VIII.9 Hydrogen Fuel Quality Research and Development

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Fiscal Year (FY) 2012 Objectives

- Determine the allowable levels of hydrogen fuel contaminants in support of the development of science-based international standards for hydrogen fuel quality (International Organization for Standardization [ISO] TC197 WG-12).
- Validate the ASTM International test method for determining low levels of non-hydrogen constituents.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Codes and Standards section (3.7) of the Fuel Technologies Program 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

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards sub-program section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 21 - Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies. (4Q, 2012)
- Milestone 26 - Revised (Society of Automotive Engineers/ISO) hydrogen quality guidelines adopted. (4Q, 2010)

FY 2012 Accomplishments

- Performed baseline tests with 2010 and 2015 DOE target platinum loadings for fuel cell anodes.
- Completed test to determine CO tolerance using 0.05 mg Pt/cm^2 anode loadings.
- Measured the impact of hydrogen sulfide and ammonia at the levels in the ISO hydrogen fuel specification in an operating fuel cell.
- Validated newly developed ASTM method using Fourier transform infrared (FTIR) to measure trace contaminants in hydrogen.

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Introduction

For the past six years, open discussions and/or meetings have been held and are still on-going with manufacturers, hydrogen suppliers, other test facilities from the north America team and international collaborators regarding experimental results, fuel clean-up cost, modeling, and analytical techniques to help determine levels of constituents for the development of an international standard for hydrogen fuel quality (ISO TC197 WG-12). Significant progress has been made. The process for the fuel standard is entering final stages as a result of the technical accomplishments.

Approach

Our approach utilizes our expertise in ultra-low impurity measurement and analysis for single-cell testing and methodology development for data collection and analysis. This work is in support of the development of consensus standards for fuel quality with the ISO TC197 WG-12 international team. We also provide technical feedback and guidance to collaborators on selection of materials, calibration techniques, test methods, and data analysis.

Results

In FY 2012, tests using a common membrane electrode assembly (MEA) containing 0.1/0.4 mg Pt/cm^2 at the anode and cathode, respectively were completed. These results while providing valuable insights for understanding mechanisms, are not in line with the DOE targets. The 2010 and 2015 target loadings have 0.05 mg Pt/cm^2 at the anode. We identified a commercial supplier to provide us with samples at the target loadings. The initial tests results indicated that these low-loaded MEAs had durability and performance comparable to the common MEA and therefore further tests using these MEAs were initiated. The CO tolerance of the low-loaded anode varied with temperature as shown in Figure 1. At 80^oC, the MEA could tolerate >100 ppb CO, while the tolerance was 75 ppb at 60^oC and <500 ppb at 45^oC. We also observed a lower tolerance limit for NH_3 and H_2S. The common MEA tolerated 4 ppb H_2S and 100 ppb NH_3 for 100 h with <1% (<7 mV decay) performance decay. At 100% relative humidity with an anode loading of 0.05 mg Pt/cm^2, there is an ≈11 mV decay, while at 25% relative humidity this increases to 20 mV (clearly more sensitive than common MEA). The losses increased as the relative humidity was lowered and with NH_3, the life test showed approximately 50 mV loss within the first 100 hours. The voltage-current-resistance indicated similar findings and the impedance suggested the ionomer was mostly responsible for this voltage loss.

A significant portion of FY 2012 effort included participation in the validation of an ASTM test method using FTIR to measure trace contaminants in gaseous hydrogen. This technique can identify unknown materials, determine the quality or consistency of a sample and quantify the components in a mixture, since no two molecular structures have the same infrared spectra. This method was chosen for multiple reasons such as it being a powerful tool to quantify multiple gaseous species without the need for chromatography to separate contaminants. In addition, hydrogen is not infrared active, so there is no interference when probing other constituents. This method is also precise with a short analysis time and sensitivity can be increased by running multiple scans. We focused on NH_3 and H_2O in these measurements and obtained several spectra at various concentrations. A calibration curve was built by diluting down a known contaminant standard and obtaining the spectra. Figures 2 and 3 are examples of these findings. The calibration curves allowed the detection limits to be determined and verified.

Conclusions and Future Directions

In FY 2012, baseline tests on MEAs with DOE target loadings (i.e. anode = 0.05 mg Pt/cm^2) were performed in order to qualify these materials before introducing contaminants at the fuel specification levels. In addition, various tests using CO, H_2S and NH_3 were performed. The CO tolerance increased with increasing temperature while the H_2S tolerance decreased with decreasing relative humidity.

Our future work plans will focus on testing the existing hydrogen fuel specifications on ultra-low platinum loading as well as state-of-the-art materials including nano-structured thin film-based MEAs. Uncertainty in the fuel tolerance of state-of-the-art materials can potentially be a detriment to fuel cell systems and their viability. We plan to address this issue by:

1. Focusing on coupling the tolerance to fuel impurities as a function of platinum loading and/or state-of-the-art materials.
2. Actively participating in other ASTM methods development.
3. Contributing to other working groups such as:

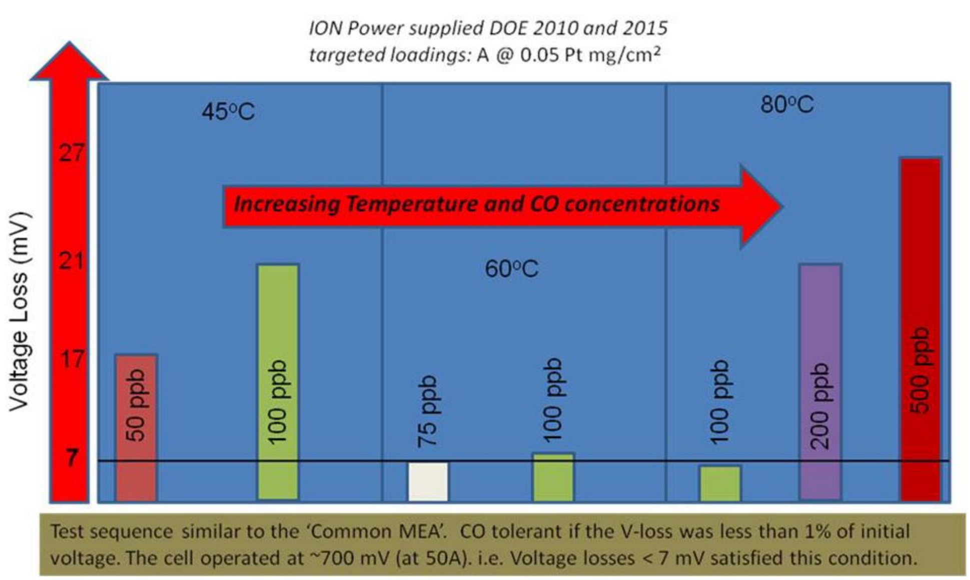

FIGURE 1. Voltage loss due to CO impurity in fuel at various temperatures using an anode loading of 0.05 mg Pt/cm^2

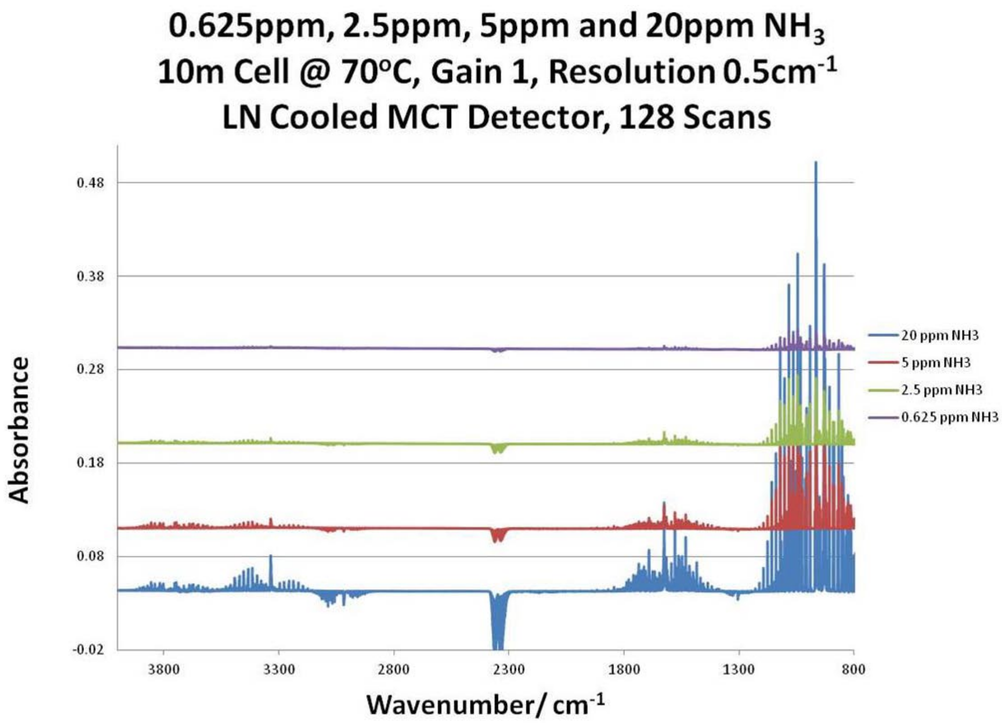

FIGURE 2. FTIR measurements of spectra for multiple H_2O concentrations

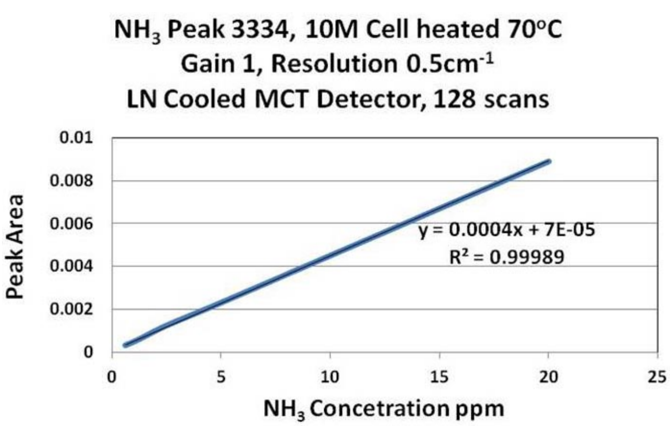

FIGURE 3. A calibration curve produced from different NH_3 concentrations

- TC 197/WG 13 – Hydrogen detection apparatus - Stationary applications
- TC 197/WG 14 – Hydrogen fuel - Product Specification - Proton exchange membrane (PEM) fuel cell applications for stationary appliances

FY 2012 Publications/Presentations

1. PEMFC Poisoning with CO: Measuring Tolerance vs. Temperature and Low Platinum Loadings, Tommy Rockward, Calita Quesada, Karen Rau, and Fernando Garzon, 220^{th} Electrochemical Society Meeting, Boston, MA.