CASE
CASE WESTERN RESERVE UNIVERSITY

Model Compound Studies of Fuel Cell Membrane Degradation

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DOE Briefing

Outline

1. Motivation
2. Literature Review of Fuel Cell Durability
3. Experiments and Methodology
4. Results and Discussions
5. Working Conclusions

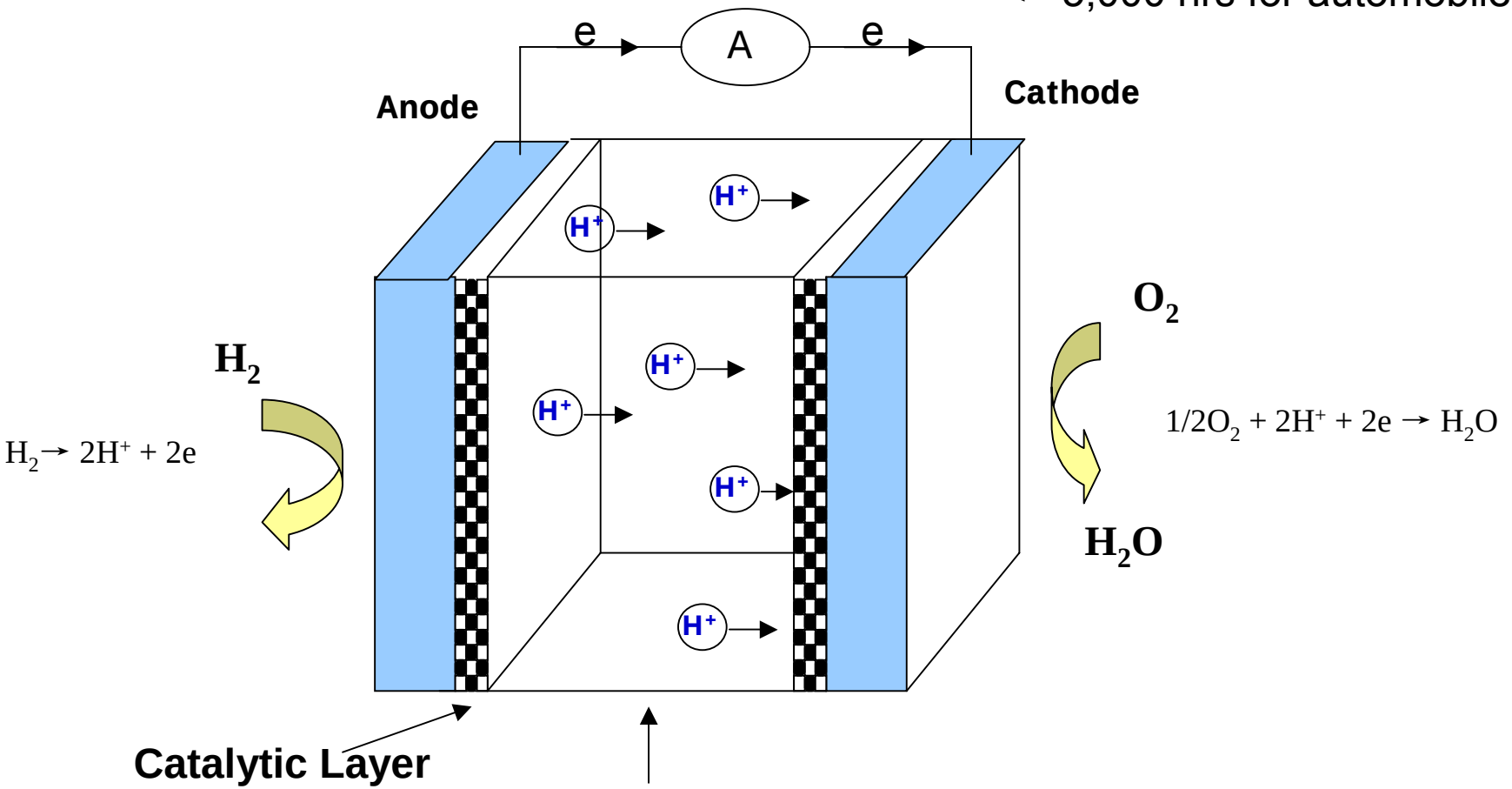
Motivation

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

Typical Life Time Number

- < 20,000 hrs for stationary
- < 5,000 hrs for automobiles



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Prior-Art of Fuel Cell Failure

1. Fuel Cell System

- Poisoning / loss → Failure of catalyst
- Scorching / contamination → Failure of plate

2. Mechanical Failure of Membrane

- Stress created by thermal / hydration cycling
- Failure at contact points in assembly
- Pin-hole formation

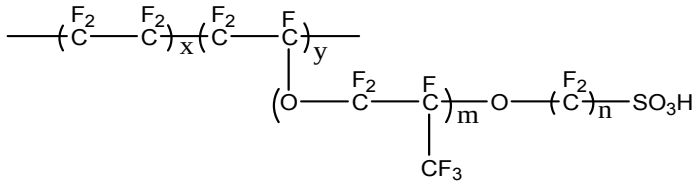
3. Chemical Degradation of Membrane

- Membrane thinning
- Fluoride leaching of perfluorinated membrane
- H_2O_2, $\cdot OH$, and $\cdot OOH$ formation and attack on membrane

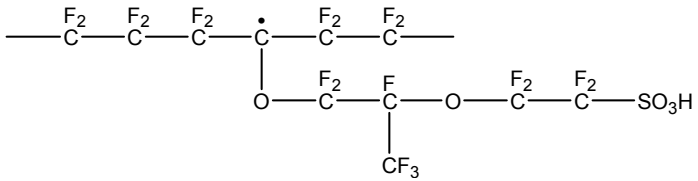
Prior-Art of Membrane Degradation

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

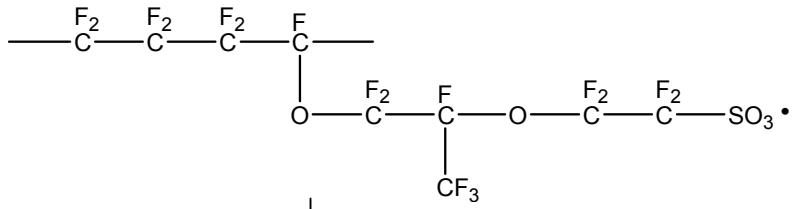
Nafion Ionomer



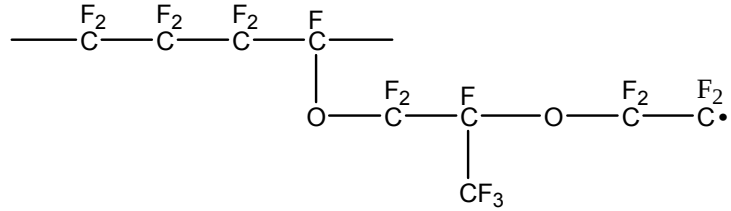
Copper Ion | **H_2O_2**



Fe^{3+} | **H_2O_2**



$-1/2O_2$ | **$-SO_2$**

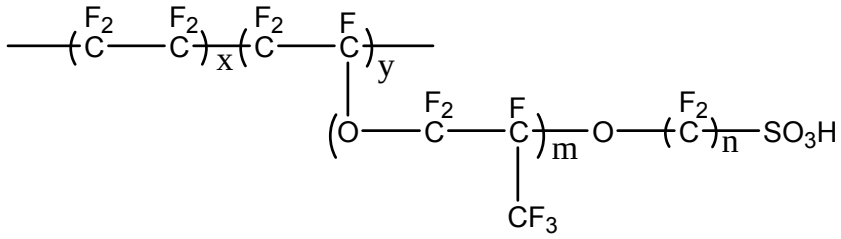


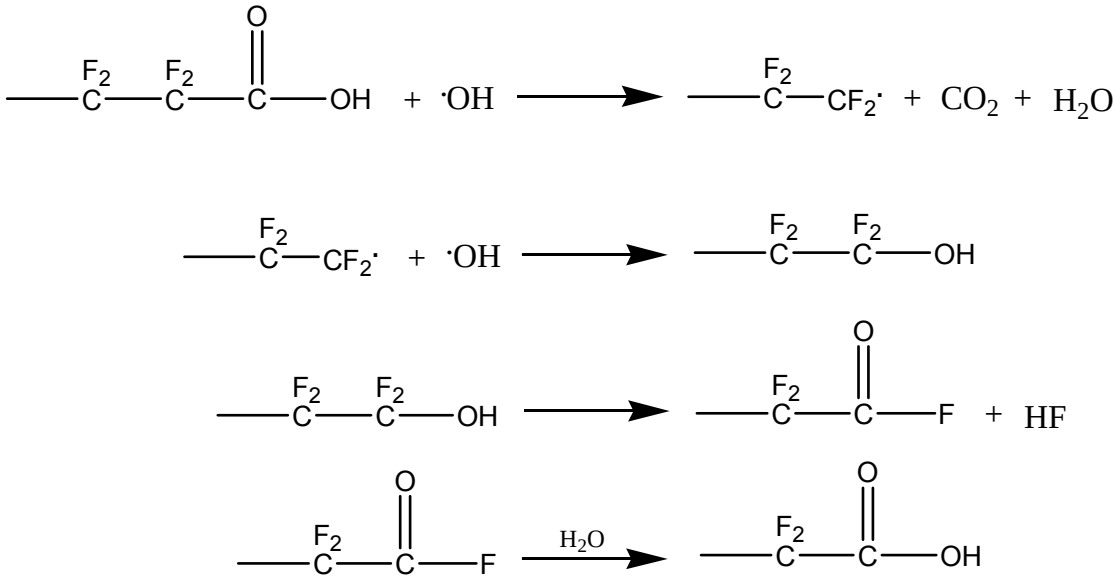
S. Schlick et al., Spring 2005, ACS National Meeting, San Diego CA

Prior-Art of Membrane Degradation

Main Chain Unzipping of Nafion from End Group

Nafion Ionomer





Curtin et al, J. Power Sources, 2004, 131, 41
Pianca et al, J. Fluorine Chem., 1999, 95, 71

Prior-Art of Membrane Degradation

Main Chain Unzipping of Nafion from End Group

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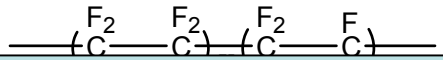
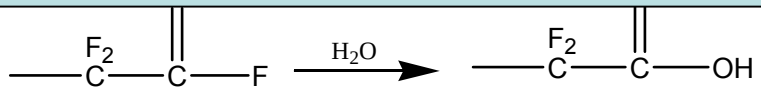


The DuPont-suggested mechanism is supported by their work, which shows that as COOH groups are fluorinated, the level of fluoride generated under lab or operating conditions decreases linearly.

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
Pianca et al, J. Fluorine Chem., 1999, 95, 71

Prior-Art of Membrane Degradation

Controversial Issues of Degradation Studies

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_2O_2: concentration of H_2O_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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Experiments and Methodology

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 ·**OH** radical source

vs.

UV/H_2O_2 photolysis as a metal-free ·**OH** radical source

Experiments and Methodology

Fenton's Reaction

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + {}^{\bullet}OOH$$

Harsh Conditions

- **Fe^{2+}**: 400 mM [in $Fe(SO_4)_2(NH_4)_2{\cdot}6H_2O$]
- **H_2O_2**: 400 mM
- **MC**: 100 mM
- **H_2O**: total volume is 50 ml.

Milder Conditions

- **Fe^{2+}**: 30 ppm = ca 0.54 mM
- **H_2O_2**: 400 mM
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Experiments and Methodology

Fenton's Reaction

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- **MC**: 100 mM
- **H_2O**: total volume is 50 ml.

Our initial reaction conditions

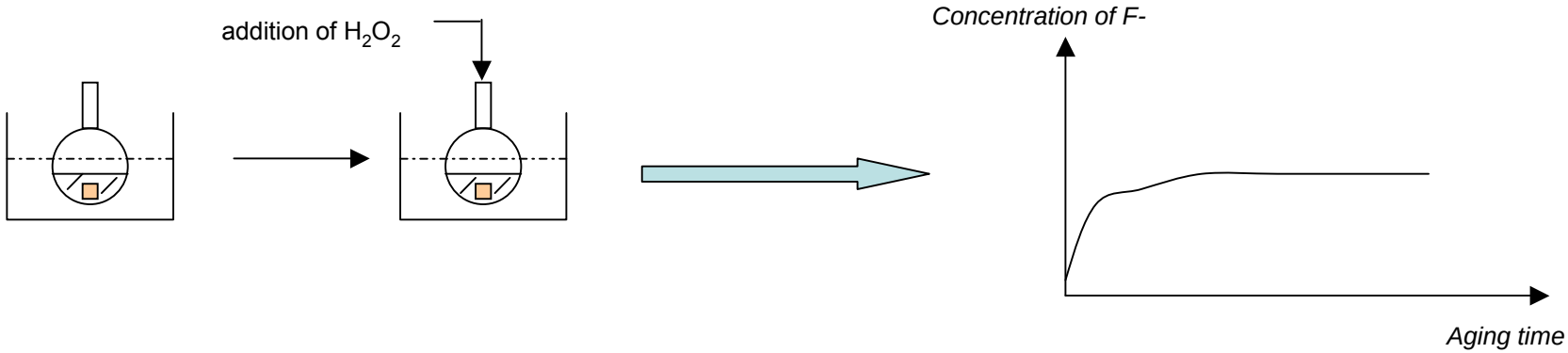
Milder Conditions

- **Fe^{2+}**: 30 ppm = ca 0.54 mM
- **H_2O_2**: 400 mM
- **MC**: 100 mM
- **H_2O**: total volume is 50 ml.

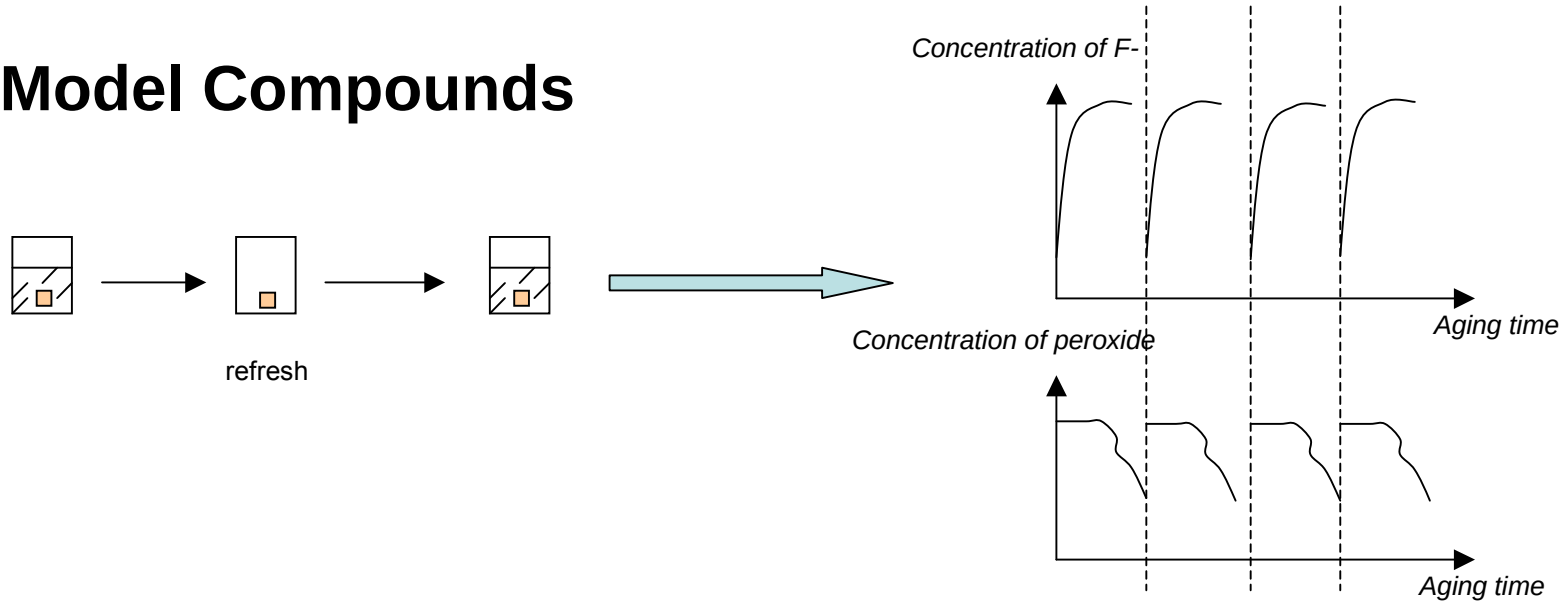
Matches DuPont's Reaction conditions

Aging Experiment Procedure

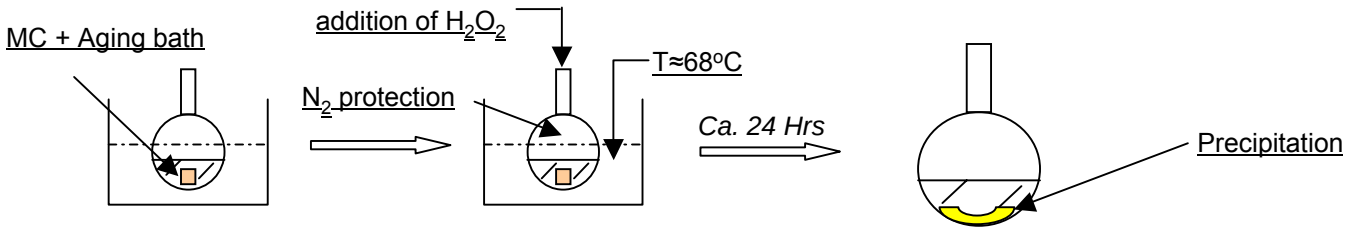
Membrane Film Samples



Model Compounds



Model Compound Separation Scheme



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

Filtration

Oil Phase | Water Phase → *F- Measurement*

Washing by EDTA

Extraction by 1-Butanol

Rotavaporation to take out 1-Butanol

Oil Phase → *F- Measurement check whether F- was carried over*

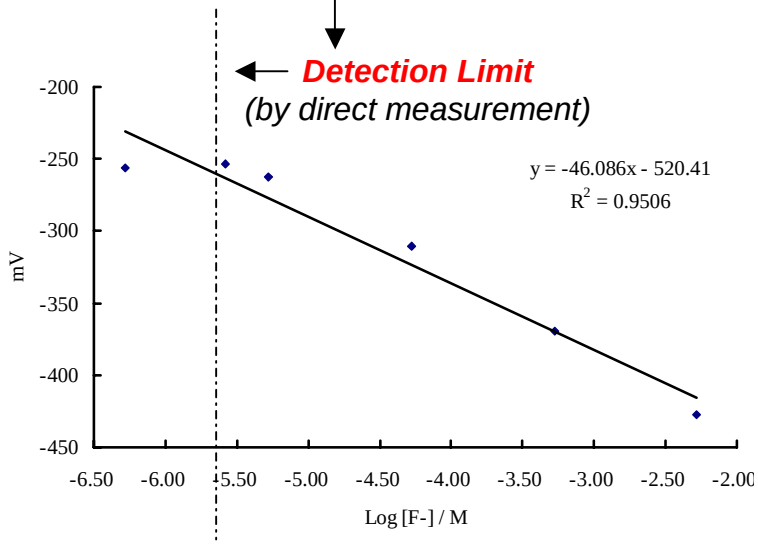
^{19}F NMR

Fluoride Concentration Measurement

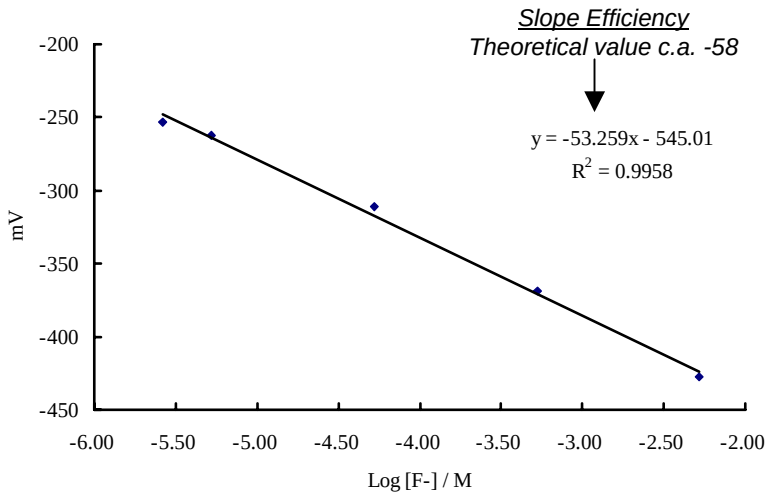
F^- Ion Selective Electrode (ISE)

Concentrations and ISE readings

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

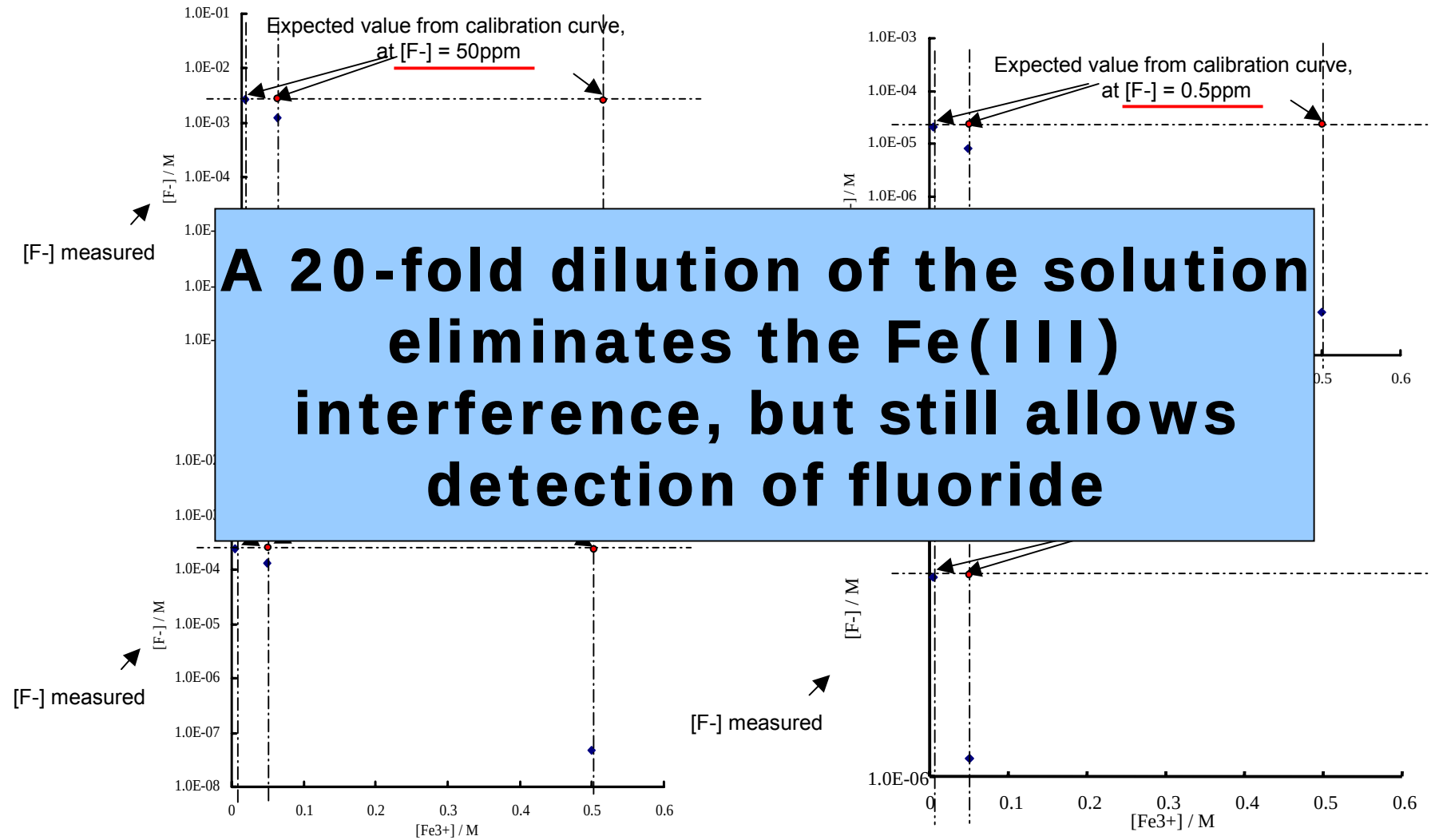


Full Concentration Range



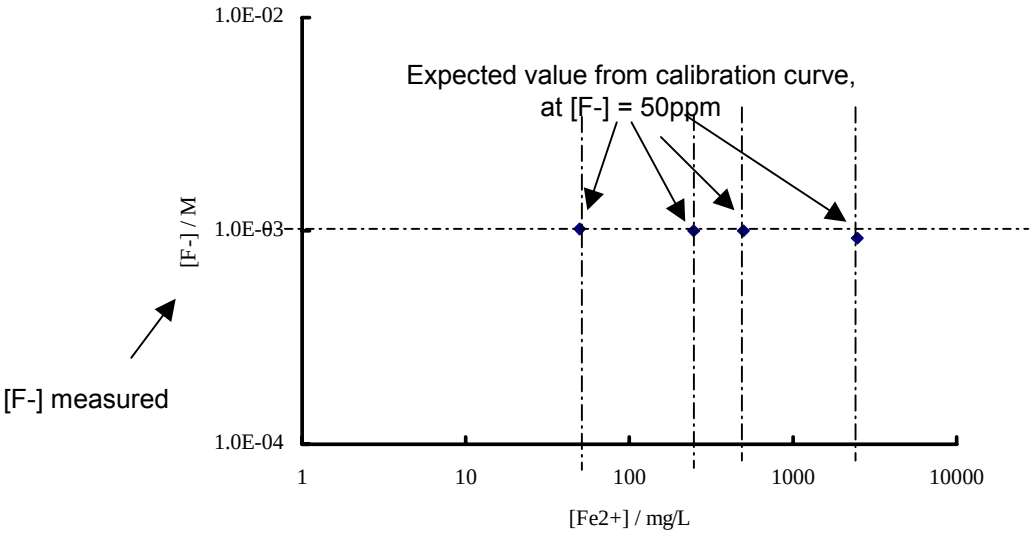
Working Concentration Range

Interference of Fe^{3+} on ISE



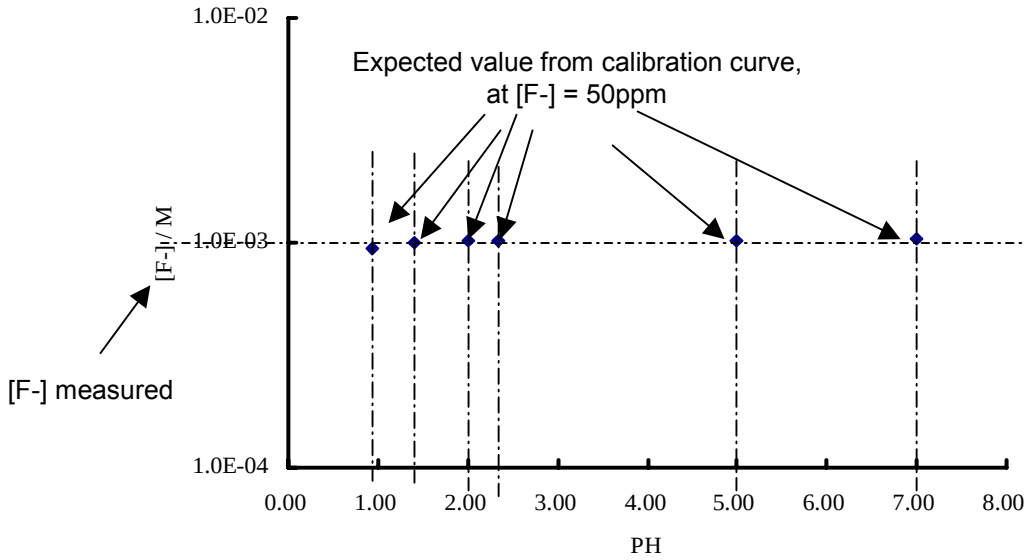
A 20-fold dilution of the solution eliminates the Fe(III) interference, but still allows detection of fluoride

Other Interference Factors?



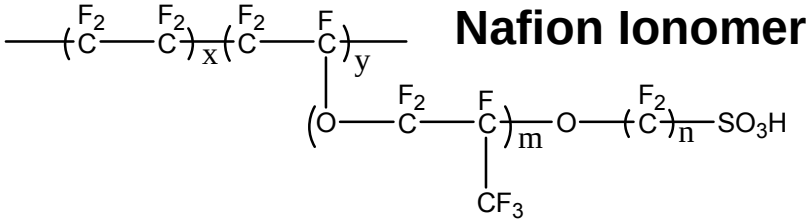
No Interference from Fe(II)

No pH effect

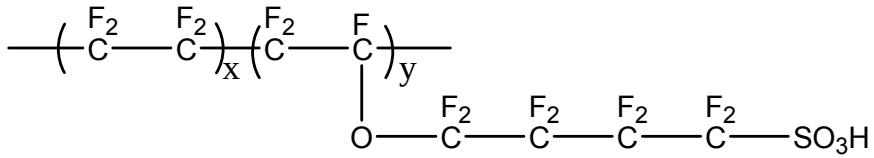


Materials

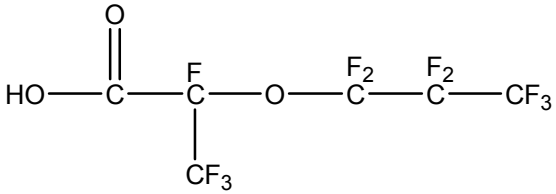
Nafion Ionomer



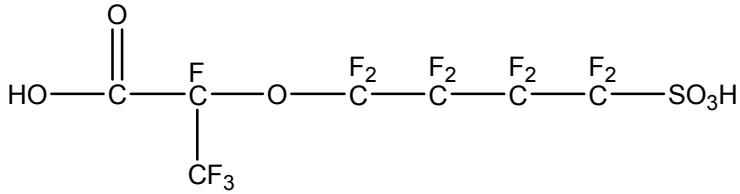
3M Ionomer



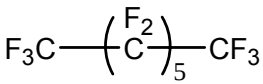
MC1



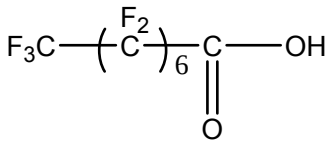
MC2



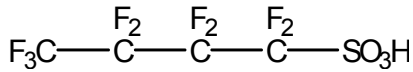
MC3



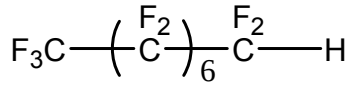
MC4



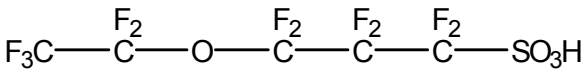
MC5



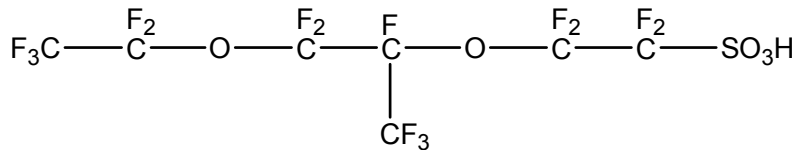
MC6



MC7



MC8



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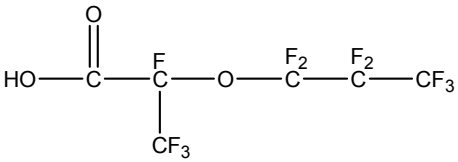
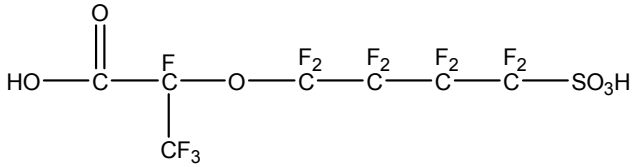
Fluoride Leaching of MCs

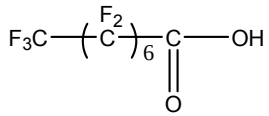
MC1



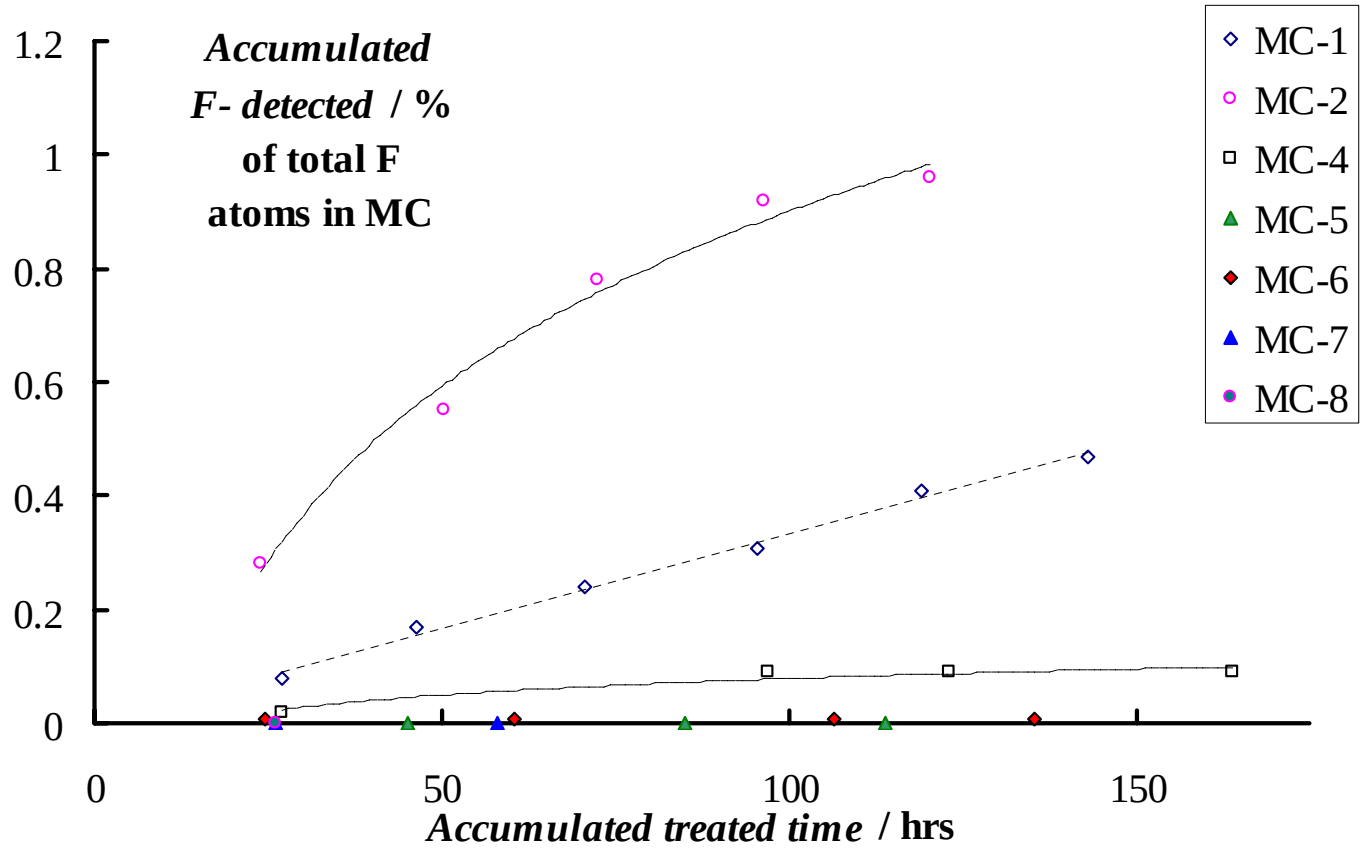
MC2



MC4



Under "harsh" Fenton Conditions



Comparison of MCs and Ionomers

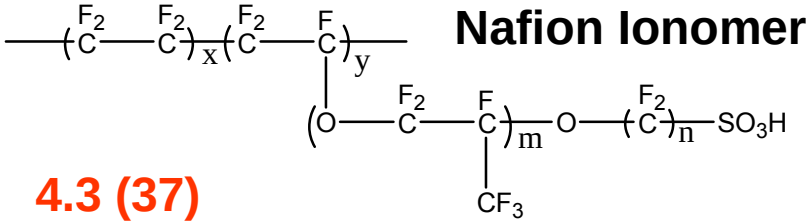
Generated under "Harsh Fenton's Conditions"

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

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

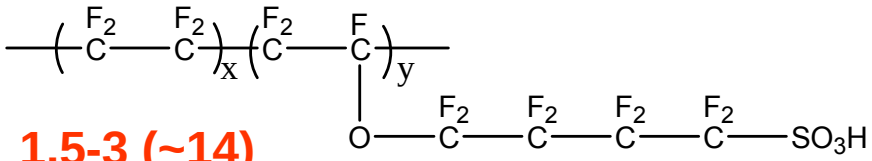
Materials – Relative Decomposition Rates

Nafion Ionomer



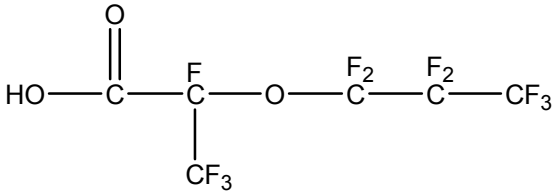
4.3 (37)

3M Ionomer



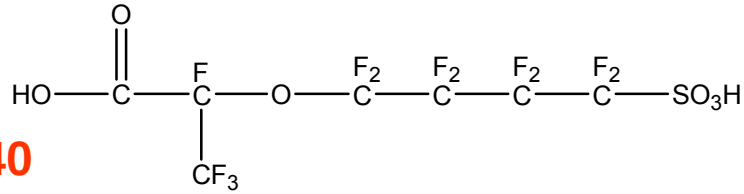
1.5-3 (~14)

MC1



11

MC2



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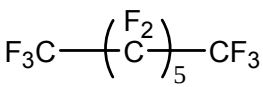
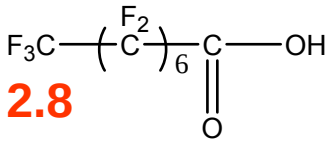
MC3



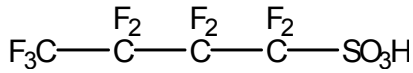
Not tested

MC4



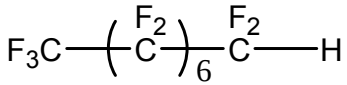
2.8

MC5



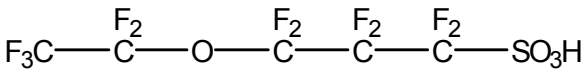
1.1

MC6



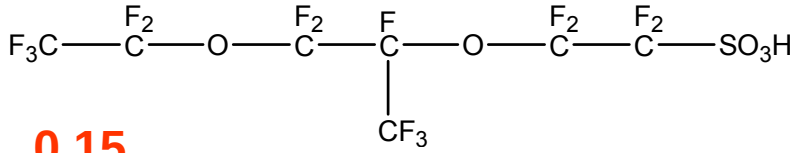
1.0 (defined)

MC7



0.3

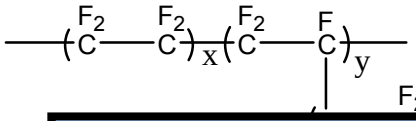
MC8



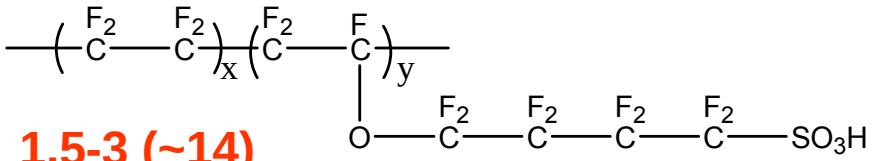
0.15

Materials – Relative Decomposition Rates

Nafion Ionomer



3M Ionomer



1.5-3 (~14)

Comparison of MC5 and MC6

Results argue against literature

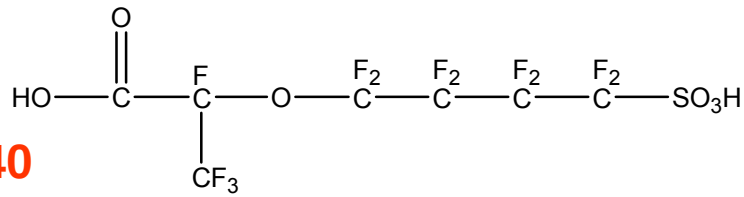
Suggestion of sulfonic acid as

Cite for radical attack in the

Presence of Fe Ions

(Similarly, MC7,8 low values)

MC2



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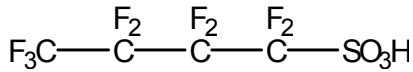
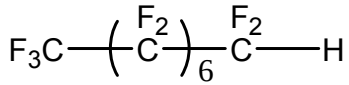
MC5

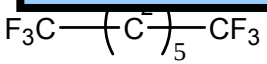


1.1

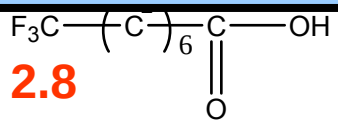
MC6



1.0 (defined)

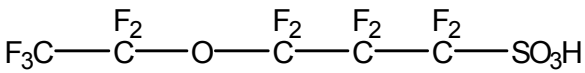


Not tested



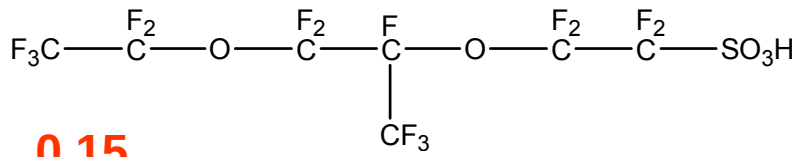
2.8

MC7



0.3

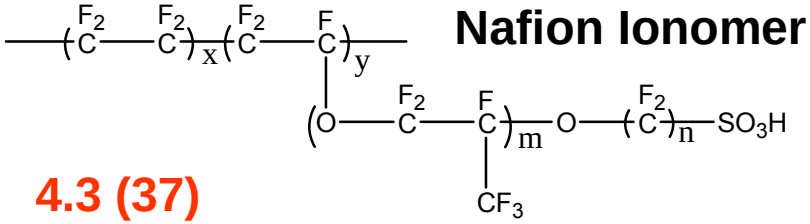
MC8



0.15

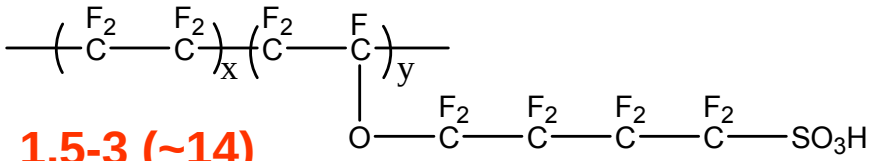
Materials – Relative Decomposition Rates

Nafion Ionomer



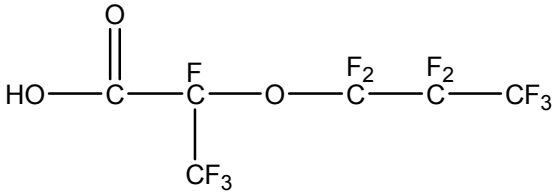
4.3 (37)

3M Ionomer



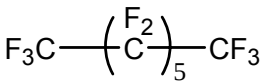
1.5-3 (~14)

MC1



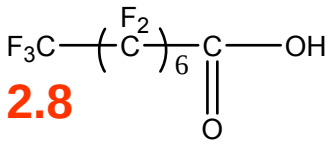
11

MC3



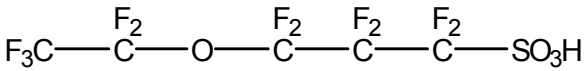
Not tested

MC4



2.8

MC7



0.3

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

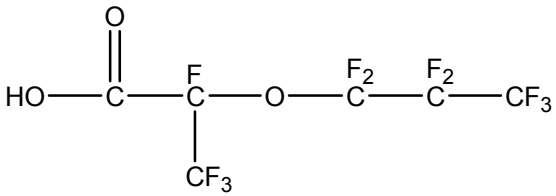
Suggests that the branched side chains
In Nafion are fragile

Materials – Relative Decomposition Rates

Branched perfluoroethers <u>in the presence of carboxylic acids</u> appear to be More fragile than their linear counterparts (MC1, 2 *vs.* MC4,5)

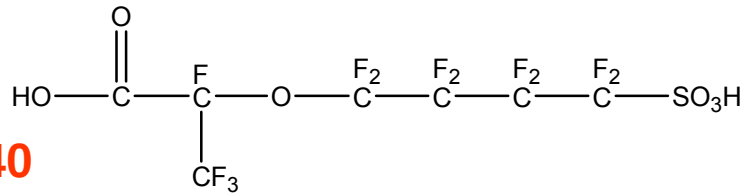
The perfluoroisopropylidene branches alone do not appear to be significant Triggers for decomposition, but appear to work in synergy with carboxylate groups. (MC7,8 *vs.* MC1,2)

MC1



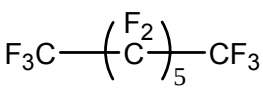
11

MC2



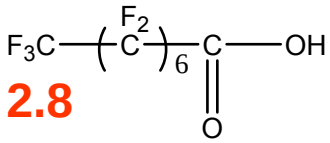
40

MC3



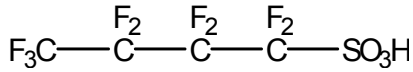
Not tested

MC4



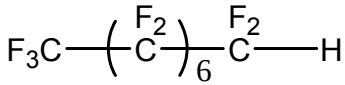
2.8

MC5



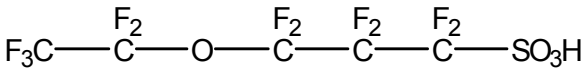
1.1

MC6



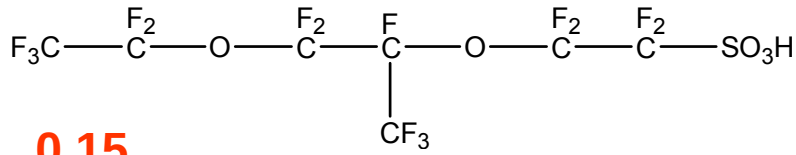
1.0 (defined)

MC7



0.3

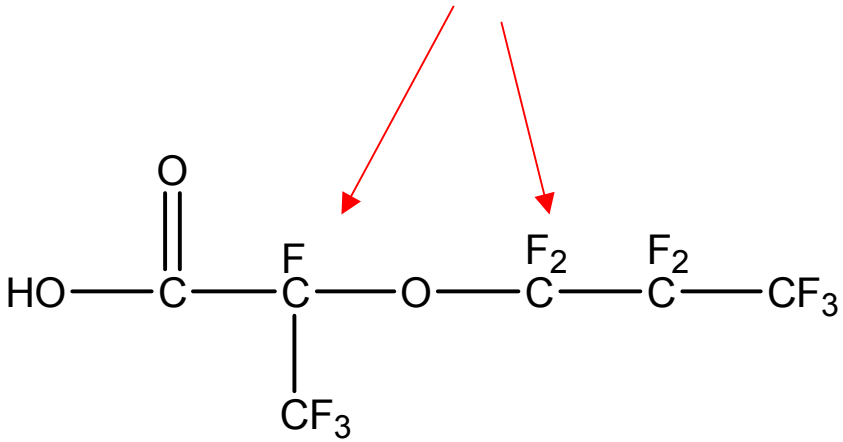
MC8



0.15

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 **

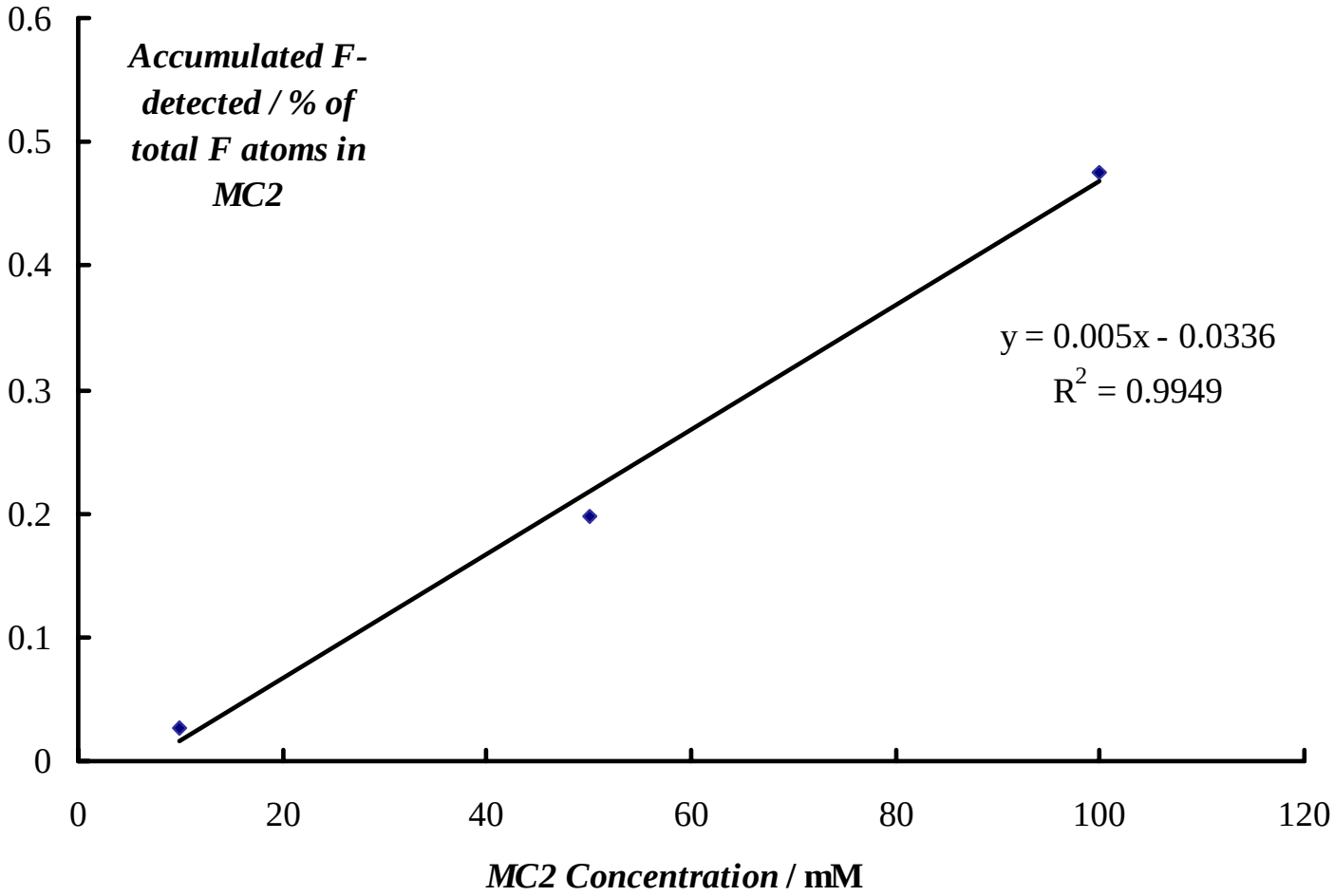


Perhaps true for C-F bonds as well

* R. Atkinson, *Chem Rev*, **1985**, *85*, 69-201
** D. L. Cooper, *Atmos.Env.*, **1992**, *26A*, 1331-4

MC Fluoride Results *vs.* Concentration

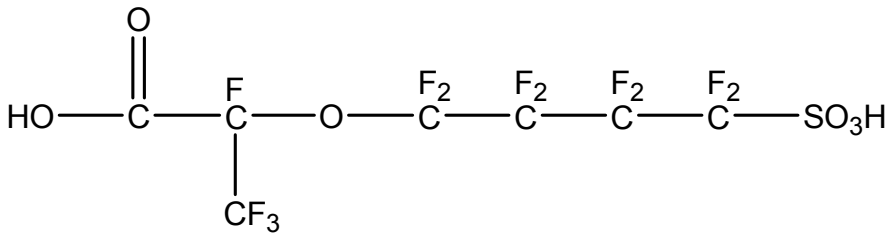
Concentration effects appear to be unimportant*



* Will test lower reactivity MCs as well

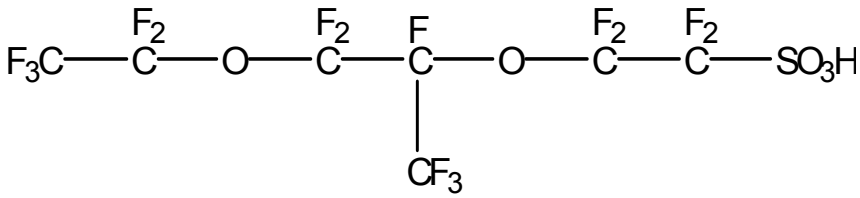
Comparison of MC Degradation w/o Iron

MC2



	MC2-Original Sample	MC2-1HR	MC2-H2O2-1HR
[F] / M	6.09E-04	5.94E-04	3.49E-03
[F] / ppm	< 10 ppm	< 10 ppm	ca 65ppm
% of total F atom	NA	Negligible	0.26

MC8



	MC8-Original Sample	MC8-1HR	MC8-H2O2-1HR
[F] / M	2.37E-05	2.48E-05	1.01E-04
[F] / ppm	ca 0.5 ppm	ca 0.5ppm	ca 2.5 ppm
% of total F atom	NA	Negligible	0.0051

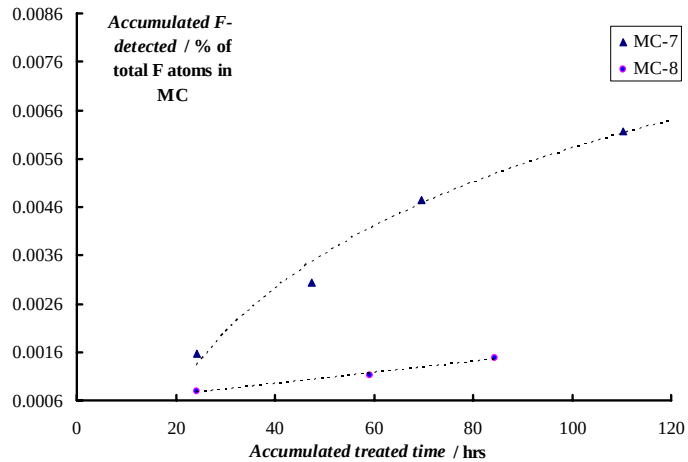
Reactivity Ratios Similar to those with Fenton's Agent

Current Fluorocarbon Degradation Studies

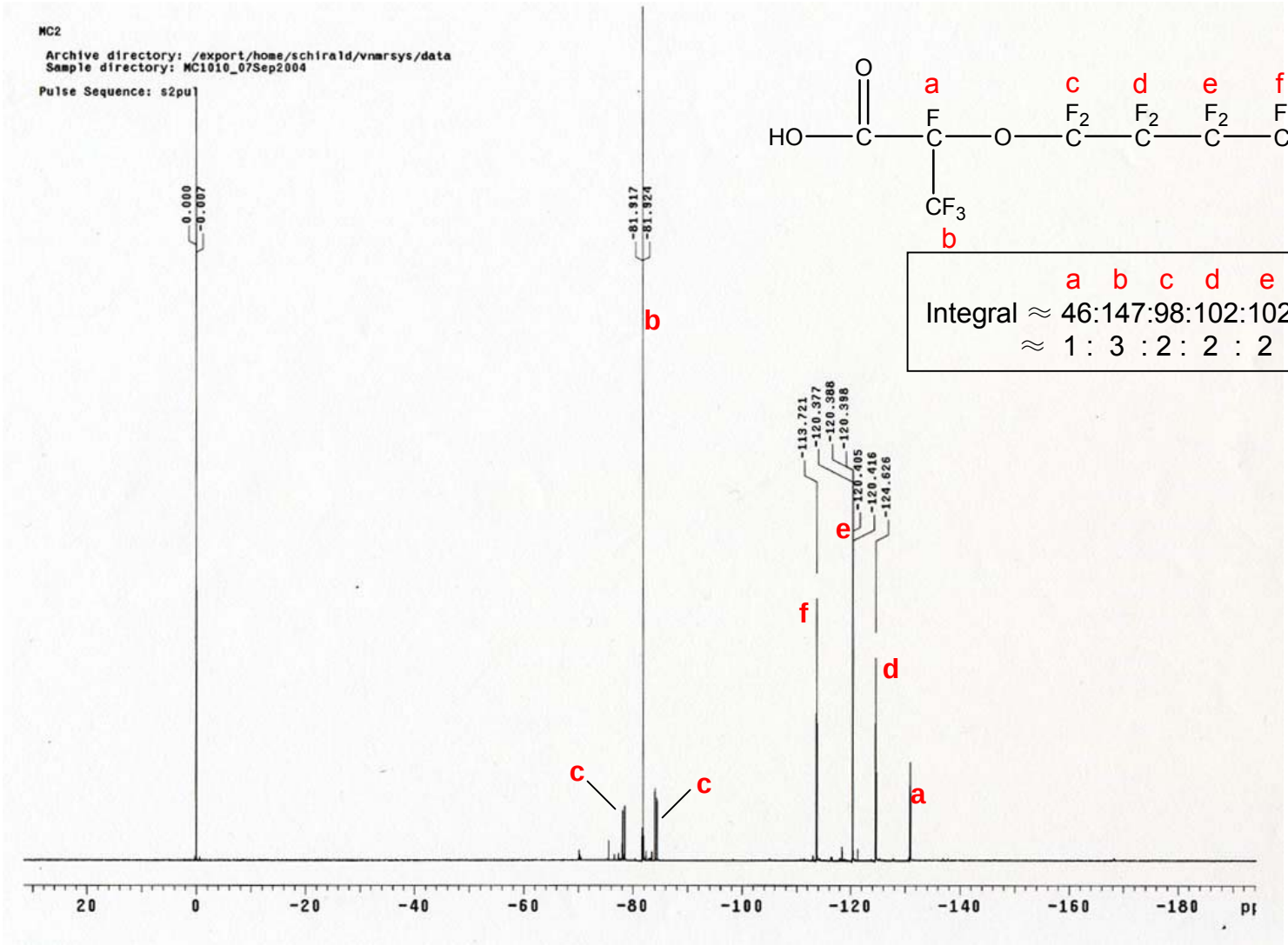
- Replicating MC studies under “Mild Fenton’s conditions”
- Additional solubility studies
- Additional hydrogen peroxide photolysis experiments
- Effect of copper ions?
- TEMPO/ESR Trapping of MC decomposition radicals

- NMR and LC/MS analysis of MC degradation products

MC7,8 behave Similarly under Mild and Harsh Fenton’s conditions

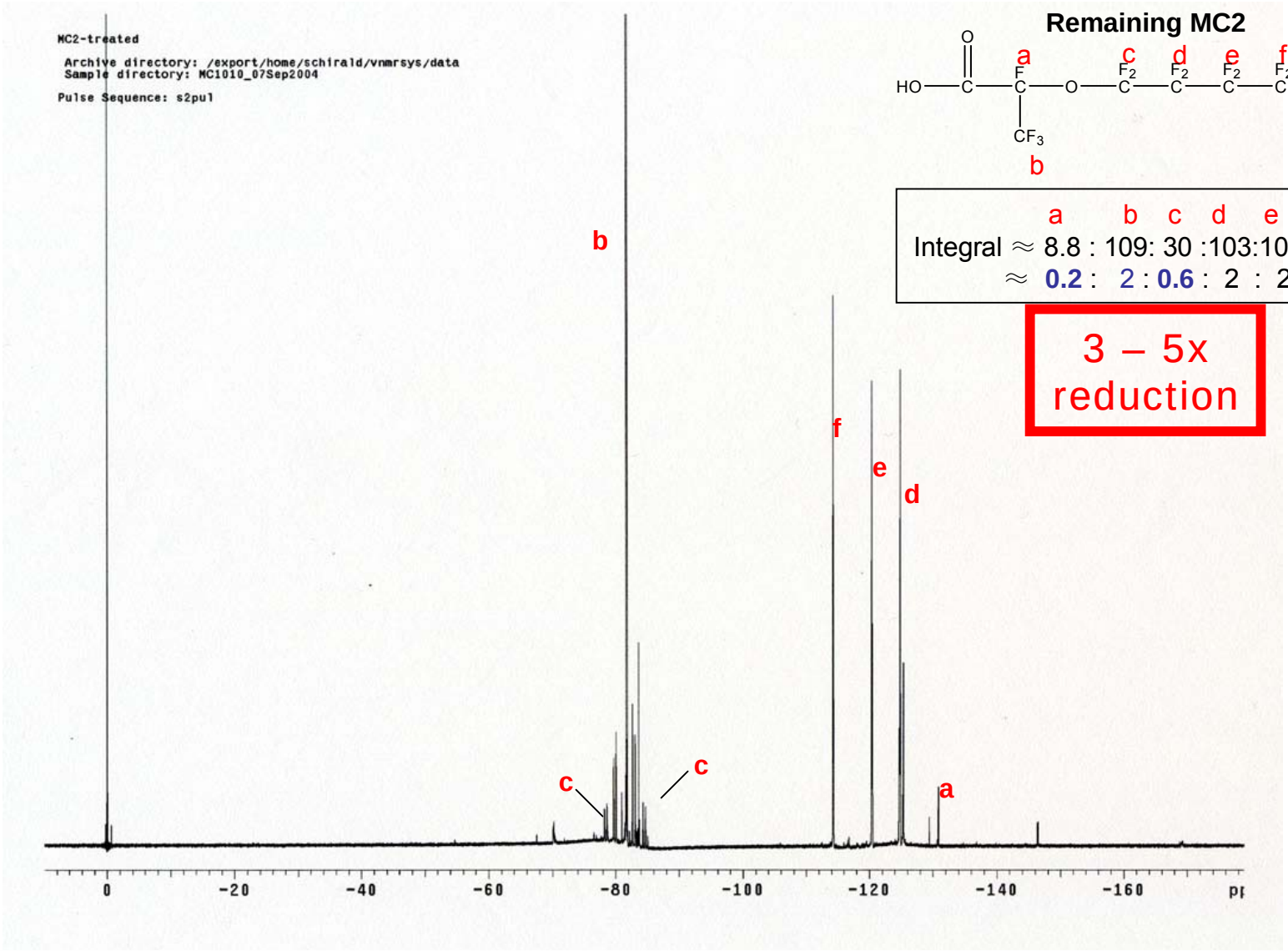


^{19}F NMR of MC2 – Before Degradation



	a	b	c	d	e	f
Integral ≈	46	147	98	102	102	100
≈	1	3	2	2	2	2

^{19}F NMR of MC2 – Fenton's Aged Sample

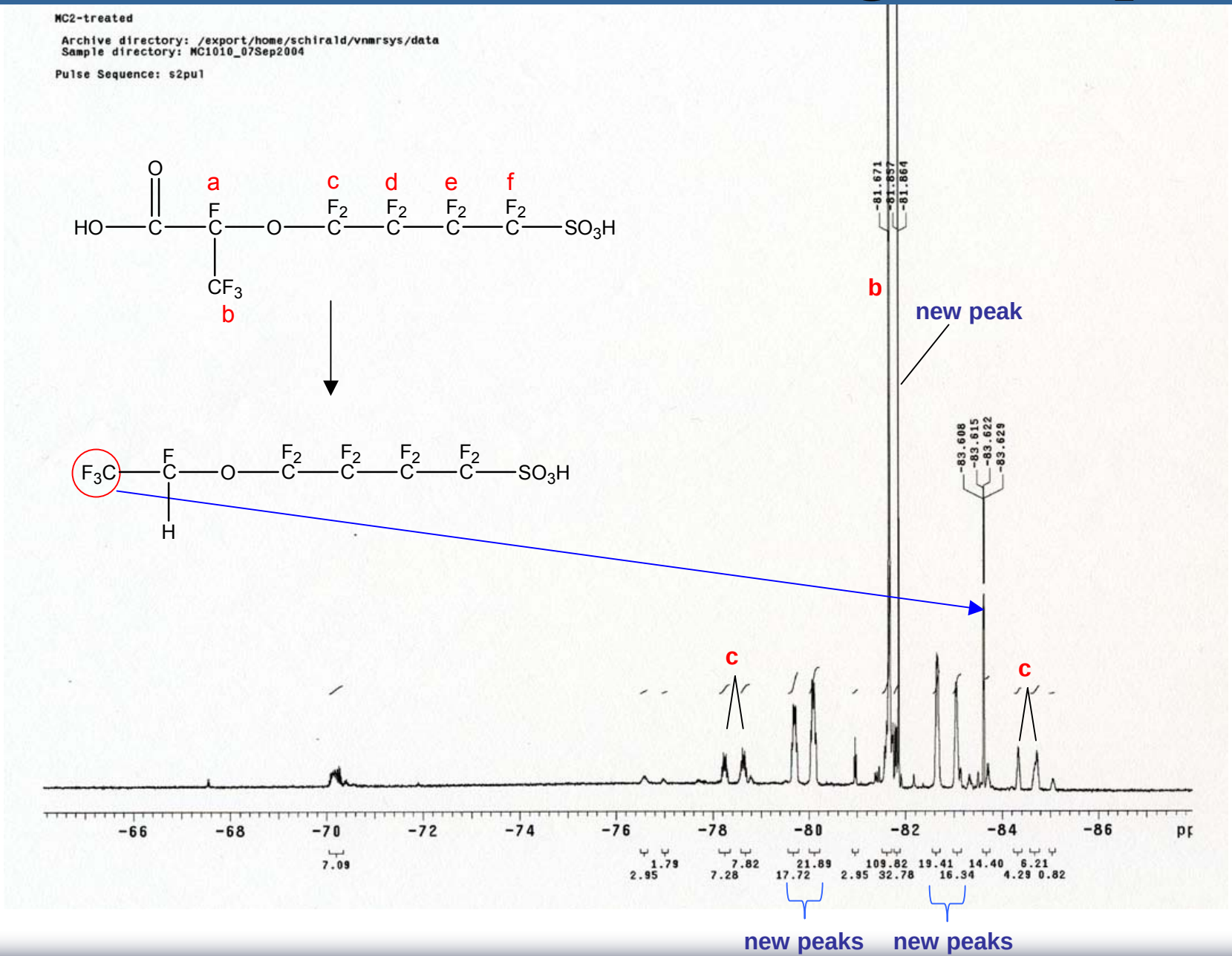


Remaining MC2

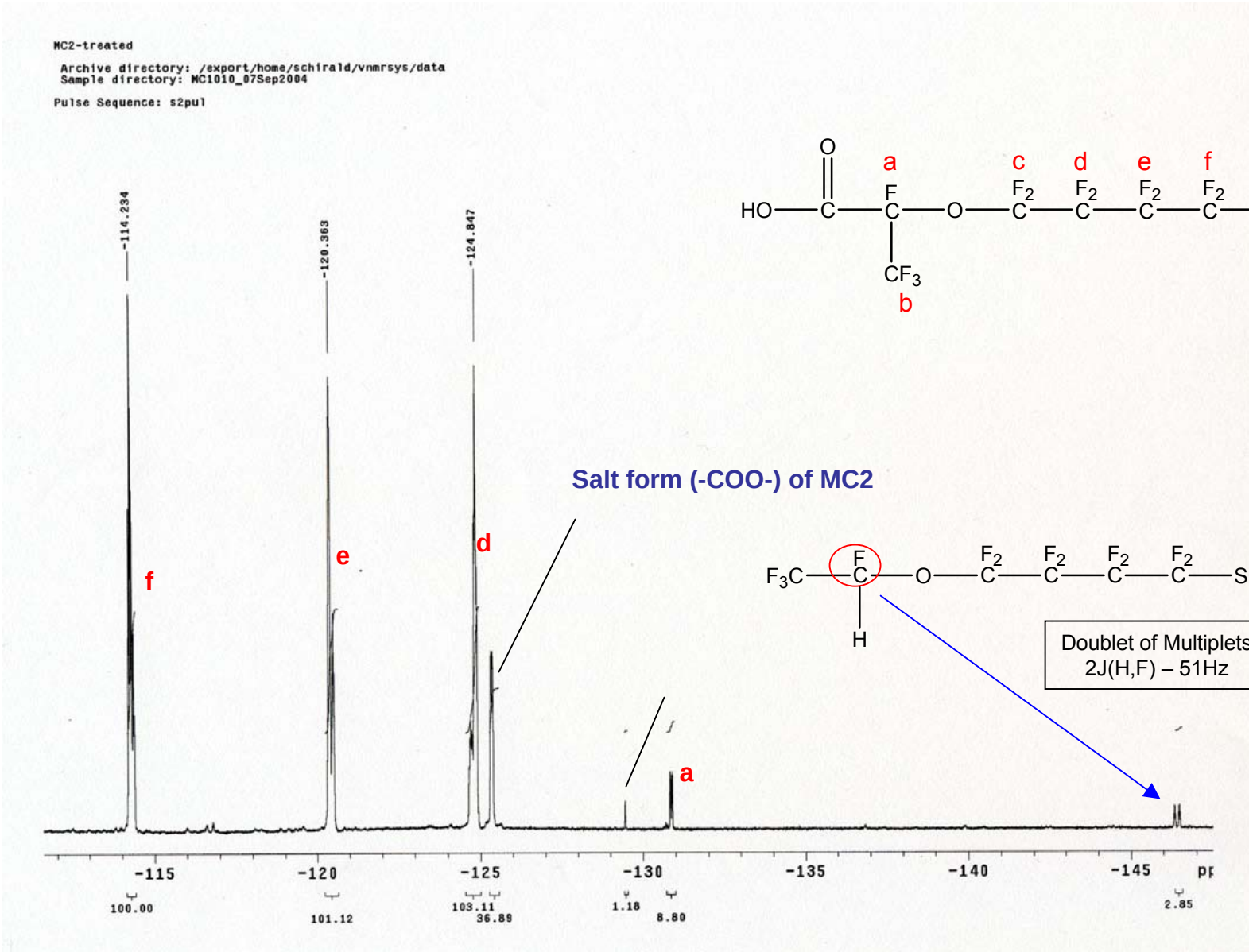
	a	b	c	d	e	f
Integral ≈	8.8 :	109:	30 :	103:	101:	100
≈	**0.2** :	2 :	**0.6** :	2 :	2 :	2

3 – 5x reduction

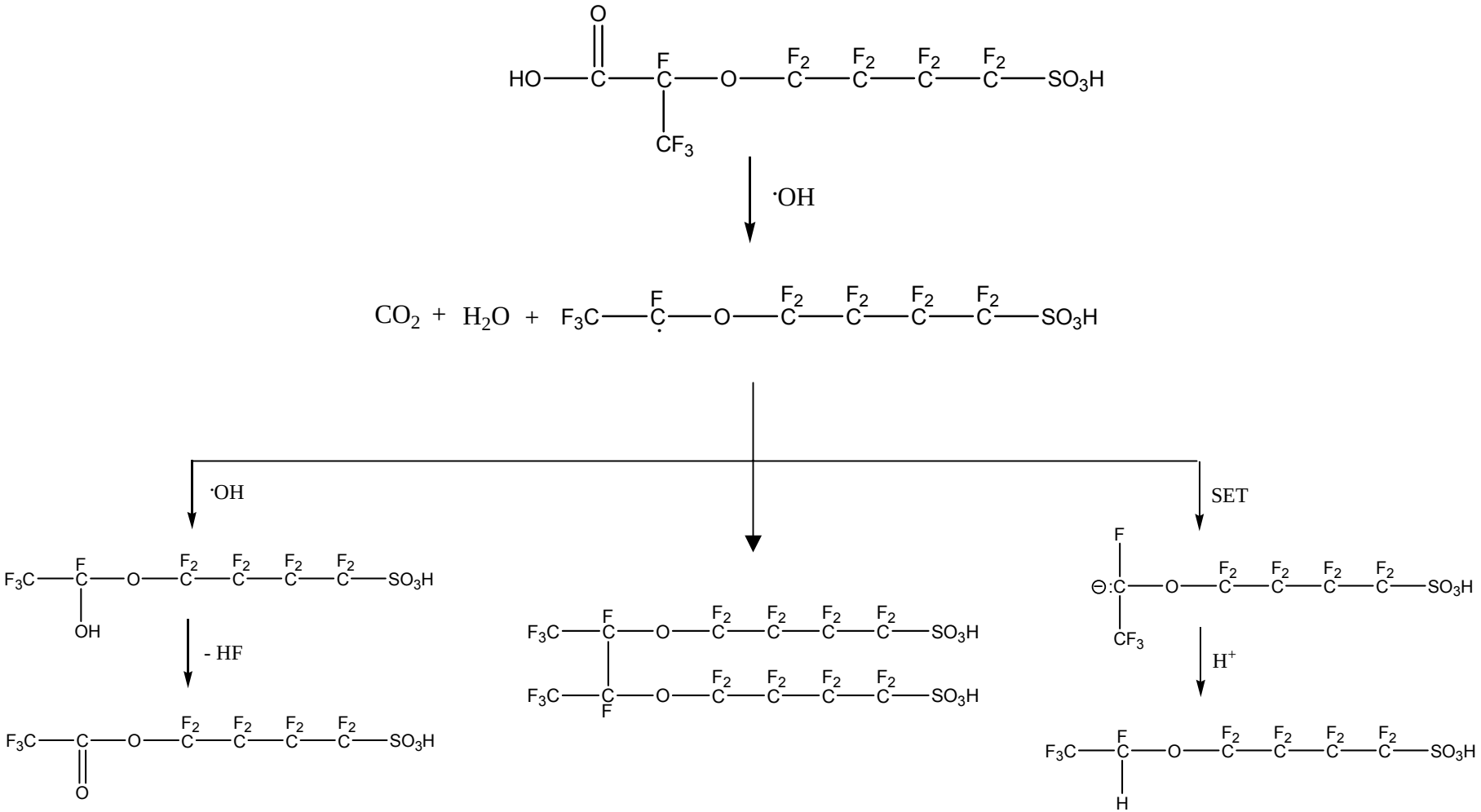
^{19}F NMR of MC2 – Fenton's Aged Sample



^{19}F NMR of MC2 – Fenton's Aged Sample



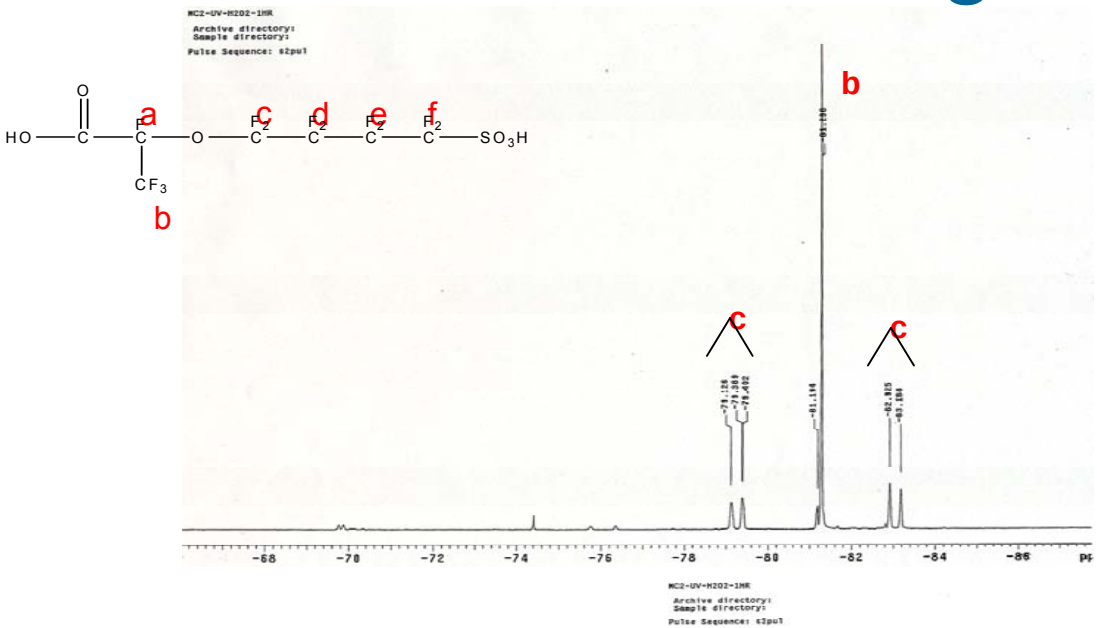
Possible Reaction Routes of MC2

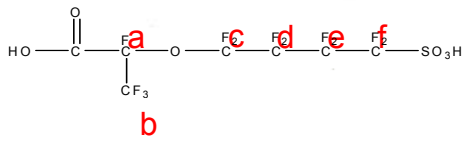


Route 1 **Route 2** **Route 3**

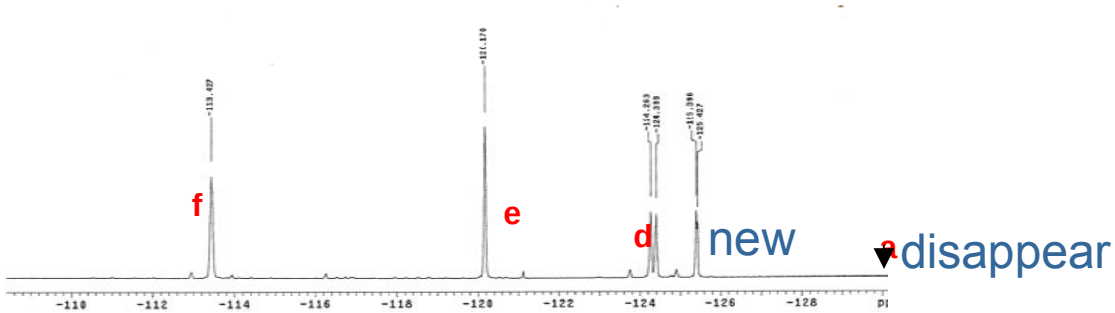
UV/H_2O_2 Photolysis Degradation

^{19}F NMR of Degraded MC2



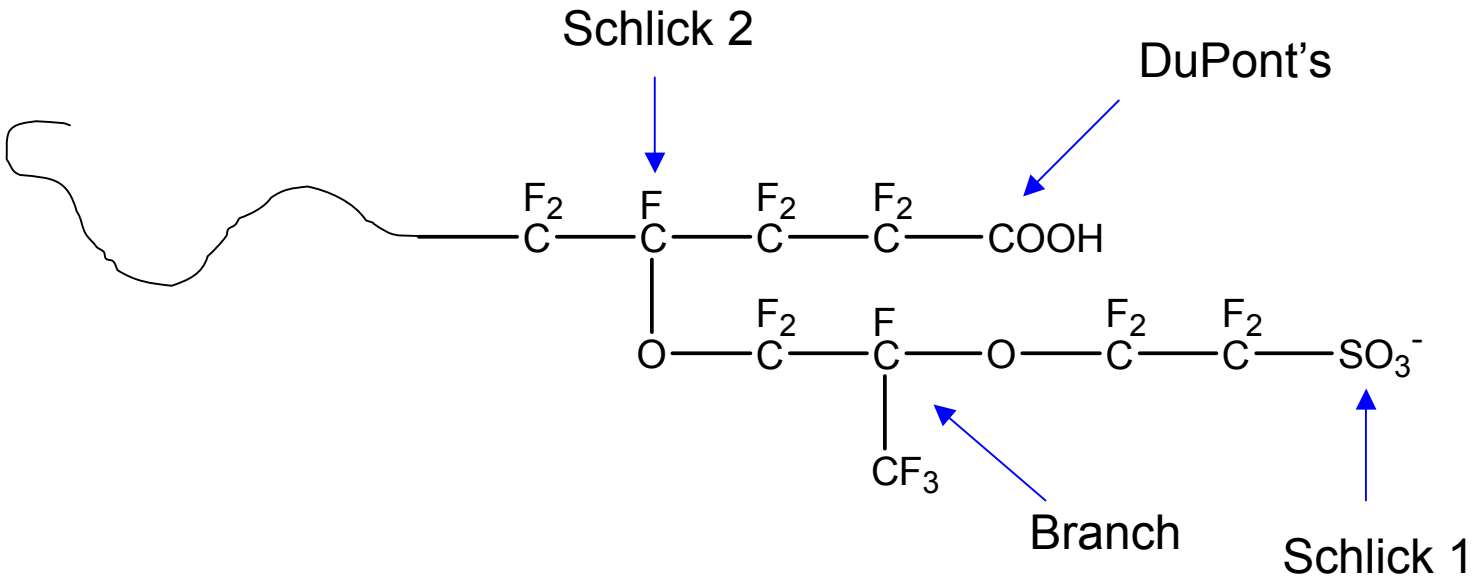


Peak a appears to Disappear under UV/H^2O_2 photolysis



Working Conclusions – May 2005

Results: Comparison With Literature



- ✓ **Appear not to support Schlick 1**
- ✓ **Appear not to support Schlick 2**
- ✓ **DuPont's mechanism supported**
- ✓ **Side chain degradation appears to be important as well**
- ✓ **Branches potentially destabilizing**

What about Other PEM Materials?

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

Acknowledgement

- ✓**Financial Support Provided by DOE (Contract # DE-FC36-03GO13098)**

- ✓**Drs Mike Hicks, Mike Yandrasits, Tom Kestner - 3M**

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