LA-UR-12-23022
Approved for public release; distribution is unlimited.

Title: Hydrogen Fuel Quality

Author(s): Rockward, Tommy

Intended for: Report

Hydrogen Fuel Quality

Tommy Rockward (Primary Contact), C. Quesada, K. Rau, F. Garzon, R. Mukundan, and C. Padró
Los Alamos National Laboratory (LANL)
P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 667-9587
E-mail: trock@lanl.gov

DOE Managers (Headquarters)

HQ: DOE Technology Development Manager: Antonio Ruiz
Phone: (202) 586-0729; Fax: (202) 586-9811
E-mail: Antonio.Ruiz@ee.doe.gov

Project Start Date: October 1, 2011

Project End Date: September 30, 2015

Objectives

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

Technical Barriers

This project addresses the following technical barriers from the 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 RCS
(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 26 - 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 FTIR to measure trace contaminants in hydrogen

Introduction

For the past 6 years, open discussions and/or meetings have been held and are still on-going with OEM, 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 was to utilize our expertise in ultra-low impurity measurement and analysis capabilities for the single cell testing and through useful collaborations on methodologies for data collection and analysis 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 FY12, we completed test using a common MEA containing 0.1/0.4 mg Pt/cm^2 at the anode and cathode, respectively. These results prove useful for understanding mechanism, but 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 did not indicate ant issues with durability and performance comparable to the Common MEA and therefore we went forward with the tests in this effort. And, base on those MEAs we found that the CO tolerance varied with temperature. At 80^{o}C, the MEA could tolerate >100 ppb CO. While the tolerance at 60^{o}C was 75 ppb and 45^{o}C could not tolerate 50 ppb. This is shown in figure 1. We also observed a bigger challenge for NH_3 and H_2S. The common MEA tolerated 4 ppb H_2S and 100 ppb NH_3 for 100h. At 100% RH with 0.05 mg Pt/cm^2 there is~11mV decay, while 25% RH reduces 20mV (clearly more sensitive than common MEA). The losses increased as the relative humidity was lowered. And with NH_3, the life test showed approximately 50mV loss within the first 100 hours. The VIR indicated similar findings and the impedance suggested the ionomer was mostly responsible.

We also spend a significant portion of FY12 participating in the validation of an ASTM test method using FTIR to measure trace contaminants in gaseous hydrogen. Because no two molecular structures have the same IR spectra, this technique can identify unknown materials, determine the quality or consistency of a sample and quantify the components in a mixture. 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 IR active so there is no interference when probing other constituents, the method is precise and sensitivity can be increased by running multiple scans, and measurements are taken very quickly. We focused on NH_3 and H_20 in these measurements. We measured several spectra at various concentrations. Use these spectra a calibration curve was built by using a known contaminant standard and diluting it down using the same balance gas. 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 FY12, we were able to perform baseline test on MEAs with DOE target loadings (i.e.0.05 mg Pt/cm^2) in order to qualify these materials before introducing contaminants from the fuel specification. In addition, we were performed various test using CO, H_2S and NH_3. We measured the CO tolerance in an operating fuel cell to be…

Our future work plans will focus on testing the existing hydrogen fuel specifications on DOE targets for ultra-low platinum loadings as well as novel materials. This uncertainty 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. Joining in other working groups such as:

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. **Investigating the Impact of Low Levels of Sulfur Compounds on the Fuel Cell Performance**, Tommy Rockward, John Davey, Eric L. Brosha, and Fernando H. Garzon, 218th Electrochemical Society Meeting, Las Vegas, NV

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

Acronyms

MEA-Membrane-Electrode Assembly
DOE-Department of Energy
ASTM- American Society for Testing and Materials
FTIR-- Fourier Transform Infrared
OEM-Original Equipment Manufacturer
ISO International Standards Organization
TC197/ Technical Committee
WG-12-Working Group
LN Liquid Nitrogen
MCT-Mercury, Cadmium, Telluride
AST- Accelerated Stress Test

Figures

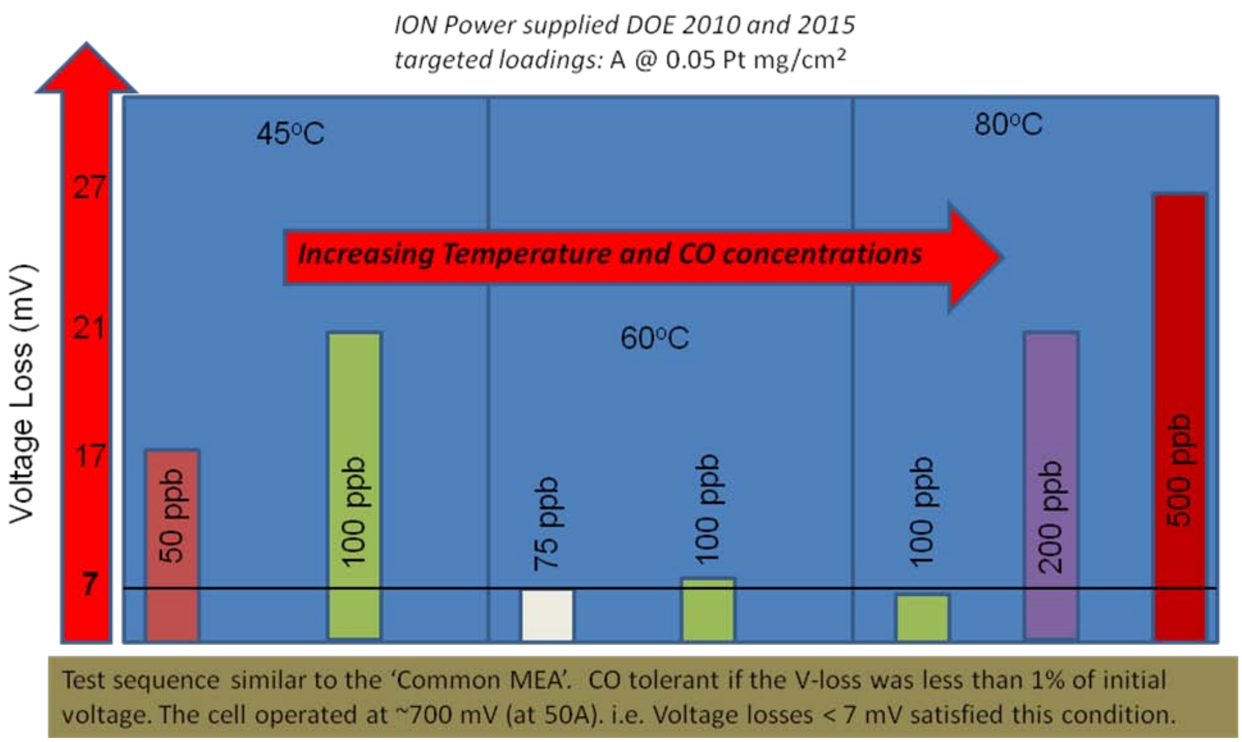

Figure 1. Voltage loss due to CO versus temperature using the 0.05 mg Pt/cm^2.

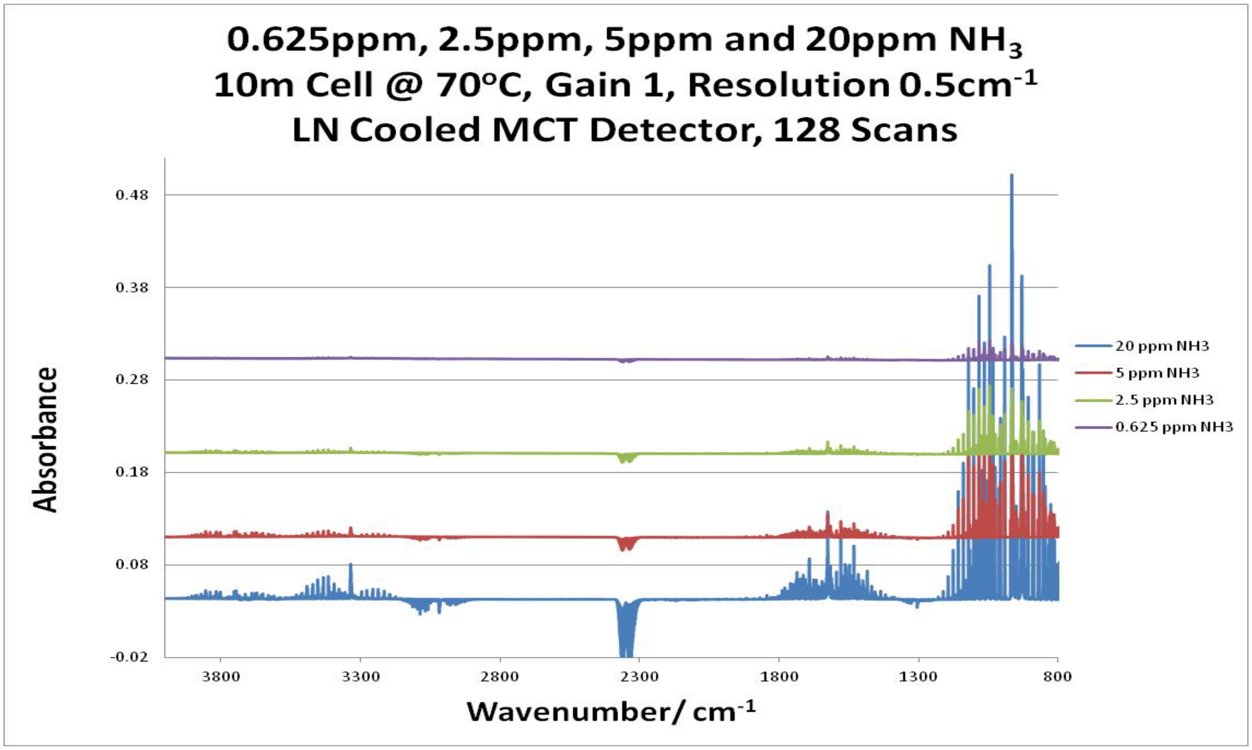

Figure 2. FTIR measurements of spectra for multiple H_20 concentrations.

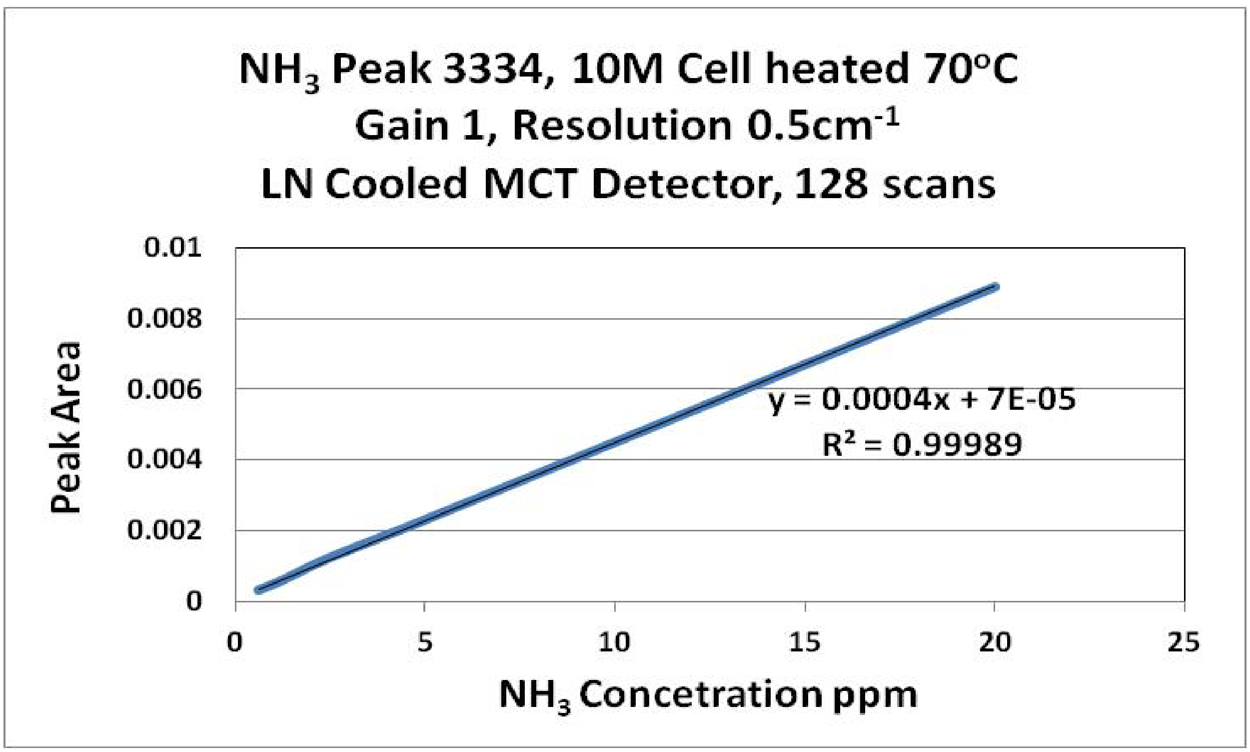

Figure 3. A calibration curved produced from different NH_3 concentrations.