Assessment of PEMFC
Durability by Effluent Analysis

Thesis for the degree of Philosophiae Doctor

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Norwegian University of Science and Technology
Department of Chemistry
Acknowledgement

Shortly after the start of my career as a researcher at SINTEF Chemistry, I met Professor Signe Kjelstrup. Her encouragement to pursue a doctorate degree as well being able to find funding for a project with a relevant research topic, made this PhD work possible. The original project, funded by Nordisk Industrieforskning, was given the ambitious title “A novel membrane for the polymer electrolyte fuel cell”. At the project start, the performance and durability of a polyvinylidene fluoride polymer functionalized by irradiation grafting was evaluated. It was quickly verified that the durability of this membrane was vastly inferior to the state of the art perfluorinated alternatives. At this stage in the project, Professor Kjelstrup gave me the freedom to redefine the project. I resolved to use my knowledge in fluorine chemistry as a basis; to evaluate durability of PEM fuel cells by monitoring fluorine emission rates. This shifted the focus of the project towards analytical chemistry, and my work more peripheral to the rest of her research group. Undoubtedly, I was forced to work more independently. Nevertheless, her support for my work was always felt and her intellect and quick perception made it easy to follow and provide constructive feedback on my progress. Thank you, Signe!

As a young researcher with ownership in several running projects, it was never an option to leave SINTEF full time to work on the PhD project. My research managers at SINTEF Materials and Chemistry provided the possibility of working part time at SINTEF. Although a challenging combination, the overlap between PhD project and SINTEF project work made this an interesting combination. The transition back to working full time at SINTEF was also without complications. Thank you, Torstein Haarberg, Rune Bredesen and Arne Petter Ratvik.

My mentor at SINTEF was Chief Scientist Kalman Nagy. He taught me everything I know about fluorine chemistry and ion-selective electrodes. His knowledge extends beyond the scientific aspects; he taught me how to establish good relations with potential project partners in industry. We have shared many social occasions, the highlights probably found at his wine farm in Somlószölös in Hungary. I cannot
possibly acknowledge Kalman without mention of his elegant and charming wife, Randi. Thank you, Kalman and Randi.

My work at SINTEF has always been a large part of my life; science is in many ways a cruel mistress and takes a substantial amount of your time. It is therefore paramount to have a good working environment where your colleagues also are your friends. There are people at work that fill my every need of friendship, and I could not wish for a better place to spend my days. Thank you, Arne Petter Ratvik, Christian Schoning, Egil Skybakmoen, Asbjorn Solheim, Ove Bjorn Paulsen, Karen Sende Osen, Steffen Moller-Holst, Anders Odegard, Ann Mari Svensson, Magnus Thomassen, Bjarte Arne Oye, Sverre Rolseth, and Julian Tolchard. The list goes on and on...

In 2007, Sissel and I (and our two-year old male German Shepherd Dog, Gringo) decided to expand our family. I still vividly remember the statement “There’s more in here” from our first ultrasound examination. February 18, 2008 Thomas and Erik Nybroen Aarhaug were born. Our lives were suddenly turned upside down; priorities completely transferred, work included. Suddenly, work had to be performed during working hours. Books and publications were stopped being dragged to and from work. This was probably for the better, since these were mostly transported to and not read at home. Of course, this also delayed the completion of this thesis work, as full working days left little time for work on the thesis. Although there are times when I wonder how to find strength and patience for my twin boys, they bring a dimension to my life I cherish to a point I did not believe to be possible. In times of trouble and despair, the shift of focus from yourself to your kids puts everything into perspective and makes everything all right; your kids are what’s important and all else is secondary. It makes things simple when one’s mind tries to complicate them. Although the dogs are gone, Sissel and I both miss all our three German Shepherds. We hope one day to find the time to yet again be proud owners of a German Shepherd Dog. Thank you Sissel, you are the cornerstone of my life, the rock solid hub that keeps everything in place when I spin around during my ups and downs. Thank you Thomas and Erik for making my life so much richer! I can’t wait to spend the rest of my life trying to be a good father, safely guiding you through what is good, but also what is not so good in life.
My personality is of an expansive nature: I always tend to find new and exciting things in science to pursue. In SINTEF, the freedom of pursuit is almost unlimited. This is, for me, often at the cost of sufficient scientific depth and sustainability on the individual topics. This thesis project forced me to work more fundamentally, and the boundaries given by the thesis work has felt comfortable. I can now enter this topic with a feeling of self-confidence and with a genuine desire to know more. I appreciate the opportunity given to me to perform this thesis project.
Summary

A review of literature relevant for the understanding of chemical degradation in Polymer Electrolyte Membrane (PEM) systems was conducted. The proposed pathways to the formation of chemical species suspected of causing degradation were summarized. The structures of the most common PerFluorinated Sulfonic Acid (PFSA) ionomers were presented. The proposed mechanisms of chemical degradation were listed with reference to their point of attack on the ionomer structure. The role of Fluoride Emission Rate (FER) as a metric for chemical degradation rate was discussed. Several papers present results where fluorocarbon fragments are present in the effluent water. The quantification of these fragments was scarce, but results indicate that their amount may depend on fuel cell test hardware as well as the test operating conditions.

A novel methodology for simultaneous analysis of fluorine and fluoride were presented. By alkaline fusion, the fluorocarbons were digested and fluorine completely recovered as fluoride. Fluoride concentrations were then estimated for both digested and untreated samples by means of potentiometric analysis. By application of a fluoride selective electrode in acidic media, improved sensitivity was obtained. The proposed methodology was evaluated statistically. Using PolyTetraFluoroEthylene (PTFE) as a model compound, excellent recovery of fluorine was documented.

A review of papers presenting FER data was performed and the results were summarized with reference to the operating conditions testing were conducted. FER data span several decades in magnitude. A non-accelerated durability experiment was conducted to evaluate both FER as well as total Fluorine Emission Rates (FtER) throughout the experiment. Cathode and anode effluents were scrubbed in sodium hydroxide gas bubblers. In addition, a fluoride selective electrode was mounted in an anode gas bubbler in order to continuously monitor the accumulated fluoride concentration. The results show that the FtER to FER ratio is significantly higher than one. For the cathode FtER was initially high and decreasing with time. Cathodic FER
Summary was increasing although less pronounced than the FtER decrease. As a result a decreasing FtER to FER ration was found. At the anode, a correlation between online FER and the FER found from batch analysis was found; both increasing with time. Cathodic FtER and FER were always higher than their anode equivalent. No correlation with fuel cell performance data was found. The results showed that for the non-accelerated test protocol applied, significant amounts of fluorocarbons leaves the fuel cell. Further, the ratio of FtER to FER also changed with time, suggesting that the FER metric does not represent a constant fraction of the ionomer loss throughout the experiment.

An accelerated durability experiment was conducted in order to evaluate FER as a function of gas flow rates at Open Circuit Voltage. It was found that a five-fold increase in gas flow rates resulted in FER that was more than five times higher. It was speculated that the increase in FER was caused by increased gas cross-over. For both gas flow levels, FER was sharply decreasing with time. Performance losses were higher for high gas flow rates, although a direct correlation between performance data and FER could not be obtained.

Experimental design was applied in order to evaluate several operational parameters and their impact on fuel cell performance and durability. An ON/OFF accelerated protocol was applied. Gas humidification level, clamping pressure and pressurized operation were used as input parameters. It was found that 100 % humidified reactant gases and pressurized operation gave superior performance and durability. FER was lower for high humidification, but higher for pressurized operation. In other words, the lowest FER was not found for the experiment showing superior durability.

Interestingly, similar FER was recorded for repeated experiments where carbon flow fields were replaced with stainless steel ones. SER was found to be much higher than FER. As the ionomer structure suggests SER to be significantly lower than FER, it was believe that the ionomer was not the only source of sulfur. Sulfur levels were initially high, and highest for experiments with 100 % humidified gases. After an initial decay, SER nevertheless stabilized at a higher level than FER. It was not understood why the assumed contamination of sulfur did not wash out with time. An attempt to evaluate the background levels of fluoride and sulfate in the fuel cell test rig was attempted. It was found that significant levels of both were present at the test startup. Purging with inert gas did however reduce the fluoride and sulfate levels to
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Nomenclature

CI  Current Interrupt
DFT  Density Functional Theory
DMPO  DiMethyl Pyrroline Oxide
ECSA  ElectroChemical Surface Area
EIS  Electrochemical Impedance Spectroscopy
EMPA  Electron MicroProbe Analysis
EMF  ElectroMotive Force
ESR  Electron Spin Resonance spectroscopy
EW  Equivalent Weight
FER  Fluoride Emission Rate
F-ISE  Fluoride-Ion Selective Electrode
FRR  Fluoride Release Rate
FtER  Total Fluorine Emission Rate
FTIR  Fourier Transform Infrared Spectroscopy
IEC  Ion-Exchange Capacity
HFR  High Frequency Resistance
ISE  Ion-Selective Electrode
LC  Liquid Chromatography
LOD  Limit Of Detection
LOQ  Limit Of Quantification
MEA  Membrane Electrode Assembly
MS  Mass Spectrometry
MW  Molecular Weight
NHE  Normal Hydrogen Electrode
NMR  Nuclear Magnetic Resonance
OCV  Open Circuit Voltage
ORR  Oxygen Reduction Reaction
PFSA  Proton Conducting Sulfonic Acid
PSSA  PolyStyrene Sulfonic Acid
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>PolyTetraFluoeroEthylene</td>
</tr>
<tr>
<td>RDS</td>
<td>Rate Determining Step</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SD</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SER</td>
<td>Sulfur Emission Rate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFA</td>
<td>TriFluoroAcetic acid</td>
</tr>
<tr>
<td>TFE</td>
<td>TetraFluoroEthylene</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TISAB</td>
<td>Total Ionic Strength Adjustment Buffer</td>
</tr>
<tr>
<td>TOF-SIMS</td>
<td>Time-Of-Flight Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>USFCC</td>
<td>US Fuel Cell Council</td>
</tr>
<tr>
<td>WER</td>
<td>Water Emission Rate</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
1 Introduction

Although the principles of fuel cells were discovered and described as early as 1838 by German scientist G.F. Schönbein [1], it was not until 1955 that W. Thomas Grubb of General Electric first explored the concept of a Proton-Exchange Membrane Fuel Cell (PEMFC). The first attempt at a solid polymer electrolyte was synthesized by condensation of phenolsulfonic acid and formaldehyde. The polymer was brittle and hydrolyzed readily, yielding sulfuric acid [2]. These setbacks were the reason why the Gemini 1-4 missions used batteries rather than fuel cells. Partially sulfonated polystyrene was also explored, but did not show much improvement neither chemically nor mechanically. The first membrane to be implemented at a power source system level was prepared by cross-linking or grafting styrene-divinylbenzene into a matrix of fluorocarbon followed by sulfonation. Although some difficulties had to be overcome in its first application in the Gemini 5 mission in 1965, this membrane type successfully served the remainder of the Gemini missions. The requirement for a reactant gas humidification system for PEMFC contributed to the decision of using alkaline fuel cells for the subsequent Apollo and Space Shuttle NASA missions. Despite the initial failure in space applications, research was conducted to improve durability of the solid polymer electrolyte. It was found that an alpha C-H bond present in the styrene-divinylbenzene structure was limiting for membrane lifetime [2]. The first efforts to eliminate this C-H bond involved the use of polystyrene sulfonic acid (PSSA) membranes. With the introduction of Nafion® in 1966, focus was heavily shifted towards perfluorinated aliphatic structures. Although most commercial applications of PEMFCs have made use of Nafion® or derivatives thereof, Ballard Power Systems, Inc. is still using trifluorostyrene and substituted trifluorostyrene copolymer membranes.

1.1 Perspectives on PEMFC commercialization

PEMFC systems are today commercially available. For transportation, forklifts have shown to be a niche market well suited for PEM fuel cells in a hybrid configuration with batteries. Although the author of this thesis first drove a PEM fuel cell car in 2005,
they are still not commercially available for purchase. But the technology is maturing fast: a Mercedes-Benz 2011 B-Class F Cell car has been available in California through a three-year lease plan at $849 per month. It should be noted that only 70 cars were available for the cities of Los Angeles and San Francisco combined. Moreover, The H2Moves Scandinavia project, supported by the EU-program FCH JU, will for the period 2011-2013 demonstrate 10 fuel cell cars of this type in the Oslo region, and SINTEF Oslo will have one of the cars at its disposal for a year. These demonstration projects will provide invaluable feedback to the car manufacturers which will eventually make the cost of fuel cell cars competitive.

In order to assess the cost-effectiveness of fuel cell systems projected cost analysis at an assumed representative manufacturing rate must be performed. U.S. Department of Energy (DOE) has since 2006 contracted Direct Technologies Inc. (DTI) and TIAX LLX (TIAX) independently to carry out annual fuel cell system cost analysis. Marcinkoski et. al. [3] have reviewed the latest available reports. The analysis is performed on an 80 kWnet system utilizing hydrogen gas as fuel, manufactured at a rate of 500,000 systems annually. Non-technical variables are held constant in order to avoid the impact of cost fluctuation outside the technical domain. As an example, the cost of platinum group metal (PGM) is held constant at $ 35 g⁻¹.

Some of the cost driving items in the most recent cost analyses are shown in Table 1:
Table 1. Selected high cost items of a 80 kWnet PEMFC system from recent DTI and TIAX reports.

<table>
<thead>
<tr>
<th>Selected high cost items</th>
<th>DTI 2010 (US$ per kWnet)</th>
<th>TIAX 2008 (US$ per kWnet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer electrolyte membrane</td>
<td>2.88</td>
<td>2.38</td>
</tr>
<tr>
<td>Catalyst ink and application</td>
<td>8.69</td>
<td>15.43</td>
</tr>
<tr>
<td>Gas diffusion layers</td>
<td>3.03</td>
<td>2.04</td>
</tr>
<tr>
<td>Membrane electrode assembly</td>
<td>3.91</td>
<td>2.56</td>
</tr>
<tr>
<td>Bipolar plates</td>
<td>5.68</td>
<td>2.72</td>
</tr>
<tr>
<td>Air compressor/expander/motor</td>
<td>8.07</td>
<td>7.69</td>
</tr>
<tr>
<td>Membrane air humidifier</td>
<td>1.18</td>
<td>2.29</td>
</tr>
<tr>
<td>Hydrogen sensors</td>
<td>2.47</td>
<td>0.5</td>
</tr>
<tr>
<td>System assembly and testing</td>
<td>1.38</td>
<td>4.03</td>
</tr>
<tr>
<td>Overall estimated cost</td>
<td>51.38</td>
<td>57.48</td>
</tr>
</tbody>
</table>

As expected, the noble metal catalyst contributes significantly to the PEMFC cost. Due to intensive effort towards reducing the catalyst loading in fuel cell systems, this figure has been substantially lowered in the last two years. The 2008 TIAX report estimated catalyst cost to constitute approximately 60% of the overall stack cost.

It is interesting to note that the cost of the polymer electrolyte is lower than all the other components of the PEMFC assembly. The 2008 DTI estimate is based on Gore™ type technology where a 25 µm thick expanded PTFE (ePTFE) film is functionalized with Nafion® type ionomer. The cost of Nafion® is for 500,000 stack units per year estimated to be $ 92 kg⁻¹ or $ 17 m⁻² processed, whereas the ePTFE is estimated at about $ 6 m⁻². The preliminary TIAX estimate for 2010 is based on a 20 µm 3M ePTFE reinforced membrane with a cost of about 19 $ m⁻². As seen from in Table 2, the DOE technical targets for 2010 and 2015 are already met. The materials cost was found to constitute approx. 85% of the overall membrane cost.
Table 2. Some relevant DOE Technical targets\textsuperscript{1} for PEMFC.

<table>
<thead>
<tr>
<th>Component</th>
<th>2005 status</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 kWe stack H\textsubscript{2}</td>
<td>110 $/kWe</td>
<td>45 $/kWe</td>
<td>30 $/kWe</td>
</tr>
<tr>
<td>Electrocatalyst ($15/g Pt, &lt; 0.2 g/kWe)</td>
<td>55 $/kW</td>
<td>5 $/kW</td>
<td>3 $/kW</td>
</tr>
<tr>
<td>MEA</td>
<td>60 $/kW</td>
<td>10 $/kW</td>
<td>5 $/kW</td>
</tr>
<tr>
<td>Bipolar plate</td>
<td>10 $/kW</td>
<td>5 $/kW</td>
<td>3 $/kW</td>
</tr>
<tr>
<td>Membrane</td>
<td>25 $/m\textsuperscript{2}</td>
<td>20 $/m\textsuperscript{2}</td>
<td>20 $/m\textsuperscript{2}</td>
</tr>
<tr>
<td>GDL</td>
<td>15 $/m\textsuperscript{2}</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Another important aspect for fuel cell commercialization is durability. The DOE target for 2010 for automotive applications, and unchanged for 2015, is 5000 hours of operation under cycling at 80 °C according to DOE durability protocols. This target is expected to be equivalent to 150,000 miles or 240,000 km on the road. In hybrid systems better durability has been obtained, but as of 2005 the DOE achieved durability status for unbuffered operation was reported to be only 2000 hours. Comparably; for stationary applications the 2011 DOE target is 40,000 hours. As of 2005, 20,000 hours was achieved.

The cost of perfluorinated ionomers has been perceived as high, and this has at least partly been caused of an expensive fluorination process. The membrane cost of the PEMFC system of course reflects that the membrane thickness has been significantly reduced. The economic analyses show that currently the other PEMFC components are more cost driving than the membrane itself. The reduced membrane thickness has the benefit of improved power density, but has a negative effect on durability. In addition to reduced mechanical stability, the increased cross-over of gases enhances chemical degradation of the membrane. The durability for stationary as well as transient operation of PEMFC is far from reaching their respective targets.

1.2 Motivation and aims

The economical considerations before mentioned demonstrate that the membrane is vital component for the commercialization of PEMFC technology. As perfluorinated or

\textsuperscript{1}http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf
partly fluorinated ionomers are currently state-of-the-art technology, the fluoride emission rates are an important metric for the evaluation of ionomer stability.

The motivation for this thesis work originated from the significant discrepancy found in literature when it comes to results from the commonly used Fluoride Emission Rate (FER) method to evaluate PEM fuel cell durability. The emission rates found in literature span several orders of magnitude, and although some of this variation could be ascribed to fuel cell hardware and testing conditions, there is still reason to believe that FER was influenced by factors not yet understood. Analysis of effluent waters by Nuclear Magnetic Resonance (NMR) or Mass Spectrometry (MS) has indicated the presence of fluorocarbons. Quantitative analysis of these fluorocarbons has remained scarce, and upholding the common perception that fluorine leaving the PEMFC can be recovered mainly as fluoride. A main aim for this thesis work has been to provide quantitative data on the emission of fluorocarbons from PEMFCs.

Another challenge for FER analysis has been the low concentration of fluoride found in effluent water. The most commonly used methodology for fluoride analysis is by means of a fluoride-selective electrode potentiometry. The detection limit for this method is in the range 100 to 200 ppb and, unless high degradation rates are observed, will result in low analytical performance. Another source of error often neglected is the interference by Fe\(^{3+}\). In Fenton testing where hydrogen peroxide and ferrous or ferric ions are added to degrade the perfluorosulfonic acid ionomer, ferric ions will form complexes with fluoride. Unless this is remedied by using a complexing agent, the fluoride concentration estimate will be too low.

SINTEF has since the 1960s worked closely with the Norwegian aluminium industry when it comes to environmental aspects of primary aluminium production. Assessment of fluorine emission to the environment has been central in this work, and this has resulted in the development of the SINTALYZER automated analytical system. The system uses an ion selective electrode to quantify fluoride potentiometrically. Samples obtained near and at aluminium primary production locations contain Al\(^{3+}\) ions that, similar to Fe\(^{3+}\), complexes fluoride. SINTEF therefore developed a proprietary acidic
wet chemical method to counteract complexation. Another benefit of this method is improved sensitivity; limit of detection (LOD) and limit of quantification (LOQ) has been found to be 6 and 9 ppb respectively. The SINTALYZER system incorporates several sample digestion methods. In this way, fluorine is recovered as fluoride for subsequent analysis. Although primary developed for samples relevant for aluminium primary production, these procedures have been verified to recover fluorine from fluorocarbon containing materials like ski wax. It was therefore an aim of this thesis work to develop more sensitive fluorine and fluoride analysis methodology, applicable to PEMFC durability research.

1.3 Organization of the thesis

The thesis is organized in an introductory chapter and six subsequent chapters. The first of these, Chapter 2, gives the state of the art of characterization of chemical degradation of fluoropolymer membranes and defines the questions to be investigated in the chapters to follow. This chapter is special in the way that it gives the scientific introduction to the remaining chapters. It is written in the format of a review, and is intended to be published as such a paper.

Chapter 2: Chemical degradation of fluorinated ionomers in Polymer Electrolyte Membrane systems


This chapter reviews literature relevant for chemical degradation of Perfluorinated Sulfonic Acid (PFSA) membranes. The fundamental chemical reactions proposed to contribute to chemical degradation are listed. Structural assessment of PFSA ionomers were made with respect to the proposed points of attack. In addition, the mechanisms of attack are reviewed. Suggested activities for further improved understanding of chemical degradation are proposed.
Chapter 3: Determination of fluorine in PTFE and Nafion® by alkaline fusion and fluoride-selective electrode potentiometry


This paper describes the fluorine and fluoride analysis methodology applied in order to assess FER and Total Fluorine Emission Rates (FtER). Method evaluation was performed in order to document analytical performance.

Chapter 4: Degradation of Polymer Electrolyte Membrane Fuel Cells Monitored by Fluorine and Fluoride Emission Rates


The methodology established in Chapter 3 was applied to a long term durability experiment. As improved quantification levels for fluorine and fluoride were documented, a non-accelerated experiment was chosen. The FER and FtER were compared to the fuel cell performance data. The paper also summarizes FER data previously published.

Chapter 5: Degradation Rates of PEM Fuel Cells Running at Open Circuit Voltage


Open Circuit Voltage (OCV) hold experiments are known to induce very high chemical degradation rates. In this experiment, FER was evaluated as a function of the reactant gas flows. In addition to the observed OCV decay rates and change in membrane resistance, FER was correlated with fuel cell peak effect losses.

Chapter 6: PEMFC Degradation Assessed by Effluent Analysis from Designed Experiments

This paper describes the application of experimental design to fuel cell durability research. Three fuel cell operational parameters: reactant gas relative humidity, fuel cell clamping pressure and reactant gas pressurized operation, were used as input. In addition to performance data, FER and Sulfur Emission Rates (SER) were used as response parameters. Liquid Ion Chromatography was used to analyse fluoride and sulfate in frequently sampled effluent water.

Chapter 7: Patent: Method for potentiometric analysis of fluoride in biological materials

The SINTALYZER system and its analytical methodology were previously sold commercially under a Non-Disclosure Agreement (NDA). A prerequisite for using the SINTALYZER for this thesis work was therefore to evaluate intellectual property protection. This initiated a patenting process by this author in capacity of being the SINTALYZER Project Manager at SINTEF for the last decade. This process concluded that considerable parts of the SINTALYZER system were no longer patentable. An international patent application, PCT/NO09/00313, was however issued for direct analysis of fluoride of biological samples by acid extraction. This patent is currently licensed by Metrohm AG, Switzerland. Although the patent does not cover the application of SINTALYZER to fuel cell durability research, it is included in this thesis for two reasons; firstly, it inevitably became part of the PhD project, and secondly the patent describes in larger detail than found elsewhere in the thesis the acidic wet chemistry used by the SINTALYZER.

1.4 References


2 Chemical Degradation of Fluorinated Ionomers in Polymer Electrolyte Membrane Systems

2.1 Summary

2.1.1 Summary of degradation mechanisms proposed
A summary of the suggested chemical degradation pathways suggested is presented, classified according to the reactive species involved.

Hydroxyl radicals
The hydroxyl radicals are considered to be one of the most reactive species inside a fuel cell. They will readily digest non-perfluorinated end groups in the ionomer structure initiated by hydrogen abstraction. It has also been proposed by Delaney et al. [1] that hydroxyl radicals are capable of abstracting fluorine from the ionomer main chain under dry conditions. Density Function Theory (DFT) calculations has however indicated that this is unlikely [2, 3]. A mechanism where the C-S bond connecting the sulfonic acid functional group to the side chain is broken by hydrolysis, has been proposed by Cipollini [4]. Coms [2] also suggested attack on the sulfonic acid group by hydroxyl radicals. He proposed a mechanism where under dry conditions, hydrogen abstraction occurred. The finding of Trifluoro Acetic Acid (TFA) in fuel cell effluents was by Chen et al. [5] taken as evidence for attack on the secondary ether bridge of the side chain by hydroxyl radicals. Zhou et al. [6] performed experiments with model ionomer compounds exposed to Fenton testing. They concluded that the ether bridge connecting the side chain to the main chain was attacked by hydroxyl radicals.

Hydroperoxyl radicals
The hydroperoxyl radicals are believed to be more abundant than hydroxyl radicals, especially under operating conditions of high humidity levels [2, 4]. Their potency is however considered to be lower than the hydroxyl radicals as seen in Table 9. While Coms [2] has suggested that they have no active part in chemical degradation Delaney
et al. [1] and Cipollini [4] claim they are ascribed to the fast decomposition of end groups, especially under wet conditions.

**Hydrogen peroxide**

The high stability of PFSA ionomers in concentrated solutions of hydrogen peroxide suggests that hydrogen peroxide does not directly attack the ionomer structure. Hydrogen peroxide is, however, an intermediate to radical formation. The role of hydrogen peroxide in chemical degradation has been disputed by Mittal et al. [7] and Liu et al. [8]. Coms [2] have suggested that under dry conditions, for a proton bearing sulfonic acid group, hydrogen peroxide is capable of attack on the sulfonic acid group in the capacity of being a strong alpha effect nucleophile.

**Hydrogen radicals**

Hydrogen radicals have been proposed to be formed by reaction of molecular hydrogen with hydroxyl radicals [2, 9]. According to Table 9, the hydrogen radical is less potent than the hydroxyl radical. Fluorine abstraction is however thermodynamically driven by the formation of the very strong H-F bond. Density Functional Theory (DFT) calculations by Coms [2] suggested this pathway to be likely. Work by Huang et al. [10] has suggested hydrogenation of main chain -CF₂ groups near the anode.

**Metallic impurities**

Although impurities like iron, copper and titanium have been shown to have an impact on chemical degradation in the capacity of being Fenton active [11], their impact in capacity as a counter ion of the ionomer is not well documented. Kadirov et al. [12] have shown decreased stability of PFSA ionomers ion-exchanged with Fe³⁺, even in the absence of hydrogen peroxide giving source to radicals via Fenton reactions.

Table 3 summarizes the mechanisms of chemical degradation proposed in literature.
### Table 3. Summary of degradation mechanisms for main chain (MC) and side chain (SC).

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Mechanism</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>·H</td>
<td>F abstraction</td>
<td>Dry*</td>
<td>[2]</td>
</tr>
<tr>
<td>MC-end group</td>
<td>·OH₂</td>
<td>H abstraction</td>
<td>Wet</td>
<td>[1, 4]</td>
</tr>
<tr>
<td>MC</td>
<td>·OH</td>
<td>F abstraction</td>
<td>Dry</td>
<td>[1]</td>
</tr>
<tr>
<td>MC</td>
<td>·OH</td>
<td>H abstraction</td>
<td>Wet</td>
<td>[1, 2, 4, 13-15]</td>
</tr>
<tr>
<td>SC -SO₃(H)</td>
<td>·OH</td>
<td>C-S (hydrolysis)</td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>SC</td>
<td>·OH</td>
<td>C-C breakage</td>
<td>Dry</td>
<td>[5]</td>
</tr>
<tr>
<td>SC-SO₃H</td>
<td>·OH</td>
<td>H abstraction</td>
<td>Dry</td>
<td>[2]</td>
</tr>
<tr>
<td>SC-SO₃H</td>
<td>H₂O₂</td>
<td>S-O</td>
<td>Dry</td>
<td>[2]</td>
</tr>
<tr>
<td>SC</td>
<td>·OH</td>
<td>C-O-C</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>SC-SO₃⁻</td>
<td>Fe³⁺</td>
<td>C-S</td>
<td>Wet</td>
<td>[12]</td>
</tr>
</tbody>
</table>

*hydrogen radical formation function of ·OH concentration

The mechanisms are illustrated in Figure 1 for dry and wet conditions.

![Figure 1. Chemical attack on PFSA generic structure under humidified and dry conditions. Hydroxyl radicals are indicated with red, hydroperoxyl radicals with green and hydrogen radicals with blue.](image-url)
2.2 Introduction

This paper aims to review literature relevant to the understanding of chemical degradation of Perfluoro Sulfonic Acid (PFSA) ionomers. There are reviews available on the subject of PEM technology durability [16-18], where chemical degradation is treated alongside mechanical and performance degradation. These topics are all interlocked, and the understanding of PEM technology durability requires all topics to be addressed. This review attempts to go into more detail with respect to chemical degradation.

An introduction to PFSA ionomers and the commercially available variants are first given, followed by literature presenting experimental evidence of chemical degradation. The possible pathways to formation of reactive species that are suspected to contribute to chemical degradation in PEM fuel cells are then presented. Proposed mechanisms of degradation are then presented followed by mitigation of chemical degradation.

For ease of reading, a summary of the proposed degradation mechanisms are given in Table 3. A graphical illustration of the chemical attack on a common PFSA is attempted in Figure 1.

2.3 Perfluorinated membranes

2.3.1 Nafion®

DuPont introduced Nafion® in the 1960’s aiming at fuel cell applications in space [19]. It saw a large application in chlor-alkali production, before fuel cell research and development again started dominating Nafion® membrane development twenty years ago. Nafion® is a copolymer of tetrafluoroethylene (TFE, MW = 100 g mol⁻¹), and perfluoro(4-methyl-3,6-dioxa-7-octene-1-sulfonyl fluoride) (MW = 446 g mol⁻¹). The generic structure of the repetitive unit is shown in Figure 2.
Figure 2. Generic Nafion® structure. Carboxylic acid end group inserted to illustrate location in structure. The number of x groups is selected according to the EW of the structure. The y group introduces a secondary ether bridge as well as a –CF₃ group, and the z group is used to control the length of the side chain.

The polymer is converted into an ionomer - an ion conducting polymer - by hydrolysis of the sulfonfyl fluoride group by treatment in alkali hydroxide to an alkali sulfonate form. Acid treatment is then applied in order to convert the ionomer to acid form. The relative amount of the co-monomers determines the equivalent weight (EW) of the copolymer. Typically EW is in the range 800-1500 g [15]. According to the inventor of Nafion®, Walther Grot [20], a copolymer with EW = 1046 g has approximately 140 ion conducting groups per molecule. The estimated molecular weight is thus in the range of 150,000 g mol⁻¹. As Nafion® does not form a true solution, common methodology for MW assessment like light scattering and gel permeation chromatography cannot be applied, resulting in a large variance of MW estimates reported [21].

2.3.2 PFSA derivates of Nafion®

Table 4 lists some commercial derivates of Nafion® [22].

Table 4. List of commercial PFSA. The group indexes x, y and z are illustrated in Figure 2.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®, Flemion™, Aciplex™</td>
<td>6-10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Dow™, Aquion™</td>
<td>3-10</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3M</td>
<td>3-10</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>Asahi-Kasei</td>
<td>3-10</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>
In addition to the variation in EW, length and branching of the side chain is varied for the different PFSA brands.

2.3.3 Proton conduction in PFSA
The morphology of Nafion® is still being investigated. An early visualization of the hydrated Nafion® structure is given by the Cluster-Network model [21]. In this model, the hydrophilic sulfonic acid groups form spherical clusters, often referred to as inverted micelles, with a diameter of 4 nm. These clusters are interconnected with narrow (1 nm) channels thus providing a water percolation network available for conduction of protons and other cations. The mechanisms of proton conductivity in Nafion® has been evaluated by Pivovar et al. [23]. The morphology of the membrane is strongly dependent of the water content. Gottesfeld et al. [24] evaluated Nafion® water uptake, and found that Nafion® 117 boiled in water to uptake roughly 22 water molecules per sulfonic acid group. From saturated vapor, only 14 water molecules were taken up. This discontinuity was explained by that vapor phase condensation of water being less favorable at the hydrophobic surface of the membrane. The thermal history of the samples investigated has been evocated as a plausible reason for the apparent Schroeder paradox occurrence in the case of Nafion® [25].

The hydrophilic/phobic orientation is important when it comes to chemical degradation. The orientation of the ionomer has influence on which part of the structure will be available for attack by reactive species. The hydration state of the ionomer and the uniformity of humidification are both important factors when it comes to chemical degradation rates. The development of membranes with lower EW, and thus higher proton conductivity and water uptake, has resulted in reduced durability [18].

2.3.4 Chemical stability of perfluorinated membranes
The inherent chemical and thermal stability of perfluorinated polymers stem from the carbon fluorine bond strength. The bond strengths of C-F and C-H are on average 460 and 410 kJ mol⁻¹, respectively. Due to the inherent stability of the polymer backbone, the side chain has been considered as a likely target for chemical attack. The C-F bond strength decreases from primary to tertiary organization [2, 14]. It is therefore likely that backbone fluoride abstraction would occur at the carbon connecting the side chain to the backbone. While Schiraldi et al. [14] suggested that ether bridge α-
carbon forms weaker C-F bonds, Coms’ [2] calculations show that an oxygen adjacent to the C-F bond actually strengthens it. Further, the C-C and C-O bonds were found to be stronger than their hydrocarbon equivalents. The finding of complete side chain fragments in fuel cell effluents is in evidence of the C-O bond connecting the side chain to the backbone being broken [26].

The ether bridges and the length of the side chain have been suspected weaknesses of the structure. Branching of the side chain, group y in Figure 2, has also been debated as a possible weakness of the structure. The group introduces both an ether bridge as well as a tertiary C-F bond. Both Chen et al. [5] as well as Ghassemzadeh et al. [27] have given experimental evidence of increased degradation rates originating from this group. Coms [2] suggested that structural orientation due to water solubility might affect degradation rates. Escobedo et al. [28] did not, however, find significant difference in chemical stability between branched and non-branched model ionomer fragments. According to Coms [2], the C-S bond is the weakest bond found in the structure. Model studies of trifluoromethanesulfonic (triflic) and methanesulfonic acid found the C-S bond of triflic acid to be weaker. It was therefore argued that the C-S bond is weakened by the strong electron withdrawing effect of the three fluorine atoms bonded to the carbon atom in addition to the similar effect of the three oxygen atoms bonded to the sulfur atom.

The manufacturing processes of perfluorinated ionomers does not necessarily result in completely fluorinated products. End groups like carboxylic acid are often introduced [29]. Model compound experiments have shown that the chemical stability of structures containing carboxylic groups are inferior to those containing sulfonic acid groups [14, 28]. For each copolymer molecule, there are two possibilities of end groups on the backbone of the ionomer structure.

### 2.4 Experimental assessment of chemical degradation

#### 2.4.1 Introduction

With the introduction of Perfluorinated Sulfonic Acid (PFSA) membranes, the lifetime of fuel cells improved from hundreds to thousands of hours. LaConti et al. [30] reported 60,000 hours of stable operation for Nafion® 120 (250 µm thickness) in the seventies. Improvements in performance and proton conductivity, however, led to the application of thinner membranes with lower equivalent weight, reducing
durability [18]. Nevertheless, Cleghorn et al. [31] has reported 26,300 hours of stationary operation for a Gore™ Select® membrane with 35 µm thickness. With the durability reported, there is an obvious need for accelerated lifetime testing. Current targets for durability are 5,000 and 40,000 hours for transport and stationary applications respectively. There are several operating conditions known to adversely reduce membrane lifetime. The challenge of running accelerated tests is to correlate the effects of accelerated degradation with degradation inflicted when running at normal operating conditions [32].

Chemical degradation is very often coupled with mechanical degradation of the membrane, as mechanical properties of the membrane are deteriorated by chemical attack. Mechanical properties are also degraded, typically by transients in the hydration state. In a fuel cell test, it is difficult to decouple the effects of chemical and mechanical degradation. *Ex-situ* testing has been shown to be useful for evaluating the chemical stability of ionomers, as it effectively discriminates between chemical and mechanical degradation. *Ex-situ* characterization is limited by the fact that samples characterized represent the average of any effect inflicted during the sampling interval.

### 2.4.2 Overview of main parameters impacting chemical degradation rates

**Effect of temperature**

Operating temperature has a high impact on chemical degradation rates. While the intrinsic thermal stability of PFSA membranes in inert and air atmosphere is excellent [33] under 100 °C, chemical degradation rates are drastically increased in the same temperature range. Based on activation energy calculations, LaConti [30] estimated degradation rates to double for every 10 °C increase in operating temperature.

**Effect of relative humidity**

It is generally observed that chemical degradation rates are increased with reduced humidification of the reactant gases [34, 35]. Humidification is interlinked with operating temperature, and non-uniformity of humidification levels within the membrane are more pronounced at elevated temperatures.
2.4 Experimental assessment of chemical degradation

**Effect of operating pressure**
Although pressurized operation is favorable when it comes to water management of the fuel cell, increased chemical degradation is expected due to the increased cross-over of gases from one electrode to the other.

**Effect of reactant gas cross-over**
Of paramount importance to chemical degradation is the cross-over of reactants to the opposite electrode. The membrane permeability to molecular hydrogen is approximately twice that of molecular oxygen [36]. Permeability is hugely dependent on the membrane thickness, but also fuel cell operating conditions. Inaba [37] evaluated the molecular hydrogen cross-over as a function of operating temperature, relative humidity and pressure. He found the cross-over to increase with all parameters, pressure having the greatest influence on cross-over rates. Molecular oxygen permeation rates in Nafion® have also been evaluated [38, 39] as function of operating conditions.

**Effect of load setting**
As will be discussed in detail in Chapter 2.5, the load setting will influence the electrochemical processes occurring at the electrodes. Indirectly, the load setting will affect fuel utilization and reactant gas concentration profiles through the flow fields. Mittal et al. [40] decoupled the effect of current density from gas-cross over, arguing that the production rate of protons and water at the electrode might affect the degradation rate.

2.4.3 **Assessment of chemical degradation**

**Terminology**
Methodologies for assessment of chemical degradation are often classified in terms of *in-situ* and *ex-situ* techniques. *Online* and *post mortem* techniques are alternate terms for basically the same classifications. A methodology is often classified according to being destructive or non-destructive. For *ex-situ* testing, this classification is normally superfluous as indicated by the *post mortem* analogy. For *online* testing, it is important that the methodology applied does not leave a history that will affect the remainder of the durability test. The methodology applied might to various extents be destructive to the fuel cell, or indirectly affect the test result by requiring a change in
operating conditions for the duration of the methodology applied. If neither is the case, the methodology is often characterized as non-destructive.

**Fluoride emission rate**
The Fluoride Emission Rate (FER), *aka* Fluoride Release Rates (FRR), is one of the most commonly used metrics for chemical degradation rate assessment. Potentiometry [41] as well as Ion Chromatography (IC) [5, 35] are the most common methodologies applied for FER assessment. The good analytical performance achieved by cheap and simple instrumentation makes potentiometry attractive. The FER has no impact on the durability experiment as analysis is performed on effluent water. Fragments of fluorocarbons are frequently found in effluents [5, 26, 28]. Therefore, ionomer mass loss cannot be calculated directly from the accumulated fluoride concentration in effluents. The application of FER to fuel cell durability has been reviewed by Aarhaug *et al.* [42].

**Sulfur emission rate**
Less frequently encountered in literature is the Sulfur Emission Rate (SER). Theoretically, the ratio of SER to FER could provide valuable information with respect to the structural break down of the electrolyte membrane. Published data has, however, not proven to be valuable in this respect [5, 35, 37, 43, 44].

**Hydrogen gas cross-over**
The permeation rate of hydrogen to the cathode is often used as end-of-test criterion in durability testing. The permeation rate is commonly found by measuring the current from oxidizing molecular hydrogen at the cathode. A stop of the test is required, as nitrogen gas has to be administered to the cathode. Standardized testing conditions are provided by USFCC [45]. Optionally, the permeation rate can be found by cathode gas analysis.

**Gravimetry**
Loss of ionomer can be found gravimetrically if care is taken to perform measurements under conditions that provide identical water content of the MEA. Degradation, however, has been shown to change the water uptake characteristics of the ionomer [46, 47]. Indirectly, loss of ionomer can be found by dividing the accumulated mass of fluorine released by the theoretical fluorine content of the MEA.
2.4 Experimental assessment of chemical degradation

Microscopy
Scanning electron microscopy (SEM) micrographs are frequently used to illustrate the change in membrane thickness as a result of degradation [36]. Transmission electron microscopy (TEM) has sufficient resolution to identify the ionomer phase of the electrodes [48, 49]. It is thus a valuable tool for assessment of chemical degradation relating to the electrodes.

Ion-exchange capacity
A change in the specific ion-exchange capacity (IEC) of the membrane might be indicative of a degradation mechanism that selectively attacks the ionomer structure. The IEC is found by titrimetry [50].

Electrochemical characterization
Chemical degradation of the ionomer phase in the electrodes will affect the proton conductivity and thus reduce performance. The ElectroChemical Surface Area (ECSA) of the electrodes is assessed by means of cyclic voltammetry [43]. If only moderate oxidation potential is applied, the methodology can be considered non-destructive. The cathode must, however, be flushed with nitrogen gas thus causing a stop in the experiment where no current is drawn from the fuel cell. ECSA does not discriminate between losses from catalyst and ionomer, making interpretation of chemical degradation difficult. In combination with TEM microscopy where the catalyst losses can be estimated, information on chemical degradation of the ionomer can be obtained [43].

Electrochemical Impedance Spectroscopy (EIS) is performed by perturbation of the system load set point. This is performed under normal operation, thus within reasonable amplitudes of either voltage or current, the method can be considered non-destructive. EIS is extensively used for modeling of charge transport and diffusion in the fuel cell [51, 52]. For chemical degradation, EIS data contain information of the proton conductivity of both the bulk membrane as well as the electrodes for a given hydration state. Of particular interest to chemical degradation is the existence of an inductive loop in the low frequency range. Modeling of electrode processes has shown correlation between this loop and hydrogen peroxide formation at the electrodes [53].
Membrane resistivity
Membrane resistivity accounts for most of the ohmic losses in the fuel cell. Thinning of the membrane by degradation would, in the case where specific IEC is sustained, lead to reduced resistance. If the membrane proton conductive groups are selectively attacked, resistance would increase. Membrane resistance varies with water content, thus a comparison must be made at operating conditions with expected identical hydration states. Ohmic losses can be estimated by Current Interrupt (CI) [54] methodology, High Frequency Resistance (HFR) or EIS.

2.4.4 Experimental results contributing to the understanding of chemical degradation

Physical characterization
LaConti et al. [30] performed long-term experiments with PEM stacks using Nafion® 120 membranes (250 µm thickness). These experiments were performed with hydrogen and oxygen as reactants, dead-ended and pressurized to 5 bar for 60,000 hours. Post mortem characterization of the membrane showed that mechanical characteristics of the membrane had deteriorated. Although the water content of the membrane had increased, the IEC was not significantly altered. The experiment was also performed under accelerating conditions where the operating temperature was increased from 60 to 100 °C. After 5000 hours, less than 0.1 % membrane deterioration was observed. Scherer et al. [55] performed water electrolysis experiments by stacking four Nafion® 117 membranes (175 µm thickness). They only found significant evidence of membrane degradation at the cathode. Membrane thickness was reduced to about 70 % of original thickness. The relative IEC was reduced to 55% suggesting the degradation of the membrane to attack the sulfonic acid groups selectively. Stücki et al. [56] evaluated durability of 100 kW PEM water electrolyzers incorporating Nafion® 117 membranes. He found membrane thinning to be limiting for lifetime. The area specific IEC was found to be proportional to the membrane thickness; suggesting homogeneous thinning of the membrane from the hydrogen side. No correlation between FER and lifetime was found. Huang et al. [10] showed evidence of ionomer degradation, by X-ray Photoelectron Spectroscopy (XPS) characterization, in the hydrogen potential region of the fuel cells. The observed formation of -HCF- and -CCF- was ascribed to interactions between carbon, fluorine and hydrogen. Ghassemzadeh et al. [57] applied Magic Angle Spinning
(MAS) $^{19}\text{F}$ and $^{13}\text{C}$ Nuclear Magnetic Resonance (NMR) to evaluate degradation of Nafion® and Hyflon™ for in-situ durability testing. Loss of signal intensity was observed for the OCF$_2$, SCF$_2$, CF$_3$ and CF groups located on the side chain. Signal intensity was retained for the main chain tertiary fluorine (CF), suggesting that the ether bridge connecting the side chain to the backbone has not been degraded. As all signals were normalized with respect to that of CF$_2$, main chain degradation other than for CF could not be evaluated. As Nafion® membranes of various thicknesses were tested; it was found that degradation was more pronounced for thinner membranes. It was speculated that this could be explained by increased gas cross-over and/or degradation localized at the electrode-membrane interface. For the thin Hyflon™ membrane, expected higher durability was explained by 1) lower relative gas cross over due to less swelling and 2) shorter side chains, ie. lack of secondary OCF$_2$ group.

**Chemical indication of selective degradation**

Xie et al. [43] monitored both fluoride and sulfate in effluents of a durability experiment at high humidity conditions. While the sulfate concentration varied between 50 and 100 ppb, the fluoride concentration had a concentration interval between 50 and 450 ppb. A voltage excursion to higher values resulting in a threefold increase in fluoride concentration did not feature a sulfate equivalent. Aarhaug et al. [58] found the background levels of sulfate in Gore™ Select® MEAs to be high. After 100 hours of operation, SER stabilized at a level still higher than FER. In another durability experiment, Aarhaug et al. [35] also found SER to be higher than FER. It was speculated that sulfate from the production process of the MEA dominates the concentration in the effluents. Alas, FER to SER analysis has so far not provided useful information about any possible selective attack on the ionomer side chain.

**Open Circuit Voltage (OCV) hold experiments**

One of the most commonly used protocols for accelerated degradation is OCV hold. As the only reactant consumption is by cross-over, the reactant concentrations remain fairly uniform throughout the flow channels. As no water is produced, it is possible to keep the membrane hydration uniform. The most commonly used metrics for OCV hold is gas cross-over and FER. Post mortem SEM analysis is often applied to evaluate the dimensional change in membrane thickness. Results by Liu et al. [32]
show that membrane thinning for OCV hold tests is fairly uniform. The degradation rate was also high; the membrane thickness was reduced from 25 to approx. 6 µm in 200 hours. Aarhaug et al. [59] have shown that FER is a function of the gas flows applied. Liu et al. [36] evaluated the impact of reactant gas partial pressures on FER. They found a second order dependence on hydrogen partial pressure but only first order dependence of oxygen partial pressure. It was concluded that the effective gas cross over rate was strongly linked to the degradation rate observed.

Both Aarhaug et al. [59] and Liu et al. [32] have documented a sharply declining FER with time for OCV hold experiments. An increasing FER with time has been documented by Liu et al. [36] and Cipollini [4]. Chen et al. [5] evaluated FER for OCV experiments at three humidification levels: 82, 55 and 36 %. While the two highest levels showed a constant, if not slightly increasing FER, the low setting showed an almost tenfold increase. For this setting, FER was initially high then stabilizing at approx 80 % of the initial rate. TriFluoro Acetic acid (TFA) fragments, at a ratio 1/10 that of FER was observed for the low humidification setting. While the TFA rate was close to detection limit for the 55 % setting, it was not detected for the high humidity experiments. FTIR analysis of the sample showed that the signal intensity ratio for the two ether bridges was changed. Furthermore, an increase in carboxylic acid groups, as well as evidence of S-O-S cross bonding was observed. The authors suggested that under dry condition, TFA was formed from the “y group” of the Nafion® side chain (Figure 2).

Endoh et al. [60] performed OCV hold experiments at both full and low humidity conditions. It was verified that degradation rates were higher for low humidity conditions. Post mortem FTIR analysis of the membrane showed a higher concentration of carboxylic acid end groups near the anode. A platinum band was observable near the cathode, but no correlation between carboxylic acid concentration and the location of this band was found.

Mittal et al. [13] evaluated the effect of membrane thickness on degradation rates for OCV hold experiments. An increase in FER with increasing membrane thickness was observed from 25 to 175 µm. For thicker membranes, a decreasing FER was found. Comparable FER was found for membrane thicknesses of 50 and 525 µm. Assuming the tenfold increase in thickness has the consequence of a tenfold reduction in reactant crossover, the results are contradictory to other results where FER appeared to be a function of the reactant concentration [59, 61]. Mittal et al. further explored this
phenomenon in a bilayer configuration where a single electrode was sandwiched between membranes of various thicknesses. It was found for both molecular hydrogen and oxygen that while the opposite electrode thickness was kept at 50 µm, an increase in FER was found when increasing the membrane thickness from 25 to 350 µm. It was speculated that FER could be dependent on both formation of radicals as well as the degradation rate of the ionomer. A maximum in FER at a given membrane thickness was thought to represent a shift in Rate Determining Step (RDS); up to a certain cross over rate, degradation rate is the RDS thus increasing with increasing membrane bulk volume. At a certain membrane thickness, reactant gas cross over became the limiting factor and FER thus decreased with a further increase in membrane thickness.

Fenton et al. [62] evaluated the effect of relative humidity on FER. For a Nafion® 112 membrane (thickness 51 µm) maintained at 90 °C, the highest FER was found for a 30 % relative humidity setting. It was speculated that lower relative humidity setting of 10 % would dislocate less Pt into the membrane, thus reducing the number of sites of radical formation.

Fenton’s reagent
H.J.H Fenton reported as early as 1894 on the strong oxidative potential of the combination of ferrous iron and hydrogen peroxide towards tartaric acid [63]. The potency of the mixture has later been claimed to originate from the formation of radicals [11, 64]. The presence of ferrous iron promotes the conversion of hydrogen peroxide into hydroxyl radicals and water (R. 8). The resulting ferric ions react with hydrogen peroxide to form hydroperoxyl radicals (R.9). Alternatively, hydroperoxyl radicals can be formed from the reaction between hydroxyl radicals and hydrogen peroxide (R. 10). Ferric iron can also react with hydroperoxyl radicals to form ferrous iron and molecular oxygen (R. 12) [65]. While hydrogen peroxide is consumed in the process, iron is cycled between the two oxidation states and thus does not need replenishment. Other Fenton active metals are Cu^{2+} and Ti^{3+} [11]. Platinum has been shown to produce radicals when used it fuel cell electrodes [66]. Due to the more facile decomposition of hydrogen peroxide to molecular oxygen and water in the presence of platinum metal, its Fenton activity is considered to be low compared to that of Fe^{2+} [36]. From the reduction potentials listed in Table 9 it can be seen that
only the hydroxyl radical is more potent than hydrogen peroxide itself as a part of the hydrogen peroxide/water redox couple.

The Fenton test has been extensively used to evaluate ionomer stability. The strongly oxidizing environment was initially expected to simulate that of actual fuel cell operation. PFSA ionomers show high degree of stability in concentrated hydrogen peroxide [65]. LaConti et al. [30] explored the effect of hydrogen peroxide and ferrous iron concentrations on polystyrene sulfonic acid (PSSA) membranes. Liu et al. [8] found a linear correlation between FER and hydrogen peroxide concentration. Kinumoto et al. [65] evaluated individual decomposition ratios of C-F bonds and -SO₃ groups for Nafion® membranes immersed in 30 % hydrogen peroxide at 80 °C, ion exchanged for several cations. The decomposition ratios were calculated from fluoride and sulfate concentrations measured by Ion Chromatography (IC). The alkali and alkaline earth ions showed no effect on degradation ratios. For the transition metals, Cr³⁺ and Co²⁺ showed identical decomposition ratios as H⁺-Nafion®. The effect of Cu²⁺ and especially Fe²⁺ was significant. After nine days, the degradation ratios of C-F and -SO₃ were 68 and 33 % respectively. For H⁺-Nafion®, the ratios were 1 and 7 % after 5.5 days. In addition to the increased degradation rate, the results indicated that C-F bond attack was more pronounced when Fenton reagent was applied. Chen et al. [67] investigated the effect of temperature on the fluoride emission rate (FER) for a Fenton experiment with concentrations of 30 % hydrogen peroxide and 30 ppm Fe²⁺ respectively. They found that an increase in temperature from 60 to 70 °C doubled the FER. Increasing the temperature from 70 to 80 °C saw almost 2.5 times increase in FER. Furthermore, the effect of Fe²⁺ concentration was evaluated. Interestingly, the highest Fe²⁺ concentration of 300 ppm resulted in the lowest FER. It was speculated that higher iron concentrations would change the degradation mechanism so that more fluorinated fragments were produced. Thus, FER would not be representative for the actual degradation rates. Aarhaug et al. [42] has documented substantial amounts of fragments present in effluents by monitoring both total fluorine as well as fluoride emission rates. Analysis of fluorinated fragments found in Fenton experiments has been performed. The fact that the same fragments have been observed [26, 28] for both Fenton and fuel cell experiments has been supportive of the use of ex-situ testing of ionomer stability. Table 5 lists fragments detected by ¹⁹F Nuclear Magnetic Resonance (NMR) and Mass Spectrometry (MS):
### Table 5. Fragments detected in fuel cell effluents and Fenton solutions.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Analytical method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO₂C-CF(CF₃)OCF₂CF₂-SO₃H</td>
<td>NMR, MS</td>
<td>[26, 28]</td>
</tr>
<tr>
<td>HCF(CF₃)OCF₂CF₂-SO₃H</td>
<td>MS</td>
<td>[26]</td>
</tr>
<tr>
<td>HO₂C-CF₂-SO₃H</td>
<td>NMR</td>
<td>[28]</td>
</tr>
<tr>
<td>CF₂CO₂H</td>
<td>NMR</td>
<td>[28]</td>
</tr>
</tbody>
</table>

According to quantitative NMR assessment by Healy et al. [26], the largest fragment was present in significant quantities relative to the fluoride ion. The largest fragment was believed to originate from the side chain detached, whereas the other fragments stem from decomposition of the side chain.

DuPont performed Fenton experiments where model compounds according to Table 6 were used [28]:

### Table 6. DuPont model experiment fragments.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Structure</th>
<th>% Fluorine released as F⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>CF₃CF₂OCF₂CF(CF₃)OCF₂CF₂SO₃H</td>
<td>0.005</td>
</tr>
<tr>
<td>#2</td>
<td>CF₃CF₂OCF₂CF(CF₃)OCF₂CF₂COOH</td>
<td>1.907</td>
</tr>
<tr>
<td>#3</td>
<td>CF₃-(CF-O-CF₂CF₂SO₃)-COOH</td>
<td>0.655</td>
</tr>
<tr>
<td>#4</td>
<td>CF₃-(CF-O-CF₂CF(CF₃)CF₂SO₃)-COOH</td>
<td>0.391</td>
</tr>
</tbody>
</table>

Experiments with the two first fragments were performed in order to evaluate the stability of carboxylic acid versus sulfonic acid end groups. It was found that while fragment #1 was close to inert, fragment #2 almost completely disintegrated. Similar experiments were performed by Schiraldi et al. [14] to the same conclusion.

Experiments with fragments #3 and #4 were performed in order to evaluate if branching and/or length of the side chain would affect its stability. From the results shown in Table 6 it was concluded that there was no significant difference in stability between fragment #3 and #4; Nafion® should not be inherently less stable than other ionomers with a shorter, unbranched side chain. Zhou et al. [6] also approached Fenton mechanistically by means of model compounds. It was found that FER was at
least one order of magnitude higher for compounds containing carboxylic acid groups. The FER was also found to be non-zero for compounds without carboxylic acid end groups. Fragment analysis by Liquid Chromatography Mass Spectrometry (LC-MS) showed no -SO$_3$ group loss. The mechanistic point of attack was further explored by fragment analysis from Fenton testing of two model compounds MC7 and MC8. The model compounds were chosen for their structural similarity to DOW/3M and Nafion® structures respectively. Their structure and the result of the LC-MS fragment analysis is shown in Table 7.

**Table 7. Model compounds and their fragments produced by Fenton testing.**

<table>
<thead>
<tr>
<th>MC7</th>
<th>MC8</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$CF$_2$-O-CF$_2$CF$_2$CF$_2$-SO$_3$H</td>
<td>CF$_3$CF$_2$-O-CF$_2$CF(CF$_3$)-O-CF$_2$CF$_2$-SO$_3$H</td>
</tr>
<tr>
<td>HOOC-CF$_2$CF$_2$CF$_2$-SO$_3$H</td>
<td>HOOC-CF(CF$_3$)-O-CF$_2$CF$_2$-SO$_3$H</td>
</tr>
<tr>
<td>F$_3$C-COOH (TFA)</td>
<td>CF$_3$-CF(CF$_3$)-O-CF$_2$CF$_2$-SO$_3$H</td>
</tr>
<tr>
<td>HOOC-CF$_2$-O-CF$_2$CF$_2$CF$_2$-SO$_3$H</td>
<td>CF$_3$-CH(CF$_3$)-O-CF$_2$CF$_2$-SO$_3$H</td>
</tr>
<tr>
<td>CF$_2$CF$_2$CF$_2$-SO$_3$H</td>
<td>H-CF$_2$-O-CF$_2$CF$_2$-SO$_3$H</td>
</tr>
</tbody>
</table>

The fragments produced for both MCs have in common that they all require at least one ether cleavage reaction. FER data showed that these compounds lost less than 0.01% of their fluoride inventory. MC7 showed higher FER than MC8, although the difference in FER was small. The authors did not address why MC8 with two ether bridges did not appear to be more vulnerable to attack. The comparison of MC7 and MC8 to equivalent compounds with one carboxylic acid group revealed that the degradation reactions appeared to be 500 times faster with the end groups present than with the rate of degradation from ether cleavage reactions.

Incomplete fluorination of the PFSA membrane during production introduces end groups [29] containing C-H bonds that are less stable than C-F [15]. Attempts to chemically stabilize the ionomer were performed by reducing the number of end groups. Escobedo et al. [28] reported a linear correlation between the number of end groups and FER. The ordinate intercept was at 10% FER, suggesting that there must be at least one additional path to the degrading of Nafion® other than end group attack.
For in-situ fuel cell testing, the same correlation between number of end groups and degradation has not been established [4]. For some fuel cell testing conditions, improved durability has been obtained when reducing the number of end groups [1]. For accelerated testing conditions like OCV hold and automotive cycles, hardly any improvement is observable. The latter, especially, has put focus on the fact that for Fenton testing, the membrane is always 100 % humidified.

Kadirov et al. [12] evaluated the effect of ultraviolet (UV) light induced radical formation on PFSA ionomers. Irradiation by UV light results in homolysis of hydrogen peroxide (reverse R. 11). Electron Spin Resonance (ESR) spectroscopy analysis showed membrane derived radical formation only for membranes neutralized with Fenton active cations. Radical formation was observed for Fe$^{2+}$ neutralized membranes in the presence of hydrogen peroxide, but also for Fe$^{3+}$ neutralized membranes without hydrogen peroxide present. The radicals detected were of type ROCF$_2$CF$_2$. and their concentration was found to increase with a decreasing Fe$^{3+}$ concentration.

As Fe$^{2+}$ in the presence of hydrogen peroxide will be oxidized according to R. 8, the authors speculated that Fe$^{3+}$ takes part in a reaction scheme according to R. 1.

\[
R - O - CF_2CF_2SO_3^- + Fe^{3+} \rightarrow R - O - CF_2CF_2SO_3^\cdot + Fe^{2+}
\]

The radical would subsequently recombine and by release of SO$_2$ and O$_2$ to form the radical detected. In order to further evaluate the effect of Fe$^{2+}$ counter ions on degradation, Zhou et al. [6] compared conventional Fenton testing with UV radiation based radical formation. For model compounds containing carboxylic acid groups, FER was registered even without addition of hydrogen peroxide. FER increased when hydrogen peroxide was added. Decarboxylation facilitated by UV light was suggested as the cause of degradation. Without reference to any experimental comparison performed, Zhou et al. [6] concluded that there was no significant difference between Fenton test and UV degradation tests. It is not clear whether a comparison of fragments produced for the two methods was performed.

There are several approaches to performing Fenton testing when it comes to administration of Fenton reagent and hydrogen peroxide. Kundu et al. [68] evaluated two methods of Fe$^{2+}$ administration. By ion-exchanging PFSA samples with Fe$^{2+}$
prior to immersion in hydrogen peroxide, the surface of the ionomer appeared “foamy” after degradation. For the more conventional method of adding samples to hydrogen peroxide solutions containing Fe$^{3+}$, severe changes in morphology were observed. SEM images showed the formation of holes and bubbles as well as tearing. Chemical degradation, represented by FER and weight loss, was found to be similar for the two methods. No change in Equivalent Weight (EW) was observable, but viscosity measurements of the dissolved degraded samples indicated a reduction in Molecular Weight (MW). Zhou et al. [6] immersed PFSA samples in Fe$^{2+}$ before slowly adding hydrogen peroxide. According to Walling [11], this will limit the formation of hydrogen peroxide by reverse homolysis (R. 11) but will also reduce the consumption of hydroxyl radicals by reaction with hydrogen peroxide to form hydroperoxyl radicals (R. 10). It was verified by Zhou et al. [6] that slow addition of hydrogen peroxide yielded higher FER, thus suggesting a higher concentration of hydroxyl radicals in the Fenton solution.

Despite the apparent chemical stability of PFSA in concentrated hydrogen peroxide, Qiao et al. evaluated structural changes to membranes of varying equivalent weights [47]. For these experiments, PFSA samples were pretreated, by boiling in hydrogen peroxide and sulfuric acid, in order to remove any impurities. After treatment with 3 % hydrogen peroxide at 80 °C for three weeks, the proton conductivity of the membrane with EW 900 was reduced to 50 % of the initial value. The membranes of EW 1000 and 1100 showed similar trends albeit less pronounced. The trend was verified by studying the membrane water uptake. FTIR analysis revealed an emerging band at 1440 cm$^{-1}$ that was identified as S-O-S cross-linking. Thermogravimetric Analysis (TGA) also revealed that the decomposition temperature of the -SO$_3$ group shifted to lower values with time. These findings are consistent with the loss of proton conductivity and water uptake of the membranes. They are also consistent with ionomer stability in hydrogen peroxide, as the reduced number of sulfonic acid groups will remain undetected by the FER metric.

Structural modification assessment of Nafion® after Fenton treatment has been reported by several authors. Kinumoto et al. [65] found from FTIR analysis that the normalized absorbance of C-F, C-O-C and -SO$_3$ did not change significantly, suggesting that both side chain and back bone were decomposed. A small but emerging peak at 1460 cm$^{-1}$ was attributed to formation of SO$_2$-O-SO$_2$ or -SO$_2$F groups. With the small absorbance observed, the release of sulfate was assumed to be
more facile. NMR studies by the same author verified the non-specificity of attack; after initial attack the whole molecule is decomposed. Chen et al.[67] found a weak absorption peak at 1436 cm\(^{-1}\) attributing this to the S-O-S cross-linking suggested by Qiao et al. [47]. Both FTIR and XPS data indicated a loss of -CF\(_2\) groups. The XPS data also indicated loss of sulfur from the membrane. Increased oxygen to carbon ratio was attributed to added oxygen from the radical attack by formation of carboxyl and/or carbonyl groups.

Ghassemzadeh et al. [27] evaluated degradation in Nafion\(^\circledR\) and Hyflon\(^\text{TM}\) by solid-state \(^{19}\text{F}\) NMR spectroscopy. Due to a peak-broadening effect observed by the presence of iron ions in the samples, the initial Fe\(^{2+}\) concentration of the Fenton test was kept low in order to retain spectral features vital to the evaluation of structural degradation. The comparative study indicated that degradation was less pronounced in Hyflon\(^\text{TM}\) membranes. For both membranes, tertiary fluorine (CF) signal for the main chain was virtually unchanged after the Fenton test. The biggest signal losses were for both membranes that of the SCF\(_2\) group. The more pronounced loss for Nafion\(^\circledR\) was ascribed to the possibility of additional attack on the tertiary fluorine of the side chain. Loss of OCF\(_2\) signal was found to originate from the secondary ether bridge thus indirectly causing loss of SCF\(_2\) signal. Ghassemzadeh et al. [27] further evaluated the fluoride content of the Fenton test samples by \(^{19}\text{F}\) NMR spectroscopy. Almost identical FER were calculated for Nafion\(^\circledR\) 112 and Hyflon\(^\text{TM}\). No other fluorine containing species were found. As only the Nafion\(^\circledR\) membrane was chemically stabilized by main chain end group capping, it was argued that the degradation rate for Nafion\(^\circledR\) was contributed by side chain attack. The almost similar FER for the Hyflon\(^\text{TM}\) membrane was explained by contributions from both end group as well as side chain attack.

**Hydrogen peroxide exposure by flow cell configuration**

One inherent problem with Fenton ex-situ testing is the constancy of the hydrogen peroxide concentration during the test. Continuous flow experiment with constant hydrogen peroxide concentration has therefore been used as an alternative. Mittal et al. [7] used untreated Nafion\(^\circledR\) 117 membranes to separate flows of 300 ppm liquid hydrogen peroxide and dry nitrogen gas, recording a FER of \(7.6 \times 10^{-7} \text{ g F}^{-} \text{ cm}^{-2} \text{ h}^{-1}\). No increase in FER was observable for an experiment where the hydrogen peroxide concentration was increased to 0.3 %.

When adding one Pt/C electrode to the cell
assembly, hydrogen peroxide was fed to the active and passive electrode alternately. In both configurations a 2.5 fold increase in FER was observable. When hydrogen peroxide was fed to the active and passive sides, the exit hydrogen peroxide concentrations were 25 and 150 ppm respectively. For experiments performed with two electrodes and hydrogen and oxygen as reactants, a 25-fold increase in FER was observed. The authors concluded that not much degradation could be ascribed to hydrogen peroxide generated in fuel cells, given limited Fenton activity from the Pt/C catalyst and the low contamination level of Fe in the membrane. Liu et al. [8] evaluated the effect of catalyst in flow configuration with 10 % hydrogen peroxide and nitrogen gas on each side of a Nafion® 112 membrane maintained at 90 °C. As seen in Table 8, variation in the use of catalyst was performed on the nitrogen side to avoid hydrogen peroxide decomposition upon entry. The use of carbon support did not increase FER noticeably compared to the bare membrane, and it was thus concluded that the carbon, Vulcan XC-72R, did not show Fenton activity. Platinum, 0.4 mg cm$^{-2}$ on carbon support, was shown to be Fenton active. By ion-exchanging 10 % of the membrane capacity with Fe$^{2+}$ high FER, comparable to normal fuel cell operation at OCV, was found. The effect of hydrogen peroxide concentration on FER was found to be proportional up to 10 ppm. For higher concentrations of hydrogen peroxide only a small increase in FER was observed. It was speculated that this could be due to insufficient Fe$^{2+}$ available for radical formation, or that hydrogen peroxide was consumed by the reaction with hydroxyl radicals to form less potent hydroperoxyl radicals. Liu et al. concluded that given the approximately 5 ppm contamination levels of Fe$^{2+}$ found in membranes, hydrogen peroxide formed in the fuel cell is not the main contributor to degradation.

Table 8. Cell configurations and corresponding FER values. Membrane location indicated by ||.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>FER (10$^{-8}$ g F$^{-}$ cm$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>C</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Pt/C</td>
</tr>
<tr>
<td>N$_2$</td>
<td>10 % Fe$^{2+}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Pt/C</td>
</tr>
</tbody>
</table>
Vapor phase hydrogen peroxide experiments
Reactant gas humidification level is known to have a large impact on degradation rates [34]. Administration of batch Fenton’s test or flow hydrogen peroxide configuration does not allow for evaluation of degradation rates as a function of humidification level. Hommura et al. [69] exposed membrane samples to vapor phase hydrogen peroxide, where the temperature and relative humidity of the sample chamber was 120 °C and approx. 14 %, respectively. During the course of 700 hours of exposure to hydrogen peroxide vapor a uniformly increasing FER was observable, peaking at $3 \times 10^{-6}$ g F$^{-1}$ cm$^{-2}$ h$^{-1}$. The corresponding sample weight loss was 25 %. The authors interpreted the increasing FER to an increased number of points-of-attack per molecule. This assumption was verified by FTIR analysis showing an increasing number of carboxylic acid groups in the membrane sample with time. Size Exclusion Chromatography (SEC) verified that the molecular weight had decreased to 10 % of the value of the virgin samples. Based on the decrease in molecular weight and the weight loss of the sample, each molecule had an estimated 14 severed points for the full duration of the experiment. With an expected maximum of two carboxylic end groups possible from the manufacturing process, severe main chain scission was assumed. The experiment was also performed with samples ion-exchanged with Fe$^{2+}$. A membrane containing 30 ppm Fe$^{2+}$ lost 25 % of its initial weight in about 275 hours. A correlation between Fe$^{2+}$ concentration and carboxylic acid group formation was verified by FTIR analysis. Extrapolating this correlation to zero Fe$^{2+}$ concentration also illustrated the high degradation rate observable in hydrogen peroxide vapor only. The authors did not speculate on the degradation mechanism involved. According to Vogel et al. [70], hydrogen peroxide vapor at 80 °C decomposes to two hydroxyl radicals. Kinetic data for the homolysis of (reverse R. 11) hydrogen peroxide indicate, however, a very low kinetic constant for this reaction [71]. Delaney et al. [1] performed vapor phase hydrogen peroxide experiments directly comparable to Fenton’s test by using similar concentrations of hydrogen peroxide and Fe$^{2+}$. Non-stabilized membranes as well as membranes stabilized by fluorine end group capping were compared. It was found for vapor phase experiments that stabilization of the membrane had no effect on degradation. Membrane weight loss was higher for vapor phase experiments. It was argued that different degradation mechanisms were dominating for vapor and liquid phase experiments; carboxylic end
group attack is not the only point-of-attack in vapor phase experiments. FTIR characterization of the samples showed that only vapor phase experiment samples showed an increase in carboxylic groups, this being indicative of backbone scission. The effect of Fe$^{2+}$ concentration was found to be similar for both phase experiments. Hydrogen peroxide concentration, however, showed a larger impact on membrane weight loss. Delaney et al. [1] speculated that the conversion of hydroxyl radicals to hydroperoxyl radicals (R. 10) was less efficient in vapor phase. Whereas hydroxyl radicals are capable of both backbone scission as well as end group attack, the hydroperoxyl radicals are limited to end group attack [4]. A combination of the two tests in the vapor then liquid phase sequence was shown to have larger sample weight loss than the individual tests. It was argued that the combination simulated the high degradation rates observable for automotive load cycles.

2.5 The chemistry of degradation

2.5.1 Introduction

There are several mechanisms involved in chemical degradation of PFSA ionomers. Fuel cell geometrical parameters, operating parameters and the chemical nature of the fuel cell components used are all of importance for the chemical degradation observed. Research performed on the topic of chemical degradation represents a set of parameters that cannot necessarily be projected to other conditions. An example here is ex-situ degradation of ionomers. These sets do, however, contribute to the understanding of chemical degradation. They represent a pathway to chemical degradation for a given set of parameters. In order to improve lifetime of a particular fuel cell application, it is vital to find the main contributions to degradation. Only then can significant improvement be made. In chemical degradation, it is believed that radicals formed in-situ are the source of most degradation observed. There are several pathways to radical formation in fuel cells.
2.5.2 Hydrogen peroxide pathway

Sources of hydrogen peroxide

Oxygen Reduction Reaction

The Oxygen Reduction Reaction (ORR) is complex and offers several pathways from molecular oxygen to water. Ideally on a platinum catalyst, the reaction occurs by direct 4-electron transfer according to the following reaction [72]:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23 \text{ V} \]  

Alternatively, the reduction can follow a pathway where hydrogen peroxide is an intermediate:

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.70 \text{ V} \]  
\[ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.76 \text{ V} \]

The electrocatalytic mechanism is not fully understood, but two pathways are suggested [73]:

<table>
<thead>
<tr>
<th>Dissociative (4-electron pathway):</th>
<th>R. 5</th>
<th>Associative (2-electron pathway):</th>
<th>R. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2}O_2 + Pt \rightarrow Pt - O )</td>
<td>( Pt + O_2 \rightarrow Pt - O_2 )</td>
<td>( Pt - O + H^+ + e^- \rightarrow Pt - OH )</td>
<td>( Pt - O_2 + H^+ + e^- \rightarrow Pt - O_2H )</td>
</tr>
<tr>
<td>( Pt - O + H^+ + e^- \rightarrow Pt - OH )</td>
<td>( Pt - OH + H^+ + e^- \rightarrow Pt - H_2O )</td>
<td>( Pt - O + H^+ + e^- \rightarrow Pt - OH )</td>
<td>( Pt - OH + H^+ + e^- \rightarrow Pt - H_2O )</td>
</tr>
</tbody>
</table>

In the dissociative pathway, the oxygen-oxygen bond is broken as oxygen is absorbed to the platinum surface. In the associative pathway, the oxygen-oxygen bond is broken after molecular oxygen is adsorbed to the surface. The dissociative and associative pathways have been calculated using density functional theory [74] for low and high current density, respectively. Hydrogen peroxide formation is therefore mainly associated with higher load settings at bulk platinum. In the operational voltage range of fuel cells, the hydrogen peroxide yield is considered to be low even for carbon supported catalysts [30, 75]. Inaba et al. [37] showed that for Vulcan XC-
72 supported platinum catalyst that the yield was found to be no larger than 2 % for loadings greater than 5 % wt. platinum in the voltage range 0.6-0.8 V. The effect of dispersion was also evaluated by applying various loadings of 20 % wt. Pt/C. SEM imaging of the electrodes found the degree of agglomeration of catalyst to vary with loading. The hydrogen peroxide yield was found to increase with decreasing loading. This was explained by the fact that higher agglomeration would give a higher probability for desorbed hydrogen peroxide to be further reduced to water or to be catalytically decomposed at adjacent platinum sites rather than escaping the electrode surface. Inaba et al. [76] further evaluated the size effect of catalyst particles. No size effect was observed; the highest mass activity was found for 1 nm particles. Surprisingly, the hydrogen peroxide yield increased with particle size. The catalyst support itself might influence the ORR mechanism as shown by Xu et al. [77]. These results indicate that the catalyst support catalyzes the reduction of hydrogen peroxide to water, allowing for a 4-electron pathway via the peroxide intermediate.

The electrochemical surface area of the fuel cell cathode decreases with time. It is therefore likely that hydrogen peroxide formation at the cathode will increase with time. Another factor likely to increase is the contamination of the electrode surface. Schmidt [75] showed that a large increase in hydrogen peroxide yield was obtained by adding ppm levels of chloride to the cathode air supply. As adsorbed chloride reduces the number of adjacent catalytic sites required to break the O-O bond, the probability of hydrogen peroxide formation increases.

**Oxygen Evolution Reaction**

In water electrolysis, Reaction R. 4 is expected to produce hydrogen peroxide at operating voltages above 1.76 V.

**Direct formation at electrodes**

Durability studies showing enhanced degradation [30], or even in-situ detection [78] of hydrogen peroxide at the anode gave evidence of another possible source of hydrogen peroxide in the fuel cell. Whereas the anode voltage is favorable for molecular oxygen reduction, the platinum surface is saturated with hydrogen, effectively preventing O-O bond breakage. A pathway was suggested by LaConti [30]:
2.5 The chemistry of degradation

\[ Pt + \frac{1}{2}H_2 \rightarrow Pt - H \]

\[ Pt - H + O_2 \rightarrow Pt - HO_2 \]

\[ Pt - O_2H + Pt - H \rightarrow 2Pt + H_2O_2 \]

One requirement for this pathway is that molecular oxygen must be available at the anode. With the exception of air bleed applied to the anode, cross-over from the cathode is the only source of molecular oxygen. The cross-over rate is primarily dependent on membrane thickness [78], but the rate is also influenced by temperature, partial pressures and membrane hydration state [37]. Inaba [37] detected 0.05 ppm hydrogen peroxide at the anode only, for an experiment where fuel cell degradation was shown to be higher at this electrode. Formation of hydrogen peroxide at the cathode at voltages higher than the standard reduction potential of 0.7 V, requires a non-electrochemical pathway to peroxide formation. LaConti et al. [30] detected hydrogen peroxide in an experiment where hydrogen gas containing 5 % oxygen gas was bubbled through a 3M H_2SO_4 solution in the presence of platinized platinum. Often observable in Scanning Electron Microscopy (SEM) post mortem analysis is the formation of a platinum band inside the membrane near the cathode. Liu et al. [36] showed the location of this band to be a function of the hydrogen and oxygen partial pressures; the partial pressures dictates the potential profile across the membrane and thus where Pt^{2+} is reduced to Pt. This band is a possible location of heterogeneous catalysis of hydrogen and oxygen gas into hydrogen peroxide.

**Sinks of hydrogen peroxide**

Hydrogen peroxide is not stable, and decomposes readily into molecular oxygen and water. This reaction is catalyzed by most transition metals and typical catalysts include manganese oxide, silver and platinum [79]. The decomposition at the platinum electrodes in fuel cells is expected to be efficient and thus preventing hydrogen peroxide escaping the fuel cell in the electrode effluent water. Mittal et al. [80] used single electrode experiments to evaluate the decomposition efficiency, and was able to detect low concentration of hydrogen peroxide in the effluent of the passive electrode. Liu et al. [8] estimated that for a hydrogen peroxide flow cell
experiment that around 8% of the hydrogen peroxide was decomposed at the Pt/C electrode.

Hydrogen peroxide is known to decompose in the presence of a heterogeneous catalyst according to the following reaction:

\[ M^{n+} + H_2O_2 + H^+ \rightarrow M^{(n+1)+} + \cdot OH + H_2O \]  \hspace{1cm} \text{(R. 8)}

The oxidized metal cation and/or the hydroxyl radical can further react with hydrogen peroxide to form hydroperoxyl radical according to:

\[ M^{(n+1)+} + H_2O_2 \rightarrow M^{n+} + \cdot O_2H + H^+ \]  \hspace{1cm} \text{(R. 9)}

\[ \cdot OH + H_2O_2 \rightarrow \cdot O_2H + H_2O \]  \hspace{1cm} \text{(R. 10)}

Hydrogen peroxide may also be formed by the recombination of hydroxyl radicals [11]:

\[ \cdot OH + \cdot OH \rightarrow H_2O_2 \]  \hspace{1cm} \text{(R. 11)}

According to Cipollini [4] the following reaction might also contribute to cycling \( M^{3+} \) back to \( M^{2+} \), thus further consuming hydrogen peroxide:

\[ 2M^{n+} + H_2O_2 \rightarrow 2M^{(n+1)+} + 2H^+ + O_2 \]  \hspace{1cm} \text{(R. 12)}

In the case of \( \text{Fe}^{2+}, \text{Cu}^{2+} \) and \( \text{Ti}^{3+} \) being the catalyst, the resulting hydroxyl and hydroperoxyl radical activities are high. This is often referred to as Fenton reagent [2, 11, 81]. It has been shown that platinum is Fenton active by detecting hydroxyl radicals at a platinum cathode by electron paramagnetic spin resonance (ESR) trapping [66]. Liu et al. [36] evaluated the membrane degradation in a fuel cell assembly where hydrogen peroxide was administered in liquid form. They concluded that Pt/C was a far less efficient Fenton reagent than \( \text{Fe}^{2+} \), due to the more facile pathway of hydrogen peroxide decomposition to molecular oxygen and water. It should be emphasized that this comparison was made for metallic and not ionic platinum.

### 2.5.3 Direct radical formation pathway

Both hydroxyl and hydroperoxyl radicals are possible intermediates of the ORR, as seen in R. 5 and R. 6. Molecular oxygen crossed-over from the cathode can also be
reduced according to ORR. By analogy with the pathway proposed for formation of hydrogen peroxide (R. 7), complete reduction to water is less likely to proceed on a platinum surface covered with adsorbed hydrogen. Platinum particles that have migrated from the electrodes are possible catalytic sites for the reaction between molecular hydrogen and oxygen to form radicals. The actual distance from the electrodes will reflect the potential of the catalyst [36, 82]. Burlatsky et al. [82] performed quantum chemical calculation of ORR intermediates. Calculations showed that for low potentials, hydrogen peroxide formation takes place. Before dissociation however, a hydroxyl radical was released. For high potentials, calculations showed that after formation of a hydroperoxyl group at the platinum surface a hydroxyl radical was the most favorable pathway. Burlatsky et al. concluded that direct radical formation could occur at either high or low potentials, but because of documented hydrogen peroxide formation in fuel cells, the selectivity of the low potential path could be lower. Liu et al. [8] performed reversed hydrogen pumping experiments, evaluating radical formation by degradation of the electrolyte membrane. Sweeping the cathode potential from 0 V to where oxygen evolution occurred, no degradation was apparent before formation of molecular oxygen took place. Administering oxygen gas to the cathode, the degradation rate appeared to be independent of the cathode voltage. Mittal et al. [40] performed experiments with only one active electrode to evaluate radical formation. They found similar degradation rates for anode-only and cathode-only modes, suggesting radical formation to be independent of the electrode voltage. The rates were, however, only similar when the anode had been pre-exposed to air. In the cases where the anode was not, a degradation rate two orders of magnitude lower than that of the cathode was observed for more than 45 minutes until similar degradation rates were finally observed. The formation of hydroxyl and hydroperoxyl radicals have been verified by Vogel et al. [70]. For Fenton experiments, hydroxyl radicals were directly detectable by ESR. By means of DiMethyl Pyrroline Oxide (DMPO) spin-trapping, both radicals could be detected. The hydroxyl radical was found to be more abundant. A life time of approx. 30 minutes in argon atmosphere was indicated for these radicals. Endoh et al. [60] evaluated hydroxyl radical formation rates for various catalysts. For OCV hold tests under low relative humidity conditions, hydroxyl radicals were trapped with DMPO and detected by ESR. While radical formation was observable for two commercially supported catalysts, no radical formation was found for “clean” Pt deposited in-situ.
Discerning radical formation from either direct or indirect hydrogen peroxide pathway has not been documented. It can be expected that several operational parameters may influence the reaction pathway.

### 2.5.4 Hydrogen radical formation

According to Coms [2], formation of hydrogen radicals is plausible at the anode:

$$H_2 + \cdot OH \rightarrow \cdot H + H_2O$$

$$k = 4.7 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$$ \hspace{1cm} R. 13

Stücki et al. [56] suggested that cathodic reduction of C-F by molecular hydrogen could take place in PEM water electrolyzers. Vogel et al. [70] has verified the existence of hydrogen radicals in operating fuel cells by in-situ ESR spin-trap studies.

### 2.5.5 Reduction potentials of degrading species

To illustrate the potency of the degrading species, their standard reduction potentials are given in Table 9.

**Table 9. Standard reduction potentials.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Standard reduction potential (versus NHE)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \cdot OH + H^+ + e^- \rightarrow H_2O )</td>
<td>2.59 V</td>
<td>[83]</td>
</tr>
<tr>
<td>( \cdot H + H^+ + e^- \rightarrow H_2 )</td>
<td>2.3 V</td>
<td>[64]</td>
</tr>
<tr>
<td>( H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O )</td>
<td>1.74 V</td>
<td>[83]</td>
</tr>
<tr>
<td>( \cdot O_2H + H^+ + e^- \rightarrow H_2O_2 )</td>
<td>1.48 V</td>
<td>[83]</td>
</tr>
</tbody>
</table>

### 2.6 The mechanisms of chemical degradation

#### 2.6.1 Introduction

This chapter presents the suggested mechanisms of chemical degradation found in literature. This follows from the experimental work from which they are proposed, but also the literature that deals with the formation of the reactive species as well as experimental evidence of the formation of these species.

#### 2.6.2 End group attack

According to Pianca et al. [29], the end groups listed in Table 10 are likely to be encountered in PFSA.
End group attack is exemplified by carboxylic acid reactivity according to Curtin et al. [15]. Hydroxyl radicals abstract hydrogen from the carboxylic acid group producing a perfluorocarbon radical (R. 14). This radical reacts with another hydroxyl radical to produce an acid fluoride that rearranges to an acyl fluoride (R. 15). The acyl fluoride finally hydrolyses to form a carboxylic acid group (R. 16).

\[
R - \text{CF}_2 - \text{COOH} + \cdot \text{OH} \rightarrow R - \text{CF}_2 \cdot + \text{CO}_2 + \text{H}_2 \text{O} \quad \text{R. 14}
\]

\[
R - \text{CF}_2 \cdot + \cdot \text{OH} \rightarrow R - \text{CF}_2 \text{OH} \rightarrow R - \text{COF} + \text{HF} \quad \text{R. 15}
\]

\[
R - \text{COF} + \text{H}_2 \text{O} \rightarrow R - \text{COOH} + \text{HF} \quad \text{R. 16}
\]

As seen from R. 14 to R. 16 the polymer chain is shortened by -CF2- released as CO2 and HF, while the end group is retained as carboxylic acid. As one end group is replaced by another, the overall number of end groups remains fairly constant. This process, also known as main chain unzipping [69], consumes polymer molecules from the initiation of unzipping at either one or two end groups of the molecule, until the entire backbone is digested. The side groups will eventually be released and the ether bridge forms an end group prone to further attack. The experimental evidence of complete, and fragments of the side chains [28] as well as sulfate found in effluents [43] supports this mechanism. As complete molecules are removed from the structure, the EW and IEC are retained. The mechanism is considered to have a constant rate due to the number of end groups retained.

### Table 10. End groups encountered in PFSA.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid</td>
<td>-CF2-COOH</td>
</tr>
<tr>
<td>Amide</td>
<td>-CF2-CONH2</td>
</tr>
<tr>
<td>Perfluorovinyl</td>
<td>-CF2-CF=CF2</td>
</tr>
<tr>
<td>Acyl fluoride</td>
<td>-CF2-COF</td>
</tr>
<tr>
<td>Difluoro methyl</td>
<td>-CF2-CF2H</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-CF2-CH2-CH3</td>
</tr>
</tbody>
</table>
Coms [2] has pointed out that the subsequent reaction by highly reactive radical species present in low concentration, is not very likely. He proposed that the radical reacts with the more abundant hydrogen peroxide functioning as a hydrogen donor:

\[ CF_2 \cdot + H_2O_2 \rightarrow CHF_2 + \cdot O_2H \]  

The -CHF₂ group is not stable against attack from hydroxyl radicals and proposed revision of the mechanism only involves the intermediate species. Thermodynamic calculations by Coms et al. [84] show that hydrogen abstraction from carboxylic acid by hydroperoxyl radicals is an endothermic reaction, and thus hydroxyl radicals only take part in the end group attacks.

2.6.3 Side chain attack

Although sulfate is reported in fuel cell effluents [43], this does not necessarily imply that the attack is initiated at the sulfonic acid group. As seen from 2.6.2, end group attack can result in sulfate release provided the entire structure is digested. Chen et al. [5] found sulfur emission rates to be low in OCV hold experiments, arguing that direct C-S bond attack was unlikely. Fragments of the side chain containing the sulfonic acid group were also found in effluents [28], suggesting that attack is initiated elsewhere. Reaction between sulfonic acid groups has been documented for Fenton tests; Quiao et al. [47] and Chen et al. [50] reported evidence of S-O-S cross binding, while Kinumoto et al. [65] suggested a presence of SO₂-O-SO₂.

Cipollini [4] argued that hydroxyl radicals are potent enough to attack the weak C-S bond. By hydrolysis, the sulfonic acid group is removed and the adjacent -CF₂ group is converted to a carboxylic acid end group. Zhou et al. [6] performed Fenton experiments on model compounds without finding evidence of C-S bond breakage. After radiating samples with UV, Kadirov et al. [12] proposed that C-S bond breakage occurs due to the effect of Fe³⁺ as a counter ion. Although Pozio et al. [85] has documented an effect on the use of stainless fuel cell components on degradation rates, the effect of the low ppm range impurity levels on degradation, either via Fenton activity or by Fe³⁺ sulfonyl group attack, is expected to be low [8].

Coms [2] argued that the hydroxyl radical is sufficiently potent in order to abstract hydrogen from the associated -SO₃H group, thus suggesting a hydration level dependency. The resulting sulfonyl radical would then decompose, releasing the -SO₃ group. Further, he argued that hydrogen peroxide, in the capacity of being a very
strong alpha-effect nucleophile, could react with the -SO$_3$H group to form sulfonyl peroxide according to:

$$ R - CF_2 - CF - SO_3H + H_2O_2 \rightarrow R - CF_2 - CF - SO_2 - O - OH + H_2O \quad \text{R. 18} $$

This peroxy acid could then combine with a -SO$_3$H group to form bissulfonyl peroxide, SO$_2$-O-O-SO$_2$. This structure would subsequently decompose via O-O bond homolysis, resulting in two radicals that would commence degrading the two side groups simultaneously.

Ghassemzadeh et al. has shown for both ex-situ [27] and in-situ [57] durability testing that the side chain is more susceptible to chemical attack. In addition to loss of signal intensity from OCF$_2$ and SCF$_2$ groups, the NMR analysis showed that the tertiary fluorine signal losses of the side chain were much higher than those of the main chain. Chen et al. [5] found TFA in fuel cell effluents, and FTIR characterization was indicative of a change in intensity of the two ether bridges of Nafion®. It was proposed that the hydroxyl radical would attack the side chain where the -CF$_3$ group is attached. The proposed mechanism is shown in Table 11.

**Table 11. Side chain attack according to Chen. MC and SC indicate main and side chains respectively.**

<table>
<thead>
<tr>
<th>MC $-O- CF_2 - CF(CF_3) - O - (CF_2)_2 - SO_3H + OH \rightarrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MC</strong> $- O - CF_2 \cdot$</td>
</tr>
<tr>
<td>$HC - CF(CF_3) - O - (CF_2)_2 - SO_3H$</td>
</tr>
<tr>
<td><strong>MC $- O - CF_2 \cdot + H_2O$</strong></td>
</tr>
<tr>
<td>$OC(CF_3) - O - (CF_2)_2 - SO_3H \xrightarrow{\text{hydrolysis}}$</td>
</tr>
<tr>
<td><strong>Unzipping (R. 15 and R. 16) &gt; MC cleavage</strong></td>
</tr>
<tr>
<td>$CF_3 - CO - OH + HO - (CF_2)_2 - SO_3H$</td>
</tr>
</tbody>
</table>

The resulting radical reacts further according to the unzipping mechanism described in 2.6.2. The cleavage of the main chain will result in two end groups, thus increasing the overall number of end groups and thereby increasing the degradation rate. The fragment containing the sulfonyl acid group eventually splits off TFA. Based on the TFA analysis, the authors claim this mechanism is favored by low humidity conditions. By comparing TFA emission rate to FER, it was concluded that main chain scission is the main contributor to degradation under the given operating conditions.
conditions. Although no mechanistic explanation to humidity dependence was given by these authors, Coms [2] has suggested that observed reactivity due to side chain branching could be explained by the altered hydrophilic properties of the chain. It was not indicated by Chen et al. [5] whether the tertiary C-F bond of the side chain was the target of hydroxyl radical attack. Calculations by Coms [2] indicate that these C-F bonds are actually strengthened by the adjacent ether bridge.

The suggested degradation of functional groups in membranes would result in reduced IEC. Fenton testing performed by Qiao et al. [47] showed that both water uptake and proton conductivity was reduced with time. Kinumoto et al. [65] argued that S-O-S formation would be small compared to the fraction of sulfonic acid released, thus having only a minor impact on IEC.

2.6.4 Main chain attack

Experimental evidence of main chain scission is found in data showing an increasing number of carboxylic acid groups in the ionomer with time. This has been particularly evident in vapor phase hydrogen peroxide experiments. Delaney et al. [1] performed such experiments in the presence of Fe$^{2+}$, where hydroxyl radicals would attack the tertiary C-F bonds of the main chain. It was also mentioned that thermodynamic studies by others, although no reference was given, suggests that the C-F attack might occur on the side chain and then propagate to cleave the main chain. Hommura et al. [69] performed similar experiments in the absence of Fe$^{2+}$. The carboxylic acid group formation rate was substantial, thus suggesting that hydrogen peroxide in the vapor phase is capable of attacking the ionomer. The authors concluded that main chain scission accounted for the increase in carboxylic acid groups formed, although no mechanism was suggested.

Coms [2] calculated reaction enthalpies of fluorine abstraction by hydroxyl radicals and the possibility of C-F attack was found to be very unlikely. Density functional theory (DFT) calculations by Mitov et al. [3] also showed fluorine abstraction to be unlikely. Coms [2] further suggested the formation of hydrogen radicals at the anode by reaction of molecular hydrogen with hydroxyl radicals (R. 13). This has also been suggested by Orkin et al. [9]. According to Table 9, the hydrogen radical is less potent than the hydroxyl radical. Fluorine abstraction is however thermodynamically driven by the formation of the very strong H-F bond. Kinetic calculations have shown that abstractions of secondary and tertiary C-F bonds should be feasible. XPS studies by
Huang et al. [10] suggested hydrogenation of main chain -CF₂ groups near the anode. This was interpreted as interaction with hydrogen or carbon atoms. The presence of hydrogen radicals in fuel cells has been verified experimentally [70].

### 2.6.5 Radical formation and attack

As described in Section 2.5, radical formation can have several pathways. In addition to formation at the electrodes, formation can occur at Fe²⁺, Cu²⁺ and Ti³⁺ cations trapped in the membrane. A contamination level of a few ppm of metal ions can be expected in commercial MEAs. Also, Pt particles dislocated from the electrodes are possible sites of radical formation. Cipollini [4] speculates that localized attack of the membrane occurs at the Pt band formed, thus explaining the homogeneous thinning of the membrane observed in durability experiments. However, Endoh et al. [34] found formation of carboxylic acid end groups to be higher near the anode rather than in the vicinity of the Pt band.

As seen from R. 10, hydroxyl radicals are converted to hydroperoxyl radicals. The conversion is dependent on the hydrogen peroxide concentration; for Fenton testing, the hydroperoxyl radical is considered to be the predominant species [2, 4]. Walling [11] indicated that slow addition of hydrogen peroxide to a solution containing Fe²⁺ would minimize the consumption of hydroxyl radicals by R. 10 and R. 11. The conversion is important due to the difference in radical reactivity. Whereas this difference is generally accepted, the role of each radical in degradation remains disputed. Coms [2] argues that hydroperoxyl radicals have no impact on degradation whereas Cipollini [4] considers the radical sufficiently potent for end group attack. Delaney et al. [1] suggests the increased degradation rate found in vapor phase hydrogen peroxide exposure could be explained by a higher fraction of hydroxyl radicals being present.

### 2.6.6 Impact of morphology

Chemical degradation rates are not only governed by the possible reaction pathways. The availability of the sites of attack also influences the degradation rate. The hydrophobic main chain and the hydrophilic side chain of the ionomer will rearrange according to the local water content of the membrane. In a fully hydrated state, the ion clusters will provide only limited access to the hydrophobic main chain. The remarkable stability of PFSA ionomers in Fenton’s reagent can be seen in connection with the limited availability of the end groups found on the main chain for chemical
attack by radicals in the water phase. Cipollini [4] envisages the onset of degradation as slow hydrolysis of the C-S bond of side chain by hydroxyl radicals. From the water phase, there are initially more sulfonic acid groups than carboxylic acid end groups available for attack. With a low hydrogen peroxide concentration and low number of end groups, the probability of reaction between sulfonic acid group and hydroxyl radicals are higher. As the side chain is consumed, the main chain is split, introducing two end groups for each sulfonic acid group hydrolyzed. The consumed side chain will eventually expose more of the hydrophilic end groups to the radicals, and the degradation rate gets a boost from the prevailing hydroperoxyl radicals attacking the end groups.

2.6.7 Impact of hydration level

In addition to the effect of water level on morphology, the hydration level also affects the solvation of the proton in the membrane. Perfluorosulfonic acids are superacids, and for a fully humidified membrane the sulfuric acid group will remain completely deprotonated. Modeling efforts by Li et al. [86] have shown that four water molecules are required to support significant ionization. According to Mittelsteadt et al. [87] this coordination number is only achieved for RH settings higher than 60%. Under dry operating conditions, Coms [2] argues that proton bearing sulfonic acid groups are vulnerable to attack by both hydroxyl radicals as well as hydrogen peroxide. The carboxylic acid on the other hand is a weak acid that is expected to remain associated even under dry conditions. The possibility of hydrogen abstraction from carboxylic acid should therefore be independent of hydration level.

The observed increase in degradation rates under low humidity conditions [34] and vapor phase hydrogen peroxide [1, 69] has not been well understood. A concentration effect of hydrogen peroxide was suggested by LaConti [30]. Liu et al. [8] performed hydrogen peroxide flow cell experiments and concluded that increased hydrogen peroxide concentration in fuel cells could not account for increased degradation rates observable under dry operating conditions. For gas phase hydrogen peroxide experiments, it is more likely that radicals in the vapor phase attacks the hydrophobic main chain directly. As the increased degradation rates observed is not consistent with the constant number of end groups in the ionomer, main chain scission is plausible. Delaney et al. [1] suggested tertiary C-F bond cleavage by hydroxyl radical. It is also likely that fewer hydroxyl radicals are converted to hydroperoxyl radicals in the vapor
phase, thus providing a more aggressive chemical attack. As the hydroxyl radical attack on the main chain is found to be unlikely by some [2, 70], an alternative route to main chain scission could be fluorine abstraction by hydrogen radicals.

Delaney et al. [1] performed the vapor phase hydrogen peroxide in sequence with conventional Fenton test. While each of the tests resulted in less of 10 % ionomer loss, the combined test resulted in more than 90 % ionomer loss. The combined efficiency was explained by formation of large numbers of carboxylic acid groups in the vapor phase by main chain scission, possibly by abstraction of fluoride from tertiary C-F bonds. In wet conditions, the end groups are readily attacked by the abundant hydroperoxyl radicals.

2.6.8 Assessment of degradation rates
The high degradation rates found by Delaney et al. [1] for the vapor and liquid phase sequential Fenton test give a good indication of rates of each individual mechanism. Apparently, a large number of end groups are formed during the vapor phase of the test. The attack on these end groups is much faster in the wet phase. Cipollini [4] speculated that the rate of reactions are of the following order:

\[
\cdot \text{OH} + H_2O_2 > \cdot \text{OH} + \text{−C}O\text{OH} > \text{O}_2\text{H} + \text{−C}O\text{OH} \gg \cdot \text{OH} + \text{−CS}
\]

Zhou et al. [6] performed model compound experiments in order to evaluate degradation pathways. He came to the conclusion that carboxylic acid end group attack was approximately 500 times faster than that of ether bridge cleavage. Due to the lack of conformity for test conditions used in published durability work, it is difficult to compare the degradation rates reported. For FER, Aarhaug et al. [42] showed the large variance in the emission rates. Another problem with the FER metric is the ignored total fluoride emission rate. As indicated by Healy et al. [26] and Aarhaug et al. [42], this fraction may be significant. Chen et al. [5] speculated that this fraction might also change with test conditions, making FER even less reliable as a metric for chemical degradation.

2.6.9 Mitigation of chemical degradation
The chemically stabilized Nafion® series from DuPont has significantly reduced the number of end groups in the membrane. While improved stability was observed in Fenton testing, little or no improvement was observable for in-situ testing [1]. While several mechanisms have been proposed in Chapter 2.6, there is no obvious structural
stabilization that can be performed in order to prevent chemical attack on the structure. Aoki et al. [88] reported Fenton testing with platinum exchanged membranes gave lower FER than membranes in the proton form. Further, the effect was verified in model experiments with molecular hydrogen and oxygen reactants at Pt/C electrodes showed reduced FER when the membrane separating the electrodes were Pt exchanged. The authors concluded that Pt dispersed membranes would improve durability by scavenging hydrogen peroxide and/or hydroxyl radicals.

Coms et al. [84] evaluated the use of Ce³⁺ and Mn²⁺ as scavengers of species contributing to chemical degradation. These mitigants will consume hydroxyl radicals according to R. 19 and R. 20.

\[
\begin{align*}
Ce^{3+} + \cdot \text{OH} + H^+ & \rightarrow H_2O + Ce^{4+} \\
Mn^{2+} + \cdot \text{OH} + H^+ & \rightarrow H_2O + Mn^{3+}
\end{align*}
\]

where \(k = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}\) R. 19

\(k = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}\) R. 20

Important for the applicability is the regeneration of the mitigants. This is accomplished via reactions R. 21 to R. 24 for Ce:

\[
\begin{align*}
Ce^{4+} + H_2O_2 & \xrightarrow{k_1} Ce^{3+} + \cdot O_2H + H^+ \\
Ce^{4+} + \cdot O_2H & \xrightarrow{k_2} Ce^{3+} + O_2 + H^+ \\
2Ce^{4+} + H_2 & \xrightarrow{Pt} 2 Ce^{3+} + 2H^+ \\
2Ce^{4+} + H_2O & \xrightarrow{Pt} 2 Ce^{3+} + 4H^+ + O_2
\end{align*}
\]

where \(k_1 = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}\) R. 21

\(k_2/k_1 = 13 \pm 2\) R. 22

fast R. 23

slow R. 24

and R. 25 to R. 26 for Mn:

\[
\begin{align*}
Mn^{3+} + H_2O_2 & \xrightarrow{k_3} Mn^{2+} + \cdot O_2H + H^+ \\
Mn^{3+} + \cdot O_2H & \xrightarrow{k_4} Mn^{2+} + O_2 + H^+
\end{align*}
\]

where \(k_3 = 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}\) R. 25

\(k_4 > k_3\) R. 26

The redox potentials of Ce⁴⁺/Ce³⁺ and Mn³⁺/Mn²⁺ are 1.44 and 1.5 V versus NHE respectively [84].

The mitigation effect of Ce and Mn was evaluated by incorporation into both the membrane and electrodes. For Ce, Electron MicroProbe Analysis (EMPMA) of MEA cross sections revealed that Ce migrated into the center of the membrane. It was hypothesized that this occurred during the hot pressing of the MEA. After 200 hours
of testing at OCV, the Ce signal was reduced to approx. 50%. The Ce had migrated out of the active area to the membrane outside the active electrode area. By incorporation into the electrodes, it was found that Ce$^{3+}$ was about four times as effective as Mn$^{2+}$ as a mitigant. This was found to correspond well with the rate constants given for R. 19 to R. 26.

A comparison between an unmitigated MEA with one where electrodes were oversprayed with Ce$^{3+}$, amounting to complexation of approx. 1% of the sulfonic acid groups of the membrane, was made. It was found that mitigation reduced the voltage loss by a factor of 20 and the FER nearly 1000 fold. While the unmitigated MEA lost nearly 40% of its original fluoride inventory, this figure was only 0.2% for the mitigated membrane. The unmitigated membrane showed a thinning from 50 to 35 µm. The oversprayed MEA was further compared with a MEA where the membrane was ion-exchanged with a 16-fold increase in Ce$^{3+}$ loading. Interestingly, the same effect on voltage loss and FER was observed.

The mechanism of scavenging was evaluated by using a hydrogen peroxide flow cell configuration. By measuring the exit concentration it was established that Ce$^{3+}$ is not a hydrogen peroxide decomposer. By evaluating FER, it became clear that Ce$^{3+}$ is not Fenton active. The mitigation effect of Ce$^{3+}$ is therefore a result of radical scavenging.

The performance losses associated with Ce$^{3+}$ were finally evaluated for various loadings. It was found that performance losses increased with loading. An increase in specific resistance was also observed, but the IR corrected voltages showed that the losses could not be explained by this increase alone. Whereas the high loadings showed unacceptable performance losses, Coms [84] concluded that the lower loadings were a good compromise between enhanced durability and reduced performance.

### 2.7 Conclusions

#### 2.7.1 Main parameters contributing to chemical degradation rates

It is well documented that gas cross-over rates of molecular hydrogen and oxygen to the opposite electrodes are important parameters for the degradation rate observed. It is therefore important that these parameters are evaluated when reporting chemical degradation rates. Temperature is another factor known to accelerate degradation. It is always coupled with water management and thus requires careful planning of
humidification control when changing the temperature set point of an experiment. Temperature also changes the gas cross over rate, and the effect from this must also be taken into consideration.

The hydration state of the membrane appears to be paramount for the lifetime of the fuel cell. It has been shown by Delaney et al. [1] that combined testing in vapor and liquid hydrogen peroxide is detrimental to ionomer stability. It appears that main chain attack is accelerated under dry conditions producing an increasing number of unstable end groups. In the wet phase the digestion of the same groups commences faster, possibly due to a larger concentration of reactive species in this phase. Coms [2] has further suggested several pathways for attack on the sulfonic acid when protonized at dry conditions.

**The role of the reactive species in chemical degradation**

The role of hydrogen peroxide in chemical degradation appears to be less important than what was suggested in early durability work. The *in-situ* formation rate of hydrogen peroxide looks to be limited by the facile decomposition at Pt electrodes. Also, there are direct pathways to radical formation. A predominance for anode side degradation as well as degradation rates independent of cathode potential suggest a limited role of ORR in hydrogen peroxide formation. For the vapor phase hydrogen peroxide experiments, it is still uncertain whether the radical action or direct attack by hydrogen peroxide on -SO₃H is the main source of degradation.

To discern the role of the various radicals in chemical degradation is difficult. The main reason is the challenging task of detecting these species *in-situ*, as well as being able to generate them quantitatively *ex-situ*. Published work agree that the hydroxyl radical is the main culprit of chemical degradation. The role of hydroperoxyl radical is still debated.

The enhanced degradation rates observable under humidity cycling suggests different mechanisms prevail under each conditions. It has been shown that end groups are formed during the dry phase. Also, attack on the -SO₃H group has been shown to be plausible. In the wet phase, these groups are rapidly consumed, possibly by faster reaction kinetics or by greater abundance of reactive species.

**2.7.2 Variations over the PFSA structure**

Although it has been speculated that the length of the side chain as well as the presence of an additional ether bridge could be possible sources of chemical attack,
this review has not found substantial evidence to support this. The presence in TFA in effluent water reported by Chen et al. [5] made this author review old liquid chromatography data for experiments performed under dry conditions. In none of the approximately 50 samples investigated was TFA found.

2.7.3 Metrics used for chemical degradation rate assessment

It has been shown by several authors that fluoride emission only represents a fraction of the total fluorine emission from the fuel cell. As it appears that the fluoride fraction varies with the test conditions, this further diminishes the validity of using FER as a measure for chemical degradation. It has been shown by Aarhaug et al. [42] that both FER and total fluorine emission rates can be analyzed by batch analysis of the same samples. Chen et al. [5] documented simultaneous analysis of fluoride, TFA and sulfate by liquid chromatography. Additional methodology, although more complicated, can be applied to analyze the fluorinated fractions in the fuel cell effluents.

The SER metric has been used infrequently. More frequent reporting of SER in conjunction with FER and FtER would probably reveal valuable information about the stability of the PFSA ionomer.

2.7.4 The need for standardized testing

The main obstacle for the comparison of work presenting chemical degradation rates is the lack of standardization in testing. With the establishment of standard testing, experimental work on chemical degradation could have been performed on standardized sets of parameters. These parameters include fuel cell geometry, operating conditions, fuel cell components as well as the metrics used to evaluate chemical degradation. In order evaluate certain aspects of chemical degradation, relevant parameters should be systematically varied. Reference to standard test conditions should be presented.

Fuel cell test standardization is a work in progress. Protocols are available from FCTESTNET, USFCC, JARI as well as DOE already exists. Improved harmonization between the research groupings in Europe, U.S. and Japan would further improve research performed aiming at improving the durability of PEM fuel cells.
2.7.5 Fenton testing

The liquid phase Fenton testing has seen limited correlation with in-situ testing, especially when it comes to FER and the number of end groups quantified. For Fenton testing, FER is the primary metric used. Although the liquid administration of hydrogen peroxide has inherent limitations when it comes to the hydration state of the ionomer as well as the concentration stability of hydrogen peroxide, there are other metrics that could more frequently be applied for this test:

1. Ex-situ characterization of the sample in order to evaluate the number of end groups as well as structural changes inflicted by the test.
2. IEC assessment should be performed in order to evaluate changes in EW.
3. In addition to FER; SER and FtER metrics should be applied in order to evaluate the fluoride losses from the ionomer. A complexing agent should be used in order to avoid complexation of fluoride with Fe\(^{3+}\).
4. Qualitative and quantitative assessment of the fluorinated fragments of the test solution.
5. Ionomer mass loss assessment. The mass loss should be correlated with FtER and/or quantitative fraction assessment in addition to FER. For mass losses, sample extraction should be alternatively performed in order to evaluate the fraction of ionomer chains not released from the sample into the test solution.

The vapor phase hydrogen peroxide exposure of PFSA ionomers has shown to enhance chemical degradation. This test makes it possible to evaluate ionomer stability as a function of hydration state. Performing this type of testing with application of the metrics listed above should provide valuable information about the degradation mechanism.

2.7.6 In-situ testing

Efforts should be made to standardize test conditions for better comparability of results. Establishing standardized test metrics would also be beneficial, albeit more difficult to implement.

Comparison of different PFSA ionomers

Although it appears that chemical attack on PFSA ionomers could be at locations similar for all known PFSA, it is nevertheless of interest to explore this further.
Although membranes of similar thickness would be an obvious choice, the gas cross-over rate for each ionomer must be established. The EW of the membranes should also be comparable. It is of particular interest to evaluate ionomer with and without a secondary ether bridge. Additional metrics like FtER, SER and fragment analysis should be applied in addition to FER and TFA emission rates. FTIR analysis should be applied \textit{post mortem} in order to evaluate any structural changes to the membranes; end group count and location predominance, and any possible sulfur group interactions.

\textbf{Further evaluation of the FER metric}

Standardized test conditions should be used to evaluate the correlation between FER and FtER. A better understanding of the factors influential to this ratio could be useful. FER is a sensitive, fast and cost efficient methodology well suited for fuel cell durability studies. Once knowledge about the fraction of the total fluorine loss from the ionomer it represents for various conditions is established, its use can be better justified.

\textbf{Further evaluation of the SER metric}

It appears that SER values do not correlate well with the sulfur content of the ionomer. It is possible that sulfuric acid used in the production process might contribute to a high background not easily flushed out of the system. In the case of high SER, experiments should be conducted with the aim of flushing sulfate out of the system. In addition to inert flushing, cell operation with load is a possibility, particularly under high humidity conditions. Once a low background is established SER should be evaluated against fragment analysis. As with the FER metric, an understanding of what fraction SER represent of the total sulfur emission rate should be established.

\textbf{2.8 Acknowledgement}

Nordisk Industriforskning, SINTEF Materials and chemistry and NTNU, Department of Chemistry is gratefully acknowledged for financial support to this work. Professor Signe Kjelstrup, NTNU and Dr. Rémy Sellin, CNRS, is acknowledged for valuable input to this review.
2.9 References


3 Determination of Fluorine in PTFE and Nafion® by Alkaline Fusion and Fluoride-selective Electrode Potentiometry

3.1 Abstract

In order to be able to estimate both fluoride emission rates as well as total fluorine emission rates in the context of fuel cell durability studies, a sensitive method for fluorine digestion and analysis is proposed.

By alkaline fusion of the organic matrix, the fluorine is recovered as fluoride. Quantification is then performed by a standard addition method by means of a Fluoride Ion-Selective Electrode (F-ISE). The method is applicable for a wide range of samples containing fluorinated hydrocarbons. Examples are PolyTetraFluoroethylene (PTFE)-based ski waxes, lubricants, bones of farm animals and biological samples. The analytical performance of the method is illustrated by analysis of samples of PTFE pellets in the mass range 5-250 mg. In order to improve sensitivity for the fluoride detection, masking of the lanthanum fluoride leakage from the fluoride electrode was performed. Of more than fifty samples analyzed, only two deviate more than 2 % from 100 % fluorine recovery. To illustrate the applicability of the method for electrochemical energy conversion applications, samples containing liquid Nafion® in the range 1-8 mg were analyzed. Although the recovery was on average 105 %, this error is explained by the fact the Nafion® source is a volatile solution where sample masses are not easily controlled. The Limit Of Detection (LOD) was estimated to be 6.2 µg L\(^{-1}\), whereas the Limit Of Quantification (LOQ) for the methodology was estimated to be 8.6 µg L\(^{-1}\). The result verifies the method’s ability to recover fluorine from Nafion® ionomers. The method evaluation gives proof of excellent analytical performance. The sensitivity is sufficient to analyze the fluoride concentrations found in effluent from fuel cells based on fluoropolymer ionomers. The proposed methodology thus renders evaluation of both fluoride and total fluorine emission rates using the same analytical principle.
3.2 Introduction

Methodologies for the determination of total fluorine in a wide range of analytical matrices have been developed during the past century. The Willard-Winter [1] methodology gave motivation for faster and less complicated methods, some of these listed by Ma [2]. The most common procedure for cleavage of organically bound fluorine has been alkaline fusion. Before the entry of the Fluoride Ion-Selective Electrode (F-ISE), colorimetric titration was the dominating analytical technique for the analysis of recovered fluoride [1-4]. The F-ISE gave rise to faster methods of higher analytical performance. The combination of alkaline fusion and potentiometric determination has seen applications in geology [5, 6], biological samples [5, 7] and nutrition [8]. F-ISE application in biological matrices with sodium peroxide [9] or no digestion [10] has been reported. The quantification of fluoride by standard addition calibration has evolved from Gran’s Plot [6, 11, 12] and two-point standard addition [5, 7, 12] to multi-addition calibration [13, 14] now implemented in commercially available equipment.

The chlorine-alkaline electrolysis technology gave rise to development of proton conducting perfluorinated membranes. Due to the excellent chemical stability of these fluoropolymers, they have been applied in Proton Exchange Membrane (PEM) electrochemical energy conversion systems.

Characterization of fluoropolymers involves advanced techniques like Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), often in combination with Mass Spectrometry (MS). The thermal stability of fluoropolymers can be investigated by ThermoGravimetric Analysis (TGA) [15]. For durability investigations, combination with FTIR [15] renders possible the speciation of fluorine from degradation as a function of temperature. Chemical degradation proceeds through several steps and eventually terminates in formation of hydrogen fluoride. The ratio of fluorine to fluoride reveals information about the degradation mechanism.

Determination of fluorine content in Teflon by combustion by oxygen and titrimetric determination has been reported [4]. The use of alkaline fusion followed by F-ISE potentiometric determination has also been previously reported for soil and biological samples [5, 7]. The limit of detection was reported to be 3 ppm fluoride [5]. No
previous work of quantitative decomposition of Nafion® or similar ionomers is known to the authors.

In this work we investigate the analytical performance of an alkaline fusion potentiometric determination of fluorine content in PTFE and Nafion®. According to Baumann [16], the ion-selective electrode sensitivity is mainly limited by fluoride release from the lanthanum fluoride membrane used in the electrode. By removal of this contribution by complexation it is possible to increase sensitivity from the ppm to the ppb level. Lingane [17] argued that although the solubility of lanthanum fluoride increases with lowered pH, the mass of fluoride released is actually reduced. This was explained by the fact that while fluoride was associated with protons to form hydrofluoric acid, the lanthanum ions near the electrode further suppress dissolution of the lanthanum fluoride. As the main interference for the F-ISE is the hydroxyl ion, the selectivity of the electrode is excellent at low pH. The work by Moritz et al. on flow injection analysis of fluoride has shown that F-ISE kinetics is superior at low pH [18]. As equilibrium between electrode and solution is quickly established, the potentiometric analysis is significantly faster than for conventional fluoride analysis utilizing a Total Ionic Strength Adjustment Buffer (TISAB) [19]. In our proposed method, a hydrochloric acid solution of concentration 0.5 M was chosen. A pH of about 0.3 is well compatible with the arguments for acidic analysis of fluoride above mentioned. The pH dependence of the free fluoride concentration in solution is reduced towards lower pH [20], reducing the need for pH buffering when adding standard solution. Further, this eliminates the need for addition of supporting electrolyte to establish sufficient ionic strength of the analytical solution.

Nafion® ionomers have a water content dependent on ambient temperature and humidity. For method evaluation the water content introduces errors, as Nafion® sample masses will vary with their ambient conditions. PTFE has therefore been used as a model compound to establish the analytical performance. The PTFE decomposition methodology is verified by statistical evaluation, using the software package AMIQAS [21, 22]. After evaluation, the methodology has been applied to Nafion® in the form of liquid ionomer to verify the applicability of the method to proton conducting ionomers.
This methodology has been applied in a durability study where both fluorine and total fluorine emission rates has been evaluated with respect to operating conditions and performance degradation [23].

3.3 Experimental

3.3.1 Sample digestion

For PTFE digestion, fine powder in the range 5 to 250 mg was transferred to nickel crucibles and covered with 5 g NaOH pellets. For Nafion® digestion, a 5 % wt. solution in the range 40 to 260 µL was transferred by micropipette to nickel crucibles. After evaporation of the solvents, 5 g NaOH pellets were added to the crucibles. The crucibles were lidded and placed in an oven. The oven temperature was ramped to 560 °C in two hours and dwelled at 560 ± 20° C for another two hours. The oven cooling ramp depends on the thermal mass of the oven, but is not significant for the experiment. After cooling the samples were dissolved in 75 mL water at 70-80 °C for 24 hours before being transferred quantitatively to volumetric flasks.

Reagents

DuPont fine powder 636-N was used for experiments of PTFE degradation. The source of Nafion® ionomer was Liquion solution N-1105 containing 5% wt. Nafion® ionomer of equivalent weight 1100. The Nafion® solution is a mixture of 75 % wt. isopropanol and 20 % water. The Nafion® content is within 4.95 to 5.05 % wt. The density of the solution is 860 g L^{-1}. Analytical grade NaOH (Baker) was used for sample digestion. Fluoride standard (1 g L^{-1}) was prepared from analytical grade NaF (Merck). Analysis was performed in 0.5 M hydrochloric acid (analytical grade). All sample preparation and dissolution was performed with distilled water.

Apparatus

For digestion of samples Naber N60/14 or Entech SF-4/17 ovens were used. These ovens follow strict calibration routines. The samples were digested in 100 mL nickel lidded crucibles. Fluoride analysis was performed using Metrohm 781 Ion-meter, Metrohm 799 Titrator for standard additions and finally a Metrohm 824 Sample changer. The Sartorius CP224S balance used had a 0.1 mg resolution.
Analysis of fluoride
Aliquots of the diluted samples were transferred to a measuring beaker containing hydrochloric acid (50 mL, 0.5 M). After initial electrode ElectroMotive Force (EMF) was recorded, three standard additions by NaF standard was performed. The additions were calculated dynamically so that the change in electrode voltage was in the order of 10 mV. All samples were analyzed with at least one replication, preferably with different aliquots. To illustrate the analytical performance, no results were omitted by outlier evaluation.

3.4 Results and discussion

3.4.1 Digestion of PTFE
The result of 54 consecutive digestions of PTFE is shown in Table 12. Aliquots used were in the range 0.2-3 mL. Dilution was done to 1000 mL. The mean value of the percent recovery is 100.2. The mean relative standard deviation is 1 %. Of the 54 individual analyses, only two deviate more than 2 % from complete recovery.
Table 12. Digestion of PTFE.

<table>
<thead>
<tr>
<th>m PTFE [g]</th>
<th>N</th>
<th>m F- cr. [mg]</th>
<th>m F- meas. [mg]</th>
<th>Recovery [%]</th>
<th>SD [mg]</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0469</td>
<td>2</td>
<td>35.6</td>
<td>36.0</td>
<td>101.0</td>
<td>0.48</td>
<td>1.3</td>
</tr>
<tr>
<td>0.0983</td>
<td>2</td>
<td>74.7</td>
<td>74.3</td>
<td>99.4</td>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1627</td>
<td>2</td>
<td>123.7</td>
<td>125.0</td>
<td>101.1</td>
<td>0.13</td>
<td>0.1</td>
</tr>
<tr>
<td>0.0302</td>
<td>4</td>
<td>23.0</td>
<td>23.2</td>
<td>101.1</td>
<td>0.26</td>
<td>1.1</td>
</tr>
<tr>
<td>0.0594</td>
<td>4</td>
<td>45.1</td>
<td>44.7</td>
<td>98.9</td>
<td>0.65</td>
<td>1.5</td>
</tr>
<tr>
<td>0.0900</td>
<td>4</td>
<td>68.4</td>
<td>67.9</td>
<td>99.3</td>
<td>0.57</td>
<td>0.8</td>
</tr>
<tr>
<td>0.0050</td>
<td>4</td>
<td>3.8</td>
<td>3.9</td>
<td>102.4</td>
<td>0.06</td>
<td>1.5</td>
</tr>
<tr>
<td>0.0103</td>
<td>4</td>
<td>7.8</td>
<td>7.9</td>
<td>100.4</td>
<td>0.07</td>
<td>0.9</td>
</tr>
<tr>
<td>0.0203</td>
<td>4</td>
<td>15.4</td>
<td>15.4</td>
<td>100.1</td>
<td>0.26</td>
<td>1.7</td>
</tr>
<tr>
<td>0.0348</td>
<td>4</td>
<td>26.4</td>
<td>26.4</td>
<td>100.0</td>
<td>0.08</td>
<td>0.3</td>
</tr>
<tr>
<td>0.0590</td>
<td>4</td>
<td>44.8</td>
<td>44.9</td>
<td>100.2</td>
<td>0.24</td>
<td>0.5</td>
</tr>
<tr>
<td>0.0924</td>
<td>4</td>
<td>70.2</td>
<td>69.7</td>
<td>99.3</td>
<td>0.21</td>
<td>0.3</td>
</tr>
<tr>
<td>0.1668</td>
<td>4</td>
<td>126.8</td>
<td>126.8</td>
<td>100.0</td>
<td>2.27</td>
<td>1.8</td>
</tr>
<tr>
<td>0.2125</td>
<td>4</td>
<td>161.5</td>
<td>164.4</td>
<td>101.8</td>
<td>3.28</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2517</td>
<td>4</td>
<td>191.3</td>
<td>187.4</td>
<td>98.0</td>
<td>0.86</td>
<td>0.5</td>
</tr>
</tbody>
</table>

N indicates replicate measurements in the mean value, m F- cr. is the theoretical mass of fluoride in the crucible. m F- meas. is the experimentally obtained result. Recovery is the per cent recovery of fluorine.

Statistical analysis is performed on the dataset [21, 22]. A weighted linear regression relates the true value with the measured fluoride concentrations in the crucible. This constitutes a method evaluation function (MEF). The MEF gives information about concentration dependent as well as concentration independent errors in the analysis. Ideally, the MEF should have a slope of unity and an intercept equal to zero. A prerequisite to MEF evaluation is a normal distribution of the data. The normal distribution is shown in Figure 3. The AMIQAS normal score test shows that the data is normally distributed relative to a five per cent significance limit. The weight used is the inverse square of the mean value. The correlation is calculated to be 0.9798. At a 5 % confidence, this is higher than the limit of 0.9778.
Another prerequisite to MEF evaluation is that the standardized residual between the measured value and their mean at each concentration level should be independent of concentration. This is done by performing a weighted regression. The residual plot of the data is shown in Figure 4. The weight used is the inverse square of the mean value. The reference value is true fluorine content in sample. Figure 4 indicates that only at a true content of 161.5 mg fluorine is a residual of more than two standard deviations observed for the applied weight.
With a verified normal distribution of the results, the MEF was found by weighted linear regression. The MEF is shown in Figure 5. The ideal MEF of slope 1 and intercept 0 is indicated by a solid line. The estimated MEF indicated by a dotted line. The estimated MEF has a slope of 0.9970 and an intercept of 0.0947. The weight used was the inverse square of the mean value. The linear correlation between reference (true) values and the observed (measured) values was found to be $R^2 = 0.9991$. 

**Figure 4. Standardized residuals.**

[Image of a standardized residuals graph]
3.4 Results and discussion

Figure 5. Method Evaluation Function.

A MEF slope close to 1 indicates that the method in the range 5-250 mg PTFE is virtually independent of sample mass. An intercept of 94.7 µg indicates a positive systematic error, independent of sample mass. The error is significant and contributes 2.1 per cent to the lowest sample mass. The error is related to the blank value of the method evaluation and will be discussed separately.

The test conclusion is that neither slope nor intercept of the MEF is significantly deviating from 1 and zero respectively. The method is therefore in analytical control within the range 5-250 mg true fluorine content.

Digestion of Nafion®

Results from the digestion of Nafion® are shown in Table 13.
Table 13. Digestion of Nafion® ionomer.

<table>
<thead>
<tr>
<th>V Nafion [µL]</th>
<th>V Aliquot [mL]</th>
<th>m F⁻ cr. [mg]</th>
<th>m F⁻ meas. [mg]</th>
<th>Recovery [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>5</td>
<td>1.173</td>
<td>1.200</td>
<td>102.3</td>
</tr>
<tr>
<td>40</td>
<td>10</td>
<td>1.173</td>
<td>1.220</td>
<td>104.0</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>2.346</td>
<td>2.550</td>
<td>108.7</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>2.346</td>
<td>2.547</td>
<td>108.6</td>
</tr>
<tr>
<td>120</td>
<td>5</td>
<td>3.519</td>
<td>3.728</td>
<td>105.9</td>
</tr>
<tr>
<td>120</td>
<td>10</td>
<td>3.519</td>
<td>3.754</td>
<td>106.7</td>
</tr>
<tr>
<td>160</td>
<td>5</td>
<td>4.692</td>
<td>5.158</td>
<td>109.9</td>
</tr>
<tr>
<td>160</td>
<td>10</td>
<td>4.692</td>
<td>5.262</td>
<td>112.1</td>
</tr>
<tr>
<td>205</td>
<td>5</td>
<td>6.012</td>
<td>6.102</td>
<td>101.5</td>
</tr>
<tr>
<td>205</td>
<td>10</td>
<td>6.012</td>
<td>6.065</td>
<td>100.9</td>
</tr>
<tr>
<td>260</td>
<td>5</td>
<td>7.625</td>
<td>8.055</td>
<td>105.6</td>
</tr>
<tr>
<td>260</td>
<td>10</td>
<td>7.625</td>
<td>8.001</td>
<td>104.9</td>
</tr>
</tbody>
</table>

“V Nafion” is the added volume of ionomer solution to the crucible, m F⁻ cr. is the true mass of fluoride calculated from the theoretical content in Nafion® solution 5 % wt. m F⁻ meas. is the experimentally obtained mass.

Aliquots used were the volume of the dilution used in analysis. Dilution was 250 mL. The average recovery for the 12 measurements is 105.9 %. These values are corrected for a blank value as described in the next section. It is seen from the last column in Table 13 that the recovery varies from 100.9 to 109.9. Uncertainties are introduced by adding the volumes with micropipettes. The solution is volatile and the Nafion® content could be higher than 5 % wt. The volumes of column 1 in Table 13 shows the calibration of pipettes with Nafion® solution of settings in the range 50 to 300 µL. Prior to use, the calibration of the pipettes with water verified the pipette setpoints to be within quoted accuracy. There are thus significant errors associated with these volumes. The digestion of Nafion® ionomer was performed in order to illustrate that the applicability of the method to complete breakdown of the organic matrix and recovery of the fluorine. The digestion applies for Nafion® membranes as well. However, the water content of membranes is a function of temperature and humidity.
Therefore the accurate fluorine content is difficult to obtain unless using a controlled atmosphere.

**Estimation of blank**

Distilled water and chemicals used introduce a blank value of fluoride that must be subtracted from the analytical result. For the potentiometric analysis with the buffers used, the blank value in the analysis beaker is 0.25 µg fluoride. Since digestion is performed by considerable amounts of NaOH, the blank value is to some extent dependent on the aliquot used.

The estimate of the blank value is done by performing the analysis without the introduction of a source of fluorine. Since the values are low and close to the detection limit of the analytical method, numerous repetitions of the experiment need be performed in order to establish this value. The value is a function of the aliquots and hence must be performed for the aliquots used in the experiments.

For the PTFE digestion, a blank value of 0.3 µg could be subtracted from the analytical result with aliquots in the range 0.2-3 mL. However, this amounts to less than two per cent for the lowest mass analyzed. For higher masses, the blank value is negligible. Since 2% is within relative error of the analysis, value correction is ignored.

For the Nafion® ionomer digestion, the blank value is considerably higher due to the aliquots in the range 5-10 mL. A blank value for the aliquots 5 and 10 mL was found to be 0.6 µg in the analysis beaker. This value is used in the blank value correction of the results.

**Method sensitivity**

Based on the IUPAC definition, the limit of detection (LOD\textsubscript{IUPAC}) is the blank value added three times the standard deviation of the mean of 20 replicate measurements of the blank performed the same day. Similarly, the limit of quantification (LOQ\textsubscript{IUPAC}) is defined as the blank value added 10 times the standard deviation of the mean. The blank value presented in this work is estimated from blank values based on individual experiments with different aliquots used. Although the estimate is based on more than 20 measurements, 20 individual experiments at each aliquot are not performed. Neither were these performed on the same day.
For the restrictions given, LOD was found to be 6.2 µg L⁻¹. The LOQ estimate is 8.6 µg L⁻¹.

### 3.5 Conclusion

The proposed methodology for recovery of fluorine in perfluorinated hydrocarbons and ionomers shows excellent analytical performance. The potentiometric analysis of fluoride shows very good sensitivity. For fuel cell durability studies both fluoride and total fluorine emission rates can be evaluated applying the same analytical methodology for fluoride quantification.

### 3.6 Acknowledgement

Nordic Energy Research is acknowledged for financially supporting the corresponding author's PhD project. Dr. Karsten N. Thomsen is acknowledged for the introduction to AMIQAS.

### 3.7 References


3.7 References


4 Degradation of Polymer Electrolyte Membrane Fuel Cells Monitored by Fluorine and Fluoride Emission Rates

4.1 Abstract

An experiment was performed in order to characterize degradation of Polymer Electrolyte Membrane Fuel Cells (PEMFC) by means of fluorine and fluoride emission rates. Apart from intermittent polarization scans to characterize system performance, the experiment was performed under constant operating conditions chosen in order to avoid any acceleration of degradation rates. During the experiment, the cathode effluent was scrubbed by passing it though an absorbent. The absorbent was analyzed for both total fluorine and fluoride. The anode effluent was scrubbed in a container where a fluoride-selective electrode was installed for assessment of the accumulated fluoride concentration. The absorbent was periodically replaced and analyzed for total fluorine and fluoride.

For both electrodes, the experiment shows increasing Fluoride Emission Rates (FER) with time. FER clearly reflects the increased degradation associated with the Open Circuit Voltage (OCV) excursions observed. An enhanced degradation was observed for operation under dry conditions. No correlation between FER and operational current density was found. An increase in FER with time could be explained by an increased reactant cross over with time.

A Fenton test was performed to evaluate the Total Fluoride Emission Rate (FtER) to FER ratio for accelerated ex-situ testing. A ratio higher than 1 was found, suggesting that total decomposition of the ionomer into CO₂, HF and H₂SO₄ does not occur. FtER estimates are for all samples equal or higher than the FER estimate. On the cathode, FtER is initially more than twice the FER emission rates from both electrodes, suggesting that there are more fluorine containing fragments in the effluents initially. The overall fluorine and fluoride losses amount to an ionomer loss of 7.1 % and 4.7 % respectively. Higher FtER at the cathode could be explained by the higher flow rates due to the use of air as oxidant.
For the durability experiment performed, the combined averaged cathode and anode \( \text{FtER} \) and \( \text{FER} \) up to 1078 hours were found to be 153.3 and 98.9 ng F\(^-\) cm\(^{-2}\) h\(^{-1}\), respectively. The averaged ratio \( \text{FtER} \) to \( \text{FER} \) is thus 1.6. The \( \text{FER} \) average correlate well with other published data.

This work shows that not all fluorine leaves the fuel cell as fluoride. The relative amount of fluorine to fluoride decreases with time. This might be due to a change in degradation mechanism. To justify the use of \( \text{FER} \) as a metric for chemical degradation, knowledge about the ratio \( \text{FtER} \) to \( \text{FER} \) should be established. This work has shown that this ratio changes with time, thus rendering \( \text{FER} \) less reliable as a metric.

### 4.2 Introduction

Commercially available Membrane Electrode Assemblies (MEAs) for Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are almost exclusively produced from perfluorinated hydrocarbons substituted for proton conduction. The excellent thermal and chemical stability provided by the perfluorination is known from PolyTetraFluoroEthylene (PTFE). The electrochemical energy conversion taking place in fuel cells does, however, involve redox conditions capable of degrading the perfluorinated ionomers used in the electrolyte membrane and the proton conducting phase of the electrodes. Durability is today the biggest obstacle for commercialization of PEMFC technology. Extensive efforts have been made to understand the chemical degradation mechanisms occurring in fuel cells. As fuel cells are of an integrated nature, monitoring of degradation rates are challenging. For chemical degradation, a well-established methodology for rate estimation is the use of Fluoride Emission Rates (FER), where the fluoride concentration in the fuel cell exhaust water is monitored.

Degradation of fluoropolymers results in the release of fluoride and possibly ionomer fragments containing fluorine. Baldwin \textit{et al.} reported as early as 1990 a correlation between FER and the lifetime of Solid Polymer Fuel Cells (SPFC) and PEM electrolyzers \cite{1}. The logarithm of expected lifetime was found to have a linear correlation with the logarithm of the FER. This correlation was, however, found for membrane thicknesses in the order of 250 µm and with low reactant gas cross-over. Since then, FER has become one of the most commonly used diagnostic tools for PEM system durability. Liu \textit{et al.} \cite{2} found, by application of an accelerated test...
4.2 Introduction

protocol for Gore™ Select® Membranes, an initial increase followed by a decrease in FER with time. Fluoride analysis was performed with a Fluoride Ion-Selective Electrode (F-ISE) on the mixed effluents of the anode and cathode. This work concluded that FER does not represent membrane lifetime since degradation did not proceed isotropically. Hicks et al. [3], however, found a linear correlation between the logarithm of accelerated lifetime and the logarithm of both initial and average FER. The correlation with initial FER was found to be useful, as even accelerated lifetime could be predicted from fluoride concentration of effluents sampled at the start of the experiment.

Pozio et al. [4] used FER as a measure of degradation rate when comparing stainless steel and aluminum end plates. For experiments performed at moderate operating conditions with respect to degradation, it was found that FER was higher at the cathode when using stainless steel end plates. The pH of the cathode effluent was lower than that of the anode and similarly, the fluoride concentration in the cathode effluent was higher than that of the anode. A good correlation between pH and FER was found, suggesting that hydrogen fluoride was released to the effluent. By using aluminum end plates, FER and pH were identical at both electrodes. pH was not significantly different from the value of the inlet water. Significantly lower FER was observed, suggesting a role of stainless steel in the degradation mechanism.

Xie et al. [5] showed for moderate to high load and temperature under high humidity conditions an increase in FER with time. A sudden, threefold increase in FER found correlation with a voltage drop observed after 800 hours. The maximum fluoride concentration in the effluents was found to be 450 ppb. Healy et al. [6] gave evidence of observable scatter in FER data. Good correlation between pH and FER was again found, suggesting HF present in the effluents. An assessment of fluoride mass balance was given. It was suggested for a 25 µm thick membrane that a FER of 3 µg F⁻ cm⁻² h⁻¹ would digest the ionomer completely in 1200 hours. Liu et al. [7] investigated FER as a function of current density for an accelerated test protocol. They found that a current density of 1800 mA cm⁻² showed the lowest FER of 43 ng F⁻ cm⁻² h⁻¹. FER was fairly stable with time. The experiment was ended after 2000 hours even if the end-of-test criterion of 2 cubic centimeter hydrogen gas cross-over per minute was not reached. The membrane loss for the period was 4.4 %. At the other extreme, the OCV hold test gave the highest FER of 4 µg F⁻ cm⁻² h⁻¹. The test ended after 212 hours with a 52 % membrane loss. The FER was sharply decreasing with time. Only for the FER
obtained at a current density of 800 mA cm\(^{-2}\), was an increasing FER with time observed. Correlating FER for the four current density levels with the membrane lifetime revealed that there is a fair (R\(^2\) = 0.97) linear correlation between the logarithm of lifetime and FER respectively. Aarhaug \textit{et al.} [8] varied the gas flow rates for OCV hold experiments and found FER to be strongly dependent on this parameter. No systematic difference in anode and cathode emission rates was found, and for both flow rates applied a sharply declining emission rate trend was observed. Aarhaug \textit{et al.} [9] also evaluated FER emission for an ON/OFF accelerated protocol experiment according to FCTESQA [10]. Four experiments were performed simultaneously, systematically varying membrane thickness (18 and 35 µm) and the ON/OFF cycle period (15 and 30 minutes). The load was cycled between OCV and 0.8 A cm\(^{-2}\). For all experiments FER was increasing with time. FER was higher for the thinner membranes. It appears that the variation in FER between experiments was larger than what could be explained by the input variable variation, making interpretation of the results difficult. Aarhaug \textit{et al.} [11] also applied experimental design in order to investigate fuel cell durability as a function of reactant gas relative humidity, cell clamping pressure and pressurized operation. A fractional factorial design was applied in order to evaluate the effect of the operating parameters keeping the number of experiments low. It was found that gas relative humidity had the highest impact on FER; changing the relative humidity from 25 to 100 % reduced average FER from 295 to 108 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\). A change from ambient to pressurized operation at 1.5 barg increased average FER from 120 to 282 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\). The cell clamping pressure appeared to have less impact on FER than the other parameters; a change from 5 to 10 barg reduced average FER from 228 to 175 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\). As initial FER was high for all experiments, the system test rig background was evaluated. In a subsequent run, the system was purged with N\(_2\) and the effluent analyzed for fluoride every hour. It was found that a tenfold background level was present and that at least three hours of purging was necessary to reduce this background to an acceptable level given the FER levels of the experiments. Motupally \textit{et al.} [12] found a linear correlation between FER and reciprocal gas relative humidity. Further, a linear correlation was also found between the logarithm of FER and the reciprocal operational temperature. Liu \textit{et al.} [13] evaluated the impact of humidity on durability by varying the cathode humidification. The FER value for a humidified cathode was 0.15 µg F\(^{-}\) cm\(^{-2}\) h\(^{-1}\), whereas the value for a dry cathode was
16 ng F⁻ cm⁻² h⁻¹. The finding is in contrast to the normal perception of increasing durability with higher gas relative humidity settings. It was speculated whether higher humidification settings would allow for more contamination entering the membrane and thus contributing to degradation. To evaluate this, membranes with <1, 20 and 500 ppm Fe²⁺ were tested with both humidified and dry cathodes. The highest FER value of 0.81 µg F⁻ cm⁻² h⁻¹ was found for the membrane with 500 ppm Fe²⁺ and a dry cathode. The value for humidified cathode was 0.21 µg F⁻ cm⁻² h⁻¹. For the lower Fe²⁺ concentrations, FER values were reduced to 0.15 µg F⁻ cm⁻² h⁻¹ and 64 ng F⁻ cm⁻² h⁻¹ for 20 ppm and < 1 ppm respectively for humidified cathode. At these concentrations of Fe²⁺, the dry cathode setting again showed lowest values of FER, 12 and 13 ng F⁻ cm⁻² h⁻¹ for 20 ppm and < 1 ppm Fe²⁺ respectively. Mittal et al. [14] also evaluated the correlation between relative humidity and FER. They found FER to be 50 µg F⁻ cm⁻² h⁻¹ and 1 µg F⁻ cm⁻² h⁻¹ for 30% and 100 % relative humidity respectively. Fenton et al. [15] investigated the effect on FER for membrane thickness. They used a bi-layered setup showing that although reactant flux was reduced with membrane thickness, there was an increase in FER with membrane thickness up to a certain thickness. This was explained with increased bulk volume available for reaction. It was speculated that both bulk membrane volume as well as reactive species concentration could be rate limiting for the overall degradation process.

Table 14 summarizes FER data for durability experiments published. Where average FER is not reported, the maximum FER is given. The maximum FER values reported are not related to observed membrane failure or end-of-test condition. The FER values spans three decades, with stable as well as both increasing and decreasing time trends registered.
The use of Fenton's reagent for ionomer stability investigation is frequently reported in ex-situ papers. By immersing the ionomer in hydrogen peroxide solution, Fenton's reagent is used to observe the stability of the ionomer. Table 14 summarizes the reported FER values with A/C specified.
solution containing ppm levels of ferrous iron, peroxide radicals are effectively formed according to R. 27- R. 29 [16, 17]:

\[
Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \\
\text{R. 27}
\]

Ferric iron and/or the hydroxyl radical can further react with hydrogen peroxide to form hydroperoxyl radical according to:

\[
Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot O_2H + H^+ \\
\text{R. 28}
\]

\[
\cdot OH + H_2O_2 \rightarrow \cdot O_2H + H_2O \\
\text{R. 29}
\]

These radicals are known to degrade the ionomer, producing hydrogen fluoride. According to Curtin et al. [18], the attack occurs at partially fluorinated end groups like –CF₂H, –CF₂=CF₂ or –CF₂COOH originating from the production process. The latter end group is used as an example below where the degradation is initiated by abstraction of hydrogen from the end group:

\[
R - CF_2 - COOH + \cdot OH \rightarrow R - CF_2 \cdot + CO_2 + H_2O \\
\text{R. 30}
\]

\[
R - CF_2 \cdot + \cdot OH \rightarrow R - CF_2OH \rightarrow R - COF + HF \\
\text{R. 31}
\]

\[
R - COF + H_2O \rightarrow R - COOH + HF \\
\text{R. 32}
\]

The perfluorocarbon radical then reacts with the hydroxyl radical and via an intermediate to form a -COOH end group by reaction with water and the release of two HF molecules. A generic Nafion® ionomer structure is seen in Figure 6. The end groups are located, when present, at the start and end of the perfluorinated backbone of the molecule.

\[
\left[ (CF_2-CF_2)_x -CF-CF_2 \right]_y \\
\text{CF}_3
\]

\[
\hat{O} - CF_2-CF-O-CF_2-CF_2SO_3H
\]

\[
\text{Figure 6. Generic Nafion® structure.}
\]
The degradation mechanism described in R. 30 to R. 32 shows that the original –COOH end group is replaced by a new –COOH end group that is also available for hydrogen abstraction. Provided that hydroxy radicals are available, the fragment will decompose completely into HF, CO₂ and SO₂.

The measured fluoride concentration in the reagent solution is taken as a measure of ionomer stability. FER is occasionally calculated from this concentration, but concentrations are more frequently reported. Results are often normalized to reference materials, making comparison between experimental results difficult. For Fenton testing, high concentrations of ferric ions in the solution will interfere with the fluoride concentration assessment by fluoride-selective electrode [19]. Unless a complexing agent is used [20], the fluoride concentration of the solution will be underestimated.

A main drawback with Fenton’s test is the variation in hydrogen peroxide concentration with time. Therefore, a fuel cell configuration where liquid hydrogen peroxide is fed to one electrode has been used. Mittal et al. [21] compared FER for a liquid hydrogen peroxide (300 ppm) and nitrogen gas configuration to be 25-30 times lower than that of OCV hold testing running hydrogen and oxygen. They concluded that FER was dictated by the hydrogen gas cross over rate, questioning the influence of hydrogen peroxide on the durability of PEMFC.

FER is one of the most commonly used metrics for in-situ fuel durability studies [14, 22, 23]. However, a correlation between the number of end groups and FER has not been established [22, 24]. While chemically stabilized ionomers have shown improved durability in Fenton’s test, this is less evident for in-situ testing, typically involving transient operation. The chemistry of fuel cell degradation is obviously complex and has more pathways than those represented by the Fenton test. For in-situ testing, FER is strongly dependent on test conditions and the fuel cell components used. Table 14 shows values spanning three decades, with increasing, stable as well as decreasing trends are reported.

LaConti et al. [25] reported low-molecular-weight fluorocarbon sulfonic acids in the product water from Nafion® PEMFC stacks. Escobedo et al. [26, 27] performed Nuclear Magnetic Resonance (NMR) spectroscopy studies on water from OCV hold tests as well as Fenton tests and found fragments of the complete side chain in
addition to smaller fragments like trifluoro acetic acid. Tran et al. [28] investigated effluent water from both accelerated *ex-situ* tests with vapor phase hydrogen peroxide as well as *in-situ* tests by means of Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). They found for both cases fragments of, or complete side chains. Healy et al. [6] used both NMR as well as Mass Spectrometry (MS) to analyze water extracted from a stack tested under several conditions in addition to water from Fenton testing and found only fragments containing a sulfonic acid group. Significant masses of the fragments relative to that of fluoride ion were found, although no exact quantification was given. Chen et al. [29] analyzed effluents from OCV hold experiments and found, in cases of low humidification, significant amounts of trifluoro acetic acid. The use of FER as a metric for chemical degradation assumes complete decomposition of the fluorine content of the membrane into hydrogen fluoride. The use of FER as a metric can also be justified given a constant or known ratio of fluoride to total fluorine in the fuel cell effluents. Knowledge of this ratio has however not been established. It can be speculated that factors affecting the quantity of fluorine containing fragments leaving the fuel cell are dependent on 1) the concentration of hydroxy radicals and 2) the retention time of the fragment in a location where radicals are available for attack. The latter is most likely dependent on the reactant gas flow rate.

In this work we monitor both FER as well as total fluorine emission rate (FtER) of a fuel cell durability experiment. By quantifying the total fluorine concentration in the effluents, the ratio of total fluorine to fluoride can be monitored over time. This ratio has not previously been reported. Any change in this ratio over time could provide information about the chemical degradation occurring in the fuel cell. New methodology has been applied to sampling of total fluorine as well as fluoride in the fuel cell effluents [20]. Additionally, the accumulated fluoride content in the anode gas scrubber was monitored continuously by a mounted fluoride-selective electrode. The anode and cathode effluents were monitored individually, so that more information about the degradation rates near each electrode could be obtained.

Constant operating conditions considered not to be accelerating degradation were chosen for several reasons. Firstly, the methodology is sufficiently sensitive to the FER rates expected for non-accelerating conditions. The chosen methodology has a documented quantification level of 8.6 µg F L⁻¹, sufficient according to FER previously reported in Table 14. Secondly, constant operating conditions were chosen
in order to be able to evaluate if the ratio FER to FtER would change with time invariant of the operating conditions. Potentiostatic control was chosen since it is often speculated that hydrogen peroxide formation is voltage dependent, thus providing a constant formation rate at 0.7 V throughout the experiment.

4.3 Experimental

Fuel cell durability test

The experiment was performed with a 10 cm² stainless steel housing with parallel serpentine flow fields and pneumatic clamping pressure control. A Gore™ Primea Select® 58 membrane electrode assembly (MEA) and E-TEK ELAT V2 gas diffusion layers (GDL) were used. The cell was thermostatted at 40 °C while hydrogen and air gas streams were bubbled through deionized water at 50 °C. The active area was pressurized to 10 bar. Gas conversion was maintained at 0.8 and 0.4 for anode and cathode respectively. Minimum flows were set to 20 and 30 nmLpm. After initial pressure- and gas cross-over testing, the system load was set to 0.7 V without any break-in procedure. A polarization scan was performed every 4 hours. The scan was recorded in 15 minutes from 0.2 V to OCV in 12 steps of decreasing duration. The cell ohmic resistance was estimated by means of current interrupt (CI) technique every 12 minutes. The CI estimate was not verified by high frequency resistance (HFR) measurements and was only used to illustrate relative changes during the experiment.

Fenton test

To correlate cell testing with ex-situ Fenton testing with respect to total fluorine and fluoride emission, a 50 mm ø piece of as-received Nafion® 117 was immersed into a solution of hydrogen peroxide (30% wt p. a., 100 mL) added iron sulfate (p. a.) to 100 ppm concentration of Fe²⁺. During the 14 day test, hydrogen peroxide was replenished frequently.

Effluent scrubbing

Cathode effluent gas was scrubbed with two gas washing bottles (250 mL, porosity 100-160 µm) containing sodium hydroxide (0.5 M, 100 mL) in sequence. For the anode, similar bottles were used. The first was however equipped with a fluoride-selective and Ag/AgCl/KCl (saturated) double junction reference electrode.
Orthophosphoric acid (0.5 M, 100 mL) was used as absorbent/electrolyte in this bottle. The F-ISE was initially calibrated against fluoride standards within the relevant concentration range.

Sample alkaline fusion
In order to digest the organic fluorine containing material, alkaline fusion was used. Sample aliquots of 30 mL were transferred to lidded nickel crucibles. The anodic samples were made alkaline by addition of NaOH (5 M, p. a.). Water was evaporated from the samples before they were covered with NaOH pellets (5 g, p. a.). The crucibles were lidded and placed in an oven. The oven temperature was ramped to 560 °C in two hours and dwelled at 560 ± 20° C for another two hours. After cooling the samples were dissolved in 75 mL distilled water at 70-80 °C for 24 hours before being transferred quantitatively to volumetric flasks (250 mL). Background level assessment was performed frequently by only adding NaOH (5 M p. a., 5 mL) then following the same procedure.

Analysis of fluoride
Analysis was performed on a Metrohm setup consisting of 781 Ion meter, 799 Titrino with 1 mL burette and 824 Sample changer with sample stirrer. The 799 Titrino was used to add 1000 mg L⁻¹ (sodium) fluoride standard. Aliquots of volume 30 mL were transferred by pipette to a measuring beaker containing hydrochloric acid (0.5 M p. a., 10 mL). Deionized water was added to 50 mL total volume. After the initial electrode EMF was recorded, three standard additions by NaF standard were performed. The additions were calculated dynamically so that the change in electrode voltage was in the order of 10 mV. All samples were analyzed with at least one replicate. For the Fenton test, aliquots of 5 and 1 mL were used for FtER and FER respectively. As only the ratio of FtER to FER was reported, correction for fluoride complexation by Fe³⁺ was not performed.

Online fluoride assessment
The fluoride selective electrode was calibrated by recording the electrode voltage for several samples of orthophosphoric acid containing fluoride for the expected fluoride concentration range for the experiment. The online fluoride concentration was subsequently calculated from the electrode calibration curve. The end volume of the
sample was recorded and a correction for dilution was performed assuming constant water emission in the interval. Further, a pH correction for free fluoride was performed by correcting for the dilution by water. The pH was measured before and after sampling by means of a Metrohm pH electrode. The background concentration of fluoride for the orthophosphoric acid used was found to be 12 µg L⁻¹.

4.4 Results and discussion

4.4.1 Fuel cell durability

The fuel cell durability test was performed for approximately 1650 hours. During this period, the test was interrupted three times due to system faults. These interruptions are defined for further reference: A) between 330-360 hours the system was running at OCV, B) between 950-985 hours the system was running at OCV, while lack of air humidification increased cell resistance until previous levels were restored at 1025 hours and C) between 1440-1560 hours the cell was running at OCV. Loss of system load was the cause of all excursions to OCV. During these excursions, the cell was exposed to minimum gas flows. Cell ohmic resistance data is missing from A-C due to the system load fault.

Current density and ohmic resistance profiles for the test are shown in Figure 7.
Figure 7. Durability test progression. Red dots indicate current density recorded under 0.7 V potentiostatic control. Black dots indicate specific resistance obtained by current interrupt technique. Indicated are also the interruptions marked A-C where excursions to open circuit voltage (OCV) occurred, and also the performance decay $a_{A-C}$ calculated as average change in current density per unit time.

After 48 hours the system performance peaked at about 0.38 A cm$^{-2}$. This is an average based on the transient current density resulting from the frequent polarization scans performed. The average degradation rate up to interruption A at 330 hours was 24 µA cm$^{-2}$ h$^{-1}$. Resuming the experiment after interruption A, a performance loss of 50 mA cm$^{-2}$ was observed. From this point on, the degradation rate increased to 76 µA cm$^{-2}$ h$^{-1}$. Resuming the experiment after interruption B, a performance loss of 25 mA cm$^{-2}$ was observed. Contrary to interruption A, the change in degradation rate was basically unaltered. Resuming the experiment after interruption C, an increase in performance of about 25 mA cm$^{-2}$ was observed. The degradation rate was, however, increased more than fivefold to 380 µA cm$^{-2}$ h$^{-1}$. Cell ohmic resistance dropped rapidly the first 48 hours then more slowly down to 0.1 Ω cm$^2$. For the remainder of
the experiment, the resistance dropped very slowly to a value slightly below 0.1 Ω cm$^2$.

4.4.2 Performance degradation rates

To assess the degradation rates at various load levels, polarization scans were performed. The degradation rates calculated are shown in Figure 8.

![Figure 8. Cell performance losses. The performance losses were calculated as the change in current density per unit time for the first 1400 hours of the experiment. The following load levels were assessed: 0.8 V (red triangles), 0.6 V (green squares), 0.4 V (orange circles) and 0.2 V (blue diamonds).](image)

The performance loss rate is lowest for the 0.8 V setting with a value of 50 µA cm$^{-2}$ h$^{-1}$ and increases with load setting, i.e. lower cell voltage. The voltage losses were almost identical for the 0.4 V and 0.2 V load settings. The OCV loss for the first 900 hours the rate is 5 µV h$^{-1}$. Over 1635 hours the rate is 16 µV h$^{-1}$. This is quite high compared to other non-accelerated experiments published [30].
4.4.3 Fluorine and fluoride emission rates

Due to the higher water release rates at the cathode, sampling was performed more frequently at this electrode. Eight samples were collected in 1078 hours. The samples from the secondary scrubbers were also quantified. As the total fluorine and fluoride concentrations estimated did not contribute significantly to the overall emission rates, these samples were omitted from the results. On the anode side, four samples were collected in 1632 hours. The samples of the secondary scrubbers were quantified and the levels found too low to contribute to overall release rates, and were thus omitted.

Cathode emission

The calculated Fluoride (FER) and Total Fluorine (FtER) Emission Rates are presented in Figure 9.

![Figure 9. Cathode FtER (solid red squares) and FER (open red squares) are plotted against the primary ordinate axis. Trend lines are included for both FtER (dotted line) as well as FER (solid line) where the samples K7 (456 hours) and K15 (1078 hours) have been omitted from regression. The ratio between FtER and FER for each sample is indicated by blue triangles plotted against the secondary ordinate axis. Error bars indicate one standard deviation for the analytical result.](image-url)
The highest emission rates are found for samples recorded during interrupts A and B, samples K7 and K15. K15 is exceptionally high, suggesting that the combination of OCV and dry conditions for interrupt B enhances chemical degradation of the ionomer. Excluding these samples, the trend line indicates that FER is increasing with time. FtER, however, shows a decreasing time trend. The ratio FtER to FER is thus decreasing even more pronounced than FtER alone.

Cathodic FER is increasing from 34.9 to 53.5 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\), omitting the samples containing OCV excursions. The highest recorded FER is 141.4 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\) for the sample containing OCV excursion at dry conditions. The averaged FtER and FER for all eight samples was found to be 103.8 and 62.3 ng F\(^{-}\) cm\(^{-2}\) h\(^{-1}\), respectively. The averaged ratio FtER to FER is thus 1.7.

There are several possible sources of organically bound fluorine in the effluents. The GDL material might release PTFE that could contribute to FtER. During fuel cell break-in procedures, significant morphological changes to the ionomer phase are observed. In addition to the possibility of residue from production process, these morphological changes might contribute to FtER by release of fragments to the effluents.

**Anode emission**

The calculated Fluoride (FER) and Total Fluorine (FtER) Emission Rates are presented in Figure 10.
Figure 10. Anode FtER (solid black squares) and FER (open black squares) are plotted against the primary ordinate axis. Trend lines are included for both FtER (dotted line) as well as FER (solid line). Online FER assessment (open green squares) is plotted against the primary ordinate axis. The ratio between FtER and FER for each sample is indicated by blue triangles plotted on the secondary ordinate axis. Error bars indicate one standard deviation for the analytical result.

Similar to the cathode emission results, the sample recorded during interrupt B, A5, has the highest FtER and FER values, 55.8 and 76.7 ng F⁻ cm⁻² h⁻¹ respectively. The sample with the lowest FER, A1, is the only sample not containing an OCV excursion. Both FtER and FER trend lines show an almost identical increase with time, although a large variance for the regression is high. For the first 600 hours of the experiment, a similar trend to that of the cathode was observed: decreasing FtER and increasing FER.

The FtER to FER ratio is initially high, but then decreases significantly. The averaged FtER and FER for all four samples was found to be 48.2 and 36.9 ng F⁻ cm⁻² h⁻¹, respectively. The averaged ratio FtER to FER is thus 1.3.
Online fluoride assessment

The online FER assessment is shown in Figure 11.

Figure 11. Online FER assessment for samples A1 (blue), A3 (brown), A5 (green) and A7 (red). FER is found from the slope of the curves multiplied by the volume of the sample, and corrected for 10 cm² cell area. FER has unit ng F⁻ cm⁻² h⁻¹. In parenthesis is the corresponding FER estimate from by batch analysis of the sample. The start time of the interruptions A-C are indicated to illustrate the impact on online fluoride concentration assessment.

Initially, the electrode potential is defined by the background fluoride concentration of the electrolyte. The correlation between FER online assessment and the batch quantification is best illustrated for sample A1 where no interruptions in the experiment occurred. While the online estimate of FER is 10 ng F⁻ cm⁻² h⁻¹, the batch analysis found FER to be 17 ng F⁻ cm⁻² h⁻¹. For the three other samples, the interrupts A, B and C can be seen to change the accumulated fluoride concentration of the samples. Direct comparison between batch and online FER assessment is not applicable for samples A5 and A7. Here, the batch analyses contain the fluoride produced from interrupts B and C respectively, whereas the online assessment does not. For sample A3 the online assessment is performed by taking the slope for the sample duration, thus containing interrupt A. For batch A5, the impact of OCV in
combination with dry conditions is clearly seen by an exponential increase in the sample fluoride concentration.

From Figure 11 it can be seen that the online anode FER assessment, ignoring A3 containing stop A, indicates an increasing FER with time. This increase is smaller in magnitude than what was found for the FtER and FER by batch analysis. Online FER is generally lower than the estimates obtained from batch analysis. The online FER estimate is most likely inferior to that from batch analysis due to the uncertainties involved in calculations from electrode calibration as well as dilution and pH corrections.

**Cathode to anode emission symmetry**

For comparison, the cathode samples corresponding to the anode sampling intervals have been summed. The ratios of cathode to anode emissions are shown in Table 15.

**Table 15. Cathode and anode emission rates and their ratios. The cathode samples within the same time interval as that of the anode sample are summed for direct comparison between the electrodes.**

<table>
<thead>
<tr>
<th>Batch</th>
<th>Cathode FER</th>
<th>Cathode FtER</th>
<th>Cathode FtER:FER</th>
<th>Anode FER</th>
<th>Anode FtER</th>
<th>Anode FtER:FER</th>
<th>Cathode to Anode ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1/ΣK[1,3,5]</td>
<td>33.2</td>
<td>72.8</td>
<td>2.2</td>
<td>16.8</td>
<td>27.8</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>A3/ΣK[7,9]</td>
<td>53.2</td>
<td>81.0</td>
<td>1.5</td>
<td>24.9</td>
<td>24.8</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>A5/ΣK[11,13,15]</td>
<td>86.0</td>
<td>137.2</td>
<td>1.6</td>
<td>55.8</td>
<td>76.7</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Average</td>
<td>62.3</td>
<td>103.8</td>
<td>1.7</td>
<td>36.9</td>
<td>48.2</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

Both FtER and FER are higher at the cathode. The FtER values are, with the exception of sample A3 for which they are almost identical, higher than FER. Table 15 shows that sample A3/ΣK[7,9] has the highest ratio. The last sample, A5/ΣK[11,13,15], has the lowest ratio observed.

Cathodic FER is initially twice that of the anode. This value drops to 1.5 for the last comparable sample. Literature data on FER for individual electrodes is scarce. Aarhaug *et al.* has documented almost identical emission rates for both electrodes.
when running OCV [8] as well as higher anode emission rates running ON/OFF accelerated test protocols [31].

It has been suggested by Fenton et al. [15] that the retention time of fragments near the electrodes could influence the effective degradation of fluorocarbon fragments and thus affect the FtER to FER ratio. Gas flow rate at the electrode is therefore likely to influence the ratio. Further, it can be speculated that higher flow rates more efficiently remove fluorocarbon fragments from the MEA and into the effluents.

Cathode and anode combined emission rates and fluoride mass balance assessment

For this experiment the combined averaged cathode and anode FtER and FER up to 1078 hours is found to be 153.3 and 98.9 ng F cm\(^{-2}\) h\(^{-1}\), respectively. The averaged ratio FtER to FER is thus 1.6. Assuming the membrane density to be 2 g cm\(^{-3}\) and the fluoride content to be 75 %, this amounts to an ionomer loss of 4.7 % and 7.1 % for fluoride and total fluorine respectively.

The overall FER for this experiment is within the FER range shown in Table 14.

Water emission rates

The Water Emission Rates (WER) for the cathode and the anode are shown in Figure 12.
Initially, WER is about 2.5 times higher at the cathode. The cathode WER drops quicker than for that of the anode. As seen in Figure 12, most of this discrepancy is accounted for by the reduced water production from the performance losses. The remainder can partly be explained by the fact that for the experimental conditions used, the air flow is five times higher than the hydrogen flow. Therefore, a larger reduction in air flow than hydrogen is the result of the reduced performance. The estimated water production is calculated from the current density at 0.7 V. During the interruptions A-C, the estimate therefore assumes water production. As seen by negative values in Figure 12, the estimate is too high.

Even with the higher gas flow at the cathode, a higher WER at the anode is observed when produced water is excluded from the cathode WER estimate. This implies that there is a net flux of water from the cathode to the anode. As the electrolyte is considered to be a stronger acid than hydrogen fluoride, fluoride will prevail in the form of HF within the membrane [32]. This makes correlation of FER with
degradation at the electrodes difficult, as the net water flux in the fuel cell has an impact on the individual FER at the electrodes.

**Fenton test**

The total fluorine versus fluoride found in the solution from the test gave a ratio of 1.2. This ratio indicates that even with sufficient concentration and retention time in solution with hydroxy radicals, there will still be organically bound fluorine present in the Fenton reagent solution. The membrane sample was not visibly degraded after fourteen days, so bulk ionomer was still available for chemical attack by radicals.

### 4.4.4 Correlation between fluoride emission rates and performance data

FER is commonly used to assess chemical degradation. The membrane bulk phase is considered to be the major source of fluorine in the fuel cell. Nevertheless, degradation of the proton conducting part of the three phase area of the electrodes is a source of fluorine in the effluent. For radical formation at the electrodes, this ionomer phase would be attacked by the radicals. Loss of ionomer from the three phase area would reduce the ElectroChemical Surface Area (ECSA) and thus performance. In the case of hydrogen peroxide formation, the peroxide has sufficient lifetime to diffuse into the bulk membrane. Catalytic conversion by metal ions would be required to produce radicals that degrade the bulk membrane phase. With this route, chemical degradation can occur with limited performance losses. *Post mortem* analysis often show severe thinning of the membrane [7]. There is therefore the possibility that FER might not correlate with performance data.

The results in Figure 9 and Figure 10 show FER at both electrodes to increase with time. By the loss of 4.7% of the fluorine, it can be assumed that a slight thinning of the electrolyte membrane will increase reactant flux through the membrane somewhat. This increase is, however, counteracted by the reduced bulk mass of fluorine available for attack.

Data from Liu *et al.* [7] show a correlation between lifetime and FER. These were experiments with similar operating conditions but with a varying current density setting for each experiment. A similar trend, albeit having slightly lower correlation, can be shown between the operating current density and FER. It was investigated whether the reduced current density output of the fuel cell for this experiment would
4.5 Conclusions

For this durability experiment considered non-accelerating, it was found that a significant part of the fluorine leaving the fuel cell is organically bound. For both electrodes, an increase in FER with time is observed. No correlation between increased FER and performance was found. It is plausible that increased reactant cross-over from thinning of the membrane increases FER with time. Another source of increased FER would be the reduced FtER as more fragments are degraded to release HF. Nevertheless, some of the scatter found in published FER data could be at least partly explained by the fact that only one part of the degradation products are studied rather than the total fluorine emission. This work shows that the ratio FtER to FER ratio changes with time. A justification of the use of FER as a metric for chemical degradation requires FtER to FER ratio to be either constant or known. This work shows that even for an experiment performed at constant operating conditions, this ratio changes with time.

correlate with FER. Table 16 lists the samples with their emission rates as well as the averaged current density for the sample period. The standard deviation reflects the break-in period (sample K1, A1) as well as stops A (K7) and stop B (K15, A5). No correlation between current density and FER/FtER was found. Although this experiment progressed potentiostatically, it has been suggested that the degradation mechanism is independent of electrode potential [15].

Table 16. Averaged operational load and FER/FtER.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Timeline (h)</th>
<th>Average j (A cm$^{-2}$)</th>
<th>SD (A cm$^{-2}$)</th>
<th>FER (ng F$^{-1}$ cm$^{-2}$ h$^{-1}$)</th>
<th>FtER (ng F$^{-1}$ cm$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>97</td>
<td>0.32</td>
<td>0.09</td>
<td>34.9</td>
<td>81.4</td>
</tr>
<tr>
<td>K3</td>
<td>177</td>
<td>0.38</td>
<td>0.01</td>
<td>39.0</td>
<td>79.1</td>
</tr>
<tr>
<td>K5</td>
<td>319</td>
<td>0.37</td>
<td>0.02</td>
<td>28.8</td>
<td>60.3</td>
</tr>
<tr>
<td>K7</td>
<td>456</td>
<td>0.32</td>
<td>0.03</td>
<td>65.0</td>
<td>93.6</td>
</tr>
<tr>
<td>K9</td>
<td>585</td>
<td>0.31</td>
<td>0.02</td>
<td>40.8</td>
<td>67.7</td>
</tr>
<tr>
<td>K11</td>
<td>721</td>
<td>0.30</td>
<td>0.02</td>
<td>48.1</td>
<td>59.2</td>
</tr>
<tr>
<td>K13</td>
<td>888</td>
<td>0.29</td>
<td>0.02</td>
<td>53.5</td>
<td>76.8</td>
</tr>
<tr>
<td>K15</td>
<td>1078</td>
<td>0.24</td>
<td>0.05</td>
<td>141.4</td>
<td>245.4</td>
</tr>
<tr>
<td>A1</td>
<td>319</td>
<td>0.36</td>
<td>0.06</td>
<td>16.8</td>
<td>27.8</td>
</tr>
<tr>
<td>A3</td>
<td>585</td>
<td>0.32</td>
<td>0.03</td>
<td>24.9</td>
<td>24.8</td>
</tr>
<tr>
<td>A5</td>
<td>1078</td>
<td>0.27</td>
<td>0.04</td>
<td>55.8</td>
<td>76.7</td>
</tr>
<tr>
<td>A7</td>
<td>1632</td>
<td>0.23</td>
<td>0.02</td>
<td>37.3</td>
<td>45.8</td>
</tr>
</tbody>
</table>
In order to investigate whether the change is indicative of a change in the dominating degradation mechanism, further experiments are required. By running hydrogen and oxygen as reactants, identical gas flows at both electrodes could be used. This would elucidate further whether the effect of gas flows on F1ER to FER ratio: either retention time of fragments in locations with high radical concentrations, or the transport of fragments out of the membrane.

4.6 Acknowledgement

Nordisk Industriforskning is acknowledged for supporting this PhD work.

4.7 References


5 Degradation Rates of PEM Fuel Cells Running at Open Circuit Voltage

5.1 Abstract
Degradation experiments of PEM fuel cells running at open circuit voltage have been performed. Two levels of gas flow rates were applied. No other condition expected to give source to accelerated degradation was chosen. The change of gas flow rates was compared to drop in open circuit voltage and loss of peak effect, i.e. maximum effect obtained from the polarization curve. Further, these losses were compared to the fluoride release rates measured throughout the experiment. The results indicate that fluoride release rates contain contributions from both drop in open circuit voltage as well as loss of peak effect performance.

5.2 Introduction
Mechanisms for degradation of PEM fuel cell systems are known to be a function of operating conditions (temperature, pressure, load, humidification, fuel stoichiometry, transients), but are still poorly understood. For the assessment of degradation rates under various operating conditions, development of non-destructive characterization techniques are of great value. Non-destructive characterization techniques are scarce due to the integrated nature of fuel cells. Possible techniques for assessment of degradation are fluoride release rates (FER), Cyclic Voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Neither of these techniques is implemented into a standard test protocol for PEM fuel cell systems.

Durability studies of fuel cell systems at open circuit voltage (OCV) are normally outside the experimental window since system design often incorporates flushing of electrodes with inert gas when idling. A consequence of OCV is gas cross-over assumed to cause degradation. Although oxygen mobility is less than that of hydrogen, electrochemical reduction of oxygen to hydrogen peroxide is favored by the anode potential. Liu et al. [1] showed that CV can be use to quantify hydrogen
peroxide \textit{in-situ}, and found the amount of hydrogen peroxide to be a function of membrane thickness. Hydrogen peroxide was found mainly on the anode side.

Degradation of PEM systems is frequently reported as a consequence of hydrogen peroxide formation in the fuel cell. Although hydrogen peroxide is a strong oxidizing agent, perfluorinated sulfonic acid (PFSA) membranes are fairly stable in concentrated solutions. However, metallic contaminants like iron, copper and titanium present in the membrane are able to convert hydrogen peroxide into far more potent hydroxy and hydroperoxy radicals [2]. This so-called Fenton reaction mechanism is assumed to be a mechanism of degradation in fuel cells [1, 3-6] and, under the presumption of hydrogen peroxide transport in water, it can occur throughout the membrane.

Using FER as indicator for degradation rate is frequently reported. Degradation of PFSA occurs amongst others by chemical attack of end groups like carboxylic acid [7]. The resulting fragments are not perfluorinated and are prone to further chemical attack. Several mechanisms are available, but most of them results in hydrogen fluoride formation. This has been verified by comparison of pH with pF [4, 5]. Whereas Baldwin \textit{et al.} [8] found FER to be an excellent indicator of fuel cell lifetime, Liu \textit{et al.}[9] found little correlation between lifetime and FER. Pozio \textit{et al.} [5] reported stainless steel housings to produced higher FER than aluminum ones, suggesting a Fenton mechanism.

As the bulk content of ionomer in the fuel cell is the membrane, FER reflects mainly the fluoride losses from the electrolyte [4]. Although changed membrane resistance is a result of membrane thinning or contamination, degradation of ionomer in the electrode active area is more significant.

In our laboratory, a research program is undertaken in order to investigate the feasibility of relative and absolute FER as a non-destructive indicator of PEM fuel cell degradation. In this work, FER has been studied as a function of different flow rates at OCV under otherwise constant conditions. Except for OCV, the conditions are expected to cause minimal degradation. Earlier, similar experiments have been performed at 0.7 V [10]. The experiments aim to establish a connection between
degradation rates and FER. In addition to FER, change of FER with respect to time is compared to various operating conditions and their resulting performance degradation. By breaking down the total degradation rate into individual mechanisms, a better understanding of the correlation between degradation and FER is obtained. Experiments with the aim of differentiating degradation are currently running. To assess changes in electrode active area, characterization by CV and EIS is under implementation. Post mortem characterization with SEM and TEM will gain information of membrane thinning, catalyst agglomeration and dislocation. By performing experimental design to operating conditions, a better understanding of contributions to degradation can be obtained.

5.3 Experimental

The fuel cell used in this work was a 10 cm$^2$ active area stainless steel housing with double serpentine flow channels. The housing was pneumatically pressurized at 2 barg. Gas diffusion layers used were E-TEK ELAT V2 double sided. MEA was Gore™ Primea® Series 58. Gases used were high purity hydrogen and synthetic air. The cell temperature was maintained at 40 °C, and the anode gas was humidified at 50 °C. To characterize performance loss, polarization curves were recorded every 12 hours by a 15 minute polarization scan from 0.2 V to OCV. The OCV is here represented by voltages at zero current. During scanning the gas flow rates were conversion controlled with stoichiometries of 1.25 and 2.50 for the anode and cathode respectively. Ohmic resistance was measured by Current Interrupt (CI). During experiments, effluents from both anode and cathode side were scrubbed through sodium hydroxide (0.5 M, 100 mL) in 250 mL gas washing bottles. Scrubber absorbents were analyzed for fluoride by fluoride selective electrode potentiometry [11]. System break-in was done by running the cell conversion controlled at 0.6 volt. Once stable performance was obtained, load was turned off and gas flow fixed at the setpoints for each experiment.

Loss of performance during operation at OCV was assessed at “low” and “high” flow conditions. The “low” condition was limited by mass flow controller range of 0.02 NL min$^{-1}$ for the anode and 0.03 NL min$^{-1}$ for the cathode. For the “high” flow rate experiment, the flows were increased fivefold.
5.4 Results and discussion

The experiment at “low” flow rate was run for 1346 hours. After about 200 hours, the experiment was interrupted for 50 hours due to power failure. Under this interruption there was no flow of gases. The experiment under “high” flow rate was run for 1008 hours. In the interval between 650 and 800 hours, reduced humidification of the anode occurred. At the end of each experiment, attempts to revitalize the system by applying a voltage of 0.5 V failed.

Figure 13 shows the course of the experiments with respect to OCV and ohmic resistance. The “low” flow rate experiment shows a fairly constant decline in OCV. The ohmic resistance shows after initial break-in a slight decrease up to 500 hours of operation. From there the resistance increases for the rest of the experiment. Xie et al. [12] have reported a similar trend for changed ohmic resistance.

![Figure 13. OCV and specific resistance. The transient behavior is the result of polarization scans recorded every 12 hours. Initial ohmic resistance appears solid due to more frequent recording during system break-in.](image-url)
The “high” flow rate experiment shows a more complex OCV loss. Up to about 650 hours, the trend appears constant although at a higher rate than that of the “low” flow rate experiment. The loss of anode humidification from this point on is clearly seen by an increase in ohmic resistance as well as a sharp, non-linear loss of OCV. When the ohmic resistance is restored to initial level at 800 hours of operation, a sharp increase of OCV is observed. From this point on, the loss of OCV appears to be linear, yet of higher rate than observed prior to loss of humidification.

Figure 14 shows the performance of the “high” flow rate experiment. The polarization curves show in addition to overall performance loss, a characteristic drop in OCV.

![Figure 14. Polarization curves recorded after the number of hours given in legend. Curves 636h and 833h are prior to, and after loss of humidification. Dashed curve 734h* was recorded during loss of humidification.](image)

The drying out of MEA appears to affect both OCV as well as overall performance. The polarization curve recorded during loss of humidification shows a polarization curve shape similar to the previous. A higher loss of OCV is registered, possibly from increased cross-over. The polarization curve recorded just after humidification is
restored show severe performance loss as well as irregularities in shape. The OCV is further reduced, suggesting irreversible losses by lack of humidification. The most striking feature of these curves is the fact that the OCV is, after only 1008 hours of operation, reduced to 0.55 V.

Comparing the two experiments when it comes to losses of peak effect is illustrated in Figure 15.

![Figure 15. Fluoride release rates (left ordinate) and peak effect relative to initial value (right ordinate) for “low” and “high” flow rate experiments. C indicates cathodic FER, A anodic FER.](image)

The loss of peak effect is significantly higher for the “high” flow rate experiment. In the “low” flow rate experiment a trend of decaying peak effect loss is observed. For the “high” flow rate experiment, a more sustained loss of peak effect is observed. From Figure 13 it appears that the loss of OCV between the experiments is greater than the loss of peak effect. However, with the contribution to degradation for the “high” flow rate experiment unknown, direct comparison cannot be made.
Fluoride emission rates are presented in Figure 15. For the “low” flow rate experiment, the FER show an exponentially decaying trend. The initial rates are comparable to previous experiments run under similar conditions with a load of 0.7 V [10]. At 0.7 V, nearly constant FER was obtained. The anode and cathode release rates reveal no information on FER symmetry. The “high” flow rate experiment show initial FER of more than five times those of “low” flow rate experiments. No symmetry of FER at the anode vs. the cathode is revealed. The FER drops with time, faster than for the “low” flow rate experiment.

The experiments show that “high” flow rates yield higher loss of peak effect. A significant loss of OCV characterizes the experiment of “high” flow rate. The initial FER for the two experiments reflects the fivefold increase in flow rates. The FER decay is higher for the “high” flow rate experiment.

FER both reflects peak effect losses as well as drop in OCV through changed gas flow rates. While the order of magnitude of FER reflects the flow rates, peak effect and FER decrease with time. A decaying peak effect degradation rate is reflected by decreased FER. A sharp drop in FER correlated to sustained degradation rates cannot be explained from the given data. The correlation between OCV and FER does initially correlate to gas flow rates. If the consequence of higher gas flow is increased cross-over, this could explain the reduced OCV. Degradation of the electrolyte which would facilitate higher cross-over should, however, lead to sustained if not increasing FER. A decay in FER for accelerated lifetime test protocols is also reported by Liu et al. [9]. Liu concluded that FER could not be used to assess lifetime of PEM fuel cells due localized and mechanical nature of degradation. The results of this work give no indication of as of whether degradation of the electrolyte is symmetric. To use FER to assess this problem, knowledge of transport of fluoride in the electrolyte has to be obtained. A consequence of this is the knowledge of the water balance in the fuel cell.

The results indicate that FER could be correlated to both losses of OCV as well as performance. In order to investigate this further, more frequent sampling of effluents are required. This will expectedly reveal more information on symmetry of release from the respective electrodes. While potentiometric quantification is accurate, the dilution in 100 mL absorbents makes the sampling frequency low. Liquid
chromatography (LC) would possibly provide high enough sensitivity, and by requiring small volumes would render frequent sampling possible. The assumption that all degradation products in the effluents are represented as fluoride should be verified quantitatively by use of alkaline fusion of samples or by LC mass spectroscopy. Water production is also addressed. This is important for transport mechanisms in the fuel cells as both hydrogen fluoride and hydrogen peroxide depend on transport by water.

5.5 References


5.5 References


6 PEMFC Degradation Assessed by Effluent Analysis from Designed Experiments

6.1 Abstract

Experimental design has been applied to study PEMFC performance and durability as a function of operating conditions. Two levels of relative humidity, clamping pressure and back pressure have been systematically applied to an ON/OFF load cycle. Effluent analysis of fluoride and sulfate has been performed to correlate the emission rates to the durability observed. Background effluent levels for fuel cell test rigs were also assessed. Fluoride emission rates increase with time. The rates are higher for the experiments with back pressure, but they do not correlate well with voltage losses. High initial emission rates of sulfate are observed. After flushing with humidified inert gas, the emission rates decline but are sustained at high rates compared to fluoride. Sulfur emission rates are higher for experiments with high humidification levels. The total mass of sulfur released is higher than expected from the ionomer equivalent weight.

6.2 Introduction

Effluent analysis is frequently used to evaluate PEMFC degradation. Liu et al. [1] reported Fluoride Emission Rates (FER) with varying time trends related to the operating conditions. Aarhaug et al. [2] have observed decaying FER for experiments running at Open Circuit Voltage (OCV), while an ON/OFF test cycle in accordance with FCTestNet [3] resulted in increasing FER. Sulfur Emission Rates (SER) in combination with FER offers possible information about side chain versus backbone attack on the ionomer. Inaba et al. [4] reported FER and SER for Fenton testing of chemical stability of Nafton®, but sulfur effluent analysis data obtained under relevant conditions are scarce. Aarhaug et al. [5] has shown that MEAs and GDLs contain sulfur from manufacturing that need be removed prior to effluent analysis.

In this work, a $2^{3-1}$ designed experiment has been performed to evaluate effluent analysis as a tool in PEMFC degradation studies. Relative humidity (A), Clamping
pressure (B) and back pressure (C) were studied at two levels for Gore™ MEA and GDLs. Replicate experiments were performed. Efforts were made in order to be able to distinguish between degradation products and contributions from humidification and fuel cell components.

6.3 Experimental

6.3.1 Designed experiments

The experiment was designed with the purpose of evaluating both performance and durability. After a break-in procedure according to Gore™, the initial voltage was recorded at 0.5 A cm⁻² to determine the between-cell variance. For all experiments cell temperature was 70 °C, minimum gas flows were 50 NmLpm and hydrogen and air stoichiometries were 1.25 and 2.50 respectively. The design parameters Relative Humidity (RH), Clamping Pressure (CP) and Back Pressure (BP) were set according to Table 17:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>RH (%)</th>
<th>CP (barg)</th>
<th>BP (barg)</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 3</td>
<td>100</td>
<td>5</td>
<td>0</td>
<td>++-</td>
</tr>
<tr>
<td>Test 1</td>
<td>25</td>
<td>5</td>
<td>1.5</td>
<td>--+</td>
</tr>
<tr>
<td>Test 4</td>
<td>100</td>
<td>10</td>
<td>1.5</td>
<td>+++</td>
</tr>
<tr>
<td>Test 2</td>
<td>25</td>
<td>10</td>
<td>0</td>
<td>-+-</td>
</tr>
</tbody>
</table>

A 24 hour load cycle was applied to accelerate degradation. After applying 0.5 A cm⁻² for 8 minutes, a polarization curve was recorded at 7 current density levels from 0 to 1 A cm⁻². Then, the load was cycled between 0.8 and 0 A cm⁻² every 15 minutes for 23 hours. The load was set from 0 to 0.8 A cm⁻² in four steps in order to avoid fuel and oxidant depletion. The cycle was run for 10 days unless the end-of-test criterion of failure to sustain 0.2 V at 0.8 A cm⁻² was met. A 10 cm² cylindrical housing with double serpentine flow fields and pneumatic clamping pressure control was used in a co-flow configuration. For the first test, Test 3, the flow fields were made from carbon composite. Disassembly of the cell after the test damaged the flow fields. For the remaining tests, flow fields made from 316 stainless steel were therefore used. Condensed water was collected from both electrodes approximately every 24 hours. The water was analyzed by Ion Chromatography (IC) for fluoride and sulfate.
Conveniently, the Sulfur Emission Rates (SER) reported in this work is on a sulfate molar weight basis.

### 6.3.2 Effluent background level assessment

To separate the degradation products from other possible contributions, several experiments were performed. To establish the background level of ions for the fuel cell test rig used, the system was flushed with N₂ at 0.5 NLpm, 100 % humidified at 70 °C. CP was set to 5 barg while the cell was operated at ambient pressure. Water was frequently sampled and analyzed by IC.

To evaluate the contribution from the gas diffusion layers, an experiment was performed where the MEA was replaced by a Teflon sheet. After initial flushing of the test rig with N₂ at 0.5 NLpm, 100 % humidified at 70 °C, the 10 cm² cylindrical cell was connected and thermostatted at 70 °C. CP was set to 5 barg while the cell was operated at ambient pressure. E-TEK double sided GDLs were used.

### 6.4 Results and discussion

#### 6.4.1 Performance and durability

The initial performance at 0.5 A cm⁻² for Test 1-4 showed an average voltage of 0.71 V and with a standard deviation of 5 mV. With the Test 3 Replicate included, the average voltage was 0.705 with a standard deviation of 12 mV. Figure 16 shows the initial performance for Test 1-4 and Test 3 replicate after the test operating conditions are set.
Figure 16 clearly shows the effect from pressurized operation as Test 1 and 4 display superior performances. The reduced volumetric flows from pressurized operation for Test 1 appear to prevent the cell from drying out. Test 2, on the other hand, suffers from lack of sufficient gas humidification. Test 3 and its replicate show only fairly good reproducibility. Especially at the two highest current densities, Test 3 shows better performance.

The polarization curves after 192 hours of operation are shown in Figure 17. Performance of Test 1 is clearly inferior to Test 4 over the entire current density range. Due to the reduced experimental design, the experiment with high RH, low CP and high BP was not performed. This prevents the ability to separate the effect of CP from RH. Test 2 failed within 24 hours and are thus not present in Figure 17.
After 192 hours of operation the variance between Test 3 and its replicate is fairly low. This indicates that for an accelerated test of 200 hours of operation the flow field materials selected have little impact on durability.

The voltage losses at OCV and 0.8 A cm$^{-2}$ were evaluated for Test 1, 3 and 4. The last five minutes of three consecutive cycle load levels for six intervals were averaged and then least squares regression was used to calculate the voltage drop and standard deviation (SD). The result is shown in Table 18:

**Table 18. Overall voltage loss for Test 1, 3 and 4.**

<table>
<thead>
<tr>
<th>Test</th>
<th>OCV Loss ($\mu$V h$^{-1}$)</th>
<th>OCV SD ($\mu$V h$^{-1}$)</th>
<th>0.8 A cm$^{-2}$ Loss ($\mu$V h$^{-1}$)</th>
<th>0.8 A cm$^{-2}$ SD ($\mu$V h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>551</td>
<td>$4.00 \times 10^{-4}$</td>
<td>287</td>
<td>$5.08 \times 10^{-5}$</td>
</tr>
<tr>
<td>Test 3</td>
<td>360</td>
<td>$1.39 \times 10^{-4}$</td>
<td>500</td>
<td>$1.70 \times 10^{-4}$</td>
</tr>
<tr>
<td>Test 4</td>
<td>91.7</td>
<td>$1.41 \times 10^{-5}$</td>
<td>28.9</td>
<td>$7.75 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Test 4 shows superior durability at both load levels. Test 1 displays its highest voltage loss at OCV. This could be explained by the pressurized operation. At 0.8 A cm\(^{-2}\) the losses are higher for Test 3 than for Test 1.

When comparing durability and performance, Test 4 shows initial performance comparable to Test 1 but the durability is superior as seen from the voltage losses in Table II. Test 2 failed after less than 24 hours and shows that low gas humidification without pressurized operation is detrimental both for performance and durability. Test 3 was operated at ambient pressure and is thus not comparable with respect to performance. The voltage loss at 0.8 A cm\(^{-2}\) is according to Table 18 higher than for Test 1. By visual inspection of the polarization curves in Figure 16 and Figure 17, the losses for Test 3 and its replicate and Test 3 are comparable at 0.8 cm\(^{-2}\). It is therefore difficult to separate durability of Test 3 from Test 1.

The between-cell variance is low for the initial performance. The replicate of Test 3, even if performed with stainless steel flow fields, show good correlation with Test 3 after 192 hours of operation.

The effect of clamping pressure is not easily interpreted in the reduced experimental design. The remaining four experiments need be performed to evaluate all effects.

6.4.2 Effluent analysis

The fluoride content in the sampled water from each electrode from the start of the experiment, and was analyzed by IC and the calculated FER are shown in Figure 18:
Generally, the FER decreased after the break in procedure. As neither the test rig nor the fuel cell was flushed with inert gas prior to the experiments, initial contribution to the FER from the test rig and production residue in GDL and MEA were expected. With the exception of Test 2, the FER increased with time. The tests with high RH (Test 3 and 4) setting show lower FER than those with low RH. Test 1 show the highest FER and also the highest increase with time. Test 3 has lower FER than Test 4. One likely explanation is the increased cross-over induced by pressurized operation for Test 4. The Test 3 replicate performed with stainless steel flow fields show only marginally higher FER. FER is generally higher for the cathode side. The exception was Test 2 where the initial anode contribution to FER was almost twice that of the cathode.

The calculated SER for the experiments are shown in Figure 19:

Figure 18. Fluoride emission rates for Test 1-4 and Test 3 replicate. As Test 2 ended in less than 24 hours, the sampling rate for this experiment was approx. 6 hours.
Like FER, the initial SER is high. After the initial decline, the SER appear to be fairly constant with time. The experiments with high RH show higher SER, with Test 3 showing the highest levels. For this experiment, the initial contribution from anode was high. This was subsequently reversed. The sulfur levels are generally more than three times those of fluoride.

FER to SER ratio analysis to characterize the chemical degradation mechanism was not performed. The SER are generally more than thrice that of FER. As an example, Nafion® of equivalent weight 1100 contains 68 per cent fluorine and 3 per cent sulfur. Clearly, the sulfur levels are too high for the effluent to represent degradation of the ionomer. Comparing Test 3 with its replica shows that the between-cell variance for SER is high.

6.4.3 Correlation between durability and effluent release rates
The FER analysis show limited correlation to the durability observed. The test showing best durability, Test 4, does not show the lowest FER. One explanation is that the enhanced crossover from pressurized operation chemically degrades the electrolyte without affecting the performance. A test of longer duration would
eventually show the mechanical consequences of thinning of the membrane. Test 1 shows the highest FER rates and also the FER increasing the most with time. This correlates well with the fact that Test 1 features the highest loss of OCV. Although not quantified, it is expected that FER will correlate well with the actual gas cross-over rate.

SER show a different trend than FER. The high RH tests show highest SER. One possible reason is that high water contents more effectively washes out sulfur from the cell. More water is exiting the cell for Test 3 than for Test 4. This should however lead to decreasing and not sustained SER with time. SER does not appear to correlate with durability. Levels are high compared to what is expected from the equivalent weight of the ionomer.

**Effluent background level assessment**

The background effluent concentrations from the test rig are shown in Figure 20:

![Figure 20. Background effluent concentrations from N$_2$ purging. As the anode was autosampled at different sampling rates and volumes, only the cathode emission rates are calculated.](image-url)
Clearly, the initial emission rates for both fluoride and sulfur are significant considering the levels seen in Figure 18 and Figure 19. For effluent analysis, the test rig should therefore be flushed with inert, humidified gas until low and stable concentration levels of the effluents are registered.

The contribution from the GDLs was found to be significant as shown in Figure 21:

![Figure 21](image-url)

**Figure 21.** Contribution to effluent emission rates from fuel cell mounted with GDLs only, separated by a Teflon sheet. The cell was connected after the fourth sample was collected after about five hours.

As expected from a test rig not flushed prior to use, initial levels are high. After four hours of flushing the rates are low and when the cell with GDLs separated by a Teflon sheet are mounted, significant increases are observed. It should be noted that the cell housing was not flushed prior to mounting. As levels observed when the cell was mounted are higher than the initial levels, where the cell was mounted for the previous experiment, it is believed that the GDL contribute to the effluent emission rates.
6.5 Conclusions

The designed experiments performed show that performance and durability are superior for the conditions given by 100 % RH, 10 barg CP and 1.5 barg BP. The variable spaces selected for the designed parameters need be extended in order to find optimal operating conditions for performance and durability. FER does not appear to correlate with voltage losses at neither OCV nor 0.8 A cm$^{-2}$. For Test 4, superior durability is not reflected by a FER higher than for Test 3. It is likely that the OCV part of the ON/OFF cycle contributes more to FER than 0.8 A cm$^{-2}$ thus diminishing this effect. An increasing FER is observed for all experiments. SER levels are high and sustained. Reproducibility of the levels between experiments is satisfactory for FER but low for SER. The levels appear to be a function of the RH level rather than reflecting performance or durability. Background levels in fuel cell test stations are observed. The system should be flushed with inert, humidified gas prior to start of an experiment. The GDLs do contribute significantly to the effluent emission rates.

6.6 Acknowledgments

Dr. Steffen Møller-Holst is acknowledged for valuable discussions regarding the planning of the experimental design performed in this work.

6.7 References


7 Patent: Method for Potentiometric Analysis in Biological Material

7.1 Patent information

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7.2 Summary

The present invention concerns a method for potentiometric analysis of fluoride in biological material, where the biological material is wet extracted and analysed for fluoride content in the same beaker, and where the sample is dissolved in an acid at a pH lower than 2. Further, the invention concerns use of the method for analysis of fluorides in aluminium industry and glassworks.

7.3 Patent description

118388/CH
2009-10-15

Application no.:

Applicant: SINVENT AS

Title: “Method for potentiometric analysis of fluoride in biological materials”

7.3.1 Invention area

The invention concerns a method for analysis of fluoride with low detection limit and short analysis time for biological materials. The invention also concerns fluoride analysis in the presence of interfering species.
The invention is generic for analysis of fluoride in aqueous solutions. The invention has superior tolerance for aluminium ion interference, often the case for biological material found near primary aluminium production sites and glassworks.

7.3.2 Background of the invention

Potentiometric analysis with fluoride ion selective electrode is a well-established methodology. The benefit for this method is a low instrumental cost and fast, precise analysis.

Fluoride selective electrodes measure fluorine in the form of fluoride. Other fluorine-containing species are not detected. Since the activity of fluoride is a function of pH, this parameter must remain constant during analysis. For an analytical representation of fluoride concentration, the activity coefficient must be buffered, to keep the relation between activity and concentration constant. This is often performed by using Total Ionic Strength Adjustment Buffer (TISAB). In the pH range 5 to 5.5 the TISAB effectively counteracts changes in pH. The use of commercially available electrodes and TISAB-buffer yields a detection limit of about 1 µM. Limiting for the sensitivity is the solubility of the electrode material, lanthanum fluoride. Leakage of fluoride from the electrode into the solution was investigated by Baumann (Anal. Chim. Acta, 54 (1971) pp. 189-197). By adding thorium or zirconium the lanthanum fluoride leakage was strongly inhibited and a detection limit down to $10^{-10}$ M was observed. By using protons or lanthanum, a detection limit close to $10^{-8}$ M was obtained.

The most significant interference for fluoride selectivity of the electrode is the hydroxyl ion. Thus, the presence of hydroxyl ions will result in too high estimates of fluoride concentration.

995-997) has analysed saliva at pH 1.2 by using a differentiated cell composed of one fluoride and pH combination electrode. At the measured pH, the difference between the electrodes represents the total fluoride content in the solution, i.e. hydrogen fluoride and fluoride. The methodology requires instrumentation where two high-impedance inputs can be differentiated. Patent application GB A 2273780 indicates fluoride analysis in acids at pH < 2.

Fluoride forms complexes and precipitates with several cations. Examples include aluminium, iron, calcium and magnesium. For fluoride analysis in matrices containing interfering complexes it is necessary to add reagent that binds the cation stronger than fluoride, to release fluoride. TISAB buffers, for example, contain CDTA, a standard complexing agent for metal ions.

For fluoride analysis in biological samples, samples are traditionally pretreated by ashing, alkaline fusion or acid extraction. Ashing and alkaline fusion are generally time and cost demanding steps due to the temperature changes involved. The purpose of the present invention is to reduce time and cost of analysis. This is achieved by combining acid extraction with fast and sensitive analysis at low pH where this is performed in the one and same analysis beaker.

Acid extraction of fluoride is commonly used for analysis of biological samples. One advantage is that extraction can be performed at room temperature. This methodology has been evaluated by Stevens (Commun. Soil Sci. Plant. Anal. 26 (1995) pp. 1823-42). In order to make extraction time shorter, the use of ultrasound is possible.

7.3.3 Brief description of the invention

The invention provides a method for potentiometric analysis of fluoride in biological samples where the biological material is wet extracted and the content of fluoride is analysed in the same beaker, where the sample is dissolved in acid with a pH lower than 2.

In order to obtain low pH values, acid is employed. Hydrochloric acid is especially preferred. Because interfering cations are present (aluminium) in the sample, phosphoric acid is preferably added for complexation or
precipitation of cations as phosphates. Hydrochloric acid can be used separately or in combination with phosphoric acid. The method is applicable for continuous monitoring of fluoride.

Examples of relevant applications include analysis of fluoride in aluminium primary production and glassworks.

For determination of fluoride in biological matrices like grass and needles, samples are dried and grounded and then acid is added to extract fluorine, complexate interfering cations and to provide optimal conditions for the analysis.

7.3.4 Short description of figures

Figure 22 shows fluoride as a function of pH in pure water (25 °C).

Figure 23 shows a predominance diagram for complexation and precipitation of Al-fluorides.

7.3.5 Detailed description of the invention

By performing analysis at pH values significantly lower than the acid constant of hydrogen fluoride (HF, pKa=3.2), a low pH dependence of the fluoride concentration is obtained in addition to high ionic strength. This is illustrated with table data from Gmelin’s Handbuch der anorganischen Chemie (Vol 5: Fluorine) where the fraction of free fluoride is given as a function of pH. In the pH range 0-2 the curve has a relatively low slope.

In the low pH range the hydroxyl ion is absent. The electrode response is very fast and approximately completely selective towards fluoride. By using an accurate burette with anti-diffusion capillary preventing leakage of standard solution into the solution, small volumes of concentrated sodium fluoride can be added without significantly changing the pH. By multiple additions of standard as described by Nagy (Light Metals Proceedings, 1978, pp. 501-516) the electrode EMF is calibrated against the added concentration of sodium fluoride so that the total fluorine concentration can be calculated. Correction of the fluoride concentration with respect to pH is not significant and can therefore be omitted.
Limits of detection for this methodology are verified to be in the range of 1 ppb. Aarhaug (Metrohm Information 33 (2004) 3, pp. 16-19) reported accuracy to be better than 5 % for analysis of samples containing 10 ppb fluoride.

Complexation and precipitation of fluorides is low at low pH (Figure 23). The methodology in itself is therefore relatively tolerant towards moderate amounts of interfering metals and other cations. In cases where the amount of interferences is high, phosphoric acid is added for complexation and precipitation of cations of aluminium, iron, calcium and magnesium. This prevents precipitation of fluorides causing erroneous analysis. The method is therefore suited for several industrial applications.

The analytical method is characterized by its simple method to obtain very fast, selective and accurate method for fluoride analysis. The method has good tolerance towards interferences. For online applications the limit of detection is a function of the electrode kinetics. Thus, this methodology is very applicable for online monitoring of fluoride.

Analysis implementation

The ion selective electrode is comprised of two electrodes; an inner reference electrode and an outer fluoride selective electrode. The inner electrode is in contact with an encapsulated fluoride solution, and thus, providing a fixed response. The outer electrode is immersed into a solution of unknown fluoride concentration. The sensitivity towards fluoride is realized by a fluoride membrane connecting the outer sample and the inner fluoride solution. This membrane is very often lanthanum fluoride, sometimes doped with europium for improved conductivity. Dependent on the difference in fluoride concentration on each side of the membrane, a potential difference is established. This potential difference causes current to run, measured by an ion meter. Relative to the inner reference, the net response for the fluoride electrode is only dependent on the fluoride content of the sample.

Shielded electrode wires are used to prevent noise pickup.

To close the electric circuit, a reference electrode is needed. Normally, a silver/silver halide electrode is used. This electrode is not polarized by the fluoride content of the solution.
Multipoint standard addition methodology is used for calibration. By connecting the fluoride selective electrode to an ion meter the ElectroMotive Force (EMF) is recorded. This value is proportional to the fluoride concentration to which the electrode is exposed. This relation is given by the Nernst equation:

\[ E = E^0 - \frac{RT}{F} \ln [F^-] \]

The relation between concentration and electromotive force is logarithmic. The correlation between electromotive force and added fluoride concentration is found by regression so that the original electrode potential in solution represents its total fluoride concentration.

As mentioned before, there is no linear correlation between potential and concentration for ion selective electrodes. For regression, either a non-linear model must be used or linearization applied. According to the invention, the method uses algorithms that linearize the correlation. This is documented by Kalman Nagy (Evaluation of the Fläkt Sintalyzer, a new semi-automatic system for fluorine analysis within the aluminium industry, TMS, Denver, 1978).

To lower the pH to less than 2 a strong acid, preferably hydrochloric acid, is used. Concentrated hydrochloric acid diluted by distilled water is approximately free from fluoride, and thus, will not interfere with the analytical result. Normally, the acid strength is chosen so that pH is in the range 0-0.5.

Chloride will provide a reference point for chloride based reference electrodes, thus providing a fast response of the reference electrode. When a stable electrode potential is obtained for the electrode system, additional potentials for the added fluoride standard concentrations are recorded. This could be e.g. a sodium fluoride standard solution.

For online applications, the dynamic changes are often of interest as is absolute content of fluoride. A pre calibration of the electrode for given fluoride concentrations as before mentioned is in many cases sufficient in order to provide online concentrations of fluoride.

As hydrogen chloride is volatile, for online application in open system use of a less volatile acid as e.g. phosphoric acid is required.

For complexation and precipitation of interfering metals, phosphoric acid is used. pH is then lower than 2, preferably in the range 1 to 1.5.
Fluorine in biological materials like grass and needles is mainly found as dust in the form of NaF, AlF₃, Na₃AlF₆, CaF₂ etc. Small amounts are often organically bound. Samples are dried and finely grounded before dissolved in acid. The extraction time varies with the sample material and must be verified by comparison with material of known fluoride content.

**Example 1: Wet extraction of fluoride from needles and grass.**

The biological sample is finely ground to a sieve diameter of 0.7 mm. Masses in the range 0.5 to 2 grams are dissolved in a 1:1 mixture of hydrochloric acid (0.5 M) and phosphoric acid (0.5 M). Fluoride analysis is performed directly in the extraction beaker where the initial electrode potential is recorded followed by one or more standard additions. The sample concentration of fluoride is found by correlating the electrode potential to the added concentrations of fluoride.

**Example 2:**

Shell is removed and the meat finely ground by a hand blender or a food processor. For shrimps shells can be left on if its fluoride content should be recorded. Krill is directly ground. As the fluoride concentration will vary with the sampling location, the masses used must be adapted accordingly. This is a compromise between sufficient fluoride content and too much solid material in the analysis beaker. The mass chosen is dissolved in a 1:1 mixture of hydrochloric acid (0.5 M) and phosphoric acid (0.5 M). The extraction period is typically between 8 and 24 hours. This could be verified by comparison with another methodology like alkaline fusion. The analysis of fluoride is performed directly in the extraction beaker as described in Example 1.
7.4 Patent claims

1. Method for potentiometric analysis of fluoride in biological materials, characterized in that the biological material is wet extracted and the fluoride concentration is analyzed in the same beaker, where the sample is dissolved in an acid at a pH lower than 2.

2. Method according to claim 1, characterized by the acid being hydrochloric acid and/or phosphoric acid.

3. Method according to claim 1, characterized by adding phosphoric acid to complex or precipitate interfering cations as phosphates when present.

4. Method according to claim 1, characterized by using ultrasound in order to reduce time consumption for extraction in the acid.

5. Use of the method according to claims 1-4 for analysis of fluorides in biological samples in locations near aluminium industry and glassworks.
7.5 Figures

Figure 22. Fluoride as function of pH in water (25 °C).

Figure 23. Predominance diagram.
7.6 Patent registration letter for Norway

Sinvent AS
Postboks 4764 Sluppen
7465 Trondheim

Att.: Kåre Herje

Oslo, 11. oktober 2010

Patentsøknad i Norge nr. 2008 3858
Sinvent AS
Fremgangsmåte for potensiometrisk analyse av fluorid i biologisk materiale

Vi har herved fornøyelsen av å kunne meddele at ovennevnte patentsøknad er bevilget til patent.

Vennligst bemerk at innsgjelse mot patentet kan innleves innen 9 måneder fra bevilgningsdatoen. Hvis vi mottar slik innsgjelse vil vi informere Dem straks.

Årsavgift forfaller til betaling hvert år på innleveringsdagen (løpedagen), men kan innbetalas innen siste dag i måneden.

Vi vil sende varsler om årsavgift i god tid før betalingsfrist.

Vennligst kontroller at opplysningene stemmer med det vedlagte offisielle patentbrev.

Patentnr. 329.357
Bevilget 4. oktober 2010
Løpedag 8. september 2008
Varighet opp til 8. september 2028

Med vennlig hilsen
Bryn Aarflot AS

Hilde Barli Schattø
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Vedlegg

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KONGERIKET NORGE
The Kingdom of Norway

Patent nr.: 329357
Patent No.

I henhold til patentloven av 15 desember 1967 er Deres patent meddelt med opplysninger som angitt i vedheftet patentkrift.

This is to certify that the Norwegian Patent Office, in accordance with the Patents Act No. 9 of 15 December 1967, has granted a patent for the enclosed invention.

Jørgen Smith
direktør
Patentbrev
Viktige opplysninger

Vi gjør oppmerksom på at ditt patentbrev er utstedt på grunnlag av de opplysninger som foreligger hos Patentstyret på meddelelsesdagen. I de aller fleste tilfeller vil meddelelsen av patent være endelig. For ordens skyld gjør vi deg likevel oppmerksom på at en innsigelse mot et meddelt patent kan bli innført.

Innsigelse:
Enhver kan fremsette innsigelse mot et meddelt patent, jf patentloven (pl) § 24. Innsigelsen må være kommet inn til Patentstyret innen ni måneder fra den dagen patentet ble meddelt. Blir en innsigelse tatt til følge skal Patentstyret oppheve patentet, jf pl § 25. En endelig avgjørelse av en innsigelse kan påklages til Patentstyrets klageorgan; Annen avdeling, innen 2 måneder fra den dagen avgjørelsen ble utsendt fra Patentstyret, jf pl § 26 og § 27.

Patentets gyldighetstid:
Patentet kan opprettholdes i inntil 20 år fra den dag da patentsøknaden kom inn til Patentstyret, jf pl § 40. For legemidler og plantefarmasetylske produkter kan det i visse tilfeller søkes om inntil fem års ytterligere beskyttelse, jf pl § 62a.

Betalings av årsavgifter:
For å opprettholde et patent eller en patentsøknad må det betales årsavgift, jf pl § 40 annet ledd. Forfall av årsavgift er siste dag i den måneden søknaden ble innført, hvilket vil si at årsavgiften ikke følger kalenderåret. Avgiften kan ikke betales tidligere enn 5 mnd før den forfaller. De to første avgiftsårene forfaller samtidig med avgiften for det tredje avgiftsåret. Ved glemt betaling kan det innbetales årsavgift innen 6 mnd etter forfall mot betaling av fastsatt forhøyelse, jf pl § 41.

Hør innehaveren av patentet eller patentsøknaden betydelige vanskeligheter med å betale kan Patentstyret gi hensikt med betalingen, jf pl § 42 og patentbestemmelsene § 26-1.

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Betales ikke årsavgiften i overensstemmelse med overnevnte bestemmelser bortfaller patentet fra og med inngangen av det avgiftsåret som avgift ikke er betalt for.
Dersom noen mener at patentet ble gitt på feilaktig grunnlag, kan det kjennes ugyldig ved dom, jf pl § 52.

Oppreisning av frister:
Dersom årsavgiften ikke blir innbetalt innen seks måneder etter ordinært forfall, kan det på visse vilkår søkes om oppreisning for oversittelse av betalingsfristen, jf pl § 72 og § 73.
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(54) Beregnelse

Fremgangsmåte for potensiometrisk analyse av fluorid i biologisk materiale

(55) Avfarte

publikasjoner

D.P. Stevens at al., "Limitations of Acid Digestion Techniques for the Determination of Fluoride in Plant Material", COMMUN. SOIL. SCI. PLANT. ANAL., 26, 1995, s. 1523-42,

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J.E. Tyler et al., "The rapid measurement of fluoride concentrations in stored human saliva by means of a differential electrode cell", Archives of Oral Biology (1989), 34(12), 995-8,

J.Zhou et al., "Method for determining fluoride ion using fluoride electrode in acidic medium", Fenxi Shipinshi (2006), 26(5), 82-84 (sammendrag)

(57) Sammendrag

Foreliggende oppfinnelse vedrører en fremgangsmåte for potensiometrisk analyse av fluorid i biologisk materiale, hvor det biologiske materialet våtekstraheres og analyseres for fluoridinnhold i samme kant, og hvor prøven er oppløst i en syre ved en pH lavere enn 2. Videre vedrører oppfinnelsen anvendelse av fremgangsmåten for analyse av fluorider i aluminiumsindustri og glassverk.
ASSIGNMENT

FOR GOOD AND VALUABLE CONSIDERATION to us by SINVENT AS, and other valuable consideration, the receipt and sufficiency of which are hereby acknowledged, we, KALMAN NAGY and THOR ANDERS AARHAUG ("ASSIGNOR"), having made an invention in "METHOD FOR POTENTIOMETRIC ANALYSIS OF FLUORIDE IN BIOLOGICAL MATERIAL" ("INVENTION"), while in the employ either as an employee or consultant of SINVENT AS, a corporation organized and existing under the laws of Norway, doing business at Klabuveneien 153, Trondheim, Norway N-7465 (sometimes hereinafter called "ASSIGNEE"), do hereby ASSIGN, SELL, and CONVEY to SINVENT AS, its successors, and assigns, the entire right, title, and interest throughout the world in and to:

1. Said invention in "METHOD FOR POTENTIOMETRIC ANALYSIS OF FLUORIDE IN BIOLOGICAL MATERIAL;"


3. Patent Cooperation Treaty international application on said invention, filed as PCT Application No. PCT/NO2009/000313 on September 8, 2009, and entitled "METHOD FOR POTENTIOMETRIC ANALYSIS OF FLUORIDE IN BIOLOGICAL MATERIAL," based on and claiming priority to Norwegian Application No. 20083858 filed on September 8, 2008;

4. United States of America utility patent application on said invention, filed as U.S. Patent Application No. 13/059,704 on February 18, 2011 (Attorney’s File No. 2181-02100) and entitled "METHOD FOR POTENTIOMETRIC ANALYSIS OF FLUORIDE IN BIOLOGICAL MATERIAL," based on and claiming priority to PCT Application No. PCT/NO2009/000313 filed on September 8, 2009;

5. All applications for patent or like protection on the INVENTION that have now been or may in the future be made by us or our legal representatives, including any continuation, continuation-in-part and any other utility applications that may be based on the INVENTION, whether in the United States of America or any other place anywhere in the world;

6. All patents and like protection that have now been or may in the future be granted on the INVENTION to us or our legal representatives, whether
in the United States of America or in any other country or place anywhere in the world;

7. All substitutions for and divisions, continuations, continuations-in-part, renewals, reissues, extensions, and the like of the applications and patents and like grants, including without limitation, those obtained or permissible under past, present, and future laws and statutes;

8. All rights of action on account of past, present, and future unauthorized use of the INVENTION and for infringement of the patents and like protection;

9. The right in ASSIGNEE to file in its name applications for patents and like protection for the INVENTION in any country or countries foreign to the United States; and

10. All international rights of priority associated with the INVENTION, applications, patents, and like protection; and

we covenant that we, and our heirs, legal representatives, assigns, administrators, and executors, will, at the expense of ASSIGNEE, its successors, and assigns, execute all papers and perform such other acts as may be reasonably necessary to give ASSIGNEE, its successors, and assigns, the full benefit of this Assignment. Further, ASSIGNOR warrants that the INVENTION is not encumbered by another assignment or obligation of assignment to a third-party and that ASSIGNOR has the full ability and authority to assign and encumber the INVENTION.

********

EXECUTED on the date indicated below, opposite my signature.

Signature: Kalman Nagy

Date: May 31, 2011

Witnessed by: [Handwritten signature]

Date: May 31, 2011

[Printed Name of Witness]
*******

EXECUTED on the date indicated below, opposite my signature.

Signature: Thor Andersen Aarhaug
Date: 2011-06-07

Witnessed by: Egil Iversen
Signature
Date: 2011-06-07

Egil Iversen
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