Effect of System and Air Contaminants on PEMFC Performance and Durability

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National Renewable Energy Laboratory

June 11, 2010

2010 Annual Merit Review and Peer Evaluation Meeting

This presentation does not contain any proprietary, confidential, or otherwise restricted information

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy operated by the Alliance for Sustainable Energy, LLC
Overview

Timeline
Start: July 2009
End: September 2013
% complete: ~5%

Budget

<table>
<thead>
<tr>
<th>DOE Cost Share</th>
<th>Recipient Cost Share</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6,000,000</td>
<td>$788,850</td>
<td>$6,788,850*</td>
</tr>
<tr>
<td>88%</td>
<td>12%</td>
<td>100%</td>
</tr>
</tbody>
</table>

DOE Budget ($K)

<table>
<thead>
<tr>
<th>FY 2009</th>
<th>FY 2010</th>
<th>FY 2011</th>
<th>FY 2012</th>
<th>FY 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>1035</td>
<td>700</td>
<td>1438</td>
<td>1476</td>
<td>1351</td>
</tr>
</tbody>
</table>

Barriers

<table>
<thead>
<tr>
<th>Barrier</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Durability</td>
<td>5,000 h for Transportation 40,000 h for Stationary</td>
</tr>
<tr>
<td>B: Cost</td>
<td>$30/kW for transportation $750/kW for Stationary</td>
</tr>
</tbody>
</table>

Partners (contract date)

General Motors* (3/10)
University of South Carolina* (1/10)
Los Alamos National Laboratory* (8/09)
University of Hawaii* (TBD)
3M (N/A)

* denotes subcontractor

*Final award amounts are subject to appropriations and award negotiations.
Relevance

- Balance of plant (BOP) costs have risen in importance with decreasing stack costs.
- Contaminants from system components (GM) have been shown to affect the performance/durability of fuel cell systems.
- Durability requirements limit performance loss due to contaminants to at most a few mV over required lifetimes (1000s of hours). ~Zero impact for system contaminants.

Average cell performance of a 90kW fuel cell stack after 850+ hours of use in test vehicle. The cell performance improved after exposure to oxidation. The recoverable 25 mV voltage loss was attributed to system-based contaminants. (provided by GM)

Relevance

- Unfortunately, commercially relevant, system-derived contaminants have many potential sources.

Typical “gas wetted” components used in a PEMFC system.

Examples of common additives in automotive thermoplastics

Relevance – Background Data

• In-situ experiments have shown a clear negative impact from system-based contaminants.
• For the case shown, the impact is observed through membrane failure, voltage loss and HFR gain.
• While little has been done in the area of system contaminants, our team members have been leaders in the limited amount reported in this area.

Ex-situ experiments are effective methods for quickly screening materials.

Leachants obtained from different grades of the same family of polymers results in very different conductivities (potentially reflecting quantity and type of contaminant).

Electrochemical data, including leachant solutions, shows that system contaminants impact catalysts.

Objectives

Decrease the cost associated with system components without compromising function, fuel cell performance, or durability

- Identify and quantify system derived contaminants
- Develop *ex-situ* and *in-situ* test methods to study system components
- Identify severity of system contaminants and impact of operating conditions
- Identify poisoning mechanisms and investigate mitigation strategies
- Develop models/predictive capability
- Develop material/component catalogues based on system contaminant potential to guide system developers on future material selection
- Disseminate knowledge gained to community

### 2009-2010 Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Quantify impact of (at least 3) leaching conditions on leachants obtained from (at least 3) polymer samples.</td>
<td>09/09</td>
<td>100% complete</td>
</tr>
<tr>
<td>2</td>
<td>Compile comprehensive list of identified, plausible polymer families for fuel cell systems.</td>
<td>07/10</td>
<td>50% complete</td>
</tr>
<tr>
<td>3</td>
<td>Quantify the impact of identified leachant mixtures (at least 4) on fuel cell performance and durability.</td>
<td>09/10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Isolate electrochemically inhibiting compounds from (at least 4) polymeric leachants.</td>
<td>09/10</td>
<td></td>
</tr>
</tbody>
</table>
Approach* – Project Overview

Choose Materials (GM)

Material Leachant Study (NREL)

Analytical characterization (GM, NREL, USC)

Quick screening

Electrode (NREL, GM)

performance (CV)

Membrane (NREL, USC)

conductivity

Ex situ mechanical testing (USC, GM)

Modeling: Contamination species (USC)

ORR, kinetic studies (NREL)

In situ fuel cell performance, recovery (USC, NREL, GM)

In situ durability tests (Hawaii, LANL)

*Beyond what is presented here, our approach is driven by other input, in part, provided in supplemental slides. For example, hydrophillicity changes are not currently included in work plan.
Approach – General Terms

Our materials selection is based on issues such as exposed surface area, total mass/volume, fluid contact, function, cost, and performance implications.

Lower-cost commodity polymers are suitable for larger components such as cathode air handling systems.

Higher-cost engineering polymers are suitable for smaller, precision components such as impellers and valves and sensors.

Examples of polymer classes with generalized costs for the system

PSU>PC>PBT>PPS>PPA>PA>PPO>POM>PET>PU>UP>Phenolic>Melamine>ABS>PS>PE>PP>PVC

Higher cost

Lower cost

1 Figure generated from GM internal knowledge

Approach – Materials Prioritization

Current prioritization for perceived impact of potential system contaminants (based on GM internal knowledge)

1. Structural materials
2. Coolants*
3. Elastomers for seals
4. Elastomers for (sub)gaskets
5. Assembly aids (adhesives, lubricants)
6. Hoses
7. Membrane degradation products
8. Bipolar/end plates
9. Ions from catalyst alloys

* Limited efforts within this project, due to options and existing data.

- Strong polymer focus, as much of the system is polymer based
- Component list contains commodity materials or materials developed for other applications where issues of fuel cell contamination would not be a concern.
- Try to leverage synergies between these materials (for example: small molecule, organic leachants or common additives/processing aids)
Approach – Protocols/Testing

GM’s established test protocols used on leachant from polyamide polymer

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Method*</th>
<th>Requirement</th>
<th>Polyamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching Test</td>
<td>FCA-T0008</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Total organic content (TOC)</td>
<td>FCA-T0008</td>
<td>&lt;TBD mg/l</td>
<td>124 mg/l</td>
</tr>
<tr>
<td>Total inorganic content (TIC)</td>
<td>FCA-T0008</td>
<td>&lt;TBD mg/l</td>
<td>40 mg/l</td>
</tr>
<tr>
<td>Total surface tension</td>
<td>FCA-T0008</td>
<td>&gt;TBD mN/m</td>
<td>Not measured</td>
</tr>
<tr>
<td>Color change</td>
<td>FCA-T0008</td>
<td>no color change via UV-Vis</td>
<td>No change</td>
</tr>
<tr>
<td>Olfactory test</td>
<td>FCA-T0008</td>
<td>no odor</td>
<td>Amine</td>
</tr>
<tr>
<td>pH</td>
<td>FCA-T0008</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
<tr>
<td>Conductivity</td>
<td>FCA-T0008</td>
<td>&lt;TBD uS/cm</td>
<td>210 uS/cm</td>
</tr>
<tr>
<td>Proton conductivity test</td>
<td>FCA-T0015</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
<tr>
<td>GDL surface energy test</td>
<td>FCA-T0016</td>
<td>&gt;140° water contact angle</td>
<td>Not measured</td>
</tr>
<tr>
<td>BPP wetting contamination test</td>
<td>FCA-T0017</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
<tr>
<td>FC Cyclic voltammetry test</td>
<td>FCA-T0018</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
<tr>
<td>Analytical Characterization</td>
<td>FCA-T0008</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
<tr>
<td>Beaker CV test</td>
<td>FCA-T0019</td>
<td>TBD</td>
<td>Not measured</td>
</tr>
</tbody>
</table>

- Standard test protocols are important in evaluating materials as this approach will allow for broader studies to be performed.
- GM has put significant work in establishing test protocols and these will be disseminated to the community as part of the project.
Technical Accomplishments and Progress

• 87% of subcontract funding now in place.


• Obtained relevant materials sets.

• Initiated leachant experiments for polymeric samples.

• Applied and evaluated multiple techniques for analyzing leachants (e.g., GC-MS, FTIR-ATR, ICP-MS, pH, conductivity, TOC, contact angle).

• Established competencies for GM established test protocols.
Investigated Leaching Test Procedures:

- 2 pieces of 1x4 inches$^2$ were prepared, giving a ratio of 103 cm$^2$ to 100 ml solution
- 100 ml total of solution was used for each sample
- Three different solutions (at 80°C)
  - DI water
  - 0.1M H$_2$SO$_4$
  - 3%H$_2$O$_2$+0.1M H$_2$SO$_4$
- 5 ml aliquots were collected at:
  - 1, 7, 15, 22, 32, 45, 60 day intervals
- pH, conductivity, FTIR and GCMS were performed on each sample

Relevant Polymeric Materials Tested:

- Acrylic Buna-N Blended Rubber
- Aramid/Buna-N
- Abrasion resistant SBR Rubber (Red)
- Weather resistant EPDM Rubber (Plain black)
- FDA-compliant Silicone Rubber (Plain black)
- Corrosion resistant Viton® Fluoroelastomer
- Amber Polyurethane Sheet
- M-strength Neoprene Rubber (Plain black)
- Silicone gasket
- Teflon coated fiberglass (Furon)
### Technical Accomplishments and Progress

#### Leachant Experiments on Relevant Materials

<table>
<thead>
<tr>
<th>Control (no polymeric material)</th>
<th>in DI water</th>
<th>0.1M H₂SO₄</th>
<th>3%H₂O₂+0.1M H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Acrylic Buna-N Blended Rubber</strong> (Gasket Sheet)</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>2. Aramid/Buna-N Gasket</strong></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>3. Abrasion resistant SBR Rubber Red</strong></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>4. Weather resistance EPDM Rubber Plain black</strong></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Some material resulted in obvious change in color, smell, and turbidity, as well as precipitation formation of leachant solutions.

We present SBR Rubber as a case study material for this presentation.
Technical Accomplishments and Progress
Develop Test Methods

**SBR Rubber (Red)**

**pH**

![pH Graph]

**Conductivity**

![Conductivity Graph]

Acid solutions caused a large pH & conductivity change in material that broke down.

- In DI water
- 0.1M $\text{H}_2\text{SO}_4$
- 3%$\text{H}_2\text{O}_2$+0.1M $\text{H}_2\text{SO}_4$
Technical Accomplishments — Develop Test Methods

Gas Chromatography Mass Spectroscopy [GCMS]

Separates leachant components and identifies chemical compounds
- Aniline is major leachant in SBR (quality = 91)

FTIR / ATR – Attenuated Total Reflection

Confirms major functional groups of compounds identified by GCMS
- Aromatic rings in SBR

Chemical designation of abrasion-resistant styrene butadiene rubber (SBR)-Red

- Styrene
- Butadiene

Polymerization of monomer involves:
Chain transfer agent such as an alkyl mercaptan
Identified leachant components studied over time

GCMS Analysis - SBR rubber sample soaked in DI water at 80°C

Leachant rates may be obtained.

Identified components seem reasonable based on known polymer chemical structure and FTIR. GC-MS seems to be a good method to identify leachants.
Collaborations

PRIME

SUBCONTRACTS
General Motors (GM): Kelly O’Leary, Balsu Lakshmanan, and Rob Reid
University of South Carolina (USC): John Van Zee and Jean St. Pierre
Los Alamos National Laboratory (LANL): Tommy Rockward
University of Hawaii (UH): Rick Rocheleau
3M*: Steve Hammrock

Contaminant identification (GM)
Test method development & validation (NREL, GM, USC)
Contaminant characterization (GM, NREL, USC, LANL, UH)
Poisoning mechanisms identification (NREL, GM, USC)
Mitigation strategies investigation (NREL, GM, USC)
Model development (USC)
Model validation (USC, GM, NREL)
Data compilation and public dissemination (NREL, GM, USC, LANL, UH)

* Provide membrane degradation products
Proposed Future Work:

- Balance of plant material selection and acquisition
- MEA and flow field production
- Discussion and theoretical agreement on protocols
- Literature review of prior work
- Soak initial samples
- Analytical Characterization
- Benchmark equipment at all facilities
- Perform in-situ and ex-situ experiments on select materials
- Finalize protocols
- Initiate modeling

4/2010 - 7/2010 - 10/2010
Summary

**Relevance:** Focus on overcoming the cost and durability barriers for fuel cell systems.

**Approach:** Perform parametric studies of the effect of system contaminants on fuel cell performance and durability, identify poising mechanisms and recommend mitigation strategies, develop predictive modeling and disseminate material catalogues that benefit the fuel cell industry in making cost-benefit analyses of system components.

**Technical Accomplishments and Progress:** 85% of the subcontract and funding are in place. We obtained relevant materials set and initiated leachant experiments for over 10 polymeric samples. We initiated evaluation of various methods for analyzing leachants (e.g., GCMS, FTIR-ATR, ICP-MS, pH, conductivity, total organic content, contact angle), and established competencies mimicking GM established test protocols.

**Collaborations:** Our team has significant background data and relevant experience. It consists of a diverse team of researchers from several institutions including 2 national labs, 2 universities, and 2 industry partners.

**Proposed Future Research:** Select and study polymeric structural materials because they have the highest impact of potential system contaminants. Develop standard testing protocols and benchmarking equipment/methods.
Supplemental Slides
<table>
<thead>
<tr>
<th>Major Components Susceptible to Contamination</th>
<th>Performance Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Plate hydrophilicity/hydrophobicity</td>
<td>1. Electrode performance</td>
</tr>
<tr>
<td>2. Diffusion Media hydrophilicity/hydrophobicity</td>
<td>2. Increased membrane resistance</td>
</tr>
<tr>
<td>3. Electrode</td>
<td>3. Decreased membrane durability</td>
</tr>
<tr>
<td>4. Membrane</td>
<td>4. GDL Water management issues</td>
</tr>
</tbody>
</table>

**Learnings to Date:**

1. Continuous soak in DI water for 1000 hours is current procedure of choice. Conductivity measured 1 x/week. Odor, appearance, bubbling recorded. Shake test, pH, and conductivity are most useful quick screening methods.

2. CV is extremely useful and we’ve developed a number of techniques depending on what we’re studying. It is currently used for 2 types of experiments: a quick screen, and a recovery screen.

3. Membrane resistance work has been limited, but needs further exploration.

4. Plate hydrophilicity/hydrophobicity is too sensitive to obtain useful data.

5. Diffusion media hydrophilicity/hydrophobicity has shown little to no effects on water management.

*Source: GM*
Example Work Flow: Nylon 6,6

1. Order variety of Nylon 6,6 from 2 manufacturers: hydrolytically stabilized, 25% reinforced w/ glass, carbon, carbon rods, clay, etc

2. Soak samples in di water as soon as they arrive

3. Measure pH, H conductivity, odor, color, CV, and membrane conductivity, all in parallel. Start soaking membrane in extract for aging
   a. During steps 4 and 5, perform chemical analysis on extract and bulk material

4. If possible or beneficial, perform extended CV experiments on extracts

5. Perform in situ fuel cell experiments with and w/o current distribution, perform DOE on concentration, temperature, current, RH, and Pt loading (all on extract sln)
   a. Work on recovering with fluid circulation and potential ranges
   b. Understanding tolerances

6. Repeat 4 and 5 with select substrate chemicals

7. Measure membrane properties of aged materials

8. Decide if any durability tests should be run and which: RH cycling w/ or w/out load

9. Feed information into mechanistic understanding

10. Feed mechanisms into simple modeling

Source: GM
In-situ fuel cell experiments are then performed to evaluate effects of operating conditions as well as dosage.

**Test Conditions:**
- 80°C, 0.2 A/cm² constant current density
- MEA Pt loading: 0.2 mg/cm² anode/ 0.3 mg/cm² cathode
- 23% RH anode and cathode inlet
- 50 cm² active area, serpentine flow field, co-flow
- Contaminant dose based on the dry gas stream
- Contaminant dose limited by gas super saturation point

**Benefits of Infusion:**
- Ability to treat leachant solutions as ‘black box’, allowing delivery of all constituent contaminants at once, ignoring partitioning coefficient if vaporizing sample

**Graph:**
- 50 PPM Ethylene Glycol Infusion on Anode
- Voltage (V)
- Load Bank Voltage (V) = 0.70 V
- HFR (mOhm/cm²) = 0.22 mOhm/cm²
- 50 PPM Anode = 7.05 uL/min delivered over 90 minutes

**Source:**
Model development for air contaminants has been extensive and similar model can be applied to system contaminants.

\[
\frac{i}{i_{c,x=0}} = 1 - \frac{k''}{k'} \left( \frac{k_x}{e^{\rho} - 1} \right)
\]

\[
\frac{i}{i_{c,x=0}} = 1 + \frac{k''}{k'} \frac{-(k_{X,des} + k_X)}{\rho}
\]

or

\[
\frac{i}{i_{c,x=0}} = 1 + \frac{k''}{k'} \frac{-k_{P,des}}{\rho}
\]


J. St-Pierre, J. Power Sources, accepted.
Effect of \( \text{O}_2 \) on the adsorption \( \text{SO}_2 \) on Pt/C electrocatalyst

**Schematic of Temperature Programmed Desorption (TPD) Apparatus**

- Mass spectrometer
- Monitor: \( \text{H}_2\text{O}, \text{CO}, \text{O}_2, \text{CO}_2, \text{SO}_2 \) and \( \text{SO}_3 \)
- Vacuum pump
- Ar
- SO\(_2\)-N\(_2\)
- Pt/C catalyst
- Reactor and furnace

**Isotherm of C-SO\(_2\) compared to the SO\(_2\) adsorption (Pt-SO\(_2\) + C-SO\(_2\))**

- \( \text{O}_2-\text{He} 10\% \) for \( \text{O}_2 \) assisted desorption
- OR
- 100% \( \text{O}_2 \) for effect of \( \text{Air} \)

**TPD can aid in understanding the mechanisms of contamination on catalyst (USC).**
Sealing materials in different leachant conditions

Sealing material has disintegrated in H₂SO₄+H₂O₂ solution (perhaps too aggressive).
<table>
<thead>
<tr>
<th>Material Description</th>
<th>In DI water</th>
<th>0.1M H₂SO₄</th>
<th>3% H₂O₂ + 0.1M H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no polymeric material)</td>
<td><img src="image" alt="Control In DI water" /></td>
<td><img src="image" alt="Control 0.1M H₂SO₄" /></td>
<td><img src="image" alt="Control 3% H₂O₂ + 0.1M H₂SO₄" /></td>
</tr>
<tr>
<td><strong>5. FDA-compliant Silicone Rubber</strong> Plain black</td>
<td><img src="image" alt="FDA-compliant Silicone Rubber In DI water" /></td>
<td><img src="image" alt="FDA-compliant Silicone Rubber 0.1M H₂SO₄" /></td>
<td><img src="image" alt="FDA-compliant Silicone Rubber 3% H₂O₂ + 0.1M H₂SO₄" /></td>
</tr>
<tr>
<td><strong>6. Corrosion resistant Viton® Fluoroelastomer</strong></td>
<td><img src="image" alt="Corrosion resistant Viton® Fluoroelastomer In DI water" /></td>
<td><img src="image" alt="Corrosion resistant Viton® Fluoroelastomer 0.1M H₂SO₄" /></td>
<td><img src="image" alt="Corrosion resistant Viton® Fluoroelastomer 3% H₂O₂ + 0.1M H₂SO₄" /></td>
</tr>
<tr>
<td><strong>7. Amber Polyurethane Sheet</strong></td>
<td><img src="image" alt="Amber Polyurethane Sheet In DI water" /></td>
<td><img src="image" alt="Amber Polyurethane Sheet 0.1M H₂SO₄" /></td>
<td><img src="image" alt="Amber Polyurethane Sheet 3% H₂O₂ + 0.1M H₂SO₄" /></td>
</tr>
<tr>
<td><strong>8. M-strength Neoprene Rubber</strong> Plain black</td>
<td><img src="image" alt="M-strength Neoprene Rubber In DI water" /></td>
<td><img src="image" alt="M-strength Neoprene Rubber 0.1M H₂SO₄" /></td>
<td><img src="image" alt="M-strength Neoprene Rubber 3% H₂O₂ + 0.1M H₂SO₄" /></td>
</tr>
</tbody>
</table>
Some material resulted in obvious change in color, smell, and turbidity, as well as precipitation formation.
pH and Conductivity Measurements

Viton® Fluoroelastomer

Minimal change in pH and conductivity for an expensive fluoroelastomer.

In DI water 0.1M H₂SO₄ 3%H₂O₂+0.1M H₂SO₄
Gas Chromatography
Mass Spectroscopy [GCMS]

Coupled Technique
Inert Purge, N\textsubscript{2}
Liquid injection
Volatilized to gas
Separation along column
Components introduced into mass spectrometer
Ionized and separated in the quadrupole by m/z
Fourier Transform Infrared Spectroscopy
[FTIR/ATR]

Vibrational spectroscopy
Identify functional groups
Spectral features shift with matrix

ATR – Attenuated Total Reflection
– Liquid and solid sampling accessory
– No sample preparation
– ZnSe cell is hydrophobic, no acids
– Ge cell is acid resistant

Evanescent standing wave
– Penetrates sample by a few microns
– Better contact = Better spectra
Main leachants identified for blended rubber are siloxanes & formamide.
Aged in DI water

- **hexamethylcyclotrisiloxane**
- **Octamethylcyclotetrasiloxane**
- **decamethylcyclopentasiloxane**
- **N,N dibutyl Formamide**
- **dodecamethylohexasiloxane**
- **Tetradecamethyloctasiloxane**