VIII.5 Hydrogen Fuel Quality

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

DOE Manager
Will James
Phone: (202) 287-6223
Email: Charles.James@ee.doe.gov

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 Program through:

- Participation in working group 12 providing leadership to hydrogen fuel quality efforts
- Performing the research and development 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) 2014 Objectives

- To carry out the duties of ASTM International (ASTM) sub-committee chair for D03.14 gaseous hydrogen fuel efforts.
- To test an operating fuel cell using membrane electrode assemblies (MEAs) with ultra-low platinum loadings with impurity mixture at the levels indicated in the international standard for hydrogen fuel quality 14687-2 document (International Organization for Standardization [ISO] TC197 WG12) [1]/SAE International (SAE) J2719 [2].
- To demonstrate improved sensitivity of electrochemical analyzer to carbon monoxide.
  - Report results to the DOE
- ·To demonstrate proof-of-concept electrochemical analyzer capable of detecting low levels (few ppb) of H_2S in hydrogen fuel.
  - Report 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 RCS (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

FY 2014 Accomplishments

- Contributions to ASTM
  - Sub-committee Chair D03.14
  - Coordinated test labs for Inter-Laboratory Study (ILS) 775, ASTM D7649 - Test Method for Determination of Trace CO_2, Ar, N_2, O_2 and H_2O in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis. Chaired an ASTM national meeting.
- In-line Fuel Quality Analyzer
  - Improved sensitivity of analyzer to CO using different electrode configuration
  - Proof of concept demonstrated for H_2S analyzer using a platinum black electrode:
  - Observed response to 10 ppb H_2S
  - Demonstrated clean-up techniques after H_2S exposure

  a). Impurity testing with ultra-low platinum MEAs
  - Completed testing with ISO mixture at various relative humidities (RHs)
  - Measured impedance spectra during exposure to ISO mixture
  - Tested MEAs for CO tolerance varying the concentrations (i.e. 0.2, 0.5, and 1.0 ppm CO); results showed a similar decay as our baseline. Experiments will be revisited.

  b). DOE/Japan Automobile Research Institute (JARI) and European Union (EU) Collaboration
  - Visited the JARI test facility
  - Conducted baseline measurements using LANL MEAs with 0.05 and 0.10 mg Pt/cm^2 at the anode and cathode, respectively

- Completed tests using JARI MEAs with two different Pt loadings (MEA #1: 0.05/0.1 mg Pt/cm^2 and MEA #2: 0.3/0.3 mg Pt/cm^2 for the anode and cathode, respectively)
- Initiated collaboration with VTT Technical Research Centre of Finland
- Began installing anode recirculation system for fuel quality testing
- Discussed international round-robin tests between JARI/EU/DOE

✧ ✧ ✧ ✧ ✧

INTRODUCTION

The work performed in this project has been partitioned into four tasks: a) contributions to ASTM standards development, b) in-line fuel quality analyzer development, c) R&D for fuel quality standards development, and d) international collaborations.

The international team (ISO TC197 WG-12) for "development of a hydrogen fuel product specifications for use in proton exchange membrane fuel cell applications for road vehicles"; (ISO 14687-2:2012) [1] indicates 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.

Science-based standards have been established; however, there is still a need to provide the tools necessary to implement this standard. LANL is helping this effort by providing leadership to ASTM in developing methods to determine the impurity content in the fuel. While steam reforming natural gas will make hydrogen affordable and available, it will produce trace amounts of CO and H_2S. The ISO has a maximum allowance of 0.2 ppm for CO and 4 ppb for H_2S [1]. Although the hydrogen grade should be certified, it would be invaluable to have in-line analyzers to protect expensive fuel cell systems and components from these contaminants. LANL 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. Our goal is to provide a quick and cheap method of detection at various points in the supply chain.

APPROACH

R&D for Fuel Quality Standards

Tests were conducted on 50-cm^2 MEAs using a total platinum loading of 0.15 mg/cm^2. The MEAs were supplied by Ion Power with an anode loading of 0.03 mg Pt/cm^2, and cathode loading of 0.12 mg Pt/cm^2, and a membrane thickness of 25 µm. The gas diffusion layers used were SIGRACET® 25BC manufactured by SGL.

In one set of experiments, the MEAs were subjected to approximately 200 hours of exposure to the ISO mixture (critical contaminants) at 100% and 50% RH in an operating fuel cell. In yet another set of experiments, we varied the CO concentration while keeping the dosage constant in order to quantify the MEA's CO tolerance level.

In-line Fuel Quality Analyzer

The interaction of either H_2S or carbon monoxide in a hydrogen stream over a platinum surface results in inhibition of hydrogen dissociation, and inherently lower current output that can be measured as increasing resistance of the system. The fuel quality analyzer is composed of a active area MEA ≤5 cm^2 with platinum-based electrodes. The electrodes were modified in order to improve the analyzer's sensitivity and selectivity to adsorbates. More specifically, we employed a low surface area platinum electrode sputtered on carbon cloth, Pt black (Alfa Aesar HiSPEC™ 1000 by Johnson Matthey), or PtRu (Pt: 30 wt%, Ru: 23.3 wt%, by TKK, Japan) loaded with 0.1 mg Pt/cm^2 as our working electrode in the experiments.

The counter electrode is either a PtRu electrode or a high surface area BASF Pt-Vulcan carbon with 0.2 mg Pt/cm^2. All MEAs were hot pressed on to Nafion® 117 membrane (thickness ≈180 µm), a much thicker membrane than the traditional fuel cell membranes (thickness <50 µm) for enhanced stability and sensitivity. The PtRu or the BASF high surface area electrode was positioned as the counter/reference electrode and exposed to ultra-high purity hydrogen only, while the adsorbates were introduced at the working electrode. Stripping voltammetry is used to verify the presence of either CO or H_2S, their amount, and to oxidize those species off the electrode's surface, which inherently doubles as a regenerating tool for subsequent measurements.

Here, we report the response of a modified platinum-type electrode to ppb levels of H_2S. This 5-cm^2 MEA had a working electrode prepared from a catalyst ink made of unsupported-catalyst powder (~6.3 nm particle size) and Nafion® solution (5%, 1,100 equivalent weight). The absence of a carbon support and the large initial Pt particle size are desirable for an electrode to be durable and have a low active surface area that is ultra sensitive to adsorbates.

RESULTS

Contributions to ASTM Standards Development

Sub-Committee Chair; Officer Duties: The subcommittee 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 work items, organizing collaboration areas, submitting items for ballot, scheduling virtual meetings, handling negatives and comments, and organizing 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**.** One current standard being developed under ASTM D03.14 is "Test Method for Determination of Trace CO_2, Ar, N_2, O_2 and H_2O in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis."

ILS: 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.

In FY 2014, LANL scientists coordinated test labs for ILS 775 (ASTM D7649) through several conference calls. We also provided a data reporting format for compiling the ILS results.

In-Line Analyzer Development

As describe in FY 2013, the analyzer is designed to be operated as a hydrogen pump, with hydrogen 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. When plotted as current versus voltage, 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. Hydrogen pump experiments were performed at 30^{o}C and 100% RH using 100 sccm of hydrogen gas at each electrode without any applied backpressure to obtain a baseline. The working electrode was then exposed to either CO or H_2S, and the experimental details and results are listed in the subsections following.

a) Carbon Monoxide Exposure

We previously reported that the standard Pt electrode does get poisoned over time and decreasing the Pt loading and/or the Pt surface area can dramatically improve sensitivity to impurities. We studied various electrode conventions, and probed their responses to 200, 100, 50 and 25 ppb CO. We measured the analyzer response during the first 5 minutes of exposure using 1 minute increments and again at 1, 3, 5 and 7 hours. The shorter increments were chosen for employing the analyzer at a hydrogen filling station, while the longer periods could satisfy on-board fuel monitoring in the anode re-circulation loop.

Our experimental results from the three different working electrode configurations were successfully utilized in increasing the analyzer sensitivity. Each of the three electrodes was exposed to 200, 100, 50, and 25 ppb CO for 7 hours. The PtRu electrode did not respond to the sub-ppm levels of CO. However, the Pt black electrode did, and an observable increase in analyzer resistance occurred between 1 and 3 hours when exposed to 200 ppb CO, and less than 5 hours when exposed to 100 ppb of CO. This electrode did not respond (no change in resistance) when exposed to 50 ppb CO for up to 7 hours. Therefore the tolerance of this electrode lies in the region between 50 and 100 ppb CO. The sputtered electrode responded to each of the CO concentrations, and thus was the most sensitive of the three electrodes. For example, it responded to 100 ppb CO in less than an hour and to 25 ppb in less than 3 hours. The analyzer

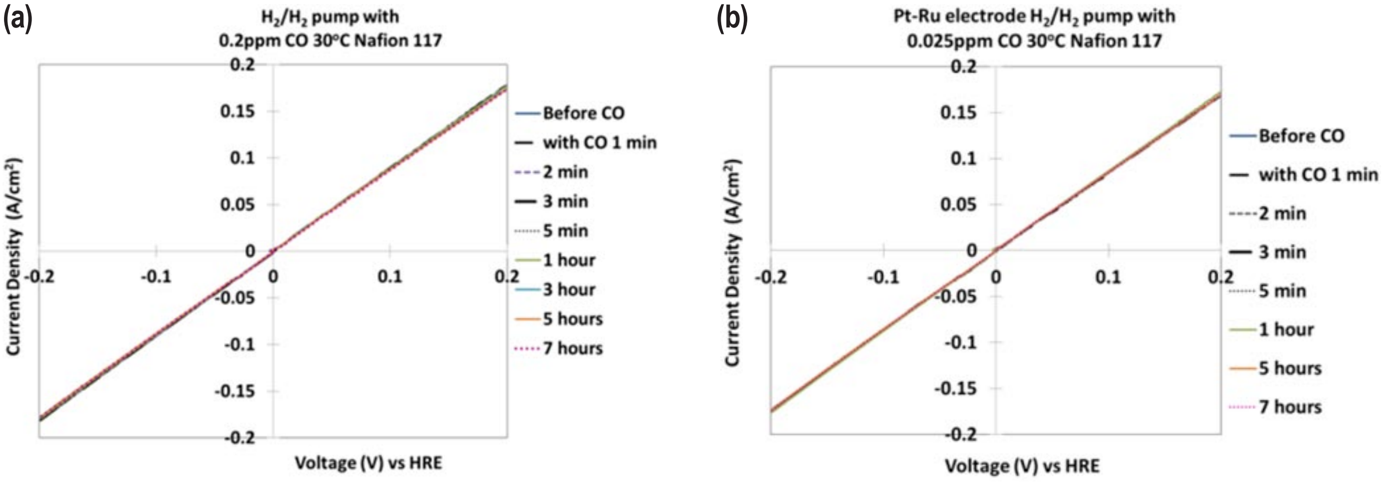

FIGURE 1. (a) and (b) show the impact of varying CO concentration on a Pt-Ru working electrode of the electrochemical analyzer.

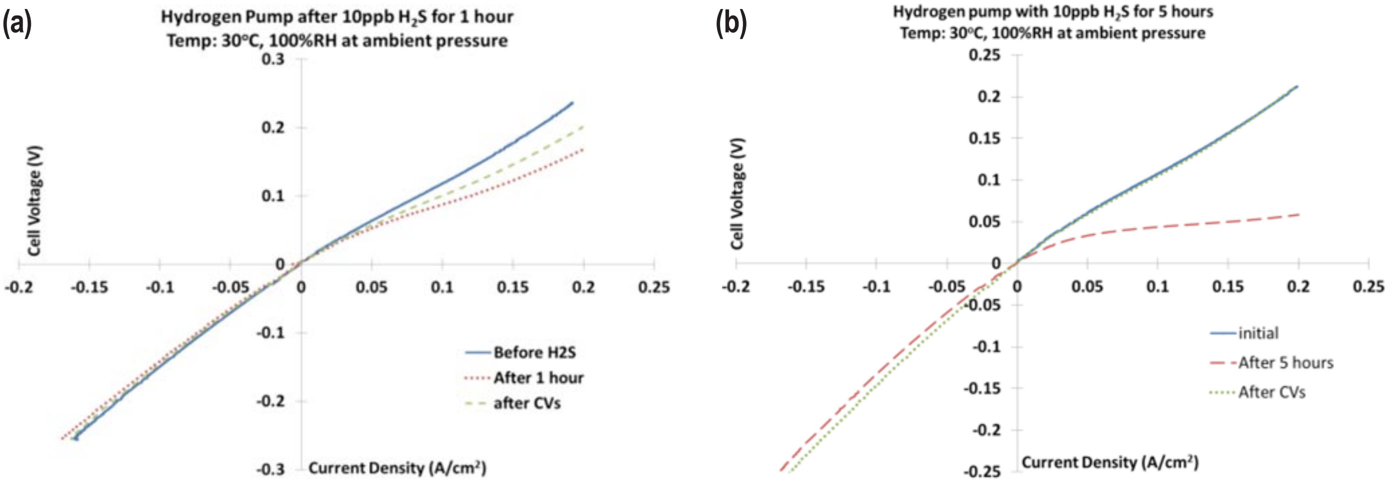

FIGURE 2. (a) and (b) demonstrate the impact of 10 ppb H_2S for 1-hr and 5-hr exposure times on a Pt black working electrode of the electrochemical analyzer.

sensitivity improved, as we hypothesized, with lower surface area electrodes. In fact, the sputtered electrode's response time was 5 times faster than the Pt black in the presence of 100 ppb CO. Figure 1 (a) and (b) show the family of current-voltage curves during exposure to 200 ppb and 25 ppb CO on the surface of a PtRu working electrode. The resistance of each remained constant throughout the duration of the experiments. This is typical for the PtRu, which can typically tolerate CO levels that exceeds the ISO concentration level for longer than 7 hours. These results indicate that by using a PtRu electrode as a psedo reference electrode and a sputtered Pt electrode as a working electrode we can design an analyzer that is sensitive to CO concentrations up to an order of magnitude lower than the current SAE CO standards (200 ppb)

b). Hydrogen Sulfide Exposure

We completed our FY 2014 milestone, which was to demonstrate the proof of concept of the analyzer to respond in the presence of 10 ppb H_2S. The current-voltage curves and cyclic voltammograms (CVs) before and after exposing the working electrode to H_2S were measured. Figure 2 shows an increase in the H_2 pumping resistance in the presence of H_2S. After four CV sweeps to 1.0 V, some of the H_2S was removed from the surface of the Pt and the H_2 pump resistance indicated a partial recovery. Figure 2 illustrates the effect of the 10 ppb H_2S over 5 hours and shows an increased degree of poisoning (larger increase in resistance) which can be completely recovered after 4 potential sweeps to 1.1 V followed by four more potential sweeps to 1.4 V. The observed resistance change is the direct result of H_2S adsorbing onto active platinum sites preventing hydrogen dissociation from occurring. Figure 2(a) and (b) demonstrate the impact of 10 ppb H_2S at 30°C, after 1 and 5 hour exposures. In Figure 2(a) the performance of the analyzer does not fully recover after CVs were run to 1.1 V, however after increasing our voltage to 1.4 V the performance returns to its original state (shown in Figure 2(b). Figure 3 illustrates the decrease in the hydrogen desorption from the Pt surface due to H_2S adsorption and its recovery after the H_2S is desorbed at the higher potentials. These results indicate that the high voltage (>1.4 V) cleaning can be utilized to reset the analyzer after prolonged H_2S exposures, while low voltage (0.6–1.0 V) can be utilized to impart selectivity to CO vs. H_2S.

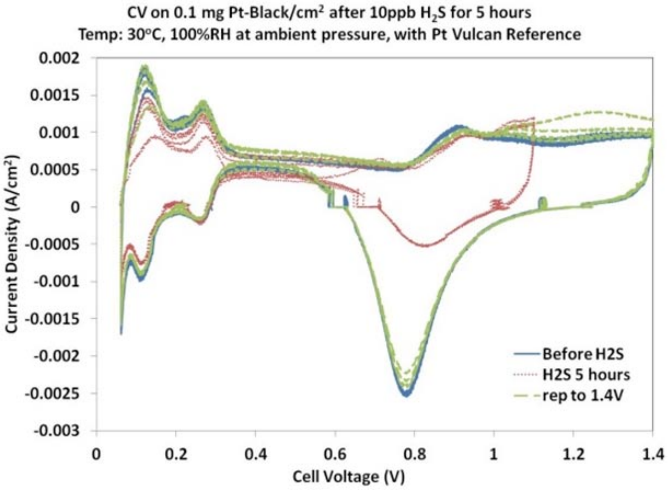

FIGURE 3. illustrates a CV of the working electrode after exposure to 10 ppb H_2S and cycled up to 1.1 V and subsequently to 1.4 V.

R&D for Fuel Quality Standards

We completed 200 hours of tests with the ISO mixture in the hydrogen fuel stream. We used low-loaded anodes (0.03 mg-Pt/cm^2) to comply with existing DOE Pt loading targets. Fuel cells were run at 80°C, using two different RHs,

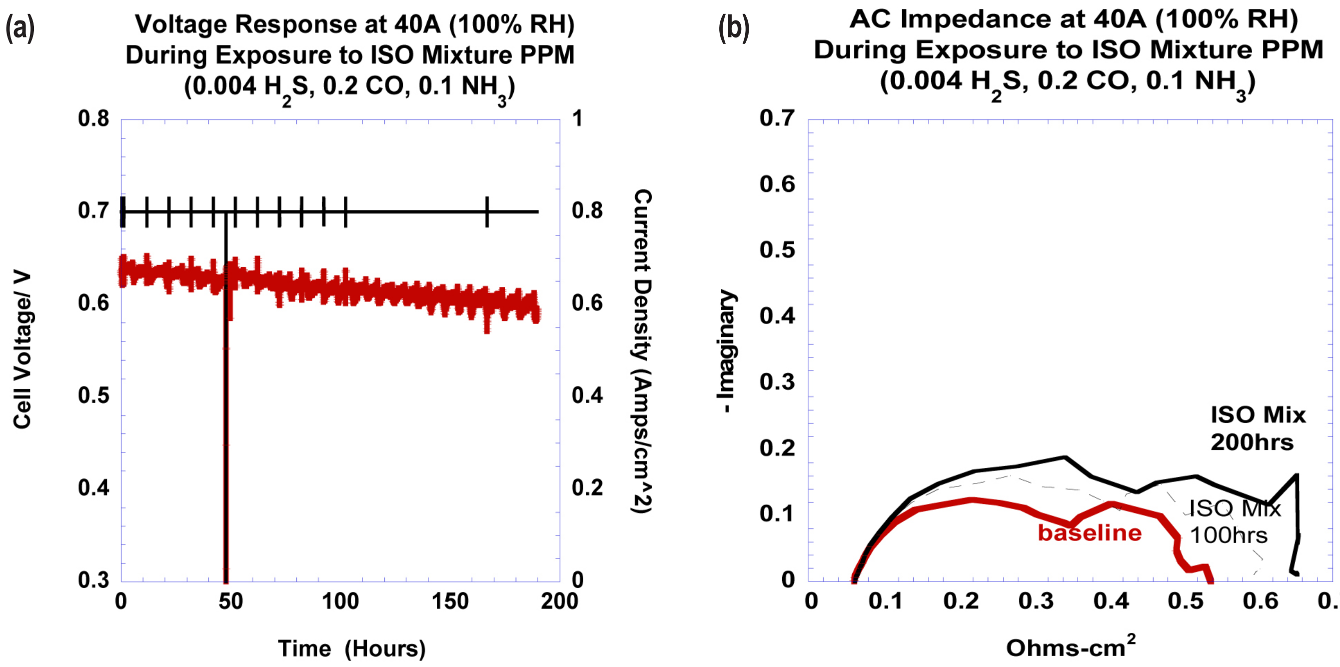

FIGURE 4. (a) shows the voltage response of an fuel cell operated at 1 A/cm^2 during exposure to 0.004 ppm H_2S, 0.2 ppm CO, and 0.1 ppm NH_3 and (b) captures its impedance spectra during the time of exposure using 0.05 and 0.1 mg Pt/cm^2 at the anode and cathode, repsectively.

with the current held at 0.8 A/cm^2. Total impedance spectra were also obtained throughout the experiments. Figures 4(a) and (b) highlight the voltage response over time of fuel cells operated at 100% RH and 30 psig back pressure and the impedance curves respectively. At 100% RH, we observed a voltage decay of 56 mV, while tests at 50% RH showed a 120 mV loss. Additional tests were conducted using MEAs with identical platinum loadings in the presence of low concentrations of CO with a focus on obtaining a tolerance level for CO. Tests were conducted using three different CO concentrations (0.2 ppm, 0.5 ppm, and 1.0 ppm). We observed a voltage decay rate similar to our baseline in each of these experiments. CVs were obtained to probe the platinum surface after each exposure. and indicated that CO was present at both electrodes, even though we intended to expose the anode only. We are currently examining this issue to determine other possible sources of CO contamination (humidifier bottles, etc..) before quantifying the CO tolerance of this low Pt-loaded MEA.

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2014, we improved the sensitivity of the analyzer to respond to 100 ppb CO in under an hour and less than 3 hours to 25 ppb CO. We also demonstrated the response of the analyzer to 10 ppb H_2S, which is 2.5 times the ISO level. However, we intend to reduce the platinum loading further to enhance both sensitivity and response time to both CO and H_2S.

In FY 2014 LANL continued to provide leadership to the ASTM Subcommittee D03.14 on Hydrogen and Fuel Cells. In FY 2014, LANL, JARI, and the EU established a working relationship. This collaboration will focus on fuel quality and durability. LANL will work on the following tasks in FY 2015.

- Continue providing leadership to ASTM efforts
- Improve response time and sensitivity of the electrochemical analyzer to CO and H_2S
- Develop a robust design for an analyzer to be utilized in a H_2 stream at a fueling station
- Perform tests with ultra-low platinum loading and state-of-the-art materials using the ISO concentration levels in DOE drive cycles using anode re-circulating systems
- Understand CO and H_2S recovery mechanisms in state-of-the-art MEAs
- Continue DOE/JARI/EU/LANL collaboration that incorporates durability and drive cycle tests in the presence of impurities

COLLABORATORS/PARTNERS

- Working Group-12 Members
- Japanese Automotive Research Institute
- European Union
- ASTM

- Air Liquide
- California Fuel Cell Partnership
- CONSCI

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