

## VIII.4 Hydrogen Fuel Quality: The Year In Review

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### Objectives

- Conduct gauge studies with testing labs and address experimental differences, thus increasing the confidence in the data.
- Create and standardize a data reporting format.
- Develop and test new analytical methods for detecting ppb levels of contaminants.
- Test the critical constituents (NH<sub>3</sub>, CO, and H<sub>2</sub>S) and provide data sets to fuel cell (FC) modelers to establish predictive mechanistic models.

### Technical Barriers

This project addresses the following technical barriers from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (I) Conflicts between Domestic and International Standards
- (N) Insufficient Technical Data to Revise Standards

### Contribution to Achievement of DOE Codes and Standards Milestones

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

- **Milestone 26:** Revised (SAE/ISO) hydrogen quality guidelines adopted. (4Q, 2010)

### Accomplishments

- Completed DOE round robin testing.
- Developed a data reporting format.
  - Accepted by ISO TC197 Working Group 12.
  - Proposed for adoption as part of standard.
- Analytical method for measuring and determining ppb levels of sulfur developed.
- Tested critical constituents (NH<sub>3</sub>, CO, and H<sub>2</sub>S).



### Introduction

In support of the DOE Energy Efficiency and Renewable Energy Office of Hydrogen, Fuel Cells & Infrastructure Technologies' Codes and Standards sub-program, LANL provides its unique expertise in materials physics and applications, chemistry, and modeling to advance the science and develop the systems required for inherently safe hydrogen components and systems. LANL also provides expertise in the collaborative development and implementation of international performance-based codes, standards and regulations.

### Approach

LANL applies its world-class expertise in materials physics and applications to address a broad range of national security needs in energy, environment, and infrastructure. This includes expertise in polymers, coatings, metallurgy, material properties (and underlying structures), material behavior at low temperatures and/or high pressures, and electronic and ionic conducting materials. The LANL team leverages the on-going multifaceted research that has spanned three decades. This includes but is not limited to a unique collection of scientific knowledge that is well-suited to providing world-class science and engineering solutions for inherently safe hydrogen systems, and the development of science-based codes and standards. We work with other organizations (both national and international) in a parallel approach to establish standards based on experimental findings.

### Results

The DOE round robin test, with participation from four universities and two national laboratories, was initiated to increase confidence in the fuel impurities data to be generated by these testing laboratories in support of the fuel quality effort. A FC test article with a

LANL in-house produced membrane electrode assembly (MEA) was assembled and initially tested at LANL according to the US Fuel Cell Council/LANL protocol. The fuel cell was sent to the test labs along with the detailed instructions. The tests performed included ‘gross leak’ test, hydrogen crossover measurements, cyclic voltammetry, and polarization curves. After all testing was completed, the test article was returned to LANL for a re-test. Figure 1 shows the excellent reproducibility of the results for voltage-current (VI) curves at 80°C for the four test labs receiving DOE funding for this activity. The round robin effort reinforced the need for timely equipment calibrations and software upgrades, and adherence to the protocol to ensure data quality.

We have also begun populating a newly developed ‘data reporting format’ using the results from the critical constituents in the hydrogen specification. Table 1 includes an excerpt from the data reporting format that is being used by all collaborators.

In our analytical method development task, we found that commercial sulfide ion probes are not suitable for measurement of trace quantities of H<sub>2</sub>S by converting the probe electromagnetic field (EMF) to sulfide ion concentration via a calibration curve even if the calibration standards are determined using titration methods. Calibration curves were found to vary greatly from standardization to standardization even for the same ion probe and isothermal conditions. The commercial probes also lacked sensitivity for sulfide ion concentrations below 10<sup>-5</sup> mole/L (M). However, trace quantities of H<sub>2</sub>S may be measured by concentrating the sulfide ion in a solution of sulfide anti-oxidant buffer if the gas flow time and flow rate are known, together with precise knowledge of the titrant concentration, titrant volume, and volume of sample, provided that isothermal conditions are maintained. Commercial

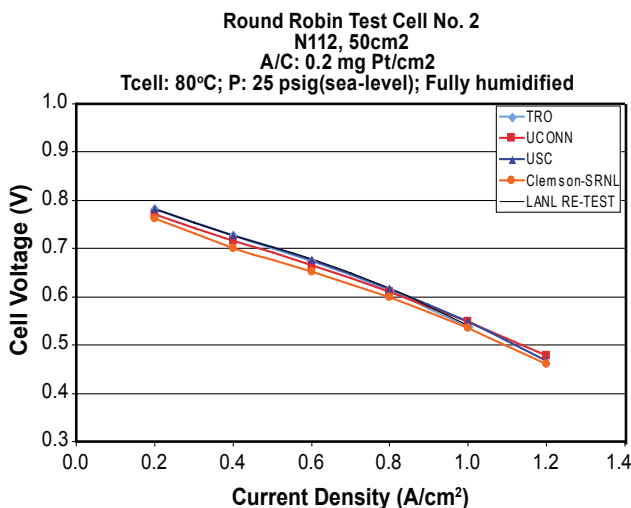


FIGURE 1. Round Robin Results Between Test Sites at 80°C and 25 PSIG

TABLE 1. Data Reporting Format Excerpt: FC Operating Conditions

FC Operating Conditions	
Diagnostic Identifier (e.g. MEA 012)	LANL_TR040908
Gas Type	
Anode Gas Composition & Quality (e.g. 100% H <sub>2</sub> , 99.999%)	electrolysis grade
Cathode Gas Composition & Quality (e.g. oilless compressor, in-house produced)	oilless compressor
Stoichiometry Mode	
Flow Tracking (yes / no)	yes
Flows	
Anode Stoich (e.g. 1.2 or N/A)	1.2
Cathode Stoich (e.g. 2.0, or N/A)	2.0
Anode Fixed Flow (e.g. 1,200 sccm, or N/A)	N/A
Cathode Fixed Flow (e.g. 3 NL/min, N/A)	N/A
Minimum Flow	
Minimum anode flow setpoint (e.g. 80 sccm, or flow at 0.2 A/cm <sup>2</sup> )	80 sccm
Minimum cathode flow setpoint (e.g. 80 sccm, or flow at 0.2 A/cm <sup>2</sup> )	343 sccm

N/A - not applicable

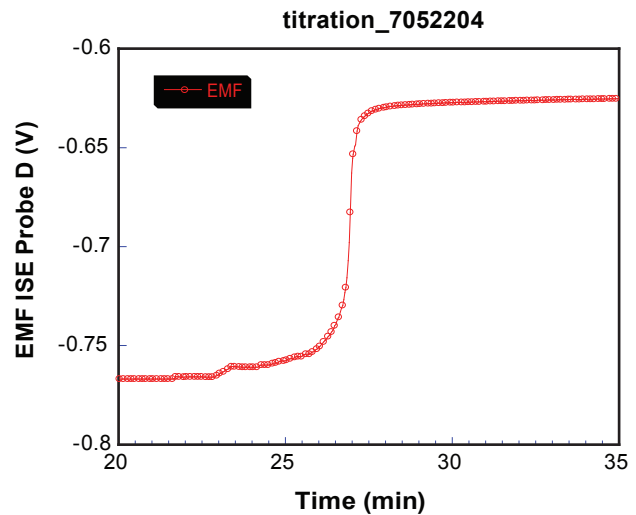


FIGURE 2. Use of Pb(NO<sub>3</sub>)<sub>2</sub> at a Concentration 10x of Anticipated [S<sup>2-</sup>] may be Titrated Using the Ion Probe as an Endpoint Indicator

sulfide ion probes may be used as an endpoint indicator for titrations. By titrating a solution of known volume with a known concentration of Pb(NO<sub>3</sub>)<sub>2</sub>, the concentration of the sulfide ion in solution [S<sup>2-</sup>] may be determined with far greater accuracy than could possibly be achieved by immersing a calibrated ion probe and calculating [S<sup>2-</sup>] from the measured EMF. Figure 2 shows the ion probe response after a titration was performed.

## Conclusions and Future Directions

Our technical objectives for Fiscal Year 2008 were achieved. We are now focusing on populating the data sheets with high-quality data on the effects of impurities on fuel cell performance, and further development of analytical methods for determination of very low concentrations of contaminants/impurities. Objectives for next year include but are not limited to the following:

- Completion of the final report on DOE round robin testing.
- Finalization of the data reporting format (awaiting input from the Japan Automotive Research Institute, European Union, and Korea).
- Optimization of the previously discussed analytical method and its modification for other critical constituents.
- Continue testing the critical constituents (NH<sub>3</sub>, CO, and H<sub>2</sub>S) and populating the test matrix.
- Continue providing data sets and interacting with FC modelers.

## FY 2008 Publications/Presentations

1. Tommy Rockward, Idoia G. Urdampilleta, Francisco A. Uribe, Eric L. Brosha, Bryan S. Pivovar, and Fernando H. Garzon, "The Effects of Multiple Contaminants on Polymer Electrolyte Fuel Cells", *ECS Transactions*, 2007; v.11, no.1, p.821-829.
2. Idoia G. Urdampilleta, Francisco A. Uribe, Tommy Rockward, Eric L. Brosha, Bryan S. Pivovar and Fernando H. Garzon, "PEMFC Poisoning with H<sub>2</sub>S: Dependence on Operating Conditions", *ECS Transactions*, 2007; v.11, no.1, p.831-842.
3. Eric Brosha, Tommy Rockward, Francisco Uribe, and Fernando Garzon, "Development of Analytical Techniques to Study H<sub>2</sub>S Poisoning of PEMFCs and Components (abstract submitted to 2008 Fuel Cell Seminar).
4. Tommy Rockward, WG-12 Presentation, October 2007, San Antonio, TX.
5. Tommy Rockward, WG-12 Presentation, August 2007, Argonne, IL.
6. Tommy Rockward, Hydrogen Quality Meeting, Washington, D.C.