Radiation grafted ETFE based membranes for fuel cells improved mechanical and oxidative stability

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Radiation grafted ETFE based membranes for fuel cells: improved mechanical and oxidative stability

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presented by
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Zürich, 2009
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Summary

One of the most important issues to level up the fuel cell technology to a commercially attractive level is the reduction of the costs of the base materials. In addition to the need of noble metal as catalyst (platinum), the fuel cell membranes are still an expensive component in the fuel cell system. The state-of-the-art and commercially available Nafion® membrane for fuel cell is expensive (600 US$/m²)\(^{(1)}\), whereas the DOE’s 2010 targeted price for membranes (automotive application) is 40 US$/m²\(^{(2)}\). Radiation grafted membranes are potentially cheaper. Styrene/divinylbenzene (DVB) based poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) membranes obtained by the radiation induced grafting technique has been developed at PSI\(^*\) and the performance and properties have been steadily optimized. Thus, this membrane shows a good performance and durability of thousands of hours at 80°C in steady conditions\(^{(3, 4)}\). However, the FEP base material shows limitations concerning mechanical stability and resistance to irradiation. This study is devoted to the optimization and improvement of the mechanical and oxidative stability of radiation grafted membranes for the polymer electrolyte fuel cell (PEFC), using ETFE film with a thickness of 25 µm as base polymer.

The ETFE base film was selected because of its superior mechanical stability and higher resistance to irradiation induced damage. The ETFE base film was electron beam pre-irradiated, subsequently grafted with styrene and then sulfonated in order to provide proton conductivity. The tensile tests, \textit{ex situ} chemical degradation and single fuel cell tests confirmed the advantages of using ETFE base material over the FEP base film. Indeed, an uncrosslinked ETFE-g-styrene sulfonic acid membrane was operated for more than 150 h, which is three times longer than for a similar FEP based membrane, which performs only 50 h.

One part of the work was directed towards understanding the grafting process, especially the relation between the graft level and the synthesis parameters. Optimal grafting conditions were then established based on the whole kinetic study performed, which were proving to yield the highest graft levels. Furthermore, an evaluation of the \textit{ex situ} properties (IEC, conductivity, water uptake, mechanical properties and dimensional stability) versus the graft level was carried out.

\(^*\) Paul Scherrer Institut
The main part of this work was devoted to the improvement of the oxidative stability of ETFE based membranes. A systematic investigation of the effect of crosslinking with divinylbenzene (DVB) on the properties of various styrene grafted ETFE based films and membranes was carried out. Selected grafted films and membranes, obtained under the same synthesis conditions (irradiation dose, temperature, solvent composition, total monomer concentration) and of the same graft level (25 % by weight) but with varying DVB concentration in the initial grafting solution were characterized for this purpose. The influence of the crosslinker content on the \textit{ex situ} properties of various films and membranes, namely dimensional stability, chemical composition, crystallinity, thermal stability, conductivity and mechanical properties, was investigated. Furthermore, the single fuel cell performance characteristics of the ETFE-\textit{g}-styrene/DVB membranes were studied in order to find the optimum DVB monomer content. The obtained results revealed that comparable performance to that of Nafion®112 membrane is reached using a DVB to styrene ratio of 5:95 (v/v) in the initial grafting solution. Therefore, a first long term test with this optimized membrane over a period of 2185 h was carried out. Electrochemical characterization over the operating-time and \textit{post mortem} analysis using fourier transformed infrared spectroscopy (FTIR) at the end of test were performed to evaluate the membrane.

A novel approach based on the increase of the intrinsic oxidative stability of uncrosslinked membranes by the co-grafting of styrene with methacrylonitrile (MAN), which possesses a protected $\alpha$-position and strong dipolar pendant nitrile group, was investigated. Membranes based on ETFE-\textit{g}-styrene/MAN were characterized for their \textit{ex situ} relevant fuel cell properties (IEC, water uptake, conductivity and dimensional stability), and the fuel cell performance and durability of the membrane electrode assemblies (MEAs) were evaluated and compared against those of ETFE-\textit{g}-styrene membranes. The obtained membranes have exploitable conductivities over 50 mS cm$^{-1}$ with lower hydration numbers in comparison to a Nafion®112 membrane and the water uptake shows a dependency on the content of MAN in the graft component. The \textit{post mortem} analysis reveals the existence of carboxylic acid, which is attributed to the hydrolysis of a fraction of the nitrile groups. The extent of nitrile group hydrolysis over the tested active area was found to be significant near to the oxygen inlet. Fuel cell tests showed a marked improvement in the lifetime of the co-grafted styrene/MAN over the styrene based membranes. Thus, we believe that MAN improves the oxidative stability of styrene grafted ETFE membranes. In addition, ETFE-\textit{g}-styrene/MAN membranes show comparable performance to Nafion®112 membrane and only a slight decrease at high
current densities was observed. The membrane preparation based on the copolymerization of styrene and MAN shows promising results and offers the opportunity of tuning the MAN and crosslinker content to enhance the oxidative and dimensional stability of the resulting fuel cell membranes. As far as we are aware, this is the first combination of these two monomers in proton exchange membranes for the fuel cell application.
Zusammenfassung


Ein Aspekt der vorliegenden Arbeit war die Beschreibung des Pfropfprozesses, insbesondere der Beziehung zwischen den Reaktionsbedingungen und dem daraus

* Paul Scherrer Institut


Ein neuer Ansatz, basierend auf der Erhöhung der intrinsischen oxidativen Stabilität unvernetzter Membranen durch Copropfung von Styrol mit Methacrylnitril (MAN), das eine geschützte α-Position und eine stark dipolare Nitrilgruppe aufweist, wurde entwickelt. ETFE-g-Styrol/MAN-Membranen wurden in Bezug auf ihre ex situ-Daten (IEC, Wasseraufnahmekapazität, Leitfähigkeit und Dimensionsstabilität) charakterisiert, die Leistung in der Brennstoffzelle und die Beständigkeit der Membran-Elektroden-Einheiten (MEA) untersucht und mit den Daten für ETFE-g-Styrol-Membranen verglichen. Die untersuchten Membranen wiesen eine Protonenleitfähigkeit von über 50 mS·cm⁻¹ auf bei einer im Vergleich zu Nafion®112 niedrigeren Wasseraufnahme pro Sulfonsäuregruppe. Die Wasseraufnahmekapazität zeigt eine Abhängigkeit vom MAN-Gehalt auf. Bei der durchgeführten post mortem-Analyse konnten Carbonsäuren nachgewiesen werden, die durch Hydrolyse der Nitrilgruppe gebildet werden können.
# List of symbols and abbreviations

## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Activity</td>
<td>[-]</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
<td>[m²]</td>
</tr>
<tr>
<td>ε</td>
<td>Electrode potential</td>
<td>[V]</td>
</tr>
<tr>
<td>ε°</td>
<td>Standard electrode potential</td>
<td>[V]</td>
</tr>
<tr>
<td>η_{act}</td>
<td>Activation overpotential</td>
<td>[V]</td>
</tr>
<tr>
<td>η_{Ohm}</td>
<td>Ohmic overpotential</td>
<td>[V]</td>
</tr>
<tr>
<td>η_{int}</td>
<td>mass transport overpotential</td>
<td>[V]</td>
</tr>
<tr>
<td>η</td>
<td>Efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs Free Energy</td>
<td>[J·mol⁻¹]</td>
</tr>
<tr>
<td>ΔH</td>
<td>Enthalpy</td>
<td>[J·mol⁻¹]</td>
</tr>
<tr>
<td>ΔH_{f}</td>
<td>Heat of fusion</td>
<td>[J·g⁻¹]</td>
</tr>
<tr>
<td>i</td>
<td>Current</td>
<td>[A]</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
<td>[A·m⁻²]</td>
</tr>
<tr>
<td>ΔG°</td>
<td>Standard free energy</td>
<td>[J·mol⁻¹]</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant = 96487</td>
<td>[C·mol⁻¹]</td>
</tr>
<tr>
<td>k_{p}</td>
<td>Propagation rate coefficient</td>
<td>[L·mol⁻¹·s⁻¹]</td>
</tr>
<tr>
<td>k_{t}</td>
<td>Termination rate coefficient</td>
<td>[L·mol⁻¹·s⁻¹]</td>
</tr>
<tr>
<td>λ</td>
<td>Hydration number</td>
<td>[-]</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons</td>
<td>[-]</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant = 8.314</td>
<td>[J·mol⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>R_{Ω}</td>
<td>Ohmic resistance</td>
<td>[Ω·m²]</td>
</tr>
<tr>
<td>R_{pol}</td>
<td>Polarization resistance</td>
<td>[Ω·m²]</td>
</tr>
<tr>
<td>ΔS</td>
<td>Reaction entropy</td>
<td>[J·mol⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>T_{g}</td>
<td>Glass transition temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>T_{m}</td>
<td>Melting temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>U</td>
<td>Cell voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>U₀</td>
<td>Voltage at open circuit</td>
<td>[V]</td>
</tr>
</tbody>
</table>
\[ W_{el} \quad \text{Electrical work} \quad [J \cdot \text{mol}^{-1}] \]
\[ X_n \quad \text{Monomer ratio} \quad [-] \]
\[ Z \quad \text{Impedance} \quad [\Omega \cdot \text{m}^2] \]
\[ Z_{\text{real}} \quad \text{Real part of the impedance} \quad [\Omega \cdot \text{m}^2] \]
\[ Z_{\text{im}} \quad \text{Imaginary part of the impedance} \quad [\Omega \cdot \text{m}^2] \]

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
</tr>
<tr>
<td>AMS</td>
<td>( \alpha )-methylstyrene</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection spectroscopy</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DIPB</td>
<td>1,3-diisopropenylbenzene</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>emf</td>
<td>Electromotive force</td>
</tr>
<tr>
<td>EPSA</td>
<td>Electrochemical platinum surface area</td>
</tr>
<tr>
<td>ETFE</td>
<td>Poly(ethylene-alt-tetrafluoroethylene)</td>
</tr>
<tr>
<td>FEP</td>
<td>Poly(tetrafluoroethylene-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
</tr>
<tr>
<td>GE</td>
<td>General Electric</td>
</tr>
<tr>
<td>GL</td>
<td>Graft Level</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen Oxidation Reaction</td>
</tr>
<tr>
<td>IDT</td>
<td>Initial degradation temperature</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion Exchange Capacity</td>
</tr>
<tr>
<td>MAN</td>
<td>Methacrylonitrile</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>MRDT</td>
<td>Maximum rate degradation temperature</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric Acid Fuel Cell</td>
</tr>
<tr>
<td>PBI</td>
<td>Poly(benzimidazole)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEEK</td>
<td>Poly(aryl ether ketone)</td>
</tr>
<tr>
<td>PEFC</td>
<td>Polymer Electrolyte Fuel Cell</td>
</tr>
<tr>
<td>PES</td>
<td>Poly(ether sulfone)</td>
</tr>
<tr>
<td>PFA</td>
<td>Poly(tetrafluoroethylene-co-perfluoropropylvinylether)</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorinated sulfonic acid</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPZ</td>
<td>Poly(phosphazene)</td>
</tr>
<tr>
<td>PSSA</td>
<td>Polystyrene sulfonic acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>PVDF-co-HFP</td>
<td>Poly(vinylidene fluoride-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>PVF</td>
<td>Polyvinylfluoride</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>SPI</td>
<td>Sulfonated polyimide</td>
</tr>
<tr>
<td>TD</td>
<td>Transverse direction</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TFE</td>
<td>Tetrafluoroethylene</td>
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I Motivation & structure of the thesis

I.1. Motivation

The proton exchange membrane is the heart of the low temperature fuel cell system. The stability and the reliability of the polymer electrolyte fuel cell (PEFC) is one of the crucial issues to bring the fuel cell technology to commercial level. Extensive work is directed in multidisciplinary fields towards resolving main challenging problems, which are still making this technology too expensive to penetrate the market easily. In addition to the environmental argument for the use of fuel cells, the economical argument is the most limiting factor. Thus, the development of cost effective proton exchange membrane is one of the main challenges and substantial research is devoted to the replacement of the state-of-the-art and expensive perfluorinated Nafion®. The radiation induced grafting technique in combination with low cost materials (either fluorinated or partially fluorinated polymers) is a very attractive technique in that sense. This technique is very versatile, well established as an industrial process and allows the functionalization of the base material and the introduction of the desired property (proton conductivity). Furthermore, the attractiveness of the radiation induced grafting technique is based on the possibility to easily tune and control several parameters to reach the desired property in a wide range.

The Electrochemistry Laboratory (ECL) is devoted to development of low-cost polymer electrolyte membranes and extensive work to improve the mechanical and oxidative stability is carried out. Thus, the investigation was directed for over a decade towards the improvement of the styrene/DVB (DVB: crosslinker) radiation grafted poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) based membranes and promising achievements were made\(^3\). Recently, the partially fluorinated poly (ethylene-alt-tetrafluoroethylene) (ETFE) has been chosen as an alternative base polymer film to increase the mechanical integrity and to reduce the impact of irradiation on the obtained membranes. The ETFE base film possesses several advantages in comparison with the FEP base film\(^5\). In fact, ETFE base film is available at high molecular weight, which induces consequently an improvement of its mechanical properties (tensile strength, elongation at break) (Figure I.1).

Being a partially fluorinated polymer instead of perfluorinated polymer, the ETFE base film on one hand requires lower irradiation doses to form radicals and achieve the desired graft level, and on the other hand enhances the grafting kinetics due to the increased monomer solubility\(^5\). In addition to the better mechanical properties, the \textit{ex situ} chemical degradation and single fuel cell tests confirmed the benefits of using ETFE
base material over the FEP base film. Indeed, an ETFE-g-polystyrene based membrane was operated for more than 150 h and this operating-time is three times longer than for the FEP-g-polystyrene based ones, which perform only 50 h at an operation temperature of 80 °C (temperature necessary for automotive application). We note that these membranes can last much longer at lower operation temperature of 40 °C.

The first objective of this work was to investigate the radiation grafting of styrene/DVB into ETFE based films and to correlate the two key parameters, namely the graft level and extent of crosslinking to the different structural changes of the membranes and their ex situ and in situ fuel cell relevant properties. Therefore, a systematic study was carried out based on two key parameters which are the graft level and the crosslinker content. We attempted to have a control over the different membrane preparation steps (radiation → grafting → sulfonation) to have reproducible results at optimum conditions. The overall goal at that stage was to have a precise and concise view on the ex situ parameters which have the highest impact on fuel cell application, and to build a quantitative specification of our membranes. The main target was the optimization of the system to increase the stability under fuel cell conditions in combination with good performance at an operation temperature of 80 °C.

![Figure I.1: Comparison of the tensile tests of ETFE and FEP base film, both with a thickness of 25 µm (from Dupont®). Measurements performed at 100 mm·min⁻¹ crosshead speed for samples with initial dimensions of 10 cm x 1 cm (Details in paragraph III.5).](image)

The second target was related to the quantification of the inhomogeneities due to the use of technical products (e.g., base film). So far, no investigation was reported on the change of the thickness of the base material over both direction (machining (extrusion) direction and transverse direction). The interest was focused on the changes on the
dimensions and the distribution of the different component over the grafted area of the films, which may cause localized stress within the system.

The third objective was devoted to the increase of the oxidative stability prior to any crosslinking by copolymerization. The aim is to select new comonomers to styrene to increase the stability of the resulting membrane under fuel cell conditions, while keeping the performance comparable to the state-of-the-art, i.e., Nafion®112 membrane.

I.2. Structure of the Thesis

This study deals with radiation induced grafting directed towards the development of proton exchange membranes for fuel cells. Therefore, the first part of the introduction is devoted to the basics of fuel cells, while the second part is focused on the polymer electrolyte fuel cells. Moreover, the proton exchange membranes are discussed in details and the different types, research trends and state-of-the-art and commercially available ones are presented. Likewise, the radiation grafting process is discussed in a sub-chapter, which summarizes the different used base materials and gives an overview of the different systems and approaches investigated. In addition the properties of the radiation grafted membranes are presented and emphasized.

All the chemicals and materials used in this thesis are summarized in the experimental Chapter, which gives also an overview of the characterization techniques and preparation procedures. Thereafter, Chapter IV concerns the effect of different grafting parameters on the kinetics, where the results of fitting with a mathematical model are presented and discussed. Thus, a detailed study on the influence of grafting parameters (temperature, water content, irradiation dose, monomer and crosslinker concentration) was performed for a better control and understanding of the system.

The ex situ characterization of the radiation grafted films and resulting membranes using different techniques are organized into two different chapters, namely the structural investigation (Chapter V), and the relevant properties for fuel cell application (Chapter VI). Thus, Chapter V deals with the different changes in the structure of the membrane (crystallinity, thermal stability, composition and dimensional changes) due to irradiation, grafting, sulfonation and crosslinking. Chapter VI is devoted to the investigation of the graft level and crosslinking effects on the ex situ relevant properties for fuel cell application such as the ion exchange capacity (IEC), conductivity, mechanical properties, chemical and dimensional stability.
The exposure of the membranes to stress during fuel cell operation is very complex (hydration/dehydration, mechanical stress, aggressive species (HO‘, HOO‘)). Therefore, fuel cell tests are crucial to evaluate the membrane performance and durability under real conditions. Chapter VII is directed towards single fuel cell tests, and in situ characterization of membrane-electrodes assemblies (MEAs) is presented more in detail. The influence of the graft level and crosslinker content on the performance and in situ properties of single fuel cells are addressed. Moreover, long term tests were performed with the optimized membranes and the ex situ and in situ membrane properties are discussed. Post mortem analysis at the end of test was also carried out and degradation mapping is presented.

Several groups work on the development of new radiation grafted membranes to improve the oxidative stability under fuel cell operation conditions by the use of some new monomer combinations with low cost impact. However, only few of them are reporting fuel cells tests of their systems. In the final Chapter a novel approach based on the use of styrene/methacrylonitrile as the graft component is presented and selected membranes were characterized for their ex situ fuel cell relevant properties. Likewise, in situ characterization of the MEAs based on these membranes was carried out and a comparison with ETFE-g-polystyrene based membranes is drawn.
II General introduction

“Three-quarters of the world’s poorest citizens, those living on less than $2 per day are dependent on the environment for a significant part of their daily livelihoods. Climate change, therefore, adds a real urgency to the efforts of the many institutions that work to improve the lives of the poor”\(^{(6)}\).

The climatic changes and global warming are now facts, which start to have a direct and indirect impact in the world. The origin and scenarios of the climatic changes and environmental problems are still under “debate”, but the problem seems to be associated with the growing energy demand. Nonetheless, the direct combustion of fuels for transportation and heating are assumed to contribute to more than 50% of greenhouse gas emission. These activities generate a significant fraction of air pollutant emission (carbon monoxide, volatile organic compounds and nitrogen oxides…) and contribute negatively on the air quality (health problem). It is interesting to keep in mind that half of the primary fossil energy use in the world accounts for the transportation sector, which is assumed to increase because of the world’s growing demand due in part to the new emerging countries like India and China\(^{(7)}\).

Is “energy” a poisoned gift (Trojan Horse) for the actual social well-being?

The energy supply security based on crude oil is another issue of paramount importance, which is closely related to the so-called peak-oil (declining oil resources), to geopolitical crisis and to the increase of the world demand. Recently, the increase of crude oil price (maximum reached ~ 147 $ / barrel) and the devaluation of the US dollar due to the American financial crisis in 2007-2008 (sub prime mortgage crisis) have brought several direct or indirect problems that all countries have to face. Hence, global policies directed towards the development and support of existing and new strategies based on different sustainable and renewable energy systems to reduce the impact of oil in all life sectors are crucial issues.

In the transportation sector, fuel cells are probably the most promising candidate to compete with conventional combustion engines\(^{(8)}\). Moreover, the fuel cells can also be possibly very attractive in other application sectors, such as stationary power generation and portable applications. The fuel cell technology is currently emerging as an efficient alternative power source to the combustion engines. In fact, this technology possesses an additional and major advantage over the air pollution of conventional combustion engines. Indeed, the fuel cell is based on a highly environmental friendly process (ultra-low emission). This claims of course the use of hydrogen gas produced in purely
ecological processes (no emission of greenhouse gas either during production or transportation), using sustainable energy forms (solar energy, wind energy, hydraulic power plants, biomass and waste…).

The polymer electrolyte fuel cell (PEFC) is a particularly promising candidate due to the exhibited higher power density in comparison with the other fuel cell types\(^9\). PEFCs possess good start-stop capabilities and operate under low-temperature (60-80 °C), but need platinum as catalyst. Likewise, the state-of-the-art of proton exchange membranes used in fuel cell based on fluorinated polymers are still expensive materials. The requirements of such materials are closely selected to ensure a higher chemical, thermal and mechanical stability under fuel cell operating conditions. In this chapter, the different general notions of fuel cell (principle of fuel cells, kinetics, thermodynamics) are discussed in detail.

II.1. Fuel cells basics

II.1.1. Definition and classification

A fuel cell follows the same principle as conventional power plants, which is a continuous transformation of the chemically stored energy in a fuel to electrical energy. However, Fuel cell offers the advantage of converting the chemical energy stored into electrical energy in one step (conversion in conventional power plants: Chemical energy (combustion) $\rightarrow$ mechanical energy $\rightarrow$ electrical energy). The permanent consumption of a supplied fuel by the fuel cell is the key parameter to differentiate it from secondary batteries (there is always need of recharging via applying an external voltage)\(^8,9\).

The major types of fuel cells are based upon the same electrochemical principles and can be differentiated by their electrolyte and the operating temperature (Table II.1):

- polymer electrolyte fuel cell (PEFC)
- alkaline fuel cell (AFC)
- phosphoric acid fuel cell (PAFC)
- molten carbonate fuel cell (MCFC)
- solid oxide fuel cell (SOFC)

Due to the operating conditions and used materials, each fuel cell type show advantages and drawbacks. Nonetheless, the arguments for choosing any type are closely related to the application and the needed power density. The common challenges and targeted objectives for all fuel cells are directed towards the improvements of the costs, reliability and durability.
### Table II.1: Description of major fuel cell types$^{(6)}$.

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Electrolyte</th>
<th>Operating temperature [$^\circ$C]</th>
<th>Fuel</th>
<th>Catalyst</th>
<th>Electric efficiency [%]</th>
<th>Power range / application</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEFC</td>
<td>Solid polymer (e.g. Nafion®)</td>
<td>50-100</td>
<td>H$_2$</td>
<td>Pt</td>
<td>35-45</td>
<td>5-250 kW / Automotive and portable application</td>
</tr>
<tr>
<td>AFC</td>
<td>KOH</td>
<td>60-120</td>
<td>Pure H$_2$</td>
<td>Pt, Ag</td>
<td>35-55</td>
<td>&lt;5 kW / military, space</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid</td>
<td>~220</td>
<td>H$_2$</td>
<td>Pt</td>
<td>40</td>
<td>200 kW / combined heat and power generation</td>
</tr>
<tr>
<td>MCFC</td>
<td>Lithium and potassium carbonate</td>
<td>~650</td>
<td>H$_2$, CO, CH$_4$</td>
<td>Ni</td>
<td>&gt; 50</td>
<td>200 kW-MW / combined heat and power generation</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide electrolyte (e.g. Zirconia)</td>
<td>~1000</td>
<td>H$_2$, CO, CH$_4$</td>
<td>Perovskites (ceramic)</td>
<td>&gt; 50</td>
<td>2 kW-MW / combined heat and power generation</td>
</tr>
</tbody>
</table>

**II.1.2. Fuel cell operation principle**

A fuel cell can be described as a galvanic cell, following the same principle as an electrochemical battery. It consists of two electrodes separated by an ion conducting medium (electrolyte) (Figure II.1).

![Figure II.1: Simplified schematic of a fuel cell.](image-url)
The fuel and the oxidant are fed continuously to the anode and cathode compartment, respectively. At each electrode an electrochemical half cell reaction takes place, with the help of a catalyst (Table II.2). The electrolyte layer ensures the separation and electronic isolation of both compartments, where the half cell reactions take place. Depending on the fuel and the mobile charge carrier, the half cell reactions differ dramatically, affecting the efficiency of the system. Indeed, the charge carriers are either positive ions (PEFC, PAFC), or negative ions migrating from one compartment to the other (either from the anode to the cathode or vice versa). Therefore, the produced water (liquid or gaseous) can be located either at the anode or the cathode side and removed either with the depleted fuel or oxidant. Consequently, the effective advantages and disadvantages of each cell type are intrinsic and unique.

Table II.2: Description of major fuel cell type reactions and charge carrier.

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Charge carrier</th>
<th>Anode reaction</th>
<th>Cathode reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEFC</td>
<td>H⁺</td>
<td>( H_2 \rightarrow 2H^+ + 2e^- )</td>
<td>( \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O )</td>
</tr>
<tr>
<td>AFC</td>
<td>OH⁻</td>
<td>( H_2 + 2OH^- \rightarrow 2H_2O + 2e^- )</td>
<td>( \frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- )</td>
</tr>
<tr>
<td>PAFC</td>
<td>H⁺</td>
<td>( H_2 \rightarrow 2H^+ + 2e^- )</td>
<td>( \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O )</td>
</tr>
<tr>
<td>MCFC</td>
<td>( CO_3^{2-} )</td>
<td>( H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- )</td>
<td>( \frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} )</td>
</tr>
<tr>
<td>SOFC</td>
<td>O²⁻</td>
<td>( H_2 + O²^- \rightarrow H_2O + 2e^- )</td>
<td>( \frac{1}{2} O_2 + 2e^- \rightarrow O²^- )</td>
</tr>
</tbody>
</table>

II.2. Polymer Electrolyte Fuel Cell (PEFC)

The core unit of the PEFC is formed by the membrane-electrode assembly (MEA), which is confined in a sandwich configuration between two conducting plates. The electrodes consist of a gas diffusion layer (GDL) and a catalyst layer located between the membrane and the GDL. The electrical current is collected from the cell by means of current collectors. These conducting plates contain integrated flow fields for the optimal distribution of the gases over the MEA, and the removal of the depleted gases and products out of the cell (Figure II.2).

The electrochemical reaction in each compartment takes place at the interfacial active layer between the GDL and the membrane, which contains the so called triple phase boundary (ensures the coexistence of ionic and electronic conductivity and gas access). The hydrogen oxidation reaction (HOR) takes place at the anode, where protons and electrons are produced. The protons migrate through the membrane to the cathode, while the electrons are drained out of the cell through the external circuit to the cathode.
current collector. At the cathode, the oxygen reduction reaction (ORR) takes place by the reaction of oxygen with protons (migrating internally) and electrons (migrating externally) to form water.

![Schematic of an MEA consisting of catalyst layer, membrane and gas diffusion layer.](image)

The following subchapters deal with the components, thermodynamics, kinetics and efficiency of the PEFC.

**II.2.1. Components of the PEFC**

**A. Polymer electrolyte membranes**

In PEFCs a thin solid polymer electrolyte membrane is the heart of the MEA. The solid polymer electrolyte should fulfil several important requirements, including being an electronic insulator, gas barrier between the two electrodes and allowing rapid proton transport at high current densities\(^{(10)}\).

Proton exchange membrane fuel cells were developed and used for the first time in the 1960s by General Electric (GE) for the NASA Gemini program, providing electricity and drinking water for the space missions. However, the type of membrane used was based on polystyrene sulfonic acid, which suffers from high oxidative degradation, in addition to the limitations related to the water management in the fuel cell. Improved
durability was achieved by the perfluorinated sulfonic acid membranes developed by Dupont under the trade name Nafion® in the late 1960s (Figure II.3)\(^{(11)}\).

The state of the art, Nafion®, is a copolymer of tetrafluoroethylene (TFE) and perfluoro-3,6-dioxa-4-methyl-7-octen-sulfonic acid. The PTFE-like backbone ensures a high chemical inertness, while the side chain provides the proton exchange capability. The Nafion® membranes are available with different proton exchange capacities and thicknesses marketed as Nafion®120, 117, 112 etc\(^{(8)}\).

![Chemical structure of Nafion®.](image)

The proton transfer in the polymer electrolyte membrane from the anode side to the cathode is a complicated process. Fundamentally, the major difficulty is to provide a pathway for the protons to flow. Two principal proton transport mechanisms are known, the so called “vehicle mechanism” and the “proton hopping”. In the first mechanism, the proton diffuses through the medium together with a “vehicle” (e.g. H\(_3\)O\(^+\) in the case of water)\(^{(12)}\). Concerning the second mechanism, the proton is transferred from one water molecule to the next by hydrogen bonding. The proton transport is the most important membrane property, which can be a limiting factor reducing efficiency and fuel cell performance. The most direct impact on such transport mechanisms in the electrolyte membranes is the drying out of the membrane, which can be balanced by humidifying the incoming reactants. In order to reduce significantly the resistance of the electrolyte, the use of thinner membranes is favored, accepting an increase of gas crossover and a decrease in mechanical robustness.

**B. Electrodes and gas diffusion layers**

Due to the moderate operating temperature of the PEFC (up to 80 °C), a catalyst based on noble metal is needed to accelerate the reactions occurring at the anode and cathode side. So far, platinum and platinum alloys have proven to possess the highest activity for both, hydrogen oxidation and oxygen reduction reactions. To ensure large reaction surface area, the catalysts consisting of particles (diameter of few nm) are
deposited on fine carbon particles (diameter of ~50 nm\(^8\)).

As pointed out previously, the reaction in each compartment takes place at the triple phase boundary at the active layer, where the catalyst particles are in good contact with the proton and electron conducting phases (Figure II.4). Likewise, the accessibility of the gases to the catalyst has to be ensured. The Pt/C particles are usually impregnated with ionomer to effectively improve the ionic conductivity between all the catalyst particles and the membrane. Thereby, the control of the morphology and the structure of the triple phase boundary are essential prerequisites to achieve high fuel cell power densities with reduced cost (lower catalyst loading\(^{13}\)).

![Figure II.4: Triple phase boundary at the membrane electrode interface.](image)

The gas diffusion layer (GDL) is characterized by its porosity (~50\%) and serves as a diffusion medium employed to provide accessibility of the reactants in a homogeneous distribution over the active area. Likewise, the GDL is conducting the electrons to or from (consumed or produced) the catalyst layer to the flow field plates. The GDL also plays an important role in the transport of the produced water through the cathode, during the PEFC operation, which has a direct impact on the performance losses (liquid water can hinder the accessibility of gases to the catalyst layer). For that aim, the hydrophobicity of the diffusion medium is increased by incorporating PTFE (Teflon\(^\circledR\)), which reduces their wettability and improves the water management in the PEFC.

**C. Flow field plates**

Both electrode sides of the MEA are covered by flow field plates, where the contact to each electrode is ensured separately. Common materials for flow field plates are stainless steel and graphite (used in this work), while the former is favourable from the
manufacturing prospective, the latter is preferred to avoid corrosion problems. Their main functionalities are to distribute the gases, to conduct the electrical current and the heat and to facilitate the water and thermal management within the cell. To fulfil these requirements channels are machined into the graphite plate to form the flow field. There are different flow field designs and geometries, which were proposed by numerous manufacturers and research groups, ranging from the most simplest to highly complicated designs (Figure II.5)\(^{(14)}\).

![Flow field geometries](image)

Figure II.5: Example of flow field geometries for fuel cell; a) parallel flow field geometry; b) serpentine flow field geometry.

**II.2.2. Thermodynamics**

In the PEFC, the hydrogen oxidation reaction (HOR) takes place at the anode side (Eq. II.1) while the oxygen reduction reaction occurs at the cathode side (Eq. II.2):

\[
\begin{align*}
\text{H}_2 & \rightarrow 2\text{H}^+ + 2\text{e}^- \quad (\text{II.1}) \\
2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2 & \rightarrow \text{H}_2\text{O} \quad (\text{II.2})
\end{align*}
\]

The overall electrochemical reaction of a PEFC, which is given by the combination of the half equations ((II.1) and (II.2), is:

\[
\begin{align*}
\text{H}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{H}_2\text{O} \quad (\text{II.3})
\end{align*}
\]

As stated previously, the PEFC converts the chemical energy stored within a fuel and oxidant to electrical energy. The limits on how much of internal energy (first law of
thermodynamics) can be transformed into electrical energy is expressed by the Gibbs-Helmholtz enthalpy (Gibbs free energy, II.4, combination of the first and second law of thermodynamics):

\[ \Delta G = \Delta H - T \Delta S \]  

Where \( \Delta G \) is the Gibbs free energy, \( \Delta H \) the change in enthalpy of the system and \( \Delta S \) the entropy due to the disorder of the system. A negative \( \Delta G \) is a sign of energetically favorable reaction.

The achievable electrical work \( W_{el} \) in the electrochemical reaction is expressed by:

\[ \Delta G = W_{el} = -nFE \]  

Where \( E \) is the electromotive force (emf), \( F \) is the charge carried by a mole of electrons (Faraday’s number (\( F = 96480 \text{ As}\cdot\text{mol}^{-1} \)) and \( n \) is the number of electrons in the overall reaction (\( n = 4 \)).

The electromotive force is dependant on the temperature and the activity of the compounds involved in the reaction, which is described by the so called Nernst equation:\(^{(15)}\):

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_{product}}{a_{reactant}} \]  

Where \( T \) is the absolute temperature value and \( R \) is the ideal gas constant (\( R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \)).

The emf of an electrochemical cell can be expressed by the use of the electrode potentials (\( \varepsilon \)) of the half reactions occurring in both compartments:\(^{(15)}\):

\[ E = \varepsilon_{red} - \varepsilon_{ox} \]  

Where (\( \varepsilon_{ox} \)) and (\( \varepsilon_{red} \)) are the electrode potentials of the oxidation and reduction half cell reactions, respectively.

The standard electrode potential \( \varepsilon_{red}^0 \) and \( \varepsilon_{ox}^0 \) of the reduction and oxidation half reactions, respectively, under standard conditions (\( T= 298 \text{ K}, p = 1 \text{ bar} \)) can be easily
calculated from thermodynamic data. Thus, values of 0.00 V and 1.23 V are determined for the $\varepsilon^0_{\text{ox}}$ (hydrogen oxidation reaction (HOR)) and $\varepsilon^0_{\text{red}}$ (oxygen reduction reaction (ORR)), respectively. Thus, the reversible voltage generated by the overall cell reaction under standard-state conditions is 1.23V.

### II.2.3. Kinetics

The electrochemical reactions in the PEFC involve the charge transfer between the electrode and the chemical species. Thus, the current $i$ is a direct measure of the electrochemical reaction rate. Because the electrochemical reaction occurs only at the interface, the current density is more fundamental than the current, when describing the electrochemical reaction kinetics.

The current-voltage curves (polarization curves) are measured to characterize the fuel cell performance (Figure II.6). The current-voltage curve is divided into three regions, where the voltage losses are controlled by various processes. The region (I) of the current-voltage curve is dominated by kinetic effects. The region (II) is assumed to be mainly due to the ohmic loss effects, while mass transport limitations are responsible for the region (III). Thus, the drop in cell voltage can be described as:

$$U = U_0 - \eta_{\text{act}(\text{HOR})} - \eta_{\text{act}(\text{ORR})} - \eta_{\text{mt}(\text{HOR})} - \eta_{\text{mt}(\text{ORR})} - \eta_{\text{Ohm}}$$  \hspace{1cm} (II.8)

Where $U_0$ is the voltage at open circuit, $\eta_{\text{act}(\text{HOR})}$ and $\eta_{\text{act}(\text{ORR})}$ are the activation overpotentials of the anodic and cathodic half cell reaction, respectively. $\eta_{\text{mt}(\text{HOR})}$ and $\eta_{\text{mt}(\text{ORR})}$ are the mass transport overpotentials for the anode and the cathode, respectively, while $\eta_{\text{Ohm}}$ accounts for the Ohmic overpotential.

We note that the value of the voltage at open circuit $U_0$ is less than the ideal and reversible voltage (Figure II.6). One of the reasons for this observed discrepancy is the side reactions occurring at the cathode (formation of hydrogen peroxides).\(^\text{(16-18)}\)

It is well known that the Butler-Volmer fundamental equation (II.9) is used as the primary step to explain how the voltage losses are related to the current density in electrochemical systems:
Where $j_0$ is the exchange current density and $b_+$ and $b_-$ are the Tafel slopes for the anodic and cathodic reactions, respectively. The Tafel slope provides information about the mechanism of the reaction, while the exchange current density gives insights about the rate constant of the redox reaction\(^\text{15}\).

![Figure II.6: Schematic of a current-voltage curve of a PEFC, showing the characteristic regions and the loss contributions of different processes.](image)

**II.2.4. Efficiency**

The efficiency $\eta$ of a conversion process is generally described as:

$$\eta = \frac{\text{useful energy}}{\text{total energy}} \quad \text{(II.10)}$$

In the fuel cell, the overall efficiency $\eta$ of energy conversion (practical efficiency) may be calculated as:

$$\eta = \eta_{\text{thermo}} \cdot \eta_{\text{voltage}} \cdot \eta_{\text{fuel}} \quad \text{(II.11)}$$

Where $\eta_{\text{thermo}}$ is the ideal thermodynamic efficiency, $\eta_{\text{voltage}}$ is the voltage efficiency and $\eta_{\text{fuel}}$ is the Faradaic and fuel utilisation efficiency.

The reversible thermodynamic efficiency of the electrochemical reaction can be determined by:
II General introduction

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

(II.12)

Where \( \Delta G \) (free energy which is related to the \( \text{emf} \) (II.5)) is the the produced electrical energy and \( \Delta H \) (reaction enthalpy) is the energy released in form of heat from the chemical reaction.

Due to the mentioned losses in the voltage occurring in the fuel cell (section II.2.3), the voltage efficiency is described as the ratio of the actual cell voltage under load \( U \) and the thermodynamically reversible cell voltage (emf):

\[
\eta_{\text{voltage}} = \frac{U}{\text{emf}}
\]

(II.13)

The Faradaic efficiency accounts for the efficiency of current generation from the reactants participating in the electrochemical reaction:

\[
\eta_{\text{Faradaic}} = \frac{I}{nF \upsilon}
\]

(II.14)

Where \( I \) is the current generated by the fuel cell, \( n \) is the number of exchanged electrons, \( F \) is the Faraday constant and \( \upsilon \) is the rate at which the fuel is supplied (\( \text{mol} \cdot \text{s}^{-1} \)). With the denominator term being the theoretical current output assuming that 100% of supplied fuel is converted during the process.

Due to parasitic reaction or to the fact that some of the fuel flows through the fuel cell without reacting, the Faradaic efficiency has to take into account the fuel utilization efficiency, which is described by the factor:

\[
\mu_{\text{fuel}} = \frac{\text{consumed fuel}}{\text{fuel input}}
\]

(II.15)

Thus, the fuel conversion efficiency in the fuel cell is given by:

\[
\eta_{\text{fuel}} = \eta_{\text{Faradaic}} \cdot \mu_{\text{fuel}}
\]

(II.16)

II.3. Proton exchange membranes for fuel cells

Research efforts are devoted to enhance the cost effectiveness, reliability and durability of proton exchange membranes (PEM) for \( \text{H}_2/\text{O}_2 \) fuel cell. Tremendous achievement in this field was reached if compared with the first membrane employed in the \textit{Gemini} space program in the early 1960s. Depending on the targeted application (automotive, stationary or portable power), the membrane should fulfil unique
requirements and be able to operate under specific conditions. In this section, the general aspects of polymer electrolyte membranes will be introduced. Moreover, the properties, requirements and problems to overcome will be discussed.

II.3.1. Properties and classification

The polymer electrolyte membranes directed to the fuel cell application have to fulfil several requirements under specific operating conditions\(^{(10)}\). The membrane should possess intrinsic characteristics:

- low permeability to fuel and oxidant
- low electronic conductivity
- good thermal stability
- good mechanical stability in both, dry and hydrated state
- good chemical stability
- good interfacial properties
- low cost

Other aspects of the PEM are their requirements in relation to their functionality in fuel cell. Critical items related to that for water swollen membranes are:

- High proton conductivity (~ 0.1 S·cm\(^{-1}\))
- Water management
- Capability of fabrication into MEAs

The current state of the art PEM is Nafion\(^\circledR\) type, which is the first perfluorinated sulfonic acid (PFSA) membrane tested in the late 1960s as perm-selective separator in chlor-alkali electrolyzers \(^{(19)}\). The second generation of Nafion\(^\circledR\) based membranes were improved in terms of performance and lifetime in comparison with the first generation employed in the Gemini space program (PEM based on polystyrene sulfonic acid). In addition to Nafion\(^\circledR\), other perfluorinated electrolyte membranes (PFSA), with outstanding properties are commercially available from different companies. Those materials can be considered as poly(tetrafluoroethylene) (PTFE) derivatives, which possess perfluoroether side chains with sulfonic acid end groups (Figure II.7).
II General introduction

The major drawback of these perfluorinated membranes is the high cost (600-700 US$·m$^{-2}$), which is related to the rather complicated fluorine chemistry involved in this technology\(^{(1)}\). A different approach was then introduced by Ballard in their BAM3G based membrane, which shows superior performance under specific conditions in comparison with Nafion®117 and Dow® membranes (Figure II.8)\(^{(20)}\).

![Figure II.7: Chemical structures of perfluorinated polymer electrolyte membranes (PFSA).](image)

On the other hand, different approaches are devoted to produce a cheaper material than the perfluorinated commercially available membranes. Thus, hydrocarbon polymers were presented as a promising alternative to obtain PEM (e.g., automotive application). The attractiveness of such membrane is due to the cost effectiveness of these materials in comparison to the perfluorinated polymers and their thermal (above 80°C) and chemical stability.

Research activities were directed towards development of sulfonated polymers, such as polystyrene and derivatives\(^{(21)}\), polyimide (PI)\(^{(22-24)}\), poly(ether ether ketone) (PEEK)\(^{(23, 25-28)}\), poly(ether sulfone) (PES)\(^{(29, 30)}\), poly(sulfone)\(^{(31-33)}\), poly(benzimidazole) (PBI)\(^{(34, 35)}\), poly(phosphazene) (PPZ)\(^{(36, 37)}\), and others\(^{(38-40)}\) (Figure II.9).
The challenge for these membranes is to enhance their performance (proton conductivity), with keeping the intrinsic advantages of the base material (mechanical, thermal and chemical stability). Therefore, the degree of sulfonation is the key parameter in most cases. The increase of the ion exchange capacity (IEC) induces an increase of the membrane swelling, while the mechanical properties are negatively affected\(^{41}\). In addition, the long term stability under fuel cell conditions of these membrane types is still to be deeply investigated, with respect to their chemical stability, reactant crossover and other relevant fuel cell parameters.

![Chemical structures of hydrocarbon polymers used in the PEFC.](image)

Figure II.9: Examples of hydrocarbon polymers used in the PEFC.

The other attractive and cost effective alternative is based on the chemical modification of commercially available base polymers (non-fluorinated, partially fluorinated and perfluorinated polymers), which are extruded already into thin films. The technique is based on radiation induced grafting of these polymers with functionalized monomers (Figure II.10)\(^{42, 43}\).
II General introduction

Figure II.10: Example structure of radiation grafted membrane based on sulfonated FEP-g-polystyrene (FEP is poly(tetrafluoroethylene-co-hexafluoropropylene).

The irradiation can be carried out using an electron-beam\(^{(44, 45)}\), X-ray\(^{(46, 47)}\) or \(\gamma\)-rays\(^{(48, 49)}\) sources under different conditions and procedures. Radiation grafting is a well established technology, which already reached industrialization step. This technology is mostly devoted to polymerization, crosslinking and patterning. Many areas of applications may be cited. The desalination of water, biomaterials treatment, separation and extraction, environmental waste treatments, etc.\(^{(50)}\). The different aspects of this process will be discussed more in detail in the paragraph II.4.

**II.3.2. Water management and degradation in PEFC**

Membrane degradation is one of the most important factors limiting the lifetime and durability of the PEFC, and causing MEA failure under fuel cell operating conditions. The degradation mechanism in the membrane is a complex process which is assumed to be the combination of chemical and physical degradation.

There is general agreement that the chemical degradation occurring in the membrane is due to the formation of highly active oxidative species, formed during fuel cell operation. It is believed also that the \(\text{H}_2\text{O}_2\) formed at both electrodes decomposes into active radicals (‘OH, ‘OOH). The \(\text{H}_2\text{O}_2\) formation was found to be dependant on the operating temperature and on the humidity\(^{(51)}\). Still, there is a debate about the mechanisms and the absolute concentration of \(\text{H}_2\text{O}_2\) formed, which are involved in the membrane attack\(^{(16-18, 52-54)}\). Furthermore, it was shown that the presence of some impurity cations (Fe\(^{2+}\), Cu\(^{2+}\)…) in the membrane can have an accelerative effect on the formation of hydroxyl and hydroperoxy radicals (Eq. II.17, II.18) and on the membrane degradation\(^{(52, 55)}\).

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

(EII.17)
Depending on the type of the membrane, the degradation mechanisms may change totally, due to the difference in the chemical structure and the susceptibility of the membrane to peroxide attack. The PFSA membranes have been found to be sensitive to peroxide radical attack in the -COOH terminal bonds, which then initiate the decomposition “unzipping-mechanism”:\(^\text{(56)}\):

\[
{^\text{\cdot}OH + H_2O_2 \longrightarrow H_2O + {^\text{\cdot}OOH}} \quad \text{(II.18)}
\]

\[
R_i -\text{CF}_2\text{COOH} + {^\text{\cdot}OH} \longrightarrow R_i -\text{CF}_2^\cdot + \text{CO}_2 + H_2O \quad \text{(II.19)}
\]

\[
R_i -\text{CF}_2^\cdot + {^\text{\cdot}OH} \longrightarrow R_i -\text{CF}_2\text{OH} \longrightarrow R_i -\text{COF} + \text{HF} \quad \text{(II.20)}
\]

\[
R_i -\text{COF} + H_2O \longrightarrow R_i -\text{COOH} + \text{HF} \quad \text{(II.21)}
\]

The decomposition begins at the chain ends of the membrane polymers and due to the regeneration by hydrolysis of the –COF group, the PFSA unit is decomposed by radical depolymerization reactions called ‘unzipping mechanism’. In addition, a main chain scission is found to occur in the PFSA membranes. It was suggested that the ether bonds in the side chain was a vulnerable point, which may be attacked\(^\text{(56, 57)}\).

For the membrane based on polystyrene sulfonic acid (PSSA), the degradation mechanism was built on the weakness of the hydrogen in alpha position of the styrene group\(^\text{(58)}\). The model molecule was a para-toluenesulfonic acid and the \(^\text{\cdot}OH\) radicals were generated by photolysis of H\(_2\)O\(_2\). The products of the reaction of these radicals with the para-toluenesulfonic acid molecules were investigated by electron paramagnetic resonance spectroscopy (EPR). It was stated that the \(\alpha\)-hydrogen was a very sensitive atom to be cleaved after the attack of \(^\text{\cdot}OH\) radical on the aromatic ring, and thereafter the radical is created in the main polymer chain, leading finally to chain scission (Figure II.11). Nonetheless, this model can not explain all chemical degradation phenomena occurring for the PSSA based membranes, and how it is progressing under fuel cell operating conditions.
Chemical degradation is not the only factor leading to MEA failure, but is combined with other physical factors inducing acceleration in the deterioration of the membrane. Membrane thinning and pinhole formation were found to occur under fuel cell operating conditions\(^{59, 60}\). In fact, the MEA is put initially under compressive stress, which induces a time-dependent deformation (i.e., creep). The initial physical properties of membranes are the crucial parameters determining their thermal and mechanical stability. Thus, the glass transition temperature, elongation at break and tensile strength are very important parameters. All these parameters are affected by the hydration state, which implies that their response to hot/wet and hot/dry states will be complex under fuel cell operating conditions. Likewise, the dimensional stability during humidity cycles may have a non-negligible effect on the microcrack formation at longer term testing. Another common MEA failure is the microcrack formation at the catalyst layer edges region, in the boundary region between the reactive and non-reactive zones of the membrane\(^{61}\).

The conventional durability fuel cell tests last more than thousand hours, without including the design and components development. To evaluate the potential and durability of membranes in a fuel cell in more efficient and rapid way, new robust protocols for short-term testing are needed. A review on the different accelerated degradation protocols (humidity cycling, start/stop cycles, Fenton reagent, OCV...) can be found elsewhere\(^{57}\).

The water transport is a complex phenomenon in the proton exchange membranes. Proper water management is an important parameter of membranes, since it is closely related to the performance losses and has a long term effect on the cell degradation rate. Dealing with the PEFC, two major issues have to be overcome, namely removal of generated liquid water (from the flow channels and gas diffusion layer (GDL)) and preventing dehydration of the membrane (electro-osmotic drag). The water management complexity comes from the fact that there are several key parts in the fuel cell which may need or not need the presence of water. Hence, the three phase boundary at both
electrodes and the membrane bulk needs the liquid water (conductivity), but its presence has to be avoided in the GDL and catalyst layer (decrease of mass transport) (Figure II.4).

The water transport within the membrane in a practical fuel cell is governed by a mixed transport process occurring between the anode and cathode side. On the one hand, water is transported from the anode to the cathode via an electro-osmotic drag, which depends on the nature of the polymer and temperature\(^{8}\). On the other hand, water diffuses from the cathode to the anode and vice versa, depending on the difference in water activity between both electrodes. Therefore, the humidification of the gases can help to reduce the risk of partial dehydration of the membrane. Additionally, the water management is complicated by the local current density distribution\(^{62}\).

**II.3.3. Challenges**

The main problems facing the proton exchanges membranes are closely related to the durability and reliability of such materials under fuel cell operating conditions. Therefore, the research targets are closely related to the functionality of the membrane in the fuel cell and its requirements:

- reduced costs
- high ionic conductivity
- improved water management
- reduced gas permeability
- improved wet/dry cycling stability of the membrane
- high chemical stability under fuel cell operating conditions and at high temperatures (up to 120°C).
- increased mechanical and dimensional stability
- improved interfacial properties of the membrane

Different approaches were presented to improve the different properties of the proton exchange membrane fuel cell. The major challenge in this case is to find a compromise between these properties and requirements in the most efficient way. It will be shown in the following chapters that the improvement of some properties can have a negative effect on the others. Moreover, a lot of work is also devoted to the development of the other fuel cell components (catalyst layer, GDL and bipolar plates), to improve the reliability and lifetime of electrical power systems.

The need of operating the fuel cell vehicle at a temperature of around 120°C is related to the efficiency of the catalyst layer (at that temperature the electrode kinetics are
enhanced and the CO-poisoning is reduced\(^{(63)}\). Several membranes were developed to operate at high temperature, such as the phosphoric-acid-doped poly(benzimidazole), hybrid Nafion® and sulfonated PEEK with incorporated ZrP \(^{(64-67)}\). Hybrid membranes were presented based on the combination of existing organic membranes with different inorganic components (hygroscopic oxides) to improve the cell performance at low relative humidity (RH). Thus, the incorporation of SiO\(_2\) and SiO\(_2\)−SZ (SZ: supported sulfated zirconia particles) into Nafion® for example was found to improve the ion exchange capacity (IEC) value, water uptake, proton conductivity, fuel cell performance and the membrane-electrode interface\(^{(68, 69)}\). Other membrane composites were presented based on sulfonated PEEK and various silica-containing molecules or macromolecules (composites of sulfonated PEEK with sulfonated diphenylsilanediol (S-DPSDO), silylated and sulfonated PEEK)\(^{(70)}\). In fact, hybridizing polymers in fuel cells is based on three major approaches\(^{(71)}\):

- use of a non-conducting polymer to improve the mechanical properties;
- incorporation of a conducting or a non-conducting inorganic phase to improve thermal stability along with conductive and water uptake properties;
- incorporation of a compound which is easily oxidized, to limit the degradation of the conducting polymer.

Other parameters like the internal resistance was reduced by the use of thinner membranes, whereas both average conductivity and water management were improved\(^{(63)}\). Likewise, reinforced membranes with improved dimensional stability and tensile strength based on incorporation of sulfonated polyimide (SPI) into PTFE (porous polytetrafluoroethylene) membrane was presented\(^{(72)}\). Another PTFE-reinforced membrane based on sulfonated poly (ether ether ketone) (SPEEK) was fabricated by the use of a thin protective layer (Pt-SiO\(_2\) and Nafion® resin) and a base layer (silica supported platinum catalyst (Pt-SiO\(_2\))), which were assumed to reduce reactant crossover and to prevent the SPEEK resin degradation due to the increase of dimensional stability and the tolerance of Nafion® resin to H\(_2\)O\(_2\)\(^{(73)}\).
II.4. Radiation induced grafting

The stability and reliability of the proton exchange membrane for fuel cells is one of the crucial issues to bring this technology from the prototype to the commercial level. Likewise, the development of cost effective proton exchange membranes to replace the expensive state-of-the-art perfluorinated membrane Nafion® is another main challenge. The radiation induced grafting of either fluorinated or partially fluorinated low cost polymers offers several advantages\(^4\). The radiation induced grafting is a versatile technique which allows the functionalization of the base material by the introduction of the suited property (proton conductivity). The attractiveness of this technique is based on the possibility to easily tune and control several parameters in a wide range.

The radiation grafting involves the use of different radiation types (electron-beam, \(\gamma\)-rays and X-rays), and may be carried out using different methods. These methods are divided into three categories: \(a\) simultaneous radiation grafting, \(b\) pre-irradiation in air (alkylperoxide method), \(c\) pre-irradiation in vacuum or inert gas atmosphere (trapped radicals method) (Figure II.12).

![Figure II.12: Preparation routes for radiation grafted films\(^{45}\).](image)

These methods can be separated into two major types, simultaneous and pre-irradiation method. In the simultaneous method, the backbone polymer and the monomer
are exposed at the same time (one-step grafting procedure), while the pre-irradiation method is a two-step grafting procedure\textsuperscript{(45)}. In this work the pre-irradiation method in air was selected for the preparation of the proton exchange membranes (easy and versatile method allowing the irradiation of big size films, which can be store at - 80 °C for several months until use). The choice of the base material, the irradiation process and the used monomers in the radiation grafting will be further discussed.

**II.4.1. Base polymers and irradiation effect**

A lot of work has been performed on the radiation induced grafting of different commercially available base materials (Table II.3). The starting materials are technical products, meaning that their properties are largely directed by the economic necessities of the production process\textsuperscript{(74)}.

Several studies were carried out based on perfluorinated polymers such as PTFE\textsuperscript{(75-77)}, FEP\textsuperscript{(78-81)}, PFA\textsuperscript{(82, 83)} and partially fluorinated base materials such as PVDF\textsuperscript{(84, 85)}, ETFE \textsuperscript{(5, 74, 86, 87)} and others \textsuperscript{(88)}. The radiation grafting was directed towards the use of perfluorinated and partially fluorinated polymers in the preparation of proton exchange membranes for fuel cell, due to their outstanding and unique combination of useful properties\textsuperscript{(89, 90)}:

- high thermal stability
- hydrophobicity
- resistance to ageing and to oxidation
- chemical inertness
- low permeability to gas
- hydrolytic stability
- low flammability
- high surface energy

Nevertheless, there are similarities and differences between the perfluorinated and partially fluorinated polymers due to the existence of C-H bonds in the latter. The high polarity of the C-F bond contribute strongly to the observed stability of fluoropolymers\textsuperscript{(91)}. When subjected to ionizing radiation, the fluoropolymers may undergo different changes in the chemical and physical properties. The mechanism and the extent of changes are relative to the nature of the fluoropolymers, their intrinsic properties, and to the irradiation conditions.
Table II.3: Common base polymer films used for radiation grafted fuel cell membranes\(^{(4)}\).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Repeating unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perfluorinated polymers</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Polytetrafluoroethylene                          | PTFE         | \[
\text{CF}_2\text{CF}_2\]_n                                                  |
| Poly(tetrafluoroethylene-co-hexafluoropropylene) | FEP          | \[
\text{CF}_2\text{CF}_2\]_n \[\text{CF}_2\text{CF}\]_m \[\text{CF}_3\]       |
| Poly(tetrafluoroethylene-co-perfluoropropylvinylether) | PFA         | \[
\text{CF}_2\text{CF}_2\]_n \[\text{CF}_2\text{CF}\]_m \[\text{OC}_{3}\text{F}_7\] |
| **Partially fluorinated polymers**                |              |                                                                                 |
| Polyvinylidenefluoride                           | PVDF         | \[
\text{CF}_2\text{CH}_2\]_n                                                  |
| Poly(vinylidenefluoride-co-hexafluoropropylene)  | PVDF-co-HFP  | \[
\text{CF}_2\text{CH}_2\]_n \[\text{CF}_2\text{CF}\]_m \[\text{CF}_3\]       |
| Poly(ethylene-alt-tetrafluoroethylene)           | ETFE         | \[
\text{CH}_2\text{CH}_2\]_n \[\text{CF}_2\text{CF}_2\]_n                   |
| Polyvinylfluoride                                | PVF          | \[
\text{CH}_2\text{CHF}\]_n                                                  |
| **Hydrocarbon polymers**                         |              |                                                                                 |
| Polyethylene                                     | PE           | \[
\text{CH}_2\text{CH}_2\]_n                                                  |

The irradiation of polymers in general leads to the formation of active species, which depending on the conditions may be radicals or ionic species\(^{(92)}\). The formed active species result from either homolytic or heterolytic bond scission reactions. The active sites formed in the long polymer chain tend to be highly selective in nature. Thus, the reaction of produced active species is either dominated by crosslinking, chain scission, or
by other chemical changes (formation of oxidative degradation products (hydroperoxide, acid fluoride and many others))\(^{74, 92}\). For the grafting process, the lifetime of the active species (radicals or ions) is of major importance and can be controlled easily, either by reducing the temperature or working under vacuum (e.g. irradiated ETFE, FEP and PVDF stored from -18 to -60 °C for a period of 4 months to 1 year)\(^{80, 93}\).

The choice of the base polymer is of crucial interest in the radiation grafting process. Indeed, it was shown that the base polymer has a direct effect on the ex situ properties of the styrene grafted membranes, such as ion exchange capacity (IEC), water uptake, conductivity, etc\(^{94}\). To begin with, each of the base materials possesses a different chemical structure and intrinsic properties (crystallinity, melting point, molecular weigh, etc). Therefore, based on which characteristic property is selected for comparison, some of them may show better or worse ex situ properties (Table II.4).

Table II.4: properties and specification of some fluoropolymers base films\(^{94}\).

<table>
<thead>
<tr>
<th>Name</th>
<th>Supplier</th>
<th>Density (g·cm(^{-3}))</th>
<th>Thickness (µm)</th>
<th>Melting point (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>DuPont</td>
<td>2.17</td>
<td>50</td>
<td>332</td>
<td>38</td>
</tr>
<tr>
<td>FEP</td>
<td>DuPont</td>
<td>2.15</td>
<td>25</td>
<td>270</td>
<td>26</td>
</tr>
<tr>
<td>PFA</td>
<td>Dupont</td>
<td>2.15</td>
<td>25</td>
<td>306</td>
<td>27</td>
</tr>
<tr>
<td>ETFE</td>
<td>Asahi Glass</td>
<td>1.73</td>
<td>25</td>
<td>257</td>
<td>34</td>
</tr>
<tr>
<td>PVDF</td>
<td>Kureha</td>
<td>1.76</td>
<td>25</td>
<td>177</td>
<td>46</td>
</tr>
</tbody>
</table>

The irradiation was shown to affect the mechanical properties of the base polymers, and the resistance to the radiation induced chain scission is following the sequence (the films were \(\gamma\)-ray irradiated in air at room temperature with a dose ranging from 0 to 52 kGy)\(^{94}\):

\[
\text{FEP} < \text{PFA} < \text{ETFE} < \text{PVDF}
\]

Higher \(\leftarrow\) radiation damage \(\rightarrow\) Lower

It is clear that the partially fluorinated polymers are more radiation resistant than the perfluorinated ones, due to crosslinking occurring mainly upon \(\gamma\)-ray irradiation. Although, in general the fluorinated polymers possess good thermal, mechanical and chemical stability, nonetheless, the most widely available perfluorinated PTFE was found to be very sensitive to high energy radiation. Indeed, PTFE is prone to severe degradation when irradiated with high energy radiation\(^{94}\). The irradiation sensitivity of PTFE is due
to the formation of acid fluoride (COF) group, which hydrolyses under humid air to form carboxylic acid group (COOH)\(^{(95)}\).

Discussing the mechanical properties of the base polymers and the resulting grafted membranes, the sequence for the tensile strength is\(^{(94)}\):

\[
\text{FEP} < \text{PFA} < \text{ETFE} < \text{PVDF}
\]

lower $\Leftarrow$ tensile strength $\rightarrow$ Higher

The sequence for the elongation at break is given by:

\[
\text{FEP} < \text{PFA} < \text{PVDF} < \text{ETFE}
\]

lower $\Leftarrow$ elongation at break $\rightarrow$ Higher

The classification of these base films (technical products) does not take into account the difference in molecular mass between the initially used polymers during the preparation (extrusion) and other product specifications, which are very important factors. Nevertheless, based on the density values (Table II.4), we can assume that the PVDF and ETFE are based on high molecular mass polymer chains, which explains their superior mechanical properties. Moreover, the crystallinity values of the compared films are also in good agreement with the determined tensile strength sequence.

Among the different available fluoropolymers, the FEP and ETFE base material sparked our interest at Paul Scherrer Institute. It has to be emphasized at this stage that the appropriate choice of base polymer film, irradiation method and processing parameters can minimize the negative effect of the irradiation, namely chains scission.

\textbf{II.4.2. Grafting reaction and used monomers}

The pre-irradiation method used in this work was performed in the presence of air, which induces the formation of peroxide groups. When elevating the temperature, the hydroperoxide decomposes to form a radical and initiate the grafting reaction\(^{(96)}\). Assuming the $PO^*$ is the primary radical site initiated by dissociation of the alkylperoxide group\(^{(93)}\), $POM^*$ is the initiated chain, $M$ is the monomer unit, and $POM_{n}^*$ and $POM_{m}^*$ are the growing graft chains, the overall grafting process can be described kinetically as a simple free radical polymerization reaction:
Initiation: \[ POOH \xrightarrow[\Delta]{\text{\textbullet}} PO^* + \cdot OH \] \hspace{1cm} (II.22)

\[ PO^* + M \rightarrow POM^* \] \hspace{1cm} (II.23)

Propagation: \[ POM^*_n + M \rightarrow POM^*_n,1 \] \hspace{1cm} (II.24)

Where the propagation rate is given by: \[ r_p = k_p [POM^*][M] \] \hspace{1cm} (II.25)

Termination: \[ POM^*_n + POM^*_m \rightarrow \text{dead polymer chain} \] \hspace{1cm} (II.26)

Where the termination rate is given by \[ r_t = k_t [POM^*_n][POM^*_m] \] \hspace{1cm} (II.27)

The grafting reaction was pointed out to follow the so called ‘grafting front’ mechanism proposed by Chapiró\(^{(44)}\), which was revealed by probing the sulphur transversal distribution in sulfonated grafted membranes with different graft levels\(^{(48, 97)}\). The initial grafting takes place at the film surface and the grafted layer swells in the reaction medium and further grafting proceeds by the progressive diffusion of the monomer through this swollen layer, thus, the grafting front proceeds to the center of the film (Figure II.13). The grafting was found to occur mainly in the amorphous zone, whereas possible surface grafting onto the crystallites may also take place.

Figure II.13: Schematic representation of the ‘grafting front’ mechanism on irradiated films\(^{(98)}\).
Although there is a high number of monomers which were radiation grafted into different base polymers existing in the literature, we will focus only on some of them directed towards the application in fuel cell (Table II.5).

Table II.5: Monomers used for the preparation of radiation grafted membranes.

<table>
<thead>
<tr>
<th>Base film</th>
<th>Grafted monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF, FEP, crosslinked PTFE, ETFE, LDPE</td>
<td><img src="image" alt="Monomer" /></td>
</tr>
<tr>
<td>ETFE</td>
<td><img src="image" alt="Monomer" /></td>
</tr>
<tr>
<td></td>
<td>$R = \text{Me, MeO, SO}_2\text{F, CF}_3...$</td>
</tr>
<tr>
<td>ETFE</td>
<td><img src="image" alt="Monomer" /></td>
</tr>
<tr>
<td>FEP</td>
<td><img src="image" alt="Monomer" /></td>
</tr>
<tr>
<td>Crosslinked PTFE</td>
<td><img src="image" alt="Monomer" /></td>
</tr>
</tbody>
</table>

It is well known that the styrene-sulfonic acid group in the grafted membrane suffers from the weakness of the $\alpha$-hydrogen position, which is involved in the radical attack induced chain scission under fuel cell conditions$^{52, 110}$. Several strategies were developed to increase the oxidative stability and the lifetime of the radiation grafted membranes under fuel cell operation, keeping the cost effectiveness as the ultimate goal. The creation of three dimensional network by crosslinking of the grafted polymer chains was pointed out to improve the stability of the resulting grafted membranes and to reduce the degradation rate under fuel cell operating condition$^{111}$. Especially, the results reported from our group based on crosslinked styrene grafted FEP membranes with
divinylbenzene as the crosslinking agent show an improvement from cell life time of 50 h for the uncrosslinked membrane to 4000 h for the crosslinked one\(^{(3)}\). The crosslinker nature, its content and its distribution were found to play a crucial role in the physicochemical properties of the grafted membranes\(^{(111)}\). Other strategies were directed towards the use of new monomers in combination with crosslinking, to increase the oxidative stability and to overcome the weakness of the alpha-hydrogen position in the styrene based membranes\(^{(110)}\). Several authors reported on \(\alpha\)-methylstyrene/styrene\(^{(109)}\) and \(p\)-methylstyrene/tert-butylstyrene\(^{(107)}\). Recently, alternative monomers were reported and tested, such as \(\alpha,\beta,\beta\)-trifluorostyrene derivatives\(^{(106)}\) and \(\alpha\)-methylstyrene/methacrylonitrile\(^{(108)}\), which show better stability but suffer from slow grafting kinetics.

### II.4.3. Properties of radiation grafted membrane

Polymer electrolyte membranes based on the radiation grafting process involve usually styrenic monomers, which are sulfonated after the grafting reaction. The grafted chains are functionalized by sulfonic acid groups, which dissociate into mobile protons in the hydrated membrane. Therefore, phase separation occurs of the hydrophobic backbone and the hydrophilic domains formed by the pending sulfonic groups hydrated with water\(^{(94)}\).

On one hand, the membranes can be characterized based on their structural and intrinsic properties, and on the other hand based on their fuel cell relevant properties. Indeed, the \textit{ex situ} and \textit{in situ} characterization of the radiation grafted membranes is a crucial step toward the correlation between the structure and fuel cell performance and durability.

#### A. Structural characterization

The preparation of radiation grafted membranes is a multi-step process, which induces different changes on the structure, morphology and properties. The resulting membranes can be characterized \textit{ex situ} based on different criteria, which can then correlate to the \textit{in situ} fuel cell parameters. Likewise, the obtained \textit{ex situ} properties are crucial to ensure a certain quality control and as comparison tools for the selected membranes before fuel cell testing.
- Homogeneity

The radiation induced grafting process is based mostly on uncontrolled radical propagation of the grafts and consequently yields a complex morphology. Therefore, investigation of the homogeneity of the membrane is a paramount step, which must be undertaken in order to optimize the parameters affecting it. The homogeneity of the radiation grafted membranes is monitored mainly by probing the distribution of different parameters, such as the graft level, crosslinker and sulfur distribution over the grafted area and through the thickness of the membrane.

Several probing technique were used for that aim, such as X-ray microprobe analysis, X-ray fluorescence, Fourier transformed infrared spectroscopy (FTIR), attenuated total reflection spectroscopy (ATR) and micro-Raman spectroscopy. Especially, FTIR and Raman spectroscopy are very interesting and versatile tools allowing fast investigations on the homogeneous distribution of the grafted component within the membrane matrix. In addition, the thickness variation over the radiation grafted membrane area is another parameter to be controlled (dimensional stability of the membrane in the dry/wet cycles), which may play a non-negligible role on MEA stability.

- Crystallinity and thermal stability

There is a lot of work directed towards the increase of the mechanical and thermal properties of the membranes, in order to reach the convenient high temperature benchmark in fuel cell (up to 120°C). The thermal and mechanical stability of radiation grafted membranes are strongly dependant on the used base material and its chemical and physical properties. Thus, the glass transition temperature, the melting temperature and crystallinity are important parameters to be assessed using fast and reliable methods, such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The structure and morphology of the base polymers used in the radiation grafted membrane synthesis are significantly influenced by the various preparation process steps (irradiation, grafting, sulfonation, swelling) and depends on the graft level and nature of the grafted component. In fact, the crystallites in the base materials are considered as crosslinking domains, which contribute to the mechanical stability and tensile strength of the material. Therefore, the investigation of the crystallinity variation with respect to different parameters (graft level, crosslinking, water content...) is useful, in order to correlate it with the structural changes of the membranes.

The thermal stability of radiation grafted membranes is another property to be monitored for more understanding of the degradation mechanism and identify the formed
degradation products. Thereby, the coupling of TGA with FTIR-spectroscopy and/or mass spectrometry offers the opportunity to get further insight into the degradation process occurring in the membranes (118, 119).

- Mechanical properties

Mechanical integrity is one of the important prerequisites for fuel cell membranes in terms of handling and fabrication of membrane electrode assemblies (MEA). Membranes should not only be robust to overcome both the mechanical and swelling stresses in fuel cell environment but also tough to prevent crack formation.

As pointed out previously, the durability is closely related to the chemical and physical degradation of the membranes. In fact, the physical factors may lead to membrane thinning and sometimes pinhole formation. This mechanical degradation can even be accentuated by the chemical one, which accelerates the performance drop (120, 121). Moreover, the dependency of the mechanical properties of the membrane on different parameters (water content, humidity, temperature, etc.) may play a significant role on the durability of the membrane.

- Dimensional stability

The dimensions of the extruded base polymer films (perfluorinated and partially fluorinated polymers) used in radiation grafting are subjected to several changes during the membrane preparation process. The dimensions of the irradiated film increase in all directions (machining direction (extrusion), transverse direction and thickness) during the grafting reaction, whereas further increase is observed after sulfonation and swelling steps. In fact, the swelling was found to induce additional stress to the radiation grafted membranes between the hydrophilic and hydrophobic parts leading to disruption in the crystalline part (122, 123). Therefore, the crystallinity and the mechanical properties are decreasing. Dimensional stability has to be considered as important parameter having a direct impact on the reliability and mechanical integrity of the radiation grafted membrane under fuel cell conditions (124). Indeed, the changes on the dimensions of the membrane in wet/dry state cycles due to change in humidification, may have an accelerative effect upon the physical degradation of the grafted membrane (membrane thinning, pinhole formation and crack propagation (57, 121). The determination of the variation on the membrane dimensional changes in wet and dry states is a prerequisite parameter before any long term testing.
B. Fuel cell relevant properties

In the grafted membrane, the fuel cell performance is governed mainly by the proton conductivity, which is dependant on the density of sulfonic acid groups and their hydration level.

- Ion exchange capacity

The ion exchange capacity (IEC) of grafted membranes is the measure of the molar content of sulfonic acid groups per mass of the dry membrane. The IEC is determined by titration of the proton content of the membrane, after exchanging it with a salt solution (KCl solution). The IEC value is an important parameter for the proton carriers and mobility across the membrane thickness, which can be controlled by the sulfonation procedure and the graft level. Thus, a low graft level (films are only surface grafted) induces a low IEC and consequently the conductivity value is very low or even unmeasurable (observed when the center of the membrane is ungrafted).

- Water uptake

In the membrane, the acid groups dissociate into mobile charges, which can be transported via two mechanisms (paragraph II.2.1). Evidently, the proton mobility depends on the incorporation of water molecules into the sulfonated domains\(^{(125)}\). The water uptake is described as the water content (mass - %) of the swollen membrane, and is described as:

\[
\text{Water uptake} = \frac{\text{mass of water swollen membrane}}{\text{mass of the dry membrane}} \cdot 100\% \quad \text{(II.28)}
\]

The other parameter, which is used regularly to describe the hydration state of the radiation grafted membrane, is the so called hydration number:

\[
\text{Hydration number} = \frac{\text{number of water molecules}}{\text{number of sulfonic acid molecules}} \quad \text{(II.29)}
\]

The hydration number as depicted in Eq II.29 is the average number of molecules of water per sulfonic acid group.

- Ex situ conductivity
The proton transport in the membrane is a complex process, which is directed by the connectivity of the hydrophilic channels and their geometry. The conductivity is the most important parameter for fuel cell performance and application. Both mechanisms describing the proton transport in the proton exchange membranes (‘vehicle mechanism’ and ‘proton hopping’) are based on the aqueous domains. Thus, the water uptake and the hydration number govern the conductivity in the radiation grafted membranes. Moreover, the conductivity is influenced by the increase of the temperature, which induces a decrease of the water content and the hydration number. Especially, under fuel cell operating conditions (60-80°C), a partial drying of the membrane may occur, leading to a decrease of conductivity.
III EXPERIMENTAL

III.1. Membrane preparation

III.1.1. Electron-beam irradiation

The base polymer, ETFE (Tefzel® 100LZ, 25 µm thick), was purchased as a film roll from DuPont (Circleville, USA). The ETFE base polymer films were first cut into 14 cm x 16 cm rectangular samples, washed in ethanol, dried and then packaged in polyethylene bags for pre-irradiation.

The irradiation was carried out in air atmosphere with an electron beam source at LEONI Studer AG, Däniken, Switzerland (accelerating voltage of 2.2 MV, beam current of 5-20 mA, dose rate 15.1±1.1 kGy s⁻¹) (Figure III.1). After exposure, the films were stored in a freezer (-80°C) until further processing.

![Figure III.1: schematic of the electron beam source at LEONI Studer Hard AG](126)

The absorbed radiation dose is defined as the amount of energy imparted to the matter and is measured in Gray (Gy) (1 Gy = 1 J / Kg). The absorbed irradiation doses were measured by using FWT-60 Series radiographic dosimeters, containing hexa(hydroxyethyl) aminotriphenylacetonitrile (HHEVC) dye manufactured by FWT and HPI (Far West Technology Inc. and Health Physics Instruments in California, USA)(127).
III.1.2. Chemicals

The reagents used during membrane preparation were styrene (purum grade; Fluka), divinylbenzene tech. (~80% of isomers: 56.3 meta, 24.4 para-DVB and 20% of isomers 3- and 4-ethylvinylbenzene; Fluka), methacrylonitrile (MAN) (purum grade; Aldrich), isopropanol (analytical grade; Fisher Scientific), toluene (analytical grade; Fisher Scientific), dichloromethane (Merck), chlorosulfonic acid (Fluka) and ultra pure water (deionized water 0.1 μS·cm⁻¹). All monomers were used as they were received, without removal of stabilizers and inhibitors for the grafting.

III.1.3. Procedure

The grafting reactions were performed in two types of reactors for technical reasons. The first type of reactor is the medium size glass reactor (60 mL), in which the kinetic reactions were carried out, and the second is the stainless steel reactor (600 mL) where the films (6 x samples) are prepared for subsequent ex situ and in situ fuel cell tests characterization (Figure III.2).

![Figure III.2: schematic of the medium size glass reactor and the stainless steel reactor.](image)

The grafting solution and the irradiated film are placed in the reactor, and then the ensemble was purged with nitrogen for 1h. The grafting was initiated by placing the closed reactor in a preheated thermostatic bath at a fixed temperature and performed for varying reaction times. The obtained grafted films were extracted in toluene overnight,
then dried under vacuum at 80°C, and reweighed in order to determine the graft level (GL), which is the weight increase of the film after the grafting process.

The GL of each film was determined from the weight of irradiated film \((W_i)\) and grafted film \((W_g)\):

\[
GL = \frac{W_g - W_i}{W_i} \cdot 100\%
\]

(III.1)

Proton conducting membranes were prepared by sulfonation of the grafted films with chlorosulfonic acid in dichloromethane (2% (v/v)) at room temperature for 5h, followed by hydrolysis in 0.1M NaOH solution and re-protonation in 2M \(H_2SO_4\) solution. Finally, the resulting membranes were swollen in deionized water at 80°C for 2h.

### III.2. Membrane characterization

#### III.2.1. Dimensional changes

The dimensional increase in machining direction (extrusion direction), transverse direction (perpendicular to extrusion) and thickness of the grafted films and membranes was calculated from

\[
Dimensional\; increase = \frac{D_1 - D_0}{D_0} \cdot 100\%
\]

(III.2)

where \(D_0\) is the initial dimension of the pristine ETFE film and \(D_1\) is the final dimension of the film after grafting or sulfonation processes.

The thickness of the grafted films and the membranes (in wet state) were measured using a digital thickness gauge (MT12B Heidenhain, Germany) with a resolution of 0.5 \(\mu m\).

#### III.2.2. FTIR-ATR measurements

The FTIR measurements of ETFE based grafted films were performed with a Perkin Elmer FTIR System 2000 spectrometer. In addition, the Attenuated Total Reflectance (ATR) technique was used to probe the surface of the grafted films and the measurements were performed using a 45° ZnSe crystal (Graseby Specac).
The mid-IR spectra were collected at a resolution of 4 cm\(^{-1}\) and the curve-fitting was performed using GRAMS/386 software (version 7.01) from Galactic Industries. The peak fitting was selected to be a mixture of Lorenzian and Gaussian form, and a base line correction was performed prior to any fitting.

### III.2.3. Ion exchange capacity and degree of sulfonation

The IEC was measured by titration using a solution of KOH (0.05 M) by means of SM Titrino 702 machine (Metrohm). For each single experiment six discs of a diameter of 1.6 cm were punched out from membrane, the surface water was blotted and the discs were weighted in three sets of two discs. Each two discs were then immersed overnight in 40 ml KCl solution (0.5 M) to ensure a complete exchange of the H\(^+\) by the K\(^+\).

The released amount of H\(^+\) was determined by titration of the solution with 0.05 mol.l\(^{-1}\) KOH and then the discs were washed several times with deionized water to ensure the removal of any excess of salt on the surface of the samples. The discs were dried for 4 h at 80 °C in a vacuum oven, and weighted after drying (m\(_{\text{salt}}\)).

The IEC was calculated using the following equations:

\[
\text{IEC} = \frac{n(H^+)}{m_0} \quad [\text{mmol} \cdot \text{g}^{-1}] \quad (\text{III.3})
\]

\[
n(H^+) = C_{(\text{KOH})} \cdot V_{(\text{KOH})} \quad [\text{mmol}] \quad (\text{III.4})
\]

\[
m_\text{a} = m_{\text{salt}} - 38.1 \cdot n(H^+) \quad [\text{g}] \quad (\text{III.5})
\]

- n(H\(^+\)) : mole number of protons
- C\(_{(\text{KOH})}\) [mol·L\(^{-1}\)] : concentration of KOH solution (0.05 M)
- V\(_{(\text{KOH})}\) [mL] : volume of KOH solution
- m\(_{\text{salt}}\) : dry weight of discs in their salt-form
- m\(_0\) : corrected weight of the discs
- 38.1 [g·mol\(^{-1}\)] : correction of the mass obtained by subtracting the molar mass of hydrogen (1 g·mol\(^{-1}\)) from the molar mass of potassium (39.1 g·mol\(^{-1}\)).

The degree of sulfonation is determined by the calculation of the ratio of the experimental and the theoretical IEC, where the latter (IEC\(_{\text{th}}\)) is calculated by the following equations, for styrene and styrene/methacrylonitrile grafted membranes, respectively:
III Experimental

\[ IEC_{th} = \frac{\text{GL}}{M(\text{styrene}) \times 100 + (M(\text{styrene}) + M(\text{SO}_3)) \times \text{GL}} \tag{III.6} \]

\[ IEC_{th} = \frac{\text{GL}}{((M(\text{styrene}) + \frac{M(\text{MAN})}{X_n}) \times (100 + \text{GL})) + (M(\text{SO}_3) \times \text{GL})} \tag{III.7} \]

Where \( X_n \) is given by:

\[ X_n = \frac{n(\text{styrene})}{n(\text{MAN})} \tag{III.8} \]

**III.2.4. Water uptake and hydration number**

The dried discs used for the IEC measurements (previous paragraph) were then regenerated into the proton form by immersing them into an HCl (1 M) solution at room temperature for 5 h. The discs were then washed several times with water and then left in water overnight, where they were swollen in deionized water for 4 h at 80°C and weighed immediately after swelling (samples were wiped from surface water).

The water uptake was calculated according to the following equation:

\[ \text{water uptake} (\%) = \frac{m_s - m_d}{m_d} \times 100 \tag{III.9} \]

\( m_s \) : weight of the swollen discs

\( m_d \) : dry weight of discs

The hydration number \( \lambda \) is calculated from the IEC and the water uptake values according to:

\[ \lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{\text{water uptake}}{\text{IEC}} \times \frac{1}{M(H_2O)} \tag{III.10} \]
III Experimental

III.2.5. Ex situ conductivity

The *ex situ* conductivity at room temperature was measured by ac impedance spectroscopy using a Zahner IM6 (Zahner Messtechnik, Kronach, Germany) impedance spectrometer. Six fully swollen membrane discs (diameter of 2cm) were assembled in the conductivity cell (Figure III.3).

In order to reduce the contact resistance, two platinum discs (diameter = 2cm) were used which were directly connected to the electrodes. Furthermore, a good contact between platinum disc and membrane discs was ensured by applying a mechanical load of 4.5 Nm.

The discs were assembled into the conductivity cell between the two platinum discs and the cell was then connected and operated in galvanostatic mode (current = 0 A, amplitude = 5 mV) and the impedance was measured in the frequency range of 50 kHz → 1 kHz → 50 kHz.

The swollen membrane discs were assembled in a stack of n = 2,3,4,5 and 6, respectively, in order to evaluate the cell resistance and contact resistance for each stack, and then the contact resistance by extrapolation to n = 0.

From the Nyquist plot (paragraph III.8.2) and the linear regression of the impedance spectra, the ohmic resistance was determined by extrapolating the value at high frequency to the real axis.

The ohmic cell resistance was determined for each disc stack and plotted versus the number of membrane discs. By extrapolating (n = 0, no membrane) to the fitted curve we obtain the contact resistance. Since the ohmic cell resistance is the sum of the contact and the membrane resistance, the latter can be easily deduced.
Figure III.3: Conductivity cell using two platinum discs.

III.3. Differential scanning calorimetry

The investigation of the crystallinity and crystallization behavior of the grafted films and membrane were performed by means of differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 instrument under N₂ atmosphere. The DSC instrument was first calibrated with Indium (Tₘ = 156.6 °C, ∆Hᵣ = 28.5 J·g⁻¹) and lead (Tₘ = 327.5 °C) standards for the temperature and energy calibration. Prior to measurement a baseline was collected, and subtracted from the measured heating curves to reduce the signal to noise ratio and for higher accuracy.

Prior to starting, the sample holder was purged with nitrogen for 10 min to equilibrate the system and remove any remaining oxygen in the pans. The heating cycles over a range of 30-300 °C were measured at a constant heating rate of 20 °C·min⁻¹ using a constant nitrogen flow.

The obtained peaks were then integrated using the same integration temperature limits (210-272 °C) for the determination of the heat of fusion (∆Hᵣ) for ETFE based grafted films and membranes. The degree of crystallinity of the base polymer film was calculated according to the following equation:

\[
Crystallinity \, (\%) = \frac{\Delta H_f}{\Delta H_0} \times 100
\]  

(III.11)

where ∆Hᵣ is the heat of fusion determined from the peak area of the melting and ∆H₀ is the reported value of heat of fusion for a 100 % crystalline polymer (113.4 J·g⁻¹ for ETFE)¹²⁶,¹²⁸.
Since the grafting of polystyrene increases the amorphous zone, a correction was applied for the dilution effect for the determination of the inherent (intrinsic) crystallinity. Therefore, the intrinsic (inherent) crystallinity can be calculated using the following equation:

\[
inherent \ crystallinity\ (\%) = crystallinity\ (\%) \times \left(1 + \frac{GL}{100}\right) \tag{III.12}\]

### III.4. Thermogravimetric analysis

The thermal stability of the grafted films and membranes was determined by thermogravimetric analysis (TGA) measurements, where a Perkin Elmer TGA7 instrument was used under nitrogen atmosphere. The temperature and the balance calibration were performed according to the Curie point of alume and perkalloy as calibration standards.

Prior to the heat treatment, the samples in the TGA chamber were purged with nitrogen for 10 min. After that purging period, the sample was heated at a constant heating rate of 20 °C·min\(^{-1}\) over a range of 50–650 °C.

For membranes, in addition to the previously cited heat treatment another step is added, which consists in holding the temperature when it reach 100 °C for 10 minutes to remove excess water prior to TGA measurements.

The relative thermal stability of the films and membranes was evaluated in terms of the initial decomposition temperature (IDT) at which the first 2 % mass loss had occurred. The TGA curves were differentiated to determine the maximum rate decomposition temperature (MRDT), selecting the minima of the first derivative. Furthermore, the residue of decomposition was obtained, and the specific weight loss of a decomposition feature was determined by the local maxima of the first derivative.

### III.5. Mechanical tests and dimensional stability

#### III.5.1. Mechanical tests

The mechanical properties of the films and membranes based on ETFE were investigated by Universal Testing Machine Zwick Roell Z005 with a maximum test load of 5kN, cross head speed from 0.0005 to 3.000 mm·min\(^{-1}\) and a load frame height of 2059 mm (Figure III.4). The measurements were performed at a cross head speed of
100 mm·min⁻¹.

Figure III.4: Image of the sample holders in the used machine.

The membranes were converted to salt form in KCl solution (0.5 M) and then dried at 50 °C in an oven for at least 24 h. A special cutter (fixed blade) was employed for the preparation of test samples. In this work, rectangular specimens (1 cm x 10 cm) were examined. Ten specimens were prepared and measured for each film or membrane sample. All the samples were analyzed for machining (where the extrusion of pristine polymer films was employed) and transverse (perpendicular to extrusion) directions.

Tensile stress-strain characteristics are derived by monitoring both the force required to pull a material apart and the elongation that the material undergoes as a result of the applied force at a constant deformation rate. In order to convert the force and the displacement into stress-strain characteristics:

The stress is defined as:

$$\text{Stress} = \frac{\text{Force}}{\text{Area}} \quad [\text{MPa}] \quad (\text{III.13})$$

The definition of strain is:

$$\text{Strain} = \frac{\text{Extension}}{\text{Original Length}} \quad [%] \quad (\text{III.14})$$
The elastic modulus is given by:

$$\text{Modulus} = \frac{\text{Stress}}{\text{Strain}} \ [\text{MPa}] \quad (\text{III.15})$$

Yield point is defined as the lowest stress at which the strain increases without increase in stress (Figure III.5).

![Figure III.5: typical stress/strain curve obtained for ETFE grafted membranes.](image)

**III.5.2. Dimensional stability**

The dimensional stability of the radiation grafted membrane upon swelling and drying is a paramount prerequisite for the mechanical durability under fuel cell operating conditions. Thus, the determination of the variation of this property within different parameters (GL, crosslinker concentration and water content) is crucial to correlate its changes with the obtained *in situ* data in wet/dry cycles.

The dimensional stability is a measure for the variation of the different dimensions of the radiation grafted membranes (machining direction, transverse direction and thickness) in wet and dry state. A square piece of the fully swollen membrane is cut using a punching cutting tool (54 mm). Both directions (MD, TD) are well labelled. The thickness is measured quickly using a digital thickness gauge (MT12B Heidenhain, Germany) with a resolution of 0.5 µm. The membrane is then dried between tissue papers in the vacuum oven at 80 °C for 2 h. Thereafter taking out the membrane from the oven, the dimensions are measured immediately. The area and volume shrinkage is then given by:
III Experimental

\[
\text{Area change} = \frac{\text{Area(wet membrane)} - \text{Area(dry membrane)}}{\text{Area(dry membrane)}} \cdot 100\% \quad (\text{III.16})
\]

\[
\text{Volume change} = \frac{\text{Volume(wet membrane)} - \text{Volume(dry membrane)}}{\text{Volume(dry membrane)}} \cdot 100\% \quad (\text{III.17})
\]

III.6. Chemical degradation*

Membrane samples were dried and weighed and then immersed in ultra pure water overnight (water-equilibration step). Then, the samples were put into glass beakers containing a 3% H\textsubscript{2}O\textsubscript{2} aqueous solution and held for different periods at 60°C. The samples were then removed, put again in pure water and were shaken for more than 24h. Thereafter, they were washed in water and dried in the oven under vacuum overnight. In the final step, they were reweighed\textsuperscript{(129)}. Therefore, the weight loss can be calculated by the following equation:

\[
\text{Weight loss} (\%) = \frac{W_d(t)}{W_d(0)} \times 100
\]

\(W_d(0)\) : weight of the dry membrane at \(t = 0\).
\(W_d(t)\) : weight of the dry membrane after treatment.

III.7. Single fuel cell test

The surface water in the radiation grafted membrane was blotted and the membrane was assembled with ELAT\textsuperscript{®} electrodes (type LT140EWSI, E-TEK / BASF Fuel Cell, Inc.) with a noble metal loading of 0.5 mg Pt cm\textsuperscript{-2}. The membrane and the electrodes were hotpressed at 110 °C / 15 kN / 180 s to form a membrane electrode assembly (MEA). The MEAs were assembled into single cells comprising a flow field machined into graphite plates. Two different types of cells were used with different flow field geometry:

Cell design 1: in this case, only a gasket of PTFE 200 µm is used to leak tide the cell assembly (Figure III.6).

* Measurements performed by Tetsuya Yamaki and Shin-ichi Sawada from Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan.
The cell geometry used is based on an active area of 30 cm$^2$, where the flow field is a 3-fold serpentine with channel/land width of 1 mm and channel depth of 0.5 mm (Figure III.7).

It is important to note here that the gas inlet/outlet ports are located outside of the active area to prevent any stress which can be caused by the gas access onto the MEA.

**Cell design 2:** the used cell geometry is based on an active area of 16 cm$^2$, which possesses a linear gas flow field with 1 mm width. For the cell assembly, a gasket (150 µm PTFE) and sub-gasket (25 µm Kapton®) were used to prevent edge failure (Figure III.8).
It is important to note that the gas inlet / outlet ports, where the mechanical stress can be the highest are located outside of the active area in this design (Figure III.9).

After the MEA assembly, a leak test was carried out on the cell to determine the gas losses using nitrogen and to verify the mechanical integrity of the membrane. The cell was then connected and operated at a temperature of 80 °C, using pure H₂ and O₂ at a stoichiometry of 1.5 each as reactants with minimum flows of 60 (H₂) and 30 (O₂) ml·min⁻¹, respectively, and at ambient pressure. The humidification of the H₂ feed stream was controlled by the use of a bubbler heated at 80 °C, whereas the O₂ was fed to the cell dry at the same temperature. The cell was operated at a fixed current density of 500 mA·cm⁻² for at least 200 h when investigating the membrane performance⁵. For the evaluation of the lifetime of the membrane the fuel cell test was maintained until failure.

**III.8. Electrochemical characterization methods**
III. Experimental

III.8.1. Polarization curve

In order to evaluate the performance of our fuel cells, polarization curves were recorded, where the voltage output for a given current density is recorded. The fuel cell polarization curves are recorded by the means of a potentiostat / galvanostat system.

III.8.2. Electrochemical impedance spectroscopy

For fuel cell research, the electrochemical impedance spectroscopy (EIS) is a powerful characterization tool used to elucidate \textit{in situ} the origin of the performance losses, and yields information on ohmic and interfacial resistances in an MEA\(^{(5)}\).

The measurement is performed by applying a sinusoidal current perturbation and following the system voltage response. The impedance is given by the equation:

\[
Z = \frac{V(t)}{i(t)} \quad [\text{Ohm}]
\]  

(III.19)

Where,

\[
V(t) = V_0 \cos(\omega t)
\]  

(III.20)

\[
i(t) = i_0 \cos(\omega t - \varphi)
\]  

(III.21)

and

- \(i_0\) is the current amplitude.
- \(V_0\) is the voltage amplitude.
- \(\omega\) is the angular frequency.
- \(\varphi\) is the phase shift between the current response and the voltage.

Using a complex notation, the expression of the impedance becomes an addition of two parts, an imaginary and a real part:

\[
Z = Z_0 \left( \cos(\varphi) + j \sin(\varphi) \right) 
\]  

(III.22)

\[
Z = Z_{\text{real}} + Z_{\text{imag}}
\]  

(III.23)

Where, \(j\) represents the imaginary number \((j^2 = -1)\).

The impedance data are usually represented in the Nyquist plot, which is obtained by the presentation of the real part \((Z_{\text{real}})\) on the x axis and the imaginary part \((Z_{\text{imag}})\) on the y axis. The resulting spectra are semi-circle like and intercept the real axis at the low and
high frequency end (Figure III.10). EIS spectra were recorded using a Zahner IM6 or IM6e system (Zahner Messtechnik, Kronach, Germany) at a DC current density of 0.5 A.cm\(^{-2}\) in pseudo-galvanostat mode with a perturbation signal of 100 mA amplitude, in a frequency range between 100 mHz and 25 kHz. From these spectra the intercept at high frequency was interpreted as ohmic resistance (R\(_\Omega\)), while the diameter of the semicircle was interpreted as polarization resistance (R\(_{pol}\)):

\[
R_{\Omega} = \lim_{\omega \to \infty} \text{Re}(Z) \quad \omega \to \infty, \text{Im}(Z) = 0
\]

\[
R_{pol} = \lim_{\omega \to 0} \text{Re}(Z) - R_{\Omega} \quad \omega \to 0, \text{Im}(Z) = 0
\]

Figure III.10: Impedance spectrum of MEA based on ETEK-140w electrodes and Nafion®112 under the conditions described above.

The \textit{Randles} equivalent circuit model was used to evaluate the EIS experimental data (Figure III.11). In this model, the electrochemical reaction in the cathode and the anode are condensed in one reaction and the porous electrode characteristics are neglected\(^{5}\).
**III. Experimental**

**III.8.3. Cyclic voltammetry (CV)**

The electrochemical platinum surface area of the anode and cathode, respectively, were determined via CO stripping voltammetry at a cell temperature of 80 °C. In preparation of the experiment, fully humidified N\textsubscript{2} was fed to the working electrode and fully humidified H\textsubscript{2} to the opposite electrode serving as reference and counter electrode, at a flow rate of 200 ml·min\textsuperscript{-1} each for at least 1 h. After 1 h, a stable equilibrium potential of around 0.1 V is reached. Impurities on the Pt catalyst surface were removed by cycling the potential of the working electrode between 0.05 and 1 V at a sweep rate of 100 mV·s\textsuperscript{-1} four times. The potential was then set to 0.125 V and the working electrode feed gas changed from pure N\textsubscript{2} to N\textsubscript{2} / 1 % CO for 15 min to adsorb CO on the catalyst. Non adsorbing CO gas phase was subsequently removed by purging with pure N\textsubscript{2} for another 15 min, and then the CO stripping voltammetry was performed at a sweep rate of 10 mV·s\textsuperscript{-1}, followed by voltammetry cycles between 0.05 and 1 V.

From the area under the CO electro-oxidation peak the electrochemical platinum surface area was calculated, assuming a specific charge of 420 µAs·cm\textsuperscript{-2} (Pt) (Figure III.10). To obtain the specific electrochemical catalyst surface area, this value is divided by the catalyst loading of the electrodes (0.5 mg·Pt·cm\textsuperscript{-2}).

Figure III.11: *Randles* equivalent circuit model.
Figure III.10: Typical example of an *in situ* CO-stripping curve voltammogram of a Pt/carbon electrode with a catalyst loading of 0.5 mg Pt cm\(^{-2}\).

**III.8.4. Pulse resistance**

The *in situ* membrane resistance measurement during fuel cell operation was performed by means of the current pulse method developed in house at PSI\(^{[111, 130]}\). Sequences of 5 A current pulses generated by an extremely fast pulse generator (rise time < 10 ns, pulse duration 10 \(\mu\)s, decay time \(\leq 5\) ns), were superimposed on the DC current delivered by the fuel cell. The voltage transient is analyzed by a fast oscilloscope (LeCroy 9310M) in a time window of 200 to 700 ns after the pulse. The membrane resistance was calculated by implementing Ohm’s law. The description and details of this method are described elsewhere\(^{[111, 130]}\).

**III.8.5. Hydrogen permeation**

The permeability of the membrane for reactant gases during fuel cell operation is a measure of the mechanical integrity and morphological changes within the membrane. Thus, the hydrogen permeability of the radiation grafted membrane is monitored via *in situ* measurement of the hydrogen crossover rate.

In preparation of the experiment, the cell is maintained at 80 °C and the gases are kept fully humidified at the same temperature. The cell is operated on H\(_2\) / N\(_2\) mode, as described in the previous paragraph devoted to the cyclic voltammetry experiment. Fully humidified N\(_2\) was fed to the working electrode (cathode) and fully humidified H\(_2\) to the opposite electrode serving as reference and counter electrode (anode), at a flow rate of
200 ml·min\(^{-1}\) each for at least 1 h. For the measurement of the rate of H\(_2\) permeation through the membrane, the potential of the working electrode was cycled once between 100 mV and 800 mV at a sweep rate of 100 mV·min\(^{-1}\) and the current density was recorded at each potential (100, 200, 300 mV…..) after 1 min. The H\(_2\) crossover rate was measured by extrapolating the fitted curve to 0 V, where the extracted current is the limiting current for H\(_2\) permeation through the membrane from the H\(_2\) to the N\(_2\) side (Figure III.11).

![Figure III.11: Example of H\(_2\) crossover measurement.](image)

### III.9. Post mortem analysis

In order to perform a *post mortem* analysis of the tested MEA, the electrodes were separated from the membrane by immersing the MEA in water for 2h and subsequent treatment with ultrasound for at least 30 min.

The collected membranes were exchanged from the pro-tonic form in 0.5 M KCl, dried in vacuum, and the FTIR spectra were recorded with the same setting as described before (paragraph *IV.2.2*). The band peak corresponding to the S=O group in the FTIR spectra used normally in the case of FEP-based membranes was overlapping with the peaks of the ETFE backbone in our case. Therefore, the area of the aromatic peak appearing at 1494 cm\(^{-1}\) was exploited to determine the degradation as follows:

\[
\text{Degradation} = \frac{A(\text{tested}) - A(\text{untested})}{A(\text{untested})} \times 100\% \quad (\text{III.26})
\]
Where:
- $A(\text{tested})$ : the area of the aromatic peak for the non-active and active area of the tested membranes.
- $A(\text{untested})$ : the area of the aromatic peak for the non-tested area of the membrane (used for IEC and conductivity determination).

For better analysis and separation between the channel and land in the membrane, a metallic slit mask was used (Figure III.12).

Figure III.12: Metallic slit mask used for the FTIR-measurements.
IV Grafting kinetics of styrene into ETFE base film

The preparation of radiation grafted membranes in this work is based on the pre-irradiation method. Thereby, the irradiation process and the synthesis conditions should be controlled and optimized. The main objective is not only to optimize the grafting parameters to ensure a fast and efficient grafting but also to fix and control them, to obtain reproducible results and a robust process. The challenge at that point is directed towards the understanding of the radiation grafting response to the variation of several parameters of our system based on ETFE base film. It is evident that the graft polymerization is strongly influenced by the irradiation and the synthesis conditions, such as pre-irradiation dose, monomer concentration, composition of grafting solution, crosslinker concentration and reaction temperature. The grafting in the studied system (ETFE-graft-styrene) proceeds by the grafting front mechanism (paragraph II.4.2) as proposed by Chapiro\(^{(131)}\).

A simple mathematical model was selected to describe quantitatively the influence of the grafting parameters and fit the changes of the graft level (GL) versus reaction time. However, the model does not take into account the influence of transfer reactions (solvent and monomer transfer reactions) and the local differences in monomer concentration or reactivity and also volume changes during grafting. Furthermore, the effect of the homopolymer formation during the grafting reaction is ignored by this model. The following equation was used\(^{(132-135)}\):

\[
GL = \frac{r_{p0}}{\gamma} \ln \left(1 + \gamma(t - t_0)\right)
\]  

where \( r_{p0} \), the apparent initial polymerization rate, is given by:

\[
r_{p0} = k_p \left[ M \right]_0 \left[ P^* \right]_0
\]  

\( \gamma \), the radical recombination rate, which is a measure for radical lifetime, is defined as:

\[
\gamma = k_r \left[ P^* \right]_0
\]  

\( t_0 \): the delay time

* These results have been published:
$k_p$: the polymerization rate constant
$k_f$: the rate constant for bimolecular termination
$[M]_0$: monomer concentration
$[P^*]_0$: initial radical concentration

The ratio of the apparent initial polymerization rate and the characteristic radical recombination rate may be considered as an indication of the grafting efficiency\(^{(133)}\).

For the investigation of the temperature effect on the grafting reaction, in addition to the used model, the Arrhenius equation was used for the calculation of the activation energy, $E_a$:

$$k = A e^{-\frac{E_a}{RT}} \quad \text{(IV.4)}$$

Where
$k$: the rate constant
$A$: pre-exponential factor
$R$: the gas constant
$T$: the absolute temperature in K

In this chapter, the influence of the irradiation and synthesis parameters on grafting yield and grafting kinetics for radiation-induced grafting of styrene into ETFE are investigated. Thus, the influence of pre-irradiation dose, temperature, monomer concentration, and composition of grafting solution were studied. The used ETFE films (7 cm x 7 cm) were grafted in a glass reactor (60 ml reaction volume) under the following standard conditions:

- 1.5 kGy irradiation dose.
- 20\% (v/v) styrene concentration.
- 15\% (v/v) water in grafting solution.
- 65\% (v/v) isopropanol.
- 50 °C grafting temperature.
IV Grafting kinetics of styrene into ETFE base film

IV.1. Influence of the irradiation dose

The irradiation dose is a very important parameter, which strongly influences the physical properties of the base polymer. The ETFE base material is well known for its good resistance to irradiation. The dose range (1.5 - 30 kGy) selected in this investigation, does neither affect the crystallinity nor do the mechanical properties of the base materials (see chapters V and VII).

The graft level (% mass) obtained as a function of reaction time at various irradiation doses is presented in (Figure IV.1). The graft level increases with the irradiation dose. All kinetic curves show an initial increase with the reaction time and reach a quasi-plateau region, except for 30 kGy. The observed increase of the GL with the dose is a consequence of the increasing number of active sites within the polymer matrix. one can even achieve graft levels above 400 % using an irradiation dose of 30 kGy, and a significant expansion of the grafted films in all directions (machining direction, transverse direction and thickness) is observed. Nonetheless, these highly grafted samples become difficult to handle after drying due to the deterioration of their mechanical properties as observed previously for FEP based grafted films\(^{(133)}\).

Figure IV.1: Variation of graft level as a function of reaction time for different irradiation doses.

The fitting of the kinetic curves using the model described by eqn. IV.1, and the resulting kinetic parameters are shown in the Figure IV.2.
The initial rate of polymerization, $r_{p0}$, shows a considerable increase upon the increase of the irradiation dose. This was expected from the obvious increase of the amount of the created active sites (alkylperoxide groups) with the irradiation dose. Seemingly, as the irradiation dose increase, the utilization of radicals in graft initiation and subsequent chain propagation is enhanced. The characteristic radical recombination rate, $\gamma$, can be considered nearly constant within the accuracy of the fit, especially for low doses. However, at higher dose rates, the decay of radicals due to recombination and transfer reactions is expected to increase. Accordingly, the time to obtain a certain graft level is reduced by the increase of the irradiation dose. It was observed that grafting did not start instantaneously and a delay time, $t_0$, caused by slow warming of the solution and/or slow diffusion of the first monomer molecules to the reactive sites at the interior of the ETFE film, can be noticed. The value for the delay time increases almost four times, when the irradiation dose is increased from 1.5 kGy to 30 kGy. This may be attributed to a change of availability of the monomer in the grafted zone as the number of reactive sites increases.

![Figure IV.2: Kinetic parameters calculated according to Eqn. IV.1.](image)

The dependence of the initial grafting rate $r_{p0}$ on the irradiation dose, determined from the slope of the log-log plot of the initial rate of grafting versus irradiation dose is presented in the Figure (Figure IV.3).
IV Grafting kinetics of styrene into ETFE base film

![Graph of Log-Log plot of the initial rate of grafting versus irradiation dose.]

Figure IV.3: Log-Log plot of the initial rate of grafting versus irradiation dose.

From the fitting of the obtained experimental data, the dependency of the grafting rate on the irradiation dose was found to have a value of 0.51. This value is consistent with the theoretical value of 0.5 for free radical polymerization. The order of dependence was determined (by using FEP as the base polymer film) as 0.64 for styrene, 0.58 for acrylic acid and 0.53 for styrene-acrylic acid, whereas a lower value was observed for PVDF grafted with styrene (0.43)\(^{(136-140)}\).

IV.2. Influence of monomer concentration

Throughout the grafting process based on the pre-irradiation technique, the diffusion and reactivity of the monomers are the key parameters. Likewise, the homopolymer formation is a side reaction occurring during the grafting reaction, which has to be dealt with. Therefore, it is important to optimise the initial concentration of monomer in order to reach the suited GL with a low monomer concentration, to limit the side reactions in the grafting solution and thereby increasing the grafting efficiency.

The variation of graft level with reaction time at various monomer concentrations (5% to 100% (v/v)) is shown in Figure IV.4. The graft level increases dramatically with an increase in styrene concentration, until it reaches a maximum at 20 % (v/v) styrene for reaction times above 2 h, and then decreases sharply as the concentration further increases.
Interestingly, for the grafting times below 2 h, this maximum is shifted to 50 % (v/v) styrene. This effect can be attributed to the partitioning between the two phases, namely the monomer and solvent mixture ratio (the solvent is a mixture of isopropanol/water : 65/15 (v/v)) inside the polymer matrix)\(^{132}\). Based on the grafting front mechanism, the increase in graft level may be attributed to the increase in the styrene diffusion and its concentration in the grafting layers. However, at very high concentration of styrene, homopolymer formation is enhanced and the diffusion of styrene across the viscous medium is hindered. The shifting observed for the lower reaction times may be due to the induction period. Indeed, the styrene used in this study is not purified and contains, as all commercial vinylic monomers, an inhibitor, which tends to terminate the first generated radicals\(^{138}\). A similar trend was reported for the grafting of styrene into PTFE, FEP, and PFA films under identical conditions\(^{141-144}\).

The extracted kinetic parameters \( (r_{p0}, \gamma, t_0) \) from the curve fitting are shown in figure IV.5. The initial polymerization rate, \( r_{p0} \), increases considerably as the monomer concentration increases from 5 % to 50 %. As long as the monomer accessibility to the propagating sites is facilitated, the grafting proceeds smoothly. The characteristic radical recombination rate, \( \gamma \), changes slightly at the beginning; however, a dramatic change is observed with the change of monomer concentration above 20 %, which may be attributed to the decay of radicals, due to radical transfer from ETFE to solvent (homopolymer formation in the grafting solution) or otherwise favoured termination reactions. The delay time increases from 10 minutes to 30 minutes, when the styrene
concentration increases from 5 % to 20 %, and no delay is determined after 50 %. At low styrene concentration, the diffusion of the monomer is the limiting factor and with an increasing concentration of styrene, the availability of the monomer in the grafting zone increases and grafting proceeds smoothly, without any induction period and/or delay time.

The variation of the initial rate of grafting with the monomer concentration allows us to determine the order dependence of the grafting rate on the monomer concentration up to a concentration of 50 % styrene. This order was found to be 1.5, less than the value of 1.9 reported for grafted FEP films\(^{(138)}\), and higher than the value 1.2, reported for grafted PVDF film\(^{(137)}\). First order dependence of the grafting rate on the monomer concentration indicates the classical free radical polymerization kinetics. The observed complexity may be due to the extensive homopolymerization during the grafting reaction. It is known that homopolymerization may hinder the monomer diffusion to the radical sites and therefore yields lower graft levels. The maximum efficiency of grafting is reached at 20 % (v/v) of monomer concentration, whereas below and above this value the efficiency decreases.

Figure IV.5: Kinetic parameters calculated according to Eq. IV.1.
IV.3. Influence of temperature

The temperature of the grafting reaction is expected to have a significant effect on the kinetics of the reaction and on the reached graft level. The variation of graft level as a function of reaction time at different temperatures in the range of 50-90 °C is presented in figure IV.6.

![Figure IV.6: Variation of graft level as a function of reaction time for different grafting temperatures.](image)

The initial rate of grafting increases with the reaction temperature up to 60°C, and later an opposite trend is observed for the range of 70-90°C. Similarly, the degree of grafting increases with an increase of the reaction temperature up to 60°C, while after 70 °C the degree of grafting decreases considerably with increasing temperature.

In fact, the grafting is controlled by a cumulative effect of the monomer diffusion within the polymer bulk, termination of the growing polymer chains, and the deactivation of the primary radicals. As the reaction temperature increases, the monomer diffusion within the bulk also increases. This enhances the monomer accessibility to the grafting sites within the polymer bulk. Consequently, the rate of initiation and propagation is enhanced. The other aspect of grafting is that the grafted zone remains swollen in the grafting medium, which leads to high mobility of the growing chains within the matrix. Therefore, termination of the two growing chains by mutual combination becomes dominant at higher temperatures. At the same time, the primary radical termination may also be accelerated by the time the monomer reaches their vicinity. In addition to that, the increase of the reaction temperature enhances the production of homopolymer in the grafting solution and then the diffusion of the monomer is hindered. In spite of the higher
rate of initial grafting, the final graft level would decrease. A similar tendency was reported for the grafting of styrene into FEP based films and the grafting of TFS onto ETFE, FEP, PTFE, PFA, LDPE films\textsuperscript{(133, 145, 146)}.

The initial rate of grafting increases significantly with temperature (up to 80 °C), since both, the reactivity of radicals and the monomer diffusion to the grafting sites are enhanced (Figure IV.7). Moreover, an induction period is observed only up to 50 °C and the reaction proceeds without any delay time at temperatures above 50°C because of the reasons mentioned above. The characteristic decay rate of the radicals also increases linearly as the temperature increases, because recombination and transfer reactions become favourable at high temperatures. Consequently, the efficiency of grafting is decreasing with the increase of the grafting temperature.

The activation energy is determined from the plot of the initial grafting rate versus the inverse temperature, according to Equation. IV.4. The overall activation energy calculated for the temperature range of 50-80°C is 98.4 kJ/mol, which is higher than the values obtained for the similar grafting systems based on PVDF (73 kJ/mol) and FEP films (27.9 kJ/mol)\textsuperscript{(132)}. A high $E_a$ value suggests a low grafting rate and a strong dependence on temperature.

![Figure IV.7: Kinetic parameters calculated according to Eq. IV.1.](image-url)
IV.4. Influence of water content

The use of water as a non-solvent in the pre-irradiation grafting of styrene onto FEP was found to yield higher graft levels with faster kinetics. It was stated that the addition of a non-solvent or even some mineral acids and salts induced a shift in the partitioning of the monomer concentration between the liquid phase and the polymer phase\(^{(132)}\). Therefore, we investigated the role of water content (in the range of 10% to 40% (v/v)) in the initial grafting solution on the kinetics and the progress of the graft level values (Figure IV.8).

![Graph showing variation of graft level as a function of reaction time for different water content in the grafting solution.](image)

Figure IV.8: Variation of graft level as a function of reaction time for different water content in the grafting solution.

The highest graft level was achieved with concentrations of 15 % water (v/v) for reaction times below 6 h and with 10 % water (v/v) above 6 h. It is very important to note that the lower water content of a grafting solution (10 %, 15 %, and 20 %) yields a homogeneous and compatible grafting solution, while the higher water content gives an immiscible grafting solution, composed of two phases. The water rich lower phase, containing the base polymer film and the upper monomer rich phase. The grafting solution is still saturated with monomer and provides the highest possible monomer concentration in the swollen film, even if some part of monomer is consumed by homopolymerization. Therefore, it is clear that the use of lower water content in this case has an accelerative effect on the grafting onto ETFE films.

The fitting of the kinetic curves and the extracted parameters \((r_{p0}, \gamma, t_0)\) do not show a significant trend with varying the water content (Figure IV.9). Both, initial
polymerization rate and the characteristic radical recombination rate increase slightly with increasing water content of the grafting solution, due to increased swelling of polystyrene grafts with styrene. Moreover, except for 10 % water, the delay time is not a significant parameter, which is not affected by the increase of water content. Introduction of a higher amount of water to the grafting solution enhances reaction rate and no delay time is observed. This is due to the enhanced mobility of polymer segments by the influence of the swelling agents.

![Graph](image)

Figure IV.9: Kinetic parameters calculated according to Eq. IV.1.

The efficiency of the grafting is not affected by the increase of water content in the grafting solution. It seems that an optimum amount of water is required to overcome diffusion limitations of monomers and their necessity to approach the backbone active sites. However, the further increase in water content in the solution and the creation of two phases would reduce the monomer accessibility within the matrix. In this grafting system, the water as polar component improves the accessibility and the penetration of the monomer to the polymer matrix.
IV.5. Influence of crosslinker

Styrene based radiation grafted ETFE membranes are prone to degradation under fuel cell conditions and fail rapidly after only 200 h (test conditions are described in paragraph III.7). One method to increase the lifetime of such a membrane is to crosslink the grafted component, to reduce the degradation of the system by three-dimensional network creation (Figure IV.10).

Based on the previous investigation on the influence of different grafting parameters we selected the obtained optimum conditions to investigate the influence of the crosslinker concentration. Thus, grafting reactions were carried out in a stainless steel reactor under a nitrogen atmosphere, using ETFE base films irradiated to a dose of 1.5 kGy. The grafting solution consisted of 20 % (v/v) monomer (mixture of styrene and divinylbenzene (DVB)), 65 % (v/v) isopropanol and 15 % water as described previously. The DVB concentration, given as the volumetric ratio of DVB with respect to the total monomer volume (DVB + styrene) in the initial grafting solution, was varied over 0 %, 5 %, 8 %, 10 %, 15 % and 20 %. The grafting reaction was initiated by placing the reactor in a thermostatic bath at 60°C for different reaction times.

Figure IV.10: Schematic of the radiation grafting of styrene/DVB onto an ETFE base film.

The grafting of styrene into ETFE films was carried out at different DVB concentrations in the initial grafting solution. We determined that the concentration of the crosslinker in the initial grafting solution affects significantly the grafting behaviour and reaction kinetics. The obtained graft levels as a function of reaction time at several DVB
concentrations (in the initial grafting solution) for the grafting of styrene into ETFE base film are presented in figure IV.11.

At very early phases of the reaction (<8 h), the highest graft level can be achieved for 0 % DVB and thereafter the graft level decreases as the DVB concentration increases. This behaviour can be attributed to the formation of a crosslinked structure, which serves as a barrier for monomer diffusion. On the other hand, for the longer reaction times (8, 16, 24 h), the introduction of DVB at a low concentration (5 % DVB) yields the highest graft level. Beyond 5 % DVB, the graft level is found to be reduced with DVB concentration. That is to say, at a low crosslinker concentration, in the presence of water in the grafting solution, a higher graft level than with 0 % DVB in solution is observed. The increase of the graft level with the introduction of a small amount of DVB can be explained by the immobilization of growing chains, which results in the decreased chain recombination. As a consequence, the polymer chains can reach higher length and the graft level increases. Moreover, the high reactivity of the double bonds of DVB induces higher graft levels. A similar behaviour was reported previously for styrene/FEP, and p-methylstyrene/ETFE combinations\textsuperscript{(129,133)}.

\begin{figure}[h!]
\centering
\includegraphics[width=0.8\textwidth]{figure_IV.11.png}
\caption{Obtained graft levels as a function of the reaction time for different crosslinker concentrations in the grafting solution.}
\end{figure}

The kinetic parameters ($r_{p0}$, $\gamma$, $t_0$) were determined by fitting the kinetic data presented in figure IV.11 using equation IV.1. Figure IV.12 shows that both the initial polymerization rate ($r_{p0}$) and radical recombination rate ($\gamma$) decrease with increasing
DVB concentration. Owing to the reduction of the polymer swelling in the grafted parts and the creation of a three-dimensional network, which reduces the diffusion of the monomer, a slowdown of the polymerization reaction and an increase in the radical lifetime are observed as DVB concentration increases. Moreover, the delay time \( t_0 \) of the polymerization is increasing up to 5% DVB which can be again explained by the restricted monomer diffusion as DVB concentration increases. However, the delay time decreases up to 10% DVB and then levels off which is somewhat unexpected. In fact, this mathematical model does not perfectly fit to our system since it has several assumptions as mentioned in the beginning of this chapter. One of the assumptions is that there are no local differences in the monomer concentration; however, we believe that there are differences in different regions of the film in terms of monomer concentrations since the films are rolled inside the reaction tube, as a result, deviations and unexpected results are observed in some cases.

![Figure IV.12: Kinetic parameters calculated according to Eq. IV.1.](image)

The grafting of styrene into ETFE films is highly depending on the synthesis conditions. At low concentration, the water content in the solvent mixture yields a high graft level even at low monomer concentrations. The greater efficiency of the grafting reaction in an isopropanol-water mixture at low irradiation doses is favorable to achieve reasonable graft levels without deterioration of mechanical properties. An increase of reaction temperature decelerates the rate of grafting, and leads to increased homopolymer formation. To simplify the system, we determined the optimum grafting conditions for the styrene/ETFE system without using a crosslinker.
The introduction of a crosslinker (DVB) brings much more complexity to the styrene/DVB based system. Grafting kinetics based on styrene/DVB and ETFE were investigated by varying the concentration of DVB as the crosslinker. The results indicated that the concentration of DVB (with respect to total monomer volume) in the initial grafting solution shows a significant influence not only on the grafting reaction itself, but also on the characteristics of the resultant films and membranes. First of all, the addition of DVB at low concentration enhances grafting while higher concentrations of DVB induce lower graft levels. In addition, the initial polymerization rate and the radical lifetime exhibited a decrease with the increasing crosslinker content. These trends were apparently accompanied with several morphological and structural changes caused by the location and inhomogeneous distribution of crosslinker in the surface and the bulk of the ETFE based grafted film.

The detailed kinetic investigations described in this study for the grafting system of ETFE-g-styrene and ETFE-g-styrene/DVB have led to a better understanding of the preparation of homogenous membranes from ETFE films. An easy control over the grafting yield could be achieved by proper selection of reaction conditions. Based on this kinetic study, we were able to control the graft level values and also the crosslinker content. The aim is to investigate the relationship between the fuel cell *ex situ* and *in situ* properties and the structure of the radiation grafted based membranes based on fixed parameters (GL, crosslinker content).
V   ETFE-g-styrene/DVB: Structural investigation

The previous chapter dealt with the optimization of the kinetic parameters of grafting, to easily tune the graft level values precisely and in a reproducible manner. Therefore, the influence of the crosslinker content and the graft level on the properties of the radiation grafted based membranes can be studied separately. In fact, a lot of work was directed towards the effect of graft level on the properties of different membranes based on FEP and PVDF\(^{(125)}\). However, all these studies did not investigate the effect of crosslinker concentration in a systematic way, and no quantification of its content was presented. Dealing with the radiation grafting process, the extent and incorporation of the crosslinker is a complex issue. The composition analysis of our membranes is a paramount step for establishing the relationship between the in situ and ex situ properties and the content in the membrane instead of the initial concentration in the grafting solution mixture. This chapter is devoted to the investigation of the effect of the graft level and the crosslinker concentration on the structure, composition and physico-chemical properties of the grafted films and resulting membranes.

V.1. FTIR-ATR investigation of the composition of grafted films

It is of interest to determine the crosslinker content in the grafted films and the membranes to understand and to compare the differently crosslinked materials for their ex situ and relevant fuel cell properties. In fact, several studies were performed to evaluate the reactivity of the isomers in the styrene/DVB copolymers and their influence on the distribution of monomers and the mechanical properties\(^{(45, 147, 148)}\). In this study technical grade DVB, a mixture of several isomers including para-divinylbenzene, meta-divinylbenzene, para-ethylvinylbenzene and meta-ethylvinylbenzene, is employed. Indeed, the styrene and the DVB isomers have distinct and unique bands at 1486 cm\(^{-1}\) (for meta-disubstituted benzene), 1493 cm\(^{-1}\) (mono-substituted benzene) and 1510 cm\(^{-1}\) (para-disubstituted benzene), whereas the bands at wavenumber 1600 cm\(^{-1}\) and 1630 cm\(^{-1}\) are assigned to the vibrations of all aromatic rings and to the C=C stretching of pending double bonds, respectively (Figure V.1). The main obstacles for a direct quantification of the DVB content in the grafted films are the high absorbance of the ETFE base film and the quite low graft levels obtained with DVB as the only monomer at the standard reaction conditions.

To overcome these difficulties, a quantification method based on the use of homopolymer blends (poly(4-methylstyrene) and poly(3-methylstyrene)) with well known compositions as the standards, was developed for FEP based grafted films\(^{(149)}\).
Thus, empirical relationships between the relative concentrations of the species in the grafting solution and those found in the grafted films were developed. However, this method was only valid in the case of highly crosslinked FEP films (concentrations > 10 % DVB), whereas below that the molar ratios are rather over estimated. In the present investigation we developed a method for the quantification of the crosslinker (DVB) content in the grafted films based on ETFE and its real composition. The method is based on the fact that the ETFE is quite resistant to high irradiation doses in comparison with FEP (high degradation above 50 kGy). This allows to graft the pure crosslinker and to obtain reasonable graft levels.

![Comparison of the 1400-1650 cm⁻¹ region in the FTIR spectra obtained for different ETFE based grafted films.](image)

**Figure V.1**

**V.1.1. Monomers calibration model**

Samples of a defined size (6 cm x 3 cm x 25 µm) were grafted in 60 ml glass reactors and the applied grafting conditions were reported earlier (Chapter IV). Styrene grafted films with varied graft levels (GL) and measured dimensions were characterized by means of FTIR measurements. The area of the peak at the wavenumber 1493 cm⁻¹, assigned to the C=C aromatic skeleton stretch vibration for the monosubstituted benzene, is plotted versus the concentration of grafted polystyrene multiplied by the sample thickness (calibration curve) for different grafted films (figure V.2).
Figure V.2: Variation of the peak area of the band at 1493 cm\(^{-1}\) versus the concentration of grafted polystyrene multiplied by the sample thickness for different ETFE based grafted films.

Regression analysis of the obtained calibration curve gave the following analytical equation:

\[
\text{Peak area (1493 cm}^{-1}) = A \times \text{concentration} \times \text{thickness} \quad (V.1)
\]

\[R^2 = 0.94; \quad A = 438.76\]

In order to calibrate the DVB content, films irradiated with a high dose (200 kGy) were chosen to yield reasonably high graft levels with pure para-DVB and technical DVB (isomers mixture). The irradiated ETFE films with defined size (6 cm x 3 cm x 25 µm) were grafted in 60 ml glass reactors and the selected grafting conditions were used as reported earlier. The FTIR spectra of the para-DVB grafted into the ETFE base film are presented in figure V.3. The obtained bands at the wavenumber 1487 cm\(^{-1}\) and 1510 cm\(^{-1}\) are assigned to the C=C aromatic stretch vibration for meta-disubstituted benzene and for para-disubstituted benzene, respectively, were fitted (Figure V.3)(149).
Figure V.3: Comparison of the 1400-1650 cm\(^{-1}\) region in the FTIR spectrum obtained for ETFE-g-(\textit{para-DVB}) @ different graft levels.

The content of a pure \textit{para-DVB}\(^*\) grafted into ETFE base film and the calibration curve are depicted in figure V.4.

Figure V.4: Peak area of the \textit{para-DVB} band at 1510 cm\(^{-1}\) versus the concentration x thickness of ETFE-g-(\textit{para DVB}) films.

Regression analysis and fitting of the obtained calibration curve gave the following relationship:

\(^*\) Synthesis performed by Natalie Sigmund in the department of chemistry at the Technical University of Munich (diploma thesis 2006).
The same fitting was performed for the meta-DVB based grafted ETFE films and the regression analysis shows the following analytical equation:

\[ \text{Peak area (1487 cm}^{-1}) = A'' \times \text{concentration} \times \text{thickness} \]  
\[ R^2 = 0.93 ; \quad A'' = 523.55 \]  

These analytical equations (V.1, 2 and 3) allow the determination of the styrene/DVB content in the grafted films using FTIR and fitting of the corresponding bands. Nonetheless, this method does not take into account the content of non reacting pending double bonds, which is closely related to the effectiveness of crosslinking. It was observed that the content of the non reacting pending double bonds (band at 1630 cm\(^{-1}\)) increases with increasing the graft level and the DVB concentration in the initial grafting solution (Figure V.3 and 5).

Figure V.5: Comparison of the 1480-1640 cm\(^{-1}\) region in the FTIR spectrum obtained for ETFE-g-(styrene-DVB) with different DVB concentration at a fixed graft level (~ 20%).

The effectiveness and the reactivity of the second double bond in the DVB were stated to be lower than the first reacting one\(^{(148)}\). The reactivity of this bond is
significantly affected by the length of the polymer chain and was found to be prone in some cases to intramolecular crosslinking. Thus, as the polymer chain grows, the reactivity of the second double bond in DVB became lower\cite{148,150}.

**V.1.2. Effect of crosslinker content on the DVB/Styrene molar ratio in the near surface and bulk of grafted films**

The kinetic of grafting is based on the reactivity of monomers and their diffusion into the grafting medium. To understand how the changes in the composition of the grafted films in the surface (~1 µm) and through the entire bulk are affected, it is important to measure the extent of crosslinking and its distribution. The absorption spectra in transmission and ATR mode of ETFE based grafted films were investigated, and the bands were fitted to determine the molar ratio of DVB/styrene and to resolve the overlapping of the peaks of the \textit{mono}-substituted benzene (styrene) and \textit{meta}-disubstituted benzene (Figure V.6).

![Figure V.6: Example of peak fitting using GRAMS software.](image_url)

For this investigation, grafted films with different DVB concentrations (5, 8, 10, 15 and 20 % DVB (v/v) in the initial grafting solution) were prepared with fixed graft level (~ 25 %). The collected FTIR-ATR spectra were fitted and the molar ratios of DVB/styrene were then calculated.

The plotted molar ratios of DVB/styrene versus the DVB concentrations in the initial grafting solution are depicted in Figure V.7.

The following relationships were obtained by means of regression analysis, for transmission mode and ATR mode, respectively:

\[
Molar\ ratio\ (DVB/\ styrene) = 0.006 \times (%\ DVB) - 0.001; \quad R^2 = 0.95 \quad (V.4)
\]

\[
Molar\ ratio\ (DVB/\ styrene) = 0.009 \times (%\ DVB) - 0.081; \quad R^2 = 0.97 \quad (V.5)
\]

The molar ratio of DVB/styrene of the grafted films in both the surface (determined by ATR mode) and the bulk (determined by transmission mode) increases with the increase of the DVB concentration in the initial grafting solution, as depicted in Figure V.7. However, DVB is found to be enriched in the surface in comparison to the bulk of the film. The following order, in terms of DVB/styrene ratio, can be deduced:

(DVB/styrene) surface > (DVB/styrene) initial solution > (DVB/styrene) bulk
This observation confirms the dependency of the grafting reaction on both, the high reactivity of DVB and the diffusion of the monomer into the grafting (paragraph IV.5). Indeed, the more DVB is reacting on the surface, the denser will be the created three-dimensional network. Consequently, the diffusion of monomer(s) is restricted and a longer reaction time is required to accomplish the desired graft level.

The same observation was made for investigated grafted films, mainly based on styrene and FEP, by FTIR spectroscopy, using both the transmission mode and the surface sensitive ATR mode\(^{(149)}\). Results from both methods showed that a higher crosslinker content was found at the surface, expressed as the ratio of styrene to double substituted benzenes.

**V.1.3. Composition determination of para- and meta-DVB versus the graft level**

A lot of work was devoted to understand and distinguish between the reactivity of both isomers of DVB (para- and meta-DVB) and their copolymerization effectiveness with styrene. It was reported on the copolymerization of commercial DVB that para-DVB is more reactive than the meta-DVB in solution (e.g. toluene), whereas both DVB isomers are more reactive than ethylvinylbenzene\(^{(148)}\). In addition to the determination of the DVB/styrene composition of the grafted films, the issue is to understand the grafting kinetic of both isomers and their content.

Selected crosslinked ETFE-g-PS films (5% DVB in initial grafting solution) obtained at different reaction time (different graft levels) were characterized by FTIR-ATR to evaluate their composition and the concentration of crosslinker. After the fitting of the obtained spectra, the (DVB/styrene) molar ratio of the grafted films in the surface and the bulk were calculated (Figure V.8).
Figure V.8: Molar ratio of the styrene/DVB versus the graft level. The initial DVB concentration in the grafting solution is 5 % DVB.

As pointed out previously (paragraph V.1.2), the molar ratio of crosslinker in the surface is higher than in the bulk of the grafted films over the studied range of graft levels. As the graft level increases, the molar ratio DVB/styrene in the bulk does not significantly change, whereas in the surface the molar ratio values decrease up to 20 % graft level and no marked change was observed thereafter.

The molar ratios of the para-DVB/styrene, the meta-DVB/styrene and meta-DVB/para-DVB were also determined by FTIR characterization and the obtained results are presented in the Figure V.9 and 10.

Figure V.9: Molar ratio of the para-DVB and meta-DVB as function of graft level. The initial DVB concentration in the grafting solution is 5 % DVB.
Interestingly the molar ratio values of both isomers are similar at a low graft level. As the graft level increases the molar ratio of para-DVB/styrene decreases, whereas the molar ratio values of meta-DVB/styrene increase. The molar ratio of meta-DVB/para-DVB presents a more clear view of the reactivity of both isomers (Figure V.10). Considering that the starting molar ratio meta-DVB/para-DVB is 2.3 in the initial grafting solution, it is clear that the para-DVB is more reactive and is highly incorporated in the beginning of the grafting reaction. Thereafter, the incorporation of meta-DVB becomes significantly higher above 20% graft level. meta-DVB has been reported to be more effective in crosslinking than para-DVB due to the greater reactivity of the pending double bond\(^{150}\).

The grafting kinetic can be discussed taking into account the reactivity and diffusion aspects. In the beginning of grafting, the kinetics depend on the chemical reactivities of the monomers in the grafting solution. The grafting front is assumed to be formed and start to propagate into the irradiated film and the grafting becomes controlled by both reactivity and diffusion. As the three-dimensional network starts to be formed, the process becomes more and more controlled by diffusion. The formation of homopolymers in the grafting solution as byproduct may also play a role on the observed composition, since the para-DVB isomers are preferentially consumed because of their high reactivities.

![Figure V.10: Molar ratio (meta-DVB/para-DVB) as function of reaction time. Dashed line is the molar ratio (meta-DVB/para-DVB) in the initial grafting solution.](image)

Figure V.10: Molar ratio (meta-DVB/para-DVB) as function of reaction time. Dashed line is the molar ratio (meta-DVB/para-DVB) in the initial grafting solution.
V.2. Dimensional changes of the grafted films and membranes

One of the very interesting observations dealing with the pre-radiation induced grafting method for the preparation of fuel cell membranes is the occurring changes on all dimensional directions of the base material. The base material undergoes an increase in the machining direction, transverse direction and the thickness during the grafting and sulfonation steps. Thus, the assessment of these changes over the preparation steps is very important, keeping in mind their close relation with the changes on the morphology and the mechanical properties of the membrane.

V.2.1. Effect of graft level on the dimensional change

Grafting of irradiated ETFE films with initial dimensions of 16 cm x 14 cm x 25 µm was performed with the standardized procedure as described in paragraph IV.5, and the time was then varied to obtain a wide range of graft levels. The variation of the machining direction, transverse direction and thickness variation with varying the graft level of the radiation grafted ETFE films are presented in figure V.10.

![Figure V.10: Grafting induced variation of the different dimensions versus the graft level.](image)

Size increases in all dimensions after grafting (thickness, machining and transverse directions) with the increase of the graft level. Seemingly, the thickness and the machining direction were highly affected and expand more than the transverse direction. Two factors can explain the observed behaviour, which are the initial orientation (anisotropy) in the base film\(^{(151)}\), and the changes in the free volume of the material due to the relaxation of the chains, diffusion and swelling of the incorporated grafted chains.
Similar results were found for other base films such as PVDF, where the observed increase was attributed to the grafting kinetic and the dependency of the system to the monomer diffusion and swelling\(^{(152)}\).

The plot of the volume variation determined by measuring the grafted film dimensions (machining direction, transverse direction and thickness) versus the graft level (not shown) and the linear regression were carried out and the following relationship was obtained:

\[
volume \ variation \ (\%) = B \times \text{graft level} \ (%) \\
R^2 = 0.95; \quad B = 1.80
\]  

(V.6)

The same observation was made for different fluoropolymers (PTFE, PFA and FEP) where it was found that the volume variation of the grafted films increase linearly with the graft level\(^{(153)}\). Assuming that the increase of the volume is due to the incorporation of polystyrene chains, the determined slope B should be the ratio of the ETFE base film density over the grafted polystyrene density. Since the density values of ETFE and styrene are 1.73 g·cm\(^{-3}\) and 1.06 g·cm\(^{-3}\), respectively, the theoretical value of B is 1.63. The calculated value matches quite well with the theoretical one, indicating that ETFE and polystyrene form separated phases.

**V.2.2. Effect of DVB concentration on the dimensional change** *

It was of interest to evaluate the influence of the crosslinker content on the changes in the dimensions of the grafted films and membranes at a fixed graft level. For that aim, selected grafted films and membranes with a graft level of \(~25\)% and with varied crosslinker (DVB) concentration (0, 5, 8, 10, 15 and 20\% (v/v)) in the initial grafting solutions were then investigated. The change in the dimensions of both grafted films and membranes as a function of DVB concentration is presented in Figure V.11 a and b.

V ETFE-g-styrene/DVB: Structural investigation

Figure V.11: Effect of the crosslinker content on the dimensional changes (GL ~ 25 %). a) ETFE grafted films, b) ETFE based membranes. Membranes were in fully swollen state in H\textsuperscript{+} form and the measurements performed at room temperature.

All film and membrane samples were examined for their machining direction, transverse direction and thickness direction. Concerning the grafted films, there is an increase of 15.3-20.7 % in thickness while an increase of 12.3-16.5 % and of 9.8-13.6 % in machining and transverse directions, respectively, can be observed.

After sulfonation, the dimensional increase becomes more pronounced. A thickness increase of 28.1-35.2 %, an increase of 17.7-29.4 % in machining direction and 18.4-28.2% in transverse direction are observed (Figure V.11b). Apparently, the most affected dimension is the thickness in comparison with the two other dimensions. In addition, only a slight difference between the machining and the transverse directions are observed after grafting reaction and sulfonation.

It was found that the dimensional increase is almost independent of crosslinker concentration in the case of grafted films. However, concerning the membranes, the dimensional increase becomes lower with the increase of the DVB concentration. That can be resulted from the restricted free volume and the decreased swelling owing to crosslinker. Furthermore, the observed trend shows clearly that the density of the grafted domains increases inside the membrane.

V.3. Investigation of the area homogeneity

The radiation grafted membranes are based on commercial films with initial specifications (thickness, composition, physical properties). Besides the importance of the films processing, the homogeneity over the area of the starting film has an influence
on the preparation reproducibility and properties of the radiation grafted membranes\textsuperscript{(74)}.

The thickness of a pristine ETFE film initially 16 cm x 14 cm (Tefzel® 100LZ, 25 µm thick, purchased from Dupont (Circleville, USA)), was measured in 56 points over the film area as described in Figure V.12.

![Figure V.12: Schematic of the selected points for FTIR measurements and their positions.](image)

The observed thickness variation of the pristine ETFE film over the area is presented in Figure V.13. Surprisingly, the thickness of the pristine film is not constant (25 µm), but varies by 1 to 3 microns in measured points. The average and the standard deviation for the thickness from the 56 measured points are 26.5 +/- 0.8. These variations may have a considerable effect on the homogeneity of the grafted film and the density distribution of the grafts over the area.

![Figure V.13: Thickness of the pristine ETFE film.](image)
In order to illustrate the inhomogeneities over the grafted area (in terms of thickness, crosslinker composition and monomer concentration), a grafted film with 5% DVB (concentration in the initial grafting solution) and with a graft level of 25.4% was characterized by FTIR measurements in 56 points. The tested film was synthesized in a 600 ml stainless steel reactor with the use of filter paper as separator between the irradiated films (initially 16 cm x 14 cm).

The thickness of the obtained ETFE-g-styrene/DVB film shows a significant variation over the surface (Figure V.14). Indeed, there are some sections where the thickness is higher than others, yet no clear trend was observed between the middle part of the film and the edges. The average and the standard deviation for the thickness variation from the 56 measured points are 29.6 +/- 1.8.

![Figure V.14: Thickness of a ETFE-g-PS/DVB (5% DVB, graft level ~ 24.5%).](image)

The measured points and the corresponding DVB/styrene molar ratios over the grafted area are plotted in the Figure V.15. The first observation is that the distribution of molar ratios of DVB/styrene over the grafted area is relatively scattered. The average and the standard deviation for the molar ratio of DVB/styrene over the grafted area are given by 0.070 +/- 0.007.
This result shows that FTIR is as a versatile method for the determination of the homogeneity of films in terms of graft level, and also can be implemented to be used for the determination of the distribution of the crosslinker over the grafted films.

V.4. Determination of the crystallinity

The relationship between the molecular structure and the properties of the radiation grafted membrane is of considerable interest to understand the system. Crystallinity is one of the important physical properties, which plays a role in the mechanical stability of the base material. \(^{45}\)

The dependence of the crystallinity on the GL of the radiation grafted films and membranes based on styrene in combination with perfluorinated (FEP\(^{128, 154, 155}\)) and partially fluorinated (PVDF\(^{128, 152}\)) and ETFE\(^{128}\)) base films was widely investigated. The shape of the thermograms remains unaltered but changes with the increase of graft level\(^{128}\). The decrease of the inherent crystallinity with the graft level was attributed to the dilution effect mostly due to the incorporation of amorphous polystyrene\(^{154}\). Furthermore, with increasing GL, FEP-g-polystyrene demonstrates an increase of the glass transition temperature (T\(_g\)) and only slight decrease of the melting temperature (T\(_m\))\(^{156}\). We believe that mainly amorphous zones are grafted, whereas a possible surface grafting may occur in the crystallites\(^{122}\). Sulfonation and water uptake of the grafted films were found to reduce the crystallinity and the melting temperature (T\(_m\)). The increase of hydrophilicity and water content were pointed out to increase the stress in the membrane and induce a disruption and distortion of the crystallites\(^{122, 123}\). In this paragraph, the influence of irradiation dose and crosslinker concentration on the...
crystallinity of the radiation grafted films and membranes are presented.

**V.4.1. Influence of irradiation dose on the crystallinity of the base film**

When subjected to ionizing radiation, fluoropolymers may undergo different changes in the chemical and physical properties. Due to the formation of active species during the radiation either by homolytic or heterolytic bond scission reactions, the base film may be subjected to crosslinking, chain scission and the introduction of functional groups (e.g., peroxides, if O$_2$ is present) (see paragraph II.4.1).

It was reported previously that the degree of crystallinity of polymers is influenced by radiation processing\(^{(44)}\). To investigate the influence of the irradiation dose on ETFE films, pristine ETFE films were electron beam irradiated (irradiation dose: 1.5, 3, 6, 15 and 30 kGy) in air. Differential scanning calorimetry (DSC) measurements were performed and the obtained single heating curves and extracted results (crystallinity (%) and melting temperature (T$_m$)) are depicted in Figure V.16 and 17.

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Figure V.16: DSC thermograms of irradiated ETFE films and the corresponding non irradiated sample.

A broad single melting peak is present for all irradiated samples and it is clear that the melting behavior is not affected by the irradiation dose in this range. The inset shows the influence of irradiation dose on crystallinity and melting temperature (T$_m$) (Figure V.17).
Figure 17: Crystallinity and melting temperature ($T_m$) as function of irradiation dose.

It is observed that electron beam irradiation (within the limits of irradiation dose used in this study) does not yield significant changes in melting and crystallinity of ETFE films. That is to say, the melting temperature (average crystallite size) is almost constant with increasing irradiation dose, while a slight increase in crystallinity of the base film upon irradiation is determined. This may be attributed to the crystallization of mobile short-chain segments formed due to chain scission reactions. A similar behavior was reported previously for FEP, ETFE and PVDF films even for other irradiation procedures (irradiation by $\gamma$-rays, or inert atmosphere, etc.)\(^{128, 145}\). It was also reported that an initial increase in crystallinity of ETFE films (125 $\mu$m) after electron beam irradiation up to 100 kGy occurs, beyond which it decreased gradually as the dose increased (up to 1200 kGy), due to the growing crystalline defects at high doses\(^{157}\). In the same dose range, $T_m$ decreases significantly with the dose rate.

**V.4.2. Effect of the crosslinker concentration on the crystallinity**

The crystallization and melting behavior of ETFE based grafted films and membranes, with various crosslinker concentrations, were determined by the integration of the DSC melting endotherms. The variation of crystallinity and the melting temperature for both, the grafted films and membranes, are displayed in Figure V.18.

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Figure V.18: Crystallinity and melting temperature of ETFE-g-styrene/DVB grafted films and membranes versus the DVB concentration in the initial grafting solution.

The crystallinity of both the grafted films and the membranes exhibits a slight decrease with increasing DVB concentration. The stiff DVB crosslinked polystyrene chains may cause the crystal disruption leading to lower crystallinities. In fact, the change in crystallinity with increasing crosslinker concentration is not substantial. The crystallinity values of the membranes are comparably lower than those of grafted films, because of the dilution effect and crystal disruption due to water uptake during the hydrolysis steps (dimensional changes)\(^{(154)}\).

A single melting peak was observed for the differently crosslinked films and membranes. The melting temperature remains almost unaltered as the DVB concentration increases. It is important to note here that the melting point of the base material is not influenced, neither by crosslinking nor sulfonation (Figure V.18).

In order to evaluate qualitatively how the crosslinking and the creation of a three-dimensional network affect the chain mobility and the structure of the grafted films, the effect of different DVB concentration in the recrystallization process was investigated. The samples were held at 300°C for 1 min and cooled at a rate of 20 °C/min to 30 °C (Figure V.19).

Interestingly, the introduction of a crosslinker produces a multiplicity in the exothermic peaks for the crosslinked grafted films and a more complex shape is observed for a sample with 20 % DVB. We note here that the endothermic peaks of the different crosslinked membranes show just a single maximum. It is clear that the increase of the crosslinker induces a strong alteration of the recrystallization peak shape, which indicates
that crystallite growth is inhibited. In comparison with the uncrosslinked grafted film, it can be inferred that two forms of crystallites are present. The first type crystallizes easily (peak at 244-248°C) and is probably not or very slightly affected by the crosslinking of the polystyrene chains. The second crystallite type corresponds to the new appearing peaks, and is the consequence of the hindrance of the chain flexibility of the base material. It is therefore clear that even the introduction of a crosslinker into the amorphous zone introduces more rigidity to the chains of the base material and therefore the crystallization is hindered. In addition, it was stated that grafting occurs mostly in the amorphous phase of the base film and possibly at the surface of the crystallites. Likewise, the observed multiplicity in the recrystallization peak may indicate how close the crosslinked grafts are to the crystallites in the grafted films.

Figure V.19: Recrystallization of crosslinked ETFE-g-styrene/DVB films with different DVB concentrations.

V.5. Determination of Thermal stability

The thermal stability of radiation grafted films and membranes is a paramount property for fuel cell applications. The thermal behaviour of the material depends closely on its chemical and physical properties. The effect of the irradiation and the grafting with styrene were already studied in detail for several base films (FEP, PVDF, ETFE)\(^{(78, 128)}\). The radiation processing was pointed out to have a significant effect on the thermal degradation of partially fluorinated polymers (PVDF, ETFE). Likewise, the grafting

induces a new and distinct degradation step in the TGA thermograms due to the incorporated polystyrene, whereas the pattern of the base film is not affected (119, 154).

Furthermore, the degradation patterns of the grafted films were not significantly affected by the increase of the graft level. A study of the thermal degradation of sulfonated FEP-g-polystyrene membranes using coupled FTIR and mass spectrometry, revealed new degradation patterns. The observed three degradation steps were assigned to dehydration of the membrane, desulfonation and de-aromatization reactions (119). In this paragraph, a systematic study of the influence of crosslinker concentration on the thermal stability of the ETFE based grafted films and membranes will be presented. Thus, the initial decomposition temperature (IDT), the maximum rate decomposition temperature (MRDT) and specific weight loss were determined.

ETFE based styrene grafted films and membranes with varying crosslinker concentration and with fixed graft level (~ 25 %) were characterized for their thermal properties by thermogravimetric analysis (TGA) (Figure V.20 and 21).

![Figure V.20: TGA thermograms of ETFE-g-styrene/DVB films (GL ~ 25 %) with different DVB concentration in the initial grafting solution and base film.](image)

The pristine ETFE film exhibits a single step degradation. The presence of polystyrene grafts does not alter the decomposition temperature of the ETFE base polymer and the grafted film shows an additional degradation step starting at ~380°C. Several steps in the degradation pattern of the membranes, due to dehydration, desulfonation, de-aromatization and finally backbone degradation, are detected (119).
Figure V.21: TGA thermograms of ETFE-g-styrene/DVB membranes (GL ~ 25 %) with different DVB concentration in the initial grafting solution.

Similar degradation profiles are observed for the ETFE-g-styrene/DVB films with different DVB concentrations. The initial decomposition temperature (IDT), the maximum rate decomposition temperature (MRDT), the specific weight loss, and the % residue of decomposition were determined for both grafted films (Table V.1) and membranes (Table V.2).

Table V.1: Initial degradation temperature (IDT), maximum rate degradation temperature (MRDT), and specific weight loss of ETFE-g-styrene/DVB films with different DVB concentrations in the initial grafting solution and fixed graft levels (~ 25 %).

<table>
<thead>
<tr>
<th>Graft Level (%)</th>
<th>DVB (% (v/v))</th>
<th>IDT (°C)</th>
<th>MRDT (°C)</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0</td>
<td>418</td>
<td>436</td>
<td>26</td>
</tr>
<tr>
<td>26</td>
<td>5</td>
<td>404</td>
<td>433</td>
<td>26</td>
</tr>
<tr>
<td>26</td>
<td>8</td>
<td>400</td>
<td>429</td>
<td>25</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>402</td>
<td>431</td>
<td>26</td>
</tr>
<tr>
<td>27</td>
<td>15</td>
<td>394</td>
<td>426</td>
<td>25</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>403</td>
<td>431</td>
<td>25</td>
</tr>
</tbody>
</table>

As far as the grafted films are concerned, the IDT and the MRDT of the uncrosslinked film (0% DVB) are slightly higher than those of the crosslinked ones, whereas the values are very similar for the different DVB concentrations (Table V.1). This can be explained by the substantial difference in decomposition behaviour of the
linear polystyrene chains and three-dimensional networks created in the presence of a crosslinker. In fact, the number of the chain ends is higher for the crosslinked films and consequently, the probability to form polymer chains with lower molecular weight is higher, which are known to degrade more readily. The weight loss values of the grafted styrene and DVB components are more or less constant and are in agreement with the fixed graft level of these samples.

ETFE based membranes with varying DVB content exhibit a very similar degradation pattern. Moreover, similar IDT and MRDT values are obtained for the uncrosslinked (0% DVB) and the crosslinked membranes. Besides, the IDT and the MRDT are not influenced by the increasing DVB concentration and there is no clear trend (Table 2). As a consequence, the concentration of DVB in the initial grafting solution does not have a significant contribution to the thermal stability of the membranes. However, the residual weight obtained for the membranes increases with DVB concentration.

Table V.2: Initial degradation temperature (IDT), maximum rate degradation temperature (MRDT), and residue of ETFE based membranes with different DVB concentrations in the initial grafting solution and fixed graft levels (~25%).

<table>
<thead>
<tr>
<th>Graft Level (%)</th>
<th>DVB (vol %)</th>
<th>IDT (°C)</th>
<th>MRDT (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0</td>
<td>289</td>
<td>338</td>
<td>2.3</td>
</tr>
<tr>
<td>26</td>
<td>5</td>
<td>287</td>
<td>337</td>
<td>6.9</td>
</tr>
<tr>
<td>26</td>
<td>8</td>
<td>293</td>
<td>341</td>
<td>2.8</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>281</td>
<td>333</td>
<td>12.5</td>
</tr>
<tr>
<td>27</td>
<td>15</td>
<td>280</td>
<td>345</td>
<td>11.2</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>289</td>
<td>346</td>
<td>13.8</td>
</tr>
</tbody>
</table>

V.6. Conclusions

Dealing with the radiation grafting process, it is important to understand that every preparation step (irradiation, grafting, sulfonation and swelling) induces changes in the structure and the properties of the grafted films and membranes. The aim was to correlate quantitatively the key parameters (graft level and crosslinker concentration) and the structure and properties of the radiation grafted films and membranes.

A calibration model was established for determination of the crosslinker (DVB) composition and concentration using FTIR-ATR spectroscopy. The investigation of the crosslinker content in the surface and in the bulk revealed inhomogeneous distribution.
through the thickness. Higher crosslinker content was measured in the surface of the grafted film than in the entire bulk attributed mainly to the reactivity of DVB versus styrene. It was found that para-DVB is more reactive than meta-DVB, however at higher GL the ratio of meta-DVB/para-DVB increases. In addition, the homogeneity of the grafted films was studied based on the change in thickness and in the DVB content over the grafted area. The thickness of the pristine base film (technical product) was found to be inhomogeneous over the area. Thus, the grafting induces a slight increase of the inhomogeneities in the thickness and composition over the area of the grafted films. We note here that the homogeneity was improved significantly using a filter paper to separate the films during grafting.

The increase of the graft level and the crosslinker concentration were apparently accompanied with morphological and structural changes. First of all, the dimensions of the grafted films and membranes increase with increasing graft level. Nonetheless, the increase of crosslinker concentration did not significantly affect the variation in the grafted film dimensions, whereas a slight decrease was observed for the swollen membranes. Likewise, neither the thermal stability nor crystallinity of the grafted films and membranes were significantly influenced by the DVB concentration.
VI ETFE-g-styrene/DVB: Relevant properties for the fuel cell application

The ex situ relevant properties for the fuel cell application presented in this section were selected due to their direct impact on the in situ membrane-electrodes assembly (MEA) properties under fuel cell operating conditions. The ion exchange capacity gives insight about the degree of sulfonation, whereas the water uptake measures the swelling of the membrane and allows determination of the number of water molecules by sulfonic groups. In addition, the conductivity is the most important property, which directs the selection of a membrane to be further tested or not in single fuel cell test. Likewise, the mechanical properties and the dimensional stability of the radiation grafted films are important parameters, which are closely affecting the handling and the MEA preparation.

VI.1. Ion exchange capacity, water uptake and ex situ conductivity*

The first properties of interest for application in fuel cell are the IEC, water uptake and proton conductivity. In fact, these properties are interconnected to the sulfonation step, which leads to the introduction of sulfonic acid groups into the grafted polystyrene chains (Figure VI.1). The sulfonic acid dissociates in the presence of water, the resulting mobility of the protons provides the ionic conductivity of the membrane. In this paragraph, the influence of the graft level and the crosslinker content on these properties is addressed separately.

Figure VI.1: Sulfonation reaction of polystyrene (paragraph III.1.3).

* These results have been published:
VI ETFE-g-styrene/DVB: Relevant properties for the fuel cell application

VI.1.1. **Effect of graft level**

To evaluate the variation of the *ex situ* properties of styrene/DVB grafted ETFE based membranes at two crosslinker concentrations in the initial grafting solution (0 % and 5 % DVB) as a function of the graft level, selected grafted films (graft level values between 17 and 50 %) were sulfonated using the standard procedure described in paragraph III.1.3. Then, IEC, water uptake and *ex situ* conductivity were evaluated in fully swollen state at room temperature.

The IEC and water uptake of ETFE based membranes are presented in Figures VI.2 a and VI.2 b.

![Figure VI.2: Ex situ membrane properties as a function of graft level. a) Ion exchange capacity, b) water uptake. The measured ETFE based membranes were synthesised at different DVB concentrations in the initial grafting solution (0 and 5 % DVB). Reported measurements were performed for membranes in water equilibrated form at room temperature.](image-url)

The IEC and water uptake exhibit the same trend for both the uncrosslinked ETFE based membrane and the crosslinked one. The measured values of IEC are in good agreement with the theoretical values calculated based on the equation III.6 assuming that each aromatic ring contains one sulfonic acid group. The increase of the both values is obviously due to the increase of the ion exchange sites, which improve the hydrophilicity of the grafted membranes. Similarly, the IEC and water uptake increase with increasing the graft level as expected, but this increase is lower in terms of swelling compared to that of uncrosslinked membranes with comparable graft level values. Since the crosslinker induces the creation of a three-dimensional network which renders the grafted
chains less flexible and induces a decrease in the free volume. The comparison of these values and the value obtained for Nafion®112 membrane (IEC ~ 0.91 mmol·g$^{-1}$ and water uptake ~ 33.5 %) shows clearly that the water uptake of the crosslinked samples are below that value. The crosslinked grafted membrane reaches the same water uptake only at a graft level value of 48 %, whereas the uncrosslinked grafted membrane exceeds the value of Nafion®112 membrane only over a graft level of 25 %. The effect of crosslinking will be discussed in the next paragraph in more detail (VI.1.2).

The *ex situ* conductivity values determined in fully water swollen state versus the graft level are reported in the Figure VI.3 a. For both grafted type membranes, the *ex situ* conductivity shows an increase with increasing the graft level, however, the obtained values for the crosslinked samples are lower than the values reported for the uncrosslinked ETFE based membranes. The hydration number is known to be closely related to the proton mobility, since as the hydration state of the membrane increases the conductivity is increasing$^{(158)}$. The first observation is that lower values of hydration number are obtained for crosslinked grafted membranes (5 to 7 water molecules per sulfonic acid group), whereas higher values were determined for the uncrosslinked ones (6 to 13 water molecules per sulfonic acid group) (Figure VI.3 b).

![Figure VI.3: a) Conductivity versus the graft level. b) Conductivity plotted against hydration number. The measured ETFE based membranes were synthesised at different DVB concentrations in the initial grafting solution (0 and 5 % DVB). Reported measurements were performed for membranes in water equilibrated form at room temperature.](image)

The obtained values for the grafted membranes are lower than that of Nafion®112 membrane (18 water molecules per sulfonic acid group). We note here that the Nafion®112 membrane is not crosslinked. The effect of crosslinking on the conductivity
and hydration number will be discussed in the next paragraph in more detail (VI.1.2). The
grafted membranes (uncrosslinked and crosslinked) show a linear trend with increasing
hydration number, whereas the obtained slope is much higher in comparison with the one
showed for a Nafion® membrane\textsuperscript{(159,160)}, meaning that we can obtain higher conductivity
values than possible for Nafion®112 (82 mS·cm\textsuperscript{-1}) at lower hydration number values.
The reason for that is most likely due to the higher volumetric IEC of the radiation
grafted membranes (2.4 to 4.4 mmol·cm\textsuperscript{-3}) compared to that of Nafion®112
(1.6 mmol·cm\textsuperscript{-3})\textsuperscript{(161)}. However, this comparison does not take into accou
nt the differences between both types of membrane (Nafion®112 membrane and grafted ETFE
based membranes), namely chemical composition, structure, morphology,
hydrophilic/hydrophobic domains connectivity and proton transport mechanism.

**VI.1.2. Influence of crosslinker concentration**

It was of interest to evaluate the influence of the crosslinker concentration on the fuel
cell relevant properties (IEC, water uptake and conductivity). Thus, ETFE grafted films
with different DVB concentration (0, 5, 8, 10, 15 and 20 % DVB) were sulfonated. The
graft level of the different membranes was adjusted to ~ 25 % by tuning the reaction time
according to the kinetic study performed previously (paragraph IV.5). The degree of
sulfonation, the ratio of sulfonic acid groups to grafted polystyrene, was found to be 98-
100 % for lower DVB concentrations while 90-95 % for higher DVB concentrations. We
determined that the monosubstituted benzene (styrene) can be sulfonated readily;
however, sulfonation becomes difficult in the presence of the double substituted benzene
rings in the case of DVB and its isomers especially at higher concentrations.

The ion exchange capacities (IEC) and hydration number at various DVB
concentrations are depicted in Figure VI.4 a and b. IEC, the measure of total number of
sulfonic acid groups, seems to be unaffected from lower DVB concentrations (5, 8,
10 % DVB) and decreases considerably with higher DVB content. This means that the
introduced ionic sites are equally accessible through the hydrophilic domains in
crosslinked membranes regardless of the more constrained polymer structure, at least up
to 10 % DVB. Beyond that concentration, number of exchange sites decreases as deduced
from lower degree of sulfonation.
Figure VI.4: *Ex situ* membrane properties as a function of crosslinker (DVB) content in the grafting solution. a) Ion exchange capacity, b) hydration number (number of water molecules per sulfonic acid site). Reported measurements were performed for membranes (fixed graft level (~25%)) in water equilibrated form at room temperature. Data for Nafion®112 is given for comparison.

The water uptake, expressed as number of water molecules per sulfonic acid site, is substantially reduced upon crosslinking due to compact crosslinked network structure (Figure VI.4 b). Consequently, the average number of water molecules per ion exchange site, decreases substantially with the increase in DVB concentration. This number decreases almost fourfold for an increase in DVB concentration from 0 % to 20 %. The highest hydration number is found as 11 for 0 % DVB case which is considerably lower than the value reported for Nafion®112 membrane (hydration number ~ 18) water molecules per sulfonic acid site). Since the water uptake is a mass based quantity, the volume-based water uptake is higher for Nafion®112 owing to its higher density. Furthermore, the water uptake of FEP based membranes is also reported to exhibit a decreasing trend compared to the uncrosslinked membranes.(97, 112).

These observations can be related and supported by the quantitative values determined by FTIR, dimensional increase and crystallinity results. FTIR reveals the increased effective crosslinker content as the DVB concentration increases in the initial grafting solution. The rise of the incorporation of crosslinker induces the reduction of the number of the ion-exchange sites, rendering the material less hydrophilic. Furthermore, the creation of a three-dimensional network reduces the free volume available and then hinders the flexibility of the chains. As a consequence, water uptake and conductivity decrease. Besides, lower values of dimensional increase with increasing DVB concentration relate with decreased water uptake. Moreover, the decrease in crystallinity
is not crucial as DVB concentration increases. In fact, the greater mechanical stress due to the crosslinker is expected to cause a substantial decrease of crystallinity while the reduced water uptake balances that stress.

The proton conductivity shows a clear dependency on DVB concentration (Figure VI.5 a). That is to say, it decreases considerably with the increasing DVB concentration for the membranes of similar graft levels. Conductivity is around 100 mS·cm\(^{-1}\) for the uncrosslinked membrane and it is significantly lower such as 18 mS·cm\(^{-1}\) for the membrane prepared with 20 % DVB. This can be attributed to the reduced mobility of protons in the membrane with increasing DVB concentration due to decreasing water uptake. As the ionic site density is roughly constant, the decrease in conductivity is attributed to a lower proton mobility at lower hydration levels. Between conductivity and hydration level an approximately linear correlation is observed (Figure VI.5 b). For Nafion® membranes, a similar correlation is observed, yet with conductivity values shifted to higher hydration numbers\(^{158, 159}\). With the ETFE based membranes, the conductivity of Nafion®112 (82 mS·cm\(^{-1}\)) is reached at a lower hydration level. This is most probably a consequence of the higher volumetric IEC of the radiation grafted membranes (2.7 mmol·cm\(^{-3}\)) compared to that of Nafion®112 (1.6 mmol·cm\(^{-3}\))\(^{161}\).

Figure VI.5: Ex situ membrane properties as a function of crosslinker content in the grafting solution. a) Conductivity, b) Conductivity as function of hydration number. Reported measurements were performed for membranes (fixed graft level (~ 25 %)) in water equilibrated form at room temperature. Data for Nafion®112 membrane is given for comparison.
VI.2. Mechanical properties and dimensional stability

The durability of the radiation grafted membranes is based on their combined good chemical and physical stability. In fact, the mechanical properties of the base material are paramount to develop robust membranes. During the membrane preparation, the base film is subjected to stress due to the irradiation under air, grafting and sulfonation steps. Furthermore, mechanical integrity is one of the important prerequisites for fuel cell membranes in terms of handling and fabrication of membrane electrode assemblies (MEA). Membranes should be not only robust to overcome both the mechanical and swelling stresses in fuel cell environment but also elastic to prevent crack formation.

Several papers have been published on the mechanical properties of fluoropolymer films such as FEP, PTFE, ETFE, PVF, PVDF\(^{(94, 157, 162-164)}\). In addition, typical mechanical properties of radiation-grafted films based on styrene/FEP\(^{(132)}\), styrene/PVDF\(^{(162)}\) and styrene/PFA\(^{(164)}\) were reported. However, not many studies were directed systematically towards the investigation of the relationship between the effect of mechanical properties and the different others parameters like the irradiation dose, the graft level and the degree of crosslinking which are closely related to the hydration, conductivity, performance and durability.

The durability issues are closely related to the chemical and physical degradation of the membranes. In fact, the physical factors may lead to membrane thinning and sometimes pinhole formation. This mechanical degradation can even be accentuated by the chemical one, which accelerates the performance drop\(^{(120, 121)}\). Moreover, the dependency of the mechanical properties of the membrane on different parameters (water content, humidity, temperature, etc.) may play a non negligible role on the durability of the membrane. Therefore, it is of interest to determine the initial mechanical properties of the membranes which will have a direct impact on the lifetime during the fuel cell testing. Likewise, the dimensional stability upon swelling of the membrane and its behaviour in wet/dry cycles has to be considered.

It is desired to investigate the mechanical properties of ETFE based materials to enhance our knowledge and improve the relevant properties of these membranes. Therefore, a systematic study of the influence of irradiation dose, crosslinker concentration, graft level or polystyrene content on the tensile strength, elongation at break and yield strength of the ETFE based membranes was performed. Mechanical properties were recorded with respect to both parallel to the extrusion direction (machining direction) and perpendicular to the extrusion direction (transverse direction) for each sample. Furthermore, an evaluation of the effect of the membrane synthesis
process on the mechanical properties of the ETFE based membrane was carried out. The aim of this investigation is to define the limits of our base film and also determine the optimum region in terms of graft level and crosslinker concentration at which membranes exhibit desired mechanical properties, dimensional stability and other desired \textit{ex situ} properties (e.g., conductivity) at the same time.

\textbf{VI.2.1. Influence of irradiation dose on the base film}

The influence of electron beam irradiation and the variation of irradiation dose on mechanical properties of pristine ETFE film were evaluated employing irradiation doses of 1.5-200 kGy. In fact, on one hand we are interested to have quantitative data about the changes occurring to our base material and its mechanical properties. On the other hand, it is of importance to know the potential and the limits of the material under high irradiation doses for other monomer combinations (e.g., α-methylstyrene/methacrylonitrile (AMS/MAN))\textsuperscript{(108)}, which have lower grafting kinetics and afford high doses to set the maximum and optimal graft level.

To begin with, it was found that irradiation did not affect the shape of stress-strain curves, however, their characteristic values were altered (data not shown) Figure VI.6.

![Figure VI.6: Tensile stress-strain curves of ETFE films with varying irradiation doses in the MD.](image)

Figure VI.6: Tensile stress-strain curves of ETFE films with varying irradiation doses in the MD.

Figure VI.7a shows that there is no significant change in elongation at break for ETFE base films up to 50 kGy of the irradiation dose. However, as the irradiation dose increases beyond 50 kGy, the elongation at break decreases gradually. The elongation at break decreases by about 25\% of its value for the unirradiated film at an irradiation dose
of 200 kGy.

![Graph showing mechanical properties](image)

Figure VI.7: Mechanical properties of ETFE base films as function of the irradiation dose (1.5 – 200 kGy). a) Elongation at break, b) Tensile strength.

It is evident from Figure VI.7 b that the tensile strength of ETFE films is markedly reduced upon irradiation. The tensile strength of the film is almost constant for the low doses such as 1.5 and 5 kGy while a significant decrease is observed beyond 25 kGy.

In the dose range studied, it is clear that both machining and transverse directions possess the similar trend with increasing irradiation dose. On the other hand, the tensile strength values are found to be higher in machining direction (MD) compared to those of transverse direction (TD), whereas the elongation at break values show the opposite trend. Thus, the anisotropy\(^{(151)}\) of the base film and its orientation during the processing (extrusion) has beneficial impact on the tensile strength of the MD. This was confirmed by Small Angle Neutron Scattering (SANS) for the FEP base film, where perpendicular orientation of the crystalline domains to the machining direction was observed. Therefore, the structural properties of the base films based on semi-crystalline polymers are highly affected by the processing conditions\(^{(151)}\). Other mechanical properties such as the Young modulus and the yield strength are depicted in Table VI.1. It is clear that the yield strength is unaffected by the irradiation and only slight decrease of Young modulus beyond 25 kGy was observed without any clear trend.

In general, the increase of irradiation dose leads to considerable deterioration of the mechanical properties of pristine ETFE films. The observed changes in the mechanical properties with higher irradiation dose are attributed to increased radiation damage to the
trunk polymer, mainly due to chain scission in the main chains. The observed decrease is a clear sign of the changes occurring in the structure of the base film during the irradiation. Same trends were observed previously for PFA films with the irradiation dose$^{(164)}$. Consequently, elongation at break and tensile strength were reduced by irradiation and complex combination of crosslinking and chain scissions was suspected to take place under specific conditions. Also, the effect of gamma ray irradiation (0-52 kGy) on various base films including FEP, ETFE, PVDF, PVF, PTFE, crosslinked PTFE and PFA was explored in the literature and similar trends were observed$^{(94)}$.

Table. VI.1: Effect of the irradiation dose on the Young modulus and yield stress of the ETFE base film in both machining and transverse direction.

<table>
<thead>
<tr>
<th>Irradiation dose [kGy]</th>
<th>Young Modulus [MPa]</th>
<th>Yield strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>TD</td>
</tr>
<tr>
<td>0</td>
<td>866</td>
<td>855</td>
</tr>
<tr>
<td>1.5</td>
<td>905</td>
<td>835</td>
</tr>
<tr>
<td>5</td>
<td>889</td>
<td>766</td>
</tr>
<tr>
<td>10</td>
<td>836</td>
<td>785</td>
</tr>
<tr>
<td>25</td>
<td>751</td>
<td>726</td>
</tr>
<tr>
<td>50</td>
<td>768</td>
<td>757</td>
</tr>
<tr>
<td>100</td>
<td>718</td>
<td>682</td>
</tr>
<tr>
<td>200</td>
<td>784</td>
<td>757</td>
</tr>
</tbody>
</table>

Evidently, every material undergoes irreversible mechanical degradation at a certain irradiation dose. However, the corresponding maximal dose is likely depending on the irradiation mode (gamma, e-beam, X-rays…) and the initial specifications of the technical products (different suppliers and difference in composition and additives). To prevent the high loss in the mechanical properties of the irradiated film it is crucial to use low doses. Nevertheless, the ETFE film exhibits good mechanical properties up to 50 kGy whereas it undergoes substantial deterioration in both tensile strength and elongation at break at higher doses.

**VI.2.2. Effect of graft level on mechanical properties of ETFE-g-styrene/DVB membranes**

The graft level is one of the important quantities which has a direct and major effect on the different *ex situ* and *in situ* properties of the grafted films and resulting membranes. Therefore, the variation of mechanical properties and dimensional stability
with the GL were examined in detail during this study. Mainly, ETFE based grafted films and membranes with GL varying up to 50 % were investigated. Also, the DVB concentration in the initial solution was varied (0 %, 5 % and 10 % DVB).

a. **Dimensional stability**

The dimensional stability (Area and volume shrinkage) of the radiation grafted membranes with varied graft levels was measured according to the procedure presented previously (paragraph III.5), and the obtained results are depicted in Figure VI.8.

The area and the volume of the radiation grafted membranes are increasing with the increase of the graft level. Thus, the membrane after drying step shrinks in all directions (machining direction, transverse direction and thickness) and the thickness was pointed out to be highly affected. We note that the membrane dimensions after grafting and subsequent sulfonation and swelling increase considerably. Upon the increase of the GL, the ETFE based membranes swell more due to an increase of the available sulfonic acid groups, thereby the water content increases inducing the disruption of the crystallites due to the generated stress, which leads to decrease of the mechanical properties of the base material (see next paragraph). Obviously, the increase of the GL has a negative effect on the dimensional stability, thereby the specification of fuel cell membranes should be chosen carefully to ensure good functionality (conductivity and performance) at minimum graft level to reduce the losses in dimensional stability.

![Shrinkage graph](#)

**Figure VI.8:** Area and volume shrinkage versus the graft level of the ETFE-g-styrene/DVB membranes.
b. **Mechanical properties**

The mechanical properties (elongation at break, tensile strength and Young modulus) of ETFE based grafted films and membranes with different GL, varying up to 50% were investigated. As shown in the Figure VI.9, the tensile strain-stress curves collected for the grafted films in the machining direction show clearly the tendency of the yield strength to increase with the GL.

![Tensile stress-strain curves of ETFE-g-styrene/DVB films (MD) with different GL.](image)

Figure VI.9: Tensile stress-strain curves of ETFE-g-styrene/DVB films (MD) with different GL.

Upon grafting, the initial dimensions of the films change in both directions, particularly in the plane direction (paragraph V.2.1). This involves important stresses in the polymer chains, what explains the change of the elastic deformation. Indeed, with increasing GL we need a stronger load and a lower elongation before an irreversible deformation occurs.

The elongation at break decreases as the graft level increases and the values are dropping substantially in the case of crosslinked films compared to uncrosslinked ones, whereas the yield strength shows an opposite trend (Figure VI.10 a and b). Therefore, the yield strength increases with the increase of the GL, and the trend is more pronounced for the higher crosslinker (DVB) concentrations. The effect of crosslinker will be discussed separately and more in detail in the next paragraph.

Noticeable differences are observed between the mechanical properties of the machining and transverse directions of the grafted films as far as Young modulus and elongation at break are considered (Table VI.2). Thus, higher values were obtained for
the Young modulus in machining direction and the opposite trend was observed for the elongation at break values up to 21 % GL and then this tendency is inverted. Grafting and incorporation of styrene is assumed to induce large scale structures, which are driven by the immiscibility of both phases (polystyrene and base film)\(^{151}\). Therefore, based on the unchanged value of the Young modulus with the increase of the GL, the inversion between the machining and transverse direction of elongation values are not a sign of anisotropy changes in the material.

**Figure VI.10:** Mechanical properties of ETFE-g-styrene/DVB films versus the graft level in machining direction. a) Elongation at break, b) Yield strength. ETFE-g-styrene/DVB films at various DVB concentrations (0, 5 and 10 % DVB).

First of all the obtained results can be understood regarding the changes of the inherent crystallinity upon grafting, second the expansion of the dimension (MD, TD and thickness) occurring after the grafted reaction. Dealing with the semi-crystalline polymers, it was already reported that the crystallites behave as crosslinks\(^{74}\). Since the inherent crystallinity of ETFE base film is known to decreases to some extent as GL increases (paragraph V.4), the deterioration in elongation at break of the material seems to be closely related to the increase of the amorphous zone on the cost of crystalline zones\(^{151}\).

Previously, the grafting was found to occur mainly on the amorphous domains of the base film. In addition, the ETFE based grafted films behave as a two phase system based on the thermal gravimetric analysis investigation (paragraph V.5). Consequently, it is necessary to explain the mechanical properties of the grafted films by considering the mechanical properties of the two phases, polystyrene and ETFE base polymer. In fact, the
bulky pendant phenyl group creates steric hindrance which results in stiffer polymer chain. Therefore, the decrease in elongation at break is most likely due to the very stiff polystyrene chain. The observed improvement in yield strength by increasing the graft level may be attributed to the possible branching and crosslinking occurring during grafting, which stabilizes the base film and enhances its elastic deformation response.

Table VI.2: Elongation at break, yield strength and young modulus of ETFE-g-styrene/DVB films (5 % DVB) with varying GL.

<table>
<thead>
<tr>
<th>Graft level [%]</th>
<th>Elongation at break [%]</th>
<th>Young modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>TD</td>
</tr>
<tr>
<td>0</td>
<td>309</td>
<td>411</td>
</tr>
<tr>
<td>5</td>
<td>269</td>
<td>338</td>
</tr>
<tr>
<td>13</td>
<td>200</td>
<td>256</td>
</tr>
<tr>
<td>21</td>
<td>163</td>
<td>164</td>
</tr>
<tr>
<td>27</td>
<td>161</td>
<td>136</td>
</tr>
<tr>
<td>36</td>
<td>112</td>
<td>68</td>
</tr>
<tr>
<td>50</td>
<td>66</td>
<td>53</td>
</tr>
</tbody>
</table>

**VI.2.3. Influence of crosslinker concentration**

In addition to the first key parameter, namely the graft level, the crosslinker content is the second tunable quantity used for the preparation of radiation grafted membranes with suitable properties. In order to examine the influence of the crosslinker, we performed tensile tests on grafted films and membranes with a fixed graft level around 25 % with varying crosslinker (DVB) concentration in the initial grafting solution from 0 % to 15 % of DVB. As shown in the Figure VI.11, the tensile strain-stress curves for different grafted films with varied DVB concentration do not show any significant difference concerning the yield strength (data not shown). However, clear trends were observed for the other parameters (elongation at break and tensile strength).
The elongation at break decreases significantly as DVB concentration increases for both grafted films and membranes (Figure VI.12a). It is about 280 % for the uncrosslinked grafted films and it becomes 100 % for a DVB concentration of 15 %. In fact, it is to be expected that the crosslinking has a negative effect on the elongation at break of the grafted films and membranes. The observed trend may be a result of the significant changes occurring in the structure of the films by crosslinking (paragaph V.4.2). The introduction of DVB leads to a three-dimensional network structure, which lowers the chain mobility.

Figure VI.12b presents the variation of tensile strength as a function of DVB concentration in the initial grafting solution. The tensile strength of ETFE based grafted films and membranes increases with the increase of DVB concentration. The DVB is well known as a stiff crosslinker which is expected to increase the brittles of the grafted films and the resulting membranes. As a consequence, increasing DVB content is expected to cause an increase in tensile strength. The crosslinking is assumed to have a positive effect on the stabilization of the crystalline domains of the grafted films and their dimensional stability. Indeed, crosslinking did not show any significant effect on the crystallinity or on the dimensions of the grafted films and membranes.

Apparently, the yield stress does not change with the DVB concentration, and the Young modulus seems to be the same for each concentration (results not shown). Although both machining and transverse directions exhibit similar tendencies in terms of tensile strength and elongation at break, slight differences are observable. Moreover, it was observed that the mechanical properties of the grafted films are superior to their
resulting membranes in both directions. In fact, we should emphasize that the membranes are in dry form to prevent any contributions of the temperature and the humidity during the measurements.

![Graphs showing elongation at break and tensile strength vs. crosslinker concentration](image)

Figure VI.12: Effect of DVB concentration on the tensile strength of ETFE grafted films and membranes in both directions. a) Elongation at break, b) Tensile strength. Membranes are exchanged into the K$^+$ form using KCl solution (0.5 M) and drying overnight at 60 °C.

c. **Dimensional stability**

The dimensional stability of radiation grafted membranes with fixed graft level (~ 25 %) and varied crosslinker content in the initial grafting solution was investigated. The area and volume shrinkage of membranes with 0, 5, 8, 10, 15 and 20 % DVB was determined using the procedure described previously (paragraph III.5) and the obtained results are depicted in Figure VI.13.

The area and volume shrinkage follow the same trends, where a decrease is observed with the increase of the DVB concentration up to 10 % DVB and then no significant changes were observed. In fact, these obtained results are in agreement with the trends observed for the hydration number and water uptake upon crosslinking (paragraph VI.1.2). The obtained results confirm clearly that the dimensional expansion of the membranes during sulfonation steps is reduced by crosslinking (paragraph V.2.2). Thus, the increase of crosslinker content induces a reduction of the free volume available in the material due to the creation of a three-dimensional network, consequently the content of water decreases, reducing the stress generated by swelling.
Evidently, the crosslinking improves the dimensional stability of the radiation grafted membranes and reduces their area and volume shrinkage (wet $\rightarrow$ dry), respectively.

**VI.2.4. Influence of the different preparation steps on mechanical properties**

As pointed out previously, it is an important issue to evaluate the changes occurring during the overall preparation process (irradiation, grafting and sulfonation) on the mechanical properties of the base film. For this, an ETFE based membrane (5 % DVB and GL $\sim$ 25 %) and a Nafion®112 membrane are discussed (Figure VI.14a). ETFE based membranes with 5% DVB were chosen because they show the best electrochemical performances in the fuel cells in comparison with lower and higher DVB content (Chapter VII).

After the grafting process a significant decrease of the elongation at break value is observed. Thus, we observed a decrease of $\sim$ 50 % of the elongation at break value due to the grafting and then further loss ($\sim$ 13 %) occurs after the sulfonation process. However, no significant change on the tensile strength was observed after grafting, only a loss of $\sim$ 17 % occurs after sulfonation. Both the ETFE based membrane and Nafion®112 membrane show comparable tensile strength values, whereas the elongation at break of the radiation grafted membrane is $\sim$ 23 % higher.
Likewise, a comparison of the mechanical properties of the ETFE, FEP based membranes and Nafion®112 was performed and the results of tensile strength and the elongation at break values are shown in Figure VI.14b. Both tensile strength and elongation at break of Nafion®112 membrane and ETFE based membrane are higher than the FEP based membrane values. Furthermore, a comparison of the Young modulus of the different membranes (ETFE, FEP based membranes and Nafion®112 membrane) is depicted in Table VI.3.

Table VI.3: Young modulus of ETFE and FEP based membranes and Nafion®112 membrane in both directions (MD and TD). Membranes are exchanged into the K⁺ form using KCl solution (0.5 M) and dried overnight at 60 °C.

<table>
<thead>
<tr>
<th></th>
<th>MD</th>
<th>TD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE-g-styrene/DVB</td>
<td>820</td>
<td>844</td>
</tr>
<tr>
<td>FEP-g-styrene/DVB</td>
<td>880</td>
<td>974</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>567</td>
<td>575</td>
</tr>
</tbody>
</table>

The FEP based membrane shows slightly higher young’s modulus values compared to the ETFE based membrane in both directions, whereas the Nafion®112 membrane possesses the lowest young’s modulus values. Both ETFE and FEP based membranes are crosslinked.
VI.3. *Ex situ* Chemical degradation

The permeation of H₂ and O₂ through the membrane and interaction with the platinum electrocatalyst under fuel cell operating conditions results in the creation of peroxiradicals or hydroperoxiradicals (OH⁻, HOO⁻), which are an aggressive degrading agent for the membranes\(^{110,165}\). One method to pre-evaluate the chemical stability of our membranes is to apply a moderate accelerated test, where an H₂O₂ solution is used instead of the severe Fenton reagent (H₂O₂ + Fe^{2+}), which leads to extensive OH⁻ generation and excessively fast membrane degradation\(^{166}\).

The influence of the DVB concentration on the chemical stability of the ETFE and FEP based membranes with fixed graft levels of ~ 25 % and ~ 18 %, respectively, was studied. Various membranes based on ETFE with different DVB content (0, 5, 10 and 15 % DVB in the initial grafting solution) and FEP membranes (0 and 10 % DVB) were prepared and tested for their *ex situ* chemical stability by immersing them in a 3 % H₂O₂ solution at 60 °C. The IEC of all membranes was determined prior to the test and the same value of around 1.6 mmol·g⁻¹ was measured for the ETFE membranes, whereas a value of 1.3 mmol·g⁻¹ was measured for the FEP based membranes. The accelerated chemical degradation of these membranes was measured and the evolution of the weight loss is depicted in Figure VI.15.

![Figure VI.15: *Ex situ* chemical degradation of FEP-based membranes (GL ~ 18 %) and ETFE based membranes (GL ~ 25 %) with different DVB content (in the initial grafting solution) in 3 % H₂O₂ at 60 °C (lines are a guide to the eye).](image_url)

All the treated membranes show an onset of weight loss after some initial period depending on the crosslinker concentration. Based on the measured GL and assuming a
degree of sulfonation of 100 %, the calculated weight loss due to total loss of the grafted components is in accordance with the experimental values at the end of the stability test. The weight loss is most likely a consequence of polymer chain scission occurring in the membranes, the fragments of which are washed out subsequently.\(^{(166)}\)

It was stated previously that the existence of radicals (OH', HOO') in the solution may result in an attack on the styrene unit, leading to the formation of a benzyl radical and, eventually, scission of the C-C bond on the grafted polymer chain.\(^{(110)}\) Study of the decomposition products in the produced water from the fuel cell based on styrene grafted FEP membranes was performed earlier, using high-pressure liquid chromatography (HPLC), revealing mainly the formation of monomeric residues\(^{(167, 168)}\). Likewise, a Raman investigation of styrene based grafted PVDF membranes shows a loss of the poly(styrenesulfonic acid) groups after fuel cell tests\(^{(165)}\). Comparing the obtained results, the first main observation is that crosslinking generally induces an increase in the chemical stability of the ETFE and FEP based membranes. Also, the base polymer seems to have an effect on the durability of the grafted membrane, the crosslinked FEP based membrane (10 % DVB) appears to have the lowest stability among the crosslinked samples. A possible explanation can be related to the kinetics of grafting in both systems, in that the incorporation and content of crosslinker are different. Indeed, the values reported for water uptake and hydration number for FEP based membrane (10 % DVB) are 16.3 % (wt %) and ~ 6.7 water molecules per sulfonic acid group, respectively, whereas the values for ETFE (10 % DVB) are lower (14.1 % (wt %) and 4.6 water molecules per sulfonic group), suggesting that the effective crosslinking is higher in ETFE based grafted membranes. The observation that the ETFE based membrane with the highest crosslinker content (15 %) shows a lower stability compared to the membranes with lower DVB content is striking at first sight. Similar results were obtained, however, for ETFE (50 µm) based membranes grafted with p-methylstyrene/DVB. The increase of the DVB content above a critical concentration results in a drastic decrease in chemical stability\(^{(169)}\). Several factors may play a significant role in that observed behavior. In fact, higher crosslinker concentration in the grafting solution induces an increase in the number of pending double-bonds in the grafted membranes as observed by FTIR, which affect the efficiency of DVB as crosslinker\(^{(170)}\). Kinetic studies of the styrene / DVB system reveal that the reactivity of the two double bonds of DVB is not the same\(^{(171)}\). After the first double bond has reacted, the kinetic of the second one in the growing polymeric chain is much lower, yielding a fraction of non reacted double bonds in the final membrane. It has been proposed that the non reacted vinyl groups may be preferable sites of radical attack\(^{(169)}\). The grafting kinetic dependency of styrene / DVB on the monomer diffusion and the relatively faster reaction of the DVB presumably create a concentration gradient through the membrane thickness.
Indeed, the previously obtained FTIR-ATR results show clearly a higher DVB concentration close to the surface, whereas comparatively lower crosslinker content is observed in the bulk of the membrane (paragraph V.2.2). The higher extent of crosslinking may also produce a higher number of chain ends, and, consequently, the probability to form polymer branches with lower molecular weight (lower chain-length), which are more easily detached from the polymer network.

VI.4. Conclusion

The effect of the crosslinker concentration (DVB) and graft level on the ex situ relevant properties of radiation grafted and sulfonated membranes based on ETFE was investigated. On the one hand, the incorporation of DVB into the film during grafting leads to a decrease of the water uptake and conductivity of the membranes, due to an increased density of the polymer network restricting the available free volume within the material. On the other hand, the increase of the graft level as expected has a positive effect on the IEC, water uptake and conductivity values of the radiation grafted membranes. However, the dimensional stability of the membranes is negatively affected by grafting, whereas the crosslinking has an opposite effect (dimensional stability improves).

The study of the influence of the irradiation dose, the crosslinker concentration and graft level on the mechanical properties reveals that the most affected parameter is the elongation at break. Indeed, the plasticity of the ETFE based grafted films and membranes decrease drastically with the increase of the graft level and the crosslinker concentration. Furthermore the ETFE base film shows good mechanical stability at relatively high doses, which provides the opportunity to use it widely with other monomer systems which are kinetically not favorable in grafting reaction. Despite the difference on the mechanical properties between the machining and transverse directions, the same trends were observed with varying the GL and crosslinker concentration for both directions. In general, mechanical properties (tensile strength; elongation at break) of grafted films are poorer than those of pristine base polymers. Furthermore, the mechanical properties of the resulting membranes are poorer than their respective grafted films. The less we irradiate, the less we graft and crosslink the better are the mechanical properties of the resulting grafted membranes. The mechanical properties (tensile strength and elongation at break) of Nafion® 112 membrane and ETFE based membrane are fairly similar in the dried state and the latter shows slightly better elongation at break.

The ex situ chemical degradation investigation revealed that the base film has an influence on the chemical stability of radiation grafted membranes. Higher stability was
observed for ETFE based membranes over the FEP based one. In addition, low and medium extents of crosslinking yield an improvement in the stability of the grafted membranes, yet at high crosslinker content a decrease is observed.
VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

The influence of the crosslinker concentration and the graft level (GL) on the structure and the \textit{ex situ} fuel cell relevant properties were investigated and shown previously (chapter V and VI). The water uptake and the conductivity were negatively affected by an increase of the crosslinker content, whereas the dimensional stability is improved as a consequence of the formation of an increasingly tight polymer network. In addition, crosslinking results in an increase of the brittleness of the membrane. Despite the beneficial increase in conductivity with the GL, the mechanical properties and crystallinity and dimensional stability decrease.

In the present chapter, the influence of the crosslinker concentration on the \textit{in situ} fuel cell properties and performance of styrene/DVB grafted ETFE based membranes is investigated. The \textit{in situ} properties were determined using auxiliary current-pulse resistance, electrochemical impedance spectroscopy (EIS), polarization curve, H\textsubscript{2} permeation measurements and CO-stripping voltammetry. Thereafter, a durability test was carried out using the best performing membrane. The electrochemical \textit{in situ} characterization of the MEA was intermittently performed over the testing period. Furthermore, a local \textit{post mortem} analysis using FTIR was performed to yield a degradation map over the active area.

VII.1. Effect of crosslinker on fuel cell performance$^*$

In the past, the FEP based membrane was optimized with respect to its performance and chemical stability by adjusting the graft level and crosslinker content. In a study of the effect of DVB on fuel cell performance, the membrane prepared with 10 \% DVB (in the initial solution) was found to exhibit the best performance$^{(172)}$. Based on this finding, and without optimizing the crosslinker content, the influence of the graft level on the \textit{ex situ} and \textit{in situ} properties for the ETFE based membranes was investigated in detail in the past$^{(173)}$. It was shown that the increase of the GL leads to more brittle membranes, while a lower GL does not afford good conductivities. The optimum GL was identified to lie between 24 and 30 \% at those conditions. For the present investigation we selected a GL of 25 \% as an optimum value (minimising the impact of GL on the mechanical properties and dimensional stability). In this compositional range, the mechanical integrity, conductivity and performance of the grafted membranes are well-balanced$^{(173)}$.

VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

The aim of the present investigation is to relate the ex situ relevant fuel cell properties to the in situ fuel cell properties and their influence on the fuel cell performance of the styrene/DVB grafted ETFE based membranes. Furthermore, the optimum crosslinker concentration leading to the highest fuel cell performance will be investigated.

Selected membranes with fixed graft level (~ 25 %) based on different DVB concentration in the initial grafting solution, varied from 0, 2, 3, 4, 5, 6, 7, 8, 10, 15 % (v/v) (volumetric ratio of DVB with respect of the total monomer volume) were prepared based on the kinetic study shown elsewhere (see IV.5). The membrane with a DVB content of 20 % could not be tested in the single cell; it was too brittle and cracked during cell assembly. The ex situ properties of these membranes were already assessed and presented previously (see chapter VI). The membranes were assembled into MEAs and were tested in the single cell for 160h (See III.7).

VII.1.1. Polarization curve and EIS measurements

For the characterization of fuel cell performance, polarization curves were recorded at 80 °C as a first test after cell conditioning (operated for 160h at 500 mA·cm$^{-2}$) and obtaining stable performance (except uncrosslinked membrane which shows already higher degradation). Results for selected MEAs are presented in Figure VII.1.

The in situ membrane resistance was determined via the auxiliary current-pulse technique$^{130}$. The membrane resistance is notably higher for crosslinker concentrations of 10 % (136 mΩ·cm$^2$ @ 0.5 A·cm$^{-2}$) and 15 % (188 mΩ·cm$^2$ @ 0.5 A·cm$^{-2}$), with concomitant decrease in cell performance, compared to the values for the uncrosslinked and 5 % DVB crosslinked membrane, respectively (both 84 mOhm·cm$^2$ @ 0.5 A·cm$^{-2}$). The distinct increase in ohmic resistance towards higher current densities is most probably associated with partial drying of the anode side of the membrane and / or the anode-membrane interface$^{168}$. In this sense, highly crosslinked radiation grafted membranes, although having only a thickness of 35 µm, can exhibit resistance characteristics similar to those of thick Nafion® membranes$^{174}$. 
VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

Figure VII.1: Single cell performance data of selected ETFE based membranes with GL of 25 % and different extent of crosslinking. Electrodes: ELAT® (type LT140EWSI) with 0.5 mg Pt cm\(^{-2}\), cell temperature: 80 °C, reactants H\(_2\)/O\(_2\) at a stoichiometry of 1.5/1.5, atmospheric gas pressure, H\(_2\) humidified at 80 °C, O\(_2\) dry.

The lowest performance, however, is exhibited by the cell with uncrosslinked membrane, although the membrane resistance is the lowest in the series (84 m\(\Omega\cdot\text{cm}^2\) @ 0.5 A cm\(^{-2}\)), which is puzzling at first. Yet similar observations have been made for FEP based radiation grafted membranes with varying extents of crosslinking\(^{(172)}\). The phenomenon will be revisited shortly. The highest performance is obtained with the membrane prepared with 5 % DVB. Compared to identical MEAs with optimized 25 µm FEP based membrane (10 % DVB) and Nafion®112 membrane, respectively, almost identical performance and membrane resistance is achieved (Figure VII.2).
VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

Figure VII.2: Single cell performance data of the best performing ETFE based membrane, standard FEP based membrane and Nafion® 112 membrane. Electrodes: ELAT® (type LT140EWSI) with 0.5 mg Pt cm$^{-2}$, cell temperature: 80 °C, reactants H$_2$/O$_2$ at a stoichiometry of 1.5/1.5, atmospheric gas pressure, H$_2$ humidified at 80 °C, O$_2$ dry.

Fuel cell performance at various current densities for MEAs with differently crosslinked membranes is shown in Figure VII.3.

Figure VII.3: Cell performance at open circuit voltage (OCV) and selected current densities as a function of crosslinker concentration in the initial grafting solution (data extracted from cell polarization data).
The OCV is markedly lower in case of the uncrosslinked and low crosslinked membranes, which is a consequence of higher reactant crossover, leading to a more pronounced formation of a mixed potential\(^{(167)}\). At medium (0.82 A·cm\(^{-2}\)) and high (1.58 A·cm\(^{-2}\)) current densities, the higher performance losses at low and high degrees of crosslinking, respectively, become apparent. Maximum performance is obtained at intermediate crosslinking corresponding to around 5 % DVB in the grafting solution. The relevant MEA performance loss terms will be discussed in the following sections.

The ohmic resistance corrected cell voltage shows constant values for membranes prepared with 5 % DVB and above (Figure VII.4), meaning that the lower performance observed towards high crosslinking is a consequence of the higher ohmic resistance of the membranes. The electrode interfacial performance is unaffected. It is clear, however, from Figure VII.1 that the limited overall performance at low degrees of crosslinking is caused by another phenomenon.

In order to gain further insight into prevalent loss mechanisms, ac impedance spectra were recorded at a current density of 0.5 A·cm\(^{-2}\) (Figure VII.5). Quite clearly, the MEA with the uncrosslinked membrane exhibits the highest overall impedance, which is in agreement with the lowest observed performance (Figure VII.1).
The spectra for the MEAs with higher crosslinked membranes appear to be similar in shape, yet gradually shifted towards higher values on the real axis. From the impedance spectra, the ohmic resistance $R_Ω$ and polarization resistance $R_{pol}$ were extracted (for details on the method cf. Experimental section in chapter III) and plotted together with similar data obtained for FEP based membranes (Figure VII.6).

![Figure VII.5: Ac impedance spectra in Nyquist representation recorded at a DC current density of 0.5 A·cm$^{-2}$ under the experimental conditions stated in the caption of Figure VII.2, Frequency range: 0.1 Hz – 25 kHz.](image)

The trends for both types of membrane are similar. At low degrees of crosslinking, an ohmic resistance of around 100 mOhm·cm$^2$ is measured, which increases with increasing extent of crosslinking, and stronger so for the ETFE based membranes. Contrariwise, the polarization resistance decreases with increasing crosslinking. For the ETFE based membranes, the $R_{pol}$ value decreases from around 400 mOhm·cm$^2$ for the uncrosslinked membrane to a stable value of 192 mOhm·cm$^2$ for membranes prepared with 5 % DVB and above. Whereas the increasing $R_Ω$ is clearly associated with the decreasing membrane conductivity (see paragraph VI.1.2), correlating well the ohmic resistance data determined via the current-pulse technique (Figure VII.1 and Figure VII.4), the significance of $R_{pol}$ in this context is less straightforward.
It has been argued that \( R_{\text{pol}} \) is a measure for the quality of the membrane-electrode interface, based on the fact that the value appears to be influenced by MEA laminating conditions and membrane surface pretreatment\(^{(175)}\). A decreasing \( R_{\text{pol}} \) with increasing extent of crosslinking would mean that the membrane-electrode interface quality improves with crosslinking. The correlation with physico-chemical phenomena of the interface is inconclusive at this point. Our results are somewhat at variance with the finding, obtained via XPS analysis of the membrane surface, that with increasing degree of crosslinking, the membrane surface becomes more and more ‘FEP-like’, i.e., gradually lower amounts of poly(styrenesulfonic acid) (PSSA) moieties are detected\(^{(176)}\). This would contradict with the insight that the ionomer in the electrodes (Nafion®) and the PSSA domains in the membrane need to be well-connected to minimize interfacial proton transport losses. It has to be kept in mind, however, that the surface of the humidified membrane is likely to have different properties compared to the membrane surface in the UHV environment used for XPS analysis.

One aspect that needs to be pointed out in this discussion is the poor chemical stability of the low crosslinked membranes, especially the uncrosslinked one. The results presented in Figure VII.1 - 6 are based on measurements taken after 160 h of operation. This was to make sure the MEAs were properly conditioned. The membranes with low extent of degradation, however, had already experienced some degradation at this point. The ac impedance derived ohmic resistance \( R_\Omega \) of the uncrosslinked membrane increased from 70 mOhm·cm\(^2\) after 21 h of operation to 94 mOhm·cm\(^2\) after 160 h, and the polarization resistance \( R_{\text{pol}} \) increased from 277 to 411 mOhm·cm\(^2\). Despite the observed increase in resistance, even with the initial values for \( R_\Omega \) and \( R_{\text{pol}} \) the trend of decreasing

Figure VII.6: Polarization and ohmic resistance values extracted from ac impedance spectra in Figure VII.5 for ETFE based membranes. Data for FEP based membranes are from ref. (172).
ohmic resistance and increasing polarization resistance towards lower extents of crosslinking remains the same.

Based on the results obtained so far, we conclude that, in terms of cell performance, the ETFE based membrane prepared with 5 % DVB in the grafting solution offers the optimum combination of ohmic resistance and membrane-electrode interfacial properties, yielding the highest MEA performance among all the samples tested with varying degree of crosslinking. A comparison of MEA performance characteristics for an optimized ETFE (5 % DVB) and FEP (10 % DVB) based membrane, respectively, and Nafion® 112 is shown in Table VII.1.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>OCV [mV]</th>
<th>Cell Voltage @ 1.58 A·cm⁻² [mV]</th>
<th>Ohmic Resistance¹ [mOhm·cm⁻²]</th>
<th>Ohmic Resistance² [mOhm·cm⁻²]</th>
<th>Polarization Resistance² [mOhm·cm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-ETFE (5% DVB)</td>
<td>919</td>
<td>443</td>
<td>84</td>
<td>95</td>
<td>184</td>
</tr>
<tr>
<td>g-FEP (10% DVB)</td>
<td>898</td>
<td>425</td>
<td>97</td>
<td>113</td>
<td>166</td>
</tr>
<tr>
<td>Nafion® 112</td>
<td>914</td>
<td>465</td>
<td>88</td>
<td>86</td>
<td>138</td>
</tr>
</tbody>
</table>

¹ ohmic resistance determined via auxiliary current-pulse technique
² ohmic and polarization resistance determined via ac impedance spectroscopy at a current density of 0.5 A·cm⁻²

In agreement with Figure VII.1, minor performance differences of up to 40 mV at a current density of 1.58 A·cm⁻² are observed, with performance increasing in the sequence:

\[ \text{g-FEP} < \text{g-ETFE} < \text{Nafion® 112} \] (performance)

The ohmic resistances determined via the auxiliary current-pulse method have a tendency to show lower values compared to the values obtained via ac impedance spectroscopy, which is a consequence of the difference in time-domain resolution for both methods and the effect of cable inductance during ac measurements at high frequencies (> 2 kHz). However, the general trend between the different membrane types is similar: The FEP based grafted membrane shows the highest ohmic resistance, which is in accordance with the ex situ conductivity data (Table VII.2). Yet the polarization resistance, our measure for the quality of the membrane-electrode interface, varies strongly, increasing in the sequence:

\[ \text{Nafion® 112} < \text{g-FEP} < \text{g-ETFE} \] (interfacial resistance)
TABLE VII.2: \textit{ex situ} properties of different membranes. Base film thickness of ETFE and FEP is 25 µm. The DVB content refers to the concentration in the initial grafting solution.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>DVB [vol %]</th>
<th>GL [wt %]</th>
<th>IEC [mmol.g(^{-1})]</th>
<th>Water uptake(^1) [wt %]</th>
<th>Hydration number(^1) [H(_2)O/SO(_3)H]</th>
<th>Proton conductivity(^1) [mS·cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-ETFE</td>
<td>5</td>
<td>25.8</td>
<td>1.74 ± 0.08</td>
<td>21.9 ± 3.1</td>
<td>7.0 ± 0.7</td>
<td>62 ± 2</td>
</tr>
<tr>
<td>g-FEP</td>
<td>10</td>
<td>18.2</td>
<td>1.36 ± 0.06</td>
<td>16.3 ± 1.5</td>
<td>6.7 ± 0.7</td>
<td>41 ± 1</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>-</td>
<td>-</td>
<td>0.91</td>
<td>33.5 ± 1.8</td>
<td>18.0 ± 0.9</td>
<td>82 ±6</td>
</tr>
</tbody>
</table>

\(^1\) @ room temperature in liquid water equilibrated state.

The overall higher interfacial resistance for the MEAs with grafted membranes highlights the ionomer compatibility issues to the ionomer in the catalyst layer, which is Nafion®. The dissimilar characteristics for the g-FEP and g-ETFE membrane based MEAs is evident. Whereas the ohmic resistance is lower for the g-ETFE based MEA, a higher polarization resistance is observed. The data for the g-FEP membrane based MEA in Table VII.1 is at variance with the values reported in Figure VII.6. The reason is different electrodes used, i.e. different generations of ELAT® electrodes (E-TEK / BASF Fuel Cell, Inc.). The origin of the higher interfacial resistance of the g-ETFE based sample is unclear at this point. Possibly it is related to different surface properties of the two grafted membranes. In a previous study on FEP based radiation grafted membranes, we found that the impregnation of the membrane with soluble Nafion® prior to hot-pressing leads to a decrease in \(R_{\text{pol}}\), hence to an improved membrane-electrode interface. This approach is probably applicable to ETFE based membranes, too. If we take the sum of ohmic resistance \(R_\Omega\) and polarization resistance \(R_{\text{pol}}\), we obtain the low frequency intercept \((R_{1F})\) with the real axis in the Nyqvist representation of the ac impedance spectrum, which is a measure for the overall performance of the cell. \((R_{1F}, \text{to be precise},\) is a measure for the slope of the polarization curve at the given DC operating point of the cell\(^{(177)}\)). For both g-FEP and g-ETFE based MEAs, the same value of \(R_{1F} = 279\) mOhm-cm\(^2\) is obtained, indicating a compensation of the ohmic and interfacial characteristics.

Up to this point, it has to be emphasized that the uncrosslinked membrane showed substantial degradation during the time on test and failure due to excessive reactant crossover after 166 h and observed pinhole formation in the active area. Similar characteristics were observed for FEP based grafted membranes\(^{(172)}\). Yet, the FEP membrane prepared with 10 % DVB in the grafting solution yielded encouraging durability of several thousand hours\(^{(175)}\).
VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

VII.1.2. \( H_2 \) permeation and catalyst surface area

The permeability of the electrolyte membrane for reactants (\( H_2 / O_2 \)) is a property that strongly influences the rate of hydrogen peroxide and radical species formation through interaction of \( H_2 \) and \( O_2 \) on the Pt catalyst surface, and thus the rate of chemical membrane degradation\(^{(54, 178)}\). A comparison of the stability of Nafion® 112 and a non-fluorinated polyaromatic membrane (biphenyl sulfone hydrocarbon type) showed that although the polyaromatic membrane showed inferior chemical stability in an \textit{ex situ} Fenton test, it exhibited a higher chemical stability in the \textit{in situ} OCV decay test, owing to its much lower reactant permeability\(^{(179)}\). It is, therefore, important to determine the \( H_2 \) crossover rate for membranes with different extent of crosslinking (Figure VII.7).

![Figure VII.7: Hydrogen crossover current density measured at 0.5 V in \( H_2 / N_2 \) mode at a temperature of 80 °C and gas pressure of 1 bar. Both \( H_2 \) and \( N_2 \) were humidified to 100 % relative humidity.]

The crossover current density was measured at 0.5 V in \( H_2 / N_2 \) mode at temperature of 80 °C. Low crosslinked membranes show clearly a higher \( H_2 \) permeability compared to Nafion® 112 membrane. The values for ETFE and FEP based membrane, at least at a crosslinking corresponding to 10 % DVB in the grafting solution, is comparable. The obtained decrease of the hydrogen crossover with the crosslinker concentration is due to the creation of three-dimensional network leading to the decrease of the water content, (paragraph VI.1.2).

The MEA performance is governed, if \( O_2 \) is used as oxidant, mainly by the membrane resistance and the available catalyst surface area. The specific electrochemically active platinum surface area, determined via CO-stripping voltammetry, shows only little variation with the crosslinker content (Figure VII.8), with a slightly increasing trend between 2 and 15 % DVB, and indications of slightly lower values at 20 % DVB. The
measurement using the uncrosslinked membrane could not be carried out due to premature failure of the MEA. For g-FEP (10 % DVB) and Nafion® 112 membrane based MEA, values between 21 and 24 m²·g⁻¹ were obtained. The variations of catalyst surface area in this series can only account for differences in cell voltage of the order of 10 mV, the influence on the polarization characteristics (Figure VII.1) can therefore be neglected.

Figure VII.8: Specific catalyst Pt surface area determined via CO stripping voltammetry. Catalyst loading is 0.5 mg Pt cm⁻² for both anode and cathode.

VII.2. Effect of graft level

The graft level is one of the key parameters to characterize the radiation grafted membranes. The increase of the GL has an influence on the different chemical, thermal and mechanical properties of the base film. In an earlier contribution, a systematic study of the effect of graft level (GL) on the ex situ and in situ properties based on styrene/DVB grafted ETFE membranes was carried out to determine the effect on the fuel cell performance (173). However, the investigation was based on optimal conditions found for the FEP based membranes (use of 10% DVB in the initial grafting solution) and the effect on fuel cell durability was not studied. It was stated that optimum graft level in that case was between 20 to 30 %.

Despite the fact that increasing GL induces an increase of the proton conductivity of the membrane, however, the mechanical properties and the dimensional stability are affected negatively. Since the grafting conditions were modified, and the system of styrene/DVB grafted ETFE membranes was optimized, we were interested to establish how the in situ properties of the MEAs based on membranes with different graft level will be affected in a long term test. In this section, the effect of graft level on the ex situ
and in situ properties of membranes with graft levels of 25 % and 35 % were studied and characterized. The membranes are based on styrene/DVB grafted ETFE with DVB concentration in the initial grafting solution of 5 % (v/v) (volumetric ratio of DVB with respect of the total monomer volume) and were prepared using the same conditions as described in paragraph IV.5.

**VII.2.1. History plot and ex situ characterization**

The ex situ fuel cell relevant properties of the membranes (IEC, water uptake, conductivity, mechanical properties and dimensional stability) were determined. The mechanical properties in both the machining and transverse direction of the selected membranes with GL of 25 % and 35 % measured under the conditions described in the paragraph III.5.1 are presented (Table.VII.3).

Table.VII.3: comparison of the mechanical properties of the ETFE-based film and membranes with 25 % and 35 % graft level. The membranes were exchanged to K$^+$ form and dried over night prior to measurements.

<table>
<thead>
<tr>
<th>GL [%]</th>
<th>Direction</th>
<th>Elongation at break [%]</th>
<th>Tensile strength [MPa]</th>
<th>Young modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base film</td>
<td>MD</td>
<td>309</td>
<td>60</td>
<td>866</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>411</td>
<td>56</td>
<td>855</td>
</tr>
<tr>
<td>Membrane</td>
<td>25</td>
<td>MD</td>
<td>114</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>139</td>
<td>46</td>
<td>844</td>
</tr>
<tr>
<td>Membrane</td>
<td>35</td>
<td>MD</td>
<td>72</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>68</td>
<td>45</td>
<td>1154</td>
</tr>
</tbody>
</table>

In general the elongation at break and the tensile strength of the grafted membranes are lower than those of the base material. Furthermore, the tensile strength and the elongation at break decrease with the increase of the GL in both directions. The important observation is that the Young’s modulus does not change significantly for the membrane with the GL of 25 %, while the value increases for the membrane with 35 % GL. Consequently, the stiffness of the highly grafted membrane is higher. The obtained data can be qualitatively explained and related with the changes of the other ex situ properties (crystallinity, dimensional changes) affected by the grafting and sulfonation. Indeed, the grafting and sulfonation are well known to induce significant changes in the structure of the grafted membranes and noticeable decrease of the crystallinity and dimensional stability (membrane shrinking) were reported with the increase of graft level.

The ex situ membrane properties of direct interest in fuel cell application (IEC, water uptake and conductivity) were measured at fully swollen state and at room temperature (Table.VII.4). As expected, the ETFE-based membrane with higher GL shows the highest
values in terms of IEC, water uptake and conductivity, assuming 100 % degree of sulfonation of the grafted polystyrene.

Table VII.4: IEC, water uptake and conductivity of the ETFE-based membrane (5% DVB) with 25% and 35% graft level.

<table>
<thead>
<tr>
<th>Graft level [%]</th>
<th>IEC [meq·g⁻¹]</th>
<th>Water uptake [%]</th>
<th>Hydration number ( \text{n(H}_2\text{O)/n(SO}_3\text{)} )</th>
<th>Conductivity [mS·cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.6</td>
<td>18.2</td>
<td>6</td>
<td>59.4</td>
</tr>
<tr>
<td>35</td>
<td>1.8</td>
<td>31.5</td>
<td>10</td>
<td>70.0</td>
</tr>
</tbody>
</table>

1 @ room temperature in liquid water equilibrated state.

After the *ex situ* characterization of both ETFE-based membranes, the question was then to correlate these data and the *in situ* fuel cell results, and to correlate qualitatively these results to mechanical stability, interfacial properties of these membranes. Thus, fuel cell tests were performed under the same conditions as described elsewhere in paragraph III.7. However, the used cell is a differential cell, which possesses a linear gas flow field with 1 mm channel/land width and with the use of sub-gasket (25 µm Kapton®) to prevent edge failure (see Figure III.8 in paragraph III.7). Both tests based on the membranes with GL ~ 35 % (test V-516) and GL ~ 25 % (test V-513) were performed for 1004 h and 1027 h, respectively, under the same conditions. Figure VII.9 shows the history plot of both MEAs showing the change of the cell voltage and ohmic resistance over the testing time.

Based on their stable cell voltage values over the test time (Figure VII.9), no signs of membrane degradation were observed for both tests. Likewise, no significant changes were observed for the membrane resistances over the testing period. Linear regression of the cell voltage was carried out and a voltage decay rate was evaluated to be 11 µV·h⁻¹ and 13 µV·h⁻¹ for the MEA based on the membrane with the GL of 25 % and 35 %, respectively.
VII.2.2. Polarization curve and EIS measurements

Single cell performance comparing the two MEAs of test V-513 and V-516 were performed after different testing time (Figure VII.10). The MEA based on GL of 25 % membrane shows higher ohmic resistance over the testing time, whereas the MEA based on GL of 35 % shows a lower value after 332 h and then a noticeable increase was observed at the end of test, reaching the same value as the MEA with 25 % GL at 1004 h. The other observation is that the MEA V-513 shows better performance at high current densities, whereas the V-516 shows a clear deviation when it reached 1500 mA-cm\(^{-2}\). Furthermore, the MEA V-516 shows a clear decrease of its performance after 1004 h.

To more deeply investigate the origin of the performance losses in both MEAs, impedance measurements were carried out at different testing time, and the extracted results are depicted in the Figure VII.11.
The values for the ohmic resistance in both MEAs show no significant changes over the testing time. The difference in the ohmic resistance between both membrane can be understood easily taking into account the \textit{ex situ} properties (water uptake, conductivity) measured for both membranes (Table VII.4). Interestingly, the polarization resistance of the MEA V-513 (25\%) was lower initially than that of the 35\%, and then it increased over time to reach the same values after 700 h of operation. The observed differences in the interfacial properties of the MEAs with the graft level were already observed and no clear trend was found\(^{(173)}\). The bonding properties of materials are closely related to their surface and wetting properties. It was previously reported that the total surface energy of the ETFE based membranes measured by means of contact angle increased with the graft level due the sulfonic acid group content\(^{(180)}\). Therefore, the observed behaviour of the interfacial resistance has most probably to deal with the hot-pressing process during the membrane-electrodes assembly. In fact the drying of the membrane during this process, and the changes of the water content, which act as plasticizer and reduces the glass transition temperature of the membrane was pointed out to be the critical parameter\(^{(181)}\).
Figure VII.11: Comparison of the polarization and ohmic resistance of the MEAs prepared with ETFE based membranes with 25 % and 35 % GL over the testing-time extracted from ac impedance spectra (not shown). Ac impedance spectra in Nyquist representation recorded at a DC current density of 0.5 A·cm\(^{-2}\) under the experimental conditions stated in the caption of Figure VII.9, Frequency range: 0.1 Hz – 25 kHz.

**VII.2.3. H\(_2\) permeation and catalyst surface area**

Another important parameter of the mechanical integrity of the membrane is the measurement of the hydrogen permeation. As shown in the Figure VII.12, the hydrogen permeation of both membranes was similar over 350 h, and then a clear and marked increase of the permeation of the MEA V-516 (GL ~ 35 %) was observed.

This result indicates that at some point, the deterioration of the membrane and the mechanical stress occurring during the fuel cell operating conditions (local hydration and dehydration, shrinkage of the membrane) are markedly increased with the increase of the graft level. The same observation was made previously for highly crosslinked (10 % DVB) membrane with 30 % GL, where the deterioration of the membrane was observed after only 362 h testing time leading to crossover leak, whereas the membrane with lower GL (24 %) was operating without any failure up to 770 h\(^{(5)}\). Yet, no clear degradation mechanism was found to correlate the chemical degradation and mechanical integrity of the MEA. However, one suggestion of such differences can be attributed to the difference in the initial mechanical properties measured between both membranes and in the decrease of dimensional stability with the increase of the GL. In fact, there is ~ 40 % variation of the elongation at break between both membranes. Furthermore, pinhole
formation in the membrane with higher GL was observed after MEA disassembly, which obviously explain the loss in performance observed after 332 h.

![Graph](image)

Figure VII.12: Effect of the graft level on the $H_2$ crossover current density over the testing-time, measured at 0.5 V in $H_2$ / $N_2$ mode at a temperature of 80 °C and gas pressure of 1 bar. Both $H_2$ and $N_2$ were humidified to 100 % relative humidity.

VII.3. Durability test

In this study the first long term-testing of single $H_2/O_2$ cell over 2180h of an MEA assembled using an optimized ETFE-based membrane prepared by radiation-induced grafting of styrene / DVB and subsequent sulfonation with a graft level of 25 % was carried out. The in situ MEA properties were characterized over the testing period using auxiliary current-pulse resistance, electrochemical impedance spectroscopy, polarization and $H_2$ permeation.

VII.3.1. History plot and ex characterization

Based on our previous study on the effect of irradiation dose, graft level, and crosslinking, on different ex situ properties (thermal stability, mechanical stability, conductivity, etc.), a membrane optimized for performance based on radiation grafted styrene / DVB onto ETFE was defined. Furthermore, an investigation of the effect of crosslinker content on the in situ membrane properties (performance, resistance, interface, etc.) was carried out (Section VII.1). It was found that the maximum performance was reached using the membrane based on 5 % DVB (v/v). The thickness of the obtained membrane was measured and the effective extent of crosslinking (DVB)
determined by FTIR. The obtained value of the DVB/styrene molar ratio in the membrane is significantly (~50 %) higher than the value in the initial grafting solution (Table VII.5).

Table VII.5: Comparison of the DVB/styrene molar ratio in the initial grafting solution and in the grafted film measured by FTIR.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>GL [%wt]</th>
<th>Molar ratio(^1) (DVB/Styrene) in the grafting solution</th>
<th>Molar ratio(^1) (DVB/Styrene) in the grafted film</th>
<th>Thickness(^2) [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE-25</td>
<td>25.2</td>
<td>4.3 +/- 0.0</td>
<td>6.7 +/- 0.1</td>
<td>34.0 +/- 0.6</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58.0 +/- 3.0</td>
</tr>
</tbody>
</table>

\(^1\) Correspond to 5% DVB (v/v).
\(^2\) Thickness measured for the membrane in liquid water equilibrated state.

DVB is well known to be more reactive than styrene and, therefore, the consumption of DVB during the grafting reaction is faster than that of styrene\(^{171, 182, 183}\). Likewise, FTIR measurements show that the DVB is incorporated to a high degree close to the surface in comparison to the bulk of the grafted film (ATR vs. transmission measurements) (Section V.2). The thickness of the resulting grafted ETFE-based membrane measured in the wet form is lower than that of the Nafion® 112 membrane.

The ex situ properties (IEC, water uptake, conductivity and hydration number) are fundamental characteristics for fuel cell performance. Representative results for the grafted ETFE-based membrane are compared to the values of Nafion®112 (Table VII.6)\(^4\).

Table VII.6: Measured value of ion exchange capacity (IEC), water uptake, hydration number and conductivity of the ETFE-based membrane (GL ~ 25.2 %; molar ratio (styrene/DVB) ~ 6.7 %) compared with the values of Nafion®112 membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC [^{[mmol·g^{-1}]}]</th>
<th>Conductivity [^{[mS·cm^{-1}]}]</th>
<th>Water uptake [^{[%wt]}]</th>
<th>Hydration number [^{[n(H_2O)/n(SO_3^-)]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE-25</td>
<td>1.6 +/- 0.1</td>
<td>64 +/- 3</td>
<td>20.6 +/- 0.6</td>
<td>7.0 +/- 0.5</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>0.9 +/- 0.1</td>
<td>82 +/- 6</td>
<td>33.5 +/- 1.8</td>
<td>18.0 +/- 0.9</td>
</tr>
</tbody>
</table>

\(^1\) Measurements were performed in fully swollen state at room temperature.

The Nafion®112 shows higher water content and conductivity than the ETFE-based
VII Fuel cell tests of ETFE-g-styrene/DVB based membranes

membrane, while the IEC value is lower (mass based values). Furthermore, the volumetric IEC values, taking into account the difference in density between both types of membranes, were evaluated and values of 2.4 mmol·cm$^{-3}$ and 1.6 mmol·cm$^{-3}$ for the ETFE grafted membrane and for Nafion®112, respectively, were determined. It is important to note here that Nafion®112 is not a crosslinked membrane, and comparable water content and conductivity values were obtained for the uncrosslinked styrene grafted ETFE-based membrane at a graft level of 25.6 %. Thus, the lower water content in the ETFE based membrane is a consequence of crosslinking, which was quantified previously by FTIR.

After assembling the grafted ETFE-based membrane (5% DVB) into the fuel cell, an MEA durability test was performed at a constant current density of 500 mA·cm$^{-2}$. The cell performance, as indicated by the cell voltage, and the ohmic membrane resistance measured by the pulse method are shown in Figure VII.13 over the testing time.

![Figure VII.13: Single cell durability test using a radiation grafted membrane based on ETFE (5 % DVB) @500 mA·cm$^{-2}$, cell temperature 80 °C; H$_2$/O$_2$ at a stoichiometry of 1.5/1.5, atmospheric gas pressure.](image)

The evaluated drop in voltage after 1100 h was around 11 mV, whereas this value was of about 21 mV at the end of the test (2180 h). Moreover, linear regression analysis of the voltage over the testing time yields a voltage decay rate of 13 µV·h$^{-1}$. Looking more closely at the history plot, the MEA history can be divided into two intervals with different voltage decay rates, the first occurring from the beginning of the test up to 1100 h with a value of 7 µV·h$^{-1}$, and a second from 1100 h to 2100 h with a decay rate of 23 µV·h$^{-1}$. Concerning the ohmic resistance, no change was noticed for the pulse measured ohmic resistance up to 1100 h, whereas an increase of 6 % was observed up to
1508 h, and then a further increase of 7% was measured up to 2100 h. The membrane resistance increases from initially 94.5 mΩ·cm\(^2\) to ~100 mΩ·cm\(^2\) after 1100 h, and then reaches a value of ~106 mΩ·cm\(^2\) at the end of test. Both stepwise changes in resistance were observed after restarting the cell (after measuring the H\(_2\) crossover in H\(_2\)/N\(_2\) mode and water humidifiers filling), which may indicate the adverse effect of start-stop cycles and their association with degradation phenomena in our system\(^{(175, 184)}\).

The polarization curves obtained over the testing time are shown (Figure VII.14). The performance of the ETFE-based membrane and the Nafion®112 after about 500 h of operating time shows similar results. However, the measured pulse ohmic resistance of the Nafion®112 was slightly higher, even showing a marked increase at high current densities starting from 1250 mA·cm\(^{-2}\). This may be the result of a stronger dehydration by the effect of electroosmotic drag on the anode side, which induces an increase in the area resistance\(^{(168)}\). Moreover, the difference in membrane microstructure, the water transport mechanism and the membrane-electrode interface may be influential parameters\(^{(168, 185)}\). The ohmic resistance does not show any significant change up to 1174 h, where after an increase leading the ETFE-based membrane to reach the same values to those of the Nafion®112 was observed after 1968 h. However, the ETFE-based membrane does not show any marked increase in resistance at high current densities over the testing time, as observed for the Nafion®112.

![Figure VII.14: Polarization curves of the ETFE-based membrane over the testing-time at 500 mA·cm\(^{-2}\), cell temperature 80 °C; H\(_2\)/O\(_2\) at a stoichiometry of 1.5/1.5.](image-url)
The extracted open circuit voltage (OCV) values at various operating times for the MEA are shown (Figure VII.15).

Figure VII.15: Evolution of the OCV value over the testing time at 500 mA·cm\(^{-2}\), cell temperature 80°C; \(\text{H}_2/\text{O}_2\) at a stoichiometry of 1.5/1.5. Radiation grafted membrane based on ETFE (GL ~ 25%, 5 % DVB).

The first general observation is that the OCV values show two distinct levels. The first one starts from the beginning up to 815 h, whereas the second one starts from 1004 h until the end of test. Moreover, the OCV slightly decreased from 0.924 V measured at 68 h to a value of 0.920 V at 188 h, which is assumed to be a consequence of the time needed for the cell and the interface of the MEA to run-in. The observed trend for the OCV correlates with the measured changes in the decay rates of the cell voltage.

In order to resolve the different losses occurring within the MEA, electrochemical impedance spectroscopy was performed intermittently over the testing period (Figure VII.16).

From the electrochemical impedance spectra, the ohmic resistance was determined from the intersection of the impedance spectrum with the real axis at the high frequency end, whereas the polarization resistance was obtained by subtracting the ohmic resistance from the resistance value at the intersection of the spectrum with the real axis at the low frequency end.
Figure VII.16: AC impedance spectra recorded at a DC current density of 500 mA·cm$^{-2}$ after different run time shown in Nyquist representation (frequency range: 0.1 Hz – 25 kHz). Radiation grafted membrane based on ETFE (GL ~ 25%, 5% DVB).

The first observation is that the Nafion®112 based MEA exhibits both lower ohmic and polarization resistance in comparison to the MEA with grafted ETFE membrane. The higher interfacial resistance (polarization resistance) in the case of the ETFE-based membrane was already pointed out to be mainly due to the lower compatibility of these grafted membranes to the Nafion® ionomer used in the catalyst layer. The resistance values extracted from the AC impedance spectra are depicted in Figure VII.17. The ohmic resistance does not show any change up to 800 h, whereas a slight increase of ~ 4% after 1200 h was observed. The polarization resistance of the ETFE based membrane decreases slightly up to 500 h and then increases after 800 h and 1200 h, afterwards no significant change is observed after this period. The observed slight decrease in the polarization resistance up to 500 h is most probably due to the improvement of the membrane-electrode interface during run-in. The extracted data of both resistances shows an increase after 1200 h, which is a sign of deterioration of the MEA. Moreover, the obtained results are in accordance with the observed loss in the OCV at 1000 h, owing to the sensitivity of the membrane to start-stop events. We should note here that the absolute ohmic resistance values determined by EIS are slightly higher than the values measured by the current-pulse method, due to the effect of cable inductance during measurements at high frequency.
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Figure VII.17: Extracted ohmic ($R_\Omega$) and polarization resistance ($R_{pol}$) from the ac impedance spectra recorded at 500 mA·cm$^{-2}$. Radiation grafted membrane based on ETFE (GL ~ 25%, 5% DVB).

VII.3.2. $H_2$ permeation and post mortem analysis

It was also important to investigate the $H_2$ crossover of the ETFE-based grafted membrane over the testing time, due to the close cause-effect relationship existing between the rate of chemical degradation and possible changes in the morphology of the membrane and its mechanical integrity (Figure VII.18). The hydrogen crossover shows a steady increase with increasing testing time up to 2000 h, and a corresponding $H_2$ permeation rate of $> 10$ ml·min$^{-1}$ was observed at the end of test after 2180 h. These results indicate clearly that to some extent changes in the membrane morphology and integrity occur over the operating time, in accordance with other measured in situ parameters (performance, ohmic and polarization resistances) (see Figures VII.13, 15 and 17). Dealing with a grafted membrane, the water management and the hydration-dehydration states become crucial issues in the durability and mechanical integrity. Likewise, water is known to play the role of a plasticizer, allowing more mobility of the chains. Therefore, the combination of morphological changes and the chemical degradation of the graft components (see post mortem results) play a significant role in the observed increase in gas permeation. The correlation of this result with the extent of degradation occurring in the membrane will be discussed in the next section dedicated to the post mortem analysis.
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Figure VII.18: Hydrogen crossover measured electrochemically in H₂ / N₂ mode at 80 °C. Radiation grafted membrane based on ETFE (GL ~ 25%, 5 % DVB).

VII.3.3. Post-mortem analysis

The cell was disassembled and the membrane was separated from the electrode by immersing the MEA in water and use of ultrasound (Figure VII.19). The first observation is that the membrane shows an entire crack in the edge zone (the border between the active and non-active area). In fact, pinhole formation was suspected from the sudden drop of performances after 2181 h and the measured H₂ crossover (> 10 ml.min⁻¹).

Figure VII.19: Scanned image (contrast enhanced) of the membrane disassembled from the MEA after 2180h on test. Radiation grafted membrane based on ETFE (GL ~ 25%, 5 % DVB).
To begin with, it was of importance to evaluate the extent of degradation in the non-active area (Area A, B, C and D as shown in Figure VII.19), where selected points of the membrane (exchanged into $K^+$ salt form and dried) were measured by FTIR (Table VII.7).

Table VII.7: Measured degradation in the non-active area for the Area A, B, C and D.

<table>
<thead>
<tr>
<th>Area</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area (A)</td>
<td>38 +/- 14</td>
</tr>
<tr>
<td>Area (B)</td>
<td>82 +/- 14</td>
</tr>
<tr>
<td>Area (C)</td>
<td>10 +/- 6</td>
</tr>
<tr>
<td>Area (D)</td>
<td>38 +/- 10</td>
</tr>
</tbody>
</table>

The area B shows marked degradation in comparison with the other non-active zones, while both areas A and D shows similar trends and less loss was observed. Interesting results were determined for the area near the hydrogen inlet of the tested membrane (area C), where the minimum degradation occurred. These results are somewhat surprising, since previously this area (non-active) was stated as a reference for the evaluation of the degradation, since no deterioration was observed on it\(^{(186)}\). Furthermore, the marked difference in the extent of degradation between the Area B and the rest of the non-active area is not yet understood. The excessive degradation in zone B, where the crack was located and formed, raises several questions about the extent of external gas crossover (leak tightness) of the MEA and the efficiency of the used gasket. Furthermore, the elevated chemical degradation is also assumed to be due to propagation of peroxides in these areas or existence of other sub-phenomenon which occurs in the presence of some potential contaminants and $H_2/O_2$.

The dried and exchanged membrane ($K^+$ form) was then characterized by FTIR to determine the extent of degradation in the active area in all channel/land areas (53 channels and lands in total). Thus, to map the degradation on the active area, 7 points in lateral direction were measured for each channel and land, and the obtained degradation map is presented in Figure VII.20. If we consider the overall area, we find that the extent of degradation in the channels was higher than in the lands of the active area. In fact, the extent of degradation in the channels was averaged to be 18 %, while the value in the lands was about 13 %. Additionally, the obtained results do not show any significant difference or clear trend between the channels and lands when comparing only the slightly degraded zone, where the values were 11.6 % and 11.7% in the channels and lands, respectively. The averages of degradation in the highly and the slightly degraded zone were determined regardless of the channel and land area in the membrane and correspond, respectively, to 51 % and 12 %. The higher degradation features were observed in the channels and lands in the first serpentine (Channel-53 and land-52)
located near the $O_2$ entrance, between the channel-41 and -43 and in the channel-31. The observed feature brings more questions than answers, about how and why the degradation occurs at these positions and the possible formation of small pinholes. The unexpected results were on the one hand the absence of any degradation gradient between the affected channels and lands, in addition to the lack of correlation between the highly degraded active zone and the crack location in the membrane.

Figure VII.20: Map of % degradation of the ETFE based membrane (membrane disassembled from the MEA after 2180h on test) located in the active area. Radiation grafted membrane based on ETFE (GL ~ 25%, 5 % DVB).

Consequently, the crack forming in our case may be assumed to be mostly due to mechanical failure of the membrane due to stress in this area between the hydrated active and non-hydrated inactive area where high degradation was measured. Likewise, the non perfect electrodes overlap may also explain the observed crack in the edge zone. Indeed, a failure of the membrane was found to occur systematically in the perimeter region of the membrane where there may be an overlap of one electrode over the other$^{(187)}$. 
VII.4. Conclusion

The effect of the concentration of divinylbenzene (DVB), used as crosslinker and co-monomer to styrene in the grafting solution, on the \textit{in situ} properties of radiation grafted and sulfonated membranes based on 25 µm ETFE with constant graft level of ~ 25 \% was investigated. The incorporation of DVB into the film during grafting leads to the formation of crosslinks within the polymer structure.

Fuel cell performance shows a maximum using the membrane prepared with 5 \% DVB in the grafting solution. Performance is nearly equivalent to that of an optimized FEP based radiation grafted membrane and Nafion\textregistered{}112. At higher extents of crosslinking (> 5 \% DVB), performance is limited by the increasing ohmic resistance of the membrane. Also, the membranes become more brittle when highly crosslinked. The membrane corresponding to 20 \% DVB could not be tested because of crack formation in the membrane during cell assembly. Conversely, the membrane electrode assemblies (MEAs) with low crosslinked membranes are limited in performance due to the apparently poor membrane-electrode interfacial properties, as evidenced by ac impedance spectroscopy. The reason for this behavior is not clear at this stage. A partial explanation is the rapid degradation of membranes with low extent of crosslinking, in particular the uncrosslinked one, which failed after 166 h due to excessive gas crossover. In comparison with a Nafion\textregistered{}112 based MEA, the higher interfacial resistance of radiation grafted membranes, both based on ETFE and FEP, indicates an inferior compatibility of the grafted membrane with the ionomer (Nafion\textregistered{}) used in the electrodes.

An important property in this context is the reactant permeability of the membrane. In this experimental series, the \textit{in situ} \textsubscript{H}2 crossover was found to decrease with increasing extent of crosslinking. A lower rate of gas permeation through the membrane is expected to yield a higher chemical stability of the membrane, owing to the lower amount of aggressive radical species (HO•, HOO•) formed at the electrodes due to interaction of \textsubscript{H}2, \textsubscript{O}2, \textsubscript{H}2\textsubscript{O} and the Pt catalyst.

The increase of the graft level does not show any significant influence on the fuel cell performance in short term testing (< 400 h), whereas losses are observed with longer term testing. The durability of highly grafted membranes is significantly affected and noticeable losses in the performance are observed with high \textsubscript{H}2 crossover. The dimensional stability of the radiation grafted membranes may be considered as key property to be taking into account for our membranes during fuel cell operation.

A fuel cell membrane based on an optimized styrene/DVB grafted ETFE membrane with a graft level of 25 \% was characterized for its \textit{ex situ} relevant fuel cell properties...
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(IEC, water uptake, conductivity and mechanical properties). The conductivity and water uptake of the grafted membrane were shown to be lower than that of Nafion®112, while the IEC shows an opposite trend, which is mainly attributed to the different densities and the effect of crosslinking and reduced free volume available within the polymer structure. Furthermore, the ETFE-based membrane shows slightly superior mechanical properties in terms of elongation at break and tensile strength.

A durability test with the optimized ETFE-based membrane was performed in a single fuel cell over a testing period of 2180 h. The MEA shows two regimes in cell voltage loss up to 2100 h, where a sudden drop was observed after 2180 h due to crack formation in the membrane. Moreover, the tested cell shows comparable performance to that of a Nafion®112 based cell, and only slight decrease in performance at high current densities was observed up to 2000 h. The post mortem analysis reveals that the high extent of degradation was more located near to the O₂ inlet, and the membrane areas associated with flow field channels were more affected than the respective land areas. It was found that degradation occurred in the non-active area to different extent, depending on the location of the measured points, the origin of which is not understood to date. Moreover, the crack formation observed in the membrane was located at the boundary between the area which shows low degradation and the highly degraded non-active area. Consequently, the MEA at the area between the active and non-active zone, even though covered by the gasket, was subjected to crack formation.
VIII ETFE-g-styrene/MAN based membranes

FEP-g-styrene based membranes show lifetime of less than hundred hours (~ 50 h) under steady fuel cell operating conditions (80 °C). In order to increase the mechanical integrity and resistance to irradiation of the obtained membranes, FEP was substituted by partially fluorinated poly(ethylene-alt-tetrafluoroethylene) (ETFE) leading to membranes showing a lifetime of more than 150 h\(^5\). Likewise, the crosslinking of these membranes offers a way to increase the lifetime to several thousands of hours. It is well known that poly(styrenesulfonic acid) in grafted membranes suffers from the weakness of the alpha-hydrogen position which is prone to radical attack under fuel cell conditions\(^{52, 110}\). A lot of work is devoted to improve the oxidative stability of radiation grafted membranes by the use of some new monomer combinations with low cost impact. Several authors reported on styrene/acyrlonitrile\(^{188, 189}\), \(\alpha\)-methylstyrene/styrene\(^{109}\), methylstyrene/\textit{tert}-butyl styrene\(^{107}\). So far, no fuel cell experiments were shown and only \textit{ex situ} chemical stability towards \(\text{H}_2\text{O}_2\) were shown. However, the real stress occurring during fuel cell operating conditions is very complex (hydration/dehydration, mechanical stress, aggressive species (\(\text{HO}^-, \text{HOO}^-\))). Our group also focuses on different monomer combinations in order to improve the chemical stability under real fuel cell operating conditions. Hence, alternative polymers have been recently reported which are prepared with substituted styrene monomers with protected \(\alpha\)-position, like \(\alpha,\beta,\beta\)-trifluorostyrene derivatives\(^{106}\) and \(\alpha\)-methylstyrene/methacrylonitrile\(^{108}\) to reduce the membrane susceptibility to chain degradation.

Based on our previous experience and knowledge of the styrene/DVB system, a new approach was initiated to improve the stability and mechanical integrity of our grafted membranes. This synthetic approach is based on the use of a new comonomer to styrene. The copolymerization is well known to induce changes on the formed polymer and its intrinsic properties. The selected monomer was methacrylonitrile (MAN), because of its protected alpha-position and its compatibility with styrene. Furthermore, based on literature data on the activation and dissociation energies of both monomers and the thermal degradation mechanism in the resulting copolymer, it was found that the MAN content reduces considerably the back-biting (Figure VIII.1) abstraction of the \(\alpha\)-hydrogen atom\(^{190}\). Likewise, it was reported that the introduction of nitrile groups in sulfonated hydrocarbon membranes has a positive effect on their dimensional stability and may improve the adhesion to inorganic materials (catalyst, fillers)\(^{191}\).

In this study, a novel approach for the preparation of radiation grafted membranes via copolymerization of styrene and MAN is presented. The grafting kinetics of the
VIII ETFE-g-styrene/MAN based membranes

styrene/MAN system was studied and a comparison with styrene is drawn. Furthermore, several membranes were prepared and characterized for their *ex situ* relevant fuel cell properties (IEC, water uptake, conductivity). The fuel cell performance and durability of the MEAs were investigated and compared with those of a styrene based membrane. *In situ* characterization over the testing period included auxiliary current pulse-resistance, electrochemical impedance spectroscopy, polarization curves and H₂ permeation. *In post mortem* analysis a degradation map of the active area for both styrene and MAN was determined by FTIR.

![Back-bitting mechanism](image1.png)

Figure VIII.1: Back-bitting mechanism\(^{(190)}\).

**VIII.1. Grafting kinetics of styrene/MAN into ETFE film and FTIR investigation of monomers composition**

**VIII.1.1. Grafting kinetics of styrene/MAN into ETFE film**

Styrene/MAN grafting into ETFE films was carried out under the same conditions as reported earlier (see section IV.5) in glass reactors. The grafting solution consisted of 20 % (v/v) monomer (mixture of styrene/MAN: 1/1 (mol/mol)) and 80 % (v/v) isopropanol/water mixture (isopropanol/water: 7/1) (Figure VIII.2).

![Tentative structure of ETFE-g-styrene/MAN membrane](image2.png)

Figure VIII.2: Tentative structure of ETFE-g-styrene/MAN membrane.

The variation of the graft level as a function of reaction time for styrene/MAN : 1/1
(mol/mol) and for pure styrene is presented in Figure VIII.3. The reactions were carried out for various reaction times (1-24 h) and the obtained kinetic curves were fitted with a simple mathematical model as described previously (Section IV).

![Figure VIII.3: Variation of the GL with the reaction time for styrene/MAN and styrene grafted ETFE base films.](image)

MAN slows down the grafting kinetics, and lower GLs are obtained compared to the MAN free system at the same reaction time. Moreover, a comparison of both grafting kinetics and the extracted parameters after fitting (initial rate of polymerization \(R_{p0}\) and the radical recombination rate \(\gamma\)) was carried out, where both parameters show higher values as in the case of styrene based grafted films (table VIII.1).

Table VIII.1: Comparison of the values of the initial rate of polymerization \(R_{p0}\) and the radical recombination rate \(\gamma\) for ETFE-g-styrene and ETFE-g-styrene/MAN.

<table>
<thead>
<tr>
<th></th>
<th>(\log(\gamma)) (\text{[h}^{-1})</th>
<th>(\log(R_{p0})) (\text{[h}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE-g-styrene-co-MAN</td>
<td>1.53</td>
<td>3.61</td>
</tr>
<tr>
<td>ETFE-g-styrene</td>
<td>2.72</td>
<td>5.19</td>
</tr>
</tbody>
</table>

On one hand, the different grafting efficiencies are probably due to an increased termination and radical transfer reaction. Furthermore, the grafting is known to be a diffusion controlled process, which means that the diffusion, affinity and solubility of monomers with the used solvent mixture are important and play a non-negligible role on the observed trend. More investigation is needed to determine the impact of styrene/MAN composition variation in the initial grafting solution and the efficiency of the grafting
reaction.

The content of MAN in the grafted films was determined by FTIR using a calibration curve of peaks corresponding to styrene (1493 cm\(^{-1}\)) and MAN (2230 cm\(^{-1}\)) (Figure VIII.4).

![FTIR spectrum](image)

Figure VIII.4: FTIR spectrum of sulfonated ETFE-g-styrene/MAN and sulfonated ETFE-g-styrene sulfonated based membranes. The intense bands at 1000-1350 cm\(^{-1}\) are ETFE backbone signals. Graft component relevant peaks: (a) C≡N stretch vibration at 2234 cm\(^{-1}\), (b) C=C aromatic skeleton stretch vibration at 1494 cm\(^{-1}\) and (c) C-H deformation vibration of methyl at 1388 cm\(^{-1}\).

The MAN/styrene molar ratio changes in the grafted material with the GL is depicted in Figure VIII.5. The MAN/styrene molar ratio in the grafted film does not show any significant change up to 26% GL and then a decrease is measured with the increase of the GL up to 35%, and then no change occurs in the composition. Composition drift in the styrene-\textit{co}-MAN with the reaction time was also observed with other systems like the grafting of styrene-\textit{co}-acrylonitrile into ETFE\(^{(188)}\). Another non-negligible factor is related to the formation of copolymer in the solution, which is a competitive process to the grafting and which should have an influence to the observed composition drift. It is important to note here that the reactivity ratios for styrene and MAN are 0.39 and 0.32 respectively\(^{(192)}\).
Figure VIII.5: Variation of the molar ratio (MAN/styrene) with the graft level (%) of the ETFE-g-styrene/MAN film. Grafting conditions: glass reactor, irradiation dose: 1.5 KGY, 20 % (v/v) monomers, MAN/styrene : 1/1 (mol/mol), 80 % (v/v) isopropanol/water mixture (isopropanol/water: 7/1) and temperature: 60 °C.

**VIII.1.2. Effect of MAN content on the ETFE-g-styrene/MAN films composition**

The content of the MAN/styrene molar ratio in the initial grafting solution was varied (MAN/styrene : 4/1, 2/1 and 1/1). The grafted ETFE based films were obtained using the same conditions as presented previously (see section IV.5), where the graft level was kept constant around a value of 27 %. The reaction times and obtained graft levels are depicted in Table VIII.2.

Table VIII.2: The reaction time required to reach a particular graft level for different MAN concentrations using a 600 mL stainless steel reactor.

<table>
<thead>
<tr>
<th>Grafted films</th>
<th>Molar ratio (MAN/St) in the initial solution</th>
<th>GL [%wt]</th>
<th>Reaction time [h]</th>
<th>Molar ratio (MAN/St) by (FTIR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-styrene/MAN #1</td>
<td>1</td>
<td>27</td>
<td>4.5</td>
<td>0.26</td>
</tr>
<tr>
<td>g-styrene/MAN #2</td>
<td>2</td>
<td>26</td>
<td>6</td>
<td>0.31</td>
</tr>
<tr>
<td>g-styrene/MAN #3</td>
<td>4</td>
<td>27</td>
<td>7</td>
<td>0.41</td>
</tr>
</tbody>
</table>

FTIR analysis of the prepared grafted films was performed and the area of relevant bands was determined. Bands of special interest are, the $\text{C} = \text{N}$ stretch vibration at 2231 cm$^{-1}$, the $\text{C} = \text{C}$ aromatic skeleton stretch vibration for the overall benzene ring and for the mono-substituted benzene at 1602 cm$^{-1}$ and at 1495 cm$^{-1}$, respectively, and the $\text{C} = \text{H}$ deformation vibration in MAN methyl at 1388 cm$^{-1}$ (Figure VII.4). Interestingly, as the molar ratio of the MAN/styrene increases, a shift of the peaks is observed (Figure
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.

Figure VIII.6: Shifts of the \((C \equiv N)\) wavenumber observed in the FTIR spectra of the ETFE-g-styrene/MAN grafted films with different MAN content.

The important characteristic of the MAN monomer is the strong polarity of the nitrile group, which can interact with its surroundings in different ways. The increase of the MAN content increases the probability of having dimers and/or trimers of adjacent MAN. Therefore, the intra and intermolecular forces (dipolar interactions) in the grafted styrene/MAN chains and their mobility may be the origin of the shifts observed in the wavenumber of the \(C \equiv N\) group\(^{193}\).

VIII.2. *Ex situ* characterization of ETFE-g-styrene/MAN based membranes

Selected membranes with a similar graft level based on styrene/MAN were characterized for their *ex situ* fuel cell relevant properties (composition, IEC, water uptake, conductivity and dimensional stability) and compared to styrene grafted FEP and ETFE based membranes and to Nafion®112 membrane (Table VIII.3 and VIII.4).

The ETFE-g-styrene/MAN membranes #1 and #3 show a different composition in terms of incorporated MAN. The composition was determined by FTIR and confirmed by IEC values. In fact, knowing the IEC value and taking into account that only the styrene is sulfonated (assuming 100 % degree of sulfonation) the molar ratio of MAN/styrene can be deduced. The obtained values show clearly that the *g*-styrene/MAN #3 based membrane shows a higher molar ratio of MAN/styrene in comparison with the *g*-

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Table VIII.3: Characteristics of the ETFE-g-Styrene/MAN based membranes compared with ETFE-g-styrene, FEP-g-styrene and Nafion®112 membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>GL [%wt]</th>
<th>Thickness* [µm]</th>
<th>Molar ratio (MAN/St by (FTIR))</th>
<th>Area shrinkage wet→dry [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-styrene/MAN #1</td>
<td>27.4</td>
<td>34</td>
<td>0.26</td>
<td>25.9</td>
</tr>
<tr>
<td>g-styrene/MAN #3</td>
<td>27.1</td>
<td>35</td>
<td>0.41</td>
<td>17.7</td>
</tr>
<tr>
<td>g-styrene</td>
<td>20.8</td>
<td>32</td>
<td>-</td>
<td>24.2</td>
</tr>
<tr>
<td>FEP-g-styrene</td>
<td>18.0</td>
<td>34</td>
<td>-</td>
<td>29.0</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>-</td>
<td>58</td>
<td>-</td>
<td>22.9</td>
</tr>
</tbody>
</table>

* Measured in water equilibrated form.

The *ex situ* properties (IEC, water uptake and conductivity) of the g-styrene/MAN#3 based membrane are lower than those of the g-styrene/MAN #2 based membrane, which can be attributed mainly to the lower styrene sulfonic acid content (Table VIII.4). Interestingly, the water uptake and hydration number are affected less than the conductivity. The question here is related to the real contribution of the nitrile group to the proton transport and the microstructure of the hydrophilic part in the membrane. Moreover, the measured values of the area shrinkage illustrate these changes, where the sample with higher MAN content possesses a higher dimensional stability. More investigations on the state-of-water of this type of membrane are needed to illustrate and understand the system. It is very important to emphasize that the MAN group is not hydrolyzed during sulfonation, which was verified by FTIR.

TABLE VIII.4: Measured value of IEC, water uptake, hydration number and conductivity of the ETFE-based membranes (ETFE-g-styrene/MAN and ETFE-g-styrene) compared with the values of FEP-g-styrene and Nafion®112 membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC [mmol·g⁻¹]</th>
<th>Conductivity * [mS·cm⁻¹]</th>
<th>Water uptake * [%wt]</th>
<th>Hydration number [n(H₂O)/n(SO₃H)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-styrene/MAN #1</td>
<td>1.35 +/- 0.07</td>
<td>69 +/- 3</td>
<td>26.8 +/- 1.5</td>
<td>10.6 +/- 0.8</td>
</tr>
<tr>
<td>g-styrene/MAN #3</td>
<td>1.14 +/- 0.02</td>
<td>42 +/- 2</td>
<td>25.5 +/- 0.4</td>
<td>12.8 +/- 0.8</td>
</tr>
<tr>
<td>g-styrene</td>
<td>1.46 +/- 0.06</td>
<td>49 +/- 2</td>
<td>25.6 +/- 3.1</td>
<td>9.7 +/- 0.7</td>
</tr>
<tr>
<td>FEP-g-styrene⁽¹⁰⁸⁾</td>
<td>1.33 +/- 0.02</td>
<td>72 +/- 6</td>
<td>29.5 +/- 0.7</td>
<td>12.3 +/- 0.8</td>
</tr>
<tr>
<td>Nafion®112⁽⁵⁾</td>
<td>0.91</td>
<td>82 +/- 6</td>
<td>33.5 +/- 1.8</td>
<td>18.0 +/- 0.9</td>
</tr>
</tbody>
</table>

* Measurements were performed in fully swollen state at room temperature.

The comparison of the different grafted membranes with similar IEC values (ETFE-g-
styrene/MAN#1, ETFE-g-styrene and FEP-g-styrene) reveals that the styrene/MAN grafted membranes shows conductivity values comparable with that of FEP-g-styrene, whereas the value is higher than that of ETFE-g-styrene value at comparable water content (Table VIII.4). In addition to the mentioned structure of the water containing domain, two other factors may explain these results, on one hand the hydrophilicity of the nitrile group and on the other its ability to form hydrogen bonds with water.

The representative results of the grafted ETFE-based membranes compared to the values of Nafion®112 obviously show a higher IEC (mass based values), while the hydration number and water uptake are slightly lower (Table VII.4). In fact the observed lower hydration number of the grafted membranes may explain their lower conductivity values in comparison with Nafion®112.

The volume based values of IEC, taking into account the difference in densities between both types of membranes, were evaluated and values of 2.3 mmol·cm$^{-3}$, 1.9 mmol·cm$^{-3}$, 2.5 mmol·cm$^{-3}$ and 1.6 mmol·cm$^{-3}$ for ETFE-g-styrene/MAN #1, ETFE-g-styrene/MAN #3, ETFE-g-styrene and for Nafion®112 membranes, respectively, were determined. As expected, the observed elevated volumetric IEC in the case of grafted membranes in comparison with Nafion®112 do not afford a higher conductivity, which can be related directly to the lower hydration number and to the difference in the microstructure.

It is important to note here that further comparison of ETFE-g-styrene and ETFE-g-styrene/MAN based membranes, which show different graft levels, is problematic, since the extent of grafting has a direct effect on the crystallinity, area shrinkage (wet $\rightarrow$ dry) and mechanical properties.

**VIII.3. Fuel cell tests and post mortem analysis of ETFE-g-styrene/MAN based membrane**

**VIII.3.1. Fuel cell tests**

*Ex situ* characterized ETFE-g-styrene/MAN based membranes #1 and #3 and a ETFE-g-styrene membrane were assembled into the fuel cell, and the MEAs were operated at a constant current density of 500 mA·cm$^{-2}$ at 80°C and ambient pressure, using pure H$_2$ and O$_2$ in counter-flow mode at stoichiometry of 1.5. Both gases were fed at 80 °C and were fully humidified using bubblers. All membranes were leak tight at the beginning of tests and the operating time of each cell is presented in Table VIII.5.

The first observation is that the FEP-g-styrene membrane showed large gas crossover
after less than 50 h, while the same happens after less than 165 h for the ETFE-g-styrene. However, no mechanical failures (pinhole or crack formation) were observed in the case of ETFE-g-styrene/MAN based membranes and for Nafion®112 membrane. The collected cell voltage and the ohmic resistance measured by the pulse method of the grafted membranes ETFE-g-styrene and ETFE-g-styrene/MAN #1 and #3 over the testing time are shown in Figure VIII.7.

Table VIII.5: Duration of the fuel cell tests performed using ETFE-g-styrene/MAN, ETFE-g-styrene, FEP-g-styrene and Nafion®112 membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Time on test [h]</th>
<th>MEA failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-styrene/MAN #1</td>
<td>1032</td>
<td>No failure</td>
</tr>
<tr>
<td>g-styrene/MAN #3</td>
<td>1009</td>
<td>No failure</td>
</tr>
<tr>
<td>g-styrene</td>
<td>&lt; 165</td>
<td>Crossover leak &gt; 10 ml·min⁻¹</td>
</tr>
<tr>
<td>FEP-g-styrene</td>
<td>&lt; 50</td>
<td>Crossover leak &gt; 10 ml·min⁻¹</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>600</td>
<td>No failure</td>
</tr>
</tbody>
</table>

The history plot and the measured pulse resistance over the testing period of the ETFE-g-styrene/MAN and the purely styrene based membranes are shown in Figure VIII.7.
Concerning the ohmic resistance of the tested MEAs, the ETFE-g-styrene based membrane showed an increase of 34 % after 165 h, while no significant change on the values of the ETFE-g-styrene/MAN #1 and #3 resistances were observed.

The performance of the ETFE-g-styrene/MAN based membrane was evaluated by recording polarization curves over the testing time (Figure VIII.8).

![Figure VIII.8: Single cell performance of ETFE-g-styrene/MAN membranes and Nafion®112 membrane. Electrodes: ELAT® with 0.5 mg Pt cm⁻², cell temperature: 80 °C, reactants H₂/O₂ at stoichiometry of 1.5/1.5, H₂ and O₂ are humidified at 80 °C and atmospheric gas pressure.](image)

Both MEAs based on ETFE-g-styrene/MAN membranes showed no significant change in the performance up to 1000h. The sample #1 shows comparable performance to the Nafion®112 membrane, and better performance than the sample #3 (expected from the ex situ conductivity values of both samples (see table VIII.4)). The observed increase at high current densities of the ohmic resistance may be due to stronger dehydration on the anode side caused by the electroosmotic drag. Other factors, as the membrane microstructure, the water transport mechanism and the membrane-electrode interface may play an important role in the observed behaviour\(^5\).\(^165\).

To investigate the contributions of both the interfacial and membrane resistances on the performance losses in both MEAs more in detail, impedance measurements
(at current density of 500 mA·cm$^{-2}$) were carried out at different testing times, and the extracted results (ohmic and polarization resistances) are depicted in Figure VIII.9.

![Graph showing the comparison of ohmic and polarization resistances over time for ETFE-g-styrene/MAN grafted membranes.](image)

Figure VIII.9: Comparison of the polarization and ohmic resistance of the styrene/MAN grafted ETFE based membranes over the testing time. Ac impedance spectra were recorded at a current density of 500 mA·cm$^{-2}$ (frequency range: 0.1 Hz - 25 kHz).

The polarization resistance ($R_{pol}$) does not show any significant change over the testing time, the quality of the membrane-electrodes interfaces is not affected. Likewise, the increase of the MAN content does not have any additional effect on the quality of the membrane-electrodes interface. However, the polarization resistance values of MAN/styrene grafted ETFE based membranes (153 mΩ·cm$^2$ and 183 mΩ·cm$^2$) are rather lower than those of styrene based membranes (411 mΩ·cm$^2$), whereas they possess comparable values compared to those of the crosslinked styrene/DVB (5% DVB) based ETFE membranes (188 mΩ·cm$^2$) (crosslinking even improves the membrane-electrodes interface (see paragraph VII.1.1)). In fact the introduction of the strongly polar pendant nitrile groups may promote the adhesion of the grafted membrane in the MEAs$^{(191)}$. Nevertheless, these polarization resistance values are still higher by 30 % than that of Nafion®112 membrane, most probably due to the incompatibility with the used ionomer in the catalyst layer, which is Nafion (Table VIII.6).

The extracted data of the ohmic resistance ($R_{Ω}$) for the ETFE-g-styrene/MAN #1 and ETFE-g-styrene/MAN #3 do not show any significant change up to 1000 h. As measured previously by the current-pulse method, the ohmic resistance values were confirmed by EIS, and the resistance values over the testing time of sample #1 were lower than those of the sample #3.
Table VIII.6: Extracted ohmic ($R_\Omega$) and polarization resistance ($R_{pol}$) from the EIS-spectra for ETFE-g-styrene/MAN, ETFE-g-styrene and Nafion®112 membranes measured after the first 160 h operation time.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ohmic resistance [mΩ·cm$^2$]</th>
<th>Polarization resistance [mΩ·cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-styrene/MAN #1</td>
<td>108</td>
<td>153</td>
</tr>
<tr>
<td>g-styrene/MAN #3</td>
<td>138</td>
<td>188</td>
</tr>
<tr>
<td>g-styrene</td>
<td>96</td>
<td>411</td>
</tr>
<tr>
<td>Nafion®112</td>
<td>86</td>
<td>138</td>
</tr>
</tbody>
</table>

The gas crossover of the grafted membranes was pointed out to be significantly affected by the crosslinker content, water uptake and graft level, which are closely related to the rate of chemical degradation (see post mortem analysis) and the dimensional stability (shrinkage of the membrane area). The mechanical integrity of the membranes was investigated by means of hydrogen permeation measurements performed intermittently over the testing time (Figure VIII.10).

![Figure VIII.10: H$_2$ permeation of the ETFE-g-styrene/MAN membranes over the testing time measured in H$_2$/N$_2$ mode at a temperature of 80 °C and gas pressure of 1 bar (both gases were fully humidified).](image)

The hydrogen crossover does not show any significant change for both samples up to 500 h, while an increase with further operating time up to 1000 h was determined in the case of the ETFE-g-styrene/MAN #1, reaching a value of 1.2 ml-min$^{-1}$. The sample #3 with higher MAN content shows higher stability, while a slight increase of the H$_2$ permeation until the end of test was measured. The observed increase after 500 h of operation is a clear sign of the changes affecting the mechanical integrity and the
morphology in the membrane, which might be also related with chemical degradation (see postmortem analysis of sample #1 (next paragraph). As mentioned previously, the permeability of the radiation grafted membranes is closely related to the radical formation and migration, which influences the rate of chemical membrane degradation\(^{54, 178}\). Therefore, dealing with uncrosslinked grafted membrane, the dimensional stability (shrinkage of the membrane area) has a predominant effect on the hydration-dehydration states and on the permeability of the membrane. In fact, the membrane shrinkage at the same water content is significantly different for both membranes, where the value measured for the sample #1 (25.9 %) is 46 % higher than the value measured for sample #3 (17.7 %) (Table VIII.3), which may have a direct effect on the durability and mechanical integrity. The same deviation after only 362 h operation in single fuel cell test was observed for crosslinked ETFE-g-styrene based membranes (paragraph VII.2.3), where also the area shrinkage of the affected membrane was higher. Initial experiments using a rapid aging protocol under specific conditions confirm these results, showing that there is a clear trend between H\(_2\) crossover evolution over testing time and the dimensional stability (area shrinkage of the membrane between wet/dry state) of the tested membranes\(^{124}\). The change in the morphology and the mechanical stress generated when changing between the wet and dry state of the membrane may explain partly the observed increase in gas permeation. Furthermore, the increase of the content of the dipolar nitrile group present in the grafted membranes may affect the water transport due to the increase of intermolecular interactions leading to physical crosslinking of this membrane. It can be mentioned here that the measured H\(_2\) crossover of the MEA based on an uncrosslinked ETFE-g-styrene based membrane was >10 ml·min\(^{-1}\) after only 160 h.

**VIII.3.2. Post mortem analysis**

To get more insight about the observed *in situ* stability of the tested cell based on the membrane ETFE-g-styrene/MAN #1, the MEA was disassembled from the electrodes by immersing it in water and ultrasound treatment. The membrane was exchanged to K\(^+\) form using a KCl solution (0.5 M) and was dried overnight. The disassembled membrane in general shows a homogeneous area, except visible discoloration in the top part of the active area and near both gas inlets (Figure VIII.11).

The membrane was characterized by FTIR to determine the degradation extent and its location as described previously (paragraph III.9) in the non-active and active area. Surprisingly, the comparison between the spectra of the pristine part of the membrane and both active and non active part tested in the fuel cell reveals the existence of a new broad peak appearing at 1700 cm\(^{-1}\) assigned to C=O band of carboxylic acid (Figure VIII.12).
Figure VIII.11: Scanned image of the membrane ETFE-g-styrene/MAN #1 disassembled from the MEA after 1032 h.

The sulfonation conditions in our case do not affect the nitrile group and no hydrolysis of this group was observed. The origin of the observed C=O group is not yet established, but hydrolysis of the C≡N group under fuel cell operating conditions could explain in part the changes occurring in the membrane. It is well known that the nitrile group under acidic conditions undergoes partial hydrolysis, where amide group (CONH₂) is observed. Likewise, the amide group may also hydrolyses (total hydrolysis) leading to the formation of carboxylic acid group (COOH) (Figure VIII.13).

Figure VIII.12: Comparison of the spectra of the untested part of the ETFE-g-styrene/MAN #1 membrane and the tested active part in the mid IR region.
The post mortem analysis of the membrane was based on the styrene group (peak at 1493 cm\(^{-1}\)), on the nitrile group (peak at 2234 cm\(^{-1}\)) and the methyl group of MAN (peak at 1388 cm\(^{-1}\)) (Figure VIII.14, 15, 16 and 17).

The fitting of the peak at 1493 cm\(^{-1}\) (styrene) reveals high degree of degradation near to the oxygen inlet under both channel and land (Figure VIII.14).

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The fitting of the peak at 1493 cm\(^{-1}\) (styrene) reveals high degree of degradation near to the oxygen inlet under both channel and land (Figure VIII.14).
Moreover, high degradation was also observed close to the hydrogen inlet. Interestingly, the degradation maps based on the nitrile group and the methyl group show qualitatively the same degradation distribution as observed for styrene (Figure VIII.15 and 16).

![Degradation Map](image1)

Figure VIII.16: Matrix representation of the degradation located in the active area based on the MAN nitrile peak (2230 cm\(^{-1}\)).

However, the quantitative difference in degradation observed for MAN based on both functional groups (methyl and nitrile groups) is quite substantial, since the same extent of degradation was expected. The hypothesis of nitrile hydrolysis in the tested membrane is in agreement with the different extent of degradation of the nitrile and methyl band. Thus, the change occurring in the nitrile group was quantified by subtraction of the extents of degradation of the nitrile and methyl group (Figure VIII.17).

![Hydrolysis Map](image2)

Figure VIII.17: Matrix representation of the hydrolysis located in the active area.
From the extent of degradation representation, it is clear that the hydrolysis of the nitrile group is mainly located near the oxygen inlet, and was less pronounced near to the hydrogen inlet. The observed hydrolysis suggests the existence of an acidic environment in the cell, which may be assumed to be the case if the membrane dries out (e.g., high electroosmotic drag occurring during weekly polarization measurements at high current density). Considering the overall area, the extent of degradation was found to be of about 40%, 36% and 37% based on the styrene group, methyl and nitrile group, respectively. Furthermore, the extent of change in the nitrile group due to hydrolysis was of about 13% in the overall active area in the membrane.

The observed degradation pattern is in accordance with the previously scanned image of the membrane (Figure VIII.11), where the discoloured zones are a sign of extensive degradation. More investigation is needed to understand how and why the degradation occurs at these positions and if its extent is much more located at the anode or cathode side. Likewise, the nature of the new functional group appearing after fuel cell test and the possible partial or total hydrolysis of the nitrile group should be investigated more deeply.

**VIII.4. Conclusion**

Novel ETFE based membranes were successfully prepared via co-grafting of commercially available inexpensive styrene and MAN monomers. Both initial polymerization and radical recombination rate are lower in the case of styrene/MAN co-grafting as compared with the grafting of styrene only. However, the grafting kinetic of this system is much faster compared to the α-methylstyrrene/MAN system\(^{108}\). The content of MAN incorporated in the grafted membrane was determined by FTIR, and a drift of the composition was observed after a graft level of ~ 25% as the reaction time is increasing.

The obtained membranes have exploitable conductivities with lower hydration number in comparison with Nafion®112. IEC, hydration number and conductivity showed a dependency on the content of MAN in the graft component. Thus, the higher the MAN content, the lower is the conductivity. However, the dimensional stability was improved by the increase of the MAN content without any significant changes in the water content of the membranes at fixed graft level.

Single fuel cell tests showed a marked improvement in the lifetime of the co-grafted styrene/MAN over the styrene based membranes. The *in situ* MEA properties were characterized over the testing period using auxiliary current pulse-resistance,
electrochemical impedance spectroscopy, polarization and H₂ permeation. Moreover, the tested cells show comparable performance to that of Nafion®112 and only a slight decrease at high current densities was observed when increasing the MAN content. As expected, the ohmic resistance is increasing with the increase of the MAN content, whereas, no significant change on the membrane-electrodes interface quality (polarization resistance) was observed. The most important result is that the mechanical integrity (H₂ permeation) of the membrane over the testing time improves with higher MAN content.

The FTIR investigation (*post mortem* analysis) of the tested membrane reveals the existence of a C=O band which was attributed to the hydrolysis of the C≡N pendant groups to carboxylic acid groups. The extent of changes in the nitrile group over the tested active area was found to be significant in the channels and lands near to the oxygen inlet. Furthermore, the analysis shows that the degradation is higher near the gas inlets.

Membranes based on the copolymerization of styrene and MAN showed promising results under single fuel cell conditions and offer the opportunity of tuning the MAN content and the crosslinker content to enhance the oxidative stability and durability of the resulting fuel cells. The obtained results arise several questions about the degradation mechanism of these membranes and what is the role and influence of nitrile pendant groups in the system during fuel cell operating conditions.
IX General discussion & future work

IX.1. Conclusions

The radiation induced grafting technique directed towards preparation of proton exchange membranes for fuel cells was investigated in this work. The focus was on the improvement of the mechanical and oxidative stability of radiation grafted membranes and contribution to the development of cost effective membranes. Therefore, the first step was the replacement of the perfluorinated FEP base film used in PSI standard membranes by the partially fluorinated ETFE base film. Utilizing ETFE as base material, it is shown that \textit{ex situ} chemical and mechanical stability of the ETFE-$g$-styrene based membranes improve considerably. Furthermore, ETFE film shows a reduced sensitivity to higher irradiation doses under air, where no significant changes on the mechanical properties and crystallinity were observed up to an irradiation dose of 50 kGy.

First of all, all the preparation steps, namely radiation, grafting reaction, sulfonation reaction and swelling, affect the structural and mechanical properties of the grafted membranes. Thus, the crystallinity, tensile strength and elongation at break are negatively influenced by the grafting, sulfonation and swelling of the membranes. Secondly, the use of glass reactor or stainless steel reactor for the grafting reaction has a significant effect of the reached graft level, final aspect of the grafted film (wrinkled films) and their homogeneity. Hence, glass reactors were used only for studying grafting kinetics, whereas the stainless steel reactor was chosen for the preparation of membranes used for \textit{ex situ} characterization and fuel cell tests.

DVB crosslinked ETFE-$g$-styrene sulfonic acid membranes were studied in detail. In the course of the process optimization, two key parameters, namely the graft level and crosslinker content were varied. Thus, the influence of both parameters on structural changes of the membrane, \textit{ex situ} and \textit{in situ} fuel cell relevant properties was investigated.

In order to understand the system and its limitations, the effect of the graft level (GL) was investigated. It was observed that the tensile strength, crystallinity and thermal stability are not significantly affected by the increase of the graft level of the radiation grafted membranes. As expected, the ion exchange capacity, the water uptake, conductivity of the membranes improve with the graft level. However, the elongation at break, dimensional stability and the gas crossover are negatively affected. The lower limit of the GL is governed by the performance and proton conductivity of the membranes,
whereas the upper limit of the GL is mainly given by the mechanical and dimensional stability of the membranes. So far, no improvement of the membrane-electrode interface was observed with the increase of GL.

Being a prerequisite for lifetime improvement of the ETFE-g-styrene based membranes, the crosslinking contributes conveniently to reduce the extent of degradation and increase the MEA durability under fuel cell operation conditions. Thus, crosslinking with DVB was pointed out to increase dramatically the durability of the membranes. The influence of the crosslinker was studied in a systematic way to correlate the changes on the structure and the different *ex situ* and *in situ* fuel cell relevant properties. It was found that the crosslinker is not homogeneously distributed over the thickness of the grafted membrane, where a higher content was determined in the surface than the entire bulk due to the higher reactivity of DVB in comparison with styrene. *Ex situ* chemical stability in 3 % H$_2$O$_2$ solution was investigated for different DVB content revealing that the crosslinking increases the chemical stability of the grafted membrane. However, excessive crosslinking content (> 10 % DVB (v/v)) leads again to a decrease in membrane stability, which is probably a consequence of a growing number of pendant double bonds due to incomplete reaction of the second vinyl unit in DVB, representing positions of attack for aggressive radical species. Furthermore, crosslinking was found to have a negative effect on the elongation at break, swelling and conductivity of the grafted membrane. Yet, the increase of the crosslinker content has a beneficial effect on the dimensional stability (wet $\rightarrow$ dry), tensile strength, gas crossover and the interfacial properties of the MEA. In addition, no significant changes on the thermal stability and crystallinity of the grafted membrane were observed. A membrane with a GL value of 25 % and 5 % DVB (v/v) concentration in the initial grafting solution was found to exhibit comparable performance to that of a Nafion® 112 membrane. A membrane of this type was tested in the single cell for more than 2100 h without significant loss in performance.

Taking advantage of the investigation devoted to the development of ETFE-g-styrene/DVB based membranes, a novel approach was investigated in order to improve the stability of radiation grafted membranes prior to any crosslinking. Thus, MAN was selected as candidate due to its protected $\alpha$-position and strong dipolar pendant nitrile group. In comparison to the grafting kinetics of ETFE-g-styrene, the styrene/MAN system grafts with slower kinetics and both the radical recombination and initial polymerization rates are lower. However, grafting kinetics of this system is much faster compared to the $\alpha$-methylstyrene/MAN system. Depending on the MAN content in the ETFE-g-styrene/MAN based membrane, the hydration number, area shrinkage (wet $\rightarrow$ dry) and conductivity are affected. Thus, the conductivity and water uptake are reduced.
with the increase of the MAN content, whereas the dimensional stability is improved. Yet, no hydrolysis of the nitrile group was observed during the membrane preparation steps (grafting, sulfonation and swelling).

In the course of the single fuel cell tests, ETFE-g-styrene/MAN based membranes showed a superior durability in comparison with ETFE-g-styrene membranes. In fact, the latter performed only for less than 165 h, while styrene/MAN based membranes were tested for more than 1000 h without any performance loss or failures under fuel cell operation conditions. To some extent, hydrolysis of the nitrile group to carboxylic acid was observed under fuel cell operation conditions and the same phenomenon was observed for the FEP-g-AMS/MAN based membranes. The sensitivity of the membranes to hydrolysis revealed by post mortem analysis was more pronounced near the O\(_2\) gas inlet.

**IX.2. Recommendations for future work**

Taking advantage of the facilities for fuel cell testing and available developed *ex situ* and *in situ* characterization techniques, we do not focus only on the synthesis and preparation of radiation grafted membranes, but we investigate their potential and limitations under fuel cell operation conditions. In fact, there is substantial work on radiation grafted membranes by different research groups directed towards fuel cell application, however their functionality in the fuel cell and performance is yet unknown. Furthermore, the behavior of any membrane and its *in situ* properties under fuel cell operation conditions can not be deduced from *ex situ* characterization data, due to the complexity and mutual influence of different parameters. However, the steady fuel cell tests as shown in this work are time consuming and the need of accelerated *in situ* test protocols has to be considered to improve the statistics and build a comparative and fast output for the evaluation of radiation grafted membranes.

The membrane homogeneity is an important issue to improve in order to reduce the impact on other fuel cell relevant parameters and on the electrochemical performance of the resulting MEAs. Homogeneity of the technical base film is the starting point to look after, since scattering on the thickness over the area was measured and the change of the base film supplier could be an option to overcome this problem. The hotpressing prior to any irradiation could be another option, taking of course into account the possible changes of crystallinity and anisotropy of the film (machining and transverse direction).

The optimization of the styrene/MAN based membranes is another issue to focus on. In fact, the content of MAN is still to be investigated with more detail, in order to
elucidate its impact on the transport properties, mechanical, dimensional and oxidative stability. Likewise, the crosslinking is the other parameter to be investigated and optimized in order to further improve the life time of the ETFE-g-styrene/MAN based membranes. The hydrolysis of the MAN nitrile group observed under fuel cell conditions in the case of styrene/MAN and even for AMS/MAN based membranes has to be investigated. Thus, the mechanism and the conditions governing this hydrolysis have to be studied and correlated to the membrane degradation mechanism. In addition, \textit{ex situ} chemical degradation investigation of ETFE-g-styrene, ETFE-g-MAN, ETFE-g-styrene/MAN and ETFE-g-AMS/MAN based membranes in comparison with styrene/DVB based membranes will be very helpful to correlate and clarify the contribution of MAN to the stability of the membranes.

The state of water of the ETFE based grafted membranes is a paramount property to be investigated to understand and correlate the proton transport with other \textit{ex situ} parameters (graft level, crosslinking and MAN content). Thus, further understanding of the membrane microstructure and its domains (hydrophilic and hydrophobic) can be correlated with other \textit{ex situ} properties (e.g., conductivity).

In the course of the fuel cell testing and \textit{post mortem} investigation, the used fuel cell designs show the strong sensitivity of grafted membranes to degradation near the gas inlets and in the edge zone between active and inactive area of the membrane. Thus, effective protection of this zone is needed to prevent this recurrent effect during long term testing. The use of stabilizing additives (e.g., MnO$_2$) in the critical zone could be an interesting option to reduce this effect and limit the degradation.

Combining the know how acquired from the study of the standard system based on FEP-g-styrene/DVB and ETFE-g-styrene/DVB, new type of membranes can be created and developed based on the use of other substituted styrenic monomers in combination with MAN. Thus, the substitution on the styrenic ring is assumed to increase the stability of the grafted membranes. Furthermore, the polar nitrile group in the radiation grafted membranes might be involved in improving the interfacial properties and the performance at low relative humidity by incorporation of inorganic hydrophilic additives (e.g., SiO$_2$, TiO$_2$).
X References


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1997  Baccalauréat (Mathematics option)
Internships

2003-2004 (9 months) Polymer Research Laboratory CNRS-UMR 7581, Thillais (France) (Pr. Marie-Claude MILLOT)

2002 (3 months) Maghreb Polymer Company (polymer production company) Casablanca (Morocco) (Pr. Hamid KADDAHI)

Languages

Arabic: mother tongue
French: Fluent
English: Fluent
German: Basic

Awards

✓ First Poster price ‘Effect of Crosslinker Concentration on Performances and Properties of Styrene Grafted onto ETFE Based Membranes’, in the 3\textsuperscript{rd} international symposium in reactive polymers in inhomogeneous and melt interface in Dresden (Germany), September 2007.

References

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Publications and oral presentations in meetings

Publications:


Scientific reports and proceedings:

Conference presentation:


Posters:

✓ PGS-fall meeting in the University of Neuchâtel, Switzerland 2005.
✓ IRAP in Antalya, Turkey in September 2006.
✓ SCS-fall meeting in the University of Zürich, Switzerland in October 2006.
✓ Advances in Polymer Science & Technology in New Delhi, India in January 2008.