2007 DOE Hydrogen Program Annual Merit Review

Hydrogen Fuel Quality

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National Renewable Energy Laboratory

May 17, 2007

Project ID# SA4

Overview

Timeline

- Project start date: 10-1-04
- Project end date: 9-30-10
- Percent complete: 30

Budget

- Total project funding
  - DOE share: $1190K
  - Contractor share: $0K
- Funding received in FY06: $200K
- Funding for FY07: $890K

Barriers

- Codes and Standards Barriers addressed
  - Consensus national agenda on codes and standards (J,A,B,D,L)
  - Limited DOE role in development of ISO standards and inadequate representation by government and industry at international forums (F,G,H,I,K)

Partners

- FreedomCAR-Fuel Partnership C&S Technical Team
- North American H2 Fuel Quality Team
- ISO TC197 WG12, SAE J2719 WG, USFCC HQ TF, ASTM D03
- DOE Fuel Quality Working Group

Acknowledgement: North American Team for ISO TC197 WG12

- Shabbir Ahmed, Romesh Kumar, Rajesh Ahluwalia, ANL (DOE FQWG)
- Bhaskar Balasubramanian, John Lemen, Chevron (C&STT, HPTT)
- Robert Benesch, Air Liquide
- Brian Bonner, Air Products
- Bob Boyd, Linde Group (ASTM, SAE)
- Pamela Chu, NIST
- Bill Collins, UTC Fuel Cells (ISO/TC197 WG12, USFCC, SAE)
- Raul Dominguez, SCAQMD (ASTM D03)
- Tony Estrada, PG&E (ASTM D03, SAE, ISO/TC197 WG12)
- James Goodwin, Clemson University (DOE Solicitation)
- Karen Hall, NHA (ISO TC197 and WG12)
- J.P. Hsu, Smart Chemistry (ASTM D03)
- Hector Colon-Mercado, William Rhodes, SRNL (DOE Solicitation)
- Trent Molter, University of Connecticutt (DOE Solicitation)
- Jim Ohi, NREL (DOE HFCIT, C&STT)
- Rick Rocheleau, Guido Bender, University of Hawaii (ISO/TC197 WG12, DOD)
- Nikunj Gupta, Shell Hydrogen (HPTT, SAE, ASTM D03)
- Jesse Schneider, George Mitchell, Daimler-Chrysler (C&STT, SAE, ISO/TC197 WG12)
- Joe Schwartz, Praxair
- Jim Simnick, BP (ASTM, HDTT)
- Mike Steele, Fred Wagner, GM (C&STT, FCTT, SAE)
- Tommy Rockward, Ken Stroh, Francisco Uribe, LANL (FCTT, USFCC/SCTRR, DOE Solicitation)
- John Van Zee, University of South Carolina (ISO/TC197 WG12)
- Gerald Voecks, consultant to NREL (ISO/TC197 WG12)
- Silvia Wessel, Ballard Power Systems (ISO/TC197 WG12, CaFCP, USFCC)
- Doug Wheeler, consultant to University of Hawaii (ISO/TC197 WG12)
- Robert Wichert, USFCC (ISO and TC197 WG12, IEC)

Background: ISO TC197 WG12 Recent History

- 7th Meeting, Paris, June 9, 2006 (1st meeting, Tokyo, June 2004)
  - completed final editing of international guidelines for hydrogen fuel quality (ISO DTS14687-2)
    - intent and limitations of DTS carefully specified
  - discussion of R&D/testing approaches by Japan, EC, North America
    - JARI/Japan Gas Association and US/Canada harmonized
    - role of Korea identified
    - formal participation by EC through FCTESTQA and JRC/EC
    - agreement to develop collaborative R&D/testing program
- 8th meeting, November 9-10, 2006, HNEI, Honolulu, in conjunction with FC Seminar
  - presentations of detailed R&D/testing plans by Japan, North America
  - initiate consensus plan with priorities, timetables, possible task "assignments"
- 9th meeting, June 5-6 2007, Seoul, Korea
  - launch consensus R&D/testing plans

Approach: R&D/Testing Structure

Collect, evaluate, and report assemblage of data and information
Recommend H_2 fuel quality specifications

Fuel cell vehicle performance characteristics as a function of H_2 fuel contaminants

- Assessment of H_2 fuel quality
- BOP issues
- Correlation of model with vehicle
- Vehicle fuel cell pre and post test

Fuel cell performance characteristics as a function of H_2 fuel contaminants

- Single contaminant/level
- Contaminant/level combinations
- Test conditions
  - operational
  - physical
- Long duration tests
- Transient tests
- Alternate catalysts and materials

H_2 fuel quality dependence on suppliers' processing technology

- Source of H_2 fuel production
- Method of cleanup
- Alternative processes, methods for cleanup
- Technical, economic fuel quality drivers

H_2 storage media characteristics as a function of H_2 fuel contaminants

- Single contaminant/level
- Contaminant/level combinations
- Choices of materials
- Long duration tests
- Cyclic and transient tests
- Operating conditions

Analytical instrumentation to monitor H_2 fuel quality

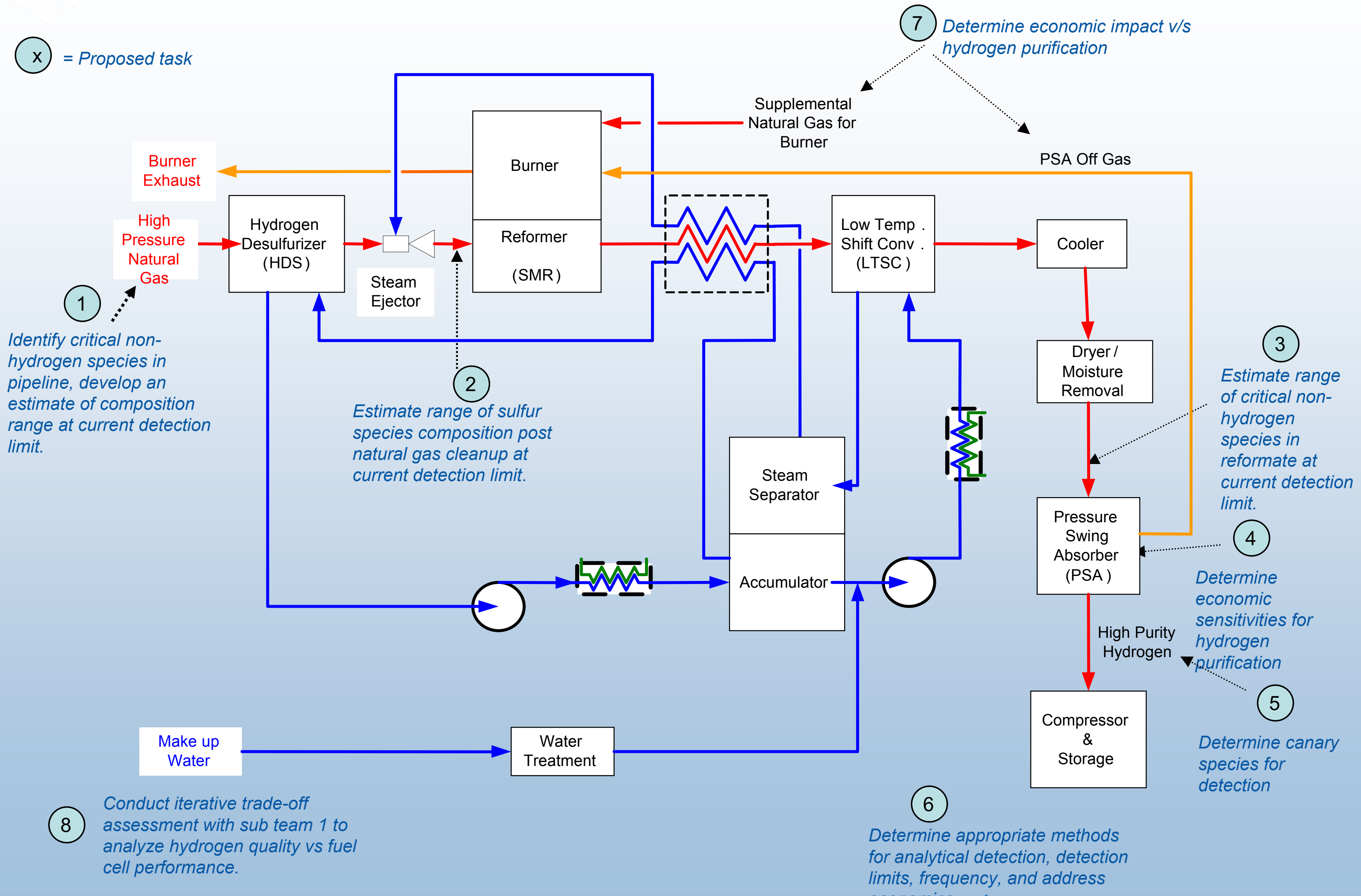
- Determine analytical parameters and constraints for key contaminants
- Identify/analyze alternative methods
- Conduct field tests

Modeling to support understanding of failure mechanisms, production/supply, material development, vehicle systems

Approach: R&D/Testing

- Conduct R&D and testing in parallel with preparation of national and international standards
  - establish collaborative program among Asia, EC, North America
  - integrate on-going and planned work (DOE solicitation winners)
  - focus on critical constituents (cost/technology drivers) for fuel cell performance and fuel cost
- Develop consensus on critical analytical methods and procedures needed to verify recommended maximum levels of contaminants (e.g., calibration gases)
  - work with ASTM D03, NIST, KIER, JIS, FCTESQA (EC), HyQ
  - establish collaborative analytic sampling and measurements effort
- Form two subteams to focus separately but iteratively on single-cell testing (performance-durability) and fuel cell system and fuel infrastructure engineering requirements and costs
  - combine data and analysis to establish consensus requirements based on trade-offs between fuel quality and fuel cost
- Form modeling subteam to develop and apply empirical model
  - focus testing and enable projection of test results, enhance understanding of mechanisms

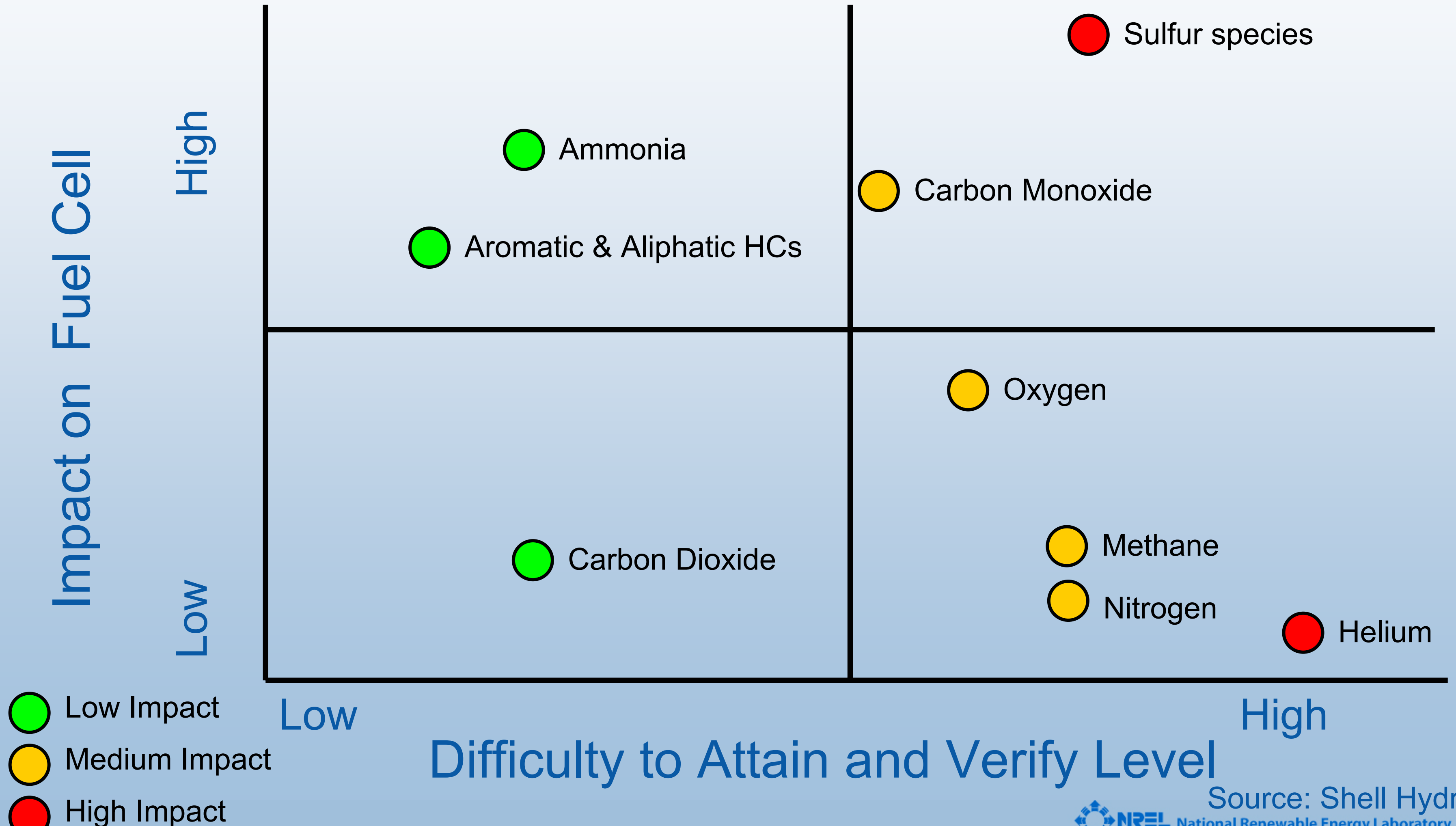
Technical Progress: Baseline Production and Purification System Defined



Source: Preliminary Information Compiled by Chevron for WG12

NREL National Renewable Energy Laboratory

Technical Accomplishments: Fuel Quality- Relative Tradeoff Drivers Identified



Source: Shell Hydrogen

Technical Accomplishment: Potential Canary Constituent Identified

- Carbon Monoxide (CO) may be possible "canary" constituent for detection at many fueling stations and production facilities using hydrocarbon feedstocks
- Subteam 2 will attempt to estimate relationship between CO concentration and other critical constituents (inerts, CH_4, S species, etc.) with respect to PSA breakthrough properties
    - Quantifiable data may be difficult to obtain from PSA adsorbent suppliers due to proprietary nature of the technology (use H_2 recovery rates as surrogate)
    - Estimate rough Order of Magnitude information for breakthrough of other critical constituents in relation to respective composition limits and to CO composition measurement
    - Address simple, cost effective analytical methodologies – when, where, and what techniques to employ?

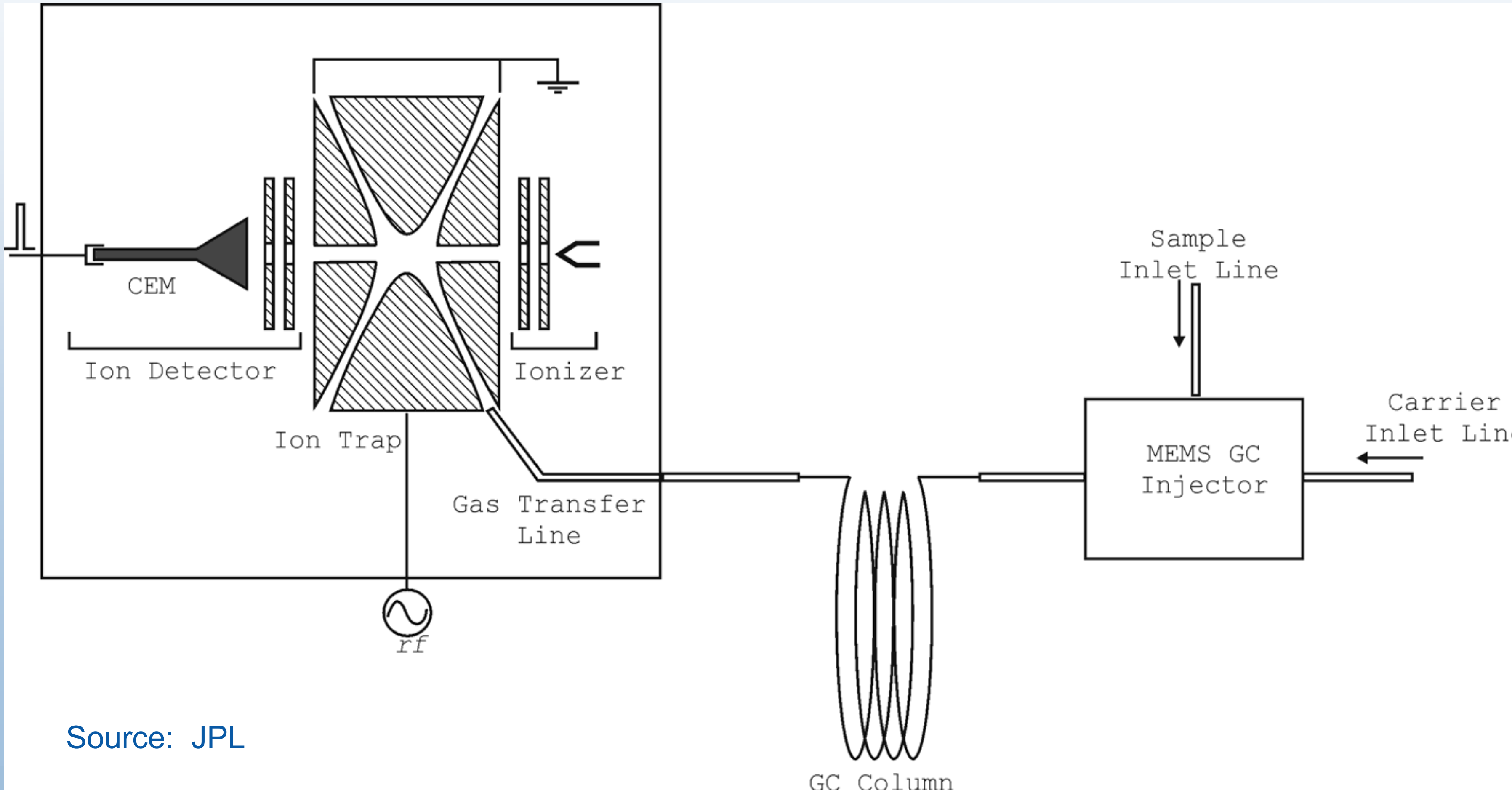
Technical Progress: ASTM Priorities for H_2 Quality Test Methods Defined and Underway

- Design, fabricate, validate 700 bar hydrogen quality sampling apparatus; prepare procedures for safe operation and measure samples
  - schematic and parts assembly under review
- Task ordering agreement under negotiation
  - sampling storage container stability study
  - beta testing of new test method using GC and multiple detectors (WK 4548) with several laboratories
  - inter-laboratory round robin testing of new ASTM analytical test methods

Source: ASTM

Technical Progress: Miniature GCMS Adapted for H2

Schematic of miniature-GCMS developed at NASA-JPL



Source: JPL

Technical Accomplishment: Composite Test Matrix

#	Baseline Tests / Ion Power / Standard GDL / LANL Standard MEA & GDL / 50mm. E-Tek Pt on carbon, 0.2m				Kinetic Effect – Anode Catalyst – Type: Pt	Pt/Alloy	Support	Anode Pt/C Ratio	Cathode Pt/C	Loading: 0.05	0.20	0.4	Cathode Catalyst loading mg/cm²
1	Ex-situ / In Performar		MEA Cross Se				C	20%			SD		
2			Other, i.e. TEM, S				C	20%			SD		
3	BOT and E		ECA	CV			C	50% 20% 20% 50%	40%	HD	HD 0.1		0.3
4			H_2 Crossover	CV			C	50% 20% 20% 50%	40%		HD 0.1		0.3
5	In-sit Perfo nce	Stand Hardw Condit	Polarization	0 to 13 (Ref 1) mA/cm²			C	50% 20% 20% 50%	40%	HD	HD 0.1		0.3
6			Durability @ mA/cm² for 100 hrs Ref 2	1000			C	50% 20% 20% 50%	40%		HD 0.1		0.3
7				600, 600, 800				50% 50%		HD			
8				200			C	50% 20% 50%					
9				Cycle, LANL Cycle			C	20%		HD			
10		Sensit	stoich, Temp C, 30psig, Stoic anode, 2.0 ca 100%RH	50									
11				60			C	50% 20% 50%					
12				80, 80, 80			C	50% 20% 20% 50%	40%		HD 0.1		0.3
13				95									
14			Anode Cathode Standard P, T	60 50				50% 50%					
15				80 50			C	50% 20% 50%					
16				100 60 50			C	50% 20% 20% 50%	40%		0.1		0.3
17			Pressure @ Standard T, stoich	1 to 2 bara / 2 bara				20%	40%		0.1		0.3
18			Stoich @ St T, P, RH, Anode/Cath	1.1 to 1.1 / 2.5				20%	40%		0.1		0.3

Future Work: Develop ISO Standard

- ISO DTS 14687-2 approved unanimously by TC197 “P” members
  - comments submitted by P members must be addressed by WG12
  - publication by mid-2007
- Committee Draft (CD)
  - due one year after approval of TS 14687-2: December 2007
  - revision of recommended allowable limits of non-hydrogen constituents
    - focus on “critical contaminants”
    - initial incorporation of test data, analysis, modeling
- Draft International Standard (DIS)
  - due one year after CD (December 2008)
- Final Draft International Standard (FDIS)
  - due one-year after DIS (December 2009)
- International Standard (IS)
  - due six months after FDIS (June 2010)

<u>note: timetable subject to approval by TC197 Secretariat</u>

Summary

- Consensus national and international fuel quality guidelines available
  - ISO Technical Specification (TS 14687-2) approved and in press
  - ISO TS and SAE J2719 are nearly identical
- Significant progress on R&D/testing to obtain data needed to convert guidelines into standards
  - Test protocol, test matrix, data reporting format adopted
  - Testing underway at LANL, HNEI
  - FQ solicitation winners integrated into overall effort
  - International collaboration underway
  - Modeling subgroup formed
- International and national standards under preparation
  - Committee draft for ISO standard
  - Updating of SAE J2719

DOE Hydrogen Program

Fuel Quality: Impurity Testing

Principal Investigator: Tommy Rockward
Los Alamos National Laboratory
May 2007

Project ID#: SA-4

Overview

- Timeline
  - Start: 10/06
  - End: 09/10
  - % complete: 10%
- Budget
  - Total project funding
    - DOE share: $500K
    - Contractor share: $0K
  - Funding received in FY06: $0K
  - Funding for FY07: $500K
- Codes and Standards Barrier addressed:
  - N. Insufficient Technical Data to Revise Standards
- Partners/Collaborators
  - HNEI, Clemson, UConn, U. South Carolina
  - ANL

Objectives

To establish and test a set of valid and reproducible experiments, geared towards producing useful data on the impacts of contaminants in the fuel stream.

To apply those learnings to help develop predictive mechanistic models.

Approach

Using LANL's decal method, we can produce Membrane-Electrode-Assemblies with different loadings.

Utilizing multiple mass-flow controllers, we are able to vary contaminant levels, and accurately measure concentrations at very low levels.

This coupled with our fuel cell experience allows testing flexibility in such a dynamic research environment.

Outline/Overview

- LANL's Decal Method
- LANL's Break-in Procedure with Results
- On-going Impurity Testing
- Round Robin Tests

LANL's Fuel Cell MEA Fabrication

Ink Catalyst Preparation (PEM, DMFC, Sprayable Inks)

Initial Membrane Treatment

Applying Catalyst (substrate, direct, GDL)

Transfer Techniques (Hot Press, Interfacial layers)

Post Membrane Treatment

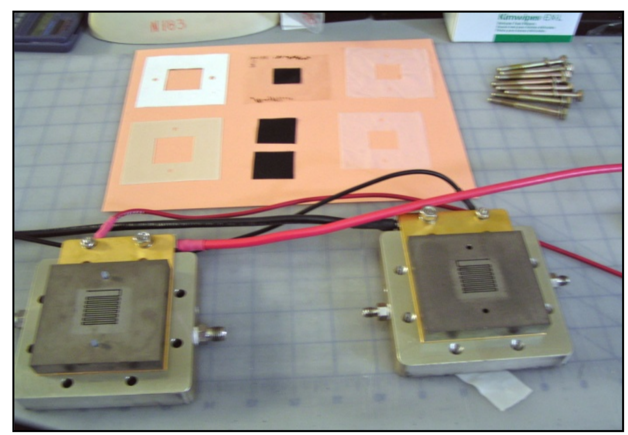
Fuel Cell Assembly

LANL's Procedure and Protocol*

- components and cell assembly

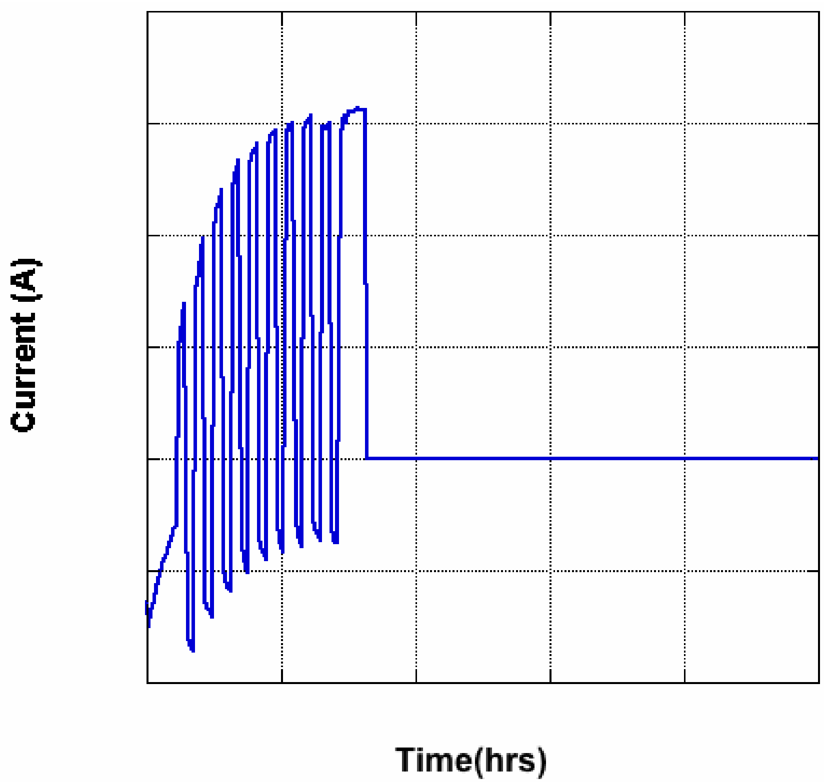
- Components
  - Various Sizes of Hardware (Typically 5 or 50 cm^2)
  - Membrane type: N112, N1135, N115 or N117
  - Pt-Loading: 0.2 mg Pt/cm^2 (20% Pt/C each electrode)
    - Loadings from weight are verified by XRF measurements
    - Profilometry and XRF for coating uniformity~5% variation
  - Backings: 1-sided and 2-sided ELAT
    - Orientation is fuel cell size dependent (water management)
  - Sealing Materials
    - Silicon gaskets & teflon masks

- Cell Assembly
  - Five layer configuration and gaskets
  - Torque
    - Star-like pattern 25 in-lbs increments to ~90 in-lbs
  - H_2 Leak Test
    - Probe exterior hardware with handheld H_2 detector
    - Dead-end hardware outlet



*Variation can be incorporated to suit hardware and/or testing scope

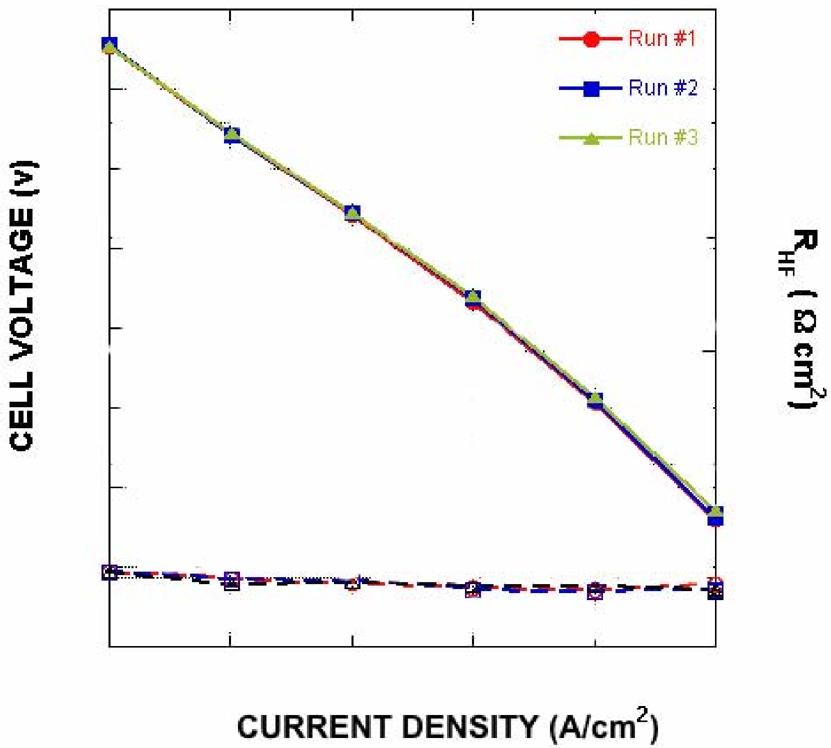
LANL’s Break-In Procedure



- Voltage cycled between 0.5V and 0.7V after soaking at 0.6V
- Cell current then held at 30A; overnight (12+ hrs)
- Cell Temp: 80^{o}C, back pressure: 25 psig (sea level), fully humidified
- H_2/Air: fixed at 696/1740 sccm
- Current and voltage versus time recorded (graph shows I vs. time)

Results are a part of on-going round robin testing

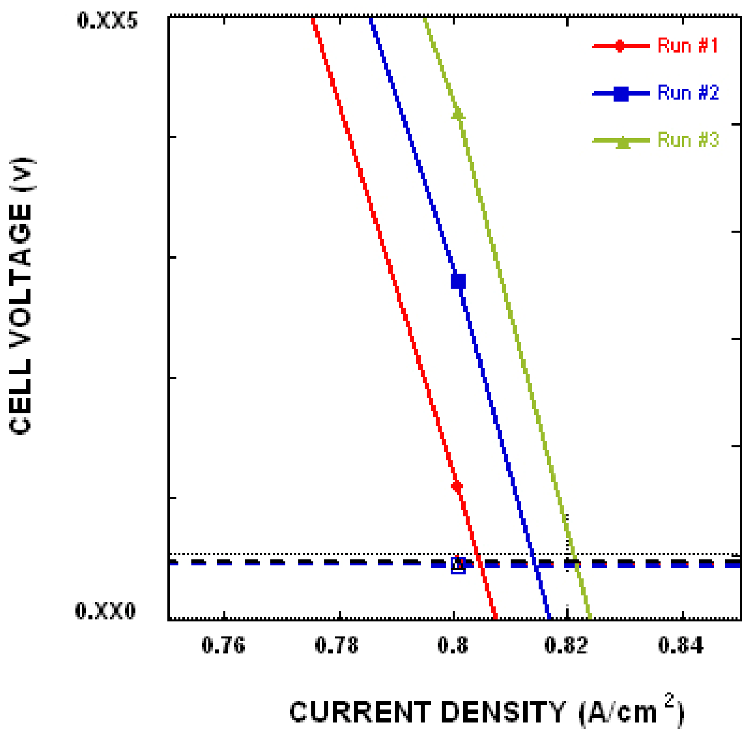
Constant Current VIR curves

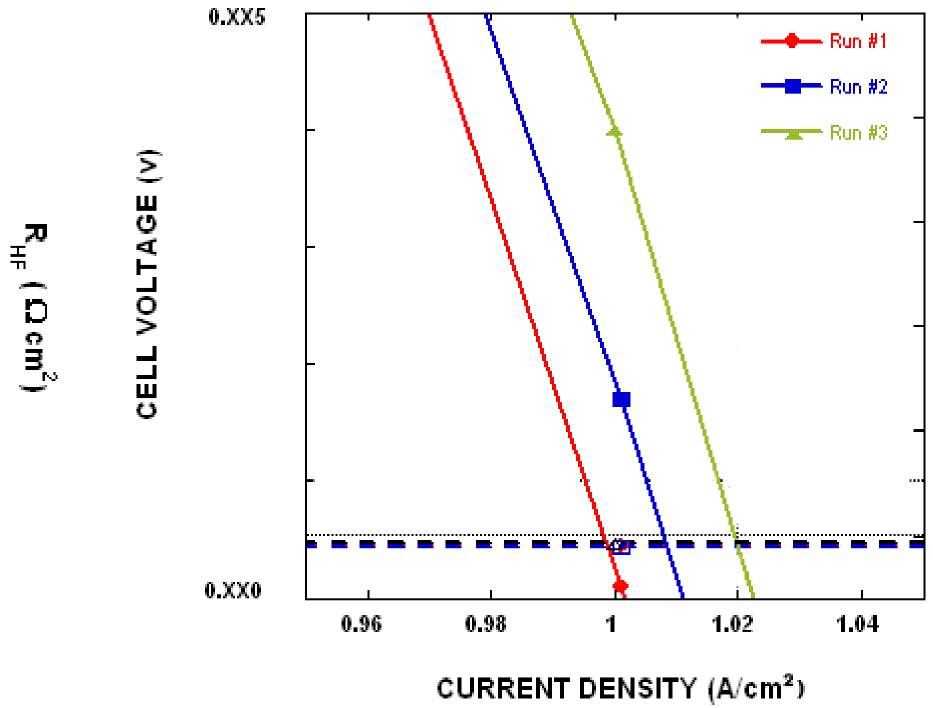


- LANL produced MEA: 0.2 mg Pt/cm^2 on both electrodes.
- H_2/Air: 1.2/2.0 stoichs
- Cell Temp: 80^{o}C, back pressure: 25 psig (sea level), fully humidified.
- Soaking time 15 min. with 5 min. for data averaging.
- Cell broke in quicker than at low temperature break-in…

Results are a part of on-going round robin testing

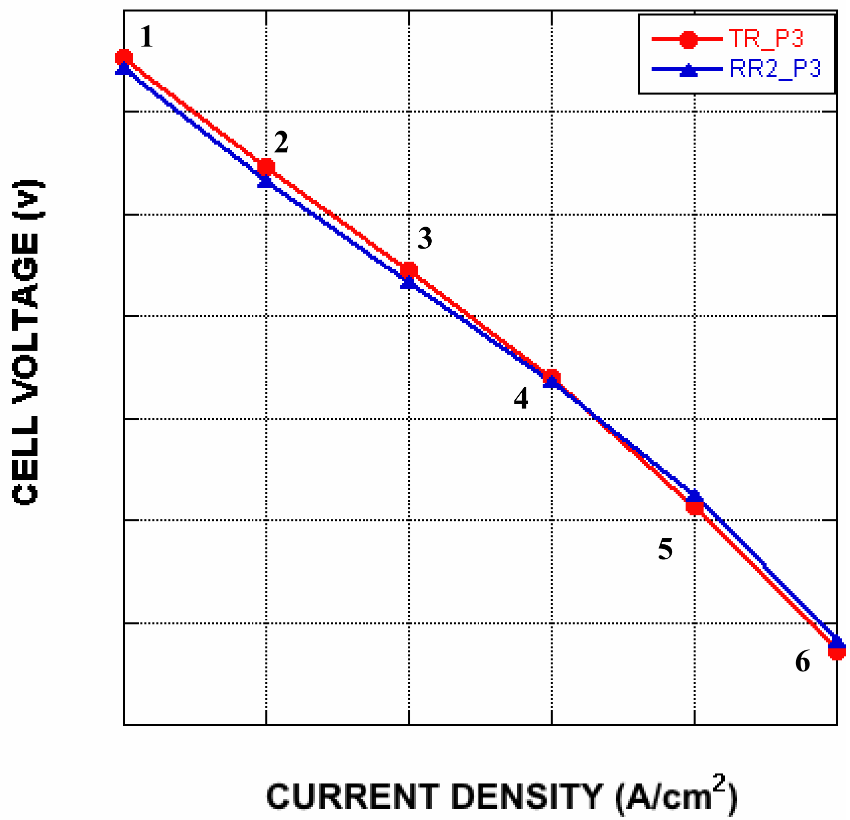
Break-in Complete
…voltage deviation < 5mV at 40A





H_2/Air: 1.2/2.0 stoichs; Cell Temp: 80ºC, back pressure: 25 psig (sea-level), fully humidified.

Cell-to-Cell Comparison

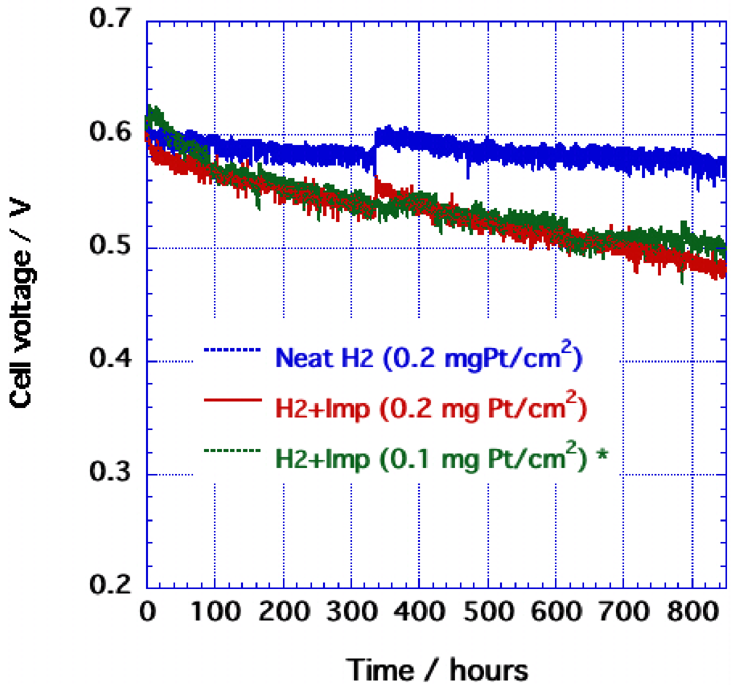


Points	+/- mV
1	4.3
2	6.7
3	5.9
4	2
5	5.5
6	4.9

Results shown reflect two different MEAs tested using identical conditions with completely different components. The cell was tested at 80°C and 25 psig with fully humidified gases. The table on the right shows the voltage deviation between the two cells.

FC Operation with FreedomCAR Fuel Specification for 2007 and 2010 anode Pt loadings

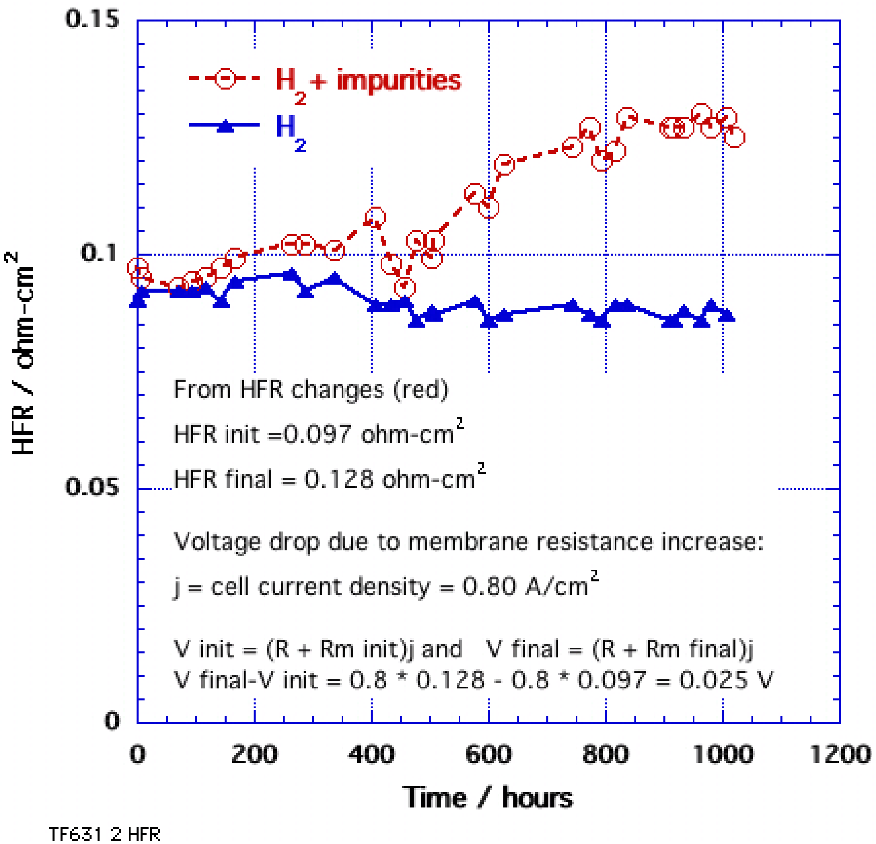
Voltage loss at 0.8 A/cm² constant current



Component	*Level*	*Level*
Hydrogen	> 99.9	> 99.9
Hydrogen Sulfide	10 ppb	10 ppb
CO	0.1 ppm	0.1 ppm
CO_2	5 ppm	5 ppm
NH_3	0 ppm	0 ppm
Ethylene (NMHC on a C1 basis)	50 ppm	50 ppm
Particulates (Conform to ISO 14687)	Not included in test	Not included in test

- *Similar losses for both Pt loadings*
- Impurities caused 100 mV performance loss after 800 hrs
- H_2S partial poisoning detected at the anode by CV
- No CO adsorption detected by CV
- Membrane conductivity also affected as indicated by increase of HFR

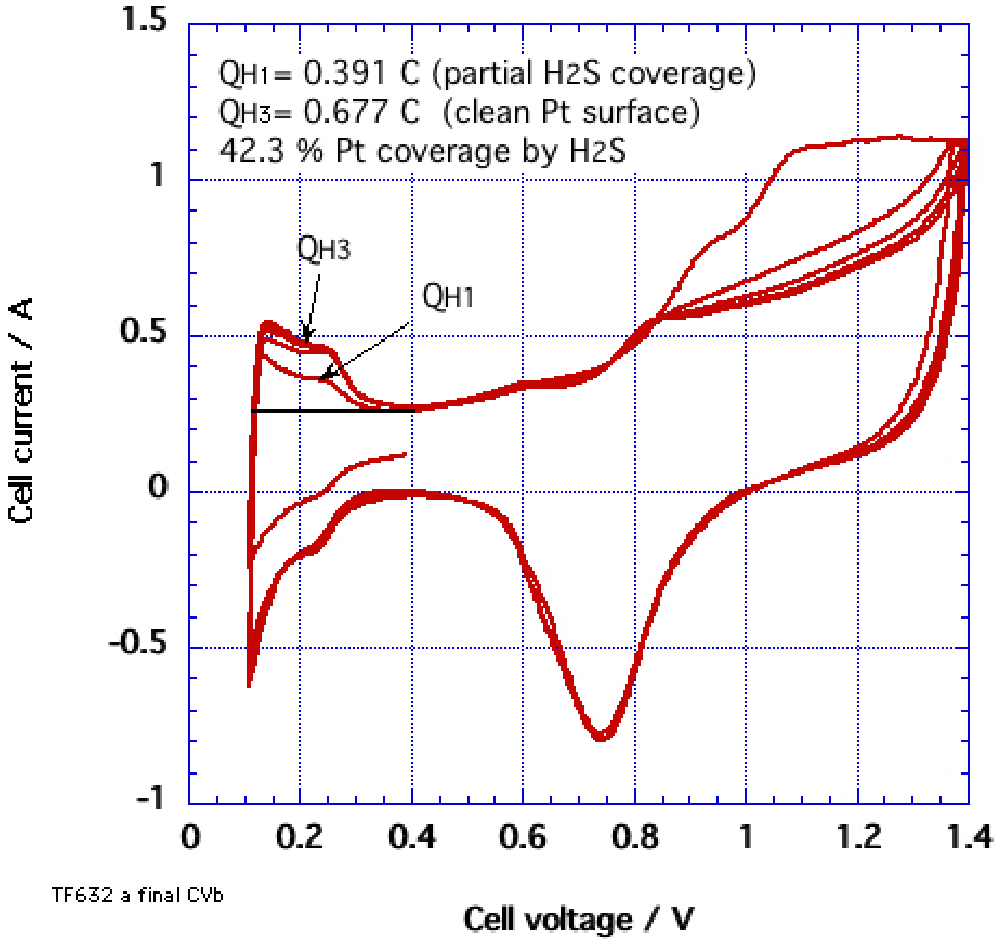
Impurity Mixture Effects On Membrane Conductivity



- High frequency resistance increases with time for impurity test mixture
- 25 mV loss from R increase
- NH_4^+ exchange for H^+ ?
- IR loss is not the only source of cell voltage drop

Ammonia gas forms cations and lowers membrane conductivity

Impurity Mixture Effects



- Cyclic voltammetry is indicative of sulfur poisoning: ~40% coverage of Pt surface
- No Evidence of CO in CV
- S adsorbed onto Pt strongly blocks CO adsorption in gas phase studies (V.D. Thomas et. al., *Surface Science*, 464 (2000) 153-164)

```
50 cm² cells / N112, 50 mV/s
Loadings: 0.2 mg Pt at each electrode
Cell Temperature: 80 °C.  PSIG: 30/30
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<u>Possible reactions:</u>

$$H_2S_{gas} + Pt \rightarrow H_2S_{Pt}$$

$$H_2S_{Pt} \rightarrow S_{Pt} + 2H^+ + 2e^- \ast$$

$$H_2S_{Pt} \rightarrow HS_{Pt} + H^+ + e^-$$

Round Robin Test

LANL has completed the first set of baseline tests.

The test cell was shipped and received at the first subsequent site, along with testing instructions. These are blind tests.

When testing is completed, the test cell will be sent to the next testing site, etc.

When all testing sites have completed the tests, the test cell will be returned to LANL for final testing. Results of all tests will be compared and reported.