Membrane Performance and Durability Overview for Automotive Fuel Cell Applications

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*Fuel Cell Activities*
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Outline

• Fuel Cell Vehicle Commercialization
  – Automotive Competitive Fuel Cell Membrane Requirements

• Proton Exchange Membranes
  – Performance: Requirements & Status
  – Durability: Requirements & Status

• Closing
Vehicle Commercialization Requirements

H1 H₂-FC Vehicle (2000):
- External humidified H₂/air
- Reduced passenger/trunk space

H3 H₂-FC Vehicle (2003):
- Internal humidification
- Reduced range & peak power

Commercialization Requirements:
- Performance – at least equal to internal combustion engine vehicles
- Durability – 6000 hours service, 10 years life
- Cost -- $5000 for power train including H₂ storage
  - About $50/kW for 100 kW system
  - Less than $10/kW target for membrane electrode assembly (supported catalyst, membrane, diffusion media, fabrication)

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Automotive FC System Operating Conditions

Fuel cell materials and design that enable higher temperature operation will be preferred in vehicle applications.

- smaller radiator
- greater packaging / styling flexibility

For a higher temperature system to be feasible, the membrane must have improved proton conductivity at low RH vs. current materials.

| Comparison of Internal Combustion Engine (ICE) vs. Fuel Cell System (FCS) |
|---------------------------------|----------------|
| **ICE**                         | **FCS**       |
| Power from system               | 80 kW         | 80 kW         |
| Heat rejected (Q)               | < 80 kW       | 100 kW (@0.6 V, including parasitics) |
| $T_{\text{ambient}}$            | 40°C          | 40°C          |
| $T_{\text{coolant}}$            | 120°C         | 80 $\rightarrow$ 95 $\rightarrow$ 120°C |
| “Q/ITD” Proportional to radiator size | <1 kW / K | 2.5 $\rightarrow$ 1.8 $\rightarrow$ 1.25 kW / K |

We ultimately want $T_{\text{coolant}}$ (FCS) as close as possible to $T_{\text{coolant}}$ (ICE), 120°C.
Effect of Cathode Outlet Pressure on Cost

- Maximum feasible operating pressure considered to be 150 kPa abs.
- Operating at higher cathode outlet pressures, to achieve higher RH, is not a cost effective or high efficiency option.
Effect of Temperature on Humidifier Size

@ 150 kPa cathode outlet

- Moving to higher temperatures solves thermal heat rejection problem.
- Moving to drier inlets enables simpler systems but does not address thermal issue.
- The dry inlet cases do not require a humidifier.
- 1st generation commercial
- 2nd generation commercial

- Higher temperature requires lower RH operating conditions to allow cost effective and packagable humidification system.
- Membrane operating at 95°C could enable a FC System that can compete with the ICE.

RH out (%)

0 10 20 30 40 50 60 70 80 90

T-stack (°C)

80 95 120

Humidifier size = 1x
Humidifier size = 2.5x
Humidifier size = 12x

RH inlet = 30%
RH inlet = dry

Not feasible. Humidifier too large.

Ideal solution, 2nd generation commercial
### Automotive FC System Operating Requirements

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>RH in (%)</th>
<th>RH out (%)</th>
<th>Q/ITD (Proportional to radiator size)</th>
<th>Membrane Conductivity</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>30</td>
<td>84</td>
<td>2.5</td>
<td>0.1 S/cm at 80% RH Commercial PFSA</td>
<td>Not competitive with ICE</td>
</tr>
<tr>
<td>95</td>
<td>30</td>
<td>55</td>
<td>1.8</td>
<td>0.1 S/cm at 50% RH Demonstrated PFSA</td>
<td>May be competitive with ICE</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>&lt;20</td>
<td>1.25</td>
<td>0.1 S/cm at &lt;20% RH (non-existent)</td>
<td>Ultimate solution</td>
</tr>
</tbody>
</table>

- Humidification system would be too large
- Radiator size 2-4 times ICE

- **0.1 S/cm at 50% RH operating at 95°C could enable a FCS that could be an “Automotive Competitive System”**
  - although it would still require a large humidifier and thermal system developments
- **0.1 S/cm at <20% RH operating at 120°C remain long term goal**
  - GM does not believe materials exist which meet initial market launch timing

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Conductivity of Polymer Electrolyte Membranes

- Sulfonated aromatic membranes are more conductive than Nafion® 1100EW at high RH, but are inferior at low RH.
- Nafion® 1100EW is not a good benchmark. Higher conductivity (lower EW PFSAs) are available.

**Benzene Sulfonic acid $H^+$-conducting group**

\[
\text{HO}_3\text{S} \quad \text{SO}_3\text{H}
\]

1.8 meq SO$_3$H/g

**Sulfonated polyarylenethioethersulfone (SPTES)**

Expected Stack Temperature-Life Profile

Assumed designed for $T_{\text{max}} = 95^\circ$C

% of Life at Stack Temperature
(not including freeze operation)

- 60 hours of life
  - max speed on hot days
  - pulling loads up hills

- The vast majority of stack life will be at 60-80°C stack temperature.
- Only 60 hours (~1%) of 5500 hr life are anticipated at 95°C.

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Automotive-Competitive Membrane Summary

- PFSA membranes with evolutionary improvements should meet needs of 1\textsuperscript{st} generation Fuel Cell Systems
  - Conductivity at 95°C & 50% RH in order to demonstrate an “Automotive Competitive System”
- Membrane needs to survive 60 hours at 95°C
  - Durability tests must properly assess membrane’s ability to do this
- Revolutionary new materials (non-PFSA membranes) are desired for 2\textsuperscript{nd}-generation automotive. These materials will relieve constraints (system complexity, operating conditions, cost) imposed by current materials.
Membrane Performance Screening

Objective: Evaluate membrane performance in a fuel cell over entire range of automotive operating conditions

Method: 50 cm² H₂-Air fuel cell test
1. Polarization Curves over range of RH (80°C, 50 kPag, 2-3 Stoichs)
   a) Wet (110% RH out)
   b) Intermediate (80% RH out)
   c) Dry (60% RH out)
2. Humidity Sweep over operating window (50 kPag, 2/2 Stoichs)
   a) 0.4 A/cm² – 80°C
   b) 0.4 A/cm² – 95°C
   c) 1.2 A/cm² – 80°C
   d) 1.2 A/cm² – 95°C

Target: Robust Operation over range of Temperature and Humidity levels
Membrane Performance Screening: Wet vs Dry

At wet conditions some HC membranes perform comparably to PFSA.

At dry conditions most HC membranes cannot run stably to 1.5 A/cm².
Membrane Performance: RH Sensitivity

- **80°C @ 1.2 A/cm²**: PFSA performance stable down to 30% RH
  HC performance dropping below 50% RH.
- **95°C @ 1.2 A/cm²**: PFSA performance dropping below 50% RH
  HC performance dropping below 100% RH.
Exchange Capacity vs. Water Uptake

Higher IECs increase conductivity, but also increase swelling

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC</th>
<th>Dry Density</th>
<th>Wt% Uptake</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mEq/cm³</td>
<td>gm/cm³</td>
<td>100 + mass H₂O/mass dry polymer</td>
<td>wet volume/dry volume</td>
</tr>
<tr>
<td>Data at 100°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 112</td>
<td>1.8 (1100 EW)</td>
<td>1.9</td>
<td>40</td>
<td>1.8</td>
</tr>
<tr>
<td>Low EW PFSA</td>
<td>2.9 (700 EW)</td>
<td>1.9</td>
<td>60</td>
<td>2.2</td>
</tr>
<tr>
<td>SPTES-50</td>
<td>2.2 (1.8 mEq/gm)</td>
<td>1.2</td>
<td>450</td>
<td>6.3</td>
</tr>
</tbody>
</table>

• Membrane should not swell excessively in liquid water at 100°C.
  – Volumetric exchange capacity more relevant than gravimetric
  – Volume swell in fuel cell stack can cause excessive mechanical force
  – Durability issues (e.g. fatigue) in wet-dry cycling
  – **Swelling of 2 suggested as screening limit**

• Important that water taken up by membrane contribute efficiently to proton conductivity!
Proton Exchange Membrane Durability

- Automotive Fuel Cells must survive 10 years and 6000h operation.
  - Electrochemically active environment
  - Transient operation
  - Start-Stop & Freeze-Thaw cycling

- We need to determine the conditions that lead to membrane failure.
- Promote development of materials that can withstand these conditions.
Why Do Membranes Fail?

Mechanical Degradation
- Stresses caused by Membrane Shrinking/Expansion with Fluctuations in Temperature or Humidity
- Stresses caused by Stack Compression & Compression Variation
- Creep/Stress Rupture

Chemical Degradation
- Polymer chain attack by radicals or other active species

Thermal Degradation
- Weakening of Membrane by Overheating (higher than operating temp)

Combined Effects of Mechanical & Chemical Degradation
Hypothesis for Membrane Mechanical Failure

- Membranes & MEAs swell after soaking in water and subsequently shrink upon drying
- In plane: tension & compression are caused as membrane constrained from shrinking & swelling cycles between wet & dry
- Fatigue from humidity cycling induced stresses causes pinholes

Accelerated Testing: *In-Situ* Humidity Cycling

- Test membranes for mechanical failure in the absence of reactive gases and electric potential
- Impose mechanical stresses on MEAs that would be experienced during fuel cell operation due to humidity fluctuations

<table>
<thead>
<tr>
<th>Materials:</th>
<th>MEA (Pt/C electrodes) &amp; Carbon Fiber Paper GDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Build:</td>
<td>50 cm² cell w/ single pass 2mm lands &amp; channels</td>
</tr>
<tr>
<td>Cycle:</td>
<td>2 min 150% RH air; 2 min 0% RH air flow</td>
</tr>
<tr>
<td>Conditions:</td>
<td>80°C, 0 kPa, 2 SLPM dry anode &amp; cathode flow</td>
</tr>
<tr>
<td>Diagnostics:</td>
<td>Physical crossover leak (failure = 10 sccm)</td>
</tr>
</tbody>
</table>
Humidity Cycling of PFSA Membranes

Humidity cycling accelerates mechanical failures in the absence of electrochemical degradation.

Homogeneous Membranes
- DuPont™ NR-111
  - 25μm, 1100EW Nafion®
- Ion Power™ N111-IP
  - 25μm, 1100EW Nafion®

Composite Membranes
- Gore™ Primea® Series 57 (Expanded PTFE Filled Reinforcement)

• Different processing methods for same polymer dramatically effects humidity cycling durability
• Mechanical reinforcement insufficient to prevent humidity cycling induced crossover leak
Humidity Cycling of Alternative Membranes

- Most research on Hydrocarbon membranes focused on performance at high temperatures and low RH
- What About Durability?

Most hydrocarbon or partially-fluorinated HC polymer membranes we’ve tested last less than 400 cycles

- Humidity cycling durability is critical when developing FC membranes
- Concepts like block copolymers & cross-linking show promise
**Chemical Degradation of Ionomer**

**Hypothesis:** Membrane degrades via reaction of (•OH) with ionomer

- Peroxide is formed as byproduct of oxygen reduction
  \[
  O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
  \]
- Peroxyl radical can be formed through decomposition of hydrogen peroxide (H₂O₂)
  \[
  H_2O_2 \xrightarrow{Fe^{++}} 2 \text{ OH}^-
  \]
- Chain “unzipping” occurs via non-fluorinated end groups (example)

*Journal of Power Sources, Volume 131, Issues 1-2, 14 May 2004, Pages 41-48, Curtin et al*

**Fuel Cell Activities**

September 14, 2006
Accelerated Membrane Chemical Durability

**Objective:** Test for chemical failure with minimal mechanical stress

**Method:** Operate at conditions that accelerate Chemical Degradation - no RH fluctuations

| Materials: | MEA (Pt/C electrodes) & Carbon Fiber Paper GDM |
| Cell Build: | 50 cm² cell w/ serpentine flow field |
| Conditions: | OCV, 95°C, 50% RH, 50 kPag, 5/5 stoich at 0.2 A/cm² equivalent flow |
| Diagnostics: | OCV, H₂ crossover current, physical leak, FRR |

**Target:**
- PFSA: < 10⁻⁸ g/hr-cm² Fluoride release rate (FRR)
- Non-PFSA: crossover diagnostic used as opposed to effluent chemical analysis
Combining Mechanical & Chemical Stresses

**Objective:** Does Electrochemical Reaction Accelerate Mechanical Failure?

- Repeat Humidity Cycling Protocol in a H₂/Air Fuel Cell
- Run constant current test at 0.1 A/cm²

<table>
<thead>
<tr>
<th>MEA</th>
<th>Cycles to Failure w/o load</th>
<th>Cycles to Failure @ 0.1 A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont™ Nafion® (NR-111)</td>
<td>4000-4500</td>
<td>800-1000</td>
</tr>
<tr>
<td>Ion Power™ Nafion® (N111-IP)</td>
<td>20000+</td>
<td>1800</td>
</tr>
<tr>
<td>Gore™ Primea</td>
<td>6000-7000</td>
<td>1300</td>
</tr>
</tbody>
</table>

- Commercial PFSA: failure accelerated >5 times under electrochemical load
- GM Benchmark: Lifetime under load = 0.7 X Lifetime in with no electrochemical load
Chemical Degradation During Humidity Cycling

Run periodically for 24h steady state at 150% RH & 0.1 A/cm$^2$

- Commercial PFSA
  - ~10X higher FRR during cycling
  - >5X acceleration of membrane failure at 0.1 A/cm$^2$
  - Mechanical stresses accelerate chemical degradation

- Robust PFSA Benchmark
  - FRR 100-1000X lower than other PFSAs
  - FRR does not increase with RH cycling
  - Mechanical stresses do not accelerate chemical degradation
Summary

• Membrane Performance
  - High membrane conductivity at low RH (< 50%) required to enable an “auto-competitive” Fuel cell System
  - 120°C remains long term target, but 95°C enables initial commercialization
  - Low EW PFSAs have potential to meet performance requirements
  - HC benzene sulfonic acid membranes not expected to meet targets

• Membrane Durability
  - Humidity cycling durability must be considered when developing membrane materials
  - Humidity cycling durability strongly dependent on processing method
  - Mechanical reinforcement not sufficient to prevent RH cycling failures
  - Humidity cycling failure is accelerated by chemical degradation
  - Mitigations strategies must be incorporated to prevent radical attack on the membrane

• High Performance Membranes exist, Mechanically Robust membranes exist, and Chemically Stable Membranes exist

→ Now we need to combine these properties into a single material
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