 mg-Pt/cm²) used in this study resulted in significantly more degradation under the same conditions. Further studies are underway using state-of-the-art MEAs subjected to fuel cell testing in the presence of fuel impurities. These results will be further augmented with testing under non steady state conditions (drive cycle transients) to determine the real impact of CO and H₂S on fuel cell performance.

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2013, a proof of concept for a CO dosage monitor capable of detecting <0.1 ppm-hour of CO was demonstrated. Fuel quality testing with low-loaded anodes (0.03 mg-Pt/cm²) indicate ≈100 mV loss at 1 A/cm² when exposed to 100 ppm CO for 50 hours and ≈200 mV loss when exposed to 4 ppb of H₂S for 50 hours. In FY 2013 LANL also provided leadership to the ASTM Subcommittee D03.14 on Hydrogen and Fuel Cells. LANL will work on the following tasks in FY 2014.

- Continue providing leadership to ASTM efforts
- Construct an electrochemical analyzer-based on the proof of concept demonstrated for the CO dosage monitor
- Expand inline analyzer proof of concept to H₂S and NH₃
- Perform tests with ultra-low platinum loading and state-of-the-art materials using the ISO concentration levels
- Understand recovery mechanisms in state-of-the-art MEAs
- Explore DOE/Japanese Automotive Research Institute/LANL collaboration that incorporates durability and drive cycle tests in the presence of impurities

COLLABORATORS/PARTNERS

- WG -12 Members
- Japanese Automotive Research Institute
- ASTM International
- Air Liquide
- California Fuel Cell Partnership
- CONSCI

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