VII.8 Hydrogen Fuel Quality

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- Jet Propulsion Laboratory/NASA, Pasadena, CA
- University of Hawaii, Honolulu, HI
- Gerald Voecks, La Crescenta, CA

Start Date: 2004
Projected End Date: 2010

Objectives

- Facilitate the development of an international hydrogen fuel quality standard for proton exchange membrane (PEM) fuel cells in land vehicles by 2010.
- Coordinate and conduct testing, research and development (R&D), and analysis to establish the data needed for consensus hydrogen fuel quality specifications for PEM fuel cells in land vehicles.
- Facilitate the development of standardized analytic methodologies and instrumentation needed to verify conformance to fuel quality specifications in international and domestic fuel quality standards.

Technical Barriers

This project addresses the following key technical barriers from the Hydrogen Codes and Standards section (3.6) of the Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

(F) Limited DOE Role in the Development of International Standards

(G) Inadequate Representation at International Forums

(H) International Competitiveness

(I) Conflicts between Domestic and International Standards

(J) Lack of National Consensus on Codes and Standards

(K) Lack of Sustained Domestic Industry Support at International Technical Committees

(N) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Codes and Standards Milestones

This project will contribute to the achievement of the following DOE Hydrogen Codes and Standards milestones from the Codes and Standards section of the HFCIT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 18** – Implement research program to support new technical committees for the key standards including fueling interface, and fuel storage. (4Q 2007)
- **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/International Organization for Standardization [SAE/ISO]) hydrogen quality guidelines adopted. (4Q 2010)

Accomplishments

- Led the North American team for ISO TC197 Working Group 12 (WG12):
  - Developed a consensus test protocol, test matrix, and data-reporting format.
  - Launched a test cell round-robin among fuel quality testing laboratories coordinated through Los Alamos National Laboratory (LANL).
  - Formed a modeling sub-team (Argonne National Laboratory [ANL], Ballard Power Systems, LANL, NREL, Institute for Fuel Cell Innovation, the University of Connecticut, the University of Hawaii, and the University of South Carolina).
- ISO TC 197 approved the international technical specification for hydrogen fuel quality.
- Harmonized international specification with SAE J2719.
- Initiated the design and fabrication of 70-MPa sampling apparatus with the Gas Technology Institute (GTI) and the American Society for Testing and Materials (ASTM).
- Launched a collaborative international fuel quality testing effort with key research organizations in North America, Asia, and the European Community (EC).

Introduction

The DOE Hydrogen Codes and Standards Program supports a comprehensive research, development, and demonstration (RD&D) effort to obtain the data needed to establish a scientific basis for the requirements incorporated in hydrogen codes and standards. This RD&D is planned, conducted, and evaluated in collaboration with industry through the U.S. FreedomCAR and Fuel Partnership, which was formed to examine and advance pre-competitive R&D of technologies to enable high-volume production of affordable hydrogen fuel cell vehicles and the national hydrogen infrastructure to support them. The codes and standards activities of the partnership are conducted through the Codes and Standards Technical Team, which adopted a roadmap to guide the RD&D.

Hydrogen fuel quality specifications must be quantified at the vehicle-station interface and must consider how the presence of small amounts of contaminants affect the performance and durability of fuel cells and the balance of plant; material compatibility of on-board and stationary hydrogen storage systems; and the operation and maintenance of hydrogen production, purification, and delivery systems. Preliminary fuel quality guidelines based on available data and information have been prepared by ISO, TS 14687-2, and SAE, J2719. Before these guidelines can become international and national standards, respectively, a comprehensive, structured R&D and testing effort is needed to determine the effects, especially the degradation mechanisms, of various contaminants on fuel cell electrodes and membranes. Implications of fuel quality on the complexity, performance, and durability of fuel cell systems and upstream infrastructure and on the cost of fuel must be understood so critical trade-offs can be assessed.

Approach

In January 2007 the ISO Technical Committee 197 (TC197) approved TS 14687-2, which contains carefully crafted language that limits its application to the pre-commercial phase of PEM fuel cell technology development. The recommended limits for non-hydrogen constituents in ISO TS 14687-2 are shown in Figure 1.

Characteristics (assay)	**Type I**	**Type II**	**Laboratory Test Methods to Consider**
	Grade D	**Grade D**	
Hydrogen Fuel Index (minimum, %)[a, b]	99.99	99.99	
Para-Hydrogen (minimum, %)	NS	95.0	
Non-Hydrogen Constituents (maximum content)			Dimensions in micromoles per mole unless otherwise stated
Total Gases[b]	100	100	
Water (H_2O)	5	5	ASTM D6348, D5454, (D1946 & D5466)[g]JIS K0225
Total Hydrocarbons[c] (C1 basis)	2	2	EPA T012, T015, ASTM (D1946 & D5466)[g], D6968, JIS K0114
Oxygen (O_2)	5	5	ASTM (D1946 & D5466)[g], JIS K0225
Helium (He), Nitrogen (N_2), Argon (Ar)	100	100	ASTM (D1946 & D5466)[g], JIS K0114
Carbon Dioxide (CO_2)	2	2	ASTM (D1946 & D5466)[g], JIS K 0114, K 0123
Carbon Monoxide (CO)	0.2	0.2	EPA 25C, ASTM (D1946 & D5466)[g], JIS K 0114, K 0123
Total Sulfur Compounds[d]	0.004[f]	0.004[f]	ASTM (D1946 & D5466)[g], D5504, JIS K 0127
Formaldehyde (HCHO)	0.01	0.01	EPA Method 11, NIOSH 2541, EPA T015, ASTM (D1946 & D5466)[g], JIS K 0114, K 0124, K 0123
Formic Acid (HCOOH)	0.2[f]	0.2[f]	ASTM (D1946 & D5466)[g], JIS K 0123, K 0127
Ammonia (NH_3)	0.1[f]	0.1[f]	ASTM (D1946 & D5466)[g], EPA T015, JIS K 0127
Total Halogenated Compounds	0.05	0.05	EPA 200.7, JIS K101
Max Particulates Size[e]	10 μm	10 μm	SCAQMD Method 301-91
Max Particulates Concentration[e]	1 μg/L @ NTP	1 μg/L @ NTP	Gravimetric (EPA IO 3.1)

[a] The hydrogen fuel index is the value obtained when the value of Total Gases (%) is subtracted from 100 %.
[b] The value of Total Gases is summation of the values of impurities listed in this table except Particulates.
[c] THC may exceed 2 micromole per mole due only to the presence of methane, provided that total gases do not exceed 100 micromole per mole.
[d] As a minimum, testing shall include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.
[e] Recommended value for Particulates is subject to sampling under realistic operational conditions and improved standardized analytical procedures.
[f] These values are based on detection limits of available instrumentation and test methods and serve as a basis for subsequent improvements in test methods and instrumentation. Recommended values for these constituents are subject to additional testing under realistic operational conditions and improved analytical procedures suitable for standardization.
[g] A new ASTM standard (WK4548) that will combine relevant portions of these two existing test methods and will utilize gas chromatography/mass spectrometry (GC/MS) to determine trace contaminants in H_2 is under development.

FIGURE 1. Recommended Limits for Non-Hydrogen Constituents, ISO TS 14687-2

During the next three years, WG12 will try to obtain sufficient test data to set fuel quality requirements that will achieve a balance between fuel quality that will not be detrimental to the performance and durability of PEM fuel cells and cost of hydrogen fuel of a quality that will not deter the commercial success of PEM fuel cell vehicles.

Results

To help develop a consensus testing and R&D effort under WG12, DOE, through NREL, formed a team of hydrogen and fuel cell experts from industry, universities, and national laboratories in the United States and Canada. The team defined a comprehensive approach to R&D and testing that will be needed to obtain data required to modify TS 14687-2 to an international standard over the next three years (see Figure 2).

Because testing for all of the non-hydrogen constituents listed in Figure 1 would be time-consuming and extremely expensive, the team defined a subset of constituents that are likely to be the major technical and economic drivers of the trade-offs between fuel quality and cost. After much discussion among the team members, industry, and other WG12 members, the team identified six "critical constituents" on which to focus the R&D and testing over the next three years: carbon monoxide (CO), sulfur (S) species, ammonia (NH_3), helium (He), methane (CH_4) and other inert gases, and particulate matter (PM) smaller than 10 microns in diameter. These constituents are those most likely to affect PEM fuel cell performance and durability, as well as the cost of hydrogen produced by steam methane reforming (SMR) and purified by pressure swing adsorption (PSA) to the levels required by TS 14687-2. WG12 has agreed to focus R&D and testing on the critical constituents identified above.

Given the need to trade off fuel cell performance and durability against the cost of delivering clean hydrogen at the fuel dispenser, the team created two sub-teams to focus expertise on each aspect of the problem. Sub-team 1 is focused on single-cell testing and obtaining data on PEM fuel cell performance and the mechanisms of cell and material degradation caused by specific critical non-hydrogen constituents in the fuel. Sub-team 2 is focused on the engineering aspects of fuel quality in both PEM fuel cell systems and in hydrogen production, purification, and delivery systems under realistic operating environments. Sub-team 2 is also collaborating with ASTM to address analytical methodology and instrumentation needs.

Sub-team 1 is attempting to bound the effects of CO, starting with a baseline of low-level CO concentration at steady-state low loads to assess cumulative coverage on the catalyst. The testing will provide essential data about the rates of accumulation, degradation, and recovery of PEM fuel cells in an automotive environment from CO in a range of 0.1 ppm to 10 ppm. Based on these tests, the sub-team will develop parametric performance descriptors, assess project performance for different conditions using accepted empirical models, and conduct cyclic tests under changed conditions to test and validate projections. In parallel to the testing, the sub-team is using a standard reporting format to search

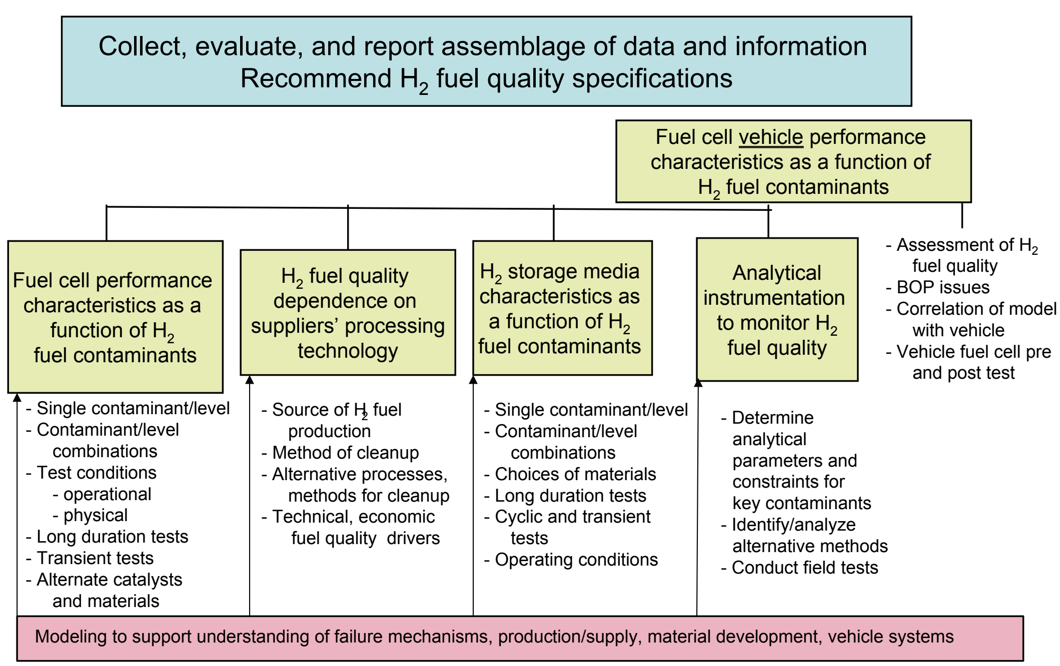

FIGURE 2. Approach to R&D and Testing

the literature and compile data from previous tests. The sub-team has also defined baseline test cells, identified commercially available membrane electrode assemblies, and developed a testing protocol and standardized data reporting format. Much of this work is based on information available from industry, universities, and national laboratories and on publications of the U.S. Fuel Cell Council (USFCC).

Sub-team 2 is working in parallel with sub-team 1 to bound the production and purification trade-offs of hydrogen fuel containing CO levels of 0.1 ppm to 10 ppm. The sub-team is preparing estimates of the cost of hydrogen by examining the recovery rates of hydrogen from SMR-PSA with CO in the range of levels given above. The sub-team determined the relative difficulty of removing contaminant species (see Figure 1), assuming production by SMR or autothermal reforming and purification by PSA. Helium, which is found in some natural gas sources in the United States, is “not possible” to remove by PSA, and CO has the highest “purification ratio for SMR.” This may provide a basis for its serving as a “canary” for other contaminant species (Figure 3).

Working with a PSA model developed by ANL, sub-team 2 is attempting to establish a relationship between CO concentration with respect to PSA breakthrough properties of other critical constituents (inerts, CH_4, S species, etc.) and estimate a rough order of magnitude of breakthrough of these constituents in relation to CO concentration for a baseline SMR-PSA system. In addition, the sub-team is addressing simple, cost-effective analytical methodologies; that is, when, where, and what techniques to employ to establish adherence to the requirements of TS 14687-2. DOE and NREL are working closely with ASTM to help develop and validate the critical sampling and measurement methodologies and instruments.

Conclusions and Future Directions

NREL will continue to support the development of an international standard for hydrogen fuel quality through ISO that is harmonized with that developed for the United States under SAE by:

Species	Adsorption Force	ISO TC 197 WG 12 (14687) Draft Spec	ATR Mol %	Purification Ratio for ATR	SMR Mol %	Purification Ratio for SMR	OVERALL EFFECT
Helium (He)	Zero	100 ppm (total inert)	500 ppm	5	500 ppm	5	NOT POSSIBLE
Hydrogen (H2)	Weak	99.99%	40-45%		75-80%		Impacts PSA recovery & Capital Cost
Oxygen (O2)		5 ppm	50 ppm	10	-	-	Impacts PSA recovery & Capital Cost
Argon (Ar)		100 ppm (total inert)	500 ppm	5	500 ppm	5	Impacts PSA recovery & Capital Cost
Nitrogen (N2)		100 ppm (total inert)	34-38%	3800	1000 ppm	10	Impacts PSA recovery & Capital Cost
Carbon Monoxide (CO)		0.2 ppm	0.1 -1 %	50000	0.1-4%	200000	Impacts PSA recovery & Capital Cost
Methane (CH4)		2 ppm (incl THC)	0.5 – 2%	10000	0.5 – 3%	15000	Impacts PSA recovery & Capital Cost
Carbon Dioxide (CO2)		2 ppm	15-17%	85000	15 -18%	90000	Relatively easier to remove
Total HC’s		2 ppm (incl CH4)	0.1 %	500	0.5%	2500	Relatively easier to remove
Ammonia	Strong	0.1 ppm	Low ppm		Low ppm		Relatively easier to remove
Total Sulfur	Strong	0.004 ppm					Relatively easier to remove
Halogenates	Strong	0.05 ppm					Relatively easier to remove
Water (H2O)	Strong	5 ppm	Dew Point		Dew Point		Relatively easier to remove

FIGURE 3. Relative Difficulty of Removing Contaminant Species

- Coordinating the North American team for testing, modeling, and analysis.
- Integrating the efforts of the laboratories funded through the recent DOE solicitation (LANL, Clemson University, and the University of Connecticut).
- Leading the North American team at ISO TC 197 WG12 meetings to convert TS 14687-2 into an international standard.

Over the next several years, the North American team will use the expertise and research facilities of many nations to work with other members of WG12 to conduct the R&D and testing in the most cost-effective way. A proposed timeline for the R&D and testing is shown in Figure 4.

FY 2007 Publications/Presentations

Publications

1. "ISO Technical Specification for Hydrogen Fuel Quality: Status and Path Forward," ECS Transactions, in press.

Presentations

1. ISO Technical Specification for Hydrogen Fuel Quality: Status and Path Forward, Fuel Cell Seminar, Honolulu, HI.

2. Hydrogen Fuel Quality R&D/Testing: North American Perspective, ISO TC197 WG12, Seoul, South Korea.

3. Hydrogen Fuel Quality, DOE/HFCIT Annual Merit Review, Washington, D.C.

4. Hydrogen Fuel Quality, DOE kickoff meeting for winners of fuel quality solicitation, Washington, D.C.

5. ISO TC197 WG12 status, meeting of North American experts, San Antonio, TX.

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– Guido Bender, Rick Rocheleau, University of Hawaii
– Robert Benesch, Air Liquide

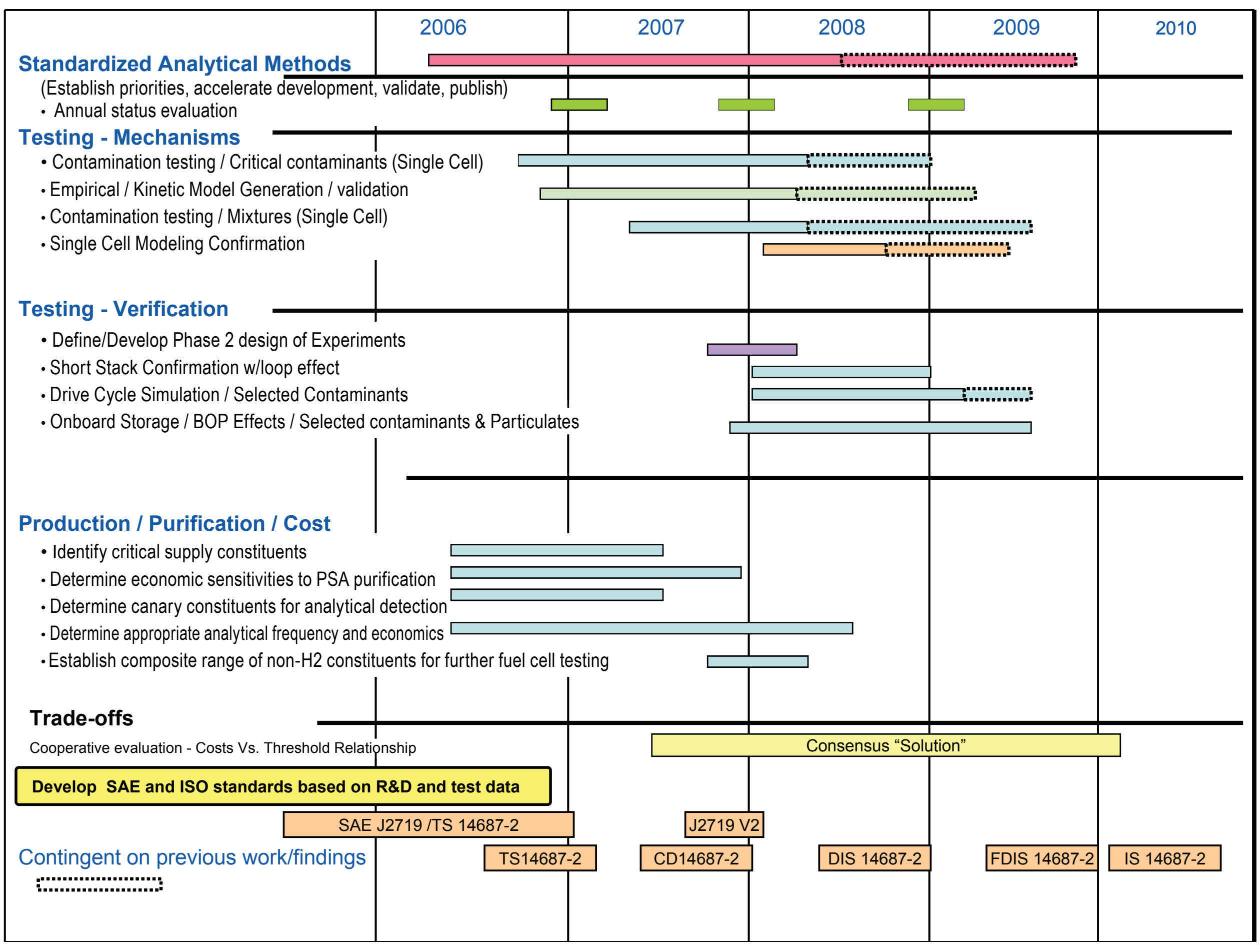

FIGURE 4. Timeline for R&D and Testing

- Bob Boyd, Linde (BOC Group)
- Pamela Chu, National Institute of Standards and Technology
- Bill Collins, UTC Power
- Hector Colon-Mercado, William Rhodes, Savannah River National Laboratory
- Raul Dominguez, South Coast Air Quality Management District
- Tony Estrada, Pacific Gas &Electric
- James Goodwin, Clemson University
- Karen Hall, National Hydrogen Association
- J.P. Hsu, Smart Chemistry
- Tom Joseph, Dave Guro, Brian Bonner, Air Products and Chemicals
- Romesh Kumar, Shabbir Ahmed, Rajesh Ahluwalia, ANL
- Trent Molter, University of Connecticut
- Tommy Rockward, Ken Stroh, Francisco Uribe, LANL
- Nikunj Gupta, Leon Rubinstein, Patrick Kilough, Shell Hydrogen
- Jesse Schneider, George Mitchell, Chrysler Group
- Joe Schwartz, Praxair
- Jim Simnick, BP
- Mike Steele, Fred Wagner, GM
- John Van Zee, Jean St. Pierre, University of South Carolina
- Gerald Voecks, consultant to NREL
- Silvia Wessel, Ballard Power Systems
- Doug Wheeler, consultant to University of Hawaii
- Robert Wichert, USFCC