Investigations on Radiation Grafted Polymer Fuel Cell Membranes:
Preparation, Characterization, Application

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You cannot escape the responsibility of tomorrow by evading it today.

Abraham Lincoln (1809 - 1865)
16th President of the United States
Summary

Fuel cells are considered as energy conversion devices on different power scales, from small units with a few Watts to supply energy for cardiac pacemakers or cell phones, over engines in automotive applications, up to combined heat and power units in the Megawatt range. Independent of the application or type of fuel cell, the development are focussed on towards higher stability and reliability and the reduction of the costs. The advantages of polymer electrolyte fuel cells (PEFC), e.g. their fast start-up, compact construction, high power density, and low working temperature, make them promising candidates as power source in mobile application. However, the PEFC reliability strongly depends on the integrity of the polymer electrolyte and catalyst. The costs of acquisition and operation of a fuel cell are significantly influenced by the use of noble metals in the catalysis (platinum) and the mechanically, thermally and chemically stable membranes as polymer electrolytes for proton conduction. Commercially available state-of-the-art membranes in PEFC, perfluorinated ionomers such as Nafion®, are still too expensive. The US Department of Energy stated target costs of 40 US$/m² for membranes in automotive applications.

Membranes prepared by radiation grafting of monomers onto prefabricated films are potentially cheaper. At Paul Scherrer Institut (PSI), styrene grafted, divinylbenzene (DVB) crosslinked, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) and poly(ethylene-alt-tetrafluoroethylene) (ETFE) based membranes were developed and their properties continuously improved. In order to improve the oxidative stability of membranes, alpha-methylstyrene (AMS) and methacrylonitrile (MAN) were used as monomers and co-grafted onto FEP base films. The subsequently prepared membranes showed less degradation in fuel cell experiments (0.057 %·h⁻¹), compared to the corresponding (uncrosslinked) styrene based membranes (1.59 %·h⁻¹). A DVB crosslinked, AMS/MAN co-grafted, FEP based membrane, showed an enhanced stability (0.015 %·h⁻¹) compared to the uncrosslinked membrane. However, the stability of the PSI benchmark concerning degradation rate, a DVB crosslinked (DVB content optimized), styrene grafted and FEP based membrane (0.010 %·h⁻¹), was not achieved.

In the present work, the graft copolymerization of AMS and MAN onto pre-irradiated FEP and ETFE base films (25 µm) was investigated. The influences of the reaction parameters on the composition and mechanical properties of grafted films, the ex situ properties, and characteristics in the fuel cell (in situ) of subsequent membranes were determined. The in situ stability of membranes was investigated by the post mortem determination of their degradation.

The temperature during the graft copolymerization of AMS and MAN onto pre-irradiated base films was reduced from previously used 60 °C to 50 °C, expecting a reduction of the depolymerization of AMS-AMS units due to the low ceiling temperature of 61 °C, determined for poly-alphamethylstyrene. Indeed, the achievable degree of grafting (DoG) for long reaction
time was higher, independent of the base film, when the graft copolymerization was performed at 50 °C. Generally, a decreasing efficiency of the graft copolymerization of AMS and MAN, given by the ratio of the apparent initial polymerization rate and the termination rate, was found for a temperature increase from 35 to 60 °C. The apparent initial polymerization rate, termination rate and front velocity were parameters in a simplified kinetic model, used to fit the experimentally determined reaction profiles. The investigation of the temperature dependence between 35 and 60 °C showed that the higher initial grafting rate goes along with a decreasing achievable degree of grafting for long reaction times. The molar ratio of AMS and MAN in the grafted polymer \( R_{m,\, graft} \) was found to be influenced by the ratio of the monomers in the grafting solution \( R_{m,\, sol} \). Independent of the used base film, the reaction profiles measured for the graft copolymerization with higher \( R_{m,\, sol} \) showed lower DoG and higher \( R_{m,\, graft} \), which enables the preparation of grafted films and subsequent membranes with \( R_{m,\, graft} \) between 0.5 and 1.1, independent of the degree of grafting.

Crosslinking of membranes was previously reported to enhance the oxidative stability of ion exchange membranes. The addition of crosslinker, DVB or diisopropenylbenzene (DIPB), to the grafting solution influenced the DoG, whereas the \( R_{m,\, graft} \) was unaffected. The apparent initial polymerization rate for the AMS/MAN co-grafting onto FEP base film was higher when low crosslinker concentrations were used and lower using high crosslinker concentration in the grafting solution, compared with the grafting without crosslinker.

The proton conductivity of radiation grafted membranes depends on the concentration of ion exchange sites and their distribution across the thickness of the membrane. Confocal Raman microscopy was established to probe the distribution of the graft components over the thickness of grafted films. The method was validated with MAN grafted onto FEP films, where the fast polymerization of MAN yields pronounced grafting fronts, which were recorded as intensity profiles and converted to concentration profiles. The co-polymerization of AMS and MAN, by contrast, proceeds very slowly and the intensity and concentration profiles show a homogeneous distribution of all components. The integral molar ratio of the monomers in the grafted polymer \( R_{m,\, graft} \) was determined for the first time by CP MAS \(^{13}\)C NMR spectroscopy and the results found to be consistent with the FTIR spectroscopic based \( R_{m,\, graft} \) within ±10 % relative standard deviation.

Mechanical stability of membranes becomes important in fuel cells, regarding temperature, humidity and pressure changes during the operation. The dimensional stability of membranes is negatively affected by grafting. However, ETFE based membranes with DoG up to 46 % show a higher dimensional stability than a Nafion® 212CS membrane. Crosslinking reduces the dimensional changes, by forming a denser, three-dimensional network. Therefore, less irradiated, grafted and crosslinked films and membranes show the better mechanical properties at room temperature and ambient humidity. Based on those result, membranes with the lowest possible DoG for a sufficient conductivity should be used. From an application point of view, the results obtained in tensile tests at 80 °C and 80 % relative humidity are more promising. The mechanical properties of an ETFE based, AMS/MAN/DVB co-grafted membrane are also decreased, compared to the pristine ETFE base film, but the decrease was less pronounced than for grafted films, compared to the corresponding base film at room temperature and ambient humidity.

The ion exchange capacity, an integral measure for the concentration of sulfonic acid groups in the membrane, and proton conductivity were found to be influenced by the DoG and \( R_{m,\, graft} \).
The influence of the $R_{m,\, graft}$ is less than that of the $DoG$, which is related to the limited adjustable $R_{m,\, graft}$ range ($\approx 0.5-1.1$), whereas the $DoG$ is predominantly limited by the required mechanical properties of membranes. The IEC increased with the $DoG$ and, at a given $DoG$, with an increasing $R_{m,\, graft}$. The influence of crosslinker (DVB) on the IEC was found to be weak, whereas the proton conductivity is significantly reduced with increasing crosslinker concentration. Membranes were characterized in situ after approximately 150 h, to ensure the operation of the fuel cell under steady state conditions. The cell voltage at a given current density (550 mA·cm$^{-2}$) increased from 0.62 to 0.67 V with increasing $DoG$ of the uncrosslinked ETFE based, AMS/MAN co-grafted membranes (21 to 50 %). A proper correlation of the in situ performance with the $R_{m,\, graft}$ was not possible, however, the performance of uncrosslinked AMS/MAN co-grafted, FEP based membranes increased by trend with the $R_{m,\, graft}$. Durability tests of membranes at constant current density (500 mA·cm$^{-2}$) confirmed the enhanced oxidation stability of AMS/MAN based membranes by a reduced degradation rate (0.035 %·h$^{-1}$) compared to styrene based membranes. The need for an alternative crosslinker (DIPB) was reflected in the further reduction of the degradation rate (0.014 %·h$^{-1}$).
Zusammenfassung


Eine Möglichkeit, kostengünstige protonenleitende Membranen herzustellen, bietet das Strahlenpfropfen von dünnen Polymerfolien mit geeigneten Monomeren. Am Paul Scherrer Institut (PSI) wurden Styrol gepfropfte, Divinylbenzol (DVB) vernetzte und auf Poly(ethylen-alt-tetrafluorethylene) (ETFE) oder Poly(tetrafluorethylen-co-hexafluorpropylen) (FEP) basierende Membranen entwickelt und in ihren Eigenschaften fortlaufend verbessert. Mit dem Ziel die oxidative Stabilität von Membranen zu erhöhen, pfropfte M. Ślaski alpha-Methylstyrol (AMS) und Methacrylnitril (MAN) auf vorbestrahlte FEP Filme. Die aus den gepfropften Filmen hergestellten Membranen zeigten in Brennstoffzellenversuchen eine deutlich geringere Degradation (0.057 % · h⁻¹) als die entsprechenden unvernetzten, auf Styrol basierenden Membranen (1.59 % · h⁻¹). Eine, bezüglich ihrer Zusammensetzung nicht optimierte, FEP basierende, mit DVB vernetzte und poly(AMS-co-MAN) gepfropfte Membran wies, im Vergleich zur unvernetzten Membran, eine erhöhte Stabilität (0.015 % · h⁻¹) unter den selben Betriebsbedingungen der Brennstoffzelle auf. Die PSI interne Bestmarke bezüglich Stabilität (0.010 % · h⁻¹), aufgestellt von einer DVB vernetzten, Styrol gepfropften und auf FEP basierten Membran, konnte jedoch nicht erreicht werden.

In der vorliegenden Arbeit wurde die Pfropfung von AMS und MAN auf vorbestrahlte FEP

Die Temperatur während der Pfpfung wurde mit dem Ziel die Depolymerisation von AM-SAM Einheiten zu reduzieren von 60 auf 50 °C reduziert. Die Ceiling-Temperatur, die konzentrationsabhängige Temperatur bei der die Polymerisation und Depolymerisation gleich schnell ablaufen, von PolyAMS liegt bei 61 °C. Der erreichter Pfpgrad (DoG) für lange Reaktionszeiten war unabhängig vom verwendeten Basisfilm, bei 50 °C höher als, unter ansonsten identischen Bedingungen, bei 60 °C. Die Effizienz der Pfpfung, gegeben aus dem Verhältnis der anfänglichen Polymerisationsgeschwindigkeit und der Geschwindigkeit der Terminierung, sinkt mit zunehmender Temperatur von 35 bis 60 °C ab. Die anfängliche Polymerisationsgeschwindigkeit, die Geschwindigkeit der Terminierung und die Wanderungsgeschwindigkeit der Pfpffront waren Parameter eines vereinfachten kinetischen Modells zur Beschreibung der Reaktionsprofile von Pfropfungen. Die Untersuchung des Temperatureinflusses auf die Pfpfkinetik zwischen 35 und 60 °C zeigte weiterhin, dass eine höhere anfängliche Polymerisationsgeschwindigkeit einhergeht mit einem abnehmenden, maximal zu erreichenden Pfpgrad für lange Reaktionszeiten. Es konnte gezeigt werden, dass eine Veränderung des molaren Verhältnisses der Monomere in der Lösung $R_m, sol$ das molare Verhältnis der Monomere im gepfpften Polymer $R_m, graft$ beeinflusst. Unabhängig vom verwendeten Basisfilm und bei gleicher Reaktionszeit wiesen gepfpfte Filme einen geringeren Pfpgrad und ein höheres $R_m, graft$ auf, wenn sie in Lösungen mit höherem $R_m, sol$ hergestellt wurden. Dies ermöglicht die Herstellung von gepfpften Filmen und schliesslich Membranen, bei denen sich unabhängig vom Pfpgrad ein $R_m, graft$ zwischen 0.5 und 1.1 einstellen lässt.

Verwendung von CP MAS $^{13}$C NMR Spektroskopie ermittelt und die berechneten Werte waren konsistent mit den auf FTIR spektrokopischen Messungen basierenden (relative Standardabweichung ±10 %).


Die Ionenaustauschkapazität (IEC), als ein Mass für die integrale Konzentration an Sulfonsäuregruppen einer Membran, und die Protonenleitfähigkeit sind abhängig vom Pfropfgrad und dem $R_{m, graft}$. Der Einfluss des $R_{m, graft}$ ist geringer als der des Pfropfgrads, da das molare Verhältnis nur in einem Bereich von ca. 0.5 bis 1.1 variert werden kann, während der Pfropfgrad nur durch die benötigten mechanischen Eigenschaften der Membran eingeschränkt wird. Die Ionenaustauschkapazität steigt mit zunehmendem Pfropfgrad und bei konstantem Pfropfgrad mit steigendem $R_{m, graft}$. Die Abhängigkeit der Protonenleitfähigkeit vom Pfropfgrad an AMS lässt sich mit den Quelleigenschaften von Membranen erklären, die ihrerseits mit der Menge an AMS korrelieren. Der Einfluss von DVB auf die IEC ist gering, wohingegen die Protonenleitfähigkeit mit steigender Vernetzerkonzentration, infolge reduzierter Wasseraufnahme und Quellung, signifikant abnimmt. Um einen stationären Zustand der Brennstoffzelle sicherzustellen, wurden in situ Charakterisierungen von Membranen nach ca. 150 h Betriebszeit bei 500 mA·cm$^{-2}$ durchgeführt. Die Zellspannung bei gegebener Stromdichte (550 mA·cm$^{-2}$) nahm nach 150 h von 0.62 auf 0.67 V zu, als der AMS/MAN Pfropfgrad der unvernetzten ETFE basierten Membranen von 21 auf 50 % anstieg. Eine einwandfreie Zuordnung der in situ Eigenschaften mit dem varierten $R_{m, graft}$ in unvernetzten Membranen war nicht möglich. Allerdings liess sich bei unvernetzten, AMS/MAN gepropften und FEP basierten Membranen mit steigendem $R_{m, graft}$ eine Trend zu höheren Zellspannungen erkennen. Die Langzeitstabilität von Membranen wurde bei konstanter Stromdichte (500 mA·cm$^{-2}$) ermittelt und die Tests bestätigten die verbesserte Oxidationsstabilität von AMS/MAN gepropften Membranen, verglichen mit den entsprechenden Styrol basierten Membranen, durch eine geringere Degradationsgeschwindigkeit (0.035 % ·h$^{-1}$). Die Notwendigkeit der Vernetzung zeigte sich durch eine weitere Abnahme der Degradationsgeschwindigkeit (0.014 % ·h$^{-1}$) beim Testen einer DIPB vernetzten, AMS/MAN gepropften, FEP basierten Membran.
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Chapter 1

General Introduction

1.1 Fuel cell basics

Fuel cells (FCs) are energy converters able to transform chemically stored energy of a fuel into electrical energy. The advantage compared to conventional power plants, such as nuclear power plants, combined heat and power stations, lignite-fired power plants, or hydroelectric power plants is the conversion without intermediate steps of heat production and/or transformation into mechanical energy. In contrast to secondary batteries, which require recharging by an external power supply, fuel has to be continuously supplied and is permanently consumed in fuel cells [1]. A short historical review is given (paragraph 1.1.1) before different types of fuel cells (paragraph 1.1.2) and especially the polymer electrolyte fuel cell (PEFC) and the reactions involved in its conversion of hydrogen and oxygen into water are discussed in paragraphs 1.2 and 1.2.2, respectively.

1.1.1 History of fuel cells in mobile application

Schönbein published in 1838/39 results on his experiments concerning the polarization behaviour of a platinum wire in contact with different atmospheres [1, 2]. At the same time Grove was working on the "gaseous voltaic battery" (Figure 1.1), a platinum catalysed galvanic conversion of hydrogen and oxygen to produce electrical energy.

![Gaseous voltaic battery by Sir. W. R. Grove (design 1842). Sulfuric acid was used as electrolyte, platinum as electrode material and hydrogen and oxygen as reactants. Picture taken from http://www.kwugirl.com/cyberspace/designhistory.html.](image)

The electrical energy produced by the serial connection of "fuel cells" was used to electrolyze water, shown at the head of Figure 1.1 by the production of oxygen and hydrogen in the two test
tubes. The electrocatalytically active surface was increased 1882 by Rayleigh using platinum gauze instead of a thin Pt foil [3]. Finally, Mond and Langer described 1889 the fuel cell with the basic improvement of using a diaphragm, e.g. earthenware or asbestos, impregnated with the electrolyte and covered on both sides with thin catalyst foils (Figure 1.2) [4].

Figure 1.2: Gas battery designed in 1889 by Mond and Langer (taken from [4]). The cell consisted of A: copper wire, E,E': ebonite plates, G,G': gastight chambers, K,K': india-rubber frames, M: earthenware plate covered with platinum leaf and the gas inlet and outlet O,O' and H,H', respectively.

The results of Mond and Langer concerning different combinations of electrode materials and the best performance obtained with "platinum sponge and especially platinum black" as "aeration plate" (electrode) on "unglazed earthenware" (diaphragm) were confirmed in 1889 by Alder Wright and Thompson [5].

Until 1937 the focus in fuel cell research was on direct conversion of the chemical energy stored in coal into electricity, using molten potassium hydroxide and carbon electrodes (W. Jacques 1896), iron electrodes in molten alkaline electrolytes (Haber and Bruner 1904) or molten silver as cathode and carbon, iron or copper as anode in a variety of electrolytes (Baur and Ehrenberg 1912) [3]. The diversity of developments after 1937 necessitated a classification of fuel cells and the differentiation is possible based on their operating temperature (low-, medium- and high temperature FCs), used electrolyte (polymer, oxide, KOH, etc.) or the fuel compatibility (hydrogen, methane, methanol). The division based on the used electrolyte is established and commonly used. Hence, the introduction of different fuel cell types in the next paragraph, their properties and the anodic and cathodic reactions taking place, is also based on the used electrolyte.

A detailed discussion of the historical development since 1937 goes beyond the scope of the present work, but some highlights are pointed out in the following. The enhancement achieved with molten carbonate fuel cells (MCFC) are linked to Douglas at General Electric Company (1960). He used free electrolyte and porous gas diffusion electrodes to achieve higher current densities with reduced electrode spacing compared to matrix type MCFC. The success of alkaline fuel cells (AFC) was driven by the research of Davtyan (carbon electrodes, anode impregnated with silver, the cathode with nickel), Bacon (1954, "double-layer" electrode, 6 kW AFC system), and based on his results Pratt & Withney Aircraft developed and licensed an AFC power plant for the NASA, used in the Apollo Command and Service Module at the space mission to the moon (1968). The polymer electrolyte fuel cell (PEFC) was developed by Grubb and Niedrach at General Electric ("Grubb-Niedrach fuel cell") and designed together with NASA and McDonnell Aircraft for the Project Gemini (Figure 1.3).

In 1966, after two years of research, General Motors Company (GMC) was able to build a FC driven vehicle called Electrovan. They implemented an Union Carbide fuel cell with a con-
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Figure 1.3: Roy Mushrush, Manager of General Electric’s Direct Energy Conversion Operation in Lynn, Mass., holds a fuel cell stack, three of which form a Gemini fuel cell system, in his right hand. The FC system (“FC battery”) was built with ninety-six individual cells, one is shown at the far left. The picture is taken from http://scienceservice.si.edu/pages/059017.htm.

Continuous power output of 5 kW and a battery assisted peak power output of 32 kW in a GMC Handivan (Figure 1.4).

Figure 1.4: The world’s first fuel cell vehicle: GMC Electrovan with 5 kW continuous power and 32 kW peak power output. The picture is taken from http://www.hybridcars.com.

Using the perfluorinated membrane Nafion® from DuPont (Figure 1.5) as solid electrolyte enhanced the lifetime and performance of PEFC. Furthermore, Nafion® was applied as ion conductor in the catalyst layer at the Los Alamos National Laboratory (1986).

The research on PEFC was triggered by its use in mobile applications with the advantage of local zero emission conversion of chemical into electrical energy. Therefore, Los Alamos National Laboratory launched a study with a fuel cell powered bus in 1986. Ballard Power Systems ran a
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Figure 1.5: Chemical structure of Nafion® (DuPont), a copolymer of tetrafluoroethylene (TFE) and perfluoro-3,6-dioxa-4-methyl-7-octen-sulfonic acid (x = 5-13.5).

Fuel cell driven bus in 1993. Daimler Benz launched a van in 1994, followed by the concept car "NECAR 4" (70 kW, based on A-class) in 1999, 30 city busses (Citaro) in Stuttgart/Germany and Madrid/Spain in 2003, 10 A-class based "F-CELL" cars in Berlin in 2009 used by customers (project: Clean Energy Partnership), and in 2009 finally started the production of the B-class "F-CELL" in a small series. Since December 2008 Opel / General Motors ran 10 "HydroGen4", which is the European version of the Chevrolet Equinox Fuel Cell (Figure 1.6), in the Clean Energy Partnership project in Berlin. Honda started in 2008 the first series production of a fuel cell vehicle by opening of the "FCX Clarity" production line at the Honda Automobile New Model Center in Takanezawa/Japan.

Figure 1.6: The Opel/GM "HydroGen4" fleet running in the Clean Energy Partnership project in Berlin. Picture taken from http://www.grueneautos.com.

The Institute for Fuel Cell Innovation of the National Research Council (NRC-IFCI) in Vancouver, British Columbia (BC) will operate, in collaboration with the Canadian Hydrogen and Fuel Cell Association, 20 fuel cell powered buses at the 2010 Vancouver Olympic Games ("hydrogen highway", details under http://www.chfca.ca). Stationary energy conversion using fuel cells is not discussed in detail in the present work. While low or high temperature PEFC are considered for transportation, backup power and primary power supply in stationary applications, all other FC types (see paragraph 1.1.2) are preferentially intended as stationary power supply. An introduction in stationary fuel cell systems is denoted from the California Stationary Fuel Cell Collaborative at the web-site http://stationaryfuelcells.org. The worldwide stationary fuel cell installation database http://www.fuelcells.org/info/databasefront.html contains information about the fuel cell type, manufacturer, power output, location, status, involved partners, etc. of approximately 1000 projects during the past 20 years.
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1.1.2 Types of fuel cells and their operating principle

In this section the major fuel cell types, their efficiency, power range, application and the reactions taking place at the anode and cathode are described. The classification by the electrolyte and operating temperature is used in the present work [3]:

- Polymer electrolyte fuel cell (PEFC)
- Alkaline fuel cell (AFC)
- Phosphoric acid fuel cell (PAFC)
- Molten carbonate fuel cell (MCFC)
- Solid oxide fuel cell (SOFC)

Microbial fuel cells (MFC) converting chemical energy available in bio-convertible substrates directly, using bacteria as catalyst, into electricity are not discussed in detail in the present work. The basic principle of producing electricity from carbohydrates in MFC was described by Allen et al. in 1993 [6]. The operation of MFC with waste water became in the spotlight about five years ago [7]. The principle and applications of MFC are overviewed in detail under http://www.microbialfuelcell.org.

The direct methanol fuel cell (DMFC) in PEFC configuration is a proton exchange fuel cell with a polymer membrane, where methanol is fed as fuel in an aqueous solution directly to the anode and oxidized to carbon dioxide. The generated protons have to be conducted through the membrane to the cathode, where oxygen is reduced and reacts with the protons to water. Diffusion of methanol to the cathode compartment (crossover) decreases the cell performance and the overall efficiency of a DMFC. A status report concerning the technology, used catalysts, catalyst characterization and the polymer electrolyte is given in [8] and the anode catalysis is reviewed in [9].

Independent of its type, a fuel cell consists of two electrodes separated by a electrolyte (ion conductor), like in an electrochemical battery. The fuel has to be fed continuously to the anode compartment and the oxidant, which is either oxygen or air, to the cathode department. The electrodes consist of catalyst supported by the GDL, enable the half cell reactions taking place at the conditions described in Table 1.1. Electrons produced at the anode are conducted via an external circuit to the cathode, while the ionic charge carrier is essential to balance the charge. Table 1.1 summarizes the characteristics, such as the used electrolyte, operating temperature, tolerated fuel, used catalyst, electric efficiency, power range, main application, and the reactions of the above listed fuel cell types [3].

A negatively charged carrier (OH$^-$, CO$_3^{2-}$, O$_2^{2-}$) has to pass the electrolyte from the cathode to the anode, while a positively charged cation (H$^+$) migrates through the electrolyte from the anode to the cathode. The assets and drawbacks of different fuel cell types are discussed elsewhere [1]. The main rationale to choose one of the described fuel cell types is based on the expected application, available fuel and required power. All fuel cell types are still under development and the main investigations are made to enhance the longevity and reliability and to reduce the costs of fuel cell systems. In the present work, membranes for polymer electrolyte fuel cells were prepared and characterized. Hence, the PEFC components are described and their kinetics, thermodynamics and efficiency are discussed in the following paragraph.
Table 1.1: Description of fuel cell types and their half cell reactions

<table>
<thead>
<tr>
<th>FC type</th>
<th>PEFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Solid polymer</td>
<td>KOH</td>
<td>Phosphoric acid</td>
<td>Li$_2$CO$_3$, K$_2$CO$_3$</td>
<td>Solid oxide</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>50-100 °C</td>
<td>60-120 °C</td>
<td>~220 °C</td>
<td>~650 °C</td>
<td>~1000 °C</td>
</tr>
<tr>
<td>Fuel</td>
<td>H$_2$</td>
<td>pure H$_2$</td>
<td>H$_2$</td>
<td>H$_2$, CO, CH$_4$</td>
<td>H$_2$, CO, CH$_4$</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt</td>
<td>Pt, Ag</td>
<td>Pt</td>
<td>Ni</td>
<td>Perovskite</td>
</tr>
<tr>
<td>Electric efficiency</td>
<td>35-45 %</td>
<td>35-55 %</td>
<td>40 %</td>
<td>&gt;50 %</td>
<td>&gt;50 %</td>
</tr>
<tr>
<td>Power range</td>
<td>5-250 kW</td>
<td>&lt;5 kW</td>
<td>~200 kW</td>
<td>200 kW-MW</td>
<td>2 kW-MW</td>
</tr>
<tr>
<td>Application</td>
<td>Automotive and portable</td>
<td>Military, space</td>
<td>Combined heat and power generation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anode reaction</th>
<th>H$_2$</th>
<th>H$_2$ + 2 OH$^-$</th>
<th>H$_2$</th>
<th>H$_2$ + CO$_2^-$</th>
<th>H$_2$ + O$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td></td>
<td>2 H$^+$ + 2 e$^-$</td>
<td>2 H$_2$O + 2 e$^-$</td>
<td>2 H$^+$ + 2 e$^-$</td>
<td>H$_2$O + CO$_2$ + 2 e$^-$</td>
<td>H$_2$O + 2 e$^-$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ionic charge carrier</th>
<th>H$^+$</th>
<th>OH$^-$</th>
<th>H$^+$</th>
<th>CO$_2^-$</th>
<th>O$_2^-$</th>
</tr>
</thead>
</table>

| Cathode reaction | $\frac{1}{2}$ O$_2$ + 2 H$^+$ + 2 e$^-$ | $\frac{1}{2}$ O$_2$ + 2 H$_2$O + 2 e$^-$ | $\frac{1}{2}$ O$_2$ + 2 H$^+$ + 2 e$^-$ | $\frac{1}{2}$ O$_2$ + CO$_2$ + 2 e$^-$ | $\frac{1}{2}$ O$_2$ + 2 e$^-$ |
|                   | ↓     | ↓     | ↓     | ↓       | ↓     |
|                   | H$_2$O | 2 OH$^-$ | H$_2$O | CO$_3^-$ | O$_2^-$ |
1.2 Polymer Electrolyte Fuel Cell (PEFC)

The core of a polymer electrolyte fuel cell (Figure 1.7) is its membrane electrode assembly (MEA). The interfacial contact between the membrane and electrodes influences the cell performance and therefore the MEA preparation is of utmost importance, cf. Figures 1.8 [10, 11, 12, 13]. The electrodes used in the present work (LT140EWSI, E-TEK, Somerset NJ, USA) consist of a gas diffusion layer (GDL) coated on one surface with platinum (0.5 mg·cm$^{-2}$), more precisely a carbon cloth electrode with 0.6 mg·cm$^{-2}$ of 20 % Pt on carbon and conductible by an ionomer. The MEA is sandwiched between the conducting plates, which collect the electrical current. The gas channels are milled into the conducting plates with a geometry (flow field) that permits on the one hand a good distribution of the gases, fuel or oxidant, over the MEA and on the other hand the removal of the reaction products in the depleted gases out of the cell. The GDL has to further ensure the uniform distribution of the gases over the entire MEA by providing diffusion paths for the gases under the channel as well as under the land to maximize catalyst utilization.

![Figure 1.7: Design of a polymer electrolyte fuel cell consisting of conducting plates with gas channels, gas diffusion layer and a membrane electrode assembly (MEA), which is a polymer membrane between two catalyst coated gas diffusion layers.](image)

The electrochemical reactions taking place at the anode, oxidation of hydrogen, and cathode, reduction of oxygen, are described in detail in paragraphs 1.2.2.2 and 1.2.2.3, respectively. The reactions proceed at the triple-phase boundary (Figure 1.8), existing at the interface between the membrane and catalyst particles. The characteristics of those domain is the coexistence of electronic and ionic conductivity and the simultaneously possible access of reactant gas to the active (platinum) surface.

An extensive triple-phase boundary is necessary to operate a fuel cell with the respective power density. The components of a fuel cell, their function and requirements are described in the
CHAPTER 1. GENERAL INTRODUCTION

Figure 1.8: The magnification (red square) illustrates the triple-phase boundary at the membrane electrode interface, which are the catalytic active platinum particles (grey) with connection to the carbon support (black, electronical contact), gas phase (yellow/red, gas phase), and ionomer phase (blue, proton pathway).

following paragraph.

1.2.1 PEFC components

The different components of a PEFC fuel cell are shown in Figure 1.7. Requirements for the membrane and its function is explained are paragraph 1.2.1.1. The electrodes, used catalysts and GDL are subject of paragraph 1.2.1.2 and the FC hardware, such as the flow field an current collector plates, is briefly discussed in paragraph 1.2.1.3.

1.2.1.1 Polymer electrolyte membranes

The half cell reactions of a PEFC are shown in Table 1.1. The (solid) polymer electrolyte, further termed membrane, has to exhibit the following properties [14, 15, 16]:

- high proton conductivity even at low humidity (>10 mS·cm⁻¹ [17])
- low permeability to the reactant gases (maximize Faradaic efficiency, cf. equation 1.21 on page 14)
- low electronic conductivity (electronical insulation of the two half cell reactions)
- good interfacial properties (contact with electrodes in the MEA)
- well-balanced water management
- low cost

Furthermore, the fuel cell environment demands additional requirements on the membrane concerning its

- mechanical (in dry and water swollen state),
- chemical and electrochemical, and
- thermal stability.
The operation of fuel cells, especially in non-stationary applications, include load, temperature and humidity changes. Those variations induce stress to the membrane, which therefore has to achieve the above mentioned stability criteria. The first polymer electrolyte fuel cell was developed by General Electric to produce electricity and drinking water for the NASA Gemini program, see paragraph 1.1.1 on page 1 and Figure 1.3. The used polystyrene sulfonic acid membrane was prone to oxidative degradation. The commercial launch of Nafion® (structure see Figure 1.5) by DuPont in the late 1960s improved the membrane’s durability under conditions of an operating fuel cell. Nafion® is still the state-of-the-art membrane and benchmark in terms of stability. Although Nafion® is the most commonly used and investigated membrane for PEFC, the structure and proton pathways in the water swollen state are subject of current research [18, 19, 20, 21].

Generally, the proton transport through a membrane is a very complex process. In low temperature polymer electrolyte fuel cells, the transfer of protons is coupled to the presence of water. In water swollen membranes either the Grotthuss or the vehicle mechanism are possible to conduct protons [22]. The movement of protons via the Grotthuss or ”proton hopping” mechanism requires a network of hydrogen bonds. The proton is thereby ”handed over” (translated) from an hydronium ion to a water molecule followed by the rotation of the formed water molecule to take up the next proton. More recent investigations based on NMR spectroscopically determined proton ”hopping” times claim a periodic series of isomerizations between \( H_3O^+ \) (Eigen cation) and \( H_2O_2^+ \) (Zundel cation) [23]. According to the vehicle mechanism the proton migrates together with a ”vehicle”, e.g. as \( H_2O \) if the ”vehicle” \( H_2O \) is used.

Since the proton transport for both mechanisms strongly depends on the presence of water, decreasing humidity or in the worst case drying out of the membrane will decrease or even inhibit proton conductivity through the membrane. Therefore, the water balance of the membrane has to be controlled by humidification of the incoming gases at operating temperature above 60 °C. The water management can be controlled by other methods, such as the direct hydration by embedding porous polyester fibres in the membrane or the use of self-humidifying membranes, e.g. Nafion impregnated with SiO\(_2\) or TiO\(_2\) particles to adsorb the formed water [2]. The proton conductivity and the membrane resistance depends strongly on the membrane’s thickness. Using thinner membranes will on the one hand reduce the resistance but on the other hand influence the mechanical properties and gas crossover negatively.

### 1.2.1.1 Membrane electrode assembly (MEA)

In the present work gas diffusion electrodes (GDE) were used to prepare the MEAs. The GDE consists of catalyst supported on a gas diffusion layer (impregnated with an ionomer), cf. Figure 1.8. The catalyst is usually made into an ink and printed on the carbon support of the GDL. Furthermore, the carbon support, most frequently used are carbon papers or carbon cloths, provides the electronic conductivity to the catalyst particles, while its contact to the ionic conductor (membrane) can be achieved by use of a binder (ionomer), e.g. Nafion, or by hot pressing of the MEA in order to enhance the contact area between the catalyst and the membrane. Supplying the catalyst particles with humidified gas requires the diffusion of these gases through the pores of the backing layer and the carbon support without flooding those pores. The flooding is avoided by impregnation of the porous structure with PTFE, which increases the hydrophobicity.
Platinum dispersed on carbon particles is the superior catalyst for the oxygen reduction reaction (ORR) at the cathode. The Pt loading at low temperature has to be sufficient high (0.20 and 0.35 mg/cm² for 20 and 40 % Pt/C [24]) to compensate for the slow ORR kinetics [25]. The use of air instead of oxygen further reduces the activity due to the lower oxygen partial pressure in air.

The anodic oxidation of hydrogen is performed best with nanosized Pt particles (2-4 nm) as catalyst supported on high-surface carbon particles [26]. Traces of carbon monoxide block the active sites on platinum at low temperature. The CO has to be oxidized to CO₂ to recover the initial active surface area. Several CO-tolerant catalysts for the hydrogen oxidation reaction (HOR) are under investigation, e.g. Pt alloyed with ruthenium.

1.2.1.3 Fuel cell hardware

Figure 1.7 illustrates the conducting plates with their gas channels. Stainless steel or graphite (used in the present work) are commonly used materials for conducting or flow field plates, named also end plates in single cells or bipolar plates in cell stacks. The bipolar or end plates are responsible for the supply of gases to the MEA and their flow field geometry determines the uniformity of the gas distribution and the local stoichiometry of the reactants. Many types of flow channel configurations are used, such as pin-type and straight, serpentine, integrated or interdigitated channels. Figure 1.9 shows the linear (parallel) and serpentine flow fields.

Furthermore, the reaction products have to be removed in the gas channels and the produced current collected via the contact area of the bipolar plates with the MEA. Finally, the bipolar (end) plates contribute significantly to the mechanical robustness of a fuel cell stack. However, the bipolar plates constitute more than 60 % of the weight and approximately 30 % of the costs in a fuel cell stack [27]. While graphite materials are prefered with respect to their corrosion resistance [15], the conductivity of metallic materials is higher (Fe alloys ≈ 5.3·10⁶ S·cm⁻¹ vs. graphite 10³ S·cm⁻¹) and the processing of stainless steel plates is more efficient. Hence, coated metallic bipolar plates with the prospect to reduce corrosion are investigated [28].

The fuel cell has to be gas-tight, wherefore the whole assembly shown in Figure 1.7 requires additional sealings. A single fuel cell has to be heated to the desired operating temperature, whereas fuel cell stacks necessitate cooling. The placing of heating or cooling devices, the gas
delivery to and the removal of the exhaust gas from the flow channel as well as the connections for controlling and monitoring the fuel cell operation yield sophisticated fuel cell architectures. The infrastructure necessary to operate a polymer electrolyte fuel cell contains a fast control unit linked to highly dynamic gas supply and heating or cooling devices, to ensure the fuel cell running in its operating optimum.

1.2.2 Fuel cell reactions

Understanding a fuel cell requires the knowledge of its fundamental reactions, e.g. the overall redox reaction (paragraph 1.2.2.1). In the present work hydrogen was used as fuel and consequently oxidized on the anode while pure oxygen was used and reduced on the cathode. Thus, the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) are introduced in paragraph 1.2.2.2 and 1.2.2.3, respectively.

1.2.2.1 Electrochemical cell

A general expression of the redox reaction taking place in an electrochemical cell is given by equation 1.1. The electrochemical cell, e.g. fuel cell, consists of an anode and cathode where the indices 1 and 2 denote the involved redox pairs.

\[
n \cdot ox_1 + m \cdot red_2 \rightarrow x \cdot red_1 + y \cdot ox_2
\]  

(1.1)

Compound \(ox_1\) is reduced and \(red_2\) oxidized during the reaction shown in equation 1.1. The equilibrium potential of each half cell reaction \(\epsilon_1\) or \(\epsilon_2\), respectively, is given by the Nernst equation 1.2 using the standard electrode potential \(\epsilon^0\) and the activity of the oxidized \(a_{ox}\) and reduced species \(a_{red}\).

\[
\epsilon_{1,2} = \epsilon_{1,2}^0 - \frac{RT}{nF} \ln \frac{a_{ox1,2}}{a_{red1,2}}
\]  

(1.2)

The Faraday constant \(F\) and number of electrons \(n\) transferred in the redox reaction have to be known. The electromotive force \(\Delta E\) of an electrochemical cell is equal to the potential difference between the two half cell reactions \(\epsilon_1\) and \(\epsilon_2\), according to equation 1.3.

\[
\Delta E = \epsilon_1 - \epsilon_2 = \epsilon_1^0 - \epsilon_2^0 + \frac{RT}{nF} \ln \frac{a_{ox1}^{n_{ox1}} \cdot a_{red2}^{n_{red2}}}{a_{red1}^{n_{red1}} \cdot a_{ox2}^{n_{ox2}}}
\]  

(1.3)

The conversion of internal energy \(dU\), described by the first law of thermodynamics \((dU = \delta Q + \delta W)\), into electrical energy is limited by the change of the Gibbs free energy \(\Delta G\), which is accessible by combining the first and second law of thermodynamics (equation 1.4). For the reaction shown in equation 1.1 the Gibbs free energy can be calculated according to equation 1.4 ("Gibbs-Helmholtz equation") from the standard Gibbs free energy \(G^0\). Since a fuel cell is a galvanic cell, the free energy of the overall reaction is converted into electrical energy and its relation to the cell voltage is shown in equation 1.5.

\[
\Delta G = \Delta H - T\Delta S = \Delta G^0 - RT \ln K = \Delta G^0 + RT \ln \frac{[ox_1]}{[ox_2]} \frac{[red_2]^b}{[red_1]^c}
\]  

(1.4)

In equation 1.4 \(\Delta H\) corresponds to the change in enthalpy, \(T\) to the absolute temperature, \(\Delta S\) to the change in entropy and \(K\) to the equilibrium constant \((K = \frac{a_{products}}{a_{reactants}})\).
The combination of equation 1.3 and 1.4 yields an expression (equation 1.5) for the maximum achievable electrical work $W_{el}$.

$$\Delta G = W_{el} = -nF\Delta E$$  \hspace{1cm} \text{(1.5)}

The fuel cell reactions take place at the cathode, exposed to neat oxygen or air, and anode, where the fuel, hydrogen in the present work, is oxidized. The reversible voltage generated in a H$_2$/O$_2$ fuel cell under standard conditions $\Delta E_0$ is 1.23 V and corresponds to the difference of the standard electrode potential of the cathodic ORR $\epsilon^0_{ORR}$ (1.23 V) and the anodic HOR $\epsilon^0_{HOR}$ (0.00 V).

### 1.2.2.2 Oxygen reduction reaction

The strong kinetic inhibition of the cathodic oxygen reduction reaction (ORR) leads to high overpotentials, up to several hundreds of millivolts, and the slow ORR kinetics is one of the most limiting factors in energy conversion efficiency of polymer electrolyte fuel cells. Mechanistic details regarding the adsorption and desorption can be found elsewhere [29, 30, 31]. Two overall pathways are possible in acidic electrolytes [2]. The direct four-electron pathway has a standard potential of $\epsilon^0 = 1.229$ V (equation 1.6). The alternative peroxide pathway is initiated by peroxide formation (equation 1.7, $\epsilon^0 = 0.67$ V) and followed either by an acidic reduction of the hydrogen peroxide (equation 1.8, $\epsilon^0 = 1.77$ V) or its disproportionation (equation 1.8).

\[
\begin{align*}
O_2 + 4 H^+ + 4 e^- &\rightarrow 2 H_2O \\
O_2 + 2 H^+ + 2 e^- &\rightarrow \text{HOOH} \\
\text{HOOH} + 2 H^+ + 2 e^- &\rightarrow 2 H_2O \\
2 \text{HOOH} &\rightarrow 2 H_2O + O_2 
\end{align*}
\]

Structure-activity relationships were investigated and discussed controversially in numerous publications. For instance the influence of the particle size [32], intercrystalline distance [33], reaction on specific active sites [34], and pretreatment [35] of the catalyst on the ORR was determined.

### 1.2.2.3 Hydrogen oxidation reaction

The oxidation of hydrogen on platinum based catalysts shows a very fast kinetics. The overall hydrogen oxidation reaction (equation 1.10) has a standard potential of $\epsilon^0 = 0$ V and combines the adsorption of H$_2$ on the catalyst surface, its dissociation and electrochemical reaction and the dissociation of H$^+$ from the catalyst [2].

$$H_2 \rightarrow 2 H^+ + 2 e^-$$  \hspace{1cm} \text{(1.10)}

The mechanism of the HOR at a catalyst M proceeds via a chemical (Tafel reaction, equation 1.11) or electrochemical (Heyrovsky reaction, equation 1.12) adsorption step followed by a discharge path of the absorbed hydrogen atom (Volmer reaction, equation 1.13) [36].

\[
\begin{align*}
H_2 + 2 M &\rightleftharpoons 2 MH \\
H_2 + M &\rightleftharpoons MH + H^+ + e^- 
\end{align*}
\]

[12]
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\[
MH \rightleftharpoons M + H^+ + e^-
\]  

(1.13)

If the catalyst M is platinum, the Tafel and Volmer mechanism is proposed with the chemical adsorption of \( H_2 \) in the Tafel reaction as rate determining step [37].

1.2.3 Operation and efficiency

The electrochemical nature of a fuel cell and the description of its equilibrium state by the Nerst equation 1.2 was mentioned in the previous paragraph. The electrochemical reaction rate is directly accessible from the current \( i \) due to the charge transfer between the electrode and the chemical species. Those electrochemical reactions in the fuel cell were shown in equation 1.11, 1.12 and 1.13 for the anode and not discussed in detail due to their complexity for the cathode. However, the reactions take place at the electrolyte-electrode interface in contact with the involved chemical species, wherefore the current density \( j \) is used to describe the electrochemical reaction kinetics.

The fuel cell performance is presented in a polarization plot, which is the graphic representation of the current density dependent cell voltage (Figure 1.10). The measured polarization curve is characterized by three regions. In the first region at low current density the curve is dominated by activation losses (kinetic effects). The slope of the polarisation curve in the intermediate current density region is predominantly affected by ohmic losses, arising due to resistive losses in the electrolyte and in the electrodes. The abrupt collapse of the cell voltage for high current density occurs as a result of mass transport limitations.

The effective cell voltage \( U \) is given by the open circuit voltage \( U_0 \) (OCV) diminished by the overpotential caused by activation (act) and mass transport (mt) effects and ohmic losses, shown in equation 1.14.

\[
U = U_0 - \eta_{act(ORR)} - \eta_{act(HOR)} - \eta_{mt(ORR)} - \eta_{mt(HOR)} - \eta_{ohm}
\]  

(1.14)

The activation overpotentials \( \eta_{act(ORR)} \) and \( \eta_{act(HOR)} \) of the cathodic and anodic half cell reactions, respectively, are associated with the current density \( j \) in the Butler-Volmer equation 1.15.

The mass transport overpotentials \( \eta_{mt(ORR)} \) and \( \eta_{mt(HOR)} \) are related to the limited transport
of oxygen to the cathode and hydrogen to the anode, respectively. The ohmic overpotential \( \eta_{\text{ohm}} \) depends in a first approximation on the resistance of the fuel cell membrane.

\[
j = j_0\left[\exp\left(\frac{\alpha_A n F \eta_{\text{act}}}{RT}\right) - \exp\left(\frac{\alpha_C n F \eta_{\text{act}}}{RT}\right)\right] = j_0\left[\exp\left(\frac{\eta_{\text{act}}}{b_+}\right) - \exp\left(\frac{\eta_{\text{act}}}{b_-}\right)\right]
\]  

(1.15)

In equation 1.15 \( j_0 \) conforms to the exchange current density in absence of net electrolysis and at zero overpotential and \( \alpha \) to the transfer coefficient of either the anodic (index A) or cathodic (index C) reaction, respectively. The simplification shown in equation 1.15 is possible by introduction of the Tafel slopes \( b_+ \) and \( b_- \) (equation 1.16) for the anodic and cathodic reactions, respectively.

\[
b_+ = \frac{RT}{\alpha_A n F} \quad \text{and} \quad b_- = \frac{RT}{\alpha_C n F}
\]  

(1.16)

While the exchange current density describes the intrinsic rate of electron transfer between the electrode and the chemical species, the Tafel slope provides mechanistic information about the reaction [38].

The efficiency \( \eta_{\text{FC}} \) of the energy conversion process in a fuel cell is given according to [39] by

\[
\eta_{\text{FC}} = \frac{\text{electrical power output} \ (P_{\text{FC}})}{\text{fuel input} \ (F_{\text{in}})}
\]  

(1.17)

or expressed by the ideal thermodynamic efficiency \( \eta_{\text{thermo}} \), the voltage efficiency \( \eta_{\text{voltage}} \) and the fuel conversion efficiency \( \eta_{\text{fuel}} \) by

\[
\eta_{\text{FC}} = \eta_{\text{thermo}} \cdot \eta_{\text{voltage}} \cdot \eta_{\text{fuel}}
\]  

(1.18)

The thermodynamic efficiency \( \eta_{\text{thermo}} \) of a given electrochemical reaction corresponds to the ratio between the produced electrical energy \( \Delta G \) and the released heat \( \Delta H \) of the chemical reaction under reversible conditions, according to

\[
\eta_{\text{thermo}} = \frac{\Delta G}{\Delta H}
\]  

(1.19)

The voltage efficiency \( \eta_{\text{voltage}} \) is defined by the effective cell voltage \( U \) (cf. equation 1.14) under load and the thermodynamically reversible cell voltage \( \Delta E \) (cf. equation 1.3) by equation 1.20.

\[
\eta_{\text{voltage}} = \frac{U}{\Delta E}
\]  

(1.20)

The fuel conversion efficiency \( \eta_{\text{fuel}} \) is similar to the Faradaic efficiency \( \eta_{\text{Faradaic}} \), also called Coulombic or current efficiency, reduced by the fuel utilization efficiency \( \mu_{\text{fuel}} \), according to equation 1.21. The fuel utilization efficiency accounts for the amount of fuel used in the electrochemical reaction (\( \mu_{\text{fuel}} = \text{consumed fuel} / \text{fuel feed} \)).

\[
\eta_{\text{fuel}} = \eta_{\text{Faradaic}} \cdot \mu_{\text{fuel}} = \frac{I}{nF \nu} \cdot \mu_{\text{fuel}}
\]  

(1.21)

The Faradaic efficiency is governed by the effective current generated in the fuel cell. The denominator term is given by the number \( n \) of exchanged electrons, the Faraday constant \( F \) and the fuel feed rate \( \nu \).
1.3 Proton exchange membranes

The research was focused on more reliable fuel cell components, since General Electric launched the first polymer electrolyte fuel cell for the NASA Gemini program in the 1960s. The introduction of Nafion® by DuPont only a few years later was a big step towards more durable membranes. The requirements for membrane vary depending on the application (stationary, portable or automotive) and the operating conditions, e.g. the temperature, humidity, constant or cyclic changed load. Today, the performance, safety and freeze start reach the requirements for the commercial launch of PEFC in automotive application [40]. However, the cruising range, reliability, longevity and weight of fuel cell systems still need to be improved and the costs has to be reduced significantly to make the PEFC commercially viable. Here, reduction of the costs, decrease of resistance at low humidity and improvement of the durability are the critical membrane targets to achieve [40].

The different types of polymer electrolyte membranes, their water management and stability is dicussed in the following.

1.3.1 Types and chemical nature of proton exchange membranes

A sulphonated polystyrene ion-exchange membrane was used in the "Grubb-Niedrach fuel cell" built at General Electric Company for the NASA Gemini mission. The oxidative stability, performance and lifetime was improved by using perflourinated sulfonic acid (PFSA) electrolyte membranes [41]. Nafion®, today in a modified version compared to the original material, is still state-of-the-art. Other derivatives of poly(tetrafluoroethylene) (PTFE) possessing perfluoroether side chains (nomenclature by [16]) are commercially available (Figure 1.11).

The major drawback of Nafion-type membranes is the high production costs of ~500 US$/m² caused by the involved fluorine chemistry [44]. To overcome the restrictions connected to the need of liquid water in PFSA membranes to conduct protons, thereby limiting the operating temperature to 100 °C, attention was paid to the modification of PFSA membranes [45]. The water management can be improved and additionally the internal resistance reduced by using thinner membranes, where the back-diffusion of water (cathode → anode) is more effective [46]. In the case of the GoreSelect® membrane a porous expanded PTFE, providing high mechanical stability to an even thin membranes (~10 µm), was impregnated with Nafion®. Recast
Nafion® membranes with hygroscopic oxides particles (SiO$_2$, TiO$_2$) increases the back-diffusion and reduces the electro-osmotic drag of water and allows operation of such composite membranes at lower humidities or higher temperature [47]. Another way towards high performance membranes was the emulsion copolymerization of $\alpha$$,\beta$$,\beta$-trifluorostyrene (TFS) with $R$ substituted TFS derivatives ($R = OR$, CN, OH, NO$_2$, CF=CF$_2$) and subsequent sulfonation by Ballard [48]. The membrane BAM3G01 (composition see [48]) outperformed Nafion® 117 or Dow® membranes based fuel cell stacks in terms of the voltage achieved at a given current density (650 mA/cm$^2$) [16].

![Chemical structure of Ballard BAMG3 membranes](image)

Figure 1.12: Chemical structures of Ballard BAMG3 membranes ($R = OR$, CN, OH, NO$_2$, CF=CF$_2$).

Nevertheless, the modification of Nafion®-like membranes did not lower the costs and an insistent demand of membranes with improved properties and of low costs pushed the research in membranes based on non-fluorinated polymers. Hydrocarbon polymers are known as thermally and chemically stable and the task is to improve their membrane properties, such as proton conductivity and water management, without affecting their intrinsic stability. A selection of sulfonated hydrocarbon polymers, investigated regarding their properties as cation exchange membranes is shown together with an incomplete list of citations in Table 1.2.

The proton conductivity and ion exchange capacity for the examples shown in Table 1.2 depend on the degree of sulfonation. An increasing degree of sulfonation, in the majority of cases indicated by the number of sulfonic acid group per repeating unit, increases the water uptake and thereby the swelling and worsens the mechanical properties. The balancing between an appropriate proton conductivity and sufficient mechanical resilience is therefore one of the challenges in membrane optimization [59].

Proton conductivity becomes possible in "dry" membranes if the proton transport mechanism is independent of free water. Sulfuric acid (H$_2$SO$_4$) and phosphoric acid (H$_3$PO$_4$) exhibit proton conductivity in their anhydrous state due to self-ionization and self-dehydration. Complexes of those acids with basic polymers are formed via hydrogen bonds. The conductivity as well as the mechanical stability of such acid-base (polymer) complex membranes depends on the acid content and they become gel-like if high acid contents are used. Poly(ethylene oxide) (PEO), poly(ethylene imine) (PEI), poly(acryl amide) (PAAM), PBI and poly(vinyl alcohol) (PVA) were used as basic polymers [45]. The replacement of water by ionic liquids (IL) is a further way to decouple the proton conductivity from the membrane’s water content. IL-based gel-type proton conducting membranes are intended for adding the advantages of IL, such as nonvolatility, good thermal and chemical stability, wide electrochemical window and nonflammability, to proton conducting membranes [66, 67].

The chemical modification of existing, already film-shaped polymers provides another possibility
Table 1.2: Selection of non fluorinated, sulfonated polymers used as membranes in fuel cells [49].

<table>
<thead>
<tr>
<th>Base polymer</th>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td><img src="image1" alt="Polystyrene Structure" /></td>
<td>[49, 50]</td>
</tr>
<tr>
<td>Polyimide (PI)</td>
<td><img src="image2" alt="Polyimide Structure" /></td>
<td>[51, 52, 53]</td>
</tr>
<tr>
<td>Poly(ether sulfone) (PES)</td>
<td><img src="image3" alt="Poly(ether sulfone) Structure" /></td>
<td>[54, 55, 56, 57]</td>
</tr>
<tr>
<td>Poly(ether ketone) (PEK, PEEK)</td>
<td><img src="image4" alt="Poly(ether ketone) Structure" /></td>
<td>[58, 59, 60]</td>
</tr>
<tr>
<td>Poly(benzimidazole) (PBI)</td>
<td><img src="image5" alt="Poly(benzimidazole) Structure" /></td>
<td>[59, 61, 62, 63]</td>
</tr>
<tr>
<td>Poly(phosphazene) (PPZ)</td>
<td><img src="image6" alt="Poly(phosphazene) Structure" /></td>
<td>[64, 65]</td>
</tr>
</tbody>
</table>

To fulfil the requirements of proton exchange membranes, which can be achieved by harsh chemical treatment, etching, or using radiation. Whereas the first two methods primarily alter the surface, high energy irradiation grafting is also able to modify the bulk [68, 69]. Electromagnetic radiation, such as γ-ray [70, 71, 72] or X-ray [73], and irradiation using charged particles, e.g. electrons [74, 75, 76, 77, 78] or swift heavy ions [79, 80], were used to activate the used base polymers [81]. Poly(styrene sulfonic acid) (PSSA) and poly(α-methylstyrene sulfonic acid-co-methacrylonitrile) grafted onto base polymers, as e.g. prepared at PSI, are shown as examples for radiation grafted membranes in Figure 1.13.

![General structures of membranes based on a) polystyrene or b) α-methylstyrene (AMS) / methacrylonitrile (MAN) copolymer, radiation grafted onto a base polymer and subsequently sulfonated.](image7)
1.3.2 Radiation grafted membranes

A selection of membranes used in polymer electrolyte fuel cells was discussed in the last paragraph. Development of membranes is carried out with the main focus on increasing the stability and reliability by simultaneously reducing the costs. Radiation grafting offers a possibility to modify a variety of chemically, mechanically and thermally stable base polymers by introduction of the required functionalities with the graft component. In simple terms, the modification of base polymers by radiation grafting with appropriate polymers corresponds to a dilution of the base material with the graft component. Thus, the "mixing" of two basically different materials and their associated physical properties becomes possible. The advantage of the radiation grafting in membrane preparation is the use of already film-shaped base polymers. An additional forming step is not necessary, since the film keep its shape during the entire membrane preparation process. The choice of base polymers in radiation grafting and their combination with a multitude of possible monomers offers the perspective to prepare tailor-made grafted polymers and, following sulfonation, membranes, fulfilling the required properties for their use in fuel cells. Monomers used for the graft polymerization either carry the required functional group, e.g. acid moieties in acrylic acid, methacrylic acid, para-sulfonyl fluoride-α, β, β-trifluorostyrene, or a post grafting modification is necessary to add the functionality, e.g. the sulfonation of grafted polystyrene or derivatives thereof to introduce dissociable acid groups.

However, before discussing a selection of base polymers (Table 1.3) used for radiation grafting and monomers (Table 1.4) able to polymerize under the grafting conditions, the general procedures and irradiation sources are reviewed in the next paragraph.

1.3.2.1 Radiation Grafting

The activation of chemically inert base films by irradiation can be performed simultaneously (a) or before the grafting (b) [74]. The activation of the base polymer by pre-irradiation (b), where the graft polymerization is carried out as second step, is possible in ambient atmosphere and therefore in the presence of oxygen (b1) or in nitrogen or argon as inert gas (b2). A general scheme of the different radiation grafting methods is shown in Figure 1.14 [75].

Simultaneous irradiation ensures a homogeneous exposure of the base polymer and monomer(s), either in bulk or solution, to the irradiation. Therefore, the radicals are generated in the base polymer as well as in the monomer units and consequently a high yield of homopolymer is obtained. Homopolymer is the polymerization product without connection to the base polymer. Regarding the pre-irradiation method (b1), the generated active species (radicals) reacts with oxygen and forms peroxyl radicals, which are stabilized as hydroperoxides after the subtraction of hydrogen atoms from present hydrogen-donors, e.g. the adjacent CH-groups in partially fluorinated base polymers or water vapor in the ambient atmosphere. In the absence of oxygen, case (b2), the radicals remain carbon based, as long as the restricted chain mobility prevents recombination. The chain mobility and the reactivity of the radicals is reduced at low temperature, wherefore the activity of irradiated base films to initiate the grafting is preserved for at least one year by storage at -80°C, cf. reported FEP radical lifetimes of more than three years [82].

The constitution of grafted films may differ in the linkage between the base polymer and graft component and the endgroup of the grafted chain depending on the pre-irradiation method (b1 vs. b2). The easier sample preparation and lower requirements on the reactors are advantages
1.3. PROTON EXCHANGE MEMBRANES

Figure 1.14: Different preparation routes for radiation grafted polymers.

which argue for the pre-irradiation grafting method in ambient air.

Grafting of monomer(s) in bulk or solution onto pre-irradiated films, which are not swellable in the monomer(s) or solvent, occurs according to the grafting front mechanism (Figure 1.15) [74].

Figure 1.15: Irradiation (1) yield active sites (radicals, red dots) within the base film. Grafting is initiated at the surfaces by polymerization of monomers (2). Further grafting (3) of active sites within the irradiated film requires diffusion of monomers through the already grafted (swollen) polymer zone. Thereby, the grafting front (green) moves from the surfaces to the interior and the grafted domain behind consists of previously grafted (dark blue) and recently added graft component (light blue). Termination begins in surface near areas (4) and further grafting (5) increases the concentration of graft component $c_{\text{graft}}$ at the film center. Grafting for a long time (6) yields homogeneously grafted films with the same $c_{\text{graft}}$ over the entire film thickness.

This mechanism basically combines polymerization, swelling of the grafted region, and diffusion
of monomers into the swollen domain to further react with internal radicals. Certainly, grafting starts at surface near active sites, which initiate the polymerization. The graft component changes the morphology of the film in the grafted zone, which thereby becomes swellable by the monomers and/or solvents. Accordingly, monomers reach by diffusion active sites within the film and start to grow new chains. The need of a grafted domain to proceed the grafting further into the film, results in a sequence of quasi-simultaneous sub-steps of polymerization, swelling and diffusion. The "grafting front" describes the innermost borderline between the pre-irradiated ungrafted polymer and the already grafted area. The coincidence of the grafting fronts, started originally at opposite surfaces, yields a grafted film able to conduct protons after its sulfonation and hydrolysis ("through-grafted" film). Further grafting increases the DoG over the entire film thickness.

Excluding chain transfer and dispropotionation, recombination of two radicals, centered at growing chain ends, will terminate the propagation, cf. equations 1.30 to 1.34. The flexibility of polymer chains increases with their length and therefore termination becomes more probable the longer the chains grow. The chain growth is initiated first at the surfaces of preirradiated films and, at any given time until termination by recombination sets in, the chains are longer in surface near regions than in the film center. Hence, the probability of recombination is slightly higher in surface near areas. Due to earlier termination of the polymerization by recombination in regions more distant from the center, where the chains still grow, the distribution of the graft components becomes more and more homogeneous the longer the grafting proceeds.

The graft-through of the films is needed to prepare membranes featuring proton conductivity at all, while a preferably homogeneous distribution of a sufficient amount of the graft component provides proton conductivity in the required range for fuel cell applications (∼0.1 S·cm$^{-1}$ [14]). The proton conductivity is introduced into the hydrophobic base films by the graft component, either carrying a hydrophilic ion exchange site (acid groups) already in the monomer or the grafted polymer is modified in an additional post-grafting step. Depending on the concentration of the ion exchange sites, "clusters" of hydrophilic domains are formed in the presence of water [83]. The interconnection of those "clusters" to a three-dimensional network provides the channels to transport protons through a membrane.

1.3.2.2 Irradiation and nature of active sites

The irradiation of polymers may lead to (a) crosslinking, (b) formation of active sites, or (c) chain scission. Which process or combination of these processes finally occurs depends on the type of base film, used radiation source, applied dose, and the present atmosphere [84]. Irradiation of poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) creates radicals by chain scission due to cleavage of the weaker C-C bond (∼372 kJmol$^{-1}$ [85]) compared to the C-F bond (531 kJmol$^{-1}$ [82]). Nevertheless, tertiary carbon radicals, main chain radicals, and side chain (CF$_3$ group) radicals formed by the cleavage of C-F bonds were found to be generated beside the chain end radicals formed by cleavage of C-C bonds during the radiation of FEP [82]. Irradiation of poly(ethylene-alt-tetrafluoroethylene) (ETFE) yields carbon based radicals from the cleavage of C-C and C-H bonds, whereas the C-H bond dissociation energy (430 kJmol$^{-1}$) is smaller than the $D_0$ of C-F bonds. However, ETFE and the structurally similar poly(vinylidene fluoride) (PVDF) tend towards crosslinking when exposed to ionizing irradiation [82].
The sources used to irradiate base polymers can be classified into [81]

- Electromagnetic radiation (photons)
  1. $\gamma$ ray, e.g. $^{60}$Co ($E_{em} = 1.25$ MeV), $^{137}$Cs ($E_{em} = 0.66$ MeV)
  2. X-ray
  3. UV irradiation (soft)

- Particulate radiation (charged particles)
  1. Electrons (used in the present work)
  2. Swift heavy ions, e.g. $^4$He, $^{197}$Au, $^{209}$Bi, etc.

Using technical electron beam facilities, irradiation becomes today a highly reproducible and fast process, where the required irradiation dose is controlled by the beam current and feed rate at a given, constant acceleration voltage. The concentration of active sites (radicals) and subsequently the concentration of backbone-side chain linkages in a grafted film increases with the applied irradiation dose.

Pre-irradiation in ambient air yields hydro peroxides formed by the reaction of the primarily induced carbon based radicals with the present oxygen and the subsequent hydrogen abstraction, as discussed above. Indeed, the nature of the active sites is important for the grafting reaction and constitution of the grafted film. The "capping" of the active sites has to be removed thermally to initiate the polymerization. Different energies (temperatures) are required to homolytically dissociate the O-O bond ($146 \text{ kJ mol}^{-1}$), heterolytically the O-H bond ($463 \text{ kJ mol}^{-1}$), or cleave the entire hydroperoxide group by homolytical C-O bond dissociation ($358 \text{ kJ mol}^{-1}$). The linkage between the base polymer and the grafted side chain will be different depending on the cleaved bond and the subsequently formed initiating radical. The nature of this linkage may substantially influence the stability of the fuel cell membrane prepared from those grafted film.

### 1.3.2.3 Base polymers used for radiation grafting

Base films used for irradiation induced grafting influence the properties of the grafted films and furthermore of the membranes prepared with these films [86]. Therefore, chemically, thermally and mechanically stable, preferably hydrophobic polymers are used, having the ability to produce stable radicals. However, the generation of stable radicals has to be accompanied with the resistance of the base polymers towards radiolytic degradation. Hydrocarbon, partially and perfluorinated polymers were used as base materials for radiation grafting (Table 1.3). Hydrocarbon polymers benefit from their cheapness, high radiation resistance and good mechanical properties [87]. Partially and perfluorinated polymers show excellent thermal and chemical properties and generate highly stable radicals when exposed to radiation [82].

Each base polymer shown in Table 1.3 possesses characteristic intrinsic physical properties, such as density, melting point, crystallinity [86] and in case of available technical products specific molecular weight distributions. The further discussion focuses on partially and perfluorinated polymers, basically due to their chemical and mechanical robustness, which is beneficial for fuel cell applications. The resistance of fluorinated base polymers to irradiation was shown by the influence of the irradiation dose (0 to 52 kGy) on the mechanical properties, namely the tensile
Table 1.3: Selection of base polymers used for radiation grafting.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrocarbon polymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>PE</td>
<td>(\left(-\text{CH}_2\text{-CH}_2\right)_n)</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>(\left(-\text{CF}_2\text{-CH}_2\right)_n)</td>
</tr>
<tr>
<td><strong>Partially fluorinated polymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>PVDF</td>
<td>(\left(-\text{CF}_2\text{-CH}_2\right)_n)</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride-co-</td>
<td>PVDF-co-HFP</td>
<td>(\left(-\text{CF}_2\text{-CH}_2\right)_n) (\left(-\text{CF}_2\text{-CF}_2\right)_m)</td>
</tr>
<tr>
<td>hexafluoropropylene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene-co-tetrafluoroethylene)</td>
<td>ETFE</td>
<td>(\left(-\text{CH}_2\text{-CF}_2\text{-CF}_2\right)_n)</td>
</tr>
<tr>
<td>Poly(vinyl fluoride)</td>
<td>PVF</td>
<td>(\left(-\text{CF}_2\text{-CF}_2\right)_n)</td>
</tr>
<tr>
<td><strong>Perfluorinated polymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>PTFE</td>
<td>(\left(-\text{CF}_2\text{-CF}_2\right)_n)</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene-co-</td>
<td>FEP</td>
<td>(\left(-\text{CF}_2\text{-CF}_2\right)_n) (\left(-\text{CF}_2\text{-CF}_2\right)_m)</td>
</tr>
<tr>
<td>hexafluoropropylene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene-co-</td>
<td>PFA</td>
<td>(\left(-\text{CF}_2\text{-CF}_2\right)_n) (\left(-\text{CF}_2\text{-CF}_2\right)_m) (\text{OCF}_2)</td>
</tr>
<tr>
<td>perfluoropropyl vinyl ether)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(chlorotrifluoroethylene)</td>
<td>PCTFE</td>
<td>(\left(-\text{CF}_2\text{-CF}_2\right)_n) (\text{Cl})</td>
</tr>
</tbody>
</table>

strength and elongation at break [86].

The radiation induced degradation decreases in the order:

\[(\text{PTFE} > \text{FEP} > \text{PFA} > \text{ETFE} > \text{PVDF})\]

While chain scission substantially occurs during irradiation in perfluorinated films, crosslinking takes place in partially fluorinated films (cf. [79, 86, 88]). PTFE was bracketed due to the known irradiation sensitivity and the formation of acid fluoride groups during its irradiation in the presence of oxygen, which subsequently hydrolyze to carboxylic acids if water is available [89, 90, 91]. The irradiated films in [86] were subsequently grafted 8 h in a styrene/divinylbenzene (DVB) solution at 60 °C. The higher grafting ability of a base film was supposed to correlate with its easier formed radicals during the pre-irradiation, assuming the same irradiation dose and radical stability. The determined grafting ability was ordered by:

\[(\text{PVDF} > \text{ETFE} > \text{FEP} > \text{PFA} > \text{PTFE})\]

In general the partially fluorinated films show the higher grafting ability. The chemical stability was tested *ex situ* by determination of the time dependent weight lost of the membranes in
30 % hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) solution at 80 °C. At a sampling rate of 4 h the initiation of degradation, given by the first decrease in weight, was determined in the order:

PVDF (12 h) > EFTE (16 h) > FEP (20 h) ≈ PFA

The higher stability of perfluorinated polymers was attributed to the shielding effect of the fluorine atom (diameter 67 pm, cf. hydrogen atom 37 pm). However, the treatment of membranes base on styrene or styrene/DVB grafted FEP and ETFE film with 3 % H\textsubscript{2}O\textsubscript{2} solution at 60 °C caused faster degradation of FEP based membranes [92]. The mechanical stability of membranes with similar proton conductivities, based on styrene/DVB grafted films, was determined in tensile tests [86]. The elongation at break is rated qualitatively from the given stress strain curves in the order:

PVDF > PFA > ETFE > FEP (≫ PTFE)

The superior mechanical properties of partially fluorinated membranes to the perfluorinated ones were tied down to the intrinsic mechanical properties of the base polymer.

The present research at Paul Scherrer Institut (PSI) focuses on FEP and ETFE as base films for membrane preparation. In the present work both base materials were investigated due to the contradictory findings concerning the \textit{ex situ} chemical stability in H\textsubscript{2}O\textsubscript{2} solution, the intrinsically better mechanical properties of ETFE, and due to the fact that the most stable membrane concerning lifetime and loss of ion exchange capacity prepared and tested at PSI was based on FEP.

The irradiation chemistry of base polymers (P) is contemplated in the following. The homolytic dissociation of any chemical bond by irradiation forms a carbon based radical \(P\cdot\) (activation) and, depending on the nature of the cleaved bond, a hydrogen (C-H bond), fluorine (C-F bond) or another carbon based (C-C bond) radical \(R\cdot\) according to

\[
P - R \xrightarrow{\text{hv}} P\cdot + R\cdot
\]  

(1.22)

The stability of the carbon based radicals \(P\cdot\) is different for the various base polymers [82]. The primary radical undergoes further reactions with present oxygen, if the irradiation is carried out in ambient air. Depending on the irradiation temperature and dose rate the formation of peroxyl radical (propagation, equation 1.23) is followed either by formation of hydroperoxide by hydrogen abstraction (termination 1, equation 1.24) or by its reaction with an carbon based radical to form a peroxide (termination 2, equation 1.25).

\[
P\cdot + O_2 \rightarrow POO\cdot
\]  

(1.23)

\[
POO\cdot + RH \rightarrow POOH + R\cdot
\]  

(1.24)

\[
POO\cdot + P\cdot \rightarrow POOP
\]  

(1.25)

The peroxides have to be decomposed (re-activated, equation 1.26) before the graft polymerization is initiated.

\[
POOP(H)\cdot \xrightarrow{\Delta} 2 PO\cdot (POO\cdot + HO\cdot)
\]  

(1.26)

The graft polymerization is performed at elevated temperature and therefore the decomposition is thermally activated as discussed in detail in the following paragraph.
1.3.2.4 Monomers used for radiation grafting

Base polymers used for radiation grafting, the required properties as well as to some extent their radiation and grafting behaviour are introduced and discussed in the previous paragraph. Monomers used for radiation grafting have to penetrate the preirradiated film to access the active sites within the film and propagate the chain growth. Hence, a low viscosity enhances the monomer diffusion into the base polymer [81]. Especially in simultaneous irradiation grafting the monomer should not form stable free radicals. The tendency of free radical formation correlates with the monomer’s dipole strength. The monomer influences the efficiency and homogeneity of the grafting. Whereas the former determines the grafting time, the latter becomes important for the conductivity of the membrane prepared from the grafted film.

The monomers applied in radiation grafting with the view to prepare fuel cell membranes from the grafted films, can be classified into acrylic and vinyl monomers (Table 1.4). The monomers are not further subdivided into reactive (radiation sensitive) and non-reactive monomers, which is more important for simultaneous irradiation grafting. More interest regarding fuel cell ap-

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Formular</th>
<th>R</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acrylic monomers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>[93, 94, 95]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>CH₃</td>
<td>[96]</td>
<td></td>
</tr>
<tr>
<td>Acrylamide</td>
<td>NH₂</td>
<td>[97]</td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>H</td>
<td>[98, 95]</td>
<td></td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>CH₃</td>
<td>[99, 100]</td>
<td></td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>[101, 102]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>CH₃</td>
<td>[103]</td>
<td></td>
</tr>
<tr>
<td>Glycidyl methacrylate</td>
<td>-</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td></td>
<td></td>
<td>[105]</td>
</tr>
<tr>
<td><strong>Vinyl monomers</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Styrene</td>
<td>H</td>
<td>[70, 106, 107, 108]</td>
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<tr>
<td>α-Methylstyrene</td>
<td>CH₃</td>
<td>[100, 109, 110]</td>
<td></td>
</tr>
<tr>
<td>α, β, β-Trifluorostyrene</td>
<td>H</td>
<td>[111, 112]</td>
<td></td>
</tr>
<tr>
<td>para-Methyl-TFS</td>
<td>CH₃</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>para-Trifluoromethyl-TFS</td>
<td>CF₃</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>para-Methoxy-FTS</td>
<td>OCH₃</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>para-Phenoxy-FTS</td>
<td>O₆H₆</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>para-Sulfonfluoride-FTS</td>
<td>SO₂F</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>para-R-FTS</td>
<td>O(CF₂)₂SO₂F</td>
<td>[115]</td>
<td></td>
</tr>
<tr>
<td>2- and 4-Vinyl pyridine</td>
<td>-</td>
<td>[116]</td>
<td></td>
</tr>
</tbody>
</table>
plication was produced by vinyl monomers. Styrene was widely used as monomer for radiation grafting onto a multitude of base polymers, e.g. FEP [70], ETFE [106, 117], PVDF [118], PFA [119] and PE [120]. The weakness of the poly(styrene sulfonic acid) side chain under the conditions of an operating fuel cell was attributed to the presence of the hydrogen atom in α-position to the benzene ring. The homolytic dissociation of this weak carbon hydrogen bond was assumed to be involved in the degradation mechanism introduced by a radical attack on the benzene ring (cf. Figure 1.16) [121]. One ansatz was to increase the chemical stability using monomers with stronger carbon-element bonds in α-position to the benzene ring, e.g. C-F bonds in TFS and its derivatives [115] or a C-C bond in AMS [110]. Shielding of the benzene ring against the primary attack of the hydroxyl radical produced in the operating fuel cell with bulky substituents, such as meta- and para-methylstyrene or para-tert-butylstyrene, was another approach towards more stable graft components. To avoid leaching of chain fragments obtained by bond scission as a result of radical attack, crosslinker was added during the graft polymerization. The integration of bifunctional crosslinker molecules in growing chains yields a three dimensional network. This crosslinked, close meshed network may be able to retain the graft component after chain scission either due to a second connection of the fragment to the network or based on the hindered diffusion. The effectiveness of this approach was shown for an FEP based styrene grafted membrane by improving the life time in a fuel cell from 50 h for the uncrosslinked to 4000 h for the DVB crosslinked membrane under the same operating conditions [108, 122].

The reactions involved in the graft polymerization are briefly discussed in the following. Once the base film is irradiated, the activity to initiate the graft polymerization is preserved for at least one year by storage of the pre-irradiated film at -80 °C. The release of "initiation active" radicals from the alkyl peroxy groups by heating the pre-irradiated film and thermal dissociation of the O-O bond is shown in equation 1.26 (initiation 1). The primary alkylperoxy radical $PO\cdot$ is able to initiate the grafting reaction in the presence of monomer $M$ (initiation 2):

$$PO\cdot + M \rightarrow POM\cdot$$

(1.27)

The initiated chain $POM\cdot$ is growing with further monomer $M$ (propagation) according to

$$POM\cdot + (n-1)M \rightarrow POM_n\cdot$$

(1.28)

with the propagation rate $r_p$ given as a function of the propagation rate constant $k_p$ and the concentrations of the initiated chain $[POM\cdot]$ and the monomer $[M]$, respectively, according to

$$r_p = k_p[POM\cdot][M]$$

(1.29)

The graft polymer chains will grow in the presence of monomer until the "active" center disappears. Excluding chain transfer (CT) reactions to a monomer $M$ (equation 1.30), to a chain transfer agent $S$ (equation 1.31) or to a polymer $P$ (equation 1.32) and the termination by disproportionation, only recombination (equation 1.31) will stop (terminate) the chain growth.

$$POM_n\cdot + M \rightarrow POM_n + M^*.$$  

(1.30)

$$POM_n\cdot + S \rightarrow POM_n + S^*.$$  

(1.31)


\[ \text{POM}_n \cdot + P_m \longrightarrow \text{POM}_n + P_m\cdot \] (1.32)

The rate for CT to the monomer is usually 10^3 times smaller than the propagation rate \( r_p \) due to the higher activation energy. The yielded \( M^\cdot \) may initiate the growth of a new chain, which is in the case of a graft polymerization not connected to the base polymer. A chain transfer agent \( S \) has to possess a weak bond that can be easily broken to form the "activated" agent \( S^\cdot \), on its part able to act as initiator. CT to a polymer chain \( P_m \) may take place at any of the \( m \) monomer units of the polymer chain by abstraction of a atom (usually a hydrogen), which forms the dead polymer chain \( \text{POM}_n \). The initiation of a growing chain by the \( P_m\cdot \) leads to a branched polymer. The termination by disproportionation is not discussed in detail, but it has to be mentioned that the terminal double bond produced at one of the involved polymer chain ends may lead to branching if this double bond participates in subsequent reactions. The termination by recombination remarkably increase the chain length:

\[ \text{POM}_n \cdot + \text{POM}_m \cdot \longrightarrow \text{POM}_{n+m} OP \] (1.33)

The termination rate \( r_t \) depends on the termination rate constant \( k_t \) and the concentrations of both chains \([\text{POM}_n\cdot]\) and \([\text{POM}_m\cdot]\) according to

\[ r_t = k_t [\text{POM}_n\cdot][\text{POM}_m\cdot] \] (1.34)

Termination by recombination may also take place during heating after the polymerization due to its intramolecular nature, where no further reactants (monomers, CT agents, etc.) have to be present, and the higher chain mobility at elevated temperature.

### 1.3.2.5 Excursion: Membrane degradation

The longevity of polymer electrolyte fuel cells depends on the stability of each individual component. Overall voltage degradation for a PEFC under constant load conditions and fully humidified reactants at 75 °C was found to be around 1-2 µV·h⁻¹. If the operating condition diverges from the "ideal" state mentioned before, e.g. by cycling load or humidity, applying start-stop cycles, lowering humidification or increasing temperature, the degradation rate may increase drastically [123]. The most critical components concerning degradation in PEFC are the membrane and the catalyst including its carbon support, the latter becomes important in start-stop cycles or fuel starvation. Degradation of the membrane increases when the humidity decreases, the fuel cell is operated under open circuit voltage (OCV), and impurities are present in or migrate into the membrane during the operation [123, 124]. Hence, the water management in an operating fuel cell is very important. The challenge is to balance the need for humidified gas at the gas inlet to prevent dehydration of the membrane caused by the electro-osmotic drag (EOD) and the inhibition of water condensation close to the gas outlet in order to keep the pores in the GDL open and allow sufficient mass transport to the electrode. The water management is additionally influenced by the local current density [125]. The net water transport within the membrane is given by the ratio of the electro-osmotic drag (EOD) and water permeation. The EOD is a water current from the anode to the cathode with the EOD coefficient \( k_{EOD} \), defined as number of water molecules transferred through the membrane per proton [126]. The EOD depends on the nature of the polymer but not its thickness and the temperature [3]. Water
permeation depends on the difference of the water activity between both electrodes. The water permeation (back diffusion) was observed to be the largest when the membrane was exposed to vapor on one and liquid water on the other side, correlating with the maximum difference in the chemical potential \[127\]. Gas crossover is discussed as main cause of hydrogen peroxide (H\(_2\)O\(_2\)) formation and degradation of fuel cell membranes by the subsequent radical chemistry \[128, 129\]. The location of H\(_2\)O\(_2\) formation is discussed controversially in literature. The formation of H\(_2\)O\(_2\) at the anode requires the diffusion of oxygen through the membrane to the anode \[130\], where the following reactions may occur:

\[
\begin{align*}
H_2 & \xrightarrow{(P)} 2H^-
\end{align*}
\]

\[
H^\cdot + O_2 \rightarrow HO_2^\cdot
\]

\[
HO_2^\cdot + H^\cdot \rightarrow H_2O_2
\]

The \(HO_2^\cdot\) may directly attack the membrane \[14, 131\] or the hydrogen peroxide diffuse into the membrane. Incomplete oxygen reduction at the cathode may also form hydrogen peroxide \[132\] according to

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]

Independent where the hydrogen peroxide formation is located, the release of hydroxyl radicals by its reaction with trace metal ions is generally accepted. The subsequent reaction of the hydroxyl radical with another H\(_2\)O\(_2\) molecule forms the hydroperoxyl radical.

\[
H_2O_2 + M^{2+} \rightarrow M^{3+} + \cdot OH + OH^-
\]

\[
\cdot OH + H_2O_2 \rightarrow H_2O + HO_2^.
\]

The mechanism of the degradation depends on the membrane type. PFSA membranes suffer from the weakness of the terminal COOH groups prone to decarboxylation, which initiate the "unzipping mechanism" \[133\]. The reaction cycle requires hydroxyl radicals to shorten the polymer chain \(P\) by one CF\(_2\) unit, releasing carbon dioxide and hydrogen fluoride. The released HF is used to determine the fluoride emission rate (FER) as measure for the degradation of PFSA membranes \[134\].

\[
P_F - CF_2 - COOH + \cdot OH \rightarrow P_F - CF_2 \cdot + CO_2 + H_2O
\]

\[
P_F - CF_2 \cdot + \cdot OH \rightarrow P_F - COF + HF
\]

\[
P_F - COF + H_2O \rightarrow P_F - COOH + HF
\]

The unzipping mechanism was formulated for radical attack onto terminal carboxylic acid groups. The ether bridges linking the main and side chain and present in the side chain of Nafion\textsuperscript{®} like membranes were also expected to be accessible by radical attack and lead to a substantial decrease in the molecular weight \[135\]. Membrane thinning was observed to be a dissolution process, proceeding from the interface between the PFSA membrane and electrode and strongly depending on the membrane position within the fuel cell and the stack \[136\].

The supposed degradation mechanism of PSSA based membranes is initiated by the attack of
a hydroxyl radical on the benzene ring forming an OH-adduct (Figure 1.16). The protonation and water abstraction yield a delocalized radical cation, which was not experimentally observed, stabilized by the release of a proton via heterolytic cleavage of the C-H bond in α position.

![Figure 1.16: Proposed mechanism for the attack of hydroxyl radicals on para-toluene sulfonic acid, a PSSA mimic [121].](image)

The radical in α position is stabilized by mesomerism and its formation is product development controlled. Alternatively, the radical in α position can be formed by direct abstraction of the α-hydrogen by a hydroperoxyl radical, which was observed recently by S. Dockheer. Further reactions of the radical may lead to chain scission, e.g. a β-fragmentation will yield a pendant double bond (in α position) and the radical is relocated to the next styrene sulfonic acid repeating unit in α position to its benzene ring.

The above shown proposed chemical degradation mechanisms are not able to take into account all observed membrane failures during fuel cell operation [135]. Assembling the membranes first in the MEA, sometimes by hot-pressing, and subsequently in the fuel cell induces compressive force, discussed in detail in paragraph 5 on page 93. While creep is a very slow, time dependent relaxation to avoid the compressive stress, cracks may be formed during temporarily overstressing the polymer. Microcrack, craze or pinhole formation yields high gas crossover and therefore enhance membrane degradation. Pinhole formation was attributed to locally different shrinkage caused by drying, electrochemical peroxide formation within the membrane and the subsequent radical attack and dissolution of the membrane [130], the roughness of the GDL [137], and membrane dissolution caused by local stress [136]. Observation of degradation in fuel cell tests under constant load and high humidity is time-consuming [123]. Therefore, the development of meaningful ex situ or accelerated in situ methods to test the chemical and / or mechanical stability attract interest of the scientific community. The discussion of pros and cons and the comparability of those methods are beyond the scope of the present work. All aspects and influences on fuel cell durability and degradation, including ex situ and accelerated in situ testing methods, are reviewed in [135].

### 1.3.2.6 En route to chemical stability: α-Methylstyrene

In the present work α-methylstyrene (AMS) and methacrylonitrile (MAN) are co-grafted onto pre-irradiated base films, namely FEP and ETFE. Hence, the historical development of this system, especially at Paul Scherrer Institut, is briefly reviewed in this paragraph.

An overview of the variety of possible monomers used for pre-irradiation grafting is shown in Table 1.4. Styrene and its grafting behaviour are well known [74] and the necessity of post-sulfonation to achieve proton conductivity, required for the application as proton exchange mem-
brane, is compensated by the favorable grafting kinetics [71]. The thermogravimetric analysis (TGA) of FEP based polystyrene (PS) grafted films showed a two step degradation, starting with the loss of polystyrene at 400-460 °C and followed by degrading the FEP phase at higher temperature. The heat of fusion, determined by differential scanning calorimetry (DSC), was reduced by increasing the degree of grafting, which suggested the dilution of the inherent FEP crystalline zones by incorporation of amorphous PS in the amorphous FEP matrix [138]. The homogeneity of polystyrene grafting across the FEP base film thickness was determined by microprobe analysis of the transversal distribution of sulfur in the membrane and found to be homogeneous for a degree of grafting of at least 26 % [72]. Ex situ properties of poly(styrene sulfonic acid) (PSSA) grafted FEP membranes were determined depending on the degree of grafting [70, 139, 140] and the used radiation dose and grafting time [141]. Surface nonhomogeneities were observed in form of bubbles for grafting of less than 11 % PS onto FEP, attributed to the incompability of hydrophilic sulfonated PS chains in the hydrophobic FEP matrix [142]. PSSA grafted, DVB crosslinked FEP based membranes showed superior performance and durability in fuel cell tests compared to uncrosslinked membranes [122, 131]. The enhanced in situ properties placed DVB crosslinked, PSSA grafted FEP based films and membranes into the focus of research. Their grafting behaviour [143] and thermal stability [144] was compared to the grafting onto ETFE and PVDF [117, 145, 146], where the orientation during the extrusion process, irradiation type and atmosphere and the grafting temperature showed a significant influence on the degree of grafting. An improvement of the lifetime of radiation grafted FEP-g-[PSSA-co-DVB] to approximately 2000 h under the conditions of an operating fuel cell was achieved by Nafton® coating of the membrane surface and hot-pressing of the MEA [11, 108, 147]. The grafting kinetics of styrene and DVB onto FEP from non-solvents was investigated and a mixture of alcohol/water found to yield the highest degree of grafting [148]. The optimum DVB concentration in the grafting solution with respect to the fuel cell performance and durability was determined to 10 vol% [149] and the surface composition determined by X-ray photoelectron spectroscopy (XPS) was strongly influenced by the DVB concentration in the grafting solution [150]. The effect of DVB crosslinking on the grafting of styrene onto ETFE and the properties of the grafted films and membranes were intensively investigated and the optimum performance was achieved using 5 vol% DVB in the grafting solution [92, 151, 152, 153]. Nematic-like ordering of the crystalline domains was observed for FEP base film by small angle neutron scattering (SANS) [154]. Growth of the amorphous domains in uncrosslinked films for degree of grafting above 15 % caused the disappearance of the nanometer domains, which was not observed in DVB crosslinked films.

Electron spin resonance (ESR) studies showed the presence of peroxy and alkyl radicals, depending on the atmosphere, and their lifetimes varied with temperature and the presence of solvent [155]. The earlier findings concerning the weakness of the α-position for hydrogen abstraction in the follow up reaction, induced by the hydroxyl radical attack to the benzene ring, cf. Figure 1.16 [121], caused the search for more stable monomers for the radiation induced grafting. Derivatives of TFS, possessing a more stable C-F bond in α-position to the benzene ring compared to the C-H bond in styrene, were grafted onto ETFE and subsequently hydrolyzed and tested in situ [115]. High irradiation doses were used to reach a sufficiently high degree of grafting. The simplest protection of the α-position is obtained by replacing the hydrogen and the related C-H bond by a methyl group by forming a stronger C-C bond in AMS, which is a readily avail-
able chemical of low cost. The chemical stability of a grafted PTFE based zinc/ferricyanide battery membrane in a strong oxidizing agent was increased by exchanging the polystyrene as graft component with polyAMS [156]. However, the irradiation and grafting conditions were not disclosed. The radical polymerization kinetics of neat AMS is poor and its ceiling temperature of 61 °C [157] renders the polymerization at higher temperatures impossible. Grafting with a sufficient degree of grafting necessitates the use of an appropriate co-monomer. The co-grafting of AMS with styrene and DVB increased the ex situ stability in 6 % H$_2$O$_2$ solution [158]. Nevertheless, co-grafting of AMS with styrene preserves the "diluted" problem of the weak α position. The copolymerization with acrylonitrile (AN) [109, 159] and MAN [110, 109, 160, 161] increased the polymerization rate of AMS.

1.4 Aim of this work

M. Ślaski introduced, during his doctoral thesis at PSI, the graft copolymerization of AMS and MAN onto FEP base films by pre-irradiation in air, route (b1) in Figure 1.14 on page 19, to prepare fuel cell membranes [162, 163]. He studied the graft copolymerization of AMS and MAN at 60 °C and identified a mixture of isopropanol and water as the best solvent for the grafting reaction, regarding the achievable DoG. An uncrosslinked FEP based, AMS/MAN co-grafted membrane was tested in situ and reached 500 h of operation under constant load at 80 °C. Post mortem analysis of the membrane demonstrated the higher stability under the conditions of an operating fuel cell, compared to the corresponding styrene based membrane, by a substantially reduced degradation, measured as loss of the ion exchange capacity.

The stability of AMS/MAN co-grafted, FEP based membranes was further increased by the addition of crosslinker, DVB or diisopropenylbenzene (DIPB), to the grafting solution, whereas the crosslinker content was not optimized [100, 110, 162]. The DVB crosslinked membrane was tested approximately 1000 h under constant operating conditions (500 mA·cm$^{-2}$) at 60 °C (≈200 h) and 80 °C (until the end of experiment) in the fuel cell. The extent of degradation was determined based on the loss of IEC to 16%, which corresponds to a degradation rate of 0.015 %·h$^{-1}$. The degradation rate of an FEP based, styrene grafted, and DVB crosslinked membrane was determined to 0.010 %·h$^{-1}$ within the first 4000 h of operation at 500 mA·cm$^{-2}$ and 80 °C [76].

Despite the achieved improvements in course of the implementation of the co-grafting of AMS and MAN, some questions remained unanswered. The influence of the reaction parameters in the graft copolymerization on the properties of the grafted film was not discussed. The reaction sequence of irradiation, graft polymerization, sulfonation and hydrolysis is denoted in Figure 1.17, using the example of AMS and MAN for the monomers and FEP for the base film.

The influence of the irradiation dose on the degree of grafting [81] and the mechanical properties [84] were reported for styrene grafted membranes. However, the effect of the irradiation dose, to which the samples were exposed during irradiation, on the properties of AMS/MAN co-grafted films was not investigated. The solvent used for the graft copolymerization was optimized in order to achieve the maximum DoG, whereas the influence of the temperature and the molar ratio was not addressed.

The integral composition of grafted films, in terms of the ratio of the monomers in the graft copolymer ($R_{m,\text{graft}}$), was previously investigated by FTIR spectroscopy. However, proton con-
1.4. AIM OF THIS WORK

Figure 1.17: Reaction sequence of radiation co-polymerization of AMS and MAN (2) onto a pre-irradiated (1) FEP base film and the subsequent sulfonation (3a) and hydrolysis (3b) of the grafted film.

...ductivity depends on the total amount of the graft component, accessible by FTIR spectroscopy, as well as on the homogeneous distribution of the grafted polymer across the thickness of the membrane. Due to the front mechanism, shown in Figure 1.15 on page 19, an inhomogeneous distribution of the graft component has to be assumed during the initial phase of grafting. Furthermore, the diffusion of AMS and MAN within the grafted film, required to reach the active sites, may be different and therefore yield local variations of the monomer ratio. Finally, the different reactivities of AMS and MAN may cause concentration inhomogeneities due to different consumption rates. To exclude the above mentioned assumptions from affecting the homogeneity of the grafting, a method is required to resolve the local composition of grafted films. The distribution of styrene in radiation grafted, FEP based and DVB crosslinked membranes was determined by microprobe measurement of the sulfur distribution, based on the assumption of (mono)-sulfonated styrene units [143]. The application of this method for AMS and MAN co-grafted membranes will facilitate the determination of the AMS distribution, whereas the local concentration of MAN is not accessible. Confocal Raman microscopy [164, 165, 166] and confocal laser scanning microscopy [167] were shown to be potential methods to investigate the local composition of thin films.

Since graft copolymerization of the two monomers yield a certain ratio of those monomers in the grafted film, the questions, how these ratio is influenced by the reaction conditions during grafting and how these ratio influence the mechanical and fuel cell relevant properties, arose. The first objective of this work was to investigate the graft copolymerization of AMS and MAN onto pre-irradiated FEP and ETFE base films with the aim to determine the influence of the associated reaction parameter on the degree of grafting and molar ratio of the monomers in the grafted polymer. Therefore, a standard procedure was established (details in paragraph 2.1.4), to ensure the reproducibility of the preparation of grafted films and membranes. The influence of reaction parameters, such as temperature, molar ratio of the monomers in the grafting solution, monomer concentration in the grafting solution, irradiation dose, and water content, on the $D_{oG}$ and $R_{m, graft}$ was of substantial interest. With the view to compare and rank the effects of varied parameters, a simple mathematical model, describing the reaction kinetics of the graft polymerization, was used to fit curves to the experimental data and calculate the rate of polymerization and termination by recombination. The question, how crosslinking effects the grafting kinetics, was also addressed.

The second part of the work was associated with the analysis of the grafted films and the determination of their composition. Besides the improvement of existing methods, e.g. FTIR
spectroscopy, the interest was focused on the investigation of the local composition of grafted films. In particular, the distribution of the graft components over the thickness of grafted films was the target. Since the crosslinker concentration in the grafted film is not accessible by FTIR spectroscopy in AMS/MAN co-grafted films, one topic in the analytical context was the search for a suitable method to detect and quantify crosslinker.  
The mechanical properties of grafted films and especially of membranes was the third objective of this work. Attention was paid to mechanical properties of membranes at conditions closely related to the conditions of an operating fuel cell. The generation of such a "fuel cell" related climate, in terms of temperature and humidity, during the tensile testing was closely connected to the commissioning of a climatic chamber, its validation and the development of a testing protocol.  
The fourth target was related to fuel cell application. The focus was on the determination of \textit{ex situ} membrane properties and their correlation with mainly two integral characteristics of grafted films, namely the $\text{DoG}$ and $R_{m,\, graft}$. On the other hand, the \textit{in situ} characterization of membranes was of interest, either to investigate their performance or determine their durability. The investigation of tested membranes (\textit{post mortem} analysis) using appropriate methods to determine the degradation and quantify the durability of membranes was the final challenge under this target.
Chapter 2

Experimental

2.1 Grafting

2.1.1 Monomers, base films and chemicals

The base polymers, FEP (Teflon® 100A, 25 µm thick) and ETFE (Tefzel® 100LZ, 25 µm thick), were purchased as film rolls from DuPont (Circleville, USA). All chemicals were used as received without any further purification. The monomers α-methylstyrene, 99 %, stabilized with 15 ppm 4-((tert-butyl)catechol, and methacrylonitrile, 99 %, stabilized with 50 ppm monomethyl ether hydroquinone, were purchased from Aldrich. Divinylbenzene (technical grade, 80 %), a mixture of 56.3 % meta- and 24.4 % para-isomer and 20 % ethylvinylbenzene, stabilized with 0.1 % 4-(tert-butyl)catechol), meta-diisopropenylbenzene (>97 %, not stabilized), isopropanol (>99.8 %), dichloromethane (>99.9 %) and chlorosulfonic acid (>98 %) were externally procured from Fluka. Potassium chloride (analytical grade) was purchased from Merck and acetone (>99 %) from Siwid AG. Water was purified by a Seralpure® system and its quality was checked by resistivity measurement (>18 MΩ).

2.1.2 General procedure

The base polymers were cut into rectangular samples (16 cm in machining direction x 14 cm in transverse direction), washed with ethanol, dried under reduced pressure at a temperature of 80 °C, and packed in zip-lock PE bags for pre-irradiation. Irradiation was performed using an electron beam and the irradiated films were stored at a temperature of -80 °C. The grafting was carried out in reactors by immersing the pre-irradiated film in a solution containing the monomer(s). The reactors were placed for the required reaction time in a water bath and heated to the desired temperature. The grafted films were washed with acetone, dried and characterized according to paragraph 2.2. The grafted films were subsequently sulfonated, hydrolyzed and the resulting proton conducting membranes were characterized ex situ and stored in water.

2.1.3 Irradiation

Irradiation was carried out in ambient atmosphere with an electron beam facility at LEONI Studer AG, Däniken, Switzerland (see figure 2.1). A dose rate of 15.1 ± 1.1 kGy·s⁻¹ was used by applying an acceleration voltage of 2.2 MeV at a beam current of 5-20 mA. In order to get comparable reaction times, irradiation doses for FEP and ETFE of 25 kGy and 3 kGy
were chosen, respectively. For some experiments the base film was irradiated up to 200 kGy, whereas doses above 50 kGy require cooling of the samples with dry ice during the irradiation process. The irradiation dose was controlled with alanine pellet dosimeters (Far West Technology Inc.). The dosimeters were placed together with the spreaded base films on aluminium plates and passed with a conveyor under the window of the scan horn (schematic drawing see Figure 2.1). The radiation dose was controlled by the velocity of the conveyor and therefore the time during which the samples were exposed to the electron beam. Immediately after irradiation the irradiated films were placed in dry ice for transportation. The irradiated films were stored in a freezer at -80 °C for several months without losing the activity to initiate the grafting polymerization.

![Figure 2.1](image)

*Figure 2.1: Photograph (left) and schematic representation (right) of the electron beam facility at LEONI Studer AG with a sample irradiation specimen.*

### 2.1.4 Graft copolymerization of AMS and MAN

The grafting was performed in two different types of reactors, depending on the experiment. To investigate reaction kinetics and determine the influence of different reaction parameters, the grafting was carried out in a glass reactor (a), where one pre-irradiated base film was immersed in approximately 60 ml of grafting solution. The preparation of up to six films of the same composition, used e.g. for tensile tests or membrane preparation and characterization, was carried out in a stainless steel reactor with a maximum volume of 650 ml (b).

Pre-irradiated films were taken from the freezer and weighed \(m_0\). In case (a) the pre-irradiated film was rolled up and placed in the glass reactor containing the grafting solution or in case (b) mounted with up to five more pre-irradiated films in an alternate arrangement with filter papers on a frame. The filter papers were soaked with grafting solution to prevent adhesion of pre-irradiated films to each other. The mounted frame was placed in a stainless steel reactor containing the grafting solution. The reactor was closed and purged with approximately 10 l/h nitrogen for one hour in order to remove oxygen. The reactor was placed in a preheated water bath for the desired reaction time. The reaction was stopped by removing the grafting solution, rinsing the reactor and grafted film(s) once with acetone and storing the grafted film(s) overnight in acetone to remove excess monomer. The grafted film was dried in a vacuum oven.
under reduced pressure at 80 °C for at least 8 h, subsequently weighed \((m_{\text{graft}})\) and stored in zip-lock PE bags.

The definition of the degree of grafting \(\text{DoG}\) and the measurement and calculation of the molar ratio \(R_m\) are described in the following paragraph. The subsequent sulfonation and hydrolysis as well as the \textit{ex situ} characterization of membranes will be content of paragraph 2.4 and 2.5, respectively.

### 2.2 Characterization of grafted films

A grafted film composed of a base film and one grafted component, e.g. polystyrene grafted onto FEP, is (integral) characterized well enough by the mass difference before and after the grafting (cf. \(\text{DoG}\)). The use of two or more monomers necessitates additionally the determination of the ratio between the different monomer units in the grafted polymer. The molar ratio \(R_m\) was chosen due to the comparability of different monomer systems because of its independence of the chemical nature of the monomers.

#### 2.2.1 Degree of grafting

An important quantity to characterize a chemical reaction is the yield, mostly accessible from the mass of the product. In case of the solid state chemistry of a grafting reaction, the yield is related to the additional mass of the grafted polymer. This additional mass is calculated as difference of the mass of the grafted film \((m_{\text{graft}})\) and the initial mass of the base film \((m_0)\). The "yield" is specified according equation 2.1 as degree of grafting \(\text{DoG}\) and related to the initial mass of the used base film.

\[
\text{DoG} = \frac{m_{\text{graft}} - m_0}{m_0} \cdot 100 \%
\]  

(2.1)

The \(\text{DoG}\) is an integral, mass based quantity and does not contain any information about the chemical nature of the grafted component, its chain length distribution, the local composition or the homogeneity of the grafted film. Additional information about the chemical nature is available from spectroscopic methods (cf. paragraph 4).

#### 2.2.2 Molar ratio

The molar ratio \(R_m\) was used to specify the ratio of the monomers, AMS and MAN, both in the grafting solution \(R_{m, \text{sol}}\) and in the grafted film \(R_{m, \text{graft}}\).

\[
R_m = \frac{n_{\text{AMS}}}{n_{\text{MAN}}} = \frac{m_{\text{AMS}} \cdot M_{\text{MAN}}}{m_{\text{MAN}} \cdot M_{\text{AMS}}} = \frac{V_{\text{AMS}} \cdot \rho_{\text{AMS}} \cdot M_{\text{MAN}}}{V_{\text{MAN}} \cdot \rho_{\text{MAN}} \cdot M_{\text{AMS}}}
\]  

(2.2)

The \(R_{m, \text{sol}}\) can be calculated according equation 2.2 using the volumes of both monomers in the grafting solution. To calculate the \(R_{m, \text{graft}}\) the molar amount or mass of each monomer in the grafted copolymer has to be determined. The molar ratio is routinely determined using FTIR spectroscopy. To validate the FTIR spectroscopic measurement with a second, independent
method, solid state NMR spectroscopy was used to investigate the $R_{m,\text{graft}}$. More advantages of the NMR spectroscopy will be mentioned in paragraph 4.2.

### 2.2.2.1 FTIR spectroscopy

Spectra were measured with a Perkin Elmer FTIR System 2000 spectrometer and evaluated with the curve fitting GRAMS/AI software, version 8.00 (Thermo Electron Corporation, Waltham, USA). The peaks were fitted by assuming a mixed Gaussian and Lorenzian shape. The standard analysis of spectra for calculating the $R_{m,\text{graft}}$ was done with fixed maxima, whereas the peak width and weighting of the Gaussian and Lorenzian contribution were calculated by the GRAMS/AI program.

Spectra of films and membranes were measured at 4 cm$^{-1}$ resolution in the mid-IR spectral range between 4000 and 400 cm$^{-1}$. Grafted films were measured three times folded to enhance the optical path length $l$ and therefore the absorbance $A$, cf. Lambert-Beer law (equation 2.3), and facilitate the quantification even for grafted films with low DoG.

$$A = -\log\left(\frac{I}{I_0}\right) = -\log(T) = \varepsilon \cdot c \cdot l$$  \hspace{1cm} (2.3)

The intensity of very strong signals based on CF-stretch vibrations of the FEP backbone between 1300 and 1100 cm$^{-1}$ and below 800 cm$^{-1}$ was also enhanced by folding, which renders the quantification impossible in those wavelength ranges. Single layers were measured to determine the membrane degradation, based on the very strong signal of the SO stretch vibration at 1040 cm$^{-1}$. Before the FTIR spectroscopic investigation the membranes were converted into the potassium salt form by cation exchange, see paragraph 2.5.2, to reduce the water uptake.

### 2.2.2.2 CP/MAS $^{13}\text{C}$-NMR spectroscopy

The CP/MAS $^{13}\text{C}$-NMR- and MAS $^{13}\text{C}$-NMR spectra were measured in the laboratory of Prof. Müller (University of Stuttgart, Germany, now University of Trento, Italy). The experiments were performed at 100.51 MHz for $^{13}\text{C}$ and 399.75 MHz for $^1\text{H}$ on an Infinity Plus 400 NMR spectrometer from the company Varian (Palo Alto). The 90° pulse length for $^{13}\text{C}$ was 2.6 $\mu$s and for $^1\text{H}$ 3.75 $\mu$s. Spectra were acquired under magic angle spinning (MAS) conditions using a 4 mm HFXXY magic-angle spinning probe at a spinning frequency of 11 or 12 kHz. The relaxation time was determined with a progressive saturation experiment and set to 5 s for cross-polarization (CP) and 30 s for single pulse experiments. The $^{13}\text{C}$ spectra were recorded using a ramped CP sequence and xy-16 pulse decoupling at a contact time $\tau$ of 5 ms [168]. For two samples, proton decoupled $^{13}\text{C}$ single pulse experiments were carried out to review the results obtained from CP/MAS experiments.
2.3 Mechanical tests and dimensional stability

Mechanical properties of pristine base, irradiated and grafted films were investigated at room temperature and ambient humidity in tensile tests (cf. paragraph 2.3.1). The tensile tests with proton-conducting membranes were performed in a climatic chamber, controlling temperature and humidity. Furthermore, the dimensional changes of membranes were determined in shrinkage and swelling experiments (paragraph 2.3.2).

2.3.1 Mechanical tests

The mechanical properties of base films, irradiated samples, grafted films and membranes were investigated using an universal testing machine Zwick Roell 1-FR005TH (Zwick GmbH & Co. KG, Ulm, Germany) with a maximum load of 5 kN. The tensile testing machine was equipped with a climatic chamber to control temperature and humidity during the experiment (left picture in Figure 2.2). The rectangular specimens were fixed at the upper and lower end between two Vulkollan® (Bayer AG) coated aluminium clamps (right picture in Figure 2.2).

![Tensile testing machine and sample holder](image)

Figure 2.2: Tensile testing machine (left) and sample holder with a 100 mm long and 10 mm wide specimen (right).

The measurements of grafted films were performed with a cross head speed of 10 mm·min$^{-1}$, until the pre-load of 0.1 N was reached, 1 mm·min$^{-1}$ in the range from 0.5 to 1 % elongation, where the Young's modulus was determined, and 100 mm·min$^{-1}$ until the sample broke. The measurements of the water swollen membranes were performed, unless otherwise specified, with 100 mm·min$^{-1}$ cross head speed from beginning of the measurement to the sample rupture.

Ten specimens were punched out from each base, irradiated and grafted film, using a cutting die with fixed blades for the simultaneous preparation of five specimens. The values denoted for the mechanical properties of a sample are the average of ten separately measured specimens. Unlike in previous investigations, membranes were used in the present work in acid form and the specimens were cut with a scalpel to prevent notches at the edges, observed when the specimens were punched out. For each membrane composition, two samples were investigated. The first sample was placed into the climatic chamber in fully hydrated form (water swollen at rt) and the second sample in dried form (1 h, 80 °C, reduced pressure). The agreement of the measured mechanical properties of both samples was used to ensure the sample equilibration.
Stress-strain curves obtained in tensile tests were used to determine the mechanical properties of the tested specimen. The Young’s modulus, tensile strength and elongation at break were denoted in Figure 2.3, exemplarily for an FEP base film, investigated in machining direction.

\[ E = \frac{\Delta \sigma}{\Delta \varepsilon} \]

Figure 2.3: Young’s modulus \( E \), tensile strength \( \sigma_{\text{max}} \) and elongation at break \( A \) shown at the stress-strain curve of a FEP base film tested in machining direction.

The stress or standard force \( \sigma \) on the ordinate in Figure 2.3 is given by the initial cross section \( (A_0) \) of the specimen and the currently measured force \( F_{\text{act}} \) according to

\[ \text{Stress} (\sigma) = \frac{\text{Actual force}}{\text{Initial cross section}} = \frac{F_{\text{act}}}{A_0} \ [\text{MPa}] \tag{2.4} \]

The abscissa is the strain \( \varepsilon \), which is calculated from the actual length \( l_{\text{act}} \) and the initial length \( l_0 \) according to

\[ \text{Strain} (\varepsilon) = \frac{\text{Extension}}{\text{Initial length}} = \frac{l_{\text{act}}}{l_0} \tag{2.5} \]

The Young’s or elastic modulus \( E \) corresponds to the slope of the stress-strain curve in the elastic, initial part maintained for small extensions. The comparability of the Young’s modulus of different samples depends strongly on the boundaries of the stress-strain curve section used to calculate the slope and the cross head speed applied to record this section. Hence, the lower and upper strain, used as boundaries, and the cross head speed are always listed together with the Young’s modulus.

Initial experiments to determine the creep modulus \( E_c \) of water swollen membranes were performed with the tensile testing machine, using the climatic chamber. The time dependent elongation of the membranes was recorded at constant load. The creep modulus \( E_c \) was calculated according to equation 2.6 after 40 h from the stress \( \sigma \) and the relative elongation \( \varepsilon \).

\[ E_c = \frac{\sigma}{\varepsilon} = \frac{\sigma \cdot l_{\text{act}}}{l_0} \tag{2.6} \]
2.3.2 Dimensional changes

A key issue in the development of membrane is the correlation of \textit{in situ} FC degradation of membranes with physical properties, available in \textit{ex situ} experiments. One approach is the correlation of \textit{in situ} mechanical membrane degradation with its \textit{ex situ} dimensional changes. Membrane’s failure due to fatigue breakage as a result of swelling and shrinkage in dry-wet cycles is assumed to be reduced for dimensionally more stable membranes. Measurement of \textit{ex situ} shrinking was performed by drying water swollen membranes 1 h under reduced pressure at 80 °C and measuring the thickness and length in machining and transverse direction before and after drying. The dimensional stability was investigated by swelling the membranes again for 8 h at 80 °C in water and measuring the wet thickness and length in machining and transverse direction. The drying/swelling cycle was repeated and the 1\textsuperscript{d} dimensional changes in thickness, machining and transverse direction as well as the area (2\textsuperscript{d}) and volumetric shrinkage (3\textsuperscript{d}) were calculated.

The one dimensional shrinkage $S_{1D}$ was calculated in thickness $\delta$, machining $MD$ and transverse direction $TD$ according to equation 2.7. The two dimensional area shrinkage and three dimensional (volume) shrinkage were calculated according to equation 2.8 and 2.9, respectively. The additional index 0 is used to specify the initial state before drying of the membrane.

$$S_{1D} = 1 - \frac{l_{1D}}{l_{0,1D}}$$ \hspace{1cm} (2.7)

$$S_{area} = 1 - \frac{l_{MD} \cdot l_{TD}}{l_{0,MD} \cdot l_{0,TD}}$$ \hspace{1cm} (2.8)

$$S_{vol} = 1 - \frac{l_{MD} \cdot l_{TD} \cdot l_{\delta}}{l_{0,MD} \cdot l_{0,TD} \cdot l_{0,\delta}}$$ \hspace{1cm} (2.9)

Determination and calculation of the membrane swelling $Q$ was identical to the procedure shown above for the shrinkage $S$. The thickness and lengths in machining and transverse direction were measured before and after swelling of the membrane for 8 h at 80 °C in water. The initial condition in the case of swelling was the water swollen state, and therefore equations 2.7, 2.8 and 2.9 were used without the pre-term ($1-$).

2.4 Sulfonation and hydrolysis

The sulfonation of grafted films was carried out with chlorosulfonic acid in dichloromethane. Up to 10 grafted films were rolled, placed into a reactor containing a 0.66 M solution of chlorosulfonic acid in dichloromethane and stirred for 6 h at rt. Afterwards, the membranes were removed and washed three times with water to remove the excess of chlorosulfonic acid. Subsequently, the membranes were hydrolyzed by stirring for 8 h at 80 °C in water, cooled down to rt and stored in water swollen state.
2.5  *Ex situ* characterization of membranes

The characterization was carried out using six discs of 20 mm diameter punched out of the water swollen membranes. The thickness of each membrane was determined with a thickness measuring gauge (Heidenhain VRZ403 and MT12B), by averaging the six single measurements of the discs.

2.5.1 Conductivity

The conductivity was measured by impedance spectroscopy (Zahner IM6/IM6e) using a conductivity cell prepared in-house. Impedance spectra of stacked membrane discs, with \( n \) numbers of membranes varied from 2 to 5, were recorded by assembling the disc stack between two platinum contact discs (electrodes) and mounting the whole stack in the conductivity cell. A piston was placed at the top of the stack and a torque wrench was used to compress the stack with \( T = 4.5 \text{ Nm} \). The stack impedance was recorded at room temperature in galvanostatic mode in a frequency range from 1 to 50 kHz, measured at zero dc current with an amplitude of 10 mV. The measured impedance data were charted in a Nyquist plot and a linear regression line was calculated through the high frequency end of the impedance arc (10 points of highest frequencies). The stack resistance \( R_n \) is given by intersection of the linear regression line with the real axis. The contact resistance between the membrane discs was assumed to be negligible. However, the contact resistance \( R_c \) between the membranes and platinum electrodes was calculated as intercept and the averaged membrane resistance \( R_{mem} \) as slope of the linear regression line, calculated for the plot of the stack resistance as a function of the number of membranes \( n_{mem} \) in the stack.

2.5.2 Ion exchange capacity

The ion exchange capacity \( IEC \) was determined three times by titration. Each sample consists of two punched membrane discs. The water swollen sample was weighed \( (m_{wet}) \) and stirred over night in 50 ml 0.5 M potassium chloride solution. The solution containing the exchanged membrane discs was titrated with potassium hydroxide solution \( (c_{KOH} = 0.05 \text{ M}) \) to pH 7 using a SM Titrino702 (Metrohm AG). The two membrane discs per sample were rinsed with water, dried under reduced pressure at 80 °C over night, and weighed \( (m_{memK}) \). The mass based \( IEC_w \) was calculated according to equation 2.10.

\[
IEC_w = \frac{n_{H^+}}{m_{memH}} = \frac{c_{KOH} \cdot V_{KOH}}{m_{memH}} \tag{2.10}
\]

The \((IEC \pm \Delta IEC)\) stated in the result chapter was calculated as average \((IEC)\) and standard deviation \((\Delta IEC)\) of the three single measurements. The mass of the protonated membrane \( m_{memH} \) is calculated from the mass of the potassium exchanged membrane \( m_{memK} \) with equation 2.11.

\[
m_{memH} = m_{memK} - (M_K - M_H) \cdot c_{KOH} \cdot V_{KOH} \tag{2.11}
\]
The calculation of the volumetric ion exchange capacity $IEC_V$ based on the volume of the water swollen membrane $V_{wet}$ is given equation 2.12. The volume is accessible from the membrane area (punched diameter 20 mm) and its thickness.

$$IEC_V = \frac{nH^+}{V_{wet}} = \frac{c_{KOH} \cdot V_{KOH}}{V_{wet}}$$ (2.12)

The volume based $IEC_V$ is preferentially used to compare membranes with different chemical compositions, e.g. different base films or grafted components and possibly different molar masses.

### 2.5.3 Swelling and hydration

The swelling $Q$ and hydration number $\lambda$ are important quantities to characterize the water uptake of membranes. The mass based swelling $Q$ is calculated from the mass difference between the wet ($m_{wet}$) and dry membrane ($m_{memH}$) according equ. 2.13.

$$Q = \frac{m_{wet} - m_{memH}}{m_{memH}}$$ (2.13)

The swelling is termed $(Q \pm \Delta Q)$ in the following, which is the average $(Q)$ and standard deviation $(\Delta Q)$ of three single measurements. The hydration is the molar ratio between the present water and the sulfonic acid groups (cf. equation 2.14).

$$\lambda = \left[ \frac{H_2O}{SO_3H} \right] = \frac{Q}{IEC_w \cdot M_{H_2O}}$$ (2.14)

The notation $(\lambda \pm \Delta \lambda)$ is used in the following, where the $\Delta \lambda$ is calculated according to the rules of error propagation.

### 2.6 In situ characterization of membranes

The ex situ characterization of membranes was necessary to (a) determine the influence of reaction parameters on FC relevant properties and (b) pre-select membranes for in situ durability tests. The pre-selection was important to minimize the quantity of membranes in time-consuming fuel cell tests.

#### 2.6.1 Preparation of membrane electrode assembly

The membranes chosen for FC tests were dried 1 h at 80 °C under reduced pressure and cut to the final size (80 x 80 mm). LT140EW1 electrodes from E-TEK (Somerset NJ, USA) with a Pt loading of 0.5 mg·cm$^{-2}$, an ELAT type carbon cloth electrode with 0.6 mg·cm$^{-2}$ of 20 % Pt on Vulcan XC72, were assembled on both the cathode and anode side. The size of the electrodes, which is equal to the electrochemically active area, was 54 x 54 mm. Some membrane electrode
assemblies (MEAs) were hot pressed. Therefore, the MEA was stacked between two pristine base films (protection of the edges), sandwiched between stainless steel plates, and hot-pressed for 3 min at 15 kN and 110 °C. Subsequently, the MEA was stacked between two Teflon gaskets (DuPont, 150 µm) and the stack was assembled into the fuel cell. The single cell, with a three fold serpentine graphite flow field and stainless steel end- or current collector plates, was tightened to 3 Nm. The leak tightness was proved by applying 3 bar$_{abs}$ on both half cells and measuring the pressure decrease after the valve was closed. The gas crossover, a measure for the membrane integrity, was checked with a pressure of 0.5 bar$_{rel}$ on the cathode side and monitoring the gas outlet on the anode side.

2.6.2 Fuel cell test: performance and durability

Two different fuel cell tests were carried out. Performance test was used as in situ characterization of membranes, while the stability of membranes was investigated in durability or long term stability tests. The degradation of the membrane was quantified after the durability test (“post mortem”).

**Performance tests:** To ensure equal conditions for the in situ characterization (membrane resistance, nitrogen crossover, polarization curve) of membranes, a test protocol was used. The FC was conditioned at 60 °C with fully humidified hydrogen (H$_2$) and oxygen (O$_2$) at 60 °C at stoichiometric flows of $\lambda_{H_2} = 1.5$ (min. flow 60 ml·min$^{-1}$) and $\lambda_{O_2} = 1.5$ (min. flow 30 ml·min$^{-1}$). The test was performed at constant current density of 500 mA·cm$^{-2}$. After 24 h an electrochemical impedance spectrum (EIS spectrum) was recorded and a polarization curve (U/I-curve) measured. Afterwards the temperatures of the cell $T_{cell}$ and the gas humidifiers $T_{H_2}$, $T_{O_2}$ were raised to 80 °C and after additional 24 h (48 h runtime) an EIS spectrum and U/I-curve were measured. The cell was operated further 96 h (runtime 148 h) at 500 mA·cm$^{-2}$ until the final characterization with EIS, U/I-curve and hydrogen crossover was carried out. The cell was subsequently removed from the test stand and the MEA disassembled. The current density and cell voltage were recorded over the entire term of the experiment and the resistance was measured at constant time intervals.

**Durability tests:** The same procedure as used for performance tests (144 h) was applied to realize durability tests (>1000 h). The FC was started up under the same conditions, 24 h at $J = 500$ mA·cm$^{-2}$ and 60 °C with 100 % humidified H$_2$ and O$_2$ at 60 °C. The temperature was subsequently increased to 80 °C ($T_{cell}$, $T_{H_2}$ and $T_{O_2}$) at $J = 500$ mA·cm$^{-2}$ and the first characterization was carried out after 24 h (EIS spectrum and U/I-curve). The resistance was measured daily, the complete characterization (EIS, U/I-curve and hydrogen crossover) and refilling of the humidifiers with water was repeated weekly.
2.6.2.1 Membrane resistance

Three different methods were used to determine the membrane resistance, while the MEA (membrane and electrodes) was tested in the fuel cell:

- **Current pulse method**: A sequence of short current pulses (5 A, 10 ns duration) was superimposed to the DC current of the fuel cell. A fast oscilloscope was used to measure the voltage transient (approximately 10 mV) 400 - 880 ns after the current pulse was switched off ($t_0 = 0$). The membrane resistance was calculated by Ohm’s law with an accuracy <5%.

- **High frequency resistance**: An online high frequency resistance (HFR) measurement at 1 kHz was possible by using an AC milliohm meter model 3566 from Tsuruga (Osaka, Japan).

- **Electrochemical impedance spectroscopy**: EI spectra of an operating fuel cell were recorded at cell temperature $T_{cell}$ in galvanostatic mode in a frequency range from 100 mHz to 25 kHz. The impedance spectra were measured at zero dc current with an amplitude of 200 mA and plotted in Nyquist representation (Figure 2.4). The membrane resistance $\Omega_{mem}$ (red arrow in Figure 2.4) is the difference between the origin and the intersection of the high frequency end of the semi-circle with the real axis of the impedance $Re(z)$. The polarization resistance $\Omega_{pol}$ (green arrow in Figure 2.4) is the opening of the semi-circle (radius).

![Figure 2.4: Nyquist plot of a FEP based, AMS/MAN co-grafted, DIPB crosslinked membrane after 715 h FC operation at 500 mA·cm$^{-2}$.](image)

2.6.2.2 Polarization curve

The dependence of the cell voltage from the current density is represented in a polarization curve (Figure 2.5). The cell voltage was recorded 30 s after the current density was fixed.
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Figure 2.5: Polarization curve (top) and ohmic resistance $R_\Omega$ (bottom) for a FEP based, AMS/MAN co-grafted, DIPB crosslinked membrane after 715 h FC operation at 500 mA cm$^{-2}$.

The measurement was started at open circuit voltage (0 mA cm$^{-2}$) and stopped when the cell voltage dropped below 0.3 V.

2.6.2.3 Hydrogen permeability

The integrity of the membrane in the MEA assembled into a fuel cell was tested by measuring the hydrogen permeation. Therefore, a constant H$_2$ flow (200 ml min$^{-1}$) was applied at the anode and the oxygen on the cathode was replaced by nitrogen, also using a constant flow of 200 ml min$^{-1}$, while the cell- and humidifier temperatures were held at 80 °C. After 60 min the fuel cell was equilibrated (voltage approximately 0.1 V) and the potential was changed in 100 mV steps from 800 to 200 mV and in 200 mV steps back. The concentration difference between the fuel cell anode and cathode forces hydrogen to diffuse through the membrane or permeate through holes in the membrane. The hydrogen is immediately oxidized at the fuel cell cathode, which becomes the anode in H$_2$/N$_2$-mode, and the resultant current is measured with the potentiostat. A linear regression analysis of the measured data and the extrapolation of the regression line results in the theoretical current $I_{0V}$ at 0 mV (intersept). The current $I_{0V}$ was used in Faraday’s law to calculate the volumetric flow rate of hydrogen $\dot{V}$. 
Chapter 3

Grafting: Influences and Kinetics

The influence of reaction parameters on the degree of grafting $DoG$ and the molar ratio in the grafted film $R_{m, \text{graft}}$ was investigated. The influence of a single parameter was tested by varying the observant parameter, while keeping all other reaction conditions constant. The grafting of MAN only (paragraph 3.1) was chosen to be investigated as a simple system first, having substantial similarity to the AMS/MAN co-grafting. The co-grafting onto FEP base film and its dependence on reaction parameters is discussed in paragraph 3.2 and onto ETFE base films in paragraph 3.3. Kinetic parameters for the co-grafting of AMS and MAN onto FEP were determined by fitting curves to the reaction profiles of various temperature $T$ and molar ratio in the grafting solution $R_{m, \text{sol}}$. The fitted curves were computed, based on a mathematical description of the grafting reaction, as shown in paragraph 3.2.3.

3.1 FEP-$g$-MAN

The grafting of MAN only was performed at 50 °C according to the standard procedure specified in paragraph 2.1.4, using a base film size of 7 x 7 cm. The grafting solution consisted of 30 vol% MAN, 50 vol% iPrOH and 20 vol% water. The time dependent $DoG$ (reaction profile) of MAN grafting at 50 °C is shown in Figure 3.1.

A value of 30 % degree of grafting was achieved in approximately two hours, which is fast compared to the co-grafting in paragraph 3.2. The MAN grafted films were used to calibrate the FTIR spectroscopic measurement and therefore the thickness increase and the absorbance at 2230 cm$^{-1}$ were measured and plotted as a function of the reaction time in Figure 4.3 on page 73. The distribution of graft components over the film thickness was investigated with MAN grafted FEP films using confocal Raman spectroscopy. The preparation of the MAN grafted films was performed according to the standard procedure, starting with an initial FEP base film size of 14 x 16 cm. The associated reaction profile is not shown, but fits closely to the data shown in Figure 3.1. The strong $DoG$ increase observed within the first 2 h leveled off and the further mass increase was slower.

3.2 FEP-$g$-[AMS-co-MAN]

M. ´Slaski performed basic experiments on the co-grafting of AMS and MAN onto pre-irradiated FEP base films and optimized the solvent for the graft copolymerization at 60 °C with re-
Figure 3.1: Time dependent degree of grafting for grafting of MAN only onto FEP base film (25 kGy, 49 cm²).

spect to the achievable degree of grafting [162]. The ex situ properties of membranes, based on AMS/MAN co-grafted films, strongly depend on the AMS content, which is reflected in the $R_{m,\text{graft}}$. In order to enhance the AMS content, the grafting temperature was reduced to 50 °C to prevent the depolymerization of AMS-AMS repeating units. Depolymerization and polymerization are balanced for an activity of the monomer equal to 1 at the ceiling temperature $T_c$, which was determined to (65±1) °C for poly-alphamethylstyrene (pAMS) [109]. By reducing the grafting temperature to 50 °C it was assumed that depolymerization of AMS-AMS units is excluded, even if the temperature locally exceed the adjusted temperature of the heating device. A comparison of the temperature effect on grafting is given in paragraph 3.2.5. The time dependence of AMS/MAN co-grafting onto FEP base film was investigated following the standard grafting procedure using small sized (49 cm²) FEP base films (Figure 3.2). The reactions were performed in glass reactors containing the grafting solution, which consisted of 30 vol% AMS/MAN with $R_{m,\text{sol}}$ of 1.5, 50 vol% iPrOH and 20 vol% water.

The reaction profile shows a steep, linear increase within the first 10 h, yielding up to approximately 25 % DoG. The following mass increase per time is lower, tantamount with a less steep slope of the reaction profile, and finally the DoG levels off at approximately 40 % DoG ("plateau"). Compared to results obtained at 60 °C in [162], the initial slope of the reaction profile is less steep at 50 °C and the maximum achievable DoG higher for long reaction times. A similar behaviour was observed during the investigation of the temperature dependence in paragraph 3.2.5.

### 3.2.1 Influence of water content

The influence of the solvent was investigated at 60 °C in [162] and a mixture of isopropanol and water was found to be the optimum solvent for the AMS/MAN co-grafting concerning the maximum achievable degree of grafting. The solubility of the monomers, DVB and isopropanol in water and their n-octanol-water partition coefficient $p_{ow}$ (see equ. 3.1) are listed in Table 3.1.
3.2. FEP-G-[AMS-CO-MAN]

Figure 3.2: Time dependent degree of grafting for co-grafting of AMS and MAN onto FEP base film (25 kGy, 49 cm²).

\[ p_{ow} = \log P = \log K_{ow} = \frac{c_{\text{oct}}}{c_{\text{H2O}}} \]  

(3.1)

The \( n \)-octanol-water partition coefficient \( p_{ow} \) describes the distribution of a compound \( x \) in an mixture of water and a hydrophobic liquid (\( n \)-octanol) and is calculated from the concentration ratio of \( x \) in the \( n \)-octanol (\( c_{\text{oct}} \)) and water phase (\( c_{\text{H2O}} \)). The values in Table 3.1 were extracted from Merck material safety data sheets according to the European Community Directive 91/155/EWG (www.chemdat.info).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility in water [mg·l⁻¹]</th>
<th>( n )-octanol-water partition coefficient ( p_{ow} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>560 @ 20 °C</td>
<td>3.27</td>
</tr>
<tr>
<td>MAN</td>
<td>25700 @ 20 °C</td>
<td>0.68</td>
</tr>
<tr>
<td>(^i)PrOH</td>
<td>( \infty )</td>
<td>0.05</td>
</tr>
<tr>
<td>DVB</td>
<td>5 @ 25 °C</td>
<td>4.18</td>
</tr>
</tbody>
</table>

The low \( p_{ow} \) of isopropanol is equivalent to a good miscibility with water. The poor solubility of AMS and DVB with water sometimes results in phase separation at rt (first column in Table 3.1). The solubility of AMS and DVB explains the formation of a second phase and the \( c_{\text{oct}}^{\text{MAN}} \) of 0.68 suggests that a considerable amount of MAN will dissolve in the hydrophobic AMS phase. A few experiments showed phase separation of the grafting solution even at 50 °C and therefore the influence of the water content in the grafting solution was re-investigated at 50 °C. A first set of reaction profiles was recorded for the graft copolymerization of AMS and MAN with different water contents in the grafting solution (Figure 3.3). 30 vol% of AMS/MAN (\( R_m, \text{sol} = 1.5 \)) were
co-grafted in a solvent mixture containing 0, 5, 10 or 20 vol% water. The total volume was kept constant by adjusting the amount of iPrOH to 70, 65, 60 or 50 vol%, respectively.

![Figure 3.3: Reaction profiles for different water contents in the grafting solution.](image)

The data points measured for grafting solutions containing 0, 5 or 10 vol% water lie on top of each other. The water did not influence the DoG within the first 10 h, while 20 vol% water approximately double the DoG. To further investigate the DoG dependence on the water content in the grafting solution, a grafting series with different water content in the solution was performed (Figure 3.4).

![Figure 3.4: Dependence of the DoG from the water content at different times.](image)

Surprisingly, the DoG for long reaction time, e.g. 42 h in Figure 3.4, was not influenced by the water content in the grafting solution. While the DoG of films grafted 5 and 10 h was significantly higher for higher water contents in the solution, the difference starts to level off for water contents above 10 vol%, if the grafting proceeds at least 21 h. It seems that the apparent initial polymerization rate $r_{p0}$ increases with increasing water content while the maximum achievable
3.2. **FEP-G-[AMS-CO-MAN]**

degree of grafting is unaffected and approximately the same for all investigated water contents in the grafting solution. On closer examination, differences in the clouding of the films was observed. In Figure 3.5 films are shown on a black background, to enhance the contrast.

*Figure 3.5: Photographs of FEP-g-[AMS-co-MAN] grafted 42 h in solutions with 0, 5, 10, 15 and 20 vol% water (from left to right) with 42±4 % DoG.*

Grafting in neat isopropanol formed a clear film, while increased water contents in the grafting solution increased clouding of the grafted films. A morphological change of the polymer film may occur during grafting in presence of water, due to the formation of hydrophilic and hydrophobic phases within the film matrix.

### 3.2.2 Influence of monomer concentration

The influence of the monomer concentration in the grafting solution on the DoG was investigated by M. Slaski at 60 °C, during the determination of solvent effects [162]. A strong DoG increase from 4 to 35 % was observed in an iPrOH/water mixture when the monomer concentration (\(R_{m, sol} = 1.5\)) was increased from 10 to 30 vol%. Only a weak DoG increase of less than 20 % was observed for a further increase of the monomer concentration up to bulk co-grafting. Considering the scale-up of the grafting procedure to a technical relevant number and size of films and especially the volume of the required reactors, the effective monomer concentration will influence directly the production costs, and, on the other hand, the heat transport, which is facilitated in the presence of solvent. Thus, low monomer concentrations between 5 and 50 vol% were re-investigated at 50 °C (Figure 3.6) in a solution containing 20 vol% water and 75 to 30 vol% iPrOH.

The sigmoidal distribution of the measured data points in Figure 3.6 point out a strong DoG increase up to 25 vol% monomer in the grafting solution, followed by a weaker increase up to 50 vol%. The optimum monomer concentration was chosen to be 30 vol%. Around 30 vol% the curve starts to level off and small concentration drifts in the grafting solution do not effect the DoG markedly. Quite contrary, variations in the monomer concentration will strongly influence the DoG in the steeper part of the sigmoidal shaped curve around and slightly below 25 vol%. The molar ratio in the grafted film \(R_{m, graft}\), shown with red diamonds in Figure 3.6, is not much influenced by the monomer concentration, at least for concentrations up to 30 vol%.

The water to isopropanol ratio changed during the experiments, while the total water concentration was unchanged in all experiments. To investigate whether the total water concentration or water to iPrOH ratio influences the DoG, two comparative grafting series were made during the preparation of DVB crosslinked films. In the first series 20 vol% water was used and the total volume was adjusted to 60 ml with iPrOH, whereas in the second series the 60 ml total volume were prepared by adding an iPrOH/water mixture with a fixed ratio of 20:50 (vol/vol).
Figure 3.6: DoG (black) and $R_{m, \text{graft}}$ (red) as a function of the monomer concentration in the grafting solution for co-grafting of AMS and MAN onto FEP base film at 50 °C (20 h).

Two equal data sets, the degree of grafting as a function of the monomer concentration, were obtained. The total water content was 20 vol% in the first series and shifted from 27 vol% water for 5 vol% monomer to 15 vol% water for 50 vol% monomer. The independence of the DoG from the water content between 15 and 27 vol% is partially confirmed by the almost equal DoG in Figure 3.4, obtained after 21 h grafting of AMS and MAN onto FEP in solutions containing 15 and 20 vol% water.

3.2.3 Excursion: Fitting model - assumptions and equations

More quantitative kinetic data will facilitate the comparison of different effects on grafting beyond the discussion based on integral numbers like the DoG or $R_{m, \text{graft}}$. To obtain kinetic parameters from measured data, e.g. mass based DoG, FTIR spectroscopy based integral composition or confocal Raman microscopy based depth resolved composition, a mathematical description of the grafting had to be developed and applied to fit curves to the experimental data. Starting point was a simple mathematic model of the grafting reaction, as described by T. Rager [169]. The mathematical description was developed based on the following assumptions:

- The composition of the grafting solution is constant regarding time (no significant consumption of monomers) and location (no concentration gradient).
- The reactivity is location-independent and volume changes are negligible.
- Termination occurs (only) via recombination of polymer-bound radicals $P\cdot$ with the rate $r_t$ according to

$$r_t = \frac{d[P\cdot]}{dt} = -k_t[P\cdot]^2$$  \hspace{1cm} (3.2)

Integration of equation 3.2 within the boundaries $t_0 = 0$ to $t = t$ results in

$$[P\cdot] = \frac{[P\cdot]_0}{1 + k_t[P\cdot]_0 t}$$  \hspace{1cm} (3.3)
The local radical concentration within the film \([P·]\) is expressed using the initial radical concentration \([P·]_0\), the recombination rate constant \(k_t\) and the reaction time \(t\).

- The rate of polymerization \(r_p\) is defined as time dependent change of the \(\text{DoG}\) by

\[
r_p = \frac{d\text{DoG}}{dt} = k_p[P·][M] \approx k_p[P·][M]_0
\]

The use of the initial monomer concentration \([M]_0\) was possible due to the approximation of constant monomer concentrations at the active sites and negligible monomer consumption. \(k_p\) is the polymerization rate constant.

- Integration of equation 3.4 within the boundaries \(t_0 = 0\) to \(t = t\) and inclusion of the local radical concentration within the film \([P·]\) expressed in equation 3.3 results in the time dependent equation:

\[
\text{DoG} = \frac{k_p[M]_0}{k_t} \ln(1 + k_t[P·]_0 t)
\]

- In consideration of the time necessary to warm up the grafting solution and for the monomers to diffuse into the film, a linear increase of the number of reactive sites in the time interval \(0 \leq t_i \leq t_0\) was assumed. The concave part of reaction profiles was described with

\[
\text{DoG} = \frac{r_{p0}}{\gamma} \ln(1 + \gamma(t - t_0))
\]

The equation was achieved by including the apparent initial polymerization rate \(r_{p0}\), according to

\[
r_{p0} = k_p[P·]_0[M]_0
\]

and the termination rate \(\gamma\), as defined in equation 3.8.

\[
\gamma = k_t[P·]_0
\]

The delay time \(t_0\) was assumed as the required period until all active sites on the base film have reacted. If the initial radical concentration is constant the factor \(r_{p0}/\gamma\) is a measure for the grafting efficiency.

The calculated curve based on the kinetic model (dashed line) and the experimentally achieved reaction profile (red points) for the co-grafting, according the standard procedure on page 34, of AMS and MAN onto FEP base film (25 kGy) at 35 °C are shown in Figure 3.7. A strong deviation of the fitted curve shape from the measured points was observed, the red line is drawn...
to guide the eyes through this measured points. The deviation between the measured data and fitted curve increases for decreasing temperature and increasing film thickness. In the previous described model, the delay time $t_0$ was included to account for the time necessary to reach the active sites within the film. This delay renders the calculation of the $DoG$ in the induction period $0 \leq t_i \leq t_0$ impossible. To overcome this restriction, the boundary conditions of the grafting front mechanism were included into the model. Since the graft reaction combines polymerization at the active sites, swelling of the grafted zone, and diffusion of monomers to the active sites inside the film, the movement of monomers in the grafted film is given by the relative rates of diffusion and the adjustment of the polymer chains in the presence of a penetrant (monomer or solvent), also referred to as relaxation [170]. The movement can be described by Fickian diffusion, if the rate of diffusion is much less than the rate of relaxation. In the case of non-Fickian or anomalous movement the diffusion and relaxation rate are comparable and both influence the penetration of the monomers and solvent. If the diffusion is very fast compared to the relaxation process of the polymer, a constant velocity of the proceeding front is observed. Here, a constant front velocity $v_f$ was found to account for the monomer transport by the grafting dependent diffusion into the pre-irradiated film. The concentration behind the front was assumed to be constant, but the film was split into 30 slices in thickness direction to account for the onset of the grafting at the film surfaces. The grafting at depth $x_0$ starts after the time $\tau_0 = x_0/v_f$, necessary for the grafting front to move from the surface to depth $x_0$. The time dependent, local degree of grafting $DoG(t, x)$ is given in equation 3.9.

$$DoG(t, x) = \begin{cases} t \leq \tau : & 0 \\ t > \tau : & \frac{r_{p0}}{\gamma} \ln(1 + \gamma(t - \tau)) \end{cases} \quad \text{with} \quad \tau = \frac{x}{v_f} \quad (3.9)$$

In a film with the thickness $d$ the two grafting fronts meet at the film center $x = d/2$ after time $T = d/2v_f$. The average graft level $\overline{DoG}$ is calculated by equation 3.10.

$$\overline{DoG}(t) = \frac{2}{d} \int_0^{d/2} DoG(t, x) dx \quad (3.10)$$

A second curve was fitted to the experimental data for the AMS/MAN co-grafting onto FEP base film at 35 $^\circ$C using the enhanced kinetic model, shown in Figure 3.7 as solid black line. The calculated curve based on the improved kinetic model is in good agreement with the experimental data. The reaction profile at 35 $^\circ$C was chosen due to the pronounced mismatch of the curve determined with the model used by Rager and the experimental data. In paragraph 3.2.5 the experimental data for higher reaction temperatures up to 80 $^\circ$C are presented together with fitted curves based on the enhanced model. The fitted curves calculated with equation 3.6 are not shown, but the conformity with the experimental reaction profiles increases with increasing temperature.

The activation energy $E_a$ was additionally investigated for the temperature effect on the grafting reaction. The Arrhenius equation 3.11 links the activation energy $E_a$ with the reaction rate constant $k$. The activation energy is accessible from the slope $(-E_a/R)$ of the regression line in the plot of $ln(r_{p0})$ as a function of inverse temperature $T^{-1}$. 

$$\ln(r_{p0}) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(k) \quad (3.11)$$
3.2. FEP-G-[AMS-CO-MAN]

Figure 3.7: Reaction profile for the grafting of FEP-g-[AMS-co-MAN] at 35 °C (red points connected with a red guideline for the eyes) and the fitted curves based on the model 1 used by Rager [169] (dashed line) and the model 2 includes the moving grafting front, developed by Gubler [171] (solid line).

\[ k = Ae^{-\frac{E_a}{RT}} \]

The rate constant \( k \) is equal to \( r_{p0} \) in the used co-grafting model.

3.2.4 Influence of molar ratio \( R_{m, sol} \)

A pivotal question was how the molar ratio in the grafting solution \( R_{m, sol} \) influences the DoG and the molar ratio in the grafted film \( R_{m, graft} \). The importance of this question is reflected in the promise of varying ex situ and in situ membrane properties by change the \( R_{m, graft} \) at a given DoG. The first set of experiments was performed, according the standard procedure on page 34 by co-grafting of AMS and MAN in various molar ratio \( R_{m, sol} \) for 20 h at 50 °C (Figure 3.8).

The DoG (black circles) decreases and the FTIR spectroscopy based \( R_{m, graft} \) (red diamond) increases if the molar ratio in solution increases. The decrease in DoG indicates the slower grafting kinetics of AMS compared with MAN, as the AMS concentration increases along with the \( R_{m, sol} \). The possibility to adjust the \( R_{m, graft} \) between 0.5 and 1.1 is more important concerning membrane preparation and its properties. The time dependence of the DoG was investigated for five different \( R_{m, sol} \) and compared with the grafting behaviour of pure MAN in Figure 3.9. The experiments were performed at 50 °C according to the standard procedure, using 30 vol% monomers in the specified molar ratio.

An increase in the AMS content, which is equal to an increase in the \( R_{m, sol} \), yields a lower DoG in the entire investigated reaction time interval of 60 h. The apparent initial polymerization rate \( r_{p0} \) and front velocity \( v_t \) were determined based on the enhanced kinetic model [171] from
CHAPTER 3. GRAFTING: INFLUENCES AND KINETICS

Figure 3.8: Dependence of the DoG and $R_{m, graft}$ from the molar ratio of the monomers in the grafting solution $R_{m, sol}$ for 20 h co-grafting of AMS and MAN onto FEP at 50 °C.

Figure 3.9: Reaction profiles for various molar ratios in the grafting solutions $R_{m, sol}$. Points indicate the experimental data and lines represent the fitted curves based on eqn. 3.10.[171]

The apparent initial polymerization rate $r_0$ decreases with increasing molar ratio in the solution, which explains the lower degree of grafting for higher $R_{m, sol}$. An interpretation of the increasing induction period for increasing $R_{m, sol}$ is possibly given by the determined decrease of the front velocity $v_f$. Assuming an average thickness of 30 µm for all films, the decreasing front velocity prolongates the penetration time $T$ from approximately 1 h for neat MAN to 20 h for a twofold excess of AMS ($R_{m, sol} = 3.0$).

The improved kinetic model is able to consider for the delay at the beginning of the grafting and therefore represents quite well the experimental data in Figure 3.9. Nevertheless, one has to keep in mind the strong simplification of the assumed kinetic model. For instance, the depletion of the more reactive monomer at the active sites and related to this a local change in the molar ratio is not taken into account. The pre-irradiation of base films in ambient atmosphere and
therefore in the presence of oxygen yields a peroxyl radical. The peroxyl radical is formed by the reaction of the primarily generated carbon based radical with oxygen. This reacts further with a hydrogen source to hydrogenperoxyl group, which has to be decomposed to initiate the graft polymerization.

The molar ratio in the grafted film $R_{m,\text{graft}}$ based on FTIR spectroscopic investigation for the samples presented in Figure 3.9 is shown in Figure 3.11. For reasons of clarity, only four series with $R_{m,\text{sol}}$ of 0.5, 1.5, 2.0 and 3.0 are presented.

Deviations from the expected values are pronounced in Figure 3.11 for films with less than 10 % DoG, evident from the experimental data for $R_{m,\text{sol}} = 3.0$ up to 20 h reaction time. However, a general tendency for increasing $R_{m,\text{graft}}$ with rising $R_{m,\text{sol}}$ in the entire investigated time interval is observed. Moreover, the important fact is the possibility to prepare grafted films with molar ratio $R_{m,\text{graft}}$ between approximately 0.5 and 1.1 independent of the degree of grafting.
3.2.5 Influence of temperature

Temperature usually has a major effect on the kinetics of chemical reactions, i.e. the proportion of reactant molecules with sufficient energy to react (E > Ea) increases with temperature as explained in detail by the Maxwell–Boltzmann distribution of molecular energies. In case of the grafting reaction, the temperature affects the reaction kinetic and the maximum achievable degree of grafting DoG. Reaction profiles were recorded each 5 °C in the temperature range from 35 to 80 °C. The experimental data for five temperatures and the corresponding curves determined based on the enhanced kinetic model are presented in Figure 3.12.

The shape of the curve changes completely for increasing temperature. The initial rate of grafting increases significantly with the temperature in the entire investigated temperature range, indeed more pronounced up to 60 °C. An interpretation of the observed behaviour based on the degree of grafting is difficult. Whereas for very short reaction times the degree of grafting seems to increase with the grafting temperature, the opposite trend is observed for very long reaction times. The intermediate reaction time interval is dominated by an increase of the DoG inversely proportional to the grafting temperature.

A more quantitative interpretation is given in Figure 3.13 by the logarithmic plot of the apparent initial polymerization rate $r_p0$ and the recombination rate $\gamma$ as functions of the inverse absolute temperature $T^{-1}$ (Arrhenius plot) and the logarithmic representation of the front velocity versus the temperature $T$ in Figure 3.14. The activation energies were calculated based on equation 3.11 from the slope $m$ of the Arrhenius plot, which is equal to $-E_a/R$.

The activation energy of the propagation, calculated for the temperature range of 35 to 80 °C, is 101 kJ·mol$^{-1}$. This value is higher than the activation energies obtained for grafting of styrene onto FEP (27.9 kJ·mol$^{-1}$) [148], ETFE (98.4 kJ·mol$^{-1}$) [172] and PVDF base film (73 kJ·mol$^{-1}$). The higher value obtained for the co-grafting suggests a comparatively low grafting rate and a stronger temperature dependence. The activation energy for the recombination was calculated to 132 kJ·mol$^{-1}$, which is higher than the activation energy of the propagation. The more pronounced dependency on the temperature of the recombination explains the decreasing degree of
Grafting is in fact a very complex interplay of initiation of polymerization at the active sites, propagation and termination of chain growth, and swelling of the grafted zone and subsequent diffusion of monomer within the swollen polymer matrix to reach further active sites. An increase in temperature facilitates diffusion and therefore monomer access to the active sites (cf. front velocity $v_f$). The higher accessibility enhances the rate of initiation and propagation which is macroscopically apparent by an increasing DoG. The propagation is represented in the kinetic approach by the apparent initial polymerization rate $r_p0$, which increases with the temperature (Figure 3.13). The mobility of the grafted chain within the swollen polymer matrix increases with temperature and chain length. Hence, termination of two growing chains by recombination will become important or even dominate at higher temperature. The high activation energy $E_A$ determined for the recombination rate $\gamma$ reflects the strong temperature dependence.

For long reaction times at higher temperatures the formation of homopolymer was observed, which additionally hindered the monomer diffusion. The effect of increasing temperature can be summarized as following: the higher rate of the initial grafting accompanies with a decreasing achievable degree of grafting for long reaction time. Similar observations were made for styrene grafting onto FEP and ETFE base film [148, 172].
3.3 ETFE-\textit{g-}[AMS-\textit{co-\textit{MAN}}]

Apparently ETFE offers some advantages over FEP, e.g. higher molecular weight, better mechanical properties due to less bulky substituents and therefore a more flexible polymer backbone, or reduced chain scission during the irradiation based on the presence of carbon-hydrogen bonds. Therefore, ETFE base film was grafted according to the procedure on page 34 and the influence of the reaction parameters on the degree of grafting investigated. The irradiation dose of 3 kGy for ETFE base films was chosen to have comparable reaction times concerning the DoG with the FEP base films irradiated with 25 kGy. According to the investigation on FEP based films in the previous paragraph, the first investigation was done with grafting of MAN only. A second series of experiments was performed to determine the influence of the irradiation dose on the degree of grafting. The influence of the monomer concentration, molar ratio of the monomers in the grafting solution $R_{m, \text{sol}}$, and the grafting temperature on the DoG and on the molar ratio in the grafted film $R_{m, \text{graft}}$ is discussed at the end of this paragraph.

3.3.1 A comparison: grafting of MAN only

According to the grafting of MAN only onto FEP base films (cf. paragraph 3.1), 30 vol\% MAN were used in a mixture of 50 vol\% \text{iPrOH} and 20 vol\% water to graft ETFE base films various times at 50 °C. The MAN grafted ETFE films (black circles in Figure 3.15) were compared to grafted FEP films (red circles in Figure 3.15) of the same initial size (14 x 16 cm).

The time dependent increase of the degree of grafting is the same for both base films, regarding the different irradiation dose of 3 kGy and 25 kGy for ETFE and FEP, respectively. The grafting of MAN only is fast and the apparent initial polymerization rate of approximately 23 $\text{\%\cdot h}^{-1}$ remarkable high compared to the co-grafting of AMS and MAN (cf. paragraph 3.2.4).

3.3.2 Influence of irradiation dose

Irradiation of polymer films results in cleavage of chemical bonds. Depending on the irradiation source, the used polymer and the irradiation dose different processes are possible, e.g. chain

![Figure 3.15: Variation of the degree of grafting as a function of reaction time for grafting of MAN only onto ETFE (3 kGy) and FEP base film (25 kGy).](image-url)
crosslinking, chain scission, production of small molecules maybe accompanied by structural changes [74, 81]. Pre-irradiation in different ambient atmosphere forms either free carbon based or hydroperoxide masked radicals. The concentration of active sites within the polymer matrix is adjustable by the irradiation dose, which has finally a significant impact on the physical properties of the base polymer and the grafted films.

The degree of grafting as a function of reaction time was investigated for irradiation doses of 3, 10 and 50 kGy. The reaction profiles in Figure 3.16 show a linear increase of the $\text{DoG}$ for short reaction times which starts to level off for longer reaction times. The increase of the $\text{DoG}$ with the irradiation dose is due to an increasing number of active sites within the irradiated base film. The influence of the irradiation dose on the mechanical properties is discussed in paragraph 5.1.

![Figure 3.16: Influence of irradiation dose on the degree of grafting for the co-grafting of AMS and MAN onto ETFE base film.](image)

### 3.3.3 Influence of monomer concentration

The monomer concentration in the grafting solution was varied from 5 to 50 vol%, using a molar ratio $R_{m, sol}$ of 1.5. The amount of $^1$PrOH was adjusted from 75 to 30 vol% to keep the total grafting volume constant at 60 ml and the water content in the solution at 20 vol%.

The obtained monomer concentration dependent $\text{DoG}$ for ETFE based films (black circles) is compared with the previously presented FEP based data (red circles) in Figure 3.17. The obtained degree of grafting is higher for ETFE than for FEP based films in the entire experimentally covered concentration range, keep in mind the different irradiation doses used for ETFE and FEP. The curve shape of the distribution is the same for both base films, although the ETFE based curve seems to be steeper around 30 vol% monomers in the grafting solution. In consequence, small concentration changes around 30 vol% monomers in the grafting solution will make a higher impact on the $\text{DoG}$ for the grafting onto ETFE. To keep the differences between the grafting experiments onto FEP and ETFE base film as small as possible, the optimum monomer concentration was also set to 30 vol% for ETFE based experiments.
3.3.4 Influence of molar ratio $R_{m,\text{sol}}$

The possibility to co-graft FEP base film with AMS and MAN at a given $DoG$ to desired molar ratio in the grafted film $R_{m,\text{graft}}$ between 0.5 and 1.1 was shown in paragraph 3.2.4. The $DoG$ and $R_{m,\text{graft}}$ dependency on the molar ratio in the grafting solution was investigated for ETFE base films as well, following the standard grafting procedure described on page 34. The experimental data obtained for a reaction time of 20 h and a monomer concentration of 30 vol% are shown in Figure 3.18, for comparison reason scaled like Figure 3.8 on page 54.

The $DoG$ obtained with ETFE base film is slightly higher for the entire tested monomer concentration range in the solution $R_{m,\text{sol}}$ than for FEP, still keep in mind the different irradiation dose of ETFE (3 kGy) and FEP (25 kGy). The molar ratio in the grafted polymer $R_{m,\text{graft}}$ increased from ca. 0.5, obtained by using 100% excess of MAN in the grafting solution, to
approximately 1 for a two- to fourfold excess of AMS in the grafting solution.

The time dependent degree of grafting was investigated following the standard procedure on page 34 for different molar ratios of the monomers in the grafting solution (Figure 3.19). The data for the grafting of MAN only, under the same reaction condition, is included as benchmark in Figure 3.19 (black circles).

The same trend as for the grafting onto FEP base film was observed. The degree of grafting is

![Figure 3.19: Time dependent degree of grafting for different molar ratio of AMS and MAN in solution $R_{m, \text{sol}}$ (ETFE base film, 3 kGy).](image)

higher within the entire investigated reaction time period for lower molar ratio of the monomers in the grafting solution. The spectrum of the accessible molar ratio in the grafted film $R_{m, \text{graft}}$ for a given degree of grafting is comparable to the one possible for FEP base film.

### 3.3.5 Influence of temperature

The influence of the grafting temperature on the degree of grafting was qualitatively and quantitatively, on the basis of reaction parameters determined from a fitting to the experimental data, discussed for the grafting onto FEP base film in paragraph 3.2.5. AMS and MAN was also co-grafted onto ETFE base film in the temperature range from 35 to 80 °C. The reaction profiles, obtained by following the standard grafting procedure, are shown in Figure 3.20.

The reaction profiles obtained for different grafting temperatures differ significantly from the one shown in Figure 3.12 for FEP. The accentuated induction time observed at low temperature for AMS/MAN co-grafting onto FEP base film is absent in the case of grafting onto ETFE base film. Whereas the curve for grafting onto FEP at 35 °C is continuously rising in the experimental temperature range, the graph for ETFE asymptotically converge to 25 % DoG. The fitting to the experimental data was performed using both models described in paragraph 3.2.3 to determine kinetic parameters. The application of the advanced fitting model, which accounts for the movement of the grafting front, produced (physical) meaningless numbers for the front velocity $v_t$. Disregarding the front velocity, the values determined for the apparent initial polymerization rate $r_{p0}$ and radical recombination rate $\gamma$ are displayed in Figure 3.21 (circles). To verify the data obtained with the advanced model, the simpler model from equation 3.6 [169],
neglecting the initial delay, was used to investigate $r_{p0}$ and $\gamma$ (diamonds in Figure 3.21).

Neither the apparent initial propagation rate $r_{p0}$ nor the termination rate $\gamma$ show a linear correlation with the absolute inverse temperature in the Arrhenius plot. Therefore, a calculation of the activation energy $E_A$ for both, the propagation and termination reaction, was not possible in the temperature range from 35 to 80 °C.
3.4 Crosslinking of [AMS-co-MAN]-grafted films

During fuel cell operation, a membrane is exposed to radicals formed as intermediates in the reactions at the electrodes or by reactions within the membrane in the presence of catalytically active impurities. Radical attack may cleave CC bonds of the side chain backbone and produce fragments, a mechanism is proposed by Hübner and Roduner [121]. Small fragments of the graft component are mobile in a water swollen membrane and eventually washed out by electro-osmosis. The loss of graft component and therefore of sulfonic acid groups is associated with a decrease in proton conductivity. Crosslinking is one way to stabilize grafted polymer chains by forming an interconnected, three dimensional network of the grafted component in the "host matrix" of the base material. The cleavage of a CC bond in a grafted, crosslinked network will produce two chain ends, still connected to the matrix, withheld in the membrane and able to further contribute to the membrane properties.

Basic investigations were carried out using divinylbenzene (DVB) and diisopropenylbenzene (DIPB) as crosslinking agent. The use of DVB as monomer in the copolymerization with styrene [173, 174, 175] and as crosslinker in the co-grafting with styrene onto FEP [131, 122, 143, 176, 146, 147, 149, 150], ETFE [177, 146, 147, 178, 172], PTFE [179] and PVDF [180] is well known. A drawback of DVB in the laboratory routine is its commercially available purity as an isomeric mixture of meta-/para-DVB and meta-/para-ethylvinylbenzene. Both isomeric DVBs act as crosslinker but with different kinetics while each of the ethylvinylbenzene isomers only propagates chain growth as mono-functional monomer. Due to the large number of possible reaction products the FTIR spectroscopic analysis of DVB crosslinked films is difficult. DIPB is commercially available as pure meta-isomer and subsequently the analysis of DIPB crosslinked films becomes simpler. The reactivity of both crosslinkers and therefore the crosslinker effectivity is different.

Since different monomers or monomer systems and various crosslinkers are used in changing combinations, the crosslinker concentration is stated in the following as mol% crosslinker with respect to the total amount of monomers (equation 3.12).

\[
c_{\text{crosslinker}} = \frac{n_{\text{crosslinker}}}{n_{\text{monomers}}} \cdot 100\% \quad \Rightarrow \quad \frac{n_{\text{DVB or DIPB}}}{n_{\text{AMS}} + n_{\text{MAN}}} \cdot 100\% \quad (3.12)
\]

3.4.1 FEP-\([\text{AMS-co-MAN-co-DVB}]\)

The influence of the crosslinker concentration on the DoG was investigated according to the standard procedure at 50 °C by varying the crosslinker concentration from 1 to 24 mol% and adjusting the amount of \(^1\text{PrOH}\) to keep the total volume constant at 60 ml. The reaction profiles of grafting in presence of various crosslinker concentrations (colored circles) are compared in Figure 3.22 with the reaction profile obtained for the preparation of uncrosslinked films (grey line).

For short reaction times below roughly 10 to 15 h the DoG increases with the DVB content and the highest DoG is obtained for the grafting in absence of DVB. Crosslinking is the formation of
a three dimensional network in the matrix of the pre-irradiated base film. The higher the extent of crosslinking, the shorter the chains between the crosslinker molecules, the narrower becomes the formed "mesh" of the grafted component, the more hindered is the monomer diffusion within the film, which finally decrease the $DoG$ with increasing DVB content in the solution. Simultaneously the higher network density, caused by higher extent of crosslinking, will immobilize the growing grafted chains and reduce the probability for recombination. In fact, the balance between the increasing diffusion limitation of the propagation and the reduced recombination due to immobilization influences the $DoG$. This leads finally to higher graft levels observed as films grafted more than 20 h in solution with crosslinker concentration below 2 mol% (in the presence of water) compared to the grafting in absence of DVB. The reduced recombination rate seems to be predominant in the case of small DVB concentrations. However, the $DoG$ still decreases with an increasing DVB concentration in the grafting solution, pointing out the prevailing of the diffusion limitation for higher crosslinker concentration. Similar behaviour was observed using DVB as crosslinking agent with styrene onto FEP [169], ETFE [172] and with methylstyrene onto ETFE [178].

3.4.2 FEP-g-[AMS-co-MAN-co-DIPB]

The influence of the DIPB crosslinker concentration on the degree of grafting was determined by performing the same set of experiments as described in the previous paragraph for the influence of the DVB concentration. The experimental obtained reaction profiles at 50 °C are shown in Figure 3.23, plotted again with the reaction profile for the preparation of uncrosslinked films as benchmark (grey line).

The similar behaviour was observed for the use of DIPB as previously for DVB. The reaction profile obtained for grafting with 1 mol% DIPB in the grafting solution is similar to the grafting without DIPB. The $DoG$ decreases with the DIPB concentration in the grafting solution for grafting times less than roughly 10 h, where diffusion limitation prevails. The longer the
3.4. CROSSLINKING OF [AMS-CO-MAN]-GRAFTED FILMS

Figure 3.23: DoG as a function of reaction time for different DIPB concentration for the co-grafting of AMS/MAN \((R_m, sol = 1.5)\) and DIPB onto FEP base film \((25 \text{ kGy})\).

grafting proceeds the higher the DoG becomes for DIPB concentrations between 2 and 12 mol% compared to the grafting in absence of DIPB. Actually, DIPB concentrations of at least 2 to 4 mol% are necessary to significantly enhance the DoG compared to the grafting without crosslinker. The crosslinking efficiency of DIPB or its the reactivity is lower compared to DVB, which explains the need of at least 12 mol% DIPB to significantly reduce the DoG compared to the grafting without crosslinker. Additionally, the concentration of pending double bonds was compared between DVB and DIPB crosslinked films, based on the FTIR spectroscopically active symmetrical C=C stretch vibration at 1630 cm \(^{-1}\). The higher concentration of pending double bonds was observed in DVB crosslinked films. The higher reactivity of DVB compared to DIPB yields a faster incorporation of a DVB monomer as chain link. The reduced flexibility of a crosslinked network lowers the probability of a contact between the second double bond and a neighboring growing chain to form a crosslink. Hence, the double bond stays pending and keeps its "reactivity".
3.4.3 Comparison

The qualitative analysis of the time dependent DoG (reaction profiles) for different DVB and DIPB concentrations is discussed above. A more quantitative interpretation is shown in Figure 3.24 by plotting the apparent initial polymerization rate \( r_{p0} \) as a function of the crosslinker concentration. The experimentally obtained reaction profiles for the grafting in the presence of DVB and DIPB in Figures 3.22 and 3.23, respectively, do not show the induction period observed in the investigation of the temperature dependence of the AMS/MAN co-grafting onto FEP base film (paragraph 3.2.5). The simplified model by Rager [169], which neglects the moving grafting front, was used to fit curves to the experimental data. Due to an increase of the degree of grafting in the entire investigated reaction interval, the fitting was independent of the termination rate \( \gamma \). Therefore, a further simplification was applied, assuming the grafting to proceed only by propagation with the apparent initial polymerization rate \( r_{p0} \) in the investigated period and neglecting the recombination. The simplification was verified based on the good agreement of the \( r_{p0} \)-value determined for the grafting without crosslinker, using the enhanced model regarding the front velocity \( v_t \) [171] (\( r_{p0} = 17.0 \, h^{-1} \), see Figure 3.13), with the value obtained for the DIPB crosslinked data set, using only the propagation (\( r_{p0} = 16.1 \, h^{-1} \)), cf. Figure 3.24.

Figure 3.24: DoG as a function of reaction time for different DIPB concentration for the grafting of AMS,MAN (\( R_m, \text{sol} = 1.5 \)) and DIPB onto FEP base film (25 kGy).

The apparent initial polymerization rate is higher for crosslinker concentration up to 2 mol% DVB and 6 mol% DIPB in the grafting solution as compared to \( r_{p0} \)-value for the grafting in absence of crosslinker. For higher crosslinker concentrations \( r_{p0} \) drops below the value for the grafting of uncrosslinked films and becomes equal for DVB and DIPB concentrations of 24 mol% in the grafting solution. The extent of crosslinking in the grafted film could not be proved directly, some reasons are discussed in the following chapter 4. Therefore the mechanical properties were investigated, known to be influenced by crosslinking (chapter 5.1.2).

The influence of the base film on the DoG was determined as a function of the crosslinker concentration at 50 °C, following the standard grafting procedure (Figure 3.25). The crosslinker concentration is plotted in logarithmic scale to enlarge the small concentration range.

At low crosslinker concentration ETFE based films yields higher DoG due to their better swelling in the grafting solution. For higher crosslinker concentrations the effect of the crosslinker be-
3.4. CROSSLINKING OF [AMS-CO-MAN]-GRAFTED FILMS

Figure 3.25: Influence of the DVB- and DIPB-concentration in the grafting solution on the DoG for AMS/MAN co-grafted FEP (25 kGy) and ETFE base films (3 kGy). The reaction time was (24.0±0.2) h.

...comes predominant and the difference between the base films levels off. The grafting behaviour of DVB and DIPB are different and therefore the crosslinker concentration and the crosslinking efficiency has to be known to specify and classify the influence of both crosslinkers.
3.5 Conclusion

Grafting onto insoluble, (pre-)irradiated base film is a combination of initiation of polymerization at active sites and propagation of polymerization by monomer diffusion to the growing chain ends carrying the active sites, which necessitates the swelling of the graft polymerized zone by the grafting solution. The complexity of the grafting reaction is demonstrated at best by showing a list of its dependencies: base material, irradiation method and dose, monomer(s), solvent(s), concentration of monomer(s), the ratio of the monomers, reaction time, the nature, concentration and addition time of crosslinker (if used), and temperature.

Usually, the influence of a varied reaction parameter on the $\text{DoG}$ and the $R_{m,\text{ graft}}$ was determined. In addition, the reaction kinetics was investigated for the influences of the grafting temperature and the molar ratio in the grafting solution. The apparent initial polymerization rate for the propagation, termination rate for the recombination, and drift velocity of the grafting front were determined by using mathematical descriptions of simplified kinetic models to fit curves to the experimental data.

Solvent effects on the co-grafting of AMS and MAN onto FEP base film were studied in a previous work at 60 °C and a mixture of isopropanol and water was found to be the optimum solvent with regard to the achievable degree of grafting. Higher AMS content was expected in the grafted films by reducing the grafting temperature to 50 °C (ceiling temperature of pAMS $T_c = 65$ °C). The addition of water accelerated the initial grafting but did not influence the achievable degree of grafting for long reaction times (42 h). The increased hydrophilicity in grafting solutions containing water may force the monomers, which are predominantly hydrophobic in nature, into the hydrophobic, not swellable pre-irradiated base film. This effect is of importance at the beginning of the grafting reaction, while its importance should fade with increasing $\text{DoG}$. Along with the $\text{DoG}$, the swellability of the grafted film and therefore the monomer access to the active sites should increase, mostly independent of the water content in the grafting solution.

The $\text{DoG}$ was increased with increasing monomer concentration in the grafting solution, while the $R_{m, \text{ graft}}$ did not change significantly. The optimum monomer concentration was chosen at 30 vol% as a compromise between a sufficient reaction rate and a minimized influence of the monomer depletion by the copolymerization on the $\text{DoG}$. Decreased $\text{DoG}$ but increased molar ratio in the grafted film ($R_{m, \text{ graft}}$) was obtained for graft polymerization with increasing molar ratio of AMS and MAN in the grafting solution ($R_{m, \text{ sol}}$) after 20 h at 50 °C. Reaction profiles measured with higher $R_{m, \text{ sol}}$ showed lower $\text{DoG}$ and higher $R_{m, \text{ graft}}$ independent of the reaction time, which enables the preparation of grafted films and subsequently membranes with $R_{m, \text{ graft}}$ between 0.5 and 1.1 independent of the degree of grafting. Fitting curves, calculated based on the mathematical description of a simplified kinetic model, to the experimental data showed decreasing apparent initial polymerization rate and front velocity with increasing $R_{m, \text{ sol}}$.

The influence of temperature on the AMS/MAN co-grafting onto FEP was investigated between 35 and 80 °C by measuring a reaction profile up to 72 h each 5 °C. Curves were calculated based on the mathematical description of a simplified kinetic model and fitted to the experimental data. The apparent initial polymerization rate, termination rate and front velocity increased with an increasing grafting temperature. The activation energies for propagation and termination were determined from the slope of the Arrhenius plots to 101 kJ·mol$^{-1}$ and 132 kJ·mol$^{-1}$, respectively. The high values obtained suggest low grafting and termination rates and high
dependence on the temperature of both reactions. In summary the investigation of the temperature dependence on the co-grafting of AMS and MAN onto FEP shows that the higher initial grafting rate goes along with a decreasing achievable degree of grafting for long reaction times. The influence of different reaction parameters on the co-grafting of AMS and MAN onto ETFE was investigated. Higher DoGs were obtained for the grafting of films irradiated to higher doses. A similar behaviour to the experiments with FEP was observed for the grafting with various monomer concentration and molar ratio in the grafting solution onto ETFE. The absence of an initial delay for all investigated temperatures in the range from 35 to 80 °C and a non-linear correlation of either the apparent initial polymerization rate or the termination rate with the inverse absolute temperature in the Arrhenius plot for the co-grafting onto ETFE were different to the results obtained with FEP base film.

DVB and DIPB were used to investigate the crosslinker effect on the co-grafting of AMS and MAN. The DoG decreased with increasing crosslinker concentration in the grafting solution, regardless of which crosslinker was used. At short reaction time below approximately 15 h the achieved DoG was lower using crosslinker compared to the grafting without crosslinking. For longer reaction times, only films which were grafted in solutions containing low crosslinker concentration yield higher DoG compared to the grafting without crosslinker, while the use of high crosslinker concentrations significantly decreased the DoG. Therefore, the apparent initial polymerization rate for both DVB and DIPB crosslinked, AMS/MAN co-grafted FEP base films were higher for small and lower for high crosslinker concentration in the grafting solution compared with the grafting without crosslinker. The observed behaviour is due to the balance between the increasing diffusion limitation of the propagation and the reduced recombination rate due to immobilization of the growing chain ends.

The co-grafting of AMS and MAN onto FEP or ETFE base films is slow compared to the grafting of styrene onto the same base films. On the other hand, homopolymer formation based on chain transfer to monomer was only observed for very long reaction times (>90 h) and preferentially in the presence of crosslinker. The reaction time needed to graft a AMS/MAN copolymer at 50 °C and $R_{m,\text{sol}}$ of 1.5 in necessary concentrations to subsequently prepare membranes which fulfill the required properties for the use in a fuel cell, is around 20 h. Hence, homopolymer formation is negligible in this time interval.

The grafted films as a "solid mixture" of two polymer phases and its morphology is still not totally understood. Small angle neutron scattering (SANS) combined with differential scanning calorimetry provide a first idea about the size of the domains formed in PS grafted FEP films. Whereas the grafting in the presence of DVB yields a structure dominated by the alternating amorphous and crystalline structure of the FEP base film, phase separation and >200 nm large domains appear for uncrosslinked films [154]. However, the SANS measurements were not able to resolve the structure on a length scale of a polymer chain. The insolubility of grafted films still render the measurement of the average chain length or chain length distribution, degree of polymerization, number average molecular weight (accessible by GPC, viscometry, pressure osmometry), weight average molecular weight (accessible by SANS, light or X-ray scattering) or the grafted chain polydispersity impossible. First experiments using solid state NMR spectroscopy successfully provide access to the molar ratio of AMS and MAN in the grafted film $R_{m,\text{graft}}$ but did not unravel structural details.
Chapter 4

Spectroscopy

Grafting films prepared according to the procedure described in paragraph 3 and proton-conducting membranes obtained by subsequently sulfonating and hydrolysing those grafted films is a relatively simple method to produce a large number of membranes with varying composition. The determination of \textit{ex situ} membrane properties (cf. paragraph 6) and the intuitive modification of the membrane preparation to optimize some of these properties is also possible after some practice. A serious scientific discussion about the correlation of varying condition during the preparation and the properties of the produced membrane necessitates the knowledge of the membrane composition. The correlation of the composition of a membrane with its properties is not only important for the preparation but also for the degradation and especially for the quantification of the extent of degradation.

The insolubility of grafted films in almost all solvents aggravates their analysis. Some spectroscopic methods are discussed in this paragraph, which were applied to characterize either the integral chemical composition, e.g. FTIR and NMR spectroscopy, or the locally resolved composition, using Raman spectroscopy in confocal setup.

4.1 FTIR spectroscopy

FTIR spectroscopy is a widely used method to characterize gaseous, liquid and solid compounds regarding their chemical composition and structural constitution. The application of FTIR spectroscopy to characterize grafted films is published in a multitude of papers \cite{71, 181, 182, 183, 110}. The integral composition of AMS/MAN co-grafted films was investigated using FTIR spectroscopy. Therefore, IR signals were assigned to different components of grafted films by comparing the spectral pattern of films with different composition, see Figure 4.1. The peak maximum, the assigned monomer unit and the vibration mode are listed in table 4.1.

In grafted films the peaks at 2235 cm\(^{-1}\) and 1498 cm\(^{-1}\) were used to quantify and calibrate MAN and AMS, respectively. The AMS signal at 1498 cm\(^{-1}\) was part of a cluster of five, in the case of DVB crosslinked films six overlapping signals (Figure 4.2), which necessitate the fitting of the whole cluster. The very weak additional DVB based signal would be located at 1511 cm\(^{-1}\).

M. Ślaski used the signal at 1600 cm\(^{-1}\) to quantify the AMS content and calculate the molar ratio \(R_{m,\text{graft}}\) \cite{162}. This signal is assigned to CH stretch vibration of hydrogen atoms bound to benzene rings, regardless of the substitution pattern of the benzene ring. In crosslinked systems, the 1600 cm\(^{-1}\) band represents the sum of either AMS/DVB or AMS/DIPB.
CHAPTER 4. SPECTROSCOPY

Figure 4.1: Comparison of FTIR spectra of FEP based films with different composition

Table 4.1: IR active vibration bands of FEP based, various grafted films

<table>
<thead>
<tr>
<th>Monomer unit</th>
<th>Peak maximum [cm$^{-1}$]</th>
<th>Vibration mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>3090 / 3060 / 3026</td>
<td>CH$_2$- / CH$_3$- stretching</td>
</tr>
<tr>
<td></td>
<td>1600 / 1580 / 1498</td>
<td>aromatic C=C stretching</td>
</tr>
<tr>
<td></td>
<td>1030</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>770 / 704</td>
<td>aromatic CH- deformation</td>
</tr>
<tr>
<td>MAN</td>
<td>2980 / 2937</td>
<td>CH$_2$- / CH$_3$- stretching</td>
</tr>
<tr>
<td></td>
<td>2235</td>
<td>CN- stretching</td>
</tr>
<tr>
<td></td>
<td>1628</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1490-1420 / 1390 / 1367</td>
<td>CH$_2$- / CH$_3$- stretching</td>
</tr>
<tr>
<td>FEP</td>
<td>2364</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1300-1100</td>
<td>CF- stretching</td>
</tr>
<tr>
<td></td>
<td>982</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>690-470</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.2: Measured and fitted curve between 1431 cm$^{-1}$ and 1511 cm$^{-1}$ (6 peaks used).
4.1. FTIR SPECTROSCOPY

**Calibration:** The FTIR spectroscopic measurement of the $R_{m,\text{graft}}$ was calibrated by measuring MAN- and [AMS-co-MAN]-grafted FEP films with different $\text{DoG}$. Pre-irradiated FEP base films (25 kGy) were grafted for various reaction times at 50 °C in a solution containing 30 vol% MAN, the reaction profile is shown in Figure 3.1 on page 46. The signal intensity (peak area) of the CN-stretch vibration was recorded and plotted versus the $\text{DoG}$ of MAN (Figure 4.3). Additionally, the thickness and the ratio of the peak areas at 2235 (MAN) and 982 cm$^{-1}$ (FEP), calculated to consider the thickness change during the grafting, are shown in Figure 4.3.

![Figure 4.3: DoG dependent thickness (black), CN-vibration intensity based on peak area (grey), and peak area based ratio of the CN- and CF-vibration intensity for MAN and FEP, respectively. Solid lines show the linear regression lines and the dashed lines the corresponding 95% confidence intervals of the area of the CN- and the ratio CN-/CF-vibration.](image)

The CN-vibration intensity / $\text{DoG}$ relation was assumed to be linear and a simple linear regression analysis was performed (solid grey line in Figure 4.3). The slope of the line through the origin was calculated to 0.5071 a.u.·%$\text{DoG}^{-1}$ ($R^2 = 0.992$). The linear regression analysis of the $\text{DoG}$ dependent CN-/CF-vibration ratio yields a line through the origin with a slope of 0.0225 %$\text{DoG}^{-1}$ ($R^2 = 0.998$).

To characterize uncrosslinked grafted films the calibration of MAN is sufficient. The $\text{DoG}$ of MAN ($\text{DoG}_{\text{MAN,tot}}$) can be calculated from the calibration curve and the $\text{DoG}$ of AMS ($\text{DoG}_{\text{AMS,tot}}$) as difference between the total, mass based $\text{DoG}$ and the $\text{DoG}$ of MAN. For grafted, crosslinked films the $\text{DoG}$ of AMS has to be calibrated as well. Hence, the crosslinker concentration is given as difference between the total, mass based $\text{DoG}$ and the sum of the infrared based $\text{DoG}_{\text{AMS,tot}}$ and $\text{DoG}_{\text{MAN,tot}}$. The deviations in the FTIR spectroscopy based calculations of the $\text{DoG}_{\text{AMS,tot}}$ and $\text{DoG}_{\text{MAN,tot}}$ were too wide to determine the small crosslinker concentrations in grafted films.
4.2 CP/MAS $^{13}\text{C}$-NMR spectroscopy

The FTIR spectroscopy based determination of the molar ratio in the grafted polymer $R_{m,\text{graft}}$ had to be cross-checked and if necessary calibrated using another independent method. M. Ślaski made use of the elementary analysis (EA) to investigate the composition ($R_{m,\text{graft}}$) of AMS/MAN copolymerized and co-grafted samples and to calibrate the FTIR spectroscopic measurement [162, 100]. The calibration based on elementary analysis becomes very complex or even impossible in the case of crosslinked grafted films. The differentiation between MAN and AMS is feasible in the copolymerized samples because of the nitrogen $n_{\text{N, tot}}$, which is present only in the MAN moiety. The molar amount of MAN $n_{\text{MAN}} = n_{\text{N, tot}}$ enables the calculation of the $n_{\text{AMS}}$ from the total carbon $n_{\text{C, tot}}$ in copolymerized samples according to equation 4.1

$$n_{\text{AMS}} = \frac{n_{\text{C, tot}} - 4 \cdot n_{\text{N, tot}}}{9}$$  \hspace{1cm} (4.1)

The FEP backbone also contains carbon and the evaluation of co-grafted films becomes more complex. Adding crosslinker, DVB or DIPB, will even worsen the calculation due to their similarity with AMS.

Another method used to analyze polymers is NMR spectroscopy. A review on perfluorinated ionomers is given by Heitner-Wirguin [184]. Therein, she describes amongst others $^1\text{H}$- and $^{19}\text{F}$ NMR spectroscopic investigations of mostly solvent swollen membranes. Healy et al. found similarities between the organic degradation fragments obtained in situ, during the fuel cell operation, and ex situ from the treatment with Fenton’s reagent by analyzing either the product water or reaction mixture by means of $^{19}\text{F}$ NMR spectroscopy [185]. Solid state $^{13}\text{C}$ NMR spectra of fluoropolymers were recorded by Liu and Schmidt-Rohr [186]. They performed cross-polarization (CP) high speed magic angle spinning (MAS) experiments, with spinning frequencies $\nu_r$ higher than 25 kHz, to obtain narrow $^{19}\text{F}$ signals by reducing the $^{19}\text{F}-^{19}\text{F}$ and $^{19}\text{F}-^{13}\text{C}$ dipolar couplings. The chemical degradation of perfluorosulfonic acid ionomer membranes was studied by Ghassemzadeh et al. using solid-state $^{19}\text{F}$ and $^{13}\text{C}$ NMR spectroscopy [187].

The CP/MAS $^{13}\text{C}$-NMR spectroscopic experiments, experimental details are denoted in paragraph 2.2.2.2, were investigated in collaboration with Prof. Müller, University of Stuttgart, Germany, now University of Trento, Italy.

4.2.1 Signal correlation

CP/MAS spectra of a MAN only and an AMS/MAN co-grafted FEP film were recorded. The peak pattern of both spectra was used to correlate the observed signals with the carbon atoms in the grafted side chain (Figure 4.4).

The peaks 1-4 were also present in the spectrum of FEP-$g$-MAN (not shown) and assigned to the carbons 1-4 in the MAN repeating unit due to the different chemical shift. The same was done with the additional signals A-E observed in the spectrum of FEP-$g$-[AMS-co-MAN]. Sidebands due to the sample spinning were not named in Figure 4.4 and the different aromatic positions (ortho, meta, para) of the phenyl ring present in the AMS repeating unit not spectroscopically resolved.
4.2. Determination of the $R_{m,\text{graft}}$

In principle, all peaks in Figure 4.4 could be used to quantify the AMS/MAN-ratio. However, the best peak separation was observed for the two quaternary carbons in alpha-position to the phenyl ring (assignment B in Figure 4.4, 33 ppm) and next to the cyano group (assignment 2 in Figure 4.4, 42 ppm). The NMR spectra section between 0 and 75 ppm showing the overlapping signals for the aliphatic carbons is plotted together with the fitted trace in Figure 4.5.

![Figure 4.4: CP/MAS $^{13}$C NMR spectroscopy: assignment of measured signals to the AMS (A-E) and MAN (1-4) repeating units.](image1)

![Figure 4.5: Chemical shift section of the aliphatic carbon signals from 0 to 70 ppm. The red curve shape displays the original trace, while the blue corresponds to the fitted trace. The fitting was performed with GRAMS AI (Thermo Electron Corporation, Waltham, USA) using the green indicated peaks and the black drawn baseline.](image2)

The integration of the peaks used to fit the experimental curve was repeated to determine the standard deviation of the fitting procedure. By using a fixed number (7) of peaks for the fitting presented in Figure 4.5 and a mixed Gaussian and Lorentzian function to model the peak shape,
the relative standard deviation was less than 0.2 % for the area and less than 0.01 % for the chemical shift.

The spectra for three grafted films with approximately 28 % degree of grafting, grafted in solutions with \( R_{\text{m,sol}} \) of 0.5, 1.5 and 3.0, were shown in Figure 4.6.

![Figure 4.6: CP/MAS \(^{13}\text{C}\)-NMR spectra of FEP-g-[AMS-co-MAN] with (27.8 ± 0.6) % DoG, prepared in grafting solutions with \( R_{\text{m,sol}} \) of 0.5, 1.5 and 3.0.](image)

The accuracy of the quantitative analysis was shown by parallelism of the cross polarization curves for the two signals of the quaternary carbons. The CP curves were obtained by varying the contact time between 1 and 10 ms, determining the peak areas of the signals at 33 and 42 ppm, and plotting the areas versus the contact times. The fluctuation of the molar ratio in the grafted polymer \( R_{\text{m,graft}} \) calculated for the different contact times \( \tau \) was less than 6 %.

The comparison of the values for the \( R_{\text{m,graft}} \) determined with FTIR- and CP/MAS NMR spectroscopy is given in Table 4.2.

<table>
<thead>
<tr>
<th>( \text{DoG}_{\text{tot}} ) [m%]</th>
<th>( R_{\text{m,sol}} )</th>
<th>( R_{\text{m,graft}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR</td>
<td>CP/MAS</td>
<td>single pulse</td>
</tr>
<tr>
<td>37.5 %</td>
<td>0.5</td>
<td>0.61</td>
</tr>
<tr>
<td>37.8 %</td>
<td>1.5</td>
<td>0.73</td>
</tr>
<tr>
<td>39.4 %</td>
<td>3.0</td>
<td>0.79</td>
</tr>
<tr>
<td>28.2 %</td>
<td>0.5</td>
<td>0.57</td>
</tr>
<tr>
<td>27.4 %</td>
<td>1.5</td>
<td>0.78</td>
</tr>
<tr>
<td>28.2 %</td>
<td>3.0</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The NMR spectroscopy based molar ratio in grafted films \( R_{\text{m,graft}} \) with 28 and 38 % \( \text{DoG}_{\text{tot}} \)
deviate ±10% from the values calculated from FTIR-spectroscopic data. A relative deviation of ±10% is acceptable, since the methods (IR, NMR) used to calculate the $R_{m,\text{graft}}$ in Tab. 4.2 are based on fundamentally different principles. The FTIR calibration with grafted films, as shown in paragraph 4.1, is sufficient and the routine analysis of $R_{m,\text{graft}}$ can be performed faster and easier by FTIR spectroscopy. Whereas the FTIR spectroscopic investigation proceeds non-destructively and without need for sample preparation, the grafted films had to be cut into small pieces and inserted into the MAS rotor for NMR spectroscopic measurements. The $R_{m,\text{graft}}$ calculated on the peak ratios obtained in single pulse experiments, performed as control experiments excluding the influence of cross polarization (last column in Table 4.2), confirmed the data achieved with CP/MAS.

### 4.2.3 Search for sign of crosslinker

The challenge to determine crosslinker in small concentrations in grafted films was mentioned in the FTIR paragraph 4.1. Signals based on DVB or DIPB vibrations were located at similar wave numbers like the peaks originated by AMS. Relevant crosslinker concentrations for the preparation of FC membranes were not detectable using FTIR spectroscopy. NMR spectroscopy, at least in solution, is very sensitive to the substitution pattern of the benzene ring. The double substituted phenyl ring in DVB or DIPB should be distinguishable from the single substituted benzene ring in AMS. The spectrum of an uncrosslinked film (green spectrum in Figure 4.2) is compared in Figure 4.7 with spectra of DVB (32.2% DoG) and DIPB (36.2% DoG) crosslinked films. The grafted films were prepared in solutions with 30 vol% monomers in a $R_{m,\text{sol}}$ of 1.5. The crosslinker concentration was 12.2 mol% DVB (black spectrum in Figure 4.2) and 10 mol% DIPB (red spectrum in Figure 4.2) in the grafting solution related to the total amount of AMS and MAN.

![Figure 4.7: CP/MAS $^{13}$C-NMR spectra of FEP-g-[AMS-co-MAN] (green), FEP-g-[AMS-co-MAN-co-DVB] (black) and FEP-g-[AMS-co-MAN-co-DIPB] (red) with $R_{m,\text{sol}}$ of 1.5.](image-url)
In case of the DVB crosslinked film a small, additional peak appears at 126.7 ppm. The spectrum for the DVB crosslinked film was obtained at 11 kHz, the spectra for the uncrosslinked and DIPB crosslinked films at 12 kHz spinning frequency, which is obvious in the shift of the spinning sidebands. No additional signal was observed in the spectrum of the DIPB crosslinked film. This observation is consistent with findings for the mechanical properties of crosslinked films (paragraph 5.1.2), where the influence of DIPB is less pronounced than that of DVB for the same concentration in the grafting solutions. DIPB seems to react slower than DVB and therefore the degree of crosslinking is higher for DVB, cf. paragraph 3.4. To finally prove the possibility to detect and quantify crosslinker (DVB, DIPB), a series of films prepared with different crosslinker content in the grafting solution und grafted to higher DoG has to be investigated.

4.3 Confocal Raman Microscopy

Ion exchange capacity is an integral measure of the sulfonic acid concentration in grafted membranes (cf. paragraph 2.5.2). The proton conductivity depends on the concentration as well as on the distance between the sulfonic acid groups and the content and mobility of water (cf. paragraph 2.5.1). A sufficient concentration of sulfonic acid groups and their homogeneous distribution are therefore important requirements for membranes with reasonably high proton conductivity. The distribution of sulfonic acid groups in the membrane is already determined by the distribution of AMS in the grafted film. The integral composition of a grafted film and therefore the homogeneity over the membrane area can be measured with FTIR spectroscopy (cf. paragraph 4.1). The homogeneity over the film thickness is not accessible with FTIR spectroscopy in transmission mode, but the measurement of surface near areas is possible in attenuated total reflection (ATR) mode. The depth of penetration \( d_p \) in an ATR setup can be calculated according to equation 4.2 [188].

\[
d_p = \frac{\lambda_1}{2\Pi \cdot \sqrt{\sin^2 \Theta - \left(\frac{n_1}{n_2}\right)^2}}
\]

The penetration depth depends on the wavelength \( \lambda_1 \) of the light, the refraction indices of the optically more dense \( n_2 \) and less dense \( n_1 \) materials, and the angle \( \Theta \) of the penetrating IR beam. Typical values for the depth of penetration range from 0.7 \( \mu \)m (low \( \lambda_1 \approx 3000 \text{ cm}^{-1} \), high \( \Theta \approx 60^\circ \)) to 4.8 \( \mu \)m (high \( \lambda_1 \approx 1000 \text{ cm}^{-1} \), low \( \Theta \approx 30^\circ \)) for two materials with refraction indices of \( n_1 = 1.5 \) and \( n_2 = 4.0 \), respectively.

FTIR spectroscopy in ATR mode was used to compare bulk- and surface near composition of grafted films, e.g. the crosslinker distribution in ETFE-\(~\text{g}~\)[St-co-DVB] [152]. Raman micro(spectro)scopy in confocal setup was chosen to measure the effective distribution of graft components over the entire film thickness.

4.3.1 Measurement setup and validation

The theory and application of confocal Raman microspectroscopy to thin polymer samples was reported by R. Tabaksblat et al. in 1992 [189]. They described qualitatively and quantitatively how the objective (magnification, numerical aperture \( NA \)) and the pinhole size influence the
4.3. CONFOCAL RAMAN MICROSCOPY

N. J. Everall calculated the true focal point $z_m$ and the depth of focus $d.o.f.$ depending on the mechanical sample displacement $\Delta$ [190]. He quantified the depth resolution $DR$, which is the refraction induced broadening of the measured thickness by transition of the incident laser beam from air ($n_1$) into a more dense material ($n_2$), according to equation 4.3.

$$DR = \Delta \cdot \left[ \frac{NA^2 (n_2^2 - 1)}{(1 - NA^2)} \right]^{1/2} - n_2$$  \hspace{1cm} (4.3)

As a consequence, he suggested the use of an oil immersion objective with a liquid having the same refraction index as the sample to minimize the refraction induced broadening [191]. Baldwin and Batchelder developed a model for confocal raman microspectroscopy by considering the effect of refraction through a planar air/sample interface and a distribution of the incident light intensity along the optical axis in the sample [192]. They calculated the illumination and collected light intensity, the latter accounting for the illumination and collection efficiency, and indicated a strong decrease of both intensities with increasing focal depth and increasing numerical aperture. A theoretical description of electromagnetic diffraction of light focused through a planar interface between two materials with different refractive indices was given by Török et al. [193, 194, 195]. The diffraction at such an interface (air/glass or air/silicon) yields a well defined main energy maximum at the focus depth, but the axial width increases and the energy density decreases. An additional correction lens, which introduces an appropriate amount of spherical aberration, compensates the spherical aberration due to diffraction at the planar interface precisely. Bruneel et al. compared theoretical results based on Baldwin and Batchelder’s model [192] with experimental data measured on PE films and found a weaker intensity decrease as predicted [164]. A better agreement with the experimental data was achieved by considering off-axis refraction effects. Furthermore, the sensitivity of Raman intensity profiles to inhomogeneity or imperfect transparency of the used polymer samples was shown.

In spite of all the above mentioned problems concerning the exact theoretical description of confocal Raman microscopy, the method was applied to characterize proton conducting membranes. Mattsson et al. investigated the distribution of (a) styrene in PVDF-$g$-SSA and (b) styrene and DVB in PVDF-$g$-[SSA-co-DVB] over the membrane thickness [165]. The degradation of uncrosslinked membranes during fuel cell tests was shown to be homogeneous over the entire depth [196, 166]. The degradation of polystyrene sulfonic acid (PSSA) grafted PVDF, FEP and ETFE based membranes was analyzed with confocal Raman microscopy by Kallio et al. and compared to results obtained with SAXS and WAXS [197]. They observed the almost complete loss of PSSA side chains and could correlate the extent of degradation with the water uptake of the membrane. Depth profiles of graft polymer membranes were recorded with an axial resolution of $<0.6 \mu m$ using confocal Laser scanning microscopy by Schmidt et al. [167]. The measuring of depth profiles via confocal fluorescence microscopy was faster than micro-Raman profiling with the same signal-to-noise ratio, but staining of membranes without intrinsically fluorescent components was necessary.

All samples used in the confocal Raman microscopic investigations listed before were at least 50 $\mu m$ thick. The depth resolution was approximately 2 $\mu m$ for transparent polymer films. In the present work a FEP base film with an initial thickness of 25 $\mu m$ was used. The thickness
of the grafted films was between 30 and 40 µm. The thin polymer films require a sophisticated microscope optics regarding confocality and depth resolution.

4.3.1.1 Measurement setup

The measurements were realized using an alpha300 R confocal Raman microscope (sketch a in Figure 4.8) linked to a UHTS 300 spectroscopic system, both manufactured by WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm/Germany. A Nd:YAG Laser (λ = 532 nm, P = 4 mW) was used for the excitation. A grating with 600 grooves/mm enabled the measurement of the spectral range between roughly -300 and 3500 rel. cm⁻¹ with the spectral center set to 1900 rel. cm⁻¹. The relative wave number (rel. cm⁻¹) refers to the energy shift of inelastic scattered Raman photons (Stokes- and anti-Stokes scattering) to the elastic scattered Rayleigh light, which is by definition 0 rel. cm⁻¹ and of the same energy as the incident laser light. Only the range between 200 and 3500 rel. cm⁻¹ was of interest for this study. The optical resolution was diffraction limited, 200 nm laterally and 500 nm vertically, and a spectral resolution down to 0.02 cm⁻¹ was possible.

![Figure 4.8: (a) Setup of the Raman microscope WITec alpha300 R. (b) Sketch of the confocal configuration with a scattered Raman beam (dashed line), originated from outside the focal plane and therefore gated out from detection by the confocal hole.](image)

The Raman microscope was equipped with a linear, piezo-driven, feedback controlled scan stage. The accuracy is denoted from the supplier with 4 nm lateral and 0.5 nm vertical and the position is controlled on all axes, using capacitive sensors. The spectra and profiles were evaluated and post processed with WITec Project software (Vers. 1.92).

4.3.1.2 Signal correlation

Spectra of films with different compositions were measured by focusing approximately 5 µm below the surface and accumulating data over 60 s integration time. The Raman active vibrations, which require non-zero polarizability with respect to the normal coordinate (vibration, rotation), were determined for each graft component by comparing the spectral pattern of films with different composition (Figure 4.9). The components of grafted films and the peak maxima of their associated vibrations are listed in Table 4.3. The integration of the peak area was found
to yield more reproducible results than the determination of the peak height. For this reason all following quantitative data based on the peak area and therefore the integration boundaries were denoted in the last two columns of Table 4.3.

Investigations of DVB and DIPB crosslinked films are described in paragraph 4.3.2.3. AMS was

![Figure 4.9: Correlation of vibrations originated from FEP-, MAN-, AMS-, DIPB- or DVB-units in films with different composition.](image)

**Table 4.3: Raman active vibration bands of FEP based, various grafted films**

<table>
<thead>
<tr>
<th>Component</th>
<th>Peak maxima ([cm^{-1}])</th>
<th>Integration from ([cm^{-1}]) to ([cm^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEP</td>
<td>288, 382, <strong>730</strong>, 1210, 1294, 1376</td>
<td>660 780</td>
</tr>
<tr>
<td>MAN</td>
<td>178, 698, <strong>2235</strong></td>
<td>2180 2300</td>
</tr>
<tr>
<td>AMS</td>
<td>683, 999, <strong>1030</strong>, 1598, 3067</td>
<td>1015 1065</td>
</tr>
<tr>
<td>DIPB</td>
<td>999, 1597, <strong>1630</strong>, 3067</td>
<td>((1615), (1065))</td>
</tr>
<tr>
<td>DVB</td>
<td>&quot;1630&quot;(weak)</td>
<td>- -</td>
</tr>
</tbody>
</table>

quantified using the peak at 1030 \(cm^{-1}\). The stronger AMS related vibration band at 1598 \(cm^{-1}\) overlaps with signals from DIPB or DVB in crosslinked films, hence the integration of that peak becomes difficult. The DVB crosslinked film shows a shoulder at 1630 \(cm^{-1}\), which indicates the presence of pendent carbon-carbon double bonds. However, the intensity of DVB originated signals was too weak to quantify the DVB content, as discussed in paragraph 4.3.2.3.

**4.3.1.3 Measurement validation**

The confocality of the microscope is very important to probe a small volume even by focusing deep into a sample. The validation of the measurement of depth resolved intensity profiles (further termed intensity profiles) was performed with an inhomogeneous AMS-\(co\)-MAN grafted FEP film. The reason for the inhomogeneity is not known, but may result from adhesion of one surface of the pre-irradiated film on the reactor wall during the grafting. The intensity
profiles were measured over a lateral distance of 30 µm and the entire thickness of the grafted film. The focusing onto the surface with white light was a big challenge and in some cases impossible. To ensure the profiling of the entire thickness, the upper and lower surface were roughly determined by using so called "focusing spectra". These Raman spectra were recorded with 2 to 5 s integration time during the movement of the scan stage, until the sample related peaks occur by focusing on the upper and disappear by passing through the lower surface. The final measurement of the depth profile was started a few microns above the roughly determined upper und stopped a few microns below the lower surface. The very dark areas above and below the two bright fronts in Figure 4.10 illustrate the measurement without the grafted film. For quantitative interpretation cf. Figure 4.12.

Figure 4.10: Intensity profiles of asymmetrically grafted FEP-g-MAN with 12 % DoG. The depth profiles were measured in both directions (1,2) over the entire film thickness.

The intensity profiles of the CN-vibration shown in Figure 4.10 were measured with a "dry" air objective (Olympus 100x, NA = 0.8) at the same position (1) in two directions (1, 2). The arrow in the sketch between the profiles marks the path of the incident laser beam. Both intensity profiles are shown with the direction of the incident laser beam on top (direction 2 was rotated 180° compared to the sketch). The second direction was measured to assure that the very weak intensity of the grafted band close to the lower surface was not caused by scattering losses. The losses appear in imperfect transparent films and increase with the penetration depth due to the longer path length in the turbid sample. The second measurement confirmed the inhomogeneous grafting and facilitated the validation with this film.

The thickness of the film was ascertained with a thickness measuring gauge to (32 ± 2) µm. The calculated thickness from the intensity profile obtained with the air objective was only (22 ± 2) µm. The deviation is accounted for by the refraction of the incident laser beam at the air / film surface [198, 199]. The focal depth \( z_m \) (equation 4.4) and the refraction index \( n \) (Snell’s law, equation 4.5) depend both on the angle on the incident \( \Theta_i \) and the refracted beam \( \Theta_t \).

\[
z_m = \frac{\tan \Theta_i}{\tan \Theta_t} \cdot \Delta \tag{4.4}
\]

\[
n = \frac{\sin \Theta_i}{\sin \Theta_t} \tag{4.5}
\]

Assuming the same refractive index for both air and film, no refraction will take place and the mechanical displacement \( \Delta \) is equal to the focal depth \( z_m \). In fact, the incident laser beam is refracted to the perpendicular of the surface by transition from air into the optically denser grafted film. Hence, the focal depth \( z_m \) becomes higher than the actual mechanical displacement \( \Delta \). The replacement of the "dry" air objective by an oil immersion objective, used with
an immersion oil having approximately the same refraction index as the grafted film, should eliminate the deviation between the focal depth \( z_m \) and the mechanical displacement \( \Delta \). The refraction index of the grafted films could not be measured, but was roughly estimated to 1.4 - 1.5, based on the refraction indices of FEP (1.34), polystyrene (1.59) and a styrene acrylonitrile copolymer (1.56 - 1.57). The intensity profiles recorded using an oil immersion objective (Zeiss 100x, NA = 1.4) and immersion oil (Merck, \( n = 1.52 \)) are shown on the right half in Figure 4.11, for both directions (1, 2) at a second position (B).

Figure 4.11: Asymmetrically grafted FEP-g-MAN with 12 % DoG. The film was measured at different positions (A, B), in two directions (1, 2), and with an air and oil immersion objective.

The thickness of (34 ± 1) \( \mu m \) calculated from the intensity profile observed with the oil immersion objective is consistent with the (32 ± 2) \( \mu m \) measured with the thickness measuring gauge. The repetition of the measurement using an air objective at a second position (B) was made to verify the asymmetrical grafting at the first position (A) and exclude the existence of a single local inhomogeneity in (A). The further presented results were acquired using the above specified oil immersion objective and immersion oil.

The depth resolved homogeneity was investigated on grafted films with different DoG. Poly-methacrylonitrile grafted onto FEP was chosen as the simplest system to start with, since the grafting of only AMS is not possible under the given reaction condition (cf. paragraph 4.3.2.1). The presence of AMS as third component in FEP-g-[AMS-co-MAN] put higher demand on the detection limit of the confocal Raman microscope than for a grafted system consisting of two components (cf. paragraph 4.3.2.2).

### 4.3.2 Intensity profiles

Depth resolved intensity profiles of either MAN grafted alone or AMS/MAN co-grafted onto FEP films were recorded with 2 s integration time per spectrum. To prevent wrinkling of free-standing films, double faced adhesive tape was used to glue the films on a glass plate. The maximum lateral displacement (180 \( \mu m \)) of the microscope stage was utilized to record 31 spectra, one spectrum every 6 \( \mu m \). The measured depth was adapted to the thickness of each sample. The measurement was started ca. 5 \( \mu m \) above the upper and stopped ca. 5 \( \mu m \) below the lower surface due to the above mentioned problems with focusing on the surfaces. The film thickness was finally defined via the intensity of the CF-vibration related to the FEP moiety. The intensity profiles below are represented as color code, the scale bar is shown in Figure 4.12.
Figure 4.12: Applied color code to illustrate the intensity of vibrations in the range from 0 cts. (black) to 850 cts. (yellow) detected with the CCD camera.

4.3.2.1 FEP-g-MAN

The preparation of MAN grafted FEP films is described in paragraph 3.1. Depth profiles of films with DoG varying from 0 % (FEP base film) to 46 % are shown in Figure 4.13. The weakly grafted films (< 15 %) point out the need for the above mentioned thickness definition via the CF vibration intensity. Whereas the intensity of the CN vibration is too weak to define surfaces, the more intense CF vibration allows the determination of the film thickness.

Figure 4.13: Intensity profiles of the CF vibration (lower series; FEP moiety) and CN vibration (upper row; MAN moiety) of FEP-g-MAN with DoG between 0 (FEP) and 46 %. A lateral section of 42 µm versus the entire thickness of each sample is representend.

The thickness increases significantly with the DoG from 25 µm for the FEP base film to ca. 40 µm for the film with 46 % DoG. The intensity of the MAN based CN vibration is very weak for the sample with 7 % DoG, increases up to 15 % DoG in the surface near area, and shows noticeable intensity in the film center for samples > 21 % DoG. The intensity of the CN vibration and therefore the concentration of MAN moieties seems homogeneously distributed over the entire film thickness for the sample with 30 % DoG and slightly higher in the center of the film grafted at 46 % DoG. The presence of a surface near domain, which includes a comparatively high intensity of the CN vibration for low DoG, and its growing towards the center of the film with increasing DoG indicates the grafting of MAN according to the front mechanism.
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4.3.2.2 FEP-\textit{g}-[AMS-co-MAN]

Based on the experience with the measurement of MAN grafted FEP films and the ability to resolve its surface near domains with higher intensity of the CN vibration ("grafting fronts"), AMS/MAN co-grafted FEP films were investigated. The AMS moiety was specified and quantified with the CH vibration at 1030 cm$^{-1}$. Within the boundaries used for the integration of the AMS based peak (1015 and 1065 cm$^{-1}$), a very strong vibration was observed for the immersion oil as well. The bright upper edge in all the intensity profiles of the CH vibration, shown in the right column in Figure 4.14, indicates the much stronger signals caused by the immersion oil. The oil was only used on the top of the upper surface between the objective and the sample and thus no absorption was measured at the lower surface. The double faced adhesive tape contacting the lower surface did not absorb in the respective spectral region. The absence of peaks related to the immersion oil at wavenumbers which do not interfere with signals from compounds of the grafted films, enable the measurement of the CH vibration at 1030 cm$^{-1}$ and ensure its origin from the AMS repeating unit. The absence of immersion oil related signals while focusing into the film was also an indication of the confocality.

![Figure 4.14: Intensity profiles of the CF vibration (left column; FEP based), CN vibration (center column; MAN based), and CH vibration (right column, AMS based) of FEP-\textit{g}-[AMS-co-MAN] with different DoG.](image)

The intensity profiles shown in Figure 4.14 were trimmed to the film thickness. The areas above and below the film, necessary to set the film interface and determine the thickness, were removed with the exception of 1 $\mu$m of the immersion oil layer above the upper surface. All AMS/MAN co-grafted films show, independently of the DoG, homogeneous distributed graft components. The overlay of the intensity profiles, shown in the same color code for the different vibrations in Figure 4.14, were combined in bitmaps using various colors for the different vibrations. The bitmaps for four different DoG were plotted on the left, the scale bars for the three observed vibration on the right side in Figure 4.15.
Figure 4.15: Overlayed signal intensities of the CF-vibration (red, FEP based), CH-vibration (blue, AMS based), and CN-vibration (yellow, MAN based), of FEP-g-[AMS-co-MAN] with different DoG.

The bitmaps of the superimposed signal intensities (Figure 4.15) shows homogeneous color distribution and confirm the uniform co-grafting of AMS and MAN.

4.3.2.3 DIPB- and DVB crosslinked FEP-g-[AMS-co-MAN]

The crosslinker forms a three dimensional network by interconnecting grafted chains. The distribution of the crosslinker affects e.g. the dimensional stability. A homogeneous distribution of the crosslinker over the grafted film and consequently over the membrane reduces the water swelling in all dimensions (thickness, machining and transverse directions). However, an inhomogeneous crosslinker distribution yields an anisotropic swelling behaviour. The determination of the crosslinker over the film thickness was investigated with DVB crosslinked films. The content of DVB in the grafting solution was 0.5 vol%, which corresponds to 1.3 mol% with respect to 30 vol% AMS and MAN in a molar ratio $R_{m,sol}$ of 1.5. The intensity profiles for films up to 43 % DoG were recorded with an integration time of 5 s per spectrum (Figure 4.16).

Figure 4.16: Intensity profiles of the CF- (FEP moiety), CN- (MAN moiety), CH- (1030 cm$^{-1}$, AMS moiety), and CH-vibration (1600-1600 cm$^{-1}$, AMS and DVB moieties) of FEP-g-[AMS-co-MAN-co-DVB] with various DoG.

For the CF- and CN- vibrations, intervals from 0 to 850 cts. were chosen, while the CH- vibra-
tion at 1030 cm\(^{-1}\) is depicted from 0 to 250 cts. and the CH- vibrations in spectral range from 1600 - 1660 cm\(^{-1}\) from 0 to 300 cts. The separation of the DVB originated, weak shoulder on the much stronger signal caused by the AMS moiety in the spectral range from 1600 - 1660 cm\(^{-1}\) was not possible. Calculated ratios between signals at 1030 cm\(^{-1}\) or 3067 cm\(^{-1}\) related to the AMS moiety and the AMS/DVB related signals around 1600 cm\(^{-1}\) provide no insight into the distribution of DVB. Hence, no statement about the distribution of DVB is possible.

### 4.3.3 Depth resolved, local degree of grafting

The intensity profiles shown before were converted into concentration profiles. The calibration of the grafted compounds, as used for the FTIR spectroscopic determination of the molar ratio in the grafted film \(R_{m,\text{graft}}\) (paragraph 2.2.2.1), failed for the confocal Raman microscopy. Imperfectly transparent samples and associated diffraction losses or variability in the laser power and subsequent changes in the Raman intensity may be reasons why the Raman intensity and the concentration or mass of the graft components did not correlate.

To avoid the problem of a general calibration, each sample was calibrated separately. Before the local degree of grafting \(\text{DoG}_{\text{local}}\) was calculated, the intensity loss due to scattering in imperfect transparent films had to be addressed. The scattering can not be mathematically captured and therefore an internal standard had to be defined. This standard has to be constant over the thickness or at least of the same concentration at the same distances from the upper and lower surface. In grafted films the base material (FEP) fulfills this requirement. The CF intensity is assumed to either be constant over the entire film thickness for homogeneous grafted films or at least equal at mirrored positions in both directions from the film center assuming the presence of grafting fronts. A linear approximation was used to fit the decrease of the CF vibration intensity over the film thickness. All CF intensities over the entire depth were used to approximate the line in homogeneous grafted films, whereas two points at the position of the CN-intensity maxima in the grafting fronts were used to approximate the line in surface grafted films. The correction is illustrated in Figure 4.17 (page 89) using the example of a homogeneous MAN grafted FEP film.
The slope of the approximated line (red) in Figure 4.17 was used to correct the intensity of MAN (black) and FEP (blue). For FEP-g-[AMS-co-MAN] the AMS intensity profile was corrected accordingly. The following procedure was used to calculate the local degree of grafting $\text{DoG}_{\text{local}}$:

- Laterally, along the x-axis (180 µm) 31 spectra were measured in 6 µm steps at depth $n$ and afterwards averaged to exclude lateral inhomogeneity. The intensity $I_{x,n}$ for the vibration of component $x$ was calculated at depth $n$ by integration of the corresponding peak in the averaged spectrum, using the boundaries listed in Table 4.3.

- The integral $\text{DoG}$ of each graft component was calculated according to equation 2.1. For FEP-g-MAN the mass of MAN was accessible from the $\text{DoG}$, while the $R_{m,\text{graft}}$ had to be used additionally for FEP-g-[AMS-co-MAN] to further divide the overall degree of grafting $\text{DoG}$ into the degree of grafting for AMS ($\text{DoG}_{\text{AMS,total}}$) and MAN ($\text{DoG}_{\text{MAN,total}}$), respectively (cf. equation 4.6).

$$\text{DoG}_{\text{AMS,total}} = \frac{\text{DoG}}{\left(\frac{1}{R_{m,\text{graft}}} \cdot \frac{M_{\text{MAN}}}{M_{\text{AMS}}} + 1\right)} \quad (4.6)$$

- The integral mass for each compound $m_{x,\text{tot}}$ was calculated according to equation 4.7 from the integral degree of grafting for the corresponding compound $\text{DoG}_{x,\text{tot}}$ and the initial mass $m_0$ of the base film.

$$m_{x,\text{tot}} = \text{DoG}_{x,\text{tot}} \cdot m_0 \quad (4.7)$$

- The integral intensity $I_{x,\text{total}}$ for component $x$ over the entire film thickness was calculated as sum of all averaged intensities $I_{x,n}$ at depth $n$ for the respective compound.

- A spectrum specific mass per intensity value $(m/I)_{x,\text{total}}$ was calculated by dividing the integral mass of one component $m_{x,\text{tot}}$ by the integral intensity of its vibration $I_{x,\text{total}}$.

- For each depth the intensity for one component $I_{x,n}$ was multiplied by its specific mass per intensity value $(m/I)_{x,\text{total}}$ to get the local mass of that component $m_{x,n}$.

- The local degree of grafting $\text{DoG}_{\text{local}}$ was calculated according to equation 2.1 from the local mass of FEP $m_{\text{FEP,n}}$ and the local mass of the grafted component. For MAN only grafted films the latter is only the local mass of MAN $m_{\text{MAN,n}}$ and for co-grafted films the sum of the local masses of AMS $m_{\text{AMS,n}}$ and MAN $m_{\text{MAN,n}}$.

The local degree of grafting $\text{DoG}_{\text{local}}$ is plotted as a function of the relative depth in concentration profiles (Figures 4.18 and 4.19). The relative depth corresponds to the measured depth, only the zero position was shifted. The shift was chosen to put the film center at the same depth, which was chosen at 25 µm for MAN only (Figure 4.18) and at 20 µm for AMS/MAN co-grafted films (Figure 4.19).

Different concentration profiles were obtained for the grafting of MAN only (Figure 4.18) and the co-grafting of AMS and MAN (Figure 4.19). The onset of the MAN grafting at the surface, the simultaneous increase of the surface near $\text{DoG}_{\text{local}}$ and the migration of the grafting fronts to the center is in agreement with the prediction of the front mechanism. The start of the grafting
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Figure 4.17: Measured (straight black line) and corrected (dotted black line) intensity profile of the CN vibration using the slope of the red line for the correction. The red line was fitted to the measured CF vibration intensity (straight blue line).

Figure 4.18: Local degree of grafting for MAN $\text{DoG}_{\text{MAN,local}}$ vs. relative depth for five FEP-g-MAN with different $\text{DoG}$ between 2 and 30 %. $\text{DoG}$.

in the film center is obvious at 15 % $\text{DoG}$ and a homogeneous distribution is reached at 30 % $\text{DoG}$. As opposed to this result, concentration profiles obtained for AMS/MAN co-grafted films did not show grafting fronts. In the measured $\text{DoG}$ range from 15 to 44 % the distribution of AMS and MAN was homogeneous over the entire film thickness. Furthermore, a film with 5 % $\text{DoG}$ was investigated and no grafting fronts were detected. However, the signal to noise ratio at 5 % $\text{DoG}$ was very low and close to the detection limit, for AMS as well as for MAN. The results become more understandable by considering the different reaction times for grafting MAN only or co-grafting AMS and MAN. After around 1 h 15 % $\text{DoG}_{\text{MAN,total}}$ were grafted. Around this stage the grafting at the film center set in and another 1.5 h later a homogeneous distribution was reached at around 30 % $\text{DoG}_{\text{MAN,total}}$. The co-grafting of 15 % $\text{DoG}$, which is the sum of $\text{DoG}_{\text{AMS,total}}$ and $\text{DoG}_{\text{MAN,total}}$, took around 6 h and 15 h in total were needed to reach 30 % $\text{DoG}$. Assuming comparable diffusion coefficients for AMS and MAN in the grafted
CHAPTER 4. SPECTROSCOPY

Figure 4.19: Local degree of grafting for AMS $\text{DoG}_{\text{AMS,local}}$ and MAN $\text{DoG}_{\text{MAN,local}}$ as a function of the relative depth for four FEP-$g$-[AMS-co-MAN] with different $\text{DoG}$ between 15 and 44 % $\text{DoG}$.

film, the observed difference was due to the slower copolymerization kinetics of AMS and MAN compared to the grafting of MAN only (cf. paragraph 3.2.4).

The most important information from the confocal Raman microscopic investigation for the membrane preparation based on AMS/MAN co-grafted FEP films is the homogeneous distribution of AMS and MAN over the entire film thickness. This homogeneity ensures after the sulfonation of the grafted films and subsequent hydrolysis a good proton conduction, even for films with low $\text{DoG}$.

4.4 Conclusion

The determination of influences of varied reaction parameters on the composition or structure of grafted films and membranes requires analytical methods able to resolve the expected changes. Grafted films are insoluble and therefore the characterization had to be done in solid state. The degree of grafting $\text{DoG}$ is an integral measure of the mass ratio between the added graft component and base film. The co-grafting of two or more monomers necessitates the determination of the ratio of the monomeric units in the grafted film or membrane. The integral ratio of AMS and MAN in grafted films was measured using FTIR spectroscopy in transmission mode, but it is still not possible to detect the small crosslinking concentration of DIPB or DVB in the presence of AMS and MAN. The decrease of the monomer and crosslinker concentration in
the grafting solution due to their consumption in the grafting reaction was measured using gas chromatography (GC) coupled with mass spectrometry (MS). The reliability of the method was restricted to grafting reactions with sufficiently high monomer and crosslinker consumption and suppressed homopolymer formation.

The measurement of the local composition is important to ensure homogeneously grafted films and furthermore a good proton conductivity of the membranes prepared by subsequent sulfonation of grafted films. FTIR spectroscopy in ATR setup allows the measurement of the surface-near composition and its comparison with the integral composition obtained in transmission mode. FTIR microscopy based determination of the locally resolved composition over the thickness of a grafted film or membrane is not possible. The depth and lateral resolution of an IR microscope is approximately 20-25 µm, if a Globar, a thermal light source made of a silicon carbide rod and heated to 1000-1650 °C (λ = 4-15 µm), is used. This resolution renders depth resolved information at the thickness of a grafted film within the DoG range of interest for FC application around 35 µm impossible. Raman microscopy in confocal setup is able to achieve a depth resolution of approximately 1 µm. The depth profiles recorded for the grafting of MAN only and AMS-co-Man reflect their different reaction kinetics. The fast polymerization of MAN yields intensity profiles and accounting for the DoG concentration profiles with pronounced grafting fronts up to 22 % DoG. The co-polymerization of AMS and MAN, by contrast, proceeds very slowly and the intensity and concentration profiles show a homogeneous distribution of all components.

The marketability of polymer electrolyte fuel cells strongly depends on the price and longevity of the catalyst and membrane. Stabilization strategies for fuel cell membranes are needed to enhance their life time under the conditions of an operating FC. Crosslinking was shown as potential way of membrane stabilization, especially for grafted membranes where the graft component is the weak point against chemical attack and mechanical or thermal stress. The knowledge of the location of the crosslinker in the grafted film and its crosslinking efficiency is important to determine the influence of crosslinking on the material properties. However, the determination of the crosslinker concentration in the grafted film or membrane is still a challenge. On the one hand, the FTIR signals of DVB and DIPB interfere with the signals originated by AMS and MAN. On the other hand, the crosslinker concentrations necessary to prepare FC membrane are very low and close to the limit of detection for FTIR as well as Raman spectroscopy.

Solid state NMR spectroscopy was used to probe the molar ratio in grafted films (\( R_{m, graft} \)) by a second, independent method and intended for determination of the crosslinker concentration in AMS/MAN co-grafted films. The molar ratio in grafted films was determined by CP MAS \(^{13}\)C NMR spectroscopy, using the ratio of the quaternary carbons in \( \alpha \)-position to the phenyl ring and cyano group for AMS and MAN, respectively. The \( R_{m, graft} \) values obtained by NMR were consistent with the FTIR spectroscopic based data within ±10 % relative standard deviation. An additional signal in a CP MAS \(^{13}\)C NMR spectrum of a FEP-\( graft \)-poly[AMS-co-MAN] prepared in a solution containing 12.2 mol% DVB was detected, but further investigations have to be done to prove the applicability of the method down to approximately 1 mol% crosslinker concentration in the grafting solution.
Chapter 5

Ex situ Mechanical Properties

In situ fuel cell testing of polymer electrolyte membranes is a demanding and time consuming procedure. A multitude of failure modes are possible during the membrane testing in the fuel cell environment. Variation in temperature, humidification, current density, gas concentration, and local concentration of reactive species often induce multiple failure modes. Therefore, it is almost impossible to correlate a single failure mode with chemical and physical membrane properties. A very rough classification into mechanically, chemically and thermically induced failures is commonly accepted, although the boundaries between the different modes become blurred considering an operating fuel cell.

The request for ex situ methods to investigate membrane properties is sustained, especially to induce a single failure mode under well defined and reproducible conditions and enable its correlation with structural properties of the membrane. The advantages of most ex situ methods over fuel cell tests are a more simple experimental setup, the selectivity concerning the failure mode and the rapidness, and for this reason higher sample throughput. Some in situ accelerated testing methods inducing predominantly a single failure mode were developed, e.g. mechanical failure during dry/wet-cycles [200, 201] or preferably chemical failure by fuel cell operation under open circuit voltage (OCV) [134, 202, 203]. An ex situ testing of the chemical stability of fuel cell membranes against (hydroxyl) radical attack was for instance realized by treatment of membranes with aqueous hydrogenperoxide (H₂O₂) solution at elevated temperature and determination of the time dependent weight loss as a measure for the membrane degradation rate [204, 205, 92].

Mechanical stability of polymer films and membranes has to be divided into dimensional stability, creep resistance and tensile behaviour. Dimensional stability in terms of swelling and shrinkage of membranes, e.g. induced by humidity changes, produces internal stress if the membrane is assembled in a fuel cell, which finally may cause crack formation. Creep of water swollen membranes, due to compressive force induced by the compaction force in a fuel cell, thins the membrane and may cause shorting. Tensile stress originates in a fuel cell from shrinkage of a membrane, which is fixed at its edges. This may either destroy the membrane electrode interface due to different shrinkage coefficient of the materials, or induce cracks if the stress exceeds the membrane’s tensile strength.

Various constitutive models were developed to mathematically describe the experimentally obtained mechanical data. G’Sell and Jonas developed a closed loop test equipment to experimentally determine the stress strain behaviour of polyethylene (PE) and poly(vinyl chloride)
(PVC) at constant true strain rate [206]. They described the true stress $\sigma$ phenomenologically as a function of true strain $\epsilon$ by using material related constants. The viscoelastic behaviour of polymers was investigated in various dynamic measurements and described in one- and three dimensional theories and models [207, 208, 209, 210, 211, 212]. The decrease of the Young’s modulus and tensile strength during hydration of Nafion 112 was experimentally shown by Kundu et al. [213]. The influence of humidification and temperature on the Young’s modulus, yield stress and tensile stress and strain was systematically investigated for Nafion 112 by Tang et al. [214]. They found that temperature has a more significant effect on the mechanical behaviour than humidity and increasing temperature as well as increasing humidity lower the Young’s modulus and the yield stress. Liu et al. investigated the mechanical properties of Nafion 117 and sulfonated poly(arylene ether sulfone) copolymer membranes and correlated the properties with the membranes morphology [215]. An important result in this study is the strong dependency of the mechanical properties on the strain rate. The experimental determination of the viscoelastic response of Nafion N1110 was studied by means of the temperature and hydration effect on the tensile creep [216]. The creep behaviour was found to depend strongly, but in a complex manner, on temperature and humidity, e.g. water acts as plasticizer at rt but stiffens Nafion at elevated temperature. Phenomenological modeling of temperature and humidity effects on the stress-strain behaviour was carried out by Kusoglu et al. [217]. They incorporated the effect of humidity on the material related constants in the model of G’Sell and Jonas [206].

The experimental determination of mechanical properties in grafted systems was done for example with poly(tetrafluoroethylene-co-perfluorovinylether) (PFA) base films, simultaneously grafted with styrene and characterized by FTIR, XRD and regarding the tensile strength and elongation at break [218]. The irradiation effect on the tensile strength of poly(vinyliden fluoride) (PVDF) and poly(ethylene-alt-tetrafluoroethylene) (ETFE) films was related to the change of crystallinity and the decreasing elongation at break to the irradiation induced crosslinking [84]. The authors proposed mechanisms for the electron-radiation induced reactions of PVDF and ETFE, respectively. Mechanical properties of membranes prepared by pre-irradiation grafting of styrene under nitrogen onto PVDF, poly(vinyl fluoride) (PVF), poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and ETFE, subsequently sulfonated and hydrolyzed, were investigated as a function of varied reaction time, solvent, styrene concentration and base film [219, 220]. The dimensional stability of styrene grafted ETFE films was found to be independent of the DVB concentration in the grafting solution, while membranes, prepared by sulfonation and hydrolysis of the crosslinked films, shows less dimensional increase enhancing the DVB concentration [152].

The mechanical properties of base and grafted films were investigated in the present work with tensile tests. Typically, the maximum possible stretching (elongation at break), the elastic behaviour (Young’s modulus) and the maximum stress achieved in the experiment (tensile strength) were investigated. Tensile tests were also performed with membranes, using in some experiments additionally a climatic chamber to control temperature and humidity. First creep tests were performed with the tensile testing machine and climatic chamber by applying a constant force and recording the resulting, time dependent sample elongation. The dimensional stability was investigated by measuring the membrane thickness and length in machining and transverse direction before and after drying or before and after swelling for the shrinkage or swelling, respectively.
5.1 Base, irradiated and grafted films

Membrane preparation by graft (co-)polymerization of monomer(s) onto the pre-irradiated base film, followed by sulfonation and subsequent hydrolysis, has to deal with the inherent physical properties of the base film. Choosing different base materials offers the possibility to change the mechanical properties of the starting material. However, the preparation of thin FEP or ETFE films by melt blow extrusion induces anisotropic behaviour to the material. The mechanical properties differ in the machining direction, where the film is elongated during the extrusion, and the transverse direction, which is perpendicular to the machining direction and parallel to the orientation of the crystalline domains, shown for FEP base film by small angle neutron scattering (SANS) [154]. The specification of the tensile strength and elongation at break from DuPont, Specification Bulletin T62-1 (FEP) and T62-4 (ETFE), are 17.2 MPa and min. 200 % for FEP and 41.4 MPa and min. 200 % for ETFE, respectively. The data obtained from in house measured stress-strain curves for FEP and ETFE in machining direction (cf. Figure 5.1) are (35±4) MPa and (219±14) % for FEP and (55±3) MPa and (322±13) % for ETFE, respectively.

The Young’s modulus was not specified by DuPont but calculated to (535±22) MPa for FEP and (977±24) MPa for ETFE from the initial slope of the curve between 0.5 and 1 % elongation. The inherent mechanical properties of ETFE base film outperform those of FEP in terms of the maximum applicable force and strain. However, the benchmark in long term fuel cell performance was achieved with an FEP based, styrene/DVB co-grafted membrane, operated 4000 h at 500 mA·cm\(^{-2}\) with a degradation rate, defined as loss in ion exchange capacity, of 0.01 %·h\(^{-1}\) [108]. Therefore, both FEP and ETFE based films were used to investigate the influence of irradiation (paragraph 5.1.1) and the degree of grafting (paragraph 5.1.2) on the mechanical properties. The dimensional stability of membranes was determined for FEP and ETFE based membranes with different composition of the grafted polymer (paragraph 5.2.1), whereas the tensile testing at 80 °C and 80 % relative humidity was calibrated with Nafion 212 (paragraph 5.2.2.1) and the first investigation of the influence of various membrane composition performed with ETFE based membranes (paragraph 5.2.2.2).

![Stress/strain curves of ETFE (DuPont, Tefzel\textsuperscript{R} 100LZ, 25 µm) and FEP (DuPont Teflon\textsuperscript{R} 100A, 25 µm) in machining (MD) and transverse direction (TD)](image)
5.1.1 Influence of irradiation on base films

As already mentioned, one has to deal with the inherent physical and chemical properties of the base material by preparing membranes on the pre-irradiation/graft co-polymerization/sulfonation sequence. The influence of irradiation on tensile strength, elongation at break and elastic modulus (Young’s modulus) of “solid” polymers like PTFE, PE and polystyrene (PS) was already described by Chapiro in 1962 [74]. The effect of high irradiation doses ranging from 100 to 1200 kGy on the tensile strength and elongation at break of PVDF and ETFE was investigated by Nasef and Dahlan [84].

The irradiation dose usually used in this work to pre-irradiate FEP or ETFE base films with an electron beam varies in the range from 3 to 30 kGy and therefore the focus was on doses below 50 kGy. To consider also trends for higher irradiation dose, a FEP film was irradiated with 210 kGy (cf. Figure 5.2) and an ETFE base films with 100 kGy (cf. Figure 5.3).

![Graph showing elongation at break, tensile strength, and Young's modulus of FEP as a function of irradiation dose.](image)

Figure 5.2: Elongation at break (top), tensile strength (center) and Young’s modulus (bottom) of FEP (DuPont, Teflon® 100A, 25 µm) as a function of irradiation dose.

The elongation at break as well as the tensile strength decrease with increasing irradiation dose. Both trends can be explained by an increasing radiation induced chain scission. The chain fragments with lower molar mass broaden the molecular weight distribution, show weaker chain-chain interactions and therefore disentangle more easily, which eventually yields earlier rupture of the polymer film. No evidence for crosslinking is obvious, which would increase the tensile strength due to the formation of a three-dimensional network. The decrease of the Young’s modulus for irradiation doses up to 17 kGy can be attributed to weaker chain-chain interactions caused by chain scission, whereas the increase for higher irradiation doses may be due to an increasing crystallinity. Shorter chains become more mobile and their mobility is further facilitated by heat formation at high irradiation doses. Hence, the chains are able to realign and grow the crystalline domain during cooling, which increases the crystallinity. It is proposed in [84] that a further increase of the irradiation dose will promote crosslinking and degradation effects.

No significant change of the elongation at break was observed for ETFE up to an irradiation
dose of 50 kGy, considering the relative standard deviation of approximately 10 %. Compared to the pristine base film, the tensile strength was slightly increased and the Young’s modulus decreased for the irradiation with 3 kGy, which is expected with initiating chain scission. The tensile strength was decreased and the Young’s modulus increased for a further increase of the irradiation dose up to 100 kGy, which is attributed to a combination of chain scission and increasing crystallinity. Similar trends were observed for ETFE, irradiated up to 200 kGy using an electron beam [172], and for PTFE, crosslinked PTFE, FEP, PFA, ETFE, PVDF and PVF irradiated with gamma rays up to 52 kGy [86].

5.1.2 Grafted films

The grafting reaction can be simplified characterized as a mixture of two phases. The base film (phase 1) is diluted with the graft component (phase 2), the extent of dilution is given by the degree of grafting. The amount of graft component embedded in the matrix of the base material strongly influences the mechanical properties.

FEP base films were irradiated and co-grafted with AMS and MAN to different degree of grafting using the standard procedure on page 33. Stress-strain curves obtained in tensile tests of grafted films with different $DoG$ (Figure 5.4) were used to calculate the elongation at break, tensile strength and Young’s modulus, cf. Figure 2.3 on page 38. The values of the elongation at break, tensile strength and Young’s modulus determined for the samples from Figure 5.4 are listed together with the corresponding relative standard deviation (RSD) in Table 5.1.

The elongation at break decreases and the yield strength increases by irradiation and furthermore by grafting of the FEP base film with increasing $DoG$ (Figure 5.4). A differential scanning calorimetry (DSC) study on polystyrene grafted ETFE films showed a decreasing inherent crystallinity of the base material during grafting [172]. Since grafting preferentially takes place in the amorphous zone of the base film [154], the decreasing elongation at break can be explained with the enlargement of the amorphous zone. A two step degradation was observed
in thermogravimetric analysis (TGA) of PS grafted ETFE films [172] and poly-[AMS-co-MAN] co-grafted FEP films (data not published). The first step correlates with the loss of the graft component below 400 °C while the second step is due to degradation of the base material. The degradation temperature of the base film was not influenced by grafting, which confirms the existence of a two phase system. The grafted AMS/MAN side chain carries methyl-, phenyl- and cyano-substituents which reduce the flexibility of the side chain backbone due to a steric hindered rotation of the carbon-carbon bonds. An increasing DoG accords to an increasing addition of the stiff poly[AMS-co-MAN] to the more flexible FEP, which possibly causes the decreasing elongation at break. On the other hand, the heating during the graft polymerization may increase the mobility of the polymer chains in the FEP matrix (phase 1) and enhance the extent of crosslinking as result of a successful recombination of two radicals located at the chain ends. The formed crosslinked network may resist the external stress by an enhanced elastic deformation, which explains the increased yield strength.

The FEP film co-grafted with 33.7 % AMS and MAN became stiff and broke at \( \varepsilon = 0.74 \% \).

Table 5.1: Mechanical properties of FEP base film, irradiated FEP film and AMS/MAN co-grafted FEP films with different DoG.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus</th>
<th>Tensile strength</th>
<th>Elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average [MPa]</td>
<td></td>
<td>Average [MPa]</td>
</tr>
<tr>
<td>base film</td>
<td>535</td>
<td>4.0</td>
<td>35.2</td>
</tr>
<tr>
<td>irradi. film</td>
<td>519</td>
<td>2.7</td>
<td>18.1</td>
</tr>
<tr>
<td>2.2 % DoG</td>
<td>619</td>
<td>3.2</td>
<td>18.6</td>
</tr>
<tr>
<td>3.1 % DoG</td>
<td>662</td>
<td>2.3</td>
<td>19.5</td>
</tr>
<tr>
<td>6.8 % DoG</td>
<td>795</td>
<td>2.8</td>
<td>21.4</td>
</tr>
<tr>
<td>33.7 % DoG</td>
<td>(1362)</td>
<td>(1.8)</td>
<td>7.9</td>
</tr>
</tbody>
</table>

The Young’s modulus was calculated for this sample between 0.5 to 0.7 % strain and therefore
put in parentheses. The Young’s modulus increases with increasing DoG, which again reflects the increasing fraction of stiff poly[AMS-co-MAN] in the host matrix of more flexible FEP.

5.2 Proton exchange membranes

The investigation of grafted films at rt and ambient humidity was performed to determine the influence of various film compositions on the mechanical properties. The correlation of \textit{ex situ} determined mechanical properties of grafted films with \textit{in situ} properties of membranes or their longevity is difficult, because the properties of a water swellable membrane at the temperature and humidity of an operating fuel cell differs strongly from the behaviour of a grafted film at ambient condition. Hence, a tensile testing procedure in a climatic chamber was validated with Nafion® 212CS and the measured mechanical properties compared to literature data [214, 215] (cf. paragraph 5.2.2). The measurement of the specimen thickness and width in the climatic chamber at the conditions used during the tensile test was not possible. Therefore, the specimen dimension in thickness and transverse direction, which corresponds to the width if the tensile test is performed in machining direction, at the used temperature and humidification was calculated from experiments performed to determine the dimensional stability (cf. paragraph 5.2.1). The dimensional stability in terms of the membrane’s change in length, area and volume during swelling and shrinkage was investigated by measuring its thickness and length in machining and transverse direction before and after hydration or before and after drying, respectively. The temperature effect on the dimensional change of a membrane was negligible between rt and 80 °C (r.h. constant) compared to the strong effect of humidity between dry and fully hydrated state (T constant) on its size. The swelling and shrinkage were assumed to be uniform and continuous between the dry and fully hydrated state. Hence, the humidity dependent rate of swelling or shrinking, which is either the increase or decrease of the length, area or volume per % r.h., was calculated from the initial and finale size. The thickness and width of the membrane at the condition used for the tensile test in the climatic chamber were calculated with the rate of swelling or shrinking and humidity change.

5.2.1 Dimensional stability

The shrinkage of membranes was tested by measuring the length in thickness, machining and transverse direction before and after drying of the swollen membrane for 1 h at 80 °C under reduced pressure. The one-dimensional (thickness, machining and transverse direction), in-plane and volumetric shrinkage were calculated according to equations 2.7, 2.8 and 2.9 on page 39 and the relative standard deviation (RSD) calculated to $\leq 5\%$ for the 1\textsuperscript{st} shrinkage and $\leq 20\%$ for the in-plane and volumetric shrinkage. The shrinkage of uncrosslinked ETFE based membranes is compared in Figure 5.5 to the shrinkage of Nafion® 212CS.

An increase of the shrinkage in all dimensions was observed for ETFE based membranes when the degree of grafting and therefore the in-plane and volumetric shrinkage increased. The highest shrinkage was observed for Nafion 212CS in thickness, machining and transverse direction and accordingly also in-plane and volumetric, compared to ETFE based, AMS/MAN co-grafted membranes up to 42 % DoG. The influence of crosslinking on the shrinkage was investigated with ETFE based, AMS/MAN co-grafted and DIPB crosslinked membranes (Figure 5.6).
membranes with (9.7±0.8), (19.7±0.8) and (29.7±0.8) % DoG were prepared at 50 °C according to the standard procedure in paragraph 2.1.4 in grafting solutions containing different DIPB concentration (0, 0.7, 2.0, 4.0 and 6.6 mol%).
The influence of DIPB on the kinetics of AMS/MAN co-grafting onto FEP base film was investigated, cf. paragraph 3.4.2 on page 64, and compared to the grafting onto ETFE in paragraph 3.4.3 on page 66. The FTIR-, NMR- and Raman spectroscopic efforts to quantify the crosslinker content in the grafted film are described at several positions in chapter 4. The shrinkage of membranes is reduced significantly by crosslinking, shown in Figure 5.6 for ETFE based membranes crosslinked with DIPB. The one-dimensional, in-plane and volumetric shrinkage decreased for an increasing DIPB concentration and decreasing DoG and was higher for the respective membranes prepared in the absence of a crosslinker. A particularly low shrinkage was observed for membranes prepared in solutions containing 0.7 mol% DIPB, in the case of (9.7±0.8) % DoG additionally in solutions with 2 mol%. This behaviour is not completely understood, but it seems that the in-plane (MD and TD) shrinkage contributes more to this phenomenon than the shrinkage along the membrane thickness.

Crosslinking reduces shrinkage, enhances the dimensional stability and is therefore expected to reduce membrane failure due to crack formation caused by humidity cycling. Rapid aging studies, combining enhanced mechanical stress caused by humidity cycling and accelerated chemical degradation due to fuel cell operation at OCV, were performed by L. Gubler et al. [200]. The membrane integrity was monitored by the hydrogen crossover and a DVB crosslinked FEP-g-SSA was tested almost 600 h without failure, whereas the respective uncrosslinked FEP-g-SSA and Nafion 112® start to fail after around 100 and 150 h, respectively.

5.2.2 Tensile tests under controlled climatic conditions

Correlation of ex situ and in situ properties often fails because of the strongly different conditions or setup used to determine them. As mentioned above, the correlation of ex situ mechanical properties determined with a poorly water swellable grafted film at rt and ambient r.h. with the in situ properties of a corresponding highly water swellable membrane in a fuel cell at 80 °C / 100 % r.h. is doomed to failure by the huge differences between the two investigated systems. To close the gap between the temperature and humidification of an operating fuel cell and during ex situ tensile tests, the further tensile tests were performed in a climatic chamber at 80 °C and 80 % relative humidity. Fundamental investigations concerning the preparation and handling of specimens, the time necessary to equilibrate the samples and the influence of cross head speed, temperature and humidity on the recorded stress-strain curves were performed. One problem observed at low cross head speed was the pulsation of the relative humidity. In Figure 5.7 the actual r.h. and stress are plotted versus the run time for a constant cross head speed of 2 mm-min⁻¹ at a reference value for the r.h. of 80 % (80 °C).

The actual r.h. varied between 75 and 90 %. A precise comparison of stress/strain curves measured for specimens of the same sample showed that the stress-strain curve is slightly shifted towards higher stress in the region of higher relative humidity. The observed increase was in the order of 0.1 MPa for a 5 % higher relative humidity. Based on the information of the supplier (Zwick GmbH & Co. KG, Ulm, Germany), the observed pulsation cannot be corrected and originated from the control cycle of the oversized humidifier combined with the relatively small climatic chamber (V = 70 l). The inaccuracy of the r.h. was estimated to ±10 % and accepted as inherent error of the method.
5.2.2 Method validation

To validate the recording of stress-strain curves in the climatic chamber, the mechanical properties of Nafion 212CS (DuPont) were investigated at different temperature and relative humidity. The measurements were performed with a cross head speed of 10 mm·min⁻¹ until the pre-load of 0.1 N was reached, 1 mm·min⁻¹ in the range from 3 to 5% elongation, where the Young’s modulus was determined, and 100 mm·min⁻¹ until the specimen broke. Values of 3 and 5% were used as lower and higher boundary, respectively, to determine the Young’s modulus due to anomalous curve progressions in the usually used smaller elongation range between 0.5 and 1%. Stress-strain curves were recorded at 30 and 80°C and at 30 and 80% relative humidity. At each T/r.h. condition two Nafion 212CS samples with eight specimens each were tested. The first sample was placed in the climatic chamber as received (dry form) and the second sample was swollen 8 h in water at 80°C before placed in the climatic chamber for the equilibration. The elongation at break, tensile strength, Young’s modulus, temperature and relative humidity for all samples were calculated as average of eight single measurements (Figure 5.8). At each T/r.h. condition two samples with different initial state (dry, wet) were used to specify the quality of the equilibration by the conformity of the obtained result. Previously performed experiments showed the necessity to equilibrate membranes for at least 12 h to get reproducible results.

Additionally, the mechanical properties of a Nafion 212CS were investigated after the membrane was swollen 8 h at 80°C in water and equilibrated 16 h in the climatic chamber at 80°C and 50% r.h.. The comparison of the determined mechanical properties with literature data turned out to be difficult, with exception of the Young’s modulus. The influence of the strain rate on the Young’s modulus was investigated at ambient conditions in [215] and the change of the Young’s modulus for strain rates between 1 and 12 mm·min⁻¹ (3 MPa) was in the same order of magnitude as the standard deviation (up to 20 MPa) of the measurements. On the other hand, the yield strength and elongation at break was influenced significantly by the strain rate. Hence,
5.2. PROTON EXCHANGE MEMBRANES

Figure 5.8: Elongation at break $A$ (top), tensile strength $\sigma_{\text{max}}$ (center) and Young’s modulus $E$ (bottom) for Nafion® 212CS at 30 °C and 80 °C and various relative humidity.

The dependency of the Young’s modulus of temperature and relative humidity was investigated at six different conditions, the results are shown in Figure 5.9, and compared to literature data in Table 5.2. At each condition two samples with eight specimens each were tested. The Young’s modulus is plotted as circle, whose area scales with the absolute value of the Young’s modulus and center point shows the averaged temperature and humidity calculated from the eight individually measured specimens. For comparison a circle (grey) with an area corresponding to 120 MPa is shown in Figure 5.9.

Figure 5.9: Dependency of the Young’s modulus of Nafion® 212CS of temperature and relative humidity. The area of the circles scales with the Young’s modulus.

Tang et al. performed tensile test with Nafion 112 at different humidities and temperatures with a cross head velocity of 10 mm-min$^{-1}$ [214] and presented all mechanical data in graphs. The values used for comparison in Table 5.2 were adapted from those graphs with an estimated un-
certainty of \( \pm 15 \) MPa. The Young’s modulus of Nafton 117-H, measured at ambient conditions with a cross head velocity of 1 mm-min\(^{-1}\) in [215], is also denoted in the last column in Table 5.2.

Table 5.2: Comparison of the Young’s modulus determined at different temperature and humidity in this work with values adapted from [214, 215].

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Humidity</th>
<th>Young’s modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([{^\circ}\text{C}])</td>
<td>([%])</td>
<td>this work</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>237±15</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>120±10</td>
</tr>
<tr>
<td>50</td>
<td>80</td>
<td>101±10</td>
</tr>
<tr>
<td>80</td>
<td>30</td>
<td>105±10</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>87±10</td>
</tr>
<tr>
<td>80</td>
<td>80</td>
<td>62±5</td>
</tr>
</tbody>
</table>

The Young’s moduli obtained at different temperatures and humidities in this work were in good agreement with the literature data in [214, 215], keeping in mind the different cross head velocity (1 vs. 10 mm-min\(^{-1}\)), specimen thickness (2 or 7 mil; 1 mil = 25.4 \(\mu\)m) or Nafton generation (112 vs. 212CS). The further measurements in the climatic chamber at elevated temperature and humidity were performed according to the validated procedure.

5.2.2.2 Measurement of ETFE based samples at 80 \({^\circ}\text{C} \) / 80 % RH

The following tensile tests were performed at 80 \({^\circ}\text{C} \) and 80 % relative humidity in machining direction according to the method validated with Nafton 212CS in terms of sample preparation (scalpel) and equilibration (\(\geq 12 \) h). The distance between the clamps and consequently the initial length in machining direction was fixed while the initial cross section \(A_0\) had to be calculated for each sample. The initial cross section \(A_0\) is the product of the thickness and width (transverse length) of the specimen and both change with temperature and humidity. The dimensional changes of the membranes between the dry and fully water swollen state were known from shrinkage and swelling experiments (cf. paragraph 5.2.1). Assuming a constant swelling or shrinkage of the membrane between the dry and fully water swollen state, the thickness and width of the specimen can be calculated for the temperature and humidity, used in the experiment. The initial width was controlled in the climatic chamber as accurately as possible in spot tests with a caliper gauge and the measured width was in good agreement with the calculated ones. The cross head velocity was chosen to 100 mm-min\(^{-1}\) during the whole experiment and the pre-load increased to 0.3 N. The changes yielded a better reproducibility and consequently the standard deviation became less. The Young’s modulus was determined in the range from 0.5 to 1 % elongation as the curve progression became regular at these conditions.

A series of ETFE based samples was investigated in machining direction at 80 \({^\circ}\text{C} \) and 80 % r.h., using the pristine base film, an AMS/MAN co-grafted film (34 % DoG), three uncrosslinked membranes with various DoG in the range from 20 to 40 % and two crosslinked membranes with 39 % DoG, which were prepared in solutions containing 1.3 mol% DVB and 0.7 mol% DIPB, respectively. The elongation at break, tensile strength and Young’s modulus for each sample
5.2. PROTON EXCHANGE MEMBRANES

were calculated as average from six individual measured specimens (Figure 5.10).

Figure 5.10: Elongation at break $A$ (top), tensile strength $\sigma_{\text{max}}$ (center) and Young’s modulus $E$ (bottom) in MD of ETFE base film, ETFE-\text{g-}[AMS-co-MAN] and ETFE-\text{g-}[AMSSA-co-MAN] membranes with various DoG, uncrosslinked and DIPB or DVB crosslinked.

The information in Figure 5.10 obtained with different samples (base and grafted films, membranes with different compositions) will be particularly discussed in the following:

- The behaviour of the poorly swellable samples, ETFE base film and AMS-co-MAN grafted film with 34 % DoG, is comparable to results obtained at r.t. and ambient humidity. The Young’s modulus increases, the tensile strength is not influenced and the elongation at break decreases during the grafting of AMS/MAN copolymer onto the FEP base film.

- Swellability of samples, introduced by sulfonation and hydrolysis, decreases all observed mechanical properties significantly, obvious in the comparison of the grafted film with 34 % DoG with its corresponding membrane (31 % DoG). By contrast the Young’s modulus increases slightly, the tensile strength significantly and the elongation at break is not influenced by the comparison of grafted films and the corresponding membranes in potassium form at ambient conditions, used in previous investigations of membrane’s mechanical properties. Testing of the mechanical properties of membranes in the presence of water, which acts as plasticizer, leads to completely different results.

- The Young’s modulus and tensile strength decrease and the elongation at break is not influenced by an increasing DoG in the case of uncrosslinked membranes. The swelling and therefore the water uptake scales with the DoG and the higher water content decreases the stiffness of the membrane. The water may form a hydration layer around the grafted chains and weaken the chain-chain interaction and therefore reduce the tensile strength (“shielding”). The statements about stiff and steric hindered grafted copolymer chains to
explain the DoG dependent behaviour of grafted films in tensile tests at rt and ambient r.h. in paragraph 5.1.2 become reversed for swellable membranes tested at higher humidity.

- The effect of crosslinking in membranes observed in the experiments at 80 °C and 80 % r.h. was the same as obvious with grafted films at rt and ambient humidity. The Young’s modulus and tensile strength increase and the elongation at break decreases due to a stiffer three-dimensional copolymer matrix.

The mechanical data obtained at 80 °C and 80 % relative humidity for ETFE based, via the pre-irradiation / graft copolymerization / sulfonation and hydrolysis procedure prepared membranes show a different dependence from the DoG than grafted films or membranes in potassium form investigated at room temperature and ambient humidity. While an increasing DoG of grafted films and K⁺-exchanged membranes impair the mechanical properties in measurements at rt and ambient humidity significantly, a beneficial effect of an increasing amount of graft component on the mechanical properties was observed for membranes at 80 °C and 80 % relative humidity. The better agreement of the conditions used during experiments in the climatic chamber and occurring in an operating fuel cell compared to the measurements at rt and ambient humidity attaches greater importance to the results obtained at 80 °C and 80 % relative humidity. Indeed, the correlation of ex situ mechanical data obtained at 80 °C and 80 % r.h. with in situ membrane properties in performance, long term stability or accelerated aging tests remains to be seen. However, the brittleness of grafted films especially with high DoG seems to be the critical stage during the preparation of proton-conducting membranes by graft copolymerization and sulfonation of pre-irradiated films.

5.2.2.3 Creep behaviour under constant load - a feasibility study

The assembly of membranes in membrane electrode assemblies (MEAs) and fuel cells (FC) is associated with the compressive force induced by the compaction force necessary to mount and seal the fuel cell. Membranes were usually dried 60 min at 60 °C under reduced pressure to facilitate their manageability and integration in FCs. The humidified gases and the water produced during the FC testing swell the membrane and create an additional compressive force due to the fixed size of the FC hardware. Water swollen membranes become more flexible and start to creep. In micro structured fuel cells, operated without gas diffusion layer, creep of the membranes into the channels was observed [221]. Creep thins the membrane and may form cracks and finally leads to failure of the fuel cell.

The static creeping of membranes was fundamentally investigated at conditions as close as possible to the ”real” conditions in an operating fuel cell, using the tensile testing machine in combination with the climatic chamber. All tests were performed at 80 °C and 80 % relative humidity by applying a constant force (stress) and measuring the time dependent elongation. Different samples were investigated and the obtained curves shown in Figure 5.11.

All specimens were tested with the same initial length (68.8 mm) and therefore the relative cross head positions was used instead of the specimen’s elongation in Figure 5.11. The creep modulus $E_c$ was calculated according to equation 2.6 on page 38 after 40 h from the stress $\sigma$ and the relative elongation $\epsilon$. The values obtained for the investigated membranes are denoted in brackets in the following list of qualitative conclusions made from the static creep tests:
5.3 CONCLUSION

Figure 5.11: Creep experiments with different membranes under varied conditions, experimental details see text. The experiments were performed at constant load and the time dependent relative cross head position was recorded.

- Very low creeping was observed for FEP based, with 20% DoG AMS/MAN co-grafted membranes tested under 0.5 N load (grey curves in Figure 5.11). Nevertheless, the creeping was more pronounced for the uncrosslinked membrane ($E_c = 14.7$ MPa, dark grey) compared to the membrane crosslinked with 1.3 mol% DVB in the grafting solution ($E_c = 41.2$ MPa, light grey).

- Further experiments were performed with a load of 3 N. The influence of temperature was investigated at 30 and 80 °C with ETFE-g-[AMSSA-co-MAN] (DoG = 40%). The temperature had a significant influence on the creep behaviour. After 40 h at 80 °C ($E_c = 17.9$ MPa) no plateau was reached and the extension was more than eight times higher compared to the specimen tested at 30 °C ($E_c = 139$ MPa).

- Creeping was more pronounced for higher DoG, obvious by comparing the uncrosslinked ETFE based, AMS/MAN co-grafted membranes with 20 ($E_c = 25.6$ MPa) and 40% DoG. The membrane with a higher DoG absorbs more water and becomes more plastic.

- Nafion®212CS shows the highest creeping of all investigated samples ($E_c = 3.80$ MPa).

The measurement of the creep modulus is highly affected by the temperature. The reduced creep resistance at higher temperature and humidity may become an important stability criterion for membranes in operating fuel cells.

5.3 Conclusion

The mechanical properties of FEP and ETFE base films were investigated in tensile tests. The mechanical anisotropy, machining versus transverse direction, of the thin base films is a caused by its processing in an extrusion blow molding process. The tensile and yield strength are higher and the elongation at break is significantly lower in machining direction while the Young’s modulus is not influenced by the extrusion direction compared to the transverse direction. The
orientation of the crystal domains in transverse direction determined in SANS measurements support those results [154]. Irradiation of the base material was performed in the present work with an electron beam and is essential to induce reactivity and therefore the basis of chemical treatment and modification. The concentration of reactive sites (radicals) and the associated reaction rate is proportional to the applied dose, if the dose is not too high. On the other hand, the mechanical properties are negatively influenced by irradiation. Elongation at break and tensile strength decreases with an increasing irradiation dose due to chain scission. The Young’s modulus decreases at low and starts to increase for high irradiation doses. The reason is homogeneous bond cleavage and radical formation for all doses combined with an enhanced chain mobility and crosslinking probability at higher irradiation doses and thus higher temperature.

Introduction of a chemically modifiable graft component into the matrix of the base material further influences the mechanical properties. Ex situ membrane properties, such as IEC, conductivity and swelling, increase with the concentration of sulfonated graft component (DoG). By contrast, the mechanical properties of grafted films and dry membranes in potassium form investigated at rt and ambient humidity are negatively influenced by grafting. The plasticity of grafted films decreases with the increase of the degree of grafting, reflected in a strong increase of the Young’s modulus and a likewise decrease in the elongation at break and tensile strength. The addition of crosslinker and its concentration in the grafting solution and consequently the concentration of interconnection in grafted films further reduce the plasticity. Membranes, investigated at r.t. and ambient humidity in potassium form, show poorer mechanical properties than their respective grafted films. Tensile test at 80 °C and 80 % r.h. with water swollen membranes in acid form yield mechanical properties measured at conditions much closer to conditions in an operating fuel cell. The tensile testing in the climatic chamber was validated with Nafion®-212CS. The Young’s moduli obtained under varied temperature and humidity are in good agreement with the literature data. The effect of grafting on the mechanical properties of membranes at 80 C° and 80 % r.h. is inverted compared to trends observed for dry potassium ion exchanged membranes at rt and ambient humidity. The enhanced water uptake at higher DoG increases the plasticity. The reduction of the elongation at break and increase of the Young’s modulus for crosslinked membranes was also observed at elevated temperature and humidity. The dimensional stability of membranes is negatively affected by grafting. Crosslinking reduces the dimensional changes in thickness, machining and transverse direction by forming a denser, three-dimensional network. The reduction of the available free volume reduces water uptake and conductivity. ETFE based membranes with DoG up to 46 % show a higher dimensional stability than a Nafion®-212CS membrane.

The less irradiated, grafted and crosslinked films and membranes show the better mechanical properties at room temperature and ambient humidity. Based on those result membranes with least possible DoG for a sufficient conductivity should be used. From an application point of view, the results obtained in tensile tests at 80 °C and 80 % relative humidity are more promising. The elongation at break is also decreased comparing an ETFE based, AMS/MAN/DVB co-grafted membrane with the pristine ETFE base film, but the tensile strength is unaffected and the Young’s modulus increases only slightly.
Chapter 6

Membrane Properties and Fuel Cell Tests

Graft copolymerization of monomers onto pre-irradiated base films and their subsequent sulfonation and hydrolysis is often stated as cost effective way to prepare tailor made fuel cell membranes [49, 68, 76, 81, 222]. The flexibility of the radiation grafting method to vary the properties of the grafted film and subsequent membrane is described in chapter 3 on page 45 ff., where the influence of various reaction parameters on the degree of grafting (DoG) and molar ratio in the grafted film ($R_{m, graft}$) is shown. Although radiation grafting offers a way to selectively optimize membranes, concerning their mechanical, chemical or thermal properties, these properties are interdependent and the optimization of one property will influence the others and not necessarily yield their optimum [152, 153, 223].

Membranes prepared by grafting of styrene (St) onto perfluoronated (FEP) and partially fluoronated (ETFE) base polymers and the dependence of the membrane properties on the preparation conditions are described in numerous publications. Exemplarily, a short overview on the progress in developing membrane structure-property relations at PSI is presented in the following. An increasing amount (DoG) of styrene grafted onto FEP base film, subsequently sulfonated, decreased the ex situ specific resistivity due to an increasing density of sulfonic acid groups (proton concentration) and hydration [71]. The ion exchange capacity (IEC) of FEP-g-SSA (SSA = styrene sulfonic acid) increased and the crystallinity decreased with an increasing DoG, assigned to considerable structural changes within the membrane [72]. A four-step weight loss of FEP-g-SSA membranes was determined by thermogravimetric analysis (TGA), combined with FTIR spectroscopy and mass spectrometry (MS) [139, 176]. While the first step corresponds to the loss of water (dehydration, 50-200 °C), the residual IEC became zero after heating the membrane in the range of the second step (desulfonation, ≈330 °C). Hence, the third step (≈450 °C) was attributed to dearomatization, associated with the complete loss of the graft component, and finally the FEP base polymer degraded (>530 °C). The transversal distribution of sulfur, which is part of the sulfonic acid group in the styrene repeating unit and therefore acts as tracer for the grafted side chain, was determined with microprobe analysis and found to be inhomogeneous for low DoG. Membranes with <15 % DoG showed higher sulfur contents in the surface near region compared to the middle part, as a consequence of the grafting front mechanism. The concentration gradient of sulfur disappeared at 26 % DoG. The comparison of FEP and ETFE based polySSA grafted membranes indicated an influence of the base polymer
on the mechanical properties [145].

To increase the membrane stability, divinylbenzene (DVB) was used as crosslinker in the graft component. An increasing DVB concentration in the grafting solution, associated with a higher DVB content in the grafted films and subsequently prepared membranes, decreased the swelling of the membranes in water [143]. The specific resistivity of DVB crosslinked, styrene grafted FEP based membranes with 19 % DoG increased with the crosslinker content in the grafting solution [131, 140]. Desulfonation of styrene grafted FEP based membranes, observed by TGA, shifted marginally to lower and dearomatization slightly to higher temperatures, when DVB was used as crosslinker [144].

Hotpressing and Nafion®-coating of DVB crosslinked FEP-g-SSA membranes resulted in a performance of membrane electrode assemblies (MEAs) based on these membranes in a H₂/O₂ fuel cell, comparable to Nafion® 112 based MEAs and lifetimes of more than 2000 h at >60 °C [11]. Hotpressing of a wet DVB crosslinked membrane (20 % DoG) with ETEK electrodes and subsequent fuel cell testing of this MEA yielded the PSI internal benchmark concerning membrane degradation rate (0.01 %IEC·h⁻¹) and time on operation (8000 h) for a fuel cell tested membrane [108]. The degradation rate was calculated within the first 4000 h of operation. Polarization curves were recorded at 60 °C for FEP based membranes, prepared with various DVB concentration in the grafting solution, immediately after starting up of the cell (24 - 48 h) [149]. The polarization curves for DVB crosslinked membranes were shifted to lower cell voltage compared to Nafion® 112. An increase of the membrane resistance and decrease of the cathodic polarization resistance was found for an increasing crosslinker content. Both parameters were found to be well-balanced, based on the FC performance, in a membrane prepared with 10 % DVB in the grafting solution. Crosslinking of ETFE based, styrene grafted membranes with 5 % DVB in the grafting solution yielded a membrane with the best balance between ohmic and polarization resistance, determined by electrochemical impedance spectroscopy (EIS) [151, 153, 152, 92]. A membrane prepared with 5 % DVB in the grafting solution was tested approximately 2000 h under constant load, showed a performance in polarization curves, comparable to those of Nafion® 112 [92]. Using chemically more stable monomers was expected to enhance the lifetime of membranes, e.g. using trifluorostyrene derivatives [115]. Certainly, the most promising approach was the use of α-methylstyrene (AMS) as monomer due to its availability and low price [162]. Although the graft polymerization of AMS was not possible under the conditions of pre-irradiation grafting, the use of methacrylonitrile (MAN) as a co-monomer increased the grafting kinetics and enabled the grafting of sufficient amount of the copolymer, necessary to introduce the required membrane properties. Furthermore, the MAN seems to have a beneficial effect onto the membrane stability. Results obtained in fuel cell experiments with uncrosslinked AMS-co-MAN based membranes outperformed uncrosslinked styrene based membranes by far [100, 110].

A detailed study of the influence of various reaction parameters on ex situ and in situ properties was carried out in the present work and is presented in paragraph 6.1 and 6.2, respectively. On the one hand, in situ membrane performance was investigated after 144 h by means of the EIS spectroscopic membrane resistance, the current density dependent voltage in polarization curve, and the hydrogen permeability, shown in paragraph 6.2.1. The duration of approximately 150 h was chosen to ensure constant operation conditions after a sufficient conditioning period of the FC. On the other hand, the long term stability of three different membranes was investigated after approximately 1000 h in single cell experiments, illustrated in paragraph 6.2.2. Finally, the
degradation of the disassembled, long term investigated membranes was determined by FTIR spectroscopy and compared to the degradation of styrene based membranes.

6.1 Ex situ membrane properties

The absence of a test facility for a fuel cell stack, with the possibility to characterize each single cell assembled in this stack and especially each membrane in one of those single cells, restricted the number of fuel cell tests and thereby of in situ membrane characterizations. Promising membrane candidates for fuel cell tests were determined by ex situ characteristics, whose relation to fuel cell performance was already known from previous investigations. Such characteristics are the ex situ proton conductivity, ion exchange capacity (IEC), water uptake and hydration number. Proton conductivity depends on the density of sulfonic acid groups and their hydration level and has a major impact on the fuel cell performance [224, 225]. The IEC is an integral measure of the proton carrier concentration. For homogeneous grafted films and subsequently prepared membranes with a homogeneous distribution of the sulfonic acid groups, the proton conductivity in the fully water swollen state increases with an increasing IEC. For surface grafted films and consequently membranes whose sulfonic acid groups are located at the surface the IEC will be well above zero while the proton conductivity cannot be measured due to a barrier for proton conduction in the ungrafted membrane center. The water uptake, based on the mass of the membrane, and hydration number, related to the molar amount of water, characterize the water concentration within a membrane. Water is essential for proton conductivity in state-of-the-art polymer membranes, e.g. Nafion®, where a hydrophilic phase is formed in the hydrophobic polymer matrix by the formation of inverse micelles, containing the sulfonic acid groups. The interconnection of those inverse micelles by channels, formed by the alignment of the SO₃-groups as "channel walls", build the routes for proton conduction in the water swollen state [226].

The influence of the degree of grafting, monomer concentration and molar ratio of the monomers in the grafting solution on the ex situ properties are described in paragraph 6.1.3 while the impact of the crosslinker concentration is discussed in paragraph 6.1.4.

Uncrosslinked membranes were prepared by radiation grafting of the base film with monomers according to the standard grafting procedure on page 34. The proton conductivity was introduced by subsequent sulfonation and hydrolysis of the grafted films at the conditions described in paragraph 2.4 on page 39. The degree of grafting was calculated according to equation 2.1 on page 35 for grafted films. The same DoG was used for the subsequently prepared membrane, without correction for the additional mass of the sulfonic acid groups. The titrimetric and electrochemical impedance spectroscopic methods used to determine the IEC and ex situ conductivity $\sigma$, respectively, are explained in paragraph 2.5 at page 40.

6.1.1 Degree of grafting

A key parameter to adjust the properties of radiation grafted films and subsequently prepared membranes are the degree of grafting. The amount of graft component added to "dilute" the base film and its homogeneous distribution determine the ion exchange capacity and the conductivity of the membrane. Hence, the parameters affecting the graft copolymerization of AMS and MAN onto pre-irradiated FEP base film (25 kGy), particularly the temperature $T$, molar ratio of the monomers in solution $R_{\text{monomer, sol}}$, monomer concentration ($c_{\text{monomer}}$) and reaction time
$t$, were varied both in grafting without crosslinker and in the presence of 1.3 mol\% (0.5 vol\%) DVB. The grafted films were subsequently sulfonated and hydrolyzed and the IEC determined by titration of the potassium ion exchanged membranes. The measured IEC (black dots) of uncrosslinked membranes is plotted in Figure 6.1 versus the DoG. The theoretical IEC of membranes with molar ratio in the grafted polymer $R_{m_{,\text{graft}}}$ of 0.5 (red line) and 1.2 (blue line) are shown for comparison in Figure 6.1, which were found to be the maximum and minimum achievable values, respectively, independent of the molar ratio of the monomers in the grafting solution (cf. paragraph 3.2.4 on page 53). The same experiment was accomplished for DVB crosslinked membranes, using 1.3 mol\% (0.5 vol\%) DVB in the grafting solution, at varied temperature, molar ratio $R_{m_{,\text{sol}}}$ and monomer concentration (Figure 6.2).

![Figure 6.1: Ion exchange capacity IEC (black dots) as a function of the degree of grafting DoG of uncrosslinked membranes, prepared under various conditions (temperature, molar ratio $R_{m_{,\text{sol}}}$, monomer concentration). The blue and red line show the theoretical IEC for membranes based on grafted films with molar ratio in polymer $R_{m_{,\text{graft}}}$ of 1.2 and 0.5, respectively.](image1)

![Figure 6.2: Ion exchange capacity IEC (black dots) as a function of the DoG of DVB (1.3 mol\%) crosslinked membranes prepared under various conditions ($T$, $R_{m_{,\text{sol}}}$, $c_{\text{monomer}}$, $t$). Theoretical IEC curves for membranes with $R_{m_{,\text{graft}}}$ of 1.2 (blue) and 0.5 (red) are additionally shown.](image2)

The uncrosslinked membranes show IEC values, with a few exceptions at low degree of grafting,
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within the expected theoretical IEC boundaries calculated for $R_{m, graft}$ of 1.2 and 0.5. The deviations from the expected values for low DoG were essentially the same for uncrosslinked and 1.3 mol% DVB crosslinked membranes. Indeed, the scattering of the measured thickness, conductivity, swelling and hydration number (Figure 6.3) was quite different, comparing membranes based on uncrosslinked (IEC shown in Figure 6.1) and with 1.3 mol% DVB crosslinked FEP-$g$-[AMS-co-MAN] (IEC shown in Figure 6.2).

![Figure 6.3: Comparison of the degree of grafting dependent thickness (black), conductivity (red), swelling (green) and hydration number (blue) of membranes based on uncrosslinked (circles) and with 1.3 mol% (0.5 vol%) DVB crosslinked FEP-$g$-[AMS-co-MAN] films (diamonds), prepared under varied reaction conditions ($T$, $R_m$, sol, $c_{monomer}$, $t$).](image)

The thickness increase was linearly dependent on the DoG. The slope of a linear regression line, starting with an intercept of 25 µm thickness for the ungrafted and subsequently not swellable
pristine base film, was calculated to 0.52 µm·%−1 for uncrosslinked and 0.38 µm·%−1 for 1.3 mol% DVB crosslinked membranes. A strong influence of the varied reaction parameters (T, Rm, sol, cmonomer, t) on the conductivity, swelling and hydration number was observed for uncrosslinked membranes, apparent by the scattering of the measured values. However, the addition of 1.3 mol% DVB to the grafting solution, which leads to crosslinking of the grafted films and subsequently sulfonated membranes, reduces the influence of the reaction parameters (T, Rm, sol, cmonomer, t) on the ex situ membrane properties. DVB crosslinking reduced the swelling and hydration number significantly, whereas the conductivity decreased only slightly. The correlation of the hydration number and the conductivity is known [227] and can explain the higher conductivity of uncrosslinked membranes by their enhanced hydration state of approximately 10 to 30 water molecules per sulfonic acid group compared to DVB crosslinked (1.3 mol%) membranes with approximately 2 to 10 water molecules per sulfonic acid group. The result for DVB crosslinked membranes was verified by ex situ characterization of a series of membranes (Figure 6.4), based on films grafted up to 65 h at 50 °C in a solution containing 30 vol% monomers (Rm, sol = 1.5) and 1.3 mol% DVB.

![Figure 6.4: Degree of grafting DoG, conductivity σ and ion exchange capacity IEC for FEP-g-[AMSSA-co-MAN-co-DVB] as a function of reaction time. The films were grafted in solutions containing 30 vol% monomers (Rm, sol=1.5) and 1.3 mol% (0.5 vol%) DVB.](image)

The conductivity and ion exchange capacity for DVB crosslinked membranes, prepared under the same reaction conditions, increased linearly with the DoG. The observed linear dependence of the conductivity and the DoG on the reaction time, shown in Figure 6.4, and thus of the conductivity on the DoG is not expected, cf. curves of the theoretical IEC for membranes with Rm, graft of 1.2 (blue) and 0.5 (red) in Figure 6.2. Nevertheless, the curves for both series coincide. The preparation of membranes with well-defined conductivity or IEC is possible, although
a considerable scattering of the *ex situ* properties of uncrosslinked membranes was observed. The grafting rate, which is the time dependent increase of the DoG, was found to be approximately the same for uncrosslinked and crosslinked films, if low crosslinker concentrations were used (cf. 3.4.1 on page 63 et seq.). However, the *ex situ* properties of uncrosslinked membranes differ significantly from those of DVB crosslinked membranes with comparable DoG.

AMS and MAN co-grafting onto ETFE base films, which were subsequently sulfonated and hydrolyzed, yields membranes used to investigate the influence of the base polymer on the *ex situ* properties of membranes (Figure 6.5).

![Figure 6.5: Degree of grafting dependent conductivity σ (black) and ion exchange capacity IEC (red) for membranes based on ETFE films and co-grafted with AMS and MAN without crosslinker. The conductivity of FEP based samples is shown for comparison (grey).](image)

As expected, the proton conductivity and ion exchange capacity increased with the DoG. ETFE based membranes showed significantly lower proton conductivity than membranes based on FEP. The swelling and hydration number for ETFE based membranes were notably lower, approximately two-thirds, than the corresponding properties determined for membranes grafted onto FEP base films, which explains the reduced proton conductivity. A comparison of the IEC, based on the (dry) mass, of ETFE and FEP based membranes is misleading, because of the different density of the materials. Nevertheless, the measured IEC for both base materials were in the same order of magnitude, even though the values obtained for FEP based membranes tend to be 10 % higher than for ETFE based membranes. The IEC depends on the integral concentration of sulfonic acid group and therefore on the integral concentration of AMS, cf. introduction of the present paragraph on page 111. The degree of grafting of AMS (DoG_{AMS}) dependent IEC and conductivity are shown in Figure 6.6, for the membranes discussed in Figure 6.5.

The IEC shows a linear correlation with the DoG_{AMS} in Figure 6.6 and the correlation coefficient $R^2$ for a simple linear regression was calculated to 1.00, compared to $R^2 = 0.96$ for the linear regression based on the overall DoG. Indeed, the correlation of the conductivity with the overall DoG ($R^2 = 0.98$) is slightly better than with the DoG_{AMS} ($R^2 = 0.97$).
6.1.2 Effect of monomer concentration

The influence of the monomer concentration on the degree of grafting and molar ratio in the grafted polymer $R_{m, \text{graft}}$ is discussed in paragraph 3.3.3, page 59. Its effect on the \textit{ex situ} membrane properties was investigated for uncrosslinked and DVB crosslinked membranes (Figure 6.7). The DVB impact was further explored using 1.3 and 5.2 mol\% DVB, related to the total molar amount of monomers in the grafting solution $n_{tot} = n_{AMS} + n_{MAN}$.

The degree of grafting increased with the monomer concentration in the grafting solution, shown by the colored bars in the lower right graph in Figure 6.7. The IEC correlates quite well with the DoG and the conductivity is related to the swelling and hydration number, as mentioned above. Therefore, the monomer concentration in the grafting solution influenced the DoG, but did not change the \textit{ex situ} properties of the membrane. Addition of crosslinker to the grafting solution significantly changed the swelling and hydration number and consequently the conductivity. Whereas the absolute amount of crosslinker, 1.3 versus 5.2 mol\% DVB, did not change the hydration number, a decrease in swelling and conductivity was observed with an increasing crosslinker content. The effect of crosslinking on swelling and conductivity was stronger than expected from the diminished DoG.

6.1.3 Effect of molar ratio $R_{m, \text{graft}}$

The effect of the molar ratio in the grafting solution $R_{m, \text{sol}}$ on the degree of grafting DoG and molar ratio in the grafted polymer $R_{m, \text{graft}}$ is shown in paragraph 3.3.4 on page 60. The DoG decreased when the $R_{m, \text{sol}}$ was increased, due to the slower grafting kinetics of AMS compared to the kinetics of MAN in the graft polymerization. Therefore, the variation of the AMS concentration in the grafting solution provides the possibility to vary the AMS content in the grafted polymer $R_{m, \text{graft}}$. The IEC depends on the concentration of sulfonic acid groups, which were introduced by an electrophilic aromatic substitution $S_E\text{Ar}$, and subsequent hydrolysis, to the
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Figure 6.7: Monomer concentration dependent ion exchange capacity IEC (diamonds), conductivity $\sigma$ (triangles), hydration number (stars) and swelling (circles) for membranes based on AMS/MAN co-grafted FEP films, subsequently sulfonated and hydrolyzed, using 0 (blue), 0.5 (green) or 2.0 mol\% DVB (red) in the grafting solution. The degree of grafting DoG is denoted with bars in the lower right graph.

benzene rings of the AMS repeating units (Figure 6.8). Finally, an increasing molar ratio in the grafted polymer $R_{m,\text{graft}}$ causes an increase of the IEC, assuming the sulfonation of all AMS units in the grafted polymer, which corresponds to a degree of sulfonation of 100 %.

Figure 6.8: Incorporation of sulfonic acid groups to the AMS repeating units in the grafted poly[AMS-co-MAN] side chains by an electrophilic aromatic substitution $S_{E,Ar}$ (sulfonation) and subsequent hydrolysis.

The dependence of the ex situ membrane properties on the molar ratio in the grafting solution $R_{m,\text{sol}}$ is illustrated in Figure 6.9.

A decreasing overall DoG and increasing $R_{m,\text{graft}}$ were observed by increasing the molar ratio of the monomers in the grafting solution (cf. paragraph 3.3.4 on page 60). The decrease of the DoG from 40 to 33 %, observed for membranes prepared with $R_{m,\text{sol}}$ of 1.0 to 2.5, is accompanied by the increase of the $R_{m,\text{graft}}$ from 0.7 to 1.1. Therefore, the $DoG_{AMS}$ was approximately constant in the $R_{m,\text{sol}}$ range from 0.5 to 2.5 (22 to 19 %) and consequently the
Figure 6.9: Ion exchange capacity IEC (green), conductivity $\sigma$ (red), overall degree of grafting DoG (blue circles) and DoG$_{AMS}$ (blue diamonds), for FEP based AMS/MAN co-grafted, subsequently sulfonated and hydrolyzed membranes, prepared with different molar ratio of the monomers in solution $R_{m,\text{sol}}$. Their $R_{m,\text{graft}}$, swelling, and hydration number are denoted with the grey lines.

IEC did not change. The proton conductivity, depending on the concentration of the sulfonic acid groups and the water content of the membrane, was constant in the same range, which may result from a well-balanced swelling, hydration number, and IEC (as a measure for the total amount of ion exchange sites). The ex situ properties of the membranes, prepared with $R_{m,\text{sol}}$ below and above the discussed range (1.0 to 2.5), were mainly determined by the change of the DoG (overall and AMS only). In those areas the IEC depends linearly on the overall DoG and the conductivity becomes zero for membranes with overall DoG of less than 7 %. ETFE based membranes were prepared with equal DoG (34 %), but using various molar ratio in the grafting solution $R_{m,\text{sol}}$ (0.5, 1.0 and 3.0), to determine the ex situ properties in dependence of their $R_{m,\text{graft}}$ (Figure 6.10).

At a given DoG, the IEC and proton conductivity increase with the molar ratio in the grafting solution $R_{m,\text{sol}}$. The IEC dependence on the AMS concentration was confirmed by its strong correlation, at a constant DoG, with the $R_{m,\text{graft}}$ (grey line in Figure 6.10).

6.1.4 Effect of crosslinker concentration

The influence of the crosslinker was discussed in paragraph 6.1.1 and 6.1.2 combined with the influence of the DoG and monomer concentration, respectively. A series of membranes, based on grafted films, which was prepared in grafting solutions containing various crosslinker concent-
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Figure 6.10: Conductivity $\sigma$ (black) and ion exchange capacity IEC (red) of ETFE based membranes, with 34 % DoG, as a function of the monomer ratio in the grafting solution $R_{m,\text{sol}}$. The molar ratio in the grafted polymer $R_{m,\text{graft}}$ is denoted by the grey line.

Figure 6.11: Degree of grafting DoG, conductivity $\sigma$ and ion exchange capacity IEC for FEP-g-[AMSSA-co-MAN-co-DVB] as a function of the DVB concentration. The films were grafted for 13 h at 50 °C in solutions containing 30 vol% monomers ($R_{m,\text{sol}}=1.5$).

Pre-irradiated FEP films were grafted for 13 h in solutions, containing varied crosslinker concentration from 0 (uncrosslinked) to 5 mol% DVB, which resulted in DoG between 30 and 12 %.
The decreased DoG caused a decrease of the IEC and conductivity, whereas the reduction of
the latter is more pronounced due to its additional dependence on the swelling and hydration
number. The higher crosslinker content in the grafting solution yields higher crosslinking of the
grafted film and subsequently prepared membrane. Although the measurement of the crosslinker
concentration in the grafted polymer is not possible, its influence on the properties of grafted
films and subsequently prepared membranes (cf. Figure 5.10 on page 105) is obvious. The
enhanced crosslinking further reduces the swellability and consequently the hydration number,
thus the previous mentioned reduction of the proton conductivity is more strongly pronounced
than the decrease of the IEC.

The observed correlation of the reaction parameters with the \textit{ex situ} properties allow the prepa-
ration of radiation grafted membranes with tailor-made properties. Compared to membranes
based on styrene, the co-grafting of AMS and MAN offers a further degree of freedom to adjust
the \textit{ex situ} membranes properties. While grafting of one monomer allows for simpler character-
ization, since the degree of grafting is sufficient to determine the integral composition, a second
co-grafted monomer increases the analytical complexity. Indeed, the possibility to adjust the
IEC or conductivity almost independently on the DoG, e.g. by variation of the $R_{m,\text{graft}}$ (cf.
Figure 6.10), is counterbalancing the effort, needed to identify the ratio of the monomers in the
grafted film.

### 6.2 Fuel cell tests

Each fuel cell component has to obtain its final qualification in an operating fuel cell. Currently,
the demand on accelerated tests and the difficulty to deduce fuel cell properties under "standard"
operating conditions from results of accelerated tests, render fuel cell test under "standard" op-
erating conditions essential. The runtime of several hundred to a few thousand hours of fuel
cell test under "standard" conditions restricts the testing capacity. Furthermore, the robustness
of the entire test equipment, necessary to observe, control and support the operating fuel cell,
determines the quality, reliability and usability of the results obtained in fuel cell experiments.
Hence, statistical evaluation of fuel cell experiments are limited by the number of available test
stands, their reliability and the time required to perform the tests.

\textit{In situ} fuel cell experiments were performed following the test procedure in paragraph 2.6.2 on
page 42. The temperature, 60 °C during the start-up phase and 80 °C while operation of the
fuel cell, was achieved using four heating cartridges, integrated into the stainless steel end plates
of the fuel cell (type Q30, Figure 6.12).

The continuous supply of humidified (r.h. $H_2, O_2 = 100\%$) gases, with the required stoichiometry
$\lambda (H_2/O_2 = 1.5/1.5)$, was ensured by controlling the gas flow, using mass flow controllers, and
the humidification, by passing the reactant gases through water filled vessels, heated to the
corresponding temperature.

The degree of grafting and molar ratio in the grafted film (and membrane) dependent perfor-
mance of membranes was investigated. The results obtained for ETFE and FEP based mem-
branes are shown in the next paragraph. Membrane durability was investigated over 1000 h,
using three different membranes. The durability tests are shown in paragraph 6.2.2, while the
determination of the degradation after the fuel cell testing is subject of paragraph 6.2.3.
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6.2.1 Fuel cell performance

The performance of membranes was investigated in situ by evaluating their current density dependent cell voltage (polarization curve). The membrane assembled in the fuel cell was characterized after operating the FC 24 h at 60 °C, corresponding to the start-up of the fuel cell, 24 h at 80 °C (48 h total runtime), measuring the initial conditions at 80 °C, and 120 h at 80 °C (144 h total runtime), determining the performance of the fuel cell under steady state conditions. The fuel cell was characterized by recording a performance curve, an electrochemical impedance spectrum, and measuring the hydrogen crossover at the end of the test (144 h total). Additionally, a history plot was recorded, to capture the events taken place during the fuel cell test, cf. the fuel cell characterizations after approximately 24, 48 and 144 h in Figure 6.13. The high frequency resistance (HFR) was continuously measured and recorded once a day, shown by the red circles in Figure 6.13. The ohmic resistance, determined in EIS measurements, is denoted for comparison. The performance of different membranes was compared by their cell voltage $U_{\text{cell}}$ or current density $I$, extracted from the performance curves at 550 mA·cm$^{-2}$ or 0.6 V, respectively. The positions in the history plot (Figure 6.13) with various values for the cell voltage, measured within a short time, correspond to the dates where the polarization curves were recorded. The polarization curves and measured high frequency resistances for the membrane whose history plot was brought up in Figure 6.13 are shown in Figure 6.14. Electrochemical impedance spectra were recorded after 24 and 144 h, to compare the fuel cell properties at 60 °C and determine the membrane resistance at 80 °C, respectively. For the applicability of the high frequency measurement, only the membrane was assumed to contribute to the high frequency resistance (HFR). The HFR was measured using an AC milliohm meter (model 3566 from Tsuruga, Osaka, Japan) or by EIS. EI spectra of the membrane, whose history plot (6.13) and polarization curve (Figure 6.14) are discussed before, were recorded (Figure 6.15) and the polarization and ohmic resistances determined to 143 (60 °C) and 185 mΩ·cm$^2$ (80 °C) and 89 (60 °C) and 79 mΩ·cm$^2$ (80 °C), respectively.

The lower ohmic resistance at 80 °C may be correlated to an improved water balance at higher temperature [228], whereas the increase of the polarization resistance with the cell temperature and test-duration (120 h) may be correlated with a deterioration of the membrane-electrode interface (cf. [172]).

The characterization experiments were performed with uncrosslinked, AMS and MAN co-grafted,
CHAPTER 6. MEMBRANE PROPERTIES AND FUEL CELL TESTS

Figure 6.13: History plot of an in situ membrane characterization experiment at 500 mA·cm⁻². The curve was recorded for an uncrosslinked FEP-g-[AMSSA-co-MAN] membrane with 31 % DoG and \( R_{m, \text{graft}} = 0.95 \). The cell voltage (blue), high frequency resistance HFR (red) and ohmic resistance from EIS measurement (black) are plotted as a function of the fuel cell runtime.

![History plot of an in situ membrane characterization experiment at 500 mA·cm⁻².](image)

Figure 6.14: Polarization curves of a FEP-g-[AMSSA-co-MAN] membrane with 31 % DoG and \( R_{m, \text{graft}} = 0.95 \) (cf. Figure 6.13). The U/I-curves were recorded after operation of the fuel cell for 24 h at 60 °C and further 24 and 120 h at 80 °C (500 mA·cm⁻²).

![Polarization curves of a FEP-g-[AMSSA-co-MAN] membrane with 31 % DoG and \( R_{m, \text{graft}} = 0.95 \) (cf. Figure 6.13).](image)

subsequently sulfonated and hydrolyzed, FEP based membranes, with (31±1) % DoG, possessing a molar ratio of the monomers in the grafted polymer \( R_{m, \text{graft}} \) between 0.45 and 0.95. The cell voltage \( U_{\text{cell}} \) at 500 mA·cm⁻² was determined from the polarization curves after 24 h (60 °C), 48 and 144 h (both at 80 °C) and compared to the cell voltage of Nafion® 212 CS (Figure 6.16). The cell voltage after 24 h at 60 °C (black circles in Figure 6.16) and 24 h at 80 °C, corresponding to the initial state at 80 °C (overall runtime 48 h̅ₜᵢₜ), increased with the molar ratio in the grafted polymer \( R_{m, \text{graft}} \). However, Nafion® 212 CS showed the highest cell
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Figure 6.15: EI spectra recorded for a FEP-g-[AMSSA-co-MAN] membrane with 31% DoG and $R_{m, graft} = 0.95$ (cf. Figure 6.13), after operating (500 mA cm$^{-2}$) the fuel cell 24 h at 60 °C and 120 h at 80 °C (total time on operation: 144 h).

Figure 6.16: Cell voltage of FEP-g-[AMSSA-co-MAN] with different $R_{m, graft}$ at 550 mA cm$^{-2}$, operated in a FC for 24 h at 60 °C (black) and further 24 (blue) or 120 h (green) at 80 °C.

The influence of the degree of grafting on the in situ properties was determined with ETFE based membranes. The ex situ properties of the investigated membranes are shown as a function of the overall DoG in Figure 6.5 and in dependence of the $DoG_{AMS}$ in Figure 6.6. The polarization curves of radiation grafted membranes and Nafion® 212 CS are shown in Figure 6.17. The polarization curves of only four (of seven) ETFE based radiation grafted membranes are displayed in Figure 6.17, for reason of clarity. The current density $I$, determined at 0.6 V, and cell voltage $U_{cell}$, read out at 550 mA cm$^{-2}$, for the ETFE based membranes denoted in 6.6
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Figure 6.17: Polarization curves of ETFE-g-[AMSSA-co-MAN] with different DoG and $R_{m,\text{graft}}$ of (0.85±0.10). The curves were recorded after approximately 144 h at 500 mA·cm$^{-2}$, including 24 h operation at 60 °C and 120 h at 80 °C.

are shown in Figure 6.18. Characterizations were accomplished after 24 h at 60 °C and another 24 and 120 h at 80 °C. An increase of the cell voltage at 550 mA·cm$^{-2}$ and the current density at 0.6 V was observed for an increasing DoG. For both, the cell voltage (@ 550 mA·cm$^{-2}$) and current density (@ 0.6 V) of ETFE based membranes, no loss was observed during the fuel cell operation at 80 °C (approximately 100 h). Therefore, the loss in cell voltage of ETFE based, AMS and MAN radiation co-grafted membranes was less than observed for FEP based mem-
branes (Figure 6.16). The cell voltage (@ 550 mA·cm$^{-2}$) at 60 °C (24 h$_{tot}$) was lower compared to the initial cell voltage at 80 °C (48 h$_{tot}$) in all characterization experiments with ETFE based radiation grafted membranes. On the contrary, the cell voltage (@ 550 mA·cm$^{-2}$) of FEP based membranes decreased slightly when the operating temperature was increased. However, the base film influenced the initial cell voltage after at 80 °C (48 h$_{tot}$) marginally. The cell voltage at 550 mA·cm$^{-2}$ was almost unchanged for ETFE based membranes, during the fuel cell operation at 80 °C (approximately 100 h).

6.2.2 Membrane durability

Different durability targets were set by the U.S. Department of Energy (DOE), Japan’s Ministry of Economy, Trade, and Industry (METI), and the European Commission. The U.S. DOE Office of Energy Efficiency and Renewable Energy’s in the "Hydrogen, Fuel Cells and Infrastructure Technologies" (HFCIT) program supports the research and technology development efforts, necessary for fuel cell technology to become commercially viable. The durability of PEFC for stationary applications were specified to 40000 h, over the full range of external temperatures (-35 °C to +40 °C) and with <10 % rated power degradation at the end of fuel cell life. The lifetime target for mobile application, with cycling and <5 % rated power degradation at the end of fuel cell life, is 5000 h. New Energy and Industrial Technology Development Organization (NEDO) of Japan’s METI set their target for the lifetime of fuel cells in vehicles to >5000 h, at a vehicle efficiency of 60 % and an operating temperature >90-100 °C. The European Hydrogen and Fuel Cell Technology Platform (HFP) aims for an efficiency of >40 % on the New European Drive Cycle, by costs of 100 Euros/kW and lifetimes for cars and buses of 5000 h and 10000 h, respectively [135].

A key issue in all FC programs, independently of their administration, is the durability, either under constant operating conditions, used for stationary applications, or with cycling, intended for mobile application. Therefore, long term in situ testing of fuel cell components is essential to determine the durability. The lifetime is accessible from durability experiments, if the end of life criterion is known. Two basically different procedures are possible to perform durability experiments. On the one hand, the fuel cell is operated until failure or reaching the end of life criterion. This method bears the risk of complete degradation of the tested component, which renders the post mortem analysis impossible. On the other hand, the durability test is stopped after a certain time, notably before failure, and the degree of degradation is investigated. The drawback of this procedure is the difficulty to extrapolate the rate of degradation within the chosen runtime, until the experiment was stopped, to the end of life criteria, as requested e.g. by the DOE.

In the present work the second procedure was chosen, leaving the possibility open to compare radiation grafted membranes with different compositions. The procedure of durability experiments is explained in paragraph 2.6.2 on page 42. The history plots of such durability tests are shown in Figures 6.19 and 6.20 for an uncrosslinked and a diisopropenylbenzene (DIPB) crosslinked membrane, respectively. During the durability test, the fuel cell was operated at constant current density (500 mA·cm$^{-2}$) and the cell voltage was recorded. Additionally, the membrane resistance, measured either by the current pulse method (Figure 6.19) or at high frequency (1 kHz) using an AC milliohm meter (Figure 6.20), is denoted in the figures and compared to the ohmic resistance, determined from EI spectra.
Figure 6.19: History plot of the cell voltage $U_{\text{cell}}$ (blue) of a fuel cell operated at constant current density (500 mA·cm$^{-2}$). The high resistance of the FEP-g-[AMSSA-co-MAN] membrane (31% DoG, $R_{m, \text{graft}} = 0.78$), was determined using the current pulse method and EIS, are denoted in the graph with the black diamonds and red circles, respectively.

Figure 6.20: History plot of the cell voltage $U_{\text{cell}}$ (blue) of a fuel cell operated at constant current density (500 mA·cm$^{-2}$). The high frequency resistance of the FEP-g-[AMSSA-co-MAN-co-DIPB] membrane (31% DoG, $R_{m, \text{graft}} = 1.03$), was determined by EIS and using an AC milliohm meter model 3566 from Tsuruga, are denoted in the graph with the black diamonds and red circles, respectively. A crosslinker concentration of 12 mol% DIPB was used in the grafting solution.

The cell voltage of the uncrosslinked membrane (Figure 6.19) decreased by 55 mV during the first 1150 h of operation, which corresponds to 8% of the initial cell voltage, measured after approximately 100 h at 80 °C (690 mV). Ca. 15 mV (2%) of this loss was attributed to a failure of the test equipment after 840 h. Due to the failure, the fuel cell was operated under open circuit voltage (OCV) for almost 20 h. The initial membrane resistance at 80 °C of 82 mΩ·cm$^2$
increased to 110 mΩ·cm² during the 1150 h of operation. An increase of 12 mΩ·cm² was observed during the operation under OCV (20 h), which exceeded the increase of the membrane resistance, determined to 8 mΩ·cm² within the first 840 h. The ohmic resistance, determined by EIS, was (98±2) mΩ·cm² for the first 840 h, increased to 118 mΩ·cm², during the period at operation under OCV, and reached 136 mΩ·cm² at the end of test (1150 h). Accelerated aging of membranes under OCV conditions is known [203] and attributed to enhanced hydrogen crossover [229, 230]. The incomplete reduction at the cathode, in the presence of H⁺, may act as source for hydrogen peroxide, cf. equation 1.38 on page 27, which initiate the membrane degradation.

No failure was observed during the durability test of the DIPB crosslinked membrane (Figure 6.20). The cell voltage decreased, over the entire test period of 1000 h at 80 °C, from 692 to 689 mV (∆U_{cell} = 0.4 %). Within the same duration, the high frequency resistance, measured at 1 kHz with a Tsuruga AC milliohm meter, increased by 8 mΩ·cm² from 120 to 128 mΩ·cm², while the ohmic resistance, measured by EIS, remained at (100±4) mΩ·cm². The hydrogen crossover of the uncrosslinked and DIPB crosslinked membrane increased by 140 % and 16 %, respectively, within the experiment.

The history plot of a further durability test, where an uncrosslinked membrane (31 % DoG, R_{m, graft} = 1.13) was assembled, is not shown. The initial cell voltage of 732 mV decreased by 80 mV (11 %) within the runtime of 1050 h. The experiment was interrupted for almost 70 h by a test stand failure, which caused FC operation at OCV for the corresponding period. The accurate contribution of the failure to the voltage loss and increase in membrane resistance was not calculated, due to a partial recovery of the fuel cell voltage within the next 150 h after the operation of the FC at OCV. The membrane resistance R_{mem} was determined with the current pulse method and by EIS (values denoted in brackets). The membrane resistance was approximately constant within the first 450 h at (97±3) mΩ·cm² ((98±4) mΩ·cm²). The R_{mem}-step, observed after operating the FC at OCV for 70 h, was 60 mΩ·cm² (68 mΩ·cm²), of which 32 mΩ·cm² (22 mΩ·cm²) were recovered within the following 150 h. The final membrane resistance was calculated to 189 mΩ·cm² (142 mΩ·cm²), resulting in an overall increase of 95 mΩ·cm² or 101 % (60 mΩ·cm² or 45 %).

The polarization resistance is accessible from electrochemical impedance spectra. A selection of EI spectra, recorded for the three membranes discussed before, are compared in Figure 6.21. The polarization resistance of the DIPB crosslinked membrane was little influenced within the duration of the durability test (∆R_{pol} = 11 mΩ·cm²), while an increase of the polarization resistance ∆R_{pol} of 50 and 150 mΩ·cm² was observed for the uncrosslinked membranes with R_{m, graft} of 0.78 and 1.13, respectively.

Crosslinking significantly increased the in situ stability, concerning the loss of cell voltage and the increase of the membrane and polarization resistance. This result is in agreement with the results obtained in [172] for styrene based, DVB crosslinked membranes and the observations made in [162] for poly[AMS-co-MAN] based membranes, crosslinked with DVB and DIPB.

### 6.2.3 Post mortem analysis and evaluation of the results

The membrane durability, investigated in the experiments described in the previous paragraph, was discussed based on the changes of the cell voltage and ohmic resistance. The investigation of properties of a single component, assembled in an operating fuel cell, is very complex, con-
CHAPTER 6. MEMBRANE PROPERTIES AND FUEL CELL TESTS

Figure 6.21: Comparison of EI spectra of two uncrosslinked membranes with 31% DoG and $R_{m, \text{graft}}$ of 0.73 and 1.13, respectively, with the EI spectra recorded for a DIPB crosslinked membrane (31% DoG, $R_{m, \text{graft}} = 1.03$).

cerning its multi component alignment. Hence, the analysis of the disassembled membrane after the durability test (post mortem) was chosen to investigate its degradation.

The optical comparison of the uncrosslinked grafted film, the basic material of the above discussed membrane with $R_{m, \text{graft}} = 1.13$, with the corresponding pristine membrane (dry, protonated form) and the disassembled membrane (dry, protonated form), is shown in Figure 6.22.

A change of the membrane appearance after the fuel cell test is observed apparent by its partial discoloration. To highlight the disappearance of turbidity, a black background was used to enhance the contrast. The appearance of clouding during the graft polymerization was shown in

Figure 6.22: Picture of the grafted film, pristine membrane and disassembled, 1000 h at 500 mA·cm$^{-2}$ tested membrane with 31% DoG and $R_{m, \text{graft}} = 1.13$.

paragraph 3.2.1, cf. Figure 3.5 on page 49, as a function of the water content in the grafting solution. The transparency of the fuel cell tested membrane, observed in almost 50% of the active area in Figure 6.22, was attributed to the a change in morphology. The transparent region looks similar to the pristine base film, whereas the grafted film, pristine and used membrane (outside the active area) showed clouding due to the graft polymerization in the presence of 20% water.

The degradation was quantified using FTIR spectroscopy, which was found to be a suitable method for post mortem analysis of disassembled membranes [172, 181]. The degradation was calculated based on the intensity of the SO stretching vibration at 1008 cm$^{-1}$, which is correlated to the concentration of sulfonic acid groups and, accordingly, to the IEC. The decrease in signal intensity, measured for the pristine $I_{\text{pristine}}$ and used membrane $I_{\text{used}}$, corresponds to the
loss of sulfonic acid groups within the runtime of the durability experiment. The degradation was calculated according to

\[
\text{Degradation} = \frac{I_{\text{pristine}} - I_{\text{used}}}{I_{\text{pristine}}} \cdot 100\% \quad (6.1)
\]

The degradation was investigated locally resolved (Figure 6.23), by sub-dividing the membrane in 49 squares (1 x 1 cm) and recording an FTIR spectrum in each of the squares. 25 measurements were located within in the active area, encircled by 24 measurements in the inactive membrane area, which was not in contact with the electrode during the fuel cell experiment.

Figure 6.23: Post mortem investigation of two uncrosslinked membranes, 31 % DoG and \(R_{m, \text{graft}}\) of 0.73 and 1.13, respectively, and a DIPB crosslinked membrane (31 % DoG, \(R_{m, \text{graft}} = 1.03\)). The degradation was calculated based on the decrease of the SO vibration at 1008 cm\(^{-1}\) and is denoted in percent of the initial intensity, measured for the pristine membrane.

The intensity of the SO stretching vibration in each of those 49 positions was correlated to the initial intensity, given by the average of ten measurements on the pristine film. The locally resolved degradation was calculated for the three membranes, tested concerning their durability, and is shown in Figure 6.23 as color coded two-dimensional degradation map. The highest degradation was observed for the uncrosslinked membranes, close to the hydrogen inlet. The membrane with an \(R_{m, \text{graft}}\) of 1.13 showed degradation up to 100 % on the active area, congruent with the transparent area, shown in Figure 6.22. The inactive area was degraded less than 12 %. The membrane with an \(R_{m, \text{graft}}\) of 0.78 showed also high degradation (>84 %) close to...
the H₂ inlet, but with a remarkably smaller area compared to the membrane with an \( R_{m, \text{graft}} \) of 1.13. The lowest degradation was determined for the DIPB crosslinked membrane. Nevertheless, higher degradation was observed close to the hydrogen inlet. It is worth mentioning that the FTIR spectroscopic investigation was performed in transmission mode. Therefore, the differentiation between the anode and cathode side was not possible and the measured intensity decrease and calculated degradation is an integral measure over the entire membrane thickness. First experiments, using confocal Raman microscopy, failed due to the pronounced clouding of the membranes and the correlated scattering losses. The signal intensity of the scattered Raman light was below the limit of detection, even focusing 2-3 \( \mu \text{m} \) below the membrane surface.

To compare the present result with degradation results, obtained in previous durability tests, the degradation rate was calculated. Therefore, the degradation, averaged for the active area of the membrane, was divided by the runtime of the durability test. This methodology does not account for the local degradation or its homogeneity, but allows the comparison of the averaged degradation of membranes, consisting of different components, cf. Figure 6.23. In previous investigations, the degradation was determined by the IEC loss of the membrane in the active area. Therefore, the active area was cut, the protons exchanged in potassium chloride solution, and the proton concentration in the solution determined by titration with potassium hydroxide solution to pH 7. The averaged degradation and degradation rate, denoted in brackets, were calculated to 56.4 % (0.054 % \( \cdot \text{h}^{-1} \)), 39.8 % (0.034 % \( \cdot \text{h}^{-1} \)) and 16.5 % (0.014 % \( \cdot \text{h}^{-1} \)) for the uncrosslinked membranes with \( R_{m, \text{graft}} \) of 1.13, \( R_{m, \text{graft}} \) of 0.78 and the DIPB crosslinked membrane with \( R_{m, \text{graft}} \) of 1.03, respectively.

The degradation was observed to be substantially higher close to hydrogen inlet, which is in accordance with results obtained in [100, 162]. However, these observation is contradictory to earlier findings with styrene based membranes, where the higher degradation was observed close to the oxygen inlet [92].

### 6.3 Conclusion

The time necessary to perform \textit{in situ} fuel cell experiments and the restriction due to a limited number of available test stands require the \textit{ex situ} characterization of membrane properties. The ion exchange capacity is an integral measure for the concentration of sulfonic acid groups in the membrane. Its correlation with the degree of grafting was known for styrene based membranes [71, 75, 143] and is shown in the present work for AMS/MAN co-grafted membranes, in consideration of the molar ratio of the monomers in the grafted polymer \( R_{m, \text{graft}} \). The influence of the \( R_{m, \text{graft}} \) is less than that of the \textit{DoG}. This is related to the adjustable \( R_{m, \text{graft}} \) range, which was determined in paragraph 3.3.4 on page 60 to vary from approximately 0.5 to 1.1. On the other hand, the \textit{DoG} is predominantly limited by the required mechanical properties of membranes (cf. Figure 5.10). The IEC increased, at a given \textit{DoG}, with an increasing \( R_{m, \text{graft}} \), based on the enhanced AMS content, which yields, after sulfonation and hydrolysis, a higher sulfonic acid group concentration (AMSSA). The influence of crosslinker (DVB) on the IEC was found to be weak, whereas the proton conductivity is significantly reduced with an increasing crosslinker concentration. Proton conductivity depends, beside the density of sulfonic acid groups and therefore the concentration of protons, on their mobility. Since the proton mobility is strongly correlated to the hydration level of the membrane [224, 225], the decrease of proton
conductivity in the presence of crosslinker is attributed to the reduced swelling and hydration number. The swelling was observed to rather correlate with the total amount of grafted component (DoG) than with its accurate composition (Rm, graft), which corroborates the stronger correlation of the proton conductivity with the overall DoG instead of the DoGAMS.

Hardly any structure-performance correlations, relating in situ determined properties with the composition of the corresponding membrane, were reported in the literature. Systematic investigations, to correlate the DVB content in the grafting solution with the performance of the corresponding membranes in fuel cells, were performed with styrene grafted FEP [149] and ETFE [92, 153] based membranes. The influence of the degree of grafting on the fuel cell performance was discussed for AMS/MAN co-grafted membranes, based on ETFE (25 µm) films. The cell voltage was extracted from polarization curves at 550 mA·cm⁻², recorded after 24 h at 60 °C (FC start-up) and after another 24 (initial conditions) and 120 h (performance) at 80 °C. The cell voltage after the FC start-up (60 °C) and after 24 h at 80 °C (initial conditions) increased slightly, from 0.56 to 0.64 V and from 0.64 to 0.68 V, respectively, when the degree of grafting increased from 21 to 50 %. Their cell voltage at 550 mA·cm⁻² after 144 h (120 h at 80 °C) increased from 0.62 to 0.67 V with an increasing DoG. Therefore, no deterioration of the membrane performance was observed within the characterization experiment at 80 °C. The influence of the molar ratio of the monomers in the radiation grafted membrane on the fuel cell performance was investigated, using FEP based membranes with 31 % DoG and Rm, graft between 0.45 and 0.95. The cell voltage at 60 °C (24 h) and after further 24 h at 80 °C increased with the Rm, graft. The deviations from the (expected) linear correlation between the Ucell and the Rm, graft may be due to errors, associated to the FTIR spectroscopic determination of the Rm, graft. However, the cell voltage after 144 h was significantly lower compared to the initial cell voltage after 48 h and did not correlate with the Rm, graft. Although a proper correlation of the in situ performance with the Rm, graft was not possible, the performance of FEP based membranes increased by trend with the Rm, graft.

In general, the observed start-up behaviour of uncrosslinked ETFE and FEP based radiation grafted membranes was completely different. Whereas the cell voltage increased for ETFE based membranes with an increasing operating temperature from 60 to 80 °C, a decrease was observed for FEP based membranes for the same temperature increase. The ohmic and polarization resistance, determined from EI spectra, showed different trends for FEP and ETFE based, AMS/MAN co-grafted membranes. Whereas the polarization resistance of FEP based membranes increased significantly and the ohmic resistance was slightly reduced by the increased temperature, ETFE based membranes showed, during the same temperature increase, a significant decrease of the ohmic resistance (>50 mΩ·cm⁻²) and an almost unchanged polarization resistance. While the observed trends for the ohmic and polarization resistance of FEP based membranes may result from a slightly improved water balance and a deterioration of the membrane-electrode interface [228, 172] at higher temperature and, with advanced operating time, ETFE based membranes may benefit from an strongly enhanced water balance, accompanied with an almost unchanged membrane-electrode interface.

The effect of crosslinker on the in situ performance was not systematically investigated. Nevertheless, the comparison of characterization experiments, performed with FEP and ETFE based, AMS and MAN co-grafted uncrosslinked membranes with 50 % DoG with corresponding membranes prepared in the presence of 1.3 mol% DVB in the grafting solution, showed an almost
unchanged cell voltage (@ 550 mA·cm$^{-2}$) but a markedly reduced current density (@ 0.6 V). The cell voltage at 550 mA·cm$^{-2}$ after 24 h was slightly higher for FEP based membranes (0.70 V) compared to ETFE based membranes (0.64 V), whereas the difference disappeared (0.68±0.02 V independent of the composition) at 80 °C. The current density (@ 0.6 V) of the uncrosslinked/DVB crosslinked membrane was higher after 24 h at 60 °C (1100/900 mA·cm$^{-2}$) for FEP based membranes than for ETFE based membranes (700/700 mA·cm$^{-2}$), whereas the discrepancy became less pronounced at 80 °C, denoted by 1200/1000 mA·cm$^{-2}$ for FEP based and 900/800 mA·cm$^{-2}$ for ETFE based membranes.

Durability experiments were performed with two uncrosslinked FEP based, AMS and MAN co-grafted membranes, possessing 31 % DoG and $R_m, graft$ of 0.78 and 1.13, respectively, and the corresponding DIPB crosslinked membrane, prepared in a solution containing 12 mol% DIPB (31 % DoG, $R_m, graft$ = 1.03). The influence of DIPB crosslinking on the stability of the membrane, under the condition of an operating fuel cell (constant current density), was clearly shown by the significantly reduced degradation, cf. Figure 6.23 on page 129. Uncrosslinked membranes showed complete loss of the graft component close to the hydrogen inlet. The calculation of the averaged degradation was performed to compare the results of the durability tests with previous investigated data of in situ stability tests (Figure 6.24). The runtime of the experiment (black bars) and the calculated average degradation rate (red bars) are denoted in Figure 6.24. It is worth mentioning that neither the homogeneity of the degradation nor incidents, with negative impact of the membrane performance (e.g. OCV conditions), were considered, using the temporally and laterally averaged degradation for comparison.

![Figure 6.24: Comparison of the degradation rate (% IEC loss per hour) and corresponding run time of PSI membranes from different generations. Generation 1 is represented by FEP based, styrene grafted membranes, uncrosslinked and co-grafted with DVB, and generation 2 by FEP based AMS/MAN co-grafted membranes, uncrosslinked and DVB or DIPB crosslinked. A ETFE based, styrene/MAN co-grafted (generation 2) membrane is shown for comparison. Excepting the tests of FEPgSt (failed), FEPgScoDVB (evaluated within the first 4000 h) and FEPgAMScoMAN (60 °C) (failed) all tests were stopped after the denoted runtime.](image-url)
6.3. CONCLUSION

The degradation rate of uncrosslinked FEP based membranes decreased when polystyrene as graft component was replaced by an AMS/MAN copolymer. The further decrease of the degradation rate for AMS/MAN co-grafted FEP based membranes was attributed to the preparation under optimized reaction conditions, e.g. the reduction of the grafting temperature to 50 °C. For comparison, an uncrosslinked ETFE based, styrene/MAN co-grafted membrane, recently investigated by H. Ben youcef, is denoted in Figure 6.24. Apart from the used base film, whose influence on the stability was not explicitly investigated, the co-grafting of styrene with MAN demonstrated a significant improvement of the stability, shown in Figure 6.24 by an averaged degradation rate in same order than observed for FEP based, AMS/MAN co-grafted membranes. The influence of crosslinking on the degradation rate, determined for membranes of generation 1 by comparing the FEP based, styrene grafted and the styrene/DVB co-grafted membranes, was almost two orders of magnitude. A similar degradation rate was determined for crosslinked membranes, disregarding their composition. Therefore, the influence of crosslinking on the degradation rate is less pronounced for AMS/MAN co-grafted membranes, even though the crosslinker concentration is still not optimized for these generation 2 membranes.

In order to render the influence of crosslinker on the performance and stability of AMS/MAN co-grafted membranes more precise, the in situ characterization of membranes with various crosslinker content is essential. Based on the results of these characterization tests, promising membrane candidates have to be investigated in durability tests, to finally investigate their degradation and the degradation rate.

The location of the highest degradation was found to be different for styrene and AMS/MAN based membranes. This suggests the existence of a different degradation mechanism, depending on the used monomer(s). The degradation mechanism was beyond the scope of the present work, but a first hint for the hydrolysis of the cyano group of the MAN repeating unit was observed from FTIR spectroscopic investigations. However, the knowledge of the degradation mechanism could be a helpful support to further improve the stability of membranes, by using appropriate monomers to suppress the degradation by the corresponding mechanism.
Chapter 7

Conclusion and Outlook

This dissertation continued the work carried out by M. Šlaski during his doctoral thesis at PSI [162]. He investigated the graft copolymerization of α-methylstyrene (AMS) and methacrylonitrile (MAN) onto pre-irradiated poly(tetrafluoroethylene-co-hexafluoropropylene)(FEP) base films at 60 °C and found an isopropanol-water mixture as best solvent concerning the achievable degree of grafting (DoG). The highest AMS content in the grafted copolymer in isopropanol/water as solvent was observed using 30 vol% of the monomers in the grafting solution. The AMS/MAN co-grafting onto FEP base films was compared at temperatures of 60 and 50 °C, based on the DoG. For short reaction time (<10 h) a similar behaviour at both temperatures was observed, while for longer reaction time the DoG at 50 °C was significantly higher. This result was attributed by M. Šlaski to the higher radical concentration at the higher temperature, favouring the termination by recombination at 60 °C. The addition of less than 1.5 vol% crosslinker, divinylbenzene (DVB) or diisopropenylbenzene (DIPB), to the grafting solution yielded a slightly increased DoG, whereas the DoG was significantly reduced for higher crosslinker content. Fuel cell experiments were performed with different FEP based membranes. Here, the increased stability of AMS/MAN grafted membranes, compared to styrene grafted membranes, was demonstrated and a reduced degradation observed when DVB was used as crosslinker.

Conclusion

The implementation of AMS and MAN in the graft polymerization resulted in a strong improvement of the in situ stability of the corresponding membranes. Nevertheless, important questions concerning the grafting reaction, composition of the grafted films, and properties of grafted films and the subsequently prepared membranes remained unanswered. Therefore, the purpose of the present work was the validation of the membrane preparation by radiation co-grafting of AMS and MAN, the development of analytical methods suitable to determine the homogeneity of grafted films, and the investigation of the crosslinker influence on the mechanical and chemical properties of membranes.

Each parameter relevant for the preparation of ion exchange membranes by the pre-irradiation of FEP or poly(ethylene-alt-tetrafluoroethylene) (ETFE) base films, their use as substrate, able to initiate a polymerization reaction in the graft copolymerization of AMS and MAN, and the subsequent sulfonation and hydrolysis of the grafted films, influences the composition and properties of the grafted films and subsequent membranes. The DoG and molar ratio of the
monomers in the grafted polymer \((R_{m, \text{graft}})\) are influenced to a greater or lesser extent by the used base film, applied irradiation dose, and solvent, temperature, monomer concentration and ratio of the monomers in the grafting solution \((R_{m, \text{sol}})\). The co-grafting of AMS and MAN onto FEP proceeds with a comparatively low rate and shows a strong temperature dependence compared to the grafting of styrene onto FEP, indicated by the higher activation energy \(E_a\) for the propagation of 101 kJ·mol\(^{-1}\) compared to 28 kJ·mol\(^{-1}\), respectively. The grafting efficiency, the ratio of the apparent initial polymerization rate and the termination rate, decreases with increasing temperature due to the high \(E_a\) of the termination by recombination (132 kJ·mol\(^{-1}\)). The initial polymerization rate decreases significantly with an increasing \(R_{m, \text{sol}}\), indicating the slower polymerization of AMS compared to the propagation of MAN.

The faster polymerization of MAN only, compared to the copolymerization of AMS and MAN, was the prerequisite for the preparation of grafted films with pronounced grafting fronts and their investigation using confocal Raman microscopy. Hence, the grafting fronts are present in FEP-\(g\)-MAN films up to 22 \% DoG. To achieve a homogeneous distribution of MAN over the entire film thickness, a degree of grafting of at least 30 \% DoG is necessary. Fortunately, the distribution of all components present in FEP-\(g\)-[AMS-co-MAN] is homogeneous, even at small DoG (15 \%). The homogeneity is an important requirement to ensure through-plane proton conductivity in the subsequently prepared membranes. Another requirement to achieve proton conductivity is a sufficient concentration of ion exchange sites, corresponding to the sulfonic acid groups in the investigated membranes. This concentration is related to the grafted amount of AMS (DoG\(_{\text{AMS}}\)), since the benzene ring, present in the AMS repeating unit, will carry the sulfonic acid group after the sulfonation of the grafted films. The ratio of the monomers in the grafted film \((R_{m, \text{graft}})\) was usually determined using FTIR spectroscopy, but is also accessible by CP MAS \(^{13}\)C NMR spectroscopy. In contrast to FTIR spectroscopic measurements, calibration is not required in NMR spectroscopic investigations, which is an advantage in the determination of graft components in a variable matrix of changing base films, graft components (AMS, MAN, DVB, DIPB) and their \(R_{m, \text{graft}}\).

Failure of membranes in fuel cell tests is usually attributed to chemical degradation or mechanical malfunction or combinations of both. The \textit{ex situ} investigation of a single failure mode, under well-defined conditions, and its correlation with \textit{in situ} membrane stability is important to enable high sample throughput in the optimization of membrane properties. Therefore, tensile test of grafted films and membranes were performed in various climatic conditions, which necessitated the commissioning and validation of a climatic chamber. The mechanical properties of grafted films, namely the elongation at break, tensile strength and Young’s modulus, at room temperature and ambient humidity are negatively influenced by irradiation and grafting. However, the Young’s modulus of membranes at fuel cell relevant climatic conditions (80 \(^\circ\)C, 80 \% relative humidity) is less influenced by irradiation and grafting compared to those of the corresponding grafted films. This is attributed to the swellability of membranes under high humidity condition, and the plastification effect of water, which almost counterbalances the negative effects of irradiation and grafting. The swelling of membranes increases with the DoG. Compared to Nafion® 212CS, the swelling of AMS/MAN-grafted ETFE and FEP based membranes is less pronounced, possessing DoG up to 46 and 35 \%, respectively.

\textit{Ex situ} mechanical properties are only one criterion for the usability of membranes in membrane electrode assemblies and their subsequent test in fuel cells. Other fuel cell relevant properties,
e.g. the ion exchange capacity, proton conductivity and hydration number, increase with the \textit{DoG}. The IEC is strongly correlated with the \textit{DoG}_{AMS} due to the location of the sulfonic acid groups at the AMS repeating units, whereas the proton conductivity is correlated with the \textit{DoG}. The latter is attributed to the dependence of the proton conductivity on the water content, which is also correlated to the \textit{DoG}. For the same reason, the IEC is not influenced by crosslinking, whereas the proton conductivity decreases with an increasing crosslinker content and therefore reduced swelling and water content of the membrane.

The cell voltage at a given current density of 500 mA cm\(^{-2}\) was used to evaluate the \textit{in situ} performance of membranes, which was the varied parameter in a series of fuel cell tests. The cell voltage increases approximately 8 \% when the \textit{DoG} is increased by a factor of 2.4. The cell voltage at constant current density increases by trend with an increased \(R_{m, 	ext{graft}}\). The durability of FEP based, AMS/MAN co-grafted membranes, investigated within 1000 h of operation under constant load, increases with crosslinking. A comparison of the degradation rate, determined in the active areas of the tested membranes, showed a reduced degradation of AMS/MAN co-grafted membranes, prepared at 50 °C (0.035 \% \cdot h\(^{-1}\)), compared to styrene grafted membranes (1.59 \% \cdot h\(^{-1}\)) and AMS/MAN co-grafted membranes, prepared at 60 °C (0.057 \% \cdot h\(^{-1}\)). The use of DIPB as crosslinker for AMS/MAN co-grafted membranes (0.014 \% \cdot h\(^{-1}\)) affects the degradation rate to the same extent, as previously shown for DVB crosslinking of AMS/MAN co-grafted membranes (0.015 \% \cdot h\(^{-1}\)) and less as shown for styrene based membranes (0.010 \% \cdot h\(^{-1}\)), compared to the corresponding uncrosslinked membranes.

From an application point of view, the most important finding is the preparation of grafted films and subsequent membranes with various \textit{DoG} and independently varied \(R_{m, 	ext{graft}}\). The different relation of the \textit{ex situ} membrane properties IEC and proton conductivity with those characteristics (\textit{DoG}, \(R_{m, 	ext{graft}}\)) allows the preparation of tailor-made membranes. Hence, the \textit{DoG} can be adjusted and the membrane properties modified by fine-tuning of the AMS content via the \(R_{m, 	ext{graft}}\).

**Outlook**

The AMS/MAN co-grafting was studied due to the higher oxidative stability observed for membranes, based on FEP films grafted with AMS and MAN [162]. Therefore, the kinetics of the co-grafting, the homogeneity of the co-grafted films, the influence of varied reaction parameters during the grafting on the mechanical properties, and the \textit{ex situ} and \textit{in situ} properties of AMS/MAN co-grafted membranes were investigated.

One can speculate, that the cyano group present in co-grafted membranes may act as hydroxyl radical scavenger and therefore enhance the lifetime of MAN or AN co-grafted membranes in the fuel cell environment. Furthermore, the electron lone pair may enable the CN group to serve as ligand and therefore bind impurity metal-ions and consequently reduce the radical formation by Fenton’s chemistry. Nevertheless, the need for the methyl protected alpha-position to either the benzene ring in AMS or the cyano group in MAN has to be further proven by replacing AMS with styrene in the co-grafting and, similarly, MAN with acrylonitrile. The results of those experiments, which are currently performed in our group, in comparison with the previously reported data obtained for styrene based membranes, will provide further insights into the importance of the methyl protection of the alpha-positions and the contribution of the cyano group to the enhanced stability of membranes, based on uncrosslinked AMS/MAN co-grafted
films. However, the results will strongly affect the further progress in membrane preparation by pre-irradiation grafting at PSI. If the methyl protection of both monomer is needless, the further development has to be focused on the optimization of styrene/AN co-grafted membranes, while the necessity of the protected alpha-position in both monomers will provoke the continuance of the present work.

The key issue in further development of AMS/MAN based membranes will be the stabilisation of the membrane by crosslinking of the grafted polymer. From the fuel cell experiments, performed in the present work, it may be speculated that the effect of crosslinking on the in situ stability exceeds the effect of the protected alpha-position to the benzene ring, taking the non-optimized crosslinker concentration in the case of AMS/MAN co-grafted membranes into consideration. Therefore, a more detailed study of the influence of crosslinker on the ex situ and in situ stability has to be performed in order to determine the optimum crosslinker content. Moreover, DVB and DIPB were used as crosslinker in the present work, whereas both consist of a disubstituted benzene ring and exhibit an intrinsic inflexibility. Therefore, the swelling, hydration and accordingly the conductivity is reduced by crosslinking. The use of aliphatic crosslinkers, possessing a certain chain length, should circumvent the strong reduction of swelling. Thus, an aliphatic crosslinker may combine the advantage of a three dimensional network, holding back fragments produced by chain scission, with a sufficiently high swelling and concomitant conductivity. However, DVB crosslinking was shown to be important to enhance the ex situ stability of styrene based membranes in hydrogen peroxide solution at 80 °C. The ex situ treatment of AMS/MAN co-grafted membranes with hydrogen peroxide will confirm or disprove the assumed chemical stability enhancement by the substitution of styrene for AMS. Even more significance will be achieved when the degradation of styrene/MAN co-grafted membranes will be used for comparison. Hence, the separation of the effects on the chemical stability of MAN and AMS in the grafted membrane, compared to styrene grafted membrane, will be possible.

The homogeneous distribution of the graft components, AMS and MAN, over the thickness of uncrosslinked, grafted films was shown by confocal Raman microscopy. Due to the low concentration of crosslinker in the grafted film, the detection and therefore the calculation of its distribution were not possible. The crosslinker concentration and its distribution in the grafted film and subsequent membrane are of utmost importance to understand and interpret the obtained crosslinker effects on the mechanical properties and in situ stability. First investigations with highly crosslinked films using CP/MAS $^{13}$C NMR spectroscopy indicate the usability of the method to determine the integral composition. The NMR spectroscopic measurement of membranes, swollen in heavy water, may enhance the mobility of the grafted polymer chains and therefore reduce the anisotropy and the correlated effects. This may enable the detection and quantification of crosslinker even in weakly crosslinked membranes.

The ex situ measurement of mechanical properties at conditions closely related to the fuel cell application, yielded results which showed different trends as those obtained with potassium exchanged membranes at room temperature and ambient conditions. The influence of the base film on the mechanical properties of grafted films is significant (rt, ambient humidity). The mechanical properties of membranes, prepared with different base films, measured at fuel cell relevant condition, will provide a piece of the puzzle to understand the influence of the base film on the stability of radiation grafted membranes. More experiments may facilitate the correla-
tion of the decrease of the degradation rate in durability experiments of crosslinked membranes with the mechanical properties at elevated humidity, where the crosslinker becomes important to enhance the tensile strength and Young’s modulus and attenuate creep.

The degradation of AMS/MAN co-grafted membranes in fuel cell tests, investigated by FTIR spectroscopy, was higher close to the hydrogen inlet. In contrast to the observation made for AMS/MAN co-grafted membranes, the degradation of styrene based membranes was higher close to the oxygen inlet. The degradation was measured over the entire thickness and across the diameter of the IR beam, not distinguishing between channel and land. Therefore, a locally resolved determination of the degradation, differentiating between anode, cathode, channel and land, will provide more insights and may enable the formulation of a degradation mechanism for AMS/MAN co-grafted membranes.

A more general concept of membrane stabilization, followed in literature, is based on the use of inorganic additives, e.g. SiO$_2$ or TiO$_2$, to enhance the water management by retaining the formed water in the membrane. Most of the previously reported attempts were doomed to failure by the leaching out of those particles. Hence, the stabilization of the particles by complexation or even by in situ formation of silicate-like or titanate-like structures may be the road to success. Crosslinking was found to change the surface of grafted membranes, e.g. concerning their chemical structure (XPS), hydrophobicity (contact angle measurement) and polarization resistance (EIS). Therefore, the modification of (bulk) grafted films by surface grafting, introduced by irradiation (UV), plasma etching, or chemically, may allow to enhance the contact between the membrane and the electrode and therefore to reduce the polarization resistance. Furthermore, surface grafting does not suffer from the need of monomers to penetrate into the film, which reduces the restrictions on the monomers in terms of polarity and solubility. One can also think about the incorporation of radical scavengers or chelating agents in a grafted surface layer, to catch the radicals before they penetrate into the membrane or withhold metal ions from accessing the membrane, respectively.

In a more general conspectus, the challenge in fuel cell development, to achieve their commercial viability, is the balance between the required durability and the associated costs. The Electrochemistry Laboratory at PSI is engaged in developing fuel cell components, testing these components in single cells, optimizing single cells and the tools required for their diagnostic investigation, and building fuel cell stacks and showing their operational reliability in fuel cell powered prototypes. This unique combination of activities allows the development of fuel cell components, e.g. in our case ion conducting membranes, by using the feedback of their in situ reliability to further improve their properties. Here, the throughput of membranes is restricted by the number of available fuel cell test stands, their reliability, and similarly by the time necessary to perform the durability tests. Therefore, the development of accelerated in situ test methods, showing correlation to the durability tests under constant and dynamic load, is required, to enhance the sample throughput and therefore improve the statistical evaluation of fuel cell test results. A general technical challenge in fuel cell testing is to assure the comparability of experiments, which depends on the proper conditions during the experiment and therefore strongly on the reliability of the test facilities, and enhance the sample throughput. Hence, the use a fuel cell stack, to simultaneously characterize a series of membranes, ensures the comparability of the results within this test, as long as the consistency of the cells in the stack is given.
# Nomenclature

## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>$a$</td>
<td>Activity</td>
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<tr>
<td>$A$</td>
<td>Area</td>
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<td>$\gamma$</td>
<td>Elongation at break</td>
<td>mm or %</td>
</tr>
<tr>
<td>$A$</td>
<td>Absorbance</td>
<td>a.u.</td>
</tr>
<tr>
<td>$b$</td>
<td>y-Intercept of a line ($y = m \cdot x + b$)</td>
<td>-</td>
</tr>
<tr>
<td>$c$ or $[\ ]$</td>
<td>Concentration</td>
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<td>$\gamma$</td>
<td>Termination rate</td>
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<td>$D_0$</td>
<td>Dissociation energy</td>
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<td>$d_p$</td>
<td>Penetration depth</td>
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<tr>
<td>$DoG$</td>
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<td>$DR$</td>
<td>Depth resolution</td>
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<td>Unit</td>
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<td>$[M]_0$</td>
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<tr>
<td>n</td>
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<td>[mol]</td>
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<td>$\nu$</td>
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<td>Resistivity</td>
<td>[Ω·m]</td>
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<td>Density</td>
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<tr>
<td>$S$</td>
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<td>[J · K$^{-1}$]</td>
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<td>$\sigma$</td>
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<td>$\sigma$</td>
<td>Stress (standard force)</td>
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<tr>
<td>$t$</td>
<td>Time</td>
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<tr>
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<td>$\tau$</td>
<td>Contact time in CP experiments</td>
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<td>$\Theta$</td>
<td>Angle between incident beam and surface perpendicular</td>
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### Indices

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</tr>
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<td>( )&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>x ( )</td>
<td>Isotope with atomic mass x</td>
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<td>Current / actual condition</td>
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<tr>
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</tr>
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<td>( )&lt;sub&gt;pristine&lt;/sub&gt;</td>
<td>Pristine membrane</td>
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</tr>
<tr>
<td>( )&lt;sub&gt;used&lt;/sub&gt;</td>
<td>Used, fuel cell tested membrane</td>
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*continued on next page*
### Symbol Description

- $(V)$ Volume based
- $(w)$ Mass based
- $(\text{wet})$ Water swollen
- $(x)$ or $(\text{x})$ Compound x

### Constants

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value [unit]</th>
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<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>$96485 , [\text{A} \cdot \text{s} \cdot \text{mol}^{-1}]$</td>
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<td>$N_A$</td>
<td>Avogadro constant</td>
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<td>$R$</td>
<td>Universal gas constant</td>
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### Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>AMS</td>
<td>$\alpha$-Methylstyrene</td>
</tr>
<tr>
<td>AMSSA</td>
<td>$\alpha$-Methylstyrene sulfonic acid</td>
</tr>
<tr>
<td>AN</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
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<tr>
<td>CCD cts.</td>
<td>Raman intensity in counts (CCD camera)</td>
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<tr>
<td>CP</td>
<td>Cross polarization</td>
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<td>CT</td>
<td>Chain transfer</td>
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<td>DC</td>
<td>Direct current</td>
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<td>DIPB</td>
<td>Diisopropenylbenzene</td>
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<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>DVB</td>
<td>Divinylbenzene</td>
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<td>EA</td>
<td>Elementary analysis</td>
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<td>EI(S)</td>
<td>Electrochemical impedance (Spectroscopy)</td>
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<td>EOD</td>
<td>Electro-osmotic drag</td>
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<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
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<td>ETFE</td>
<td>Poly(ethylene-alt-tetrafluoroethylene)</td>
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<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FEP</td>
<td>Poly(tetrafluoroethylene-co-hexafluoropropylene)</td>
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<tr>
<td>FER</td>
<td>Fluoride emission rate</td>
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<tr>
<td>FTIR</td>
<td>Fourier transformed infrared (Spectroscopy)</td>
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*continued on next page*
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<tr>
<th>Abbreviation</th>
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<td>Gas chromatography</td>
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<td>GDE</td>
<td>Gas diffusion electrodes</td>
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<td>Gas diffusion layer</td>
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<td>Gel permeation chromatography</td>
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<td>HFR</td>
<td>High frequency resistance</td>
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<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
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<td>IEC</td>
<td>Ion exchange capacity</td>
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<td>IL</td>
<td>Ionic liquid</td>
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<tr>
<td>irrad.</td>
<td>Irradiated, irradiation</td>
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<td>iPrOH</td>
<td>Isopropanol (2-propanol)</td>
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<tr>
<td>M</td>
<td>Monomer (in chemical equation)</td>
</tr>
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<td>MAN</td>
<td>Methacrylonitrile</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic angle spinning</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>MD</td>
<td>Machining direction</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MFC</td>
<td>Microbial fuel cell</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>P</td>
<td>Polymer (in chemical equation)</td>
</tr>
<tr>
<td>PAAM</td>
<td>Poly(acryl amide)</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>PBI</td>
<td>Poly(benzimidazoles)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEI</td>
<td>Poly(ethylene imine)</td>
</tr>
<tr>
<td>PEK / PEEK</td>
<td>Poly(ether ketone) / Poly(ether ether ketone)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PES</td>
<td>Poly(ether sulfone)</td>
</tr>
<tr>
<td>PFA</td>
<td>Poly(tetrafluoroethylene-co-perfluorovinylether)</td>
</tr>
<tr>
<td>PFC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perflourinated sulfonic acid</td>
</tr>
<tr>
<td>PI</td>
<td>Polymide</td>
</tr>
<tr>
<td>PPZ</td>
<td>Poly(phosphazine)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSSA</td>
<td>Poly(styrene sulfonic acid)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
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*continued on next page*
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>PVF</td>
<td>Poly(vinyl fluoride)</td>
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<tr>
<td>$R_m$</td>
<td>Molar monomer ratio</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
</tr>
<tr>
<td>r.h. (RH)</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>rt</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
</tr>
<tr>
<td>$S_E$Ar</td>
<td>Electrophilic aromatic substitution</td>
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<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
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<tr>
<td>SSA</td>
<td>Styrene sulfonic acid</td>
</tr>
<tr>
<td>St</td>
<td>Styrene</td>
</tr>
<tr>
<td>TD</td>
<td>Transverse direction</td>
</tr>
<tr>
<td>TFE</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>TFS</td>
<td>Trifluorostyrene</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>WAXS</td>
<td>Wide angle X-ray scattering</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YAG-laser</td>
<td>Yttrium-aluminum-garnet laser</td>
</tr>
</tbody>
</table>
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Articles in scientific reports

List of selected presentations

F. Wallasch, L. Gubler, G.G. Scherer, A. Wokaun. Pre-irradiation grafted films as precursor for fuel cell membranes: Preparation and characterization. 238\textsuperscript{th} National Meeting & Exposition of the American Chemical Society, Washington, DC, USA, August 16-20, 2009.


List of selected posters

- 59\textsuperscript{th} Annual Meeting of the International Society of Electrochemistry, Seville, Spain, 7-12 September, 2008.
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