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Synthesis and Alkaline Stability Study of Cationic Perfluoroalkyl Sulfonamide Model Compounds

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SYNTHESIS AND ALKALINE STABILITY STUDY OF CATIONIC PERFLUOROALKYL SULFONAMIDE MODEL COMPOUNDS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemistry

by
Yutung Chen
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Accepted by:
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ABSTRACT

Much interest exists in alkaline exchange membrane (AEM) fuel cells, not just because of the higher efficiency for the oxygen reduction reaction (ORR) under alkaline conditions, but also because of their inexpensiveness due to the possibility of using low-cost materials, such as non-platinum-group catalysts. Due to their high chemical stability and conductivity, tetrafluoroethylene (TFE)/trifluorovinyl ether (TFVE) anion-exchange copolymers having pendant cationic groups attract great attention. In many cases the cationic group, often a quaternary ammonium group, is attached to a fluoropolymer major chain via a sulfonamide linkage. Alkaline stability of these ionomers is critically important for AEM fuel-cell applications.

This research is a stability study of small-molecule cationic perfluoroalkyl sulfonamide model compounds in alkaline conditions. Model compounds are synthesized from $n$-perfluoroalkylsulfonyl fluoride and different amine precursors, followed by reaction with methyl iodide to make quaternary ammonium salts. Alkaline stability tests of the model compounds are then carried out in aqueous KOH solution at evaluated temperatures from 60-90 °C. Samples are heated starting from 60 °C for the first two days, and then the temperature is increased 10 °C every two days until reaching 90 °C. Decomposition products are identified by using high-temperature NMR spectroscopy at 65 °C, because the compounds have low solubility in water at room temperature, but in many cases will be completely dissolved at 65 °C. NMR spectroscopy is useful to detect
the formation or degradation of functional groups. From the $^1$H and $^{19}$F NMR spectra, one can investigate the decomposition mechanism of sulfonamides and the quaternary ammonium group. Two possible decomposition mechanisms exist for the quaternary ammonium group, 1) Hofmann elimination and 2) nucleophilic attack. The NMR spectra suggest that the quaternary ammonium group is the first site of decomposition in strong alkaline conditions. Moreover, the concentration of base shows a larger effect on the degradation of the quaternary ammonium salts than temperature in the tests.
DEDICATION

This document is dedicated to my parents Yah-Wei Chen and Shi-Feng Chuang, who provided endless love and support. Thank you for making me who I am. I am so lucky to have you as my parents. To my brother, Grant Chen, always encouraged me and came to visit to help me through the tough days when I got homesick. I am proud to have you as my sibling. I love my family so much. And to Siyan, who always gave me guidance that helped me through the difficult barriers on the research and accompanied with me during my tough academic years here in the United States.
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TABLE OF CONTENTS

TITILE PAGE.................................................................................................................................................i
ABSTRACT ....................................................................................................................................................... ii
DEDICATION ................................................................................................................................................... iv
ACKNOWLEDGMENTS .......................................................................................................................... v
LIST OF TABLES ........................................................................................................................................ viii
LIST OF FIGURES ....................................................................................................................................... viii
LIST OF SCHEMES .................................................................................................................................... xi

CHAPTER 1
INTRODUCTION ............................................................................................................................................. 1
  1.1 Alkaline Fuel Cells ......................................................................................................................... 1
  1.2 Anion Exchange Membranes (AEM) .......................................................................................... 4
  1.3 Scope of Work ............................................................................................................................... 7
  References ............................................................................................................................................. 12

CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF SMALL-MOLECULE CATIONIC PERFLUOROALKYL SULFONAMIDE MODEL COMPOUNDS ................................................................. 18
  2.1 Introduction .................................................................................................................................... 18
  2.2 Experimental ................................................................................................................................. 22
  2.3 Results and Discussion ................................................................................................................. 27
  References ............................................................................................................................................. 35

CHAPTER 3
ALKALINE STABILITY TEST OF CATIONIC PERFLUOROALKYL SULFONAMIDE MODEL COMPOUNDS .................................................................................................................. 38
  3.1 Introduction .................................................................................................................................... 38
  3.2 Experimental ................................................................................................................................ 43
    3.3.1 First Stability test: .................................................................................................................. 47
    3.3.3 Third stability test: ................................................................................................................... 53
    3.3.4 Zwitterion test: ....................................................................................................................... 58
    3.3.5 Findings of decomposition pathway: .................................................................................... 64
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.6 Conclusion</td>
<td>70</td>
</tr>
<tr>
<td>References</td>
<td>71</td>
</tr>
<tr>
<td>CHAPTER 4</td>
<td></td>
</tr>
<tr>
<td>CONCLUSIONS AND FUTURE WORKS</td>
<td>74</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>76</td>
</tr>
<tr>
<td>Appendix A</td>
<td></td>
</tr>
<tr>
<td>Synthesis of perfluoro-n-butyl sulfonamides &amp; quaternary ammonium salts</td>
<td>77</td>
</tr>
<tr>
<td>Appendix B</td>
<td></td>
</tr>
<tr>
<td>Stability study of perfluoro-n-butyl sulfonamide quaternary ammonium salts</td>
<td>91</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Synthesis of perfluoro-\textit{n}-butanesulfonamides from perfluoro-\textit{n}-butanesulfonyl fluoride</td>
</tr>
<tr>
<td>3.1</td>
<td>Stability of salt 2 in different molarities of aqueous KOH according to different temperatures</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Basic operation of (a) proton exchange membrane fuel cell (PEMFC) and (b) alkaline exchange membrane fuel cell (AEMFC).</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Synthesized perfluorobutylsulfonamide small-molecule model compounds.</td>
<td>21</td>
</tr>
<tr>
<td>2.2</td>
<td>Comparison of $^1$H NMR spectra of <strong>compound 3</strong> in CDCl$_3$ and <strong>Salt 2</strong> in D$_2$O at 65 °C. The position of the peak for the hydrogen adjacent to quaternary group moves downfield compared to the hydrogen atom on tertiary amine on the $^1$H NMR spectrum.</td>
<td>32</td>
</tr>
<tr>
<td>2.3</td>
<td>Bubble generated from filtration of the quaternary ammonium salt.</td>
<td>33</td>
</tr>
<tr>
<td>2.4</td>
<td>Photo of (a) <strong>Salt 1</strong> and (b) <strong>Salt 2</strong>.</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>The protons on the merge from two peaks to one peak with heating at 65°C (1) <strong>Salt 2</strong> at room temperature (2) <strong>Salt 2</strong> at 65 °C.</td>
<td>50</td>
</tr>
<tr>
<td>3.2</td>
<td>(Left) <strong>Salt 1</strong> and (Right) salt 2 in plastic vial.</td>
<td>51</td>
</tr>
<tr>
<td>3.3</td>
<td>Experiments 1-6 (from left to right) at (a) RT and (b) after 2 days heating at 90 °C.</td>
<td>53</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>$^1$H and $^{19}$F NMR spectra of alkaline stability test of <strong>Salt 2</strong> in H$_2$O at (1) RT (2) 60 °C, and (3) 80 °C .........................................................54</td>
</tr>
<tr>
<td>3.5</td>
<td>$^1$H and $^{19}$F NMR spectra of alkaline stability test of <strong>Salt 2</strong> in 1 M KOH at (1) RT (2) 60 °C, and (3) 80 °C .........................................................54</td>
</tr>
<tr>
<td>3.6</td>
<td>$^1$H and $^{19}$F NMR spectra of alkaline stability test of <strong>Salt 2</strong> in 2 M KOH at (1) RT (2) 60 °C, and (3) 80 °C .........................................................55</td>
</tr>
<tr>
<td>3.7</td>
<td>$^1$H and $^{19}$F NMR spectra of alkaline stability test of <strong>Salt 2</strong> in 4 M KOH at (1) RT (2) 60 °C, and (3) 80 °C .........................................................55</td>
</tr>
<tr>
<td>3.8</td>
<td>$^1$H and $^{19}$F NMR spectra of alkaline stability test of <strong>Salt 2</strong> in 4 M KOH at (1) RT (2) 60 °C, and (3) 80 °C .........................................................56</td>
</tr>
<tr>
<td>3.9</td>
<td>$^1$H NMR spectrum of <strong>Salt 2</strong> in a neutral solution (1) H$_2$O, then (2) 2 M KOH was added, and finally HCl is added, and (3) neutralized ...............60</td>
</tr>
<tr>
<td>3.10</td>
<td>$^{19}$F NMR spectrum of <strong>Salt 1</strong> in neutral solution (1) H$_2$O, then (2) 2 M KOH was added, and finally HCl is added, and (3) neutralized ...............61</td>
</tr>
<tr>
<td>3.11</td>
<td>$^1$H NMR spectrum of <strong>Salt 2</strong> in (1) H$_2$O, (2) 2 M KOH, and (3) neutralized .................................................................62</td>
</tr>
<tr>
<td>3.12</td>
<td>$^{19}$F NMR spectrum of <strong>Salt 2</strong> in (1) H$_2$O, (2) 2 M KOH, and (3) neutralized .................................................................63</td>
</tr>
<tr>
<td>3.13</td>
<td>$^1$H NMR spectrum of (1) decomposed $n$-C$_4$F$_9$SO$_2$N(CH$_3$)CH$_2$CH$_2$CH$_2$N(CH$_3$)$_3$ (+I(-) +(-))</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>3.14</td>
<td>$^1$H NMR spectrum of decomposed $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$N(CH$_3$)$_3$ (I$^+$) extracted by CDCl$_3$</td>
</tr>
<tr>
<td>3.15</td>
<td>Comparison of $^1$H NMR spectrum of (1) <strong>Salt 2</strong> in CDCl$_3$ and (2) decomposed <strong>Salt 2</strong> extracted by CDCl$_3$</td>
</tr>
<tr>
<td>3.16</td>
<td>$^1$H NMR spectrum of decomposed C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$N(CH$_3$)$_3$ (I$^+$) extracted by CDCl$_3$</td>
</tr>
</tbody>
</table>
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Structure of (A) polysulfone anion exchange membrane and (B) Tosflex</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Perfluorosulfonyl polymer synthesized by Pivovar and Herring</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Comparison of (A) Tosflex and (B) perfluoroalkyl sulfonamide small-molecule model compound (Salt 2)</td>
<td>8</td>
</tr>
<tr>
<td>1.4 ETFE-g-PVBtMA membrane synthesized by Herring</td>
<td>9</td>
</tr>
<tr>
<td>1.5 Degradation mechanisms of quaternary ammonium cation by hydroxide anions</td>
<td>10</td>
</tr>
<tr>
<td>2.1 Typical cationic groups used in AFCs</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Synthetic route of N-(allyl)trifluoromethanesulfonamide</td>
<td>20</td>
</tr>
<tr>
<td>2.3 Synthesis of mono and dialkylated perfluoroalkyl sulfonamides</td>
<td>21</td>
</tr>
<tr>
<td>2.4 DIPEA used as selective reagent in the alkylation of secondary amines to make tertiary amines</td>
<td>28</td>
</tr>
</tbody>
</table>
List of Schemes (Continued)

2.5 Hydrolysis due to perfluorobutanesulfonyl fluoride react with water ........ 29
2.6 Synthetic path of \( \text{C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)(CH}_2\text{)}_3\text{N(CH}_3\text{)}_2 \) .................. 29
2.7 Synthetic route of 3 different perfluorobutanesulfonamide .................. 30
2.8 Synthetic route of \( n-\text{C}_4\text{F}_9\text{SO}_2\text{NH(CH}_2\text{)}_3\text{N}^+\text{(CH}_3\text{)}_3\text{I}^- \) (Salt 1) and \( n-\text{C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)(CH}_2\text{)}_3\text{N}^+\text{(CH}_3\text{)}_3\text{I}^- \) (Salt 2) ............ 31
3.1 Propylene (FEP) graft \( N,N,N\)-trimethyl-benzenemethanaminium hydroxide membrane .......................................................... 39
3.2 Ag\(_2\)O-mediated ion exchange reaction, \( X = \text{Br or I} \) ......................... 40
3.3 Schematic of possible degradation positions of (1) the sulfonamide bond (2) the amide bond, and (3) cationic group .............................................................. 41
3.4 Presumption of bond cleavage of (1) Salt 1 and (2) Salt 2 under KOH attack ............................................................. 42
3.5 The nitrogen chiral center of Salt 2 .......................................................... 49
3.6 Zwitterion formation of Salt 1 ............................................................ 58
3.7 Degradation of quaternary ammonium group through nucleophilic substitution and Hofmann elimination ...................... 64
4.1 Structure of 3,3’-iminobis- \( (N,N\text{-dimethylpropylamine}) \) ............... 74
CHAPTER 1

INTRODUCTION

1.1 Alkaline Fuel Cells

The demand for clean non-fossil energy sources is rising because of an anticipated global shortage of fossil fuels and the raising of environmental awareness. An increasing concern about global pollution exists and a desire to find less polluting sources.¹ A fuel cell is a kind of energy conversion device that converts a fuel (e.g. hydrogen) and an oxidant (e.g. oxygen) into electrical energy and generates water as a harmless by-product.² In general, in acid conditions, hydrogen molecules enter a fuel cell at the anode and are then oxidized to hydrogen ion (H⁺). The generated electrons provide the current through an external circuit. Oxygen is reduced at the cathode and combines with electrons transported from the electrical circuit and the hydrogen ions that have traveled through the electrolyte from the anode to produce water. The electrolyte is an important part of a fuel cell; it should only allow appropriate ions to pass through or the chemical reaction may be disrupted.³
Five fuel cell types exist that may be distinguished by different kinds of electrolyte: alkaline fuel cells (AFCs), proton exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PACFs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). The AFC is different from other types of fuel cells because the reactions occur in strong base. By using aqueous KOH as a liquid electrolyte in the case of hydrogen as fuel at the anode, hydrogen is oxidized as follows (Figure 1.1):

\[
2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} + 4 \text{e}^- \quad (1.1)
\]

At the cathode, when the electrons pass around an external circuit, oxygen is reduced:

\[
\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad (1.2)
\]

The overall reaction is as follows:

\[
2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \quad (1.3)
\]

The AFC was invented by Francis Bacon by using carbon as electrodes and aqueous potassium hydroxide (KOH) as the electrolyte. The AFC was the first to be applied in practical use among these types of fuel cells. In the 1960s, alkaline fuel cells were used in the U.S. space program, including the famous NASA Apollo space program. Interest in
AFCs has expanded due to the triumph of the space program, and they also have been used in electric cars, drive fork lift trucks, and agricultural tractors.\textsuperscript{7-11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Basic operation of (a) proton exchange membrane fuel cell (PEMFC) and (b) alkaline exchange membrane fuel cell (AEMFC).}
\end{figure}

An AFC offers significant advantages over other types of fuel cell such as the following: (1) the efficiency of the electrochemical oxygen reduction reaction (ORR) is high under alkaline conditions; (2) the cost of alkaline ORR catalysts is low due to the possibility of using non-platinum metal\textsuperscript{12-13} and metal-free catalysts,\textsuperscript{14} and (3) the AFC is relatively easy to operate due to its low operating temperature (60-90 °C).\textsuperscript{9} However, using aqueous KOH as a electrolyte results in leakage problems, and carbon dioxide (CO\textsubscript{2}) in the air reacts with hydroxide ions (OH\textsuperscript{-}) to form solid potassium carbonate crystals (K\textsubscript{2}CO\textsubscript{3}) on the electrodes that decrease the efficiency of the cells.\textsuperscript{5} Therefore, researchers started to focus on using a solid polymeric alkaline exchange membrane
(AEM) that does not contain metal potassium as the hydroxide transport medium in an alkaline fuel cell to solve the problem. The polymeric AEM separates the anode and cathode and transmits OH\(^{-}\) ions between them and also minimizes the undesired effect of CO\(_2\).\textsuperscript{5,9,15}

1.2 Anion Exchange Membranes (AEM)

Anion exchange membranes have been used in water treatment applications such as seawater separation, bio-separation, and electrodialysis for decades.\textsuperscript{16-17} In recent years AEMs have been used in AFCs to overcome the problems of liquid electrolyte in AFCs. An AEM should meet the durability, harsh performance, and cost efficiency requirements needed for use in an AFC.\textsuperscript{18} The membrane performs two roles: it provides a barrier for gases and electrons and it provides a conduit for ion movement between the electrodes.\textsuperscript{5} Many different AEM types of AEMs have been synthesized that are in accord with the requirements listed above and some representative structures are shown in Scheme 1.1.

The vital challenge to preparing AEMs is the need for high hydroxide conductivity and good mechanical stability. It is difficult for the ionic conductivity of an AEM to reach the values commonly seen for PEMs due to the inherent mobility of OH\(^{-}\) ions being slower than that of hydrogen ions H\(^{+}\) (The ion mobility in water of OH\(^{-}\) = 2.69 and H\(^{+}\) = 4.67 relative to K\(^{+}\) = 1.00).\textsuperscript{20-21} Though AEM ionic conductivity can be promoted by increasing the number of cationic groups, water uptake also increases, which causes the loss of mechanical properties because of excessive swelling and
brittleness. Furthermore, the chemical durability of the cationic groups and the polymer backbone are important concerns. Therefore, rigorous control of the membrane morphology is needed.

**Scheme 1.1.** Structure of (A) polysulfone anion exchange membrane\(^{18}\) and (B) fluorinated anion exchange membrane synthesized by Toyo Soda Manufacturing Co., Ltd.\(^{23}\)

A large number of polymeric backbone structures exist, among which the following are most popular: poly(arylene ethers), polystyrenes, polyphenylenes, poly(vinyl alcohols) (PVAs), and fluorine-containing polymer.\(^{24-25}\) In some cases, ionic
groups may be included in the main chain of the polymer or as side-chains off of the polymer backbone. Due to the hydrophobicity of backbone and the hydrophilicity of the ionic groups, the membrane sometimes forms phase-separated regions that result in high stability in harsh conditions and also form ion channels that give high conductivities. In all cases, for AEM materials, backbone and cationic group must be stable in a high pH environment. Fluorinated polymers show a fair amount of promise for ion conduction on fuel cells.\textsuperscript{26} Nafion®, first described by Grot in the late 1960s,\textsuperscript{27} is the first of a class of synthetic fluorinated polymers with ionic properties that have remarkable resistance to degradation in both low and high pH conditions.\textsuperscript{28} Fluorinated polymers such as Nafion® contain highly hydrophobic backbone in contrast to the hydrophilic side chains. However, Nafion® is seldom used in alkaline fuel cells because it is not useful for OH\textsuperscript{-} transport.\textsuperscript{29} From the available perfluoroalkylsulfonyl fluoride precursor, different strategies can be employed to tether cations to the perfluoroalkylsulfonyl fluoride precursor. Pivovar and Herring have tried to modify the polymeric backbones, tether groups, and cationic groups, which are the possible sites for degradation.

\begin{center}
\includegraphics[width=\textwidth]{Scheme1.png}
\end{center}

\textbf{Scheme 1.2.} Perfluorosulfonyl polymer synthesized by Pivovar and Herring.\textsuperscript{30}

They synthesized a perfluoroalkylsulfonyl anion-exchange polymer (\textbf{Scheme 1.2})
by reaction of perfluoroalkylsulfonyl fluoride polymer (800 equivalent weight) with \(N,N,N\)-trimethylpropyldiamine, and it shows reasonable water uptake and good conductivity.\(^{30}\)

### 1.3 Scope of Work

As noted above, alkaline exchange membranes often suffer degradation of both backbone and the cationic groups.\(^{31}\) Because of this fact, the stability of AEMs in alkaline conditions is a main concern. The study of chemical stability of AEMs is often done by immersing a membrane in water and monitoring a decrease of the ion exchange capacity (IEC),\(^{32}\) ionic conductivity\(^{33}\) and water uptake.\(^{34}\) However, the IEC and conductivity may be affected by CO\(_2\) when the membrane is exposed to air, as it does not indeed demonstrate a degree of degradation of the cationic groups. Moreover, reduction of IEC does not elucidate where the decomposition is happening. Also, studies of this type may be done only on polymers, but it may be useful to study small-molecules as models to learn about chemical stability. In the past few years, NMR spectroscopy has been used as a strong method to do quantitative analysis of cationic groups of AEM.\(^{35-36}\)

This research focuses on synthesizing perfluoroalkyl sulfonamide small-molecule model compounds having a quaternary ammonium group attached to a fluoroalkyl group and studying their stability in strongly alkaline conditions at elevated temperature. **Scheme 1.3** illustrates the relationship between fluoropolymer AEMs and the small
-molecule model compounds that were studied in this work.

Scheme 1. Comparison of (A) fluorinated anion exchange membrane synthesized by Toyo Soda Manufacturing Co., Ltd.\textsuperscript{23} and (B) a representative perfluoroalkyl sulfonamide small-molecule model compound (Salt 2).

The goal is to characterize the cleavage of the sulfonamide bond, the amide bond and the quaternary ammonium groups of the model compound. The model compounds were chosen because the aforementioned fluoropolymer membranes are known to have reasonably stability in an alkaline environment, and the quaternary ammonium group shows higher resistance to alkaline conditions when compared to other types of cationic groups such as guanidium, phosphonium and sulfonium. Herring synthesized poly(ethylene-co-tetrafluoroethylene) grafted polyvinyl benzyltrimethyl ammonium (ETFE-g-PVBTMA) membrane (Scheme 1.4) and claimed OH\textsuperscript{-} conductivity as high as
Nafion® membrane along with low water uptake.\textsuperscript{34}

\[ \text{CH}_2\text{CH} \text{ETFE} \]

\[ \text{Scheme 1.4. ETFE-g-PVBTMA membrane synthesized by Herring.} \textsuperscript{34} \]

However, hydroxide ion is a very strong nucleophile, and ammonium groups possess several pathways for degradation in an alkaline environment, with the two most important being E2 elimination (Hofmann degradation) and direct nucleophilic substitution. The presence of β-hydrogen atoms allows the Hofmann elimination to occur, yielding an alkene (vinyl), an alcohol and a tertiary amine, which can account for the AEM having low thermal and chemical stability. A cationic group with no β-hydrogen atoms present, such as a benzyltrimethyl ammonium cation, may undergo direct nucleophilic attack yielding an alcohol and a tertiary amine. Scheme 1.5 illustrates these degradation pathways.

The study of small-molecule model compounds that mimic the polymers are of interest in part because they allow for the use of modern structural tools, such as NMR spectroscopy, GC/mass spectroscopy, and chromatographic techniques. For example,
Schiraldi reported on the degradation rate and mechanism of Nafion® by NMR spectroscopy using small-molecule model compounds.\(^{37}\)

**Scheme 1.5.** Degradation mechanisms of quaternary ammonium cation by hydroxide anions.\(^{38}\)

By treating Nafion® using a solution of aqueous hydrogen peroxide with ferrous iron (Fenton’s reagent), peroxide and hydroxyl radicals will be generated at temperatures that mimic fuel cell operation. Ramani *et al.* studied the degradation mechanism of a number of anion conductors under alkaline conditions [e.g. benzyl trimethylammonium, trimethylphosphonium, and tris-(2,4,6-trimethoxyphenyl) phosphonium] utilizing 2D NMR spectroscopic techniques. Benzyl trimethylammonium and tris-(2,4,6-
trimethoxyphenyl) phosphonium underwent direct nucleophilic substitution, while trimethylphosphonium underwent the Somelet-Hauser rearrangement. Moreover, NMR spectroscopy is an unbeatable method that shows where the degradation happens and which bonds are broken.

This thesis describes research on the alkaline stability of model compounds that are structurally related to fluoropolymer alkaline exchange materials.

Specifically, Chapter 2 focuses on the synthesis of different types of perfluoro-\(n\)-butyl sulfonamides followed by their reactions with methyl iodide to make quaternary ammonium salt. These salts were characterized by using NMR spectroscopy and elemental analysis.

Chapter 3 focuses on studying the alkaline stability of the perfluoro-\(n\)-butyl sulfonamide small-molecule model compounds prepared in strongly base conditions at different temperatures and different molarities of KOH. The decomposition pathways of the small-molecule model compounds have been studied. And also the characterization of the cleavage of the sulfonamide bond, the amide bond, and the decompositions of the quaternary ammonium group was studied.
References


CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF SMALL-MOLECULE CATIONIC PERFLUOROALKYL SULFONAMIDE MODEL COMPOUNDS

2.1 Introduction

An anion exchange membrane (AEM) is a solid polymer electrolyte that contains fixed cationic groups to transport anions. In the case of an AEM fuel cell, the anion to be transported is hydroxide. The membrane should satisfy the following requirements: (1) high ionic conductivity and ion exchange capacity, (2) high chemical and thermal stability (3) carrier for transporting hydroxide ions and (4) low swelling degree. Some typical cationic groups in AEMs are illustrated in Scheme 2.1. The quaternary ammonium group was reported to have reasonable stability in alkaline conditions when compared with other types of cationic groups.\(^2\)\(^3\)

In contrast to hydrocarbon polymers, fluorinated polymers are regarded as high value-added materials because to their outstanding properties.\(^4\) Because of the small size of fluorine and the electronegativity difference between fluorine and carbon atoms (F: 4.0,
C: 2.5), fluoropolymers are usually highly polar with C-F bonds.\textsuperscript{5-7} Due to the extreme properties of the fluorine atom, fluorine-containing ion-exchange polymer membranes have been widely used in fuel cells, such as fluorinated polyoxadiazoles, poly (perfluorosulfonic acids).\textsuperscript{5,8} In an effort to study the thermal stability in alkaline conditions using quick and accurate techniques such as NMR spectroscopy, cationic perfluoroalkyl sulfonamides are good candidates as small-molecule model compounds of fluoropolymers. As shown as Scheme 1.3 in Chapter 1, the cleavage of bonds and the decomposition pathways of cationic perfluoroalkyl sulfonamide model compounds in strong alkaline conditions can be easily monitored.

\textbf{Scheme 2.1.} Typical cationic groups used in AFCs.
Different types of perfluoroalkyl sulfonamide molecules have been synthesized from perfluoroalkyl sulfonyl fluoride by reaction with a suitable primary or secondary amine.\textsuperscript{9-11} Shainyan and Danilevich synthesized \(N\)-(allyl)trifluoromethanesulfonamide by using trifluoromethanesulfonyl fluoride and allylamine. Two equivalents of triethylamine were added in the reaction in order to absorb the generated hydrofluoric acid (HF) and further form the complex salt \(\text{F}_3\text{CSO}_2\text{N}^+\text{CH}_2\text{CH}=\text{CH}_2\text{Et}_3\text{N}^-\text{H}\). Then the reaction mixture was treated with hydrochloric acid to obtain the product \textbf{(Scheme 2.2)}.\textsuperscript{12}

\[
\text{CF}_3\text{SO}_2\text{F} + \text{H}_2\text{N} \xrightarrow{\text{Et}_3\text{N}} \text{Et}_3\text{N}\xrightarrow{\text{HCl}} \text{HCl} \text{CF}_3\text{S}O\text{N}^+\text{Et}_3\text{N}^-\text{Et}_3\text{N}\xrightarrow{-\text{Et}_3\text{N}}
\]

\textbf{Scheme 2.2.} Synthetic route of \(N\)-(allyl)trifluoromethanesulfonamide.\textsuperscript{12}

Lehmier and his group developed several routes to synthesize a series of different perfluoroalkyl sulfonamide molecules \textbf{(Scheme 2.3)}.\textsuperscript{13} In order to optimize the reaction conditions and the yield of the product, they modified the choice of solvents and bases used in the reaction.

Four different types of perfluoro-n-butyl sulfonamide small-molecule model compounds that were synthesized in this work by following literature procedures. The structures of the compounds are shown in \textbf{Figure 2.1}. Then compounds 3 and 4 from \textbf{Figure 3.1} were treated with methyl iodide to make quaternary ammonium salts 1 and 2 (structures shown in \textbf{Figure 2.1}) in order to study their alkaline stability \textbf{(Figure 4.1)}. 
Scheme 2.3. Synthesis of mono and dialkylated perfluoroalkyl sulfonamides.\textsuperscript{13}
Figure 5.1. Synthesized perfluoro-\textit{n}-butyl sulfonamide small-molecule model compounds.

2.2 Experimental

Nuclear Magnetic Resonance Spectroscopy

\textsuperscript{1}H and \textsuperscript{19}F NMR spectroscopic studies were acquired at ambient temperature and at high temperature (65 °C) with a JEOL ECX 300 instrument (\textsuperscript{1}H—301 MHz and \textsuperscript{19}F—283 MHz). All chemical shifts are given of the $\delta$ -scale in ppm. \textsuperscript{1}H spectra shifts are given to the proton signal of solvent used (chloroform: 7.25 ppm, water: 4.75 ppm), \textsuperscript{19}F chemical spectra shifts were referenced to CFCl\textsubscript{3} (0 ppm). The multiplicities of signals are abbreviated by the following: Coupling constants are given in Hertz (Hz) and signals are abbreviated as s (singlet), d (doublet), dd (doublet of doublets), td (triplet of doublets), q (quartet), quin (quintet), m (multiplet), br (broad).

Preparation of n-C\textsubscript{4}F\textsubscript{9}SO\textsubscript{2}NH(CH\textsubscript{2})\textsubscript{3}CH\textsubscript{3}(\textbf{Compound 1})

Perfluoro-\textit{n}-butanesulfonyl fluoride (3.0 g, 10 mmol) (Oakwood) was placed under a nitrogen atmosphere in a 150-mL two-necked, round-bottomed flask containing dry diisopropyl ether (15 mL), which was equipped with a reflux condenser. A twofold excess of \textit{n}-butylamine (1.4 g, 20 mmol) (Tokyo Chemical Industry Co., LTD.) was used as received and added slowly to the reaction mixture under ice bath conditions (5-10 °C). The reaction mixture was heated at 50 °C and stirred for 24 h. After that, the reaction mixture was cooled to room temperature and then dissolved in DCM, washed by deionized water, 0.5% HCl, saturated NaCl and 3% NaHCO\textsubscript{3}, and dried overnight with anhydrous MgSO\textsubscript{4}. The solvent was removed using rotary evaporator and a yellow
viscous liquid product was collected. The crude product was purified by reduced pressure distillation (65 mbar). A white crystal like product, 1.4 g, was collected at 119 °C. Yield is 52% based on perfluoro-n-butanesulfonyl fluoride.

\[ \text{Compound 2} \]

Preparation of \( n-\text{C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \) (Compound 2)

\( n-\text{Perfluorobutanesulfonyl fluoride} (3.0 \text{ g, 10 mmol}) \) (Oakwood) was placed under a nitrogen atmosphere in a 50-mL, two-necked, round-bottomed flask containing dry diisopropyl ether (15 mL), which was equipped with a reflux condenser. A twofold excess of \( N \)-methyl-1-butanamine (1.7 g, 20 mmol) (Tokyo Chemical Industry Co., LTD.) was added drop-by-drop slowly to the reaction mixture under ice bath condition (5-10 °C). Then the reaction mixture was heated at 50 °C and stirred for 24 h in an oil bath. After that, the reaction mixture was cooled to room temperature then dissolved in dichloromethane (DCM), washed by deionized water, 0.5% HCl, saturated NaCl and 3% NaHCO\(_3\). Then the DCM solution was dried overnight with anhydrous MgSO\(_4\). The solvent was removed using rotary evaporator and a yellow viscous liquid product was collected. The crude product was purified by distillation under 65 mbar at 40 °C and 2.3 g of clear liquid was obtained. Yield is 81% based on perfluoro-n-butanesulfonyl fluoride.
\( n-C_4F_9SO_2N(CH_2)CH_2CH_2CH_2CH_3 \) \( ^1H \) NMR (301 MHz, CDCl\(_3\)): \( \delta \) 0.97 (3H, td, \( J = 7.2, 1.6 \) Hz, -CH\(_3\)), 1.40 (2H, \( dq, J = 15.7, 8.3, 7.6 \) Hz, -CH\(_2\)CH\(_3\)), 1.64 (2H, \( dt, J = 15.7, 7.7 \) Hz, -CH\(_2\)), 3.07 (3H, s, -NC\(_2\)H\(_3\)). 3.41 (2H, s, -NCH\(_3\)CH\(_2\)).

 Preparation of \( n-C_4F_9SO_2NH(CH_2)_3N(CH_3)_2 \) (Compound 3)

Perfluoro-\( n \)-butanesulfonyl fluoride (3.0 g, 10 mmol) (Oakwood) was placed under a nitrogen atmosphere in a 150-mL, two-necked, round-bottomed flask containing dry diisopropyl ether (15 mL), which was equipped with a reflux condenser. A twofold excess of \( N,N,N \)-trimethyl-1,3 propanediamine (2.0 g, 20 mmol) (Tokyo Chemical Industry Co., LTD.) was added slowly to the reaction mixture under ice bath conditions (5-10 °C). The reaction mixture was heated at 50 °C and stirred for 24 h. After that, the reaction mixture was cooled to room temperature then dissolve in DCM, washed by deionized water, 0.5% HCl, saturated NaCl and NaHCO\(_3\), following by drying with MgSO\(_4\) overnight. The solvent was removed using a rotary evaporator, and yellow solid lump was collected. The crude product was purified by recrystallization using hot DCM, and a white crystal like material of solid was obtained. Yield is 68% based on perfluoro-\( n \)-butanesulfonyl fluoride.

\( n-C_4F_9SO_2NH(CH_2)_3N(CH_3)_2 \) \( ^1H \) NMR (301 MHz, CDCl\(_3\)): \( \delta \) 1.75 (2H, \( m, J = 5.6 \) Hz, -CH\(_2\)), 2.33 (6H, s, -N(CH\(_3\))\(_2\)), 2.63 (2H, \( t, J = 3 \) Hz, -CH\(_2\)N), 3.43 (2H, \( t, J = 6 \) Hz, -NHCH\(_2\)). \( ^19F \) NMR (283 MHz, CDCl\(_3\)): \( \delta \) -80.62 (s, CF\(_3\)), -112.68 (s, \( \alpha \)-CF\(_2\)), -121.36 (s, \( \beta \)-CF\(_2\)), -125.89 (s, \( \gamma \)-CF\(_2\)).
Preparation of $n$-$C_4F_9SO_2N(CH_2)\_3N(CH_3)\_2$ (Compound 4)

Perfluoro-$n$-butanesulfonyl fluoride (3.0 g, 10 mmol) (Oakwood) was placed under a nitrogen atmosphere in a 50-mL two-necked, round-bottomed flask containing dry diisopropyl ether (15 mL), which was equipped with a reflux condenser. A twofold excess of 3-(dimethylamino)-1-propylamine (2.3 g, 20 mmol) (Tokyo Chemical Industry Co., LTD.) was added slowly to the reaction mixture under ice bath conditions (5-10 °C). The reaction mixture was heated at 50 °C and stirred for 24 h. After that, the reaction mixture was cooled to room temperature, then dissolve in DCM, washed by deionized water, 0.5% HCl, saturated NaCl and 3% NaHCO₃, and then dried overnight with anhydrous MgSO₄. The solvent was removed using a rotary evaporator, and an orange viscous liquid product was collected. The crude product was purified by distillation under 65 mbar at 45 °C, and 2.6 g of a clear liquid was obtained. Yield is 68% based on perfluoro-$n$-butanesulfonyl fluoride.

$n$-$C_4F_9SO_2N(CH_2)\_3N(CH_3)\_2$ $^1$H NMR (301 MHz, CDCl₃): $\delta$ 1.79 (2H, m, -CH₂), 2.21 (6H, s, -N(CH₃)₂), 2.31 (2H, m, -CH₂N), 3.08 -(SO₂NCH₃). 3.47 (2H, m, NCH₃CH₂)

$^{19}$F NMR (283 MHz, CDCl₃): $\delta$ -80.65 (s, CF₃), -111.83 (s, α-CF₂), -121.38 (s, β-CF₂), -125.86 (s, γ-CF₂)

Preparation of $n$-$C_4F_9SO_2NH(CH_2)\_3N^+CH(CH_3)\_3\Gamma$ (Salt 1)

$n$-$C_4F_9SO_2NH(CH_2)\_3N(CH_3)\_2$ (1 g, 2.6 mmol) (Compound 3) was placed under a argon atmosphere in a 25-mL, one-necked, round-bottomed flask containing dry
acetonitrile (5 mL), which was equipped with a reflux condenser. Then methyl iodide (0.2 mL, 2.6 mmol) (Tokyo Chemical Industry Co., LTD.) was added to the solution. The reaction mixture was heated at 80 °C and stirred for 8 h. After that, the mixture was cooled to room temperature, and the solvent was removed using a rotary evaporator, followed by adding a small amount of ethanol (an amount that is enough to dissolve complex), then six times more of DCM than ethanol was added to the residue to recrystallize the product. A pale yellow crystal like solid (0.8g) was obtained. Yield is 60% based on **Compound 3**.

\[
n-C_4F_9SO_2NH(CH_2)3N(CH_3)_3^+I^{-} \quad ^1H \text{ NMR} (301 \text{ MHz, D}_2\text{O}) \delta 2.02 (2H, s, -CH_2), 2.83 (2H, s, -CH_2N(CH_3)_3I), 3.11 (9H, d, J = 9.7 \text{ Hz, } -N(CH_3)_3I ), 3.34 (2H, dt, J = 12.9, 7.1 \text{ Hz, } ) \\]

\[
^{19}\text{F NMR} (283 \text{ MHz, CDCl}_3): \delta -80.83 (s, CF_3), -112.93 (s, \alpha-CF_2), -121.53 (s, \beta-CF_2), -125.93 (s, \gamma-CF_2) \quad \text{Anal. Calcd. for } n-C_4F_9SO_2NH(CH_2)3N(CH_3)_3^+I^{-}: \text{ C, 22.83; H, 3.06; N, 5.32. Found: C, 22.85, H, 2.82; N, 5.22.} 
\]

**Preparation of n-C_4F_9SO_2N(CH_3)(CH_2)_2N^+(CH_3)_2I** (Salt 2)

\[
n-C_4F_9SO_2N(CH_3)(CH_2)_2N^+(CH_3)_2I \quad (\text{Compound 4}) \text{ was placed under an argon atmosphere in a 25-mL, three-necked, round-bottomed flask containing dry acetonitrile (5 mL), which were equipped with a reflux condenser. Then the methyl iodide (0.1 mL, 1.5 mmole) (Tokyo Chemical Industry Co., LTD.) was added to the solution. The reaction mixture was heated at 80 °C and stirred for 8 h. After that, the mixture was cooled to room temperature, and the solvent was removed using a rotary evaporator, followed by adding a small amount of ethanol (enough to dissolve the}\n\]
complex), then ten times more of DCM than ethanol was added to the residue to recrystallize the product. The complex was put in refrigerator to speed up the crystallization process. A pale yellow crystal like solid (0.48g) was obtained. The yield was 59% based on Compound 4.

\(\text{n-C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)}(\text{CH}_2\text{)}_3\text{N}^+\text{(CH}_3\text{)}_3\text{I}^-\) \(\text{H NMR (301 MHz, D}_2\text{O)} \delta 2.40-2.62 \ (2\text{H, m, } -\text{CH}_2\text{-}), 3.22 \ (2\text{H, } t, J = 3 \text{ Hz, } -\text{CH}_2\text{N}-), 3.34-3.54 \ (9\text{H, m, } -(\text{CH}_3)_3\text{I}), 3.60-3.79 \ (3\text{H, m, } -\text{NCH}_3\text{), 3.91} \ (2\text{H, s, } -\text{NCH}_3\text{CH}_2\text{-}).\) \(\text{F NMR (283 MHz, CDCl}_3\text{)}: \delta -80.73 \ (s, \text{CF}_3), -111.56 \ (s, \alpha\text{-CF}_2), -121.46 \ (s, \beta\text{-CF}_2), -125.78 \ (s, \gamma\text{-CF}_2).\) Anal. Calcd. For \(\text{n-C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)}(\text{CH}_2\text{)}_3\text{N}^+\text{(CH}_3\text{)}_3\text{I}^-:\) C, 24.46; H, 3.36; N, 5.19. Found: C, 24.57; H, 3.20; H, 5.09.

### 2.3 Results and Discussion

**Synthesis of Perfluoroalkyl sulfonamide.** To synthesize perfluoro-\(n\)-butyl sulfonamide model compounds, we started by using the perfluoro-\(n\)-butanesulfonyl fluoride and different amines with an excess amount of base to absorb the generated HF. At first diisopropylethylamine (DIPEA) was chosen as the base to absorb and trap the possibly generated free fluorine anion (Table 2.1). DIPEA is non-nucleophilic tertiary base that usually is used as a selective reagent for alkylation reactions between alkyl halides and secondary amines to make tertiary amines (Scheme 2.4).\(^{14}\)
But DIPEA was found to be an unsuitable base in this special reaction system. The reaction does not proceed as indicated by the fact that the peak of the SO$_2$F group at 50 ppm is still present in the $^{19}$F NMR spectrum even after a long heating period (48 hours). A change of solvent system was found not to overcome the problem as well (Table 2.1). Meanwhile, the product isolated from the reaction with DIPEA as base contains significant amounts of by-product, and it is extremely hard to purify the product with such a by-product present. From a $^{19}$F NMR investigation, a singlet peak located at -115 ppm belongs to fluoride beside sulfur of $n$-C$_{4}$F$_{9}$SO$_{3}$H, which is the hydrolysis product from the starting material, perfluoro-$n$-butanesulfonyl fluoride.$^{15}$ Sulfonfyl fluoride is very sensitive to moisture in base condition and can easily be hydrolyzed (Scheme 2.5).

Scheme 2.5. Hydrolysis due to perfluoro-$n$-butanesulfonyl fluoride react with water.
To avoid hydrolysis, all compounds were dried over 3 Å molecular sieves. Also, instead of using an external base that would form a complex that is hard to purify, an excess of one equivalent of amine was used to absorb HF (Scheme 2.6).

Scheme 2.6. Synthetic path of n-C₄F₉SO₂N(CH₃)(CH₂)₃N(CH₃)₂.

When HN(CH₃)CH₂CH₂CH₂N(CH₃)₂ was added to a solution of n-C₄F₉SO₂F at room temperature, a white gas immediately formed, and the reaction mixture became a white lump. Then heat was applied to the reaction mixture, which was left under reflux for 12 hours. The reaction mixture was cooled to room temperature, and the resulting white solid was dissolved in dichloromethane (DCM). Following washing by water, 0.5% HCl, saturated sodium chloride (NaCl), and 3% sodium bicarbonate (NaHCO₃), the DCM solution is dried over magnesium sulfate (MgSO₄). A yellow clear liquid was collected after removing DCM by a rotary evaporator. Finally the crude product was purified by distillation under 65 mbar at 40 °C, and a white clear liquid was collected. The preparation of four different perfluoroalkyl sulfonamides were followed by this synthesis method. Only the purification of n-C₄F₉SO₂NH(CH₂)₃N(CH₃)₂ has been modified because instead of obtaining a liquid, a solid was collected after washing by different solutions. The crude product in this case was purified by recrystallization using DCM.
Scheme 2.7. Synthetic route of three different perfluoro-\(\text{-}\)butanesulfonamides.

The reaction can also be carried out employing triethylamine (TEA) as an external base. The yield is as high as when carrying out the reaction with two equivalent of base.

**Synthesis of quaternary ammonium salt.** The synthesis of quaternary ammonium salts from the tertiary amines is simple, but the following purification procedure is difficult. Following direct addition of methyl iodide to perfluoro-\(\text{-}\)butyl sulfonamides under 80 °C for 8 h, the quaternary salt will be easily generated and obtained as an orange oily solid containing white crystals (Scheme 2.8). After adding a methyl group to the tertiary amine, the \(^1\)H NMR peak for the hydrogen atom on the
carbon atom adjacent to nitrogen atom on the quaternary moves downfield group due to the deshielding effect (Figure 2.2).

| Table 2.1: Synthesis of perfluorobutyl sulfonamides from perfluorobutanesulfonyl fluoride |
|---|---|---|---|---|
| Entry | Solvent | Base | Temperature | Result |
| 1 | Acetonitrile | DIPEA | 70-80 °C | Reaction not completed |
| 2 | Diisopropyl ether | DIPEA | 50 °C | Reaction not completed |
| 3 | Dry diisopropyl ether | Dry DIPEA | 50 °C | Reaction not completed |
| 4 | Dry diisopropyl ether | 2 equivalent of dry amine | 50 °C | Reaction completed |
| 5 | Dry dichloromethane | Dry TEA | 50 °C | Reaction completed |

Scheme 2.8. Synthetic route of $n$-C$_4$F$_9$SO$_2$NH(CH$_2$)$_3$N$^+$ (CH$_3$)$_3$I (Salt 1) and $n$-C$_4$F$_9$SO$_2$N(CH$_3$)(CH$_2$)$_3$N$^+$ (CH$_3$)$_3$I (Salt 2).
Figure 2.2. Comparison of $^1$H NMR spectra of compound 3 in CDCl$_3$ and Salt 2 in D$_2$O at 65 °C. The position of the peak for the hydrogen adjacent to quaternary group moves downfield compared to the hydrogen atom on tertiary amine on the $^1$H NMR spectrum.
To get rid of the impurities that give rise to small strange peaks in the $^1$H NMR spectrum of the salt, the salt was dissolved in H$_2$O and washed by DCM. But it takes two days to remove all the water by using a rotary evaporator under vacuum, and the impurity is still in the product. Using vacuum filtration to remove the impurities is also not available, because the quaternary ammonium salt is a surfactant, and the reaction mixture produces lots of bubbles under low pressure (Figure 2.3). Finally, recrystallization with ethanol and dichloromethane (ratio 1:6) was successful. The amount of ethanol should be just enough to dissolve the salt, while the amount of DCM should be much larger than the amount ethanol, and by placing the solution at low temperature conditions, such as a freezer (-5 °C), gave a better yield.

Figure 2.3: Bubble generated from filtration of the quaternary ammonium salt
In conclusion, synthesis of compounds 1-4 and salts 1-2 was completed and structures and purity confirmed by $^1$H and $^{19}$F NMR spectroscopy. Salt 1 and Salt 2 will subsequently be used for alkaline stability tests in work described in Chapter 3.
References


3.1 Introduction

Alkaline exchange membrane (AEM) fuel cells have gained much attention recently because AEMs offer advantages over proton exchange membrane fuel cells the oxygen reduction reaction (ORR) is easier under alkaline conditions, and AEM fuel cells can be less costly due to the ability to use non-noble-metal catalysts. However, the primary challenge to implementing AEM fuel cell technology is the stability of alkaline exchange membranes (AEMs) under high pH and high temperature (> 80 °C) operating conditions. Though the AEM alkaline stability has been widely studied, lots of reports focus on cationic groups connected to the backbone of the polymer and on the polymer degradation using ion-exchange capacity (IEC), ion conductivity and FT-IR as indicators of decomposition. Varcoe et al. soaked a fluorinated ethylene propylene (FEP) graft \(N,N,N\)-trimethyl-benzenemethaniminium hydroxide in water and heated it from 60 °C to
100 °C for 119 days and monitored the degradation by using the ion-exchange capacity.\textsuperscript{3}

\begin{scheme}
\centering
\begin{tikzpicture}
  \node at (0,0) {FEP (Fluorinated ethylene propylene)};
  \node at (-2,0) {FEP};
  \draw[thick] (-2,0) circle (1cm);
  \node at (-2,-1) {CH$_2$N(CH$_2$)$_3$ OH};
  \node at (-2,-2) {+};
  \node at (-2,-3) {\text{CH$_2$N(CH$_2$)$_3$ OH}};
  \node at (-2,-4) {\text{FEP(Fluorinated ethylene propylene)}};
\end{tikzpicture}
\end{scheme}

**Scheme 3.1.** Propylene (FEP) graft $N,N,N$-trimethyl-benzenemethanaminium hydroxide membrane.\textsuperscript{3}

These investigations are time-consuming, and they only provide relative data on chemical stability. Alkaline stabilities of the polymer backbone and the cationic group may play an important role in the entire AEM stability, so that the alkaline stability of the cationic group alone might not be sufficient.\textsuperscript{4,5} NMR spectroscopy is a powerful method to determine the degradation pathways of organic materials.\textsuperscript{6,7} Mohanty and Bae synthesized different kinds of quaternary ammonium cations and reacted them with silver oxide (Ag$_2$O) in water and D$_2$O to prepare quaternary ammonium hydroxide (or deuteroxide) salts.\textsuperscript{6}
After the Ag₂O-mediated ion exchange reaction, the quaternary ammonium hydroxide salts were transferred to NMR tubes sealed with parafilm, and the NMR tubes were heated from 60 to 120 °C. They recorded the NMR spectra at time intervals of 0, 24, 144, 264, 432, and 672 hours. They reported that alkyl quaternary cations are more stable than benzylic quaternary cations and more suitable for long-term use in alkaline fuel cells, and that alkyl quaternary hydroxides have lower decomposition rates, when compare with benzylic quaternary hydroxides. These experiments focused only on the stability of the cationic groups and not on the linkage between the cationic groups and the polymer backbone. However, several studies over the last few decades reported that a stronger correlation exists between the polymer backbone and cationic groups than perviously thought. For example, polysulfones are thermoplastic polymers known to be highly resistant to many severe conditions including alkaline environments at elevated temperature. But introducing a quaternary ammonium group onto a polysulfone polymer may increase the hydrophilicity of the polysulfone polymer and allow hydroxide ions access into electrophilic regions of the polymer backbone thereby increasing the efficiency of fuel cell. Stability tests can be further improved by using small molecule model compounds. Perfluoroalkyl sulfonamide model compounds such as those
prepared in the work described in Chapter 2 are suitable for carrying out alkaline stability tests, since they contain partially fluorinated chains that is similar to the repeating unit of the backbone of a fluoropolymer and also contains the ionic group that supports hydroxide transport as illustrated in Scheme 2.2 in Chapter 2.

This research seeks to develop a standardized method to study the stability of cationic model compounds in alkaline conditions. We focus on studying the decomposition of (1) the sulfonamide bond, (2) the amide group, and (3) the cationic group.

![Scheme 3.3](image)

Scheme 3.3. Schematic of possible degradation positions of (1) the sulfonamide bond (2) the amide bond, and (3) cationic group.

Salts with either hydrogen atom (Salt 1) or a methyl group (Salt 2) on sulfonamide group have been synthesized to compare this stability. Syntheses of these model compounds are described in Chapter 2. By our presumption, replacing the hydrogen atom by methyl group on the sulfonamide nitrogen atom will enhance the stability of this linkage in alkaline conditions, because this will prevent deprotonation of the sulfonamide group. Trepka reported the pK\textsubscript{a}'s of CF\textsubscript{3}SO\textsubscript{2}NH\textsubscript{2} and CF\textsubscript{3}SO\textsubscript{2}NHCH\textsubscript{3} as 6.33 and 7.56, respectively.\textsuperscript{11} Then it was predicted that the model compounds with
hydrogen atom on the sulfonamide group from Chapter 2 would also be easily deprotonated. Also, by comparison to the trifluoromethyl group in the report, Salt 1 contains a longer fluoroalkyl group that has strong electron withdrawing character, which could further stabilize the conjugate base after deprotonation, thereby making the sulfonamide more acidic. The hydrogen on the sulfonamide bond is thus predicted to react with potassium hydroxide (pKₐ = 0.5) and generate water, and deprotonation of either a sulfonamide bond or amide group should be observable in an NMR spectrum (Scheme 3.4).¹²⁻¹³

1.

![Scheme 3.4. Presumption of bond cleavage of (1) salt 1 and (2) salt 2 under KOH attack.](image)

2.

Scheme 3.4. Presumption of bond cleavage of (1) salt 1 and (2) salt 2 under KOH attack.
3.2 Experimental

Procedure for characterizing the degradation of quaternary ammonium salt: \(^1\)H and \(^{19}\)F NMR spectroscopic studies were acquired at ambient temperature and at high temperature (65 °C, 70 °C, 80 °C, 90 °C) with a JEOL ECX 300 instrument (\(^1\)H—300 MHz and \(^{19}\)F—283 MHz). All chemical shifts are given of the \(\delta\) -scale in ppm. The NMR spectra of compounds were obtained by putting a fluoropolymer liner (NORELL, Inc. #TL-5-7) filled with sample solution in a glass NMR tube with D\(_2\)O added in the glass NMR tube as an external reference and locking compound. Then the NMR tube was heated in the NMR spectrometer to the desired temperature to acquire the spectra.

Three different procedures were followed to conduct alkaline stability tests. They are described below.

First stability test: A 1 M KOH stock solution was prepared by dissolving 56.11 g KOH in 1 L deionized water. Then Salt 2 (0.054 g) was dissolved in 1 mL aqueous 1 M KOH to make a 0.1 M solution. Also 0.053 g of Salt 1 was dissolved in 1 mL aqueous 1 M KOH to make a 0.1 M solution. Both solutions were put in plastic (polypropylene) vials and sealed with parafilm to create isolated condition. Samples were heated at 60 °C for two days in an oil bath, then solutions were moved from the plastic vial and placed in glass NMR tubes to acquire NMR spectra (high temperature NMR at 60 °C). Then the solutions were returned to the plastic vial, temperature was increased by 10 °C to 70 °C and held there for another two days, then some solution was returned to the NMR tube to
acquire another NMR spectrum (high temperature NMR at 70 °C). The same procedure was continued until the decomposition temperature reached 90 °C.

Second stability test: Six different samples have been prepared. A 8.3 g amount of KI was dissolved in 50 mL deionized water to make 1 M KI stock solution. (1) Aqueous 1 M KOH (0.4 mL) was put into a fluoropolymer liner (NORELL, Inc. #TL-5-7.), then 0.022 g of Salt 2 was added to the solution to make a 0.1 M solution of salt in 1 M KOH. (2) Add 0.016 mL benzyltrimethylammonium hydroxide (40 wt% in H₂O) to a fluoropolymer liner, then add 0.024 mL of 1 M KOH solution to make 0.4 mL of a 0.1 M BTMAH solution in 1 M KOH. (3) Deionized water (0.4 mL) was put in to fluoropolymer liner then 0.022 g of Salt 2 was added to the water to make a 0.1 M solution of Salt 2. (4) A quantity of 0.016 mL of BTMAH solution was diluted by 0.024 mL deionized water to make a 0.1 M salt aqueous solution of BTMAH in water. (5) Salt 2 (0.022 g) was put in a fluoropolymer liner, and then 0.04 mL aqueous 1 M KI was added to make a 0.1 M solution of Salt 2 in 1 M KI. (6) A 0.016 mL BTMAH solution (40 wt%) was filled in fluoropolymer liner then 0.024 mL of aqueous 1 M KI was added to make 0.1 M solution in 1 M KI. All six samples were heated at 60 °C for two days in an oil bath and then taken from the oil bath, the outside of the liner was washed by acetone and hexane, and the liner was placed in a glass NMR tube contained a small amount of D₂O to achieve spectrometer lock. NMR spectra were then acquired for all samples (all NMR spectra recorded at 65 °C). After taking the NMR spectra, the liner was put back to the oil bath and the temperature is increased 10 °C to 70 °C for another two
days, then the samples were recovered to again acquire NMR data. The same procedure was repeated until the temperature reached 90 °C.

Third stability test: A series of KOH aqueous stock solutions was prepared with KOH concentration of 1 M, 2 M, 4 M and 6 M. (1) Salt 2 (22.0 mg) was placed in a fluoropolymer liner, and then 0.4 mL of deionized water was added to make a 0.1 M Salt 2 solution. (2) Fill 21.8 mg of Salt 2 in fluoropolymer liner (NORELL, Inc.#TL-5-7.), and then add 0.4 mL of 1 M aqueous stock KOH solution to make 0.1 M Salt 2 solution in 1 M KOH. The procedure was repeated by adding Salt 2 in different concentrations (1 M, 2 M, 4 M, and 6 M KOH) in fluoropolymer liners. Samples are then heated from room temperature to 60 °C for two days in an oil bath, the surface of the liner was washed using acetone and hexane, then the liner was placed in a glass NMR tube that contains D$_2$O, and then the NMR spectra were acquired (all NMR spectra recorded at 65 °C). After acquiring the NMR spectra, the liners were placed back to the oil bath, and the temperature was increased to 80 °C for another two days, and then the NMR spectra were recorded.

Zwitterion test: A 20 mg sample of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$N$^{(+)}$(CH$_3$)$_3$I$^{(-)}$ (Salt 1) was weighed and added to a glass NMR tube, and then 0.4 mL of deionized water was added to make a 0.1 M aqueous solution of Salt 1. The NMR spectrum was then acquired (all NMR spectra recorded at 65°C). Another 0.4 mL of 4 M stock KOH solution was added to make a 0.05 M solution of Salt 1 in 2 M KOH, and then another NMR spectrum was recorded. Then the solution was neutralized by adding 0.4 mL of 4 M aqueous HCl
solution, and another NMR spectrum was acquired. A similar procedure was followed with Salt 2.

**Decomposition pathway findings:** (1) Put 0.4 mL of 0.1 M solution of already decomposed $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$N$^{(+)}$(CH$_3$)$_3$I$^{(-)}$ (**Salt 1**) in 2 M KOH. Then add 0.1 M (1.6 $\mu$L) methanol to the solution to record the NMR spectrum. By comparing the NMR spectra of decomposed $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$N$^{(+)}$(CH$_3$)$_3$I$^{(-)}$, if the methanol is one of the decomposition product can be identify. Finally add 0.1 M (3.8 $\mu$L) trimethylamine to the solution, then take another NMR spectrum, and also compare the NMR spectra with previous spectra. Similar procedures were followed **Salt 2.** (2) **Salt 2** (0.1 M) was added in a 4 M KOH solution, and then shake the solution to make sure **Salt 2** is completely exposed to the base. Following neutralization of the solution, then extract the solution with CDCl$_3$ and use MgSO$_4$ to dry the CDCl$_3$ solution. Finally take the NMR spectra of the CDCl$_3$ layer the NMR spectra.

### 3.3 Results and Discussion

Sturgeon *et al.* proposed that non-deuterated solvent systems should be used in degradation studies to avoid H/D isotopic exchange that will be misunderstood as degradation of the compounds. They discovered the H/D exchange of benzyltrimethylammonium hydroxide in the D$_2$O solution from its effect on NMR spectra.$^{14}$ In an attempt to investigate the thermal stability and decomposition pathways of our model compounds in alkaline conditions, compounds were subjected in alkaline
conditions to test their thermal degradations. Water should be used in all systems instead of D$_2$O, although H$_2$O has a huge peak in the $^1$H NMR spectrum, it can be used without fear of H/D exchange.

The first stability tests on Salt 1 and Salt 2 were conducted in polypropylene plastic vials sealed with parafilm that is partially a closed system. Salt 1 and Salt 2 decomposed and made precipitates during the heating. The concentrations of salts when taking the NMR spectra are therefore not the same. In order to avoid changes in concentration caused by taking samples and putting them back into the plastic vial, a second stability test was developed. Salt 1 and Salt 2 and BTMAH were dissolved in aqueous KOH, and the solutions were placed in fluoropolymer NMR tube liners, which is more convenient than using the plastic vials. The result should be more accurate without transferring salt solutions between NMR tubes and reaction vials. The third stability test compares the alkaline stability of Salt 2 in solutions of different concentrations of KOH.

3.3.1 First Stability test:

Salt 1 and Salt 2 were dissolved in aqueous 1 M KOH, and the solutions were placed in plastic vials sealed with parafilm to create an isolated condition. These solutions were heated at different temperatures to characterize their stability in 1 M aqueous KOH solution. The Salt 1 solution remained clear with no change in the $^1$H NMR spectrum after heating to 60°C for 2 days. The solution was then heated to 70°C for 2 days, and it was observed that the solution became brown and some precipitate had formed but there was no evidence showing decomposition in the $^1$H NMR spectrum. The solution continues being heated to 80°C for 2 days and then at 90°C for 2 days. The $^1$H
NMR spectra (high temperature NMR 80 °C and 90 °C) showed the compound to be stable in 1 M KOH even when heated to 90 °C. The spectra are shown in Appendix A.

**Salt 2** was heated in a similar manner at 60 °C for 48 hours. The solution became white and cloudy, but no change was observed in the $^1$H NMR spectrum (high temperature NMR 60 °C). The solution started to become brown, and some white precipitate formed at the bottom of the tube, but still no change was observed in the $^1$H NMR spectrum after heating at 70 °C for 2 days (high temperature NMR 70 °C). Heating of solution continued at 80 °C for 2 days and at 90 °C for another 2 days. The $^1$H NMR spectrum (high temperature NMR 80 °C and 90 °C) showed the compound to be stable at 80 °C, but it started to decompose at 90 °C. The -(CH$_3$)$_3$ peak at 3.17 ppm from the trimethylammonium group had a large decrease in intensity. High-temperature is required to obtain the NMR spectra, because the compounds have low solubility in water and in aqueous KOH solutions at room temperature. Also, a nitrogen chiral center exists in **Salt 2** and the protons at the $\alpha$ carbon atom to this chiral center need high-temperature NMR spectroscopy to be resolved clearly (**Scheme 3.5**). The two protons on the carbon atom beside this nitrogen atom are diastereotopic protons that are magnetically non-equivalent. These protons have a favored conformation at room temperature, and the heat provides kinetic energy for the S-N linkage to spin which for rapid spinnings makes the protons equivalent. The hindered rotation is around the S–N bond, which has double-bond character which is responsible for slow rotation of S-N bond.$^{15,16}$ In the $^1$H NMR spectrum, the protons will merge from two peaks to one peak as temperature is increased. Moreover, due to the low solubility, the solution is not uniformly distributed in the plastic
vial, there is evidence of precipitation and multiple liquid phase formation. Meanwhile, the solution needs to be taken out and put back into the plastic vial in order to obtain NMR spectra, so the concentration and precipitate are hard to control.

Scheme 3.5. The nitrogen chiral center of Salt 2.
Figure 3.1. The protons on the merge from two peaks to one peak with heating at 65°C
(1) Salt 2 at room temperature (2) Salt 2 at 65 °C.
3.3.2 Second stability test:

Improvement: The experiments are conducted in fluoropolymer NMR tube liners to avoid the concentration changes caused by the salts being taking out and put back into plastic vials. The NMR spectrum can be taken by putting the fluoropolymer liner filled with a solution of sample in a glass NMR tube with D$_2$O added in the glass NMR tube to get better signal lock. The control groups of H$_2$O and KI as standards also prepared to compare with results using KOH. Also, the temperature should be the same to take high temperature NMR spectra for consistency. Furthermore, both $^1$H NMR and $^{19}$F NMR spectra are needed to investigate the decomposition. Six different samples were studied:

1. 0.1 M Salt 2 in 1 M KOH
2. 0.1 M Benzytrimethylammonium hydroxide (BTMAH) in 1M KOH
3. 0.1 M Salt 2 in H$_2$O
4. 0.1 M BTMAH in H\textsubscript{2}O

5. 0.1 M Salt 2 in 1 M KI

6. 0.1 M BTMAH in 1 M KI

The alkaline stability of benzyltrimethylammonium hydroxide (BTMAH) has been widely studied, and lots of papers have been published.\textsuperscript{14,17,18} To use BTMAH as a control group, the validity and accuracy of the compound results can be easily confirmed by comparison to literature reports that 0.1 and 0.01 M BTMAH in 2 M KOH heated at 80 °C result in a predicted half-life of greater than 4 years; e.g. only 10% degradation occurs after heating 5300 hours.\textsuperscript{14} The NMR spectra seem indicate that Salt 2 is stable in H\textsubscript{2}O and 1 M KOH from room temperature to 90 °C. However, when Salt 2 was added into a KI solution for a few hours, the color changed to yellow. The speculation is that the iodide exposed to air forms a small amount of iodine or tri-iodide. Salt 2 has low solubility in KI solution, even after heating the solution, according to the NMR spectrum. Also Figure 3.3 confirms that instead of dissolving in an aqueous KI solution, Salt 2 generates some brown precipitate at 90 °C. On the other hand, the BTMAH solution is stable in KI solution.
3.3.3 Third stability test:

The second stability test did not reveal much about the alkaline stability of the model compounds, so a third test was attempted. The effects of different concentrations of KOH base on model compound stability were studied. Samples were heated from room temperature to 60 °C for two days in an oil bath, and then the liners were put in glass NMR tube that contained D$_2$O to take the NMR spectrum (all NMR spectra have recorded at 65°C). After acquiring the NMR spectra, the liners were put back to the oil bath and the temperature is increased to 80 °C for another two days and takes the NMR spectrum.

1. 0.1 M Salt 2 in H$_2$O

2. 0.1 M Salt 2 in 1 M KOH
3. 0.1 M Salt 2 in 2 M KOH
4. 0.1 M Salt 2 in 4 M KOH
5. 0.1 M Salt 2 in 6 M KOH
6. 0.1 M Salt 2 in D₂O

Figure 3.4. $^1$H and $^{19}$F NMR spectra of alkaline stability test of Salt 2 in H₂O at (1) RT (2) 60 °C, and (3) 80 °C.
Figure 3.5. $^1$H and $^{19}$F NMR spectra of alkaline stability test of Salt 2 in 1M KOH at (1) RT (2) 60 °C, and (3) 80 °C.

$^1$H NMR spectrum of Salt 2 in 2 M KOH

$^{19}$F spectrum of Salt 2 in 2 M KOH

Figure 3.6. $^1$H and $^{19}$F NMR spectra of alkaline stability test of salt 2 in 2M KOH at (1) RT (2) 60 °C, and (3) 80 °C.

$^1$H NMR spectrum of Salt 2 in 4 M KOH

$^{19}$F NMR spectrum of Salt 2 in 4 M KOH
Figure 3.7. $^1$H and $^{19}$F NMR spectra of alkaline stability test of salt 2 in 4M KOH at (1) RT (2) 60 °C, and (3) 80 °C.

Figure 3.8. $^1$H and $^{19}$F NMR spectra of alkaline stability test of salt 2 in 6M KOH at (1) RT (2) 60 °C, and (3) 80 °C.

As shown in Figures 3.4 and Figure 3.5, salt 2 remains stable in H$_2$O and 1 M KOH from room temperature to 90 °C, and hardly any change observed in the $^1$H NMR and $^{19}$F NMR spectra. In 2 M KOH (Figure 3.6), salt 2 shows some evidence of decomposition in the $^{19}$F NMR spectrum, where a new peak is generated when the salt 2 sample is heated to 80 °C. The large noise of the $^{19}$F NMR spectrum is thought to be due to the precipitattion of the salt in the fluoropolymer liner. The solution becomes brown and has two separated liquid layers. As the concentration of base increase, the solubility
of Salt 2 gets lower. Interestingly, the $^1$H NMR spectrum of Salt 2 in 2 M KOH after 80°C treatment is nearly unchanged. In the 4 M KOH (Figure 3.7), Salt 2 shows degradation when heated to 60 °C. The $^1$H NMR peaks between 3.0-3.5ppm disappear and a new peak (2.1 ppm) is observed in the $^1$H NMR spectrum. The peak is determined to be trimethylamine, one of the decomposition products of Salt 2 that will be discussed later in the decomposition pathway findings (Section 3.3.5). Also, the $^{19}$F NMR spectrum shows an interesting change in the peak near -112 ppm, which is split into two peaks. This finding may indicate hydrolysis of either the S-N or N-C bond in the sulfonamide group.

Table 3.1. Stability of Salt 2 in aqueous solutions of different concentrations of aqueous KOH at different temperatures.

<table>
<thead>
<tr>
<th>Molarity</th>
<th>H₂O</th>
<th>1M KOH</th>
<th>2M KOH</th>
<th>4M KOH</th>
<th>6M KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Decompose</td>
</tr>
<tr>
<td>60</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Decompose</td>
<td>Decompose</td>
</tr>
<tr>
<td>80</td>
<td>Stable</td>
<td>Stable</td>
<td>Decompose</td>
<td>Decompose</td>
<td>Decompose</td>
</tr>
</tbody>
</table>
In 6 M KOH (Figure 3.8), Salt 2 was found to already be decomposed before the solution was heated. The $^1$H NMR spectrum is hard to read at room temperature because of the low solubility of Salt 2 after decomposition in 6 M KOH. The concentration of base has larger effect on the degradation of quaternary ammonium salt than temperature. The NMR spectra showed that Salt 2 has high stability in water and 1 M KOH even when heated at 80 °C. However, when Salt 2 is exposed to 6 M KOH even without heating, Salt 2 decompose directly. Table 3.1 summarizes the alkaline decomposition studies just described.

3.3.4 Zwitterion test:

There is no obvious observation showing the decomposition of sulfonamide group in the previous test, however it is predicted that Salt 1 might be a zwitterion$^{19}$. The pKa of NH$_2$SO$_2$CF$_3$ is 6.33 and the pKa of CH$_3$NHSO$_2$CF$_3$ is 7.56, which means the increase of the substituent group may increase the pKa but not by enough to prevent deprotonation in strong base. Moreover, as the fluoroalkyl group gets longer, the pKa of sulfonamide should be smaller due to the strong electron-withdrawing characteristic of fluoroalkyl group, which will serve to stabilize to conjugate base following deprotonation$^{11}$. The acidic proton on sulfonamide group can be easily taken off in the base condition and added back in acidic condition as illustrated in Scheme 3.6

58
Both Salt 1 and Salt 2 were tested by dissolving them in water, then adding KOH solution to study the changing on the NMR spectrum from neutral conditions to base conditions, followed by adding HCl to make the solution neutral again to see if the process is reversible. On the $^{19}$F NMR spectra of Salt 1, the shifting for each corresponding peak is thought to indicate the co-existence of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$N$^+$((CH$_3$)$_3$I$^-$ and $n$-C$_4$F$_9$SO$_2$N’CH$_2$CH$_2$CH$_2$N$^+$((CH$_3$)$_3$I$^-$ in base condition (Figure 3.9). After neutralizing the solution, the shifting peaks disappeared indicating the disappearance of $n$-C$_4$F$_9$SO$_2$N’CH$_2$CH$_2$CH$_2$N$^+$((CH$_3$)$_3$I$^-$. The original peaks maintain at the same position, which confirmed Salt 1, is zwitterion and the process is reversible. Surprisingly, Salt 2, decomposed in alkaline conditions showing in the $^{19}$F NMR spectrum, after neutralized the solution by HCl, the strange peaks on $^{19}$F NMR spectrum are even more than in the alkaline conditions. The decomposition process of Salt 2 is non-reversible. (Figure 3.10)
Figure 3.9. $^1$H NMR spectrum of Salt 2 in a neutral condition (1) H$_2$O, then (2) 2 M KOH was added, and finally HCl is added, and (3) neutralized.
Figure 3.10: $^{19}$F NMR spectrum of Salt 1 in neutral solution (1) H$_2$O, then (2) 2M KOH was added, and finally HCl is added, and (3) neutralized.
Figure 3.11. $^1\text{H}$ NMR spectrum of Salt 2 in (1) H$_2$O, (2) 2 M KOH, and (3) neutralized.
Figure 3.12. $^{19}$F NMR spectrum of Salt 2 in (1) H$_2$O, (2) 2 M KOH, and (3) neutralized.
3.3.5 Findings of decomposition pathway:

According to the proposed decomposition mechanism of the quaternary ammonium of Salt 2, there are five degradation products that may be generated from Salt 2 by Hofmann elimination and/or nucleophilic attack.\textsuperscript{20,21} The five products are listed below, and are numbered 1 to 5 (\textbf{Scheme 3.7}): 

\textbf{Nucleophilic attack}

\textbf{Hofmann elimination}

\textbf{Scheme 3.7.} Degradation of quaternary ammonium groups through nucleophilic substitution and Hofmann elimination.

1. $n$-C$_4$F$_8$SO$_2$N(CH$_3$)CH$_2$CH$_2$CH$_2$OH
2. \( n-C_4F_9SO_2N(CH_3)CH_2CH_2CH_2N(CH_3)_2 \) (compound 4)

3. \( n-C_4F_9SO_2N(CH_3)CH_2CH_2=CH_2 \)

4. CH_3OH

5. N(CH_3)_3

To determine the decomposition pathway, methanol and trimethylamine (TMA) were directly added to the already decomposed samples to compare the NMR signals from methanol and TMA with the signals generated following Salt 2 decomposition. Methanol is not one of the degradation products based on the \(^1\)H NMR spectrum. For example, a new peak is generated when methanol is added that was not present in the spectrum of the decomposed Salt 2, which means that methanol may be ruled out as a decomposition product. When TMA was added, however, the peak at 2.17 ppm became larger instead of producing a new peak (Figure 3.13). This result indicates that TMA is one of the degradation products. The perfluoro-\(n\)-butanesulfonamide alkene and/or alcohol products (1 and 3 above) are expected to be soluble in organic solvents. Salt 2 was exposed to 4 M KOH solution, and then the solution was neutralized. The neutralized solution was extracted with CDCl_3. Finally, NMR spectra were recorded on the CDCl_3 solution. From the NMR spectrum, the alkene with chemical shift between 5-6ppm was not present. The peaks of perfluoro-\(n\)-butanesulfonamide were also hard to determine due to the unusual integrals. The decomposition pathway of the compound is thus considered to be the Hofmann elimination because the four decomposition products of a nucleophilic attack should accompany each other. Methanol and TMA are surely soluble in water, but methanol was not present as one of the degradation product. The Hofmann elimination is
the favored decomposition pathway for aliphatic quaternary ammonium salts in strong basic conditions. The iodide anion was substituted by hydroxide, and finally hydroxide will attack a β-hydrogen atom to remove that hydrogen atom by base abstraction. Thus a alkene is formed by elimination. This pathway can give rise to AEM having low thermal and chemical stabilities. If no β-hydrogen atoms are present, the direct nucleophilic substitution reactions are generally thought to take place and yielding the formation of alcohol and tertiary amine groups.\(^\text{14}\)

\[ \text{Figure 3.13.} \] \(^{1}\)H NMR spectrum of (1) decomposed n-C\(_4\)F\(_9\)SO\(_2\)N(CH\(_3\))CH\(_2\)CH\(_2\)CH\(_2\)N(\(+\)\)(CH\(_3\))\(_3\)I\(_\text{(-)}\) (2) added methanol, and (3) then added TMA.
**Figure 3.14.** $^1$H NMR spectrum of decomposed n-C$_4$F$_9$SO$_2$N(CH$_3$)CH$_2$CH$_2$CH$_2$N$^{(+)\,(CH$_3$)$_3$I^{(-)}}$ extracted by CDCl$_3$. 
Figure 3.15. Comparison of $^1$H NMR spectrum of (1) Salt 2 in CDCl$_3$ and (2) decomposed Salt 2 extracted by CDCl$_3$. 
Figure 3.16. $^{19}$F NMR spectrum of decomposed n-
C$_4$F$_5$SO$_2$N(CH$_3$)CH$_2$CH$_2$CH$_2$N$^{(+)}$(CH$_3$)$_3$I$^{(-)}$ extracted by CDCl$_3$. 
3.3.6 Conclusion

In this study, the NMR spectral evidence suggests that the quaternary ammonium group in the model compounds is the first site of decomposition in strongly alkaline conditions. Contrary to an initial assumption at the beginning of this work that the hydrogen atom on the sulfonamide group will react with KOH and result in the cleavage of bonds, Salt 1 is zwitterion and does not appear to decompose in a high pH environment. From the decomposition pathway findings, the data showed that one of the nucleophilic attack mechanisms does not occur as methanol is not one of the decomposition products. It was also found that very high KOH concentrations (4-6 M) provide very challenging conditions for testing AEM stability, much more so than elevated temperature.
References


CHAPTER 4

CONCLUSIONS AND FUTURE WORKS

In this work, the thermal stability of perfluoroalkyl cationic model compounds has been studied. Different from the previous thought that hydrogen on the sulfur will cause the decomposition of sulfonamide or amine group, the bond is strong and shows high stability in 6M KOH at 90°C. Though salt 1 is zwitterion and it doesn’t degrade, the hydroxide ion reacts with dissociated H⁺ and would result in poor hydroxide conductivity in a membrane that influences the AFC performance so the methylation is still needed. Trimethylammonium group is the only degradable group found in the research. To further improve the stability, no β-hydrogen quaternary ammonium group such as N,N-dicyclohexyl-N-methyl-benzene-methanaminium, phenyltrimethylammonium and benzyltrimethylammonium can be tried to prevent the Hoffman elimination. The stability may be promoted by increasing the number of cationic groups.

Scheme 4.1 Structure of 3,3’-iminobis (N,N-dimethylpropylamine)
For example, 3,3’-iminobis (N,N-dimethylpropylamine) has two quaternary ammonium group that improved AEM ionic conductivity and may possibly increase the time of fully degradation.
APPENDICES
Appendix A

Synthesis of perfluoro-\textit{n}-butyl sulfonamides & quaternary ammonium salts

Figure A-1. $^1$H NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$CH$_3$ (Compound 1).
Figure A-2. $^{19}$F NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_3$CH$_3$ (Compound 1).
Figure A-3. $^1$H NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$CH$_3$ (Compound 2).
Figure A-4. $^{19}$F NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$CH$_3$ (Compound 2).
Figure A-5. $^1$H NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ (Compound 3).
Figure A-6. $^{19}$F NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$

(Compound 3)
Figure A-7. $^1$H NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ (Compound 4).
Figure A-8. $^{19}$F NMR spectrum (in CDCl$_3$) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$N(CH$_3$)$_2$

(Compound 4).
Figure A-9. $^1$H NMR spectrum (in D$_2$O) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$CH$_2$N$^+$($\text{CH}_3$)$_3$I (Salt 1).
Figure A-10. $^{19}$F NMR spectrum (in D$_2$O) of $n$-C$_4$F$_9$SO$_2$NHCH$_2$CH$_2$N$^+$CH$_3$)$_3$I (Salt 1).
Figure A-11. $^1$H NMR spectrum (in D$_2$O) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$N$^+$CH$_3$I$^-$ (Salt 2).
Figure A-12. $^{19}$F NMR spectrum (in D$_2$O) of $n$-C$_4$F$_9$SO$_2$N(CH$_3$)$_2$CH$_2$CH$_2$N$^+$CH$_3$)$_3$I 

(Salt 2)
Figure A-13. Elemental analysis data of Salt 1.

<table>
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<tr>
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<th>Found</th>
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<tbody>
<tr>
<td>C</td>
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</tr>
<tr>
<td>H</td>
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<tr>
<td>N</td>
<td>5.13</td>
<td>5.22</td>
</tr>
</tbody>
</table>
Figure A-14. Elemental analysis data of Salt 2.
Appendix B

Stability study of perfluoro-\textit{n}-butyl sulfonamide quaternary ammonium salts

Figure B-1. $^1$H NMR spectrum of Salt 1 in 1 M KOH at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 1).
Figure B-2. $^1$H NMR spectrum of **Salt 2** in 1 M KOH at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 1).
Figure B-3. $^1$H NMR spectrum of **Salt 2** in 1 M KOH at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-4. $^{19}$F NMR spectrum of **Salt 2** in 1 M KOH at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-5. $^1$H NMR spectrum of BTMAH in 1 M KOH at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-6. $^1$H NMR spectrum of Salt 2 in H$_2$O at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-7. $^{19}$F NMR spectrum of Salt 2 in H$_2$O at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-8. $^1$H NMR spectrum of BTMAH in H$_2$O at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-9. $^1$H NMR spectrum of Salt 2 in 1 M KI at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-10. $^{19}$F NMR spectrum of Salt 2 in 1 M KI at (1) 60$^\circ$C (2) 70$^\circ$C (3) 80$^\circ$C, and (4) 90$^\circ$C (Stability test 2).
Figure B-11. $^1$H NMR spectrum of BTMAH in 1 M KI at (1) 60 °C (2) 70 °C (3) 80 °C, and (4) 90 °C (Stability test 2).
Figure B-12. $^1$H NMR spectrum of **Salt 2** in H$_2$O at (1) RT (2) 60°C, and (3) 80°C (Stability test 3).
Figure B-13. $^{19}$F NMR spectrum of Salt 2 in H$_2$O at (1) RT (2) 60°C, and (3) 80°C (Stability test 3).
Figure B-14. $^1$H NMR spectrum of Salt 2 in 1M KOH at (1) RT (2) 60$^\circ$C, and (3) 80$^\circ$C (Stability test 3).
Figure B-15. $^{19}$F NMR spectrum of Salt 2 in 1M KOH at (1) RT (2) 60°C, and (3) 80°C (Stability test 3).
Figure B-16. $^1$H NMR spectrum of Salt 2 in 2 M KOH at (1) RT (2) 60°C, and (3) 80°C (Stability test 3).
Figure B-17. $^{19}$F NMR spectrum of Salt 2 in 2 M KOH at (1) RT (2) 60 °C, and (3) 80 °C (Stability test 3).
Figure B-18. $^1$H NMR spectrum of **Salt 2** in 4 M KOH at (1) RT, (2) 60 °C, and (3) 80 °C (Stability test 3).
Figure B-19. $^{19}$F NMR spectrum of **Salt 2** in 4 M KOH at (1) RT (2) 60 °C, and (3) 80 °C (Stability test 3).
Figure B-20. $^1$H NMR spectrum of Salt 2 in 6 M KOH at (1) RT (2) 60 °C, and (3) 80 °C (Stability test 3).
Figure B-21. $^{19}\text{F}$ NMR spectrum of **Salt 2** in 6 M KOH at (1) RT (2) 60 °C, and (3) 80 °C (Stability test 3).