Model Compound Studies of Fuel Cell Membrane Degradation

David Schiraldi, Chun Zhou
May 26, 2005
DOE Briefing
1. Motivation
2. Literature Review of Fuel Cell Durability
3. Experiments and Methodology
4. Results and Discussions
5. Working Conclusions
Motivation

1. Durability
   - a key for commercial fuel cell system

2. Degradation Mechanism(s)
   - complex degradation origins
   - ambiguous literature

3. Minimize Degradation
   - molecular design for stability
   - possibly include a stabilizer
**PEM Fuel Cell**

**Anode**

- \( 	ext{H}_2 \rightarrow 2	ext{H}^+ + 2\text{e} \)

**Cathode**

- \( \frac{1}{2}\text{O}_2 + 2	ext{H}^+ + 2\text{e} \rightarrow \text{H}_2\text{O} \)

**Typical Life Time Number**
- < 20,000 hrs for stationary
- < 5,000 hrs for automobiles
1. Motivation
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1. Fuel Cell System
   - Poisoning / loss $\rightarrow$ Failure of catalyst
   - Scorching / contamination $\rightarrow$ Failure of plate

2. Mechanical Failure of Membrane
   - Stress created by thermal / hydration cycling
   - Failure at contact points in assembly
   - Pin-hole formation

3. Chemical Degradation of Membrane
   - Membrane thinning
   - Fluoride leaching of perfluorinated membrane
   - $\text{H}_2\text{O}_2$, $\cdot\text{OH}$, and $\cdot\text{OOH}$ formation and attack on membrane
 Prior-Art of Membrane Degradation

- Suggestion Made Based on ESR / Nitroxide (TEMPO) Trapping

Nafion Ionomer

Copper Ion $\to$ H$_2$O$_2$ $\xrightarrow{\text{Fe}^{3+}}$ H$_2$O$_2$ $\xrightarrow{-1/2\text{O}_2}$ -SO$_2$

S. Schlick et al., Spring 2005, ACS National Meeting, San Diego CA
Prior-Art of Membrane Degradation

Main Chain Unzipping of Nafion from End Group

Nafion Ionomer

\[
\begin{align*}
\text{(C\text{=C})_x(\text{C}^\text{=C})_y} & \\
\text{O-C-F} & \text{m} \quad \text{O-C-SO}_2\text{H} \\
\text{CF}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{F}_2\text{C-F} & \text{C-OH} + \cdot \text{OH} \rightarrow \text{F}_2\text{-CF}_2' + \text{CO}_2 + \text{H}_2\text{O} \\
\text{F}_2\text{C-CF}_2' + \cdot \text{OH} \rightarrow \text{F}_2\text{C-C-OH} \\
\text{F}_2\text{C-C-OH} \rightarrow \text{F}_2\text{C-C-F} + \text{HF} \\
\text{F}_2\text{C-C-F} \xrightarrow{\text{H}_2\text{O}} \text{F}_2\text{C-C-OH} \\
\end{align*}
\]

Curtin et al, J. Power Sources, 2004, 131, 41
The DuPont-suggested mechanism is supported by their work, which shows that as COOH groups are fluorinated, the level of fluoride generated under lab or operating conditions decreases linearly. There is a non-zero intercept, however, suggesting a second mechanism must be operating as well.

Curtin et al, J. Power Sources, 2004, 131, 41
1. Assumption that peroxide is the major cause

2. Complicated nature of methodologies to generate ·OH radical
   - Fenton’s Reaction: chain-reaction easily altered by reactivity of reactants
   - UV/H\textsubscript{2}O\textsubscript{2}: concentration of H\textsubscript{2}O\textsubscript{2} is critical
   - No one really knows what levels of peroxy radicals exist w/in fuel cells

3. Analytical work concerning small changes in large molecules
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Our Approach:

Using small molecules as model compounds (MC) under carefully simulated reaction conditions

- Gains analytical capabilities (NMR, MS…)
- Allows better isolation of effect from different reactive site
- Fenton’s reagent to be used as the \( \cdot \text{OH} \) radical source vs.
  
  UV/H_2O_2 photolysis as a metal-free \( \cdot \text{OH} \) radical source
Fenton’s Reaction

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \]

\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{OOH} \]

**Harsh Conditions**

\[
\begin{align*}
\text{Fe}^{2+}: & \quad 400 \text{ mM [in Fe(SO}_4)_2(\text{NH}_4)_2\cdot\text{6H}_2\text{O]} } \\
\text{H}_2\text{O}_2: & \quad 400 \text{ mM } \\
\text{MC}: & \quad 100 \text{ mM } \\
\text{H}_2\text{O}: & \quad \text{total volume is 50 ml.}
\end{align*}
\]

**Milder Conditions**

\[
\begin{align*}
\text{Fe}^{2+}: & \quad 30 \text{ ppm = ca 0.54 mM } \\
\text{H}_2\text{O}_2: & \quad 400 \text{ mM } \\
\text{MC}: & \quad 100 \text{ mM } \\
\text{H}_2\text{O}: & \quad \text{total volume is 50 ml.}
\end{align*}
\]
Experiments and Methodology

Fenton’s Reaction

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\text{H}_2\text{O}_2 + \cdot\text{OH} & \rightarrow \text{H}_2\text{O} + \cdot\text{OOH}
\end{align*}
\]

Harsh Conditions

- \(\text{Fe}^{2+}\): 400 mM [in \(\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2\cdot6\text{H}_2\text{O}\)]
- \(\text{H}_2\text{O}_2\): 400 mM
- \(\text{MC}\): 100 mM
- \(\text{H}_2\text{O}\): total volume is 50 ml.

Our initial reaction conditions

Milder Conditions

- \(\text{Fe}^{2+}\): 30 ppm = ca 0.54 mM
- \(\text{H}_2\text{O}_2\): 400 mM
- \(\text{MC}\): 100 mM
- \(\text{H}_2\text{O}\): total volume is 50 ml.

Matches DuPont’s Reaction conditions
Aging Experiment Procedure

Membrane Film Samples

Addition of $\text{H}_2\text{O}_2$

Concentration of $\text{F}^-$

Aging time

Model Compounds

Refresh

Concentration of peroxide

Aging time
Control experiments show that we can recover known amounts of organic/fluoride using this procedure.

Model Compound Separation Scheme

MC + Aging bath

addition of H$_2$O$_2$

T=68°C

N$_2$ protection

Ca. 24 Hrs

Precipitation

Filtration

Oil Phase

Water Phase

F- Measurement

Washing by EDTA

Extraction by 1-Butanol

Rotavaporation to take out 1-Butanol

$^{19}$F NMR

F- Measurement check whether F- was carried over
Fluoride Concentration Measurement

**F⁻ Ion Selective Electrode (ISE)**

**Concentrations and ISE readings**

<table>
<thead>
<tr>
<th>[F⁻] in ppm</th>
<th>[F⁻] in M</th>
<th>Log [F⁻] / M</th>
<th>E / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>5.26E-07</td>
<td>-6.28</td>
<td>-256.5</td>
</tr>
<tr>
<td>0.05</td>
<td>2.63E-06</td>
<td>-5.58</td>
<td>-253.6</td>
</tr>
<tr>
<td>0.1</td>
<td>5.26E-06</td>
<td>-5.28</td>
<td>-262.2</td>
</tr>
<tr>
<td>1</td>
<td>5.26E-05</td>
<td>-4.28</td>
<td>-310.7</td>
</tr>
<tr>
<td>10</td>
<td>5.26E-04</td>
<td>-3.28</td>
<td>-369.1</td>
</tr>
<tr>
<td>100</td>
<td>5.26E-03</td>
<td>-2.28</td>
<td>-427.2</td>
</tr>
</tbody>
</table>

**Detection Limit** (by direct measurement)

- y = -46.086x - 520.41
- R² = 0.9506

**Slope Efficiency**
- Theoretical value c.a. -58
- y = -53.259x - 545.01
- R² = 0.9958

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**Full Concentration Range**

**Working Concentration Range**
Interference of Fe$^{3+}$ on ISE

A 20-fold dilution of the solution eliminates the Fe(III) interference, but still allows detection of fluoride.
Other Interference Factors?

No Interference from Fe(II)

No pH effect
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Fluoride Leaching of MCs

Under "harsh" Fenton Conditions

Accumulated
F- detected / % of total F atoms in MC

Accumulated treated time / hrs
### Comparison of MCs and Ionomers

**Generated under “Harsh Fenton’s Conditions”**

<table>
<thead>
<tr>
<th>Material</th>
<th>F- Generated per 24 hours, based on % of total fluorine content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion Ionomer</td>
<td>0.03 (0.26)</td>
</tr>
<tr>
<td>3M Ionomer</td>
<td>0.01-0.02 (~0.1)</td>
</tr>
<tr>
<td>MC 1</td>
<td>0.08</td>
</tr>
<tr>
<td>MC 2</td>
<td>0.28</td>
</tr>
<tr>
<td>MC 4</td>
<td>0.02</td>
</tr>
<tr>
<td>MC 5</td>
<td>0.008</td>
</tr>
<tr>
<td>MC 6</td>
<td>0.007</td>
</tr>
<tr>
<td>MC 7</td>
<td>0.002</td>
</tr>
<tr>
<td>MC 8</td>
<td>0.001</td>
</tr>
</tbody>
</table>

**Notes:**

* Numbers in parentheses are based on side chain content only (i.e. PTFE backbone inert)
* MC 3 not tested, expected to be “inert” and not particularly relevant
**Materials – Relative Decomposition Rates**

<table>
<thead>
<tr>
<th>Material</th>
<th>3M Ionomer</th>
<th></th>
<th>Nafion Ionomer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MC1</td>
<td>1.5-3 (~14)</td>
<td></td>
<td>4.3 (37)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC2</td>
<td>40</td>
<td></td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC3</td>
<td>2.8</td>
<td></td>
<td>Not tested</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC4</td>
<td>1.1</td>
<td></td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC5</td>
<td>1.1</td>
<td></td>
<td>1.0 (defined)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC6</td>
<td>0.3</td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC7</td>
<td>0.15</td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC8</td>
<td>0.15</td>
<td></td>
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### Materials – Relative Decomposition Rates

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<td>MC6</td>
<td></td>
<td>1.0 (defined)</td>
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</table>

Comparison of MC5 and MC6

Results argue against literature

Suggestion of sulfonic acid as Cite for radical attack in the Presence of Fe Ions

(Similarly, MC7,8 low values)

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<tr>
<th></th>
<th>11 40</th>
<th>2.8 1.1 1.0 (defined)</th>
<th>4.3 (37) 1.5-3 (~14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC8</td>
<td>0.15</td>
<td></td>
<td></td>
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</table>
Materials – Relative Decomposition Rates

Nafion Ionomer

\[ \begin{align*}
\text{HO} & \text{C} \quad \text{F} \quad \text{C} \quad \text{O} \\
\text{CF}_3 & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CF}_3
\end{align*} \]

4.3 (37)

3M Ionomer

\[ \begin{align*}
\text{F}_2 & \text{C} \quad \text{F} \quad \text{C} \quad \text{F}_2 \\
\text{O} & \text{C} \quad \text{C} \quad \text{F}_2 \quad \text{C} \quad \text{SO}_3\text{H}
\end{align*} \]

1.5-3 (~14)

Commercial perflorinated ionomers exhibit fluoride generation rates on the same order of magnitude to MCs containing carboxylic acids.

Nafion appears to degrade at a rate greater than a simple perfluorinated carboxylic acid, while the 3M ionomer appears to compete directly with such model compounds.

Suggests that the branched side chains in Nafion are fragile.

MC1

\[ \begin{align*}
\text{F}_2 & \text{C} \quad \text{F}_2 \quad \text{C} \quad \text{O} \\
\text{CF}_3 & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CF}_3
\end{align*} \]

11

MC3

\[ \begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{F}_2 \quad \text{CF}_3 \\
\text{OH} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CF}_3
\end{align*} \]

Not tested

MC4

\[ \begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{F}_2 \quad \text{CF}_3 \\
\text{OH} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CF}_3
\end{align*} \]

2.8

MC7

\[ \begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{SO}_3\text{H} \\
\text{O} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{SO}_3\text{H}
\end{align*} \]

0.3

Not tested

MC8

\[ \begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{SO}_3\text{H} \\
\text{O} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{SO}_3\text{H}
\end{align*} \]

0.3

Not tested
**Materials – Relative Decomposition Rates**

Branched perfluoroethers in the presence of carboxylic acids appear to be more fragile than their linear counterparts (MC1, 2 vs. MC4,5)

The perfluoroisopropylidene branches alone do not appear to be significant triggers for decomposition, but appear to work in synergy with carboxylate groups. (MC7,8 vs. MC1,2)

<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>MC1</th>
<th>MC2</th>
<th>MC3</th>
<th>MC4</th>
<th>MC5</th>
<th>MC6</th>
<th>MC7</th>
<th>MC8</th>
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<td>0.3</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Destabilizing Ethers?

It is known that C-H groups alpha to an Ether link are 10x more prone to attack by Hydroxyl radicals *
Also true for partially fluorinated ethers **

Perhaps true for C-F bonds as well

** D. L. Cooper, *Atmos.Env.*, 1992, 26A, 1331-4
**MC Fluoride Results vs. Concentration**

*Concentration effects appear to be unimportant*

 Accumulated F-detecte / % of total F atoms in MC2

\[ y = 0.005x - 0.0336 \]
\[ R^2 = 0.9949 \]

* Will test lower reactivity MCs as well
**Comparison of MC Degradation w/o Iron**

**MC2**

![MC2 Structure](image)

<table>
<thead>
<tr>
<th></th>
<th>MC2-Original Sample</th>
<th>MC2-1HR</th>
<th>MC2-H2O2-1HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F] / M</td>
<td>6.09E-04</td>
<td>5.94E-04</td>
<td>3.49E-03</td>
</tr>
<tr>
<td>[F] / ppm</td>
<td>&lt; 10 ppm</td>
<td>&lt; 10 ppm</td>
<td>ca 65ppm</td>
</tr>
<tr>
<td>% of total F atom</td>
<td>NA</td>
<td>Negligible</td>
<td>0.26</td>
</tr>
</tbody>
</table>

**MC8**

![MC8 Structure](image)

<table>
<thead>
<tr>
<th></th>
<th>MC8-Original Sample</th>
<th>MC8-1HR</th>
<th>MC8-H2O2-1HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F] / M</td>
<td>2.37E-05</td>
<td>2.48E-05</td>
<td>1.01E-04</td>
</tr>
<tr>
<td>[F] / ppm</td>
<td>ca 0.5 ppm</td>
<td>ca 0.5 ppm</td>
<td>ca 2.5 ppm</td>
</tr>
<tr>
<td>% of total F atom</td>
<td>NA</td>
<td>Negligible</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

**Reactivity Ratios Similar to those with Fenton’s Agent**
Current Fluorocarbon Degradation Studies

- Replicating MC studies under “Mild Fenton’s conditions”
- Additional solubility studies
- Additional hydrogen peroxide photolysis experiments
- Effect of copper ions?
- TEMPO/ESR Trapping of MC decomposition radicals

MC7,8 behave Similarly under Mild and Harsh Fenton’s conditions
$^{19}$F NMR of MC2 – Before Degradation

Integral $\approx 46:147:98:102:102:100$

$\approx 1:3:2:2:2:2$
19F NMR of MC2 – Fenton’s Aged Sample

Remaining MC2

Integral ≈ 8.8 : 109: 30:103:101:100
≈ 0.2 : 2 : 0.6 : 2 : 2 : 2

3 – 5x reduction
$^{19}$F NMR of MC2 – Fenton’s Aged Sample

MC2-treated
Archive directory: /export/home/schiraldi/vnmrsys/data
Sample directory: MC1019_07Sep2004
Pulse Sequence: s2p1

new peaks

new peaks

new peak

new peaks
$\text{19F NMR of MC2 – Fenton’s Aged Sample}$

Salt form (-COO-) of MC2

Doublet of Multiplets
$2J(H,F) = 51\text{Hz}$
Possible Reaction Routes of MC2

Route 1

Route 2

Route 3
Peak a appears to disappear under UV/H$_2$O$_2$ photolysis
Appears not to support Schlick 1
Appears not to support Schlick 2
DuPont’s mechanism supported
Side chain degradation appears to be important as well
Branches potentially destabilizing
Non-perfluorinated membranes are also of potential interest (Litt, McGrath, ...)

- Little known about structure/reactivity/durability
- Anecdotal information that Fenton’s agent destroys these materials at a rate vastly greater than live fuel cell performance losses
- Same analytical problems exist, plus no fluoride handle
- Model compound work, with nmr & LC/MS workup has begun in our lab
This research was supported in part by the Department of Energy, Cooperative Agreement No. DE-FC36-03GO13098. DOE support does not constitute an endorsement by DOE of the views expressed in this article/presentation.