2006 Annual DOE Fuel Cell Program Review

Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

Eric Brosha
Fernando Garzon (Presenter)
Bryan Pivovar
Tommy Rockward
Tom Springer
Francisco Uribe
Idoia Urdampilleta
Judith Valerio

Los Alamos National Laboratory
DOE Program Manager: Nancy Garland
LANL Program Manager: Ken Stroh

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Project Overview

Timeline

- Start: FY05
- Status: Ongoing

Barriers:

- Electrode performance decreased by impurities (fuel cell efficiency decreases)
- Higher Pt loading required to maintain performance in presence of impurities increases cost
- Durability may decrease in the presence of impurities

Budget:

FY06: 800K

Targets (2010):

- 5000 hrs durability
- 30$/kW by 2010
- 55% energy conversion efficiency
- 0.3g/kW Pt loading

Partners:

- FreedomCAR and Fuel Partnership
- USFCC

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Project Objectives

**Overall Objective:** Contribute to the understanding of the effects of fuel and air impurities on fuel cell performance

**Specific Goals:**
- Develop analytical methods for trace measurements
- Test fuel cell performance under simulated multi-component hydrogen impurity gas mixtures
- Investigate effect of impurities on catalysts and other FC components
- Develop methods to mitigate negative effects of impurities
- Develop models of fuel cell-impurity interactions
- Continue collaborations with USFCC, Fuel Cell Tech Team, Industry and other National Laboratories to foster a better understanding of impurity effects
Impurities And Their Sources in Polymer Fuel Cells

• Fuel Impurities

• Hydrogen Source and Reforming Process

  Natural gas
  Coal → CO, NH₃, H₂S, HC’s
  Fuel Oil

• Air Impurities

  * From fuel combustion pollution: SO₂, NO & NO₂, Soot
  * From natural sources: Ocean salts, dust

• Other

  * De-icers: NaCl, CaCl₂
  * Corrosion products from FC system: cations

Recent FC-Tech Team focus on gas mixtures to simulate common fuel impurities
Understanding Impurity Adsorption Effects

- Impurities may adsorb onto:
  - Pt surface
    - CO, H₂S, SO₂, Cl⁻
  - Carbon support
    - H₂S, SO₂
  - Ionomer
    - M⁺, NH₄⁺
  - Gas diffusion layer
    - Salts, wetting agents

- Impurities may block reaction sites for: chemisorption, charge transfer and/or impede protonic conduction.
- May also change GDL properties affecting mass transport.
Research Approach

- Fabricate and operate fuel cells under controlled impurity gases
  - Multi-gas mixing manifolds and FC test stations
  - Pre-blend impurity gas
  - Measure performance
    - Understand degradation mechanisms
    - Study mitigation approaches
- Develop analytical tools for studies
  - Electroanalytical methods
  - In situ diagnostics
  - Sub PPM gas analysis
- Analyze and model data
Analytical Method Development

H₂S Detector and TPD

- We have developed a reliable low cost method for sub-ppm H₂S analysis - ppb sensitivity
  - Ag/AgS Electrode Sulfide ion probe
  - Detects S⁻
    \[ \text{Ag} + S^- \rightarrow \text{AgS} + 2e^- \]
- Probe measures ppb quantities of H₂S by S⁻ concentration change
  \[ H₂S + 2NaOH_{\text{aqueous}} \overset{pH>12}{\underset{\text{r.t.}}{\rightarrow}} S^- + 2Na^+ + 2H₂O \]
- H₂S is a sticky gas: care must be taken in ppb measurements
  - Pre-treat gas lines
  - Temperature Programmed Desorption performed by heating sample at 5°C / min.

![Diagram of H₂S detection and TPD process]
XC-72R Comparison To Activated Carbon

- First experiment repeated using activated charcoal
- 0.24 wt% or 80 times greater absorption than on XC-72R form of carbon
- Form of carbon is very important in determining $H_2S$ adsorption behavior
H$_2$S Adsorption On XC-72 Carbon and E-TEK™ Pt/XC-72

Results

- XC-72 absorbs little H$_2$S at RT
- Pt 20%XC-72 adsorbs significant amounts of H$_2$S
  - $\approx$2%
  - Process exhibits slow kinetics- H$_2$S dissociative adsorption?
    \[
    H_2S_{gas} + Pt \rightarrow H_2S_{Pt}
    \]
    \[
    H_2S_{Pt} \rightarrow S_{Pt} + 2H_{Pt}
    \]
    \[
    S_{Pt} + 2H_{Pt} \rightarrow S_{Pt} + H_2
    \]
- Desorption temperature $>200^\circ$ C
Hydrogen Impurity Mixture

FreedomCar Fuel Cell Tech Team proposed hydrogen impurity spec.

<table>
<thead>
<tr>
<th>Component</th>
<th>Level</th>
<th>LANL Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>&gt; 99.9</td>
<td>95-99 *</td>
</tr>
<tr>
<td>Sulfur (as H₂S)</td>
<td>10 ppb</td>
<td>10 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>0.1 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>5 ppm</td>
<td>5 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>1 ppm</td>
<td>1 ppm</td>
</tr>
<tr>
<td>NMHC</td>
<td>100 ppm</td>
<td>50 ppm ethylene</td>
</tr>
<tr>
<td>Particulates</td>
<td>Conform to ISO 14687</td>
<td>not included in first test</td>
</tr>
</tbody>
</table>

* Includes dilution due to inert gas in stock mixtures
Milestone: Constant Current Testing of Impurity Mixture

Voltage losses of two 50 cm² equivalent cells run at 0.8 A/cm² for 1000 hours

- Impurity cell performance loss is significantly greater than hydrogen control cell
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:

Possible reactions:

\[
H_2S_{\text{gas}} + Pt \rightarrow H_2S_{Pt} \\
H_2S_{Pt} \rightarrow S_{Pt} + 2H^+ + 2e^- \\
H_2S_{Pt} \rightarrow HS_{Pt} + H^+ + e^- \\
\]

50 cm² cells / Ni12, 50 mV/s
Loadings: 0.2 mg Pt at each electrode
Cell Temperature: 80 °C. PSIG: 30/30

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Milestone: Air Effect on Anode Due To Shut-down

- Anode poisoned with 1 ppm H$_2$S
- Anode is at OCV before air exposure
- Air bled overnight
- **Cell recovered almost fully**

Possible mechanisms?

\[ S_{Pt} + H_2 \rightarrow H_2S_{gas} \uparrow \]

\[ S_{Pt} + O_2 + H_2O \rightarrow SO_3^{aq} + 2H^+_{aq} \]
Effect of OCV on Sulfur Poisoned Cathodes and Anodes

- Cells are poisoned for 50 min (2X amount of H₂S needed for full poisoning at 100% adsorption efficiency)
- The application of Open Circuit Voltage on S-poisoned electrodes indicates partial recovery

**cathode:** $SO_{2Pt} + O_2 + 2H^+ \rightarrow H_2SO_4$ ?

**anode:** $S_{Pt} + H_2 \rightarrow H_2S_{gas} \uparrow$ ?

EC9_92105

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Effect Of Cell Voltage on $\text{H}_2\text{S}$ Anode Poisoning

- Cell voltage at which $\text{H}_2\text{S}$ exposure occurs influences amount of performance loss and recovery rate
- More poisoning at low cell voltages

<table>
<thead>
<tr>
<th>Operating Voltage / V</th>
<th>$Q_{\text{anodic}}$ / C</th>
<th>$Q_{\text{oxygen reduction}}$ / C</th>
<th>$Q_{\text{Sulfur}}$ / C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>0.0315</td>
<td>0.0123</td>
<td>0.0192</td>
</tr>
<tr>
<td>0.74</td>
<td>0.0342</td>
<td>0.0108</td>
<td>0.0234</td>
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<td>0.6</td>
<td>0.0349</td>
<td>0.0109</td>
<td>0.0241</td>
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<td>0.5</td>
<td>0.0341</td>
<td>0.00977</td>
<td>0.0243</td>
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<td>0.4</td>
<td>0.0350</td>
<td>0.0107</td>
<td>0.0242</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0338</td>
<td>0.00952</td>
<td>0.0243</td>
</tr>
</tbody>
</table>
Hydrogen Oxidation Model Aids Understanding of Impurity Effects

- Dual path HOR kinetics model needed to explain H$_2$S poisoning data
- S poison acts as an irreversible H site blocker
- Old Butler-Volmer kinetics cannot explain results

DUAL HOR KINETIC PATHWAY

H$_2$ + 2Pt ⇌ 2H-Pt
TAFEL

H$_2$ + Pt ⇌ H-Pt + H$^+$ + e$^-$
HEYROVSKY

VOLMER
H-Pt ⇌ Pt + H$^+$ + e$^-$

Model results

Expt: Cell exposed to 1 ppm H$_2$S

- Model results show a distinct change in cell performance under different H$_2$S exposure times.

- S poison acts as an irreversible H site blocker.

- Dual path HOR kinetics model needed to explain H$_2$S poisoning data.

- Old Butler-Volmer kinetics cannot explain results.
Modeling NaCl Contamination

- NaCl was introduced with the air feed (at high concentration and flow rate – enough Na\(^+\) for complete exchange every 15 seconds)
- CVs show Cl\(^-\) at cathode plays no role
- HFR measures ion conductivity (combination H\(^+\) and Na\(^+\))
  - IR corrections necessary for VI agreement much larger
  - HFR (complete Na\(^+\) exchange) \(\sim 171\) m\(\Omega\)/cm\(^2\)
Summary

• H₂S in fuel test mixture is primarily responsible for anode polarization losses
  – Little effect from CO in mixture-competitive adsorption
  – Almost no adsorption onto XC-72 but other carbons behave differently
• Ammonia is ion exchanging for protons and causing conductivity losses
• SO₂-poisoned cathode can be partially cleaned at OCV
• Fuel cell operating voltage strongly affects extent of anode H₂S poisoning
• On shut-down OCV appears to be also an important factor for cleaning H₂S poisoned anode
• Air purging H₂S contaminated anode results in partial performance recovery
• Dual H oxidation pathway model provides insights in fuel cell behavior
Future Near Term Work

- Continue H$_2$S studies and begin SO$_2$ adsorption on other materials components of the fuel cell
  - Pt immersed in aqueous solution
  - Pt/XC-72R
  - Carbon paper
- Continue investigation of impurity speciation on Pt surfaces
- Determine performance threshold of H$_2$S and NH$_3$ allowed in fuel
- Elucidate cleaning mechanism by OCV in S-poisoned electrodes
- Continue development of impurity models
- Characterize effects of H$_2$S on anode durability and SO$_2$ on cathode durability
- Measure effects of Ca and Mg salt ions on fuel cell performance
- Commence particulate injection studies
Publications, Presentations and Patents


• F. Uribe and T. Rockward, "Cleaning (de-poisoning) PEMFC electrodes from strongly adsorbed species on the catalyst surface" 104229 Non-Provisional patent application (2006).

• F. Uribe and T. Rockward, "Cleaning PEMFC Electrodes with Adsorbed S-species". 208 ECS Meeting, Los Angeles, CA. October (2005)

Review Comments

• Focus on basic understanding rather than empirical testing
  – We are coupling electro-analytical studies to reaction pathway modeling for first principles understanding.
• Focus on component generated impurities rather than fuel impurities
  – LANL & ORNL have previously and are currently studying fuel cell impurity generation and membrane uptake from metallic bipolar plates. The FreedomCAR tech team has suggested this project research priorities focus on fuel impurities.
• Increase interaction with FreedomCAR Codes and Standards Team
  – We have a project member participating at all FCCS meetings and we have tested their proposed impurity limits mixture.