The Effects of Impurities on Fuel Cell Performance and Durability

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Project ID
#FC_24_Molter
Overview

Timeline
• Start March 2007
• End February 2011
• ~50% Complete

Budget
• Total project funding $2,335,725
  – DOE share $1,868,580
  – Contractor share $467,145
• Funding Received in FY07 - $350K
• Funding Received in FY08 - $550K

Barriers
• Establish Tolerance to Fuel and System Derived Impurities

Partners
• United Technologies Hamilton Sundstrand – Historical Contaminant Data
• FuelCell Energy, Inc., - Contaminant Test Support
• UConn CGFCC – Project Management, Testing
Relevance - Objectives

- **Overall Objective** – Develop an Understanding of the Effects of Various Impurities on Fuel Cell Performance and Durability
- **Specific Focus for Past Year**
  - Screening of Hydrocarbon Impurities Per Standard Test Protocols to Identify Impurities of Concern
  - Quantification of Effects on Fuel Cell Performance
  - Effects of Cations on Membrane Properties
  - Develop Fundamental Models Based on Experimental Findings

<table>
<thead>
<tr>
<th>Task</th>
<th>Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Contaminant Identification</td>
<td>• Identify specific contaminants and contaminant families present in both fuel and oxidant streams.</td>
</tr>
<tr>
<td>2.0 Analytical Method Development</td>
<td>• Development of analytical methods to study contaminants.</td>
</tr>
<tr>
<td></td>
<td>• Experimental design of analytical studies.</td>
</tr>
<tr>
<td></td>
<td>• Novel <em>in situ</em> detection methods.</td>
</tr>
<tr>
<td>3.0 Contaminant Studies</td>
<td>• Develop contaminant analytical models that explain these effects.</td>
</tr>
<tr>
<td></td>
<td>• Establish an understanding of the major contamination-controlled mechanisms that cause material degradation in PEM cells and stacks under equilibrium and especially dynamic loading conditions</td>
</tr>
<tr>
<td>4.0 Contaminant Model Development</td>
<td>• Construct material state change models that quantify that material degradation as a foundation for multiphysics modeling</td>
</tr>
<tr>
<td></td>
<td>• Establish the relationship between those mechanisms and models and the loss of PEM performance, especially voltage decay</td>
</tr>
<tr>
<td>5.0 Contaminant Model Validation</td>
<td>• Validate contaminant models through single cell experimentation using standardized test protocols.</td>
</tr>
<tr>
<td>6.0 Novel Mitigation Technologies</td>
<td>• Develop and validate novel technologies for mitigating the effects of contamination on fuel cell performance.</td>
</tr>
<tr>
<td>7.0 Outreach</td>
<td>• Conduct outreach activities to disseminate critical data, findings, models, and relationships etc. that describe the effects of certain contaminants on PEM fuel cell performance.</td>
</tr>
</tbody>
</table>
Approach

- Initiate Studies by Leveraging Existing Database From Prior Work
  - DOE Sponsored Activity
  - USFCC Data
  - Prior Electrolysis Product Experience
  - Ongoing Literature Review

- Focus on Specific Contaminants/Concentrations Identified by DOE/Others

- Use Standardized Test Protocols Where Appropriate to Investigate Contaminant Effects

- Develop Empirical Models Based on Our Findings
Project Work Plan/Deliverables

Deliverables
- Validated Contaminant Models Based on Performance and Durability Data Collected
- New Mitigation Technologies
- Outreach
- Papers, Workshops, Technical Interchange, Etc.

<table>
<thead>
<tr>
<th>Task</th>
<th>Milestone</th>
<th>Date Year/Quarter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Contaminant Identification</td>
<td>Contaminant Identification Review With DOE Sponsor &amp; Industry Focus Group</td>
<td>Y1/Q2</td>
</tr>
<tr>
<td>2.0 Analytical Method Development</td>
<td>Validate Analytical Methods For Studying Contaminants With Ersatz Gases</td>
<td>Y1/Q4</td>
</tr>
<tr>
<td>3.0 Contaminant Studies</td>
<td>Establish an Understanding of the Major Contamination-Controlled Mechanisms that Cause Material Degradation</td>
<td>Y2/Q4</td>
</tr>
<tr>
<td>4.0 Contaminant Model Development</td>
<td>Determine the Relationship Between Contaminant Mechanisms and the Loss of PEM Performance, Especially Voltage Decay.</td>
<td>Y3/Q4</td>
</tr>
<tr>
<td>5.0 Contaminant Model Validation</td>
<td>Validate Contamination Models Through Single Cell Experimentation Using Standardized Test Protocols and a DOE Approved Test Matrix</td>
<td>Y4/Q1</td>
</tr>
<tr>
<td>6.0 Novel Mitigation Technologies</td>
<td>Demonstrate Novel Technologies for Mitigating the Effects of Contamination on Fuel Cell Performance</td>
<td>Y4/Q4</td>
</tr>
<tr>
<td>7.0 Outreach</td>
<td>Dissemination of Results Through Reports (DOE Approved), Papers and Workshops</td>
<td>Continuous</td>
</tr>
<tr>
<td>8.0 Project Management and Reporting</td>
<td>Program Written Reports and Program Reviews</td>
<td>Continuous</td>
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</table>
Roles of Participants

The University of Connecticut
Connecticut Global Fuel Cell Center
Program Lead

United Technologies Hamilton Sundstrand
Advise on Fate of Contaminants

The University of Connecticut Institute for Materials Science
Gas Analyses/Surface Studies

The University of Connecticut School of Engineering
Contaminant Testing
Modeling & Mitigation Strategies

FuelCell Energy Inc.
Contaminant Identification
Fuel Cell Testing

- Electrolysis Contaminant Experience
- Prior Contaminant Studies
- Surface Studies/Equipment
- Gas Purity Analyses
- Fuel Cell Testing
- Modeling/Transport Expertise
- Industry Relationships
- Gas Contaminant Experience
- Fuel Cell Test Experience
Test Matrix
Hydrocarbons and Halogenated Compounds

• Initiate Testing With Methane – Practice Molecule
• Establish Analytical Techniques, Test Protocols, Basic Performance Models
• Export Data in Common Format to Working Groups for Further Modeling
• Contaminant Strategy
  – Near Term Focus – Hydrocarbons and Halogenated Compounds
  – Choice Based on Industry Input
  – Start With High Level – Dilute if Effects are Noted
  – Empirical Models – Near Term
  – Multi-Physics Models – Long Term
Focus on Molecules that May be Present in Hydrogen Fuel Stream

Impurity Choices Based on Industry Input & Literature Review

Determine Effects of:
- Molecule Functionality
- Molecule Size (ie. # Carbons)

Test Strategy

Test Matrix
Hydrocarbons and Halogenated Compounds

Specifications for Draft CD

<table>
<thead>
<tr>
<th>Component</th>
<th>ISO/SAE Specs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>99.97+</td>
</tr>
<tr>
<td>Sulfur (as H₂S)/total S</td>
<td>4 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>.2 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>2 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>.1 ppm</td>
</tr>
<tr>
<td>NMHC/Total HCs</td>
<td>2 ppm</td>
</tr>
<tr>
<td>Particulates</td>
<td>1 ug/L (10 um size)</td>
</tr>
<tr>
<td>Total non H₂ gases</td>
<td>&lt;.03% (300ppm)</td>
</tr>
<tr>
<td>Water</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5 ppm</td>
</tr>
<tr>
<td>He</td>
<td>300 ppm</td>
</tr>
<tr>
<td>N₂ + Ar</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>10 ppb</td>
</tr>
<tr>
<td>Formic acid</td>
<td>.2 ppm</td>
</tr>
<tr>
<td>Total halogenates</td>
<td>50 ppb</td>
</tr>
</tbody>
</table>
Test Protocol
Hydrocarbons and Halogenated Compounds

MEA Definition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (Early)</th>
<th>Value (Recent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Nafion® 212</td>
<td>Nafion® 212</td>
</tr>
<tr>
<td>Anode Loading</td>
<td>0.4 mg/cm²</td>
<td>0.4 mg/cm²</td>
</tr>
<tr>
<td>Anode Type</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
</tr>
<tr>
<td>Cathode Loading</td>
<td>0.2 mg/cm²</td>
<td>0.4 mg/cm²</td>
</tr>
<tr>
<td>Cathode Type</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
</tr>
<tr>
<td>MEA OEM</td>
<td>Ion Power</td>
<td>Ion Power</td>
</tr>
<tr>
<td>Cell Area</td>
<td>25 cm²</td>
<td>25 cm²</td>
</tr>
<tr>
<td>OEM</td>
<td>Fuel Cell Technologies</td>
<td>Fuel Cell Technologies</td>
</tr>
</tbody>
</table>

Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (Early)</th>
<th>Value (Recent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Temperature</td>
<td>80°C</td>
<td>80°C</td>
</tr>
<tr>
<td>Cathode Temperature</td>
<td>80°C</td>
<td>73°C</td>
</tr>
<tr>
<td>Cell Temperature</td>
<td>80°C</td>
<td>80°C</td>
</tr>
<tr>
<td>Anode Humidity</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode Humidity</td>
<td>100%</td>
<td>75%</td>
</tr>
<tr>
<td>Anode Stoich</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Cathode Stoich</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Anode Flow</td>
<td>Commensurate with Current Density</td>
<td></td>
</tr>
<tr>
<td>Cathode Flow</td>
<td>Commensurate with Current Density</td>
<td></td>
</tr>
<tr>
<td>Anode Pressure</td>
<td>25 psig</td>
<td>25 psig</td>
</tr>
<tr>
<td>Cathode Pressure</td>
<td>25 psig</td>
<td>25 psig</td>
</tr>
</tbody>
</table>

Strategy

- Use Commercially Available MEA's
- Start Test at High Concentration (Screening Test)
- Reduce Concentration to Projected Spec. Levels if Effects are Noted, Otherwise Move On
- Move Toward Lower Catalyst Loadings (Projected Commercial)

Cell Conditioning and Tests Performed in Accordance With Standardized Protocols

- H₂ Crossover Per Appendix 1
- ECA Measurement Per Appendix 2
- Cell Conditioning and Verification per section 3.1
- Polarization Under Standard Hardware Conditions 0 – 1.2 A/cm². Repeat 3 times.
- Durability Test at 800 mA/cm² for 100 Hours Under Standard Conditions
- Durability Test at 800 mA/cm² for 100 Hours Under Standard Conditions – except with TBD Conc.¹ contaminant in hydrogen.

¹) 5% - 100 PPM – 50 PPM
Hydrogen Fuel Preparation/Mixing
Hydrocarbons and Halogenated Compounds

Gases and High Vapor Pressure Oxygenated Compounds
Eg. Methane, Ethane, Acetaldehyde, Formaldehyde

Non-Gaseous Impurities
Eg. Formic Acid, Acetic Acid, Ethanol, Methanol, Propylene Glycol, Ethylene Glycol

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Maximum Concentration</th>
<th>Limiting the Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>100 ppm</td>
<td>MFC1</td>
</tr>
<tr>
<td>Formic acid</td>
<td>1 % molar</td>
<td>MFC1 and Saturator</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>200 ppm</td>
<td>MFC1 and energy balances</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>300 ppm</td>
<td>MFC1 and energy balances</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.8 % mol</td>
<td>Saturator</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.0 % mol</td>
<td>Saturator</td>
</tr>
</tbody>
</table>

FuelCell Energy
A United Technologies Company
Impurity Analysis
Hydrocarbons and Halogenated Compounds

Gas Chromatography (GC) of Anode Inlet/Outlet
- Quantitative Analytical Method for Impurities
- On Line Analysis, Simultaneous and Continuous Sampling
- Quantify Species Fed

NMR Evaluation of Condensate
- Anode and Cathode Side
- Periodic Sampling
  - Quantify Species Fed
  - 1H NMR, Protons in Different Chemical Environments Experience Different Shielding and Have Unique Shifts.
  - 13C NMR, Extension to Proton Spectra; Different Carbon Atoms Absorb in a Distinct Range.
In-Situ Contaminant Testing
Hydrocarbons and Halogenated Compounds

Formic Acid

Acetaldehyde
NMR Analysis of Condensate Hydrocarbons and Halogenated Compounds

NMR Analysis

Set up Characteristics:
- Online Collection of Condensate - Anode and Cathode Side (About Every 25 Hours Sample Collected)
- No Perturbation of Cell Operating Conditions

Formic Acid 100 ppm First Run
- Anode Side: Signal for Formic Acid at About 8.5 ppm
- Cathode Side: No signal for Formic Acid
In-Situ Impurity Testing
Hydrocarbons and Halogenated Compounds

- Lab Test Stand Configured for Impurities Testing
- GC Set Up for Impurity Analysis
- Second and Third Lab Test Stands Utilized for Break-In, Some Impurity Testing
Test Summary
Hydrocarbons and Halogenated Compounds

**MEA:** Ion-Power Inc.  N212®, **A/C:** 0.4/0.4 mgPt/ cm²  
**Cell Hardware:** Fuel Cell Technologies Inc.  
**Active Area:** 25 cm²  
**Test Station:** Teledyne MEDUSA

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Impurity</th>
<th>Current Density</th>
<th>RH (A/C)</th>
<th>Cell Temp</th>
<th>Flow Rates A/C</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 ppm CH₄</td>
<td>200 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>58.5/214 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>2</td>
<td>100 ppm CH₄</td>
<td>600 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>175/642 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>3</td>
<td>5 % CH₄ or 5% N₂</td>
<td>600 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>175/642 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>4</td>
<td>100 ppm CH₄</td>
<td>800 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>234/857 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>6</td>
<td>5% C₂H₆</td>
<td>600 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>175/642 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>7</td>
<td>5% C₂H₄</td>
<td>800 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>234/857 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>11</td>
<td>30 ppm CH₃CHO</td>
<td>800 mA/cm²</td>
<td>100%/100%</td>
<td>80 °C</td>
<td>181/664 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>31</td>
<td>100 ppm CH₃CHO</td>
<td>800 mA/cm²</td>
<td>100%/75%</td>
<td>80 °C</td>
<td>278/664 sccm</td>
<td>No Significant Degradation</td>
</tr>
<tr>
<td>35</td>
<td>100 ppm HCOOH</td>
<td>800 mA/cm²</td>
<td>100%/75%</td>
<td>80 °C</td>
<td>278/664 sccm</td>
<td>Significant Degradation</td>
</tr>
<tr>
<td>38</td>
<td>50 ppm HCOOH</td>
<td>800 mA/cm²</td>
<td>100%/75%</td>
<td>80 °C</td>
<td>278/664 sccm</td>
<td>Some Degradation</td>
</tr>
</tbody>
</table>
Test Summary
Hydrocarbons and Halogenated Compounds

Acetaldehyde (CH₃CHO) 100 ppm

Stability Test (100 hours with/without CH₃CHO, 100 ppm)

CELL#31 Operating Conditions:
Current Control: 800 mA/cm²
Pressure-Anode/Cathode: 25/25 psig
Temperature-Cell/Anode/Cathode: 80/80/73°C
Flow Rate-Anode/Cathode: 278/664 sccm (stoich. 2/2 at 800 mA/cm²)

No obvious performance impact was evident during testing at the 100 ppm level.
Test Summary
Hydrocarbons and Halogenated Compounds

Formic Acid (HCOOH) 100 ppm

Stability Test (100 hours with/without HCOOH, 100 ppm)
CELL#35 Operating Conditions:
Current Control: 800 mA/cm²
Pressure-Anode/Cathode: 25/25 psig
Temperature-Cell/Anode/Cathode: 80/80/73°C
Flow Rate-Anode/Cathode: 278/664 sccm (stoich. 2/2 at 800 mA/cm²)

100 ppm formic acid in the H₂ fuel stream shows some effect on fuel cell performance
Test Summary
Hydrocarbons and Halogenated Compounds

Formic Acid (HCOOH) 50 ppm

Stability Test (100 hours with/without HCOOH, 50 ppm)

CELL#38 Operating Conditions:

- Current Control: 800 mA/cm²
- Pressure-Anode/Cathode: 25/25 psig
- Temperature-Cell/Anode/Cathode: 80/80/73°C
- Flow Rate-Anode/Cathode: 278/664 sccm (stoich. 2/2 at 800 mA/cm²)

50 ppm formic acid in the H₂ fuel stream shows some effect on fuel cell performance, but less pronounced than 100 ppm.
Test Summary
Hydrocarbons and Halogenated Compounds
Formic Acid (HCOOH) 100 ppm

“Hot” Cyclic Voltammetry During Contamination
- Record the last CV cycles at each time step
- Scan Rate: 20 mV/sec, Scan Range: 0.05 – 1.0 V,
- Pressure-Anode/Cathode: 25/25 psig
- Temperature-Cell/Anode/Cathode: 80/80/73ºC
- Flow Rate-Anode/Cathode: 250/250 sccm

CVs were performed every 20 hours to characterize cathode poisoning. Last cycle of each scan is shown above. CVs show a decrease in H2 adsorption peaks and an oxidation peak at 0.6 V → Impurities present on Pt surface?

In the 1st CV cycle, Pt surface seems to be covered by adsorbents (peaks at 0.4 V and 0.6 V). Adsorbents are oxidized around 0.4 V & 0.6 V (e.g. CO) in the 1st cycle. In the next 3 cycles recovery of H2 absorption peak is observed, but evidence of surface coverage still exists.

To verify whether the absorbents can be permanently removed, two CV scans were performed at each interval. The peaks at 0.6 V are repeatable.

30 minutes between 1st and 2nd scan
Contaminated H2 in anode
After recovery with pure H$_2$ for 20 hours, hydrogen adsorption peaks are partially recovered. Further operation (up to 100 hrs) with pure H$_2$ does not result in additional recovery.

Contamination of HCOOH on the cathode is not fully recoverable just by purging pure H$_2$ through the anode.
Cell & System Hygiene Management
Hydrocarbons and Halogenated Compounds

How Do We Know That The System is Clean at the Start of a Test? Hydrocarbons are “Sticky” – Sometimes Difficult to Remove.

• New “Wetted” Cell Components
• Cleaning Procedure Adopted For Other System Components Plus Endplates, etc.

Cleaning Procedure After Contaminant Evaluation

• Acetone through tubing
• N₂ purge
• Step ramping to evaporate remaining solvent
  - 40° C, 80° C, 120° C
• N₂ purge
MEA Characterization

- Materials Characterization Techniques Used to Support Impurity Testing
- Baseline and Aged MEA’s Cation Impurity Distribution
- Collaborating With ORNL

**Scanning Electron Microscopy**:  
- Interface bonding  
- Edge effect or appearance  
- Electrode thickness  
- Membrane thickness  
- Electrode Porosity  
- Ionomer Distribution  
- Spectral Imaging (EDXS)  
- Any noticeable physical change

**Transmission Electron Microscopy**:  
- Distribution of the catalyst  
- Porosity of electrodes  
- Membrane/electrode interface  
- Ionomer distribution  
- Chemical composition of membrane and electrodes  
- Pt particles sizes and distribution  
- STEM: (HA-ADF) and EDXS mapping (at ORNL)
CCM Stability Evaluation

- Data Show Significant Spread in Performance/Depradation Rate
- Data Variability Led to a Detailed Investigation of All Potential Contributing Factors
  - Rechecked Test Rig
  - Recalibrated Test Rig
  - Rechecked Procedures
    - Assembly
    - Testing
  - Varied Pressure
  - Varied Flow Rates
  - Varied Relative Humidity
- Data Showed Variation Within and Between Lots of MEA’s
- Worked With Manufacturer & Other Labs to Identify Lots That Show More Consistent Performance
- Inter-Lab Effort Underway to Specify Generic, Stable MEA
Membrane Studies
Cationic Impurities

- Focus is on Membrane Properties Rather Than Fuel Cell Operational Tests
  - Fluids Permeability
  - Water Content
  - Ion Exchange Capacity
  - Conductivity/Ionic Resistance
  - Mechanical Properties
  - Contaminant Characterization Using SEM/EDX
- Move Down and Across Periodic Table to Examine Mass and Valence Effects of Common Ions

Key Findings
- Membrane Water Content Drops Significantly With Cation Exposure
- Membrane Water Content Decreases Significantly as We Move Down Periodic Table – Largely Due to the Change in Hydration Shell for Each Ion
- Nearly 100% of Ion Exchange Sites Consumed for Most Cation Contaminants, Sites Consumed at Low Concentration
- Permeation Rate Appears to be Linear With Pressure
- Cationic Contaminants Affect Permeability in Different Ways
  - H2, O2, N2 and H2O Reduced
- Yield Strength and Modulus Found to Increase With Contamination
- Tensile Strength and Elongation at Break Found to Decrease With Contamination

- Current Focus: Trace Contaminant Concentrations
Other Impurities

Ammonia (NH₃) Contamination

Current density: 1000 mA/cm²  
Cell: 52 C, Dew Points: 50/50 C  
Pressure: Ambient

25 ppm NH₃ introduced in H₂ causing serious degradation.  
Cycling contamination tests showed the cell performance can be recovered.

Early Hydrocarbon Studies Showed No Effects on Fuel Cell Performance. Per Tech Team Suggestion We Tested Ammonia to Evaluate an Impurity That Was Known to Show Some Effect - Ammonia.
Other Impurities

Electrochemical Characterization of the Effect of Ammonia

Cyclic Voltammetry (CV); Electrochemical Impedance Spectroscopy (EIS)

CV scans: 20 mV/s, 0.05 -1.2 V
Anode: 25 ppm NH₃ + H₂ Cathode: N₂
RH: 80%
Brief conclusions: H₂ absorption and Pt oxidation peaks decreased after introducing a trace amount of NH₃.

In-situ EIS scans (shown in the previous slide) show that NH₃ contaminated both Nafion® membrane and the electrodes. Both the membrane and the charge transfer resistances increased.
Other Impurities
Recovery After Contamination by Ammonia

CV scans: 20 mV/s, 0.05 -1.2 V
Anode: pure H₂, Cathode: N₂
RH=29%, 49%, 80%

CV scans show at low RH (<50%), cell could hardly recover just by purging pure H₂ at the anode. After staying at RH 100% for 24 hrs, recovery is greatly improved, but still not 100%.
Impurities Modeling

• Why Modeling?
  – Helps understand the mechanisms via which impurities affect the fuel cell performance.
  – Helps predict the fuel cell behavior under the influence of impurities.
    • How much performance degradation is expected?
      – For how long does the cell generate reasonable current under certain amount of impurities?
    • How is the durability is affected?
  – Assists the experimental design

• Our Strategy
  – Derive the equations which represent the transport of the impurities in the fuel cell
    • i.e. where are the impurities?
  – Derive relations for how the impurities affect the cell behavior
    • i.e. impact of conduction of protons, available catalyst surface for H₂ oxidation
  – Validate these relations and equations
  – Incorporate these equations/relations in our 3D modeling framework
Cation Transport Across the PEM - Multi-Component Formulation

- Nernst-Planck Equation
  \[ \nabla \cdot \left( -D_i \nabla c - z_i u_{m,i} F c_i \nabla \phi \right) = R_i \]
  with electro-neutrality condition:
  \[ \sum z_i c_i = 0 \]
  results in ionic charge conservation:
  \[ \sum_{j=1}^{n} \left[ F z_i \left( -D_j \nabla c - z_j u_{m,j} F c_i \nabla \phi \right) \right] = \sum_{i=1}^{n} \left( F z_i R_i \right) \]

- Multi-component mass balance;
  \[ - \frac{x_i}{RT} \nabla \mu_i - x_i z_i \frac{F}{RT} \nabla \phi = \sum_{j=1, j \neq i}^{n} \frac{x_j N_j - x_i N_j}{c_{tot} D_{ij}} \]
  where \[ - \frac{x_i}{RT} \nabla \mu = - \sum_{j=1}^{n-1} \Gamma_j \nabla x_i \]
  Thermodynamic Correction Factor
  and \[ \sum_{j=1, j \neq i}^{n} \frac{x_j N_j - x_i N_j}{c_{tot} D_{ij}} \equiv \sum_{j=1}^{n-1} B_{ij} N_i \]

\[ - \left[ \Gamma \right] \left( \nabla x \right) - \frac{F}{RT} \left[ x \right] \left[ z \right] \left( \nabla \phi \right) = \left[ B \right] \left( N \right) \]

Competitive absorption of Na\(^+\) and Cs\(^+\) into a H\(^+\) form Nafion\(^\circledR\)


F(\(\tau\)) is the fractional attainment of equilibrium by each species.

Multi-component mass transport formulation better predicts the competitive absorption.
Cationic Impurity in Operating PEFC

-Na⁺ in the Cathode-

• Multi-physics PEFC Model
  – 3D, transient: COMSOL
  – Multi-physics: Mass, momentum, species, energy, charge cons., EC kinetics
  – Solid mechanics: Impact of cations on mechanical stress (durability)

**Na⁺ Distribution:**
Migration and diffusion fluxes are in reverse direction and almost cancel each other.

**Effective Proton Conductivity:**

Uncontaminated

Predicted output: 0.42 A/cm² @ 0.7 V

Contaminated

Predicted output: 0.29 A/cm² @ 0.7 V

NaCl is fed through the air stream.
Cationic Impurity in Operating PEFC: 

\(-\text{NH}_4^+\) Distribution in Steady-State

- \(\text{NH}_3\) is fed into anode, and is assumed to fully convert into \(\text{NH}_4^+\).
- Migration and diffusion of \(\text{NH}_4^+\) results in accumulation in the cathode catalyst layer.
- Model predicts a performance drop from 0.63 to 0.43 A/cm\(^2\) at 0.7 V (due to loss of effective proton conductivity)

Transient models are being developed to investigate the recovery.
Collaborations

• Active Participant in Fuel Quality Working Group
• Collaborating With Other Test Laboratories on Topics of Mutual Interest (Fluids Mixing, MEA Quality Issues, Testing)
• Collaborating With Karren More (ORNL) on MEA Characterization
• Project Partners (UTC and FCE) Actively Supporting Project
• Working With NRC – Canada On Impurities Research Topics
• Have Visiting Scientist From an Automaker Working on Synergistic Topics
Future Work

- Comprehensive Evaluation of Formic Acid and Formaldehyde to Support ISO Standard Development
- Continued Testing Using Standard Test Protocols, MEA’s
- Target Low Catalyst Loadings (Reduction From 0.4 mg/cm2 to 0.1 mg/cm2)
- Develop an Understanding of Mechanism for Performance Impact
- Modeling of Effects/Sharing of Data
- Extension to Simple Halogenated Compounds
- Continued Study of Effects of Cations on Membrane Properties
  - Application Relevant Contamination Types/Levels
  - Commercially Relevant Membranes
  - Modeling of Effects/Sharing of Data

• 4 Year Project
• Time Phased Milestones Activities and Expertise
**Project Summary**

- **Relevance** - A Deeper Understanding of the Effects of Specific Contaminants on Fuel Cell Performance is Necessary for Successful Commercialization

- **Approach** - Our Experienced Team Is:
  - Leveraging Existing Knowledge and Systematically Investigate Certain Fuel Contaminants of Interest
  - Creating Empirical and Detailed Analytical Models to Predict the Fate of Specific Contaminants and Their Effect on Fuel Cell Performance


- **Technology Transfer/Collaborations** - Data Shared Through Papers, Workshops, Hydrogen Fuel Quality Working Group, Etc., Active Partnership with UTC and FCE, Collaboration With ORNL on Characterization, Working With NRC-Canada on Impurities Issues, Visiting Scientist From an Automaker


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