Applied Science for Electrode Cost, Performance, and Durability

Presented by: Christina Johnston
Los Alamos National Laboratory
Project ID: fc_16_johnston

Eric Brosha  Karren More
Fernando Garzon  Bruce Orler
Andrea Labouriau  Bryan Pivovar
Marilyn Hawley  Tommy Rockward
Rex Hjelm  Dennis Torraco
Yu Seung Kim  Cindy Welch
Kwan-Soo Lee  Hui Xu
Nate Mack  Piotr Zelenay

Affiliation: ORNL

Present affiliation: NREL
Present affiliation: Fuel Cell Energy

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

### Timeline

- **Start:** FY2005
- **Status:** Ongoing

### Budget

- **Funding in FY08:** $600K
- **Funding in FY09**
  - *(estimated): $600K*
- **Not cost-shared**

### Barriers Addressed

- **A. Durability**
- **B. Cost**
- **C. Electrode Performance**

### Partners

- Oak Ridge National Laboratory
- NIST Center for Neutron Research
- Los Alamos Neutron Science Center
Relevance: Objectives and Barriers Addressed

**Overall Project Objective**

To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program in meeting cost, durability and performance targets by addressing issues directly associated with electrodes (electrode science not specifically addressed by FY ‘06 call).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>Stock Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum group metal (pmg)</td>
<td>mg PGM / cm² electrode area</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Total loading</td>
<td></td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Cost</td>
<td>$ / kW</td>
<td>9</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td></td>
<td>&gt;2,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Operating temp ≤50°C</td>
<td>hours</td>
<td>NA</td>
<td>2,000</td>
</tr>
<tr>
<td>Operating temp &gt;80°C</td>
<td>hours</td>
<td>6,000 f</td>
<td>5,000 f</td>
</tr>
<tr>
<td>Electrochemical area loss</td>
<td>%</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;40</td>
<td>&lt;40</td>
</tr>
<tr>
<td>Mass activity</td>
<td>A / mg Pt @ 900 mV_elmax</td>
<td>0.20</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Specific activity</td>
<td>µA / cm² @ 900 mV_elmax</td>
<td>550</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>720</td>
<td>720</td>
</tr>
</tbody>
</table>

**FY09 Objectives**

- Explore impact of solvent choice in catalyst ink on fuel cell performance
- Relate the structural and chemical properties of the ionomer in different inks to electrode performance and structure
- Initiate use of bilayer/gradient structures in electrodes

**Barriers Addressed**

Electrode composition and structure must be understood and controlled to achieve the highest platinum utilization and durability

A. **Durability**: Assessing effect of electrode composition and processing on durability

B. **Cost**: Measuring catalyst utilization after altering electrode composition and processing

C. **Electrode Performance**: Evaluating effect of varying electrode inks and processing on the performance of fuel cells
Approach: Targets and Milestones

- Explore effect of catalyst ink composition and processing on utilization and performance
  - FY09: Wide range of solvents explored in catalyst inks; marked effect on performance observed
  - FY09: Bilayer/gradient electrode work initiated

- Use microscopy and other tools to better understand electrode structure and impact on performance
  - FY09: Structure and local chemical environment of Nafion® dispersed in different solvents examined by neutron scattering and NMR
  - FY09: TEM and HR-TEM used to examine the inks and electrode structures from different solvents

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mar 08</td>
<td>Perform gravimmetry experiments of H2S adsorption and CO adsorption to compare with heterogeneous surface area measurements obtained by ion selective electrodes (completed)</td>
</tr>
<tr>
<td>Jul 08</td>
<td>Modify MEAs processing to obtain electrochemical surface areas that vary by a factor of 3, and correlate these differences in surface area with fuel cell performance (completed)</td>
</tr>
<tr>
<td>June 09</td>
<td>Measure the total platinum surface area and ESA of MEAs prepared with two previously unstudied carbon supports, and rationalize the results compared to FY2008 data using structural and chemical information obtained through TEM and spectroscopy (ongoing)</td>
</tr>
<tr>
<td>Sept 09</td>
<td>Fabricate an MEA with a layered structure and evaluate the approach in terms of ESA versus performance (ongoing)</td>
</tr>
</tbody>
</table>
**Approach: Main Ideas and Overall Goals**

**Main Ideas**

- Well-designed electrode structures could lead to a reduction in catalyst loading, as well as improved performance and durability
- Novel materials may require novel electrode structures; understanding a “typical” Pt/C electrode structure is a good starting point

**Overall Goals of This Work**

- Study structure and chemical properties of fuel cell catalyst ink components as they interact—solvent (FY09), ionomer (FY09), carbon, platinum (future work), and relate to final electrode performance
- Evaluate ink and electrode processing procedures (e.g., drying temperature) with focus on correlating structure to performance (ongoing)
- Vary the components and processing conditions, based on this understanding, to improve fuel cell performance (ongoing)
- Combine microscopy, neutron scattering, other analysis methods, and modeling to develop structure/performance relationships (ongoing)
**Approach: Probe Fuel Cell Component Interactions at Various Length Scales**

- **Resolution, cm**
  - $10^0$, $10^{-1}$, $10^{-2}$, $10^{-3}$, $10^{-4}$, $10^{-5}$, $10^{-6}$, $10^{-7}$, $10^{-8}$

- **Resolution, nm**
  - $10^7$, $10^6$, $10^5$, $10^4$, $10^3$, $10^2$, $10^1$, $10^0$, $10^{-1}$

**Techniques Available**
- Scanning Electron Microscope
- Atomic Force Microscopy
- Transmission Electron Microscope
- X-ray Tomography
- Small Angle X-ray Scattering
- Small Angle Neutron Scattering
- NMR
- WAXS
- Cyclic Voltammetry

---

All listed techniques are available to LANL staff with appropriate expertise, either on-site or through collaborations.
MEA Preparation: Factors that Impact Electrode Morphology Development

Polymer Morphology in Dispersion

- Catalyst adding Mech. Stirring
- Drying

Initial Electrode Morphology

Cell break-in
- Drying
- Acidification
- Hot pressing

Final Electrode Morphology

- Electrochemical treatment
- Drying
- Hydrothermal effect
- Thermal effect
Approach for Evaluating Solvent Effect on Fuel Cell Electrodes

Preparation of Polymer Dispersion*

Characterization of Polymer/Pt/Carbon Dispersion
- Polymer/Solvent Interaction ($^{19}$F NMR)
- Polymer Morphology in Dispersion (SANS) and in Solid Electrode (AFM)
- Electrode Morphology (SANS, AFM and TEM)

Fuel Cell Performance
- Initial Fuel Cell Performance (Pt ORR kinetic and mass transfer region)
- Electrode Durability Test (Potential cycling test)

Motivation for FY09 Work

- Solvent choice in ink studied first
- Various dispersions of Nafion®-212 made in-house through novel method (subject of patent disclosure)
- Marked differences in fuel cell performance noted
- Kinetic and mass transport region impacted differently by solvent choice
- Questions raised about effect of nanoscale structure and interactions of electrode components

*Structures are visual aids reflecting current understanding, and may be later updated
**19F NMR of Nafion®-212 Dispersions**

- Relative main chain mobility: area of backbone to side chain: \( a/(c,e,f) \)
- Side chain mobility: 1/line width of \( c,e,f \) peak (kHz\(^{-1}\))
- Solvent dipolar interaction in parenthesis (MPa\(^{1/2}\))

- Mobility of Nafion® backbone and sidechains greatly differs from solvent to solvent
- **Glycerol**: fuel cell mass-transport enhanced; Nafion® has low overall mobility in solvent
- **NMP**: fuel cell kinetics enhanced; Nafion® has high overall mobility
- **Propylene glycol**: Intermediate behavior, but more similar to glycerol
Small-Angle Neutron Scattering of Nafion®-212 Dispersion

**NMP dispersion: Core-Shell Cylinder**

*Structures are visual aids reflecting current understanding, and may be later updated*

- Sharp interface between core and shell
- SLD* of core = ~calculated Nafion® backbone
- SLD of shell = ~solvent
- No solvent penetration into the core
- Solvent penetrates side chains (low slope)

**Glycerol dispersion: Cylinder Model**

- Less phase separation between Nafion® backbone and side chains
- Glycerol appears to penetrate Nafion® less than NMP (high slope), but some penetration may occur

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>-1.7</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>-2.0</td>
</tr>
<tr>
<td>Water/IPA (2:3)</td>
<td>-2.0</td>
</tr>
<tr>
<td>Butanediol</td>
<td>-3.3</td>
</tr>
<tr>
<td>Glycerol</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

* SLD = scattering length density

* Line represents slope corresponding to sharp interface between solvent and Nafion®

---

**Las Alamos National Laboratory**

Atomic Force Microscopy of Nafion®-212 Films Cast from Different Solvents

- Demonstrates impact of solvent on final ionomer structure, rather than just while in dispersion
- Correlation observed between phase separation (from SANS) and mobility (from NMR) in dispersions with final film morphology (from AFM)
- Ongoing studies: adding Pt/C incrementally to dispersions to see effect on resulting film structure, and effect of temperature of casting

Nafion® 212 dispersions after drying at temperatures well below respective boiling points
Comparison of Fuel Cell Tests to Model based on NMR, SANS, and AFM Results

**H₂/air Fuel Cell Tests**

**IR-corrected polarization curves**

- **Nafion-212 Dispersion Solvent**
  - N-methylpyrrolidone
  - Glycerol
  - Propylene glycol

Cell temp. 80°C; fully humidified; backpressure: 30/30 psig
Catalyst: 20% Pt/C (ETEK); 0.2/0.2 mgPt/cm², ionomer: Nafion 212

**Comparison of Fuel Cell Tests to Model based on NMR, SANS, and AFM Results**

- **From NMP dispersion**: Good performance at kinetically-controlled voltages, but poor performance at mass-transport controlled voltages
- **From glycerol dispersion**: Opposite pattern
- **From propylene glycol dispersion**: Intermediate behavior, but closer to glycerol (agrees with NMR)

---

**Main Chain Mobility**

- Water (16.0)
- 2-propanol (6.1)
- Ethylene glycol (11.0)
- NMP (12.3)
- Glycerol (12.1)
- Butanediol (10.0)
- Propylene glycol (9.4)
- Ethyleneglycol (11.0)
- 2-propanol (6.1)
- Water (16.0)

**Main Chain Mobility**

- Less phase-separated
- More phase-separated

**Model for glycerol**

**Model for NMP**
Extension of Study to Solvent Mixtures: Water/Isopropanol Dispersions of Nafion®-212

- Performance improved in both kinetic and mass-transport regions with decreased ratio of water to IPA
- Formation of continuous electrode film challenging with highest water content (Water: IPA 3:1), which could have reduced performance

H₂/air Fuel Cell Tests

IR-corrected polarization curves

Water:2-propanol

Water: IPA 1:3
Water: IPA 1:1
Water: IPA 2:3
Water: IPA 3:1

Cell temp. 80°C with fully humidified; backpressure: 30/30 psig
Catalyst: 20% Pt/C (ETEK): 0.2/0.2 mgpt/cm², ionomer: Nafion 212

Decreasing water content
Increasing performance
Nafion®/Solvent Interaction in Water: IPA Solvent Mixture (2.5 wt%)

- NMR shows that side-chain and main-chain mobility are intermediate those of water and IPA for water:IPA mixtures, as expected
- Kinetic performance of Water: IPA 1:1 and 2:3 electrodes similar to NMP (tending lower), but mass-transport better
- Mass transport performance of Water: IPA 1:1 and 2:3 electrodes similar to glycerol (tending higher); kinetic performance superior
- SANS data collected for 2:3 Water:IPA dispersion, but not fully analyzed; sphere-like structure of Nafion® observed—different than for NMP and glycerol; may help explain mass-transport difference
Effect of Dispersion Solvent on Catalyst Durability

**Water-Isopropanol-n-propanol**

- Better performance in kinetic region observed at the beginning of test from electrode made from water/isopropanol dispersion, but much higher performance degradation during potential cycling
- Question raised about impact of nanostructure resulting from different solvents on durability

**Glycerol**

- 1 A cm\(^{-2}\): ~60 mV loss
- 1 A cm\(^{-2}\): ~30 mV loss

---

**Model for glycerol**

- Less phase-separated

**Model for NMP**

- More phase-separated
TEM Micrographs of Catalyst Before and After Potential Cycling Test

- Initial particle size distributions are similar for 1:1:1 water:IPA:n-prop mixture and glycerol
- Particle growth with cycling tends to be greater for electrode from glycerol dispersion; more statistics needed
- Details of Nafion®-Pt interface may be different when formed from different solvents; lateral connectivity of Pt?

**Graph:**

- **From 1:1:1 water:IPA:n-prop:**
  - Before potential cycling
  - After 10,000 potential cycles

- **From glycerol:**
  - Before potential cycling
  - After 10,000 potential cycles

**Particle Size Distribution:**

- Average: 4.3 ± 0.9 nm
- Average: 4.9 ± 0.9 nm
- Average: 8 ± 2 nm
- Average: 7 ± 2 nm
Catalyst Ink 1: 30 vol% Nafion® + 20wt% Pt/C (E-TEK)

Catalyst Ink 2: 40 vol% Nafion® + 20wt% Pt/C (E-TEK)

MEA type 1: Ink 1 only (standard)

MEA type 2: Ink 2 (↑ Nafion® content) near GDL; Ink 1 near membrane

MEA type 3: Ink 1 (↓ Nafion® content) near GDL; Ink 2 near membrane

“The DNS calculations predict that a higher electrolyte phase volume fraction near the membrane-CL interface provides an extended active reaction zone and exhibits enhanced performance. A higher void phase fraction near the gas diffusion layer aids in better oxygen transport.”

Bilayer/Gradient Electrode Structures

**MEA type 1:** Performance only slightly decreased with decreased humidification

**MEA type 2:** Performance increased with decreased humidification

**MEA type 3:** Performance decreased with decreased humidification

- Changing Nafion® content in layer greatly impacts the performance pattern with humidity levels
- Coupled with maximizing catalyst utilization with solvents, could lead to better design of electrode at different length scales
Summary

- To date, the formation and optimization of the PEFC electrode structure is poorly understood and controlled.
- Work has begun to understand how materials properties and interactions govern electrode structure with the variation of solvent in catalyst inks.
- Fuel cell performance depends on the solvent(s) used to fabricate electrodes (cathodes in this study).
- Data from NMR demonstrate that Nafion® side-chains and main-chain have different mobilities in different solvents.
- Ionomer mobility could affect final ionomer structure, as indicated by AFM results.
- SANS data show that dispersed ionomer size and structure vary with solvent.
- Side-chain arrangement in NMP may be better oriented for interaction with Pt than glycerol (higher ECSA, higher kinetic performance).
- Glycerol, however, creates beneficial structures for mass-transport and durability—smaller Nafion® profile (SANS); less lateral Pt ion migration?
- Use of multiple inks to create bilayer/gradient structures could lead to improved performance.
Future Work

Shorter term (FY09 and early FY10)

- Use NMR, SANS, and dynamic light scattering to understand the effect of solvent on Nafion® dispersions
  - Focus: influence of co-solvent mixtures (water:IPA) on Nafion® morphology
    - NMR: molecular interactions of Nafion® with co-solvent mixtures
    - SANS: effect of water content on Nafion® morphology for co-solvent mixtures
- AFM study of impact of catalyst and temperature on ionomer film formation
- Continued fabrication and study of multilayer/gradient electrode structures
  - Add AC impedance and modeling to guide(validate) optimization of electrode layers

Longer term (FY10)

- Nafion® interactions with the catalyst in solution (dispersions) and solid (film) states:
  - Analyze SANS data (NIST) of Nafion®/catalyst dispersion in glycerol
  - NMR and SANS (NIST) will focus on Nafion®/ink interactions (in solvent)
  - NMR and SANS (LANSCE) will focus on determining Nafion® in films
- Study impact of Pt interparticle distance on Nafion® organization (patterned electrodes, neutron scattering)
- Use different carbon dimensions to determine impact of size and shape in performance of electrode layers (important for novel catalyst integration into MEAs)
- Model evolution of electrode structure with inputs gained from experiments