Automotive Perspective on PEM Evaluation

Craig Gittleman
Lab Group Manager – Membrane and Ionomer
General Motors Fuel Cell Research Lab
10 Carriage St., Honeoye Falls, NY 14472

High Temperature Membrane Working Group Meeting
May 18, 2009
Outline

• Automotive PEM FC Operating Conditions
• Performance Durability Tradeoffs
• Automotive PEM Requirements
• Evaluation Test Methods
• Performance Considerations
  ➢ Proton Transport Resistance
  ➢ Fuel Cell Performance
  ➢ Freeze Start
• Durability Considerations
  ➢ Mechanical Durability
  ➢ Chemical Durability
  ➢ Shorting
• Summary
• Acknowledgements
Fuel Cell Membrane Needs

Membranes Need Water to Conduct Protons

- Current membranes enable 80°C, low pressure system, but this limits maximum vehicle power due to heat removal capacity (radiator size)
- Minimum 95°C peak power operation needed for heat rejection
Automotive Operating Conditions

Automotive FC systems must be designed for their peak power operating point

- The hottest (& driest) conditions will exist at peak power
  - >90% of the time system will run colder & thus, wetter
- Humidity will depend on system pressure
  - While there is no universal agreement among OEM’s on automotive FC system pressure, systems are not expected to operate above 300 kPa-abs.
- The most desirable membranes will enable low pressure systems

Analysis done for most aggressive system including an effective cathode water recovery system and low cathode stoichs

- Current DOE target of 120°C requires >300 kPa-abs system to achieve 50% RH
- US OEMs currently focusing on 95°C peak power system, where RH could range from 40 - >100% RH depending on pressure
During humidity cycling
- Membrane swells/shrinks with changing relative humidity
- Repeated stressing of membrane leads to fatigue induced fracture

During fuel cell operation
- Chemical radicals generated at electrodes
- Radicals attack polymer structure of membrane
- Membrane thins, releasing HF

Membrane shorting – electronic current passes through membrane
- Caused by over-compression and/or high local potentials
- Can lead to extreme temperatures and thermal decomposition
Performance Durability Tradeoffs

Pathways to lower proton transport resistance

– More sulfonation - increased IEC (reduced EW)
  • Leads to high swelling – mechanical durability issues
– Thinner membranes
  • Higher gas crossover (efficiency penalty, accelerates failure)
  • Reduced shorting resistance
– Non-polymeric additives [Ceramics (SiO$_2$, ZrO, etc.), to increase water retention, Heteropolyacids for improved conductivity]
  • May embrittle membrane
  • May leach out and poison electrodes
– Improved membrane chemistry/morphology
  • Better pathways for proton & water transport
  • Potential to also improve durability
Performance Durability Tradeoffs

Pathways to Improved Durability

– Composite membranes [polymer supports, elastomer blends]
  • Non-conductive component increases proton transport resistance

– Chemical stabilizing additives [Ce$^{3+}$, Mn$^{2+}$]
  • Can bind to acid sites and lower conductivity
  • Can move to electrodes during operation and impact performance

– External Reinforcement
  • Can add additional electron and gas transport resistances to cell

– Lower compression (for shorting)
  • Increased contact resistance at material interfaces

– Improved membrane chemistry/morphology
  • Reduced swelling & improved strength
  • Potential to also improve performance
## Proton Exchange Membrane Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2010 target</th>
<th>DOE 2015 target</th>
<th>GM target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum operating temperature</td>
<td>°C</td>
<td>120</td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>Area specific proton transport resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum operating temp and water partial pressures from 40 to 80 kPa</td>
<td>Ohm cm$^2$</td>
<td>0.02</td>
<td>0.02</td>
<td>0.025</td>
</tr>
<tr>
<td>80°C and water partial pressures from 25 - 45 kPa</td>
<td>Ohm cm$^2$</td>
<td>0.02</td>
<td>0.02</td>
<td>0.025</td>
</tr>
<tr>
<td>30°C and water partial pressures up to 4 kPa</td>
<td>Ohm cm$^2$</td>
<td>0.03</td>
<td>0.03</td>
<td>NA</td>
</tr>
<tr>
<td>-20°C</td>
<td>Ohm cm$^2$</td>
<td>0.2</td>
<td>0.2</td>
<td>NA</td>
</tr>
<tr>
<td>Maximum Oxygen cross-over$^b$</td>
<td>mA/cm$^2$</td>
<td>2</td>
<td>2</td>
<td>NA</td>
</tr>
<tr>
<td>Maximum Hydrogen cross-over$^b$</td>
<td>mA/cm$^2$</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Minimum Electrical resistance</td>
<td>Ω*cm$^2$</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Cost (500K veh/yr)</td>
<td>$/m$²</td>
<td>20</td>
<td>20</td>
<td>10$^a$</td>
</tr>
<tr>
<td>Mechanical Durability</td>
<td>RH Cycles</td>
<td>20,000</td>
<td>20,000</td>
<td>20,000</td>
</tr>
<tr>
<td>Chemical Durability</td>
<td>hours</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Unassisted start from</td>
<td>°C</td>
<td>-40</td>
<td>-40</td>
<td>-40</td>
</tr>
</tbody>
</table>

$^a$ 1MM veh/yr

$^b$ Tested in MEA at 1 atm O$_2$ or H$_2$ at nominal stack operating temperature
### GM testing of PEMs

**Ex-situ Membrane Tests**

<table>
<thead>
<tr>
<th>Test</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Mass Uptake</td>
<td>Liquid Water Capacity</td>
</tr>
<tr>
<td>Water Isotherms</td>
<td>$\lambda$ vs. RH</td>
</tr>
<tr>
<td>Dimensional Stability</td>
<td>Volumetric Swelling &amp; Shrinking in Water</td>
</tr>
<tr>
<td>Tensile Tests</td>
<td>Elastic Modulus, Yield Strength, Tensile Strength, Elongation</td>
</tr>
<tr>
<td>Tear Tests</td>
<td>Fracture Toughness</td>
</tr>
<tr>
<td>Blister Test</td>
<td>Burst Strength, Biaxial Fatigue</td>
</tr>
<tr>
<td>Dynamic Mechanical Analysis</td>
<td>Storage/Loss $E$, $T_g$, Master Curve, Shift Factor</td>
</tr>
<tr>
<td>Shrink Tension</td>
<td>Residual Stress</td>
</tr>
<tr>
<td>Ion Exchange Capacity</td>
<td>Concentration of $SO_3H$ (or other acid)</td>
</tr>
<tr>
<td>In-plane Conductivity</td>
<td>Conductivity vs T, RH (including freeze to -40°C)</td>
</tr>
</tbody>
</table>
# GM testing of PEMs

**In-situ Membrane Tests**

<table>
<thead>
<tr>
<th>Test</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Permeability Tests</td>
<td>$\text{H}_2$, $\text{N}_2$, $\text{O}_2$ permeability/crossover</td>
</tr>
<tr>
<td>Water Transport</td>
<td>Water permeability</td>
</tr>
<tr>
<td>Electrical Resistance</td>
<td>Membrane shorting</td>
</tr>
<tr>
<td>Electrical Impedence Spectroscopy (MEA)</td>
<td>Through-plane membrane resistance and electrode proton transport resistance</td>
</tr>
<tr>
<td>Fuel Cell tests (MEA)</td>
<td>Fuel Cell performance</td>
</tr>
<tr>
<td>• Polarization curves</td>
<td></td>
</tr>
<tr>
<td>• Temperature sensitivity</td>
<td></td>
</tr>
<tr>
<td>• RH sensitivity</td>
<td></td>
</tr>
<tr>
<td>• Pressure sensitivity</td>
<td></td>
</tr>
<tr>
<td>Fuel Cell durability (MEA)</td>
<td>• Membrane mechanical durability</td>
</tr>
<tr>
<td>• RH cycling</td>
<td>• Membrane chemical durability</td>
</tr>
<tr>
<td>• OCV degradation</td>
<td>• Accelerated shorting resistance</td>
</tr>
<tr>
<td>• High Voltage – Pressure Ramp</td>
<td>• All of the above</td>
</tr>
<tr>
<td>• Accelerated Durability</td>
<td></td>
</tr>
<tr>
<td>Charge Storage (MEA)</td>
<td>Water capacity during freeze start</td>
</tr>
</tbody>
</table>
Membrane Shorting and Crossover tests

Objective: Evaluate membrane for shorting and gas crossover

Method: 50 cm$^2$ fuel cell test
- Standard electrodes, carbon fiber GDM with MPL
  - Compress to 20% GDM strain
  - Standard test: Fully humidified, room temperature, no back pressure
  - Also test under range of FC operating conditions

Shorting: $\text{N}_2/\text{N}_2$, 0.5V DC

$\text{H}_2$ Cross-over: $\text{H}_2/\text{N}_2$, 0.5V DC

Targets

<table>
<thead>
<tr>
<th>Shorting:</th>
<th>$&gt; 1000 \ \Omega \cdot \text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$ Cross-over:</td>
<td>$&lt; 5 \ \text{mA/cm}^2 \cdot \text{atm}$</td>
</tr>
</tbody>
</table>

Targets should be met at beginning of life and after durability testing
In-Situ Proton Transport Resistance using AC Impedance

Through plane membrane resistance is best indicator of membrane performance – accounts for membrane thickness & proton conductivity

– Principle: AC impedance spectrum to measure High Frequency Resistance (HFR) at real axis intercept in H₂/N₂ cell
– Run tests as a function of temperature and RH

\[ R_m = \text{HFR} - R_{\text{contact}} \]

The measured HFR needs to be corrected for contact resistance
• Run “Blank” cells using gold foil instead of PEM
• Run membranes with various thickness and extrapolate to zero thickness

• In-situ resistance of Nafion NRE-211 meets target at >100% RH
• Benchmark PFSA meets target at 75% RH
Proton Conductivity: In-Plane vs. Through-Plane

- Homogeneous membranes: GM-750 and GM-1050, through-plane conductivity agrees with the in-plane conductivity.
  - Indication of good determination of $R_{\text{contact}}$
- Non-homogeneous membrane GM-S with support layer: in-plane conductivity is about twice (50%RH) the through-plane conductivity.
  - Due to high resistance of support layer and swelling anisotropy

Beware of Focusing Solely on Conductivity

Sulfonated Perfluorocyclobutane (PFCB) Block Copolymers

- Fuel Cell testing is the best indicator of membrane performance
- Actual membrane RH is extremely sensitive to in cell water transport

In collaboration with Tetramer Technologies

Membrane Performance Screening

50 cm² H₂-Air fuel cell test (Standard GM flowfields, electrodes & GDM, counterflow)

1. Polarization Curves (V vs. i) over range of RH & temperature (50 kPag)
   - Wet (110% RH out, 80°C)
   - Intermediate (85% RH out 80°C)
   - Dry (55% RH out, 95°C)

2. Humidity Sweep at fixed temperature & current (50 kPag)
   - 1.5 A/cm² – 80°C, 95°C

3. Temperature Ramp with fixed inlet humidification (62°C dew pt., 50 kPag)
   - 0.4 A/cm², 1.2 A/cm² & 1.5 A/cm²
Freeze Start Considerations

- Membrane must conduct protons at low temperatures (to \(-40^\circ C\)) to enable freeze start – but proton transport resistance is not limiting.
- Membrane must have significant capacity for water so the water generated by ORR does not freeze in electrode pores & GDL during freeze start (thus cutting off O\(_2\) transport) before cell gets hotter than 0\(^\circ\)C.

- Both considerations are strongly dependent of hydration state of membrane at shutdown and startup strategy (especially current density).

Charge storage test

- Precondition cell at membrane \(\lambda \sim 3.5\)
- Run at -20\(^\circ\)C until voltage drops

Membrane water uptake rate at low temperature limits start-up current density and, thus, the rate that cell heats.

---

Membrane Mechanical Durability

Table 4
Membrane Mechanical Cycle and Metrics
(Test using a MEA)

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crossover*</td>
<td>Every 24 h</td>
<td>≤2 mA/cm²</td>
</tr>
<tr>
<td>Shorting resistance</td>
<td>Every 24 h</td>
<td>&gt;1,000 ohm cm²</td>
</tr>
</tbody>
</table>

* Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical hydrogen crossover method

- Results very sensitive to cell design and specific operation
  - Flow field geometry, compression, GDL, MEA processing, wetting & drying rates
- Recommend to benchmark against NRE-211 with specific set-up
  - NRE-211 should fail at ~5000 cycles
Humidity Cycling of PFSA Membranes

Test for mechanical failure with no chemical stresses

Homogeneous Membranes
- DuPont™ NRE-211
  - 25μm, 1100EW cast Nafion®
- Ion Power™ N111-IP
  - 25μm, 1100EW extruded Nafion®

Composite Membranes
- Gore™ Primea® Series 57 (Expanded PTFE filled Reinforcement)
- Gore™ Primea® 5720 (Improved Reinforcement)

• Humidity cycling accelerates mechanical failures in the absence of electrochemical degradation
• Different processing methods for same polymer dramatically effects humidity cycling durability
• Mechanical reinforcement can help prevent humidity cycling induced crossover leak, but is not required

### Tensile Properties of PFSA Membranes

- ASTM method D882

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NRE-211</th>
<th>N111-IP</th>
<th>Gore Primea® 57</th>
</tr>
</thead>
<tbody>
<tr>
<td>units</td>
<td>MD</td>
<td>TD</td>
<td>MD</td>
</tr>
</tbody>
</table>

#### 50% RH, 23°C

<table>
<thead>
<tr>
<th></th>
<th>MPa</th>
<th>MPa</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>30.5</td>
<td>28.0</td>
<td>32.6</td>
</tr>
<tr>
<td>Yield Strength (2% offset)</td>
<td>14.4</td>
<td>14.0</td>
<td>14.1</td>
</tr>
<tr>
<td>Elongation</td>
<td>253</td>
<td>235</td>
<td>176</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>272</td>
<td>253</td>
<td>304</td>
</tr>
</tbody>
</table>

#### submerged, 80°C

<table>
<thead>
<tr>
<th></th>
<th>MPa</th>
<th>MPa</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>8.9</td>
<td>9.5</td>
<td>17.2</td>
</tr>
<tr>
<td>Yield Strength (2% offset)</td>
<td>4.4</td>
<td>4.6</td>
<td>5.0</td>
</tr>
<tr>
<td>Elongation</td>
<td>159</td>
<td>188</td>
<td>193</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>23.9</td>
<td>25.1</td>
<td>45.0</td>
</tr>
</tbody>
</table>

- Tensile properties of N111-IP not superior to other PFSA membranes
- Cannot use tensile tests as predictor for mechanical durability

Blister Membrane Strength Test

Schematic of blister testing.

Quasielastic stress approximation based on Hencky’s

\[ \sigma = \frac{2p}{h} \]

where \( \sigma \) is the stress,
\( p \) is the applied pressure,
\( h \) is the thickness of the blister,
\( a \) is the radius; and
\( E \) is the modulus; relaxation

8 separate blisters with independent pressure control

Creep Blister Strength of PFSA Membranes

At stress levels expected during automotive operation extruded Nafion 111-IP outlasts Gore-Select 57 & Nafion NRE-211 by 10-100X

This ranking agrees with the ranking from humidity cycling tests.


Stress level induced by humidity cycling
Simple Mechanical Durability Screening

Tests Required

- Tensile Elongation to break at ambient conditions
- Linear Swelling in boiling water

Sanity Check: Does the membrane stretch more when dry then it swells when wet?

If facilities are not available for RH cycling or blister testing, at the very least, measure swelling and elongation to break.

Humidity Stability = strain @ break (25°C, 50%RH) / linear swelling (100°C H₂O)

Correlating HSF w/ Durability


General guidelines
- If HSF<1: find a way to reduce swelling and improve elasticity ASAP
- If 1<HSF<10: I’d still focus on reducing swelling and improving elasticity, but at least it’s worth running FC tests
- If HSF>10: material may be durable enough with MEA optimization
Screening for PEM Chemical Stability

Ex-situ Fenton’s ageing tests are not representative of in-situ fuel cell degradation

- Initial \( \text{H}_2\text{O}_2 \) concentration much higher than observed in operating fuel cells
- \( \text{H}_2\text{O}_2 \) concentration decreases rapidly with time
- Absence of \( \text{H}_2 \)
- Presence of liquid water

Consequences of depending on Fenton’s tests

- **False positives**
  - End group stabilized PFSA membranes are stable in Fenton’s solutions, but degrade rapidly in in-situ accelerated fuel cell tests [N. Cipollini, *ECS Transactions*. 11 (1), 1071 (2007); F. D. Coms, H. Liu, J. E. Owejan, *ECS Transactions*, 16 (2), 1735-1747 (2008).]
- **False negatives**
  - BPSH membranes degrade rapidly in Fenton’s solutions, but are relatively stable in in-situ accelerated fuel cell tests [Sethuraman *et al*, *JECS*, 155 (2), B119-B124 2008]
Membrane Chemical Durability

### Table 3
MEA Chemical Stability and Metrics

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Steady state OCV, single cell 25-50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total time</td>
<td>500 h</td>
</tr>
<tr>
<td>Temperature</td>
<td>90°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Anode/Cathode 30/30%</td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>Hydrogen/Air at stoics of 10/10 at 0.2 A/cm² equivalent flow</td>
</tr>
<tr>
<td>Pressure, inlet kPa abs (bara)</td>
<td>Anode 150 (1.5), Cathode 150 (1.5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻ release or equivalent for non-fluorine membranes</td>
<td>At least every 24 h</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Hydrogen Crossover (mA/cm²)*</td>
<td>Every 24 h</td>
<td>≤2 mA/cm²</td>
</tr>
<tr>
<td>OCV</td>
<td>Continuous</td>
<td>≤20% loss in OCV</td>
</tr>
<tr>
<td>High-frequency resistance</td>
<td>Every 24 h at 0.2 A/cm²</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Shorting resistance</td>
<td>Every 24 h</td>
<td>&gt;1,000 ohm cm²</td>
</tr>
</tbody>
</table>

* *Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical H2 crossover method

- Incorporation of chemical stabilizers has enabled excellent chemical stability
  - GM has developed a new OCV test that stepwise increases stress

<table>
<thead>
<tr>
<th>Step</th>
<th>duration</th>
<th>temperature</th>
<th>RH</th>
<th>All steps run at OCV in H₂/Air with stoics of 5/5 at 0.2 A/cm² equivalent flow and 150 kPa-abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 h</td>
<td>95°C</td>
<td>50%</td>
<td>All steps run at OCV in H₂/Air with stoics of 5/5 at 0.2 A/cm² equivalent flow and 150 kPa-abs</td>
</tr>
<tr>
<td>2</td>
<td>100 h</td>
<td>95°C</td>
<td>25%</td>
<td>All steps run at OCV in H₂/Air with stoics of 5/5 at 0.2 A/cm² equivalent flow and 150 kPa-abs</td>
</tr>
<tr>
<td>3</td>
<td>100 h</td>
<td>110°C</td>
<td>25%</td>
<td>All steps run at OCV in H₂/Air with stoics of 5/5 at 0.2 A/cm² equivalent flow and 150 kPa-abs</td>
</tr>
</tbody>
</table>

*Step duration and temperature include OCV at 0.2 A/cm² equivalent flow and 150 kPa-abs
Accelerated Membrane Chemical Durability

OCV testing of Nafion 1100EW membranes

- OCV 95 °C, 50% RH
- OCV 95 °C, 25% RH
- OCV 110 °C 25% RH

OC Voltage vs. Time (h)

Fluoride Release Rate (g/h·cm²)

- 1% Ce doped
- 30% Ce doped

• At short times (< 100h) & standard conditions – no separation between low & high stabilization levels
• At longer times and hotter/dryer conditions, separation is observed
Accelerated Membrane Shorting

Test Procedure
- Bare membrane or non-platinized MEA
- Sandwiched between GDL and flat graphite plates
- Conditions can be controlled – standard test is in air, ambient temp & RH (also test dry at 95ºC)
- Ramp potential from 0-5V (0.5V/s) - monitor current
- Record whether or not membrane shorts (indicated by current spike)
- Increase compression stepwise from 100 - 1200psi
- ~10 samples to get Weibull plot

Shorting Probability Comparison of GDM and PEM
Weibull

Cumulative Shorting Probability Comparison of GDM and PEM
Weibull

Membrane & GDL type & compression all impact membrane shorting
Summary

• Performance, durability and cost must all be considered when developing materials for automotive fuel cell systems.
• Measurements must be conducted at relevant operating conditions.
  ➢ US OEMs focusing on temperatures up to 95°C and humidities between 40-100% RH.
• A proper set of *ex-situ* tests can be used for initial screening of novel PEM materials.
  ➢ eg, Humidity Stability Factor and/or blister tests for mechanical durability
• *In-situ* performance and durability testing is essential for novel PEM evaluation – but results are very sensitive to MEA & cell design.
  ➢ Appropriate benchmarking is necessary.
  ➢ Collaborations for MEA preparation & evaluation are needed.
• At sub-freezing temperatures, membrane rate and amount of water uptake is just as important as membrane conductivity.
• Critical membrane failure modes of mechanical degradation, chemical degradation & shorting must be all be considered.
• Please call or write your congressmen and representatives to urge their support for continued government funding for Hydrogen Fuel Cell development.
Acknowledgements

General Motors Fuel Cell Research Labs
Frank Coms
Tim Fuller
Ruichun Jiang
Yeh-Hung Lai
Yongqiang (Ron) Li
Sean Mackinnon
Dave Masten
Mike Schoeneweiss
Eric Thompson

Giner Electrical Systems
Cortney Mittelsteadt

Virginia Tech
David Dillard
Scott Case
Michael Ellis