Hydrogen Fuel Quality


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Project ID # SCS007

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# Overview

## Timeline
- Project start date: 10/1/06
- Project end date: 9/30/16*

  *Project continuation and direction determined annually by DOE*

## Barriers
- Barriers addressed
  - I. Conflicts between Domestic and International Standards
  - N. Insufficient Technical Data to Revise Standards

## Budget
- Total project funding: 4025K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY15: 700K
- Total funding planned for FY16: 750K

## Partners/Collaborators
- Japanese Automotive Research Institute
- National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee Call
- ASTM
- SAE
- Smart Chemistry
- CEA-Liten France
- VTT- Helsinki, Finland
- IEC/TC105/Working Group 11
Project Objective 1: Hydrogen Fuel Quality

LANL has maintained three focus areas for the hydrogen fuel quality part of this project. These focus areas are centered on PEMFC testing, collaborations, and work with the ASTM.

Fuel Quality Testing:
- Utilize MEAs with 2015 DOE target loadings (A/C: 0.05/0.10 mg Pt/cm²)
- Tests the impact of fuel contaminants at the SAE J2719/ ISO 14687-2 levels
- Disseminate results

Collaborations:
- Develop and maintain US and International collaborations
  - Harmonize testing
  - Protocol and standards development

ASTM:
- Leadership within the D03.14 committee on the development of standards
- Participate in Inter Laboratory Studies (ILS)
Project Objective 2: Fuel Quality Analyzer

Relevance/Impact

The development of a device to measure impurities in the fuel stream would be useful to the fuel cell community, hydrogen fueling stations and suppliers. Such a device could prevent damage to fuel cell stacks provided it is:
- inexpensive
- sensitive to the same impurities that would poison a fuel cell stack
- quick response time to contaminants.

Approach

- This device operates as an electrochemical pump using a MEA-type configuration. (no air available)
- Use similar components to a fuel cell stack (e.g. Ionomer, PGM, and GDLs)
- Reduce overall Pt loading and utilize low surface area catalyst
- Identify best materials and their configuration
Outline

- ASTM Efforts D03.14
  - Momentum in the development of Standards
  - Challenges ahead
- Fuel Quality Testing
  - Parametric Studies
  - International Collaboration
- Fuel Quality Analyzer
  - Initial Approach and Findings
  - Prototype Status
  - Results
- Summary
- Future
8 standards are under consideration by D03.14

New ILS participants: Toyota and PNNL have expressed interest

New Spreadsheet helps track test-sites

Next meeting, Bellevue, WA, June 2016

Inter-Laboratory Studies Underway

- GC/MS
- FTIR

Challenges

- Data collection
- Some ILS sites require funding
Fuel Quality Testing

- Parametric studies as a function of operating conditions
  - Determining impurity tolerance under more realistic conditions
  - H₂ fuel recirculation system vs single pass
    - Effect of CO
    - Effect of H₂S
    - Effect of ISO mixture (NH₃, CO, H₂S)

- International Collaborations
  - Sulfur Pre-Dose Testing (CEA/LANL)
  - H₂ Fuel Recirculation System testing (VTT/LANL)
  - International Baseline Testing (CEA/VTT/LANL)
Approach: Parametric Study of CO Tolerance

<table>
<thead>
<tr>
<th>T: 80 ºC</th>
<th></th>
<th>Tolerance of [CO] in PEM Fuel Cells</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (kPa)</td>
<td>80</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>[CO] (ppm)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>RH (%)</td>
<td>32</td>
<td>50</td>
</tr>
</tbody>
</table>

- Is there a need to revise standards
  - Evaluate tolerance on MEAs with low anode loadings (0.05mg$_{pt}$/cm$^2$)
  - Compare re-circulation vs single pass
  - Effect of RH and pressure and concentration
- Abstract submitted to ECS (10/2016)
- Create database to provide data for modelers
Accomplishments: H₂ Recirculation vs Single-Pass with 200 ppb CO/H₂

- Fuel cell voltage at a current of 1A/cm² when operating under H₂ + 200 ppb CO with H₂ single pass (left) and H₂ recirculation (right) at 80°C, 100% RH, and 150kPa
- Voltage loss after 100 hrs with single pass is ~ 38 mV.
- Fuel Recirculation system loss is ~ 50 mV.
- 30% extra voltage loss due to recirculation at anode

MILESTONE:
Accomplishments: H$_2$ Recirculation vs Single-Pass with 4 ppb H$_2$S/H$_2$

- Fuel cell voltage at a current of 1A/cm$^2$ when operating under H$_2$ + 4 ppb H$_2$S with H$_2$ single pass (left) and H$_2$ recirculation (right) at 80$^\circ$C, 100% RH, and 150kPa
- Voltage loss after 100 hrs with single pass is ~ 31 mV and after 175 hrs is 47mV
- Similar losses to 200 ppb CO. Effect of recirculation expected to be similar to CO (underway)
Accomplishments: Single Pass ISO Mixture: RH dependence

- Fuel cell voltage at a current of 1A/cm² when operating under H₂ + mixture: 200 ppb CO, 4 ppb H₂S, and 100 ppb NH₃ with 100 % RH (left) and 50%RH(right) at 80°C, 100% RH, and 150kPa
- Voltage loss after 100 hrs at 100% RH is ~ 60 mV and at 50% RH is ~ 67 mV
- Consistent with previous data describing competitive adsorption between CO and H₂S.
International Collaborations:

- **IEC/ TC197 WG-11**
  - International team of experts developing a Fuel cell Testing Document (Status: DTS)
  - Next meeting hosted by DOE/LANL: June 20, 2016 in Washington D.C.
  - Member Countries: Finland, Japan, China, United Kingdom, Italy, France, Switzerland, US

- **CEA (Grenoble, France)**
  - Pre-dosing Experiments
  - Baseline Testing

- **VTT (Helsinki, Finland)**
  - H$_2$ Recirculation System
  - CO poisoning

- **Joint Research Centre**
  - Test method validation
Collaboration: CEA-LANL Pre-dosing Experiments:

What is the impact of CO in the event of an unexpected exposure to \( \text{H}_2\text{S} \)?

**MEA exposed to \( \text{H}_2\text{S} \) then CO:**

- Higher concentrations used to investigate impact in a shorter time period
- 1\textsuperscript{st} day: After 1h exposure to 20 ppm \( \text{H}_2\text{S} \) shows little response to 1 ppm CO
- 2\textsuperscript{nd} day: Subsequent exposures to CO and \( \text{H}_2\text{S} \) shows both regions are impacted
- \( \text{H}_2\text{S} \) regions are decreasing with successive exposures
- CO impacts become more severe as S coverage increases

**Data provided by CEA**
Collaboration: VTT-LANL

Scope: Evaluating impact of internal air bleeding on CO by assessing the carbon balance

25cm², 80°C, T<sub>anode/cath</sub>: 70°C/77°C
an/cath loading: 0.05/0.1 mg Pt/cm²
H₂/Air: 1.25/2.5 stoichs

- 1.86 ppm CO/H₂ introduced while cell operated at 0.4 A*cm⁻²
- For V<sub>loss</sub> < 30mV, CO₂ concentration increases (CO oxidation)
- Window of opportunity (possibly) exists at the introduction of CO
- Difficulties exist for carbon balancing because pre-existing CO₂ in the system (fuel or oxidant)

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Approach: Identifying Desirable Materials

Proof-of-Concept Shown FY15

Reference Electrode: Tolerant and Stable

- Pt: 30 wt %, Ru: 23.3 wt %, High surface area to mass ratio 3.5nm particle size
- Carbon black with 5% Nafion® painted decals

Working Electrode: Durable and Sensitive

Sputtered low loaded electrode provides stable Pt particle sizes and high sensitivity to impurities.

Desired response times obtained for both CO and H₂S at the SAE level!

*Response time < 5 minutes!!!*
Smart Milestone: Developing the Prototype

Approach:

- **Membrane Hydration Challenging:** Identifying conditions needed for constant membrane humidification
  - Characterize and confirm by measuring HFR and CV
  - Vary flow conditions
  - Vary Membrane thickness
- Determine a **fuel flow-rate** that will not compromise sensitivity or response time
Accomplishments: Membrane Hydration Tests N212 vs N117

- Fully saturated membranes yield constant HFR
- Increase in membrane resistivity during flow of dry gas evident.
- Thicker membrane (N117) maintains hydration longer.
Accomplishments: Re-designing the Hydration Scheme

- 400 ml/min of 6% H₂/Ar flow continuously overnight
- HFR reasonably stable (left)
- GDLs added: 100 cycles are shown overlapping (constant HFR achieved?)
Prototype Developed: Validation underway

Newly designed prototype developed. IP protection initiated for membrane hydration system
Testing is underway!!!
Initial results show promise,
Next step is to test at SAE/ISO levels!
Summary

1. ASTM
   - Several test methods have been published
   - Spreadsheet helped identify interested test-sites with capabilities for conducting ILS
   - Testers are looking for support
   - ASTM can purchase samples but does not provide funding

2. Hydrogen Fuel Quality
   - International collaborations underway (CEA, VTT, JRC)
     - Baseline testing complete
     - $H_2$ Impurity testing on-going and should continue (HyCoRA Project funding extended)
     - Re-Circulation testing comparisons made with single-pass results

3. Hydrogen In-Line Analyzer
   - Demonstrated hydration scheme allows for constant baseline measurements
   - Instant response observed at 50 ppm CO
Future Work

1. ASTM
   - Continue to support D03.14 efforts
   - Identify test sites with the capabilities and interest

2. Hydrogen Fuel Quality
   - Continue working on the CO Tolerance Chart
   - Continue testing re-circulation vs single-pass
   - Continue International collaborations (CEA, VTT, JRC)
     - Complete PEM FC testing protocol document
     - Complete round robin testing
     - Confirm the delivery of FC stack for impurity testing

1. Hydrogen In-Line Analyzer
   - Test using SAE/ISO limits (CO and H₂S)
   - Test response times for varying CO and H₂S concentrations
   - Correlate the response signal with CO and H₂S concentrations
Acknowledgements

- Charles (Will) James Jr, PhD; Technologies Manager
- Our International Collaborators: JRC, VTT-Finland, CEA, WG-11
- CSTT, SAE and ASTM D03.14 members
Reviewers Comments

“The project weaknesses are the apparent lack of urgency with ASTM and apparent lack of collaboration with the academic labs that developed the initial data. Recommend evaluating effectiveness of chairing ASTM sub-committee.”

The challenge of finding test sites has been overcome and now funding surfaces as an issue. The sub-committee chair cannot appropriate funding.

“Future work may be reasonable and worthwhile; however, little detail is provided in the presentation. Decision points are not described. Risks, barriers and challenges are not described.”

The AMR is a snap-shot of the Project approaches, accomplishments, and future direction. Sub-tasks are typically expanded during and throughout the year in dedicated presentations and or forums. The critical assumption made by the presenting team is that the reviewer(s) participates in those activities. Details have been presented to the Codes and Standards Tech Team (CSTT). Project ahead of schedule with all milestones.