INVESTIGATIONS OF PROTON CONDUCTING POLYMERS
AND GAS DIFFUSION ELECTRODES IN THE
POLYMER ELECTROLYTE FUEL CELL

PETER GODE

DOCTORAL THESIS

Department of Chemical Engineering and Technology
Applied Electrochemistry
Kungliga Tekniska Högskolan
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ABSTRACT

Polymer electrolyte fuel cells (PEFC) convert the chemically bound energy in a fuel, e.g. hydrogen, directly into electricity by an electrochemical process. Examples of future applications are energy conversion such as combined heat and power generation (CHP), zero emission vehicles (ZEV) and consumer electronics. One of the key components in the PEFC is the membrane / electrode assembly (MEA). Both the membrane and the electrodes consist of proton conducting polymers (ionomers). In the membrane, properties such as gas permeability, high proton conductivity and sufficient mechanical and chemical stability are of crucial importance. In the electrodes, the morphology and electrochemical characteristics are strongly affected by the ionomer content. The primary purpose of the present thesis was to develop experimental techniques and to use them to characterise proton conducting polymers and membranes for PEFC applications electrochemically at, or close to, fuel cell operating conditions. The work presented ranges from polymer synthesis to electrochemical characterisation of the MEA performance.

The use of a sulfonated dendritic polymer as the acidic component in proton conducting membranes was demonstrated. Proton conducting membranes were prepared by chemical cross-linking or in conjunction with a basic functionalised polymer, PSU-pyridine, to produce acid-base blend membranes. In order to study gas permeability a new in-situ method based on cylindrical microelectrodes was developed. An advantage of this method is that the measurements can be carried out at close to real fuel cell operating conditions, at elevated temperature and a wide range of relative humidities. The durability testing of membranes for use in a polymer electrolyte fuel cell (PEFC) has been studied in situ by a combination of galvanostatic steady-state and electrochemical impedance measurements (EIS). Long-term experiments have been compared to fast ex situ testing in 3 % H₂O₂ solution. For the direct assessment of membrane degradation, micro-Raman spectroscopy and determination of ion exchange capacity (IEC) have been used. PVDF-based membranes, radiation grafted with styrene and sulfonated, were used as model membranes. The influence of ionomer content on the structure and electrochemical characteristics of Nafion-based PEFC cathodes was also demonstrated. The electrodes were thoroughly investigated using various materials and electrochemical characterisation techniques. Electrodes having medium Nafion contents (35<x<45 wt %) showed the best performance. The mass-transport limitation was essentially due to O₂ diffusion in the agglomerates. The performance of cathodes with low Nafion content (<30 wt %) is limited by poor kinetics owing to incomplete wetting of platinum (Pt) by Nafion, by proton migration throughout the cathode as well as by O₂ diffusion in the agglomerates. At large Nafion content (>45 wt %), the cathode becomes limited by diffusion of O₂ both in the agglomerates and throughout the cathode. Furthermore, models for the membrane coupled with kinetics for the hydrogen electrode, including water concentration dependence, were developed. The models were experimentally validated using a new reference electrode approach. The membrane, as well as the hydrogen anode and cathode characteristics, was studied experimentally using steady-state measurements, current interrupt and EIS. Data obtained with the experiments were in good agreement with the modelled results.

Keywords: polymer electrolyte fuel cell, proton conducting membrane, porous electrode, gas permeability, degradation, water transport
SAMMANFATTNING


Nyckelord: polymerelektrolytbränslecell, protonledande membran, porös elektrod, gaspermeabilitet, nedbrytning, vattentransport
LIST OF PAPERS

This thesis is a summary of the following papers:

I. A novel sulfonated dendritic polymer as the acidic component in proton conducting membranes
   Submitted to Solid State Ionics

II. In-situ measurements of gas permeability in fuel cell membranes using a cylindrical microelectrode
    P. Gode, G. Lindbergh and G. Sundholm

III. Membrane durability in a PEM Fuel Cell studied using PVDF based radiation grafted membranes

IV. Influence of the composition on the structure and electrochemical characteristics of the PEFC cathode
    P. Gode, F. Jaouen, G. Lindbergh, A. Lundblad and G. Sundholm

V. Modelling and experimental studies of the membrane and hydrogen electrode in the PEFC; steady state and electrochemical impedance investigations
   K. Wiezell, G. Lindbergh and P. Gode
   Manuscript
MY CONTRIBUTION TO THE PAPERS IN THIS THESIS

All the papers in this thesis, except paper II, are the result of collaboration with several people during the past years. The opportunity to work and write papers together sometimes makes it difficult to distinguish the work of different persons. Hereby, I would like to highlight some significant contributions in the included papers that I have not been participating in:

**Paper I:** The synthesis of PSU-pyridine was carried out by Lina Karlsson and Patric Jannasch.

**Paper III:** The PVDF-g-PSSA membranes were synthesised by Nadja Walsby. Micro-Raman spectra were measured by Anders Strandroth and Hanna Ericson. The ion exchange capacity was determined by Mikael Paronen.

**Paper IV:** All the modelling work was performed by Frédéric Jaouen as well as a major part of the fuel cell experiments. Gas porosimetry was carried out by Anders Lundblad.

**Paper V:** The models were constructed by Katarina Wiezell.
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1 INTRODUCTION

During the last decades, the development of new high-performing polymers with excellent stability and ion conducting properties has allowed the field of electrochemistry to reach enhanced possibilities and today several new applications are in the focus of research. The use of polymers specifically designed for electrochemical applications has improved properties such as stability, power density, efficiency and safety in many electrochemical systems. Examples of applications at present are water purification, desalination and consumer appliances such as the Li-polymer battery. Further examples of future applications are depolarised anodes in the chlor-alkali industry, energy conversion like combined heat and power generation (CHP) and zero emission vehicles (ZEV). In many applications, the polymer electrolyte fuel cell (PEFC) is a possible candidate as power source. The system complexity and the broad knowledge required in the development of fuel cell technology have attracted a new generation of researchers with backgrounds not only in chemical engineering but also in multi-disciplines such as materials science, fluid mechanics and system integration. The potential of fuel cells as to environmental and market aspects has turned the expectations on the technology to reach levels resembling those on information technology (IT) during the late 1990s. One must consider that even if the technology is attractive in many applications, it must be competitive compared to the alternatives. However, even if the expectations are currently exaggerated, the technology may be established at least for niche applications. Finally, a profound knowledge in electrochemistry and chemical engineering is fundamental for succeeding in this field.

1.1 Working principle of the polymer electrolyte fuel cell

Overall, fuel cells convert the chemically bound energy in a fuel, e.g. hydrogen or methanol, directly into electricity by an electrochemical process. In this work hydrogen was used as fuel. A schematic sketch of the polymer electrolyte fuel cell principle, using hydrogen as fuel, is presented in Figure 1. The hydrogen reacts at the anode and electrons are transported from the anode to the cathode in an external circuit. Protons produced at the anode are transported through a proton conducting membrane, acting as electrolyte, to the cathode. At the cathode, the protons react with oxygen and electrons to produce water. The electrodes, active layers, are thin films with a heterogeneous porous structure consisting of carbon-supported Pt catalyst and proton conducting polymer. The membrane is sandwiched in between the electrodes and the membrane / electrode assembly, MEA, is placed in a fuel cell house. The cell house consists of current collectors with gas in and outlets and flow channels. Gas-backings are placed between the flow-channels and the MEA to distribute the gases uniformly. When two or more cells are stacked together, the current collectors are replaced by bipolar plates. The operating temperature of a conventional PEFC ranges up to about 80 °C even though new materials research is stretching the limits to reach temperatures above 100 °C. The main reason for the temperature limitations is the need of membrane humidification to obtain high proton conductivity. Long-term stability at enhanced temperatures is also a major challenge to overcome.
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1.2 The fuel cell membrane

The main purpose of the membrane is to act as a proton conductor but it also acts as a gas barrier to separate the hydrogen or methanol and oxygen. Important membrane properties are low gas permeability, high proton conductivity and sufficient mechanical and chemical stability. In the following subsections the recent development and general properties of proton conducting membranes are reviewed.

1.2.1 Membrane development

Perfluorinated polymers, such as Nafion (DuPont), Aciplex (Asahi Chemical Company) and Flemion (Asahi Glass Company), have successfully been used in PEFC applications because of their excellent chemical stability and high proton conductivity. Nafion was initially developed by DuPont in the late 1960s to meet the demands of the chlor-alkali industry. Later on, Nafion has found usage in a broad range of applications such as dialysis and water purification and has during the last 30 years, without doubt, become one of the major reasons for the intensive research on PEFC. The molecular structure of Nafion is presented in Figure 2. The perfluorinated backbone structure is similar to that of Teflon (PTFE) and is strongly hydrophobic. As opposed to the polymer backbone, the short spacer including the proton conducting sulfonic acid group is very hydrophilic and a micro phase separation is obtained in the membrane. As a result, the sulfonic acid groups are oriented in clusters or micelles surrounded by the hydrophobic backbone [1-5]. The material is semi-crystalline [6], and the phase separation acts as a physical cross-linking, giving the material its good mechanical properties. The microstructure and the physical properties of Nafion have been thoroughly investigated by several research groups using a broad range of
experimental techniques and mathematical models [1, 3, 7-13]. This material is therefore a benchmark commonly used as reference material when assessing the properties of newly developed membranes.

On the other hand, the high price, poor proton conductivity at elevated temperatures (>100 °C) and high permeability to methanol (DMFC applications) have prompted intensive research for new proton conducting membranes. To obtain less expensive materials, high-temperature conductive properties and low methanol permeability, proton conductors such as radiation-grafted polystyrene sulfonic acid membranes, membranes based on polybenzimidazole (PBI), sulfonated poly(ether ether ketone) (sPEEK), and sulfonated polysulfone (sPSU) among others have been in the focus of research. Recent developments have been summarised in several reviews [14-21].

Radiation-grafted membranes were early suggested as a less costly alternative to Nafion [22]. The radiation grafting approach has the potential to produce membranes with low cost on a large scale. The principle of this approach is based on radiation of a chemically and mechanically stable polymeric matrix, e.g. PVDF. During the radiation, radicals are induced in the polymer backbone and grafting is obtained by radical polymerisation when swelling the sample in styrene [22-28]. Another polymerisation approach is atom transfer radical polymerisation (ATRP), which has been investigated by Holmberg et al. [29]. In the next step, the grafted polystyrene is sulfonated, e.g. in chlorosulfonic acid [28]. In Figure 2, the molecular structure of PVDF-g-PSSA is presented. The membrane morphology and structural properties have been investigated by means of Raman, IR, ESCA, and FTIR [24, 25, 27-34]. Physical and electrochemical properties have been thoroughly studied by Lehtinen et al. [35, 36] and Kallio et al. [37, 38]. The radiation-grafted membranes show sufficiently good mechanical properties, high proton conductivity and have been successfully demonstrated in PEFC applications [22, 23, 39]. However, there are
some major drawbacks connected to these membranes. The PSSA chain is known to have poor chemical stability, especially to hydroxy radicals due to the weak α-hydrogen in the polymer chain [27, 40]. In order to increase the durability of the membranes, different fluorinated polymer matrices [28, 31, 41] and also addition of cross-linkers have been used [22-24, 32]. Another complicated drawback is the MEA fabrication. To obtain a high performing MEA with long durability, the interface between the electrode and the membrane must have good contact and the polymer in the electrodes must be compatible with the membrane with respect to swelling etc. Otherwise, accelerated degradation and delamination might take place [39]. Another example of styrene-based membranes is the BAM3G membrane developed by Ballard Advanced Materials Corp. Canada (BAM). In contrast to the PVDF-g-PSSA membranes, the chemical stability was increased by using fluorinated styrene monomers.

In many PEFC applications enhanced operating temperature (>100 °C) would be of advantage. A high temperature increases the kinetics and CO tolerance; valuable heat could also be produced. In addition the fuel cell system would be simplified, e.g. the cooling system could be smaller [19]. However, to reach such operating temperatures the membrane durability and proton conductivity at dry conditions must be improved. To meet the high-temperature demands, a new generation of proton conducting hydrocarbon polymers specially designed for high temperature applications is in the focus of research [15, 19-21]. An advantage of using heterocyclic polymers is that other compounds than water could act as proton carriers [42] and increase the conductivity at temperatures above 100 °C. The proton conductivity is mainly obtained by direct sulfonation, introduction of the sulfonic acid group by grafting or by doping with phosphoric acid [16]. An example is PBI-based membranes, having a thermally and chemically stable polymer backbone. The PBI-based membranes are some of the most promising alternatives to Nafion in high temperature PEFC. PBI membranes treated with phosphoric acid show high proton conductivity depending on doping level, water content and temperature [43, 44]. The membrane properties are strongly dependent on preparation method and today the durability, leakage of phosphoric acid etc. of these membranes still need to be proven [15]. Directly sulfonated polyimides are also under investigation [45-47]. A major drawback is the poor hydrolytic stability of the polyimide backbone in acidic environment and therefore the durability of the polyimide membranes is often limited [47].

A general problem with sulfonated arylene main-chain membranes is the tremendously high water uptake and subsequent swelling, especially in hot water [17]. In order to control the membrane swelling, crosslinks can be introduced to improve the mechanical properties [48-51]. Co-polymerisation or microstructure modification by grafting are other examples of measures taken out to reduce extensive hydration [21]. To overcome the problems related to swelling Kerres et al. have developed membranes based on blends of various acidic and basic polymers. Examples of acidic polymers utilised are sPSU, sPEEK and sulfonated poly(etherketones) (sPEK) [49, 52]. Examples of basic polymers utilised are modified PSU Udel(R) containing N-basic side groups, poly(4-vinylpyridine), and PBI [17, 49, 52-54]. In these acid/base blend membranes physical cross-linking is introduced by strong interactions between the acid and base functional groups. The physical cross-linking is much more flexible than the chemical, covalent, cross-linking and the blend membranes have turned out to have better mechanical properties in the wet state [17]. However, at
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At elevated temperatures the physical cross-linking is reduced due to reverse proton transfer with an associated increase in solubility of the sulfonated component. Kerres et al. has suggested a combination of physical and chemical cross-linking to optimise the mechanical properties with respect to reduced swelling, flexibility and mechanical strength [49, 50].

1.2.2 Gas transport

Beside the electrolytic properties, the membrane acts as a barrier to separate the reactants in the fuel cell. The diffusion coefficient \( D \) and the solubility \( c \) determine the transport properties of a given specie in the membrane. The permeability, \( P = D \cdot c \), should be as low as possible to prevent crossover of reactants. In addition, gas permeability in PEFC membranes has been discussed as a possible cause of accelerated membrane degradation due to radical formation when mixing hydrogen and oxygen [22]. Various techniques to measure gas permeability properties as a function of temperature, relative humidity and gas pressure in proton conducting membranes have been reported. The methods mainly used are the electrochemical monitoring technique (EMT) [35, 36, 55-58], the micro-disc electrode method [37, 59-64] and the analysis of permeation using gas chromatography [65-67]. The measurements are often time-consuming and difficult to carry out, in particular at conditions similar to the operating conditions of a fuel cell. The obtained mass-transport parameters measured with the mentioned methods vary considerably since the experimental conditions differ from one method to another. Most studies of transport properties in proton conducting membranes have been carried out with respect to oxygen permeation, whereas only few data on hydrogen have been reported [37, 56, 58, 62, 67].

1.2.3 Membrane durability

The PEFC membrane will function under harsh conditions not common for most synthetic polymers. The presence of water, hydrogen, oxygen and Pt catalyst at enhanced temperatures is demanding. The polymer should have long-term stability in both oxidising and reducing environments. The formation of hydroxy radicals [22, 27, 40, 68, 69] and sometimes impurities such as metal ions, able to catalyse radical formation, make the situation even more complicated. Gas crossover can play an important role in the formation of \( \text{OH}_2^- \) radicals at the anode [22]. In this mechanism, diffusion of oxygen through the membrane and formation of hydroxy radicals on the anode were assumed. As evidence for the proposed mechanism, it was shown that the degradation rate will increase when operating the fuel cell at OCP. Under such conditions, considerable amounts of oxygen can diffuse through the membrane. However, according to Ericson et al. [30] and Yu et al. [40], increased degradation was recognised close to the cathode. This shows that evaluation of the membrane durability is a great challenge since several processes are taking place simultaneously. In addition to chemical stability, physical parameters like mechanical strength, swelling and thickness of the membrane are of great importance [22, 23, 37, 70-72]. Repeated swelling and shrinking of the membrane due to condensing water might result in mechanical failure and degradation of the membrane. Furthermore, the operating conditions and the cell design parameters, e.g. humidification level of gases, uniform clamping pressure, cooling, bipolar plate materials, gaskets etc. will also affect the durability of the membrane [70, 72].
Membrane durability has been studied experimentally at fuel cell operating conditions [22, 23, 26, 27, 31, 34, 37, 40, 70, 73]. In-situ investigation of membrane resistance during long-term tests [22, 23, 26, 34, 73], and post-mortem analysis of ion exchange capacity, water uptake, conductivity [22, 23] and various spectroscopic methods have been used [27, 30, 31, 40]. In addition to the time-consuming long-term tests, accelerated degradation has been studied in-situ by Liu et al. [70] using increased operating temperature and ex-situ by soaking the membranes in hydrogen peroxide solution or Fenton’s reagent [73-75].

### 1.2.4 Water transport, water uptake and proton conductivity

Swelling, water uptake and proton conductivity are strongly dependent on the molecular structure and micro-phase separation in the membranes. Kreuer has in detail investigated the water uptake and proton transport properties of sPEEK in comparison to Nafion [76, 77]. The non-fluorinated polymer was shown to have low degree of interaction / phase separation between the hydrophilic sulfonic acid groups and could therefore incorporate water to a much higher extent than Nafion. The dependence on hydration number of non cross-linked and cross-linked sPSUs on IEC, presented in several papers [17, 48, 78, 79], has been gathered by Rozière et al. [21]. At high IECs a tremendous water uptake, up to $\lambda \approx 70-140$ water molecules per sulfonic acid group at 80 °C, was reported even for the cross-linked membranes [48]. A too large water uptake will drastically decrease the mechanical strength of the membrane. Overall, it is important to keep the water uptake as low as possible ($\lambda < 25$) but still maintaining high proton conductivity ($\lambda_{\text{Nafion}} \approx 22 \, \text{nH}_{2}\text{O} / \text{HSO}_3^-$ in the fully wet state [80]). In contrast to the mechanical strength, the proton conductivity in sulfonated membranes is favoured by increasing water content [37, 81]. Proton conduction in highly hydrated membranes takes place via the "Grotthus mechanism", involving reorganisation of the structure in which the proton is diffusing, and the “Vehicle mechanism” in the form of a hydronium ion, $\text{H}_3\text{O}^+$, i.e. water acts as a proton carrier [82]. The self-diffusion coefficient of water and the proton diffusion coefficient increase as a function of water content. As a consequence, the higher the water content, i.e. access of mobile water in the membrane, the higher the proton conductivity. The superior conductivity properties of Nafion compared to hydrocarbon polymers at dry conditions (<100 °C) is correlated to a better hydrophilic / hydrophobic separation [77].

Water management is one of the key parameters in the PEFC. A good control of parameters such as gas humidification, flooding and drying etc. is essential to obtain high performance and durability of the PEFC system. Fuel cell components such as gas-backing materials have been thoroughly investigated to optimise the water balance in the system [83-85]. In an operating fuel cell, water is dragged by the migrating protons from the anode side to the cathode. Values of the water drag coefficient in the range of 1-2.5 $\text{H}_2\text{O} / \text{H}^+$ have been reported [86]. The concentration gradient of water in the membrane, built up by the drag and the production of water at the cathode, will subsequently result in a back diffusion of water towards the anode. Experimental work on net water transport in the membrane have been reported by several groups [80, 86-89]. A common approach for modelling water transport is to describe the membrane / water system as a dilute electrolyte [90-92]. The diffusion coefficient of water, the water drag coefficient and the resistance are dependent on water content and are expressed by empirical expressions. Recently, an
implementation of the theory of concentrated solutions has commonly been used [89, 93-98]. This model approach includes binary diffusion coefficients of water, protons and sulfonic acid groups.

1.3 **Gas diffusion electrodes (GDE)**

The electrodes should be optimised to satisfy all the requirements of the reactions to take place. The electrodes are thin films with a heterogeneous porous structure consisting of carbon-supported Pt catalyst and proton conducting polymer sandwiched on the membrane. Several works have been published on different electrode fabrication techniques [99-105]. The electrode performance is in general limited by kinetics, current distribution and mass-transport processes.

1.3.1 **The complex nature of porous gas diffusion electrodes**

To obtain good kinetics, the area of the active catalyst surface is important, and this is obtained by finely dispersing the catalyst on a carbon support with large surface area [106-109]. The carbon / Pt-catalyst phase is electron conducting and a percolating network is therefore important to distribute the current evenly in the electrode. However, only the catalyst surface in contact with electrolyte is electrochemically active. A complete wetting of the catalyst with proton conducting polymer is therefore desirable to obtain a high catalyst utilisation [110-113]. Just as the catalyst phase, this proton conductive phase must be continuous throughout the electrode and have a good interfacial contact with the membrane. Electron and proton conductivity of porous electrodes has been studied by several groups [111-119]. Recently, Saab et al. presented a simple method to obtain conductivity data using electrochemical impedance spectroscopy (EIS) [118]. In their study they observed that increasing water content in the electrodes could have a negative effect on electron conductivity. Furthermore, Lefebvre et al. developed a method to study proton conductivity as a function of electrode thickness [117]. The proton conducting polymer serves a second purpose as binder to increase the mechanical properties of the electrode. Nafion is often used as proton conducting phase in the electrode and commonly the electrodes are hot-pressed onto the membrane to obtain a good interfacial contact. However, when using different kinds of polymers in the electrodes and the membrane, interfacial problems must be taken into account [39, 46, 49, 120]. Another issue is that the catalyst is covered by the proton conducting polymer and therefore the reactants, hydrogen and oxygen, are restricted to diffusing in the polymer phase to access the catalyst surface. The gas porosity throughout the electrode and the agglomerate size as well as water management are important parameters to control in order to minimise mass-transport limitations of gases in the electrodes [110, 111, 121-125]. The simultaneous presence of protons, electrons and reactants at the catalyst surface is often referred as the "three-phase contact".

Since the porous electrode is not planar but has a certain thickness and volume, the reaction rate might not be uniform throughout the electrode. In addition, the limiting processes are dependent on current density. As an example, at low current density the electrode reaction is limited by kinetics alone but when increasing the current density other limitations, in particular mass-transport phenomena, will be added. An electrode with good kinetics can have poor performance at high current density due to mass-transport limitations. The electrode composition and morphology will strongly affect
the limiting process dominating at specific operating conditions and as a consequence, two electrodes with the same catalyst content can have a huge difference in performance. Several studies on optimisation of the electrode composition have been reported [99, 110, 111, 126-135].

1.3.2 Reference electrodes
The thickness of the PEFC electrodes is in the order of 1-10 µm and the potential profile throughout the electrode is therefore not possible to measure experimentally. As a consequence, experimental investigation of the electrode performance is restricted to measurements of the total electrode potential and current density at the electrode surface. To be able to study the polarisation of a specific electrode, the use of reference electrodes is necessary. In the PEFC, the reference electrode is often a reversible or dynamic hydrogen reference electrode (RHE / DHE) placed on the membrane surface beside the anode [136, 137]. Also positioning of potential probes in the membrane between the cathode and anode has been used [137-139]. A true reference electrode should maintain its equilibrium potential independently of current density; the measured potential will then only include the working electrode polarisation and iR losses such as membrane and contact resistances. However, the distance between working and counter electrode is short in the PEFC due to the thin membrane, and the placement of the reference electrode is of crucial importance to avoid influence of potential gradients on the reference electrode potential [140-142]. Adler et al. have showed that any placement of the reference electrode beyond about three membrane thicknesses from the electrodes will measure the same potential [140]. In addition to the location of the reference electrode, geometrical aspects such as a small displacement of the electrodes will strongly affect the potential gradient resulting in large experimental errors, especially for very thin electrolytes.

An increasing number of papers has been published on reference electrodes in combination with electrochemical impedance spectroscopy (EIS) [137, 140, 141, 143]. The placement of the reference electrode is of crucial importance in this case as well. Modelling work shows that a misalignment of the working and counter electrodes of approximately 10 µm will result in errors larger than 10 % of the single electrode impedance response [143]. Due to the poor accuracy of experimental data when using reference electrodes, the most common approach when using EIS is to measure the total cell impedance. The performance of the oxygen cathode is usually studied assuming that the anode impedance can be neglected and that the membrane is acting as a pure resistance. Andreaus et al. [144] have investigated the influence of membrane thickness, equivalent weight and anode humidification on the impedance response. A low frequency loop was obtained, which was assigned to water transport in the membrane and its influence on the anode kinetics. The change in anode kinetics was assigned to a decreasing number of active sites due to drying out of the anode. The drying out of the anode has also been discussed by others [138, 144-146]. Consequently, measurements of the total cell impedance in order to evaluate the cathode performance are preferable only at low current density and at well-humidified conditions.
1.3.3 Modelling of the porous electrode
As has already been discussed, the porous PEFC electrode has a complex nature due to the various locally distributed processes taking place simultaneously in the electrode. This implies that it is difficult to evaluate the electrochemical behaviour in terms of limiting processes simply by measuring the potential and current response, dynamically or at steady-state conditions. In order to obtain a deeper understanding of the limiting processes, mathematical modelling is a useful tool. Models can be used in combination with experimental data to a) validate the model in describing steady-state and dynamic behaviour of the electrodes b) extract parameters through the fitting of the model to experimental data and c) give directions to the practical work, optimising the electrodes [147]. Several model approaches have been developed involving the cylindrical pore model [148, 149], the homogeneous model [126, 150-156], and the spherical agglomerate model [122, 123, 152, 157-163]. The modelling work on electrode performance presented in this thesis is based on steady-state and dynamic approaches to the spherical agglomerate model [122-124, 157].

1.4 The scope of this thesis
This PhD project was a part of the Swedish national research programme "Batteries and fuel cells for a better environment" funded by the Swedish Foundation for Strategic Environmental Research, MISTRA, and several Swedish companies. The work was defined to focus on characterisation of novel membranes developed within the same programme. However, since all PhD projects in the programme started within the same year and membrane development is time-consuming, no membranes were supplied during the progressing activities of this work. Therefore, the work was at an early stage focused on development of materials and electrochemical characterisation methods / methodology using commercially available membranes and materials for MEA preparation. In order to study membrane durability, PVFD-based radiation grafted PSSA membranes was used. In addition, collaboration resulted in an initial study of dendritic polymers as acidic component in proton conducting membranes. Also a base-functionalised polymer, pyridine-PSU, was used in the preparation of acid/base blend membranes.

The primary purpose of this thesis was to develop experimental techniques and to use them to characterise proton conducting polymers and membranes for PEFC applications electrochemically at, or close to, fuel cell operating conditions. Evaluation of membrane and electrode performance in operating fuel cells is a complicated issue, time-consuming and often including several experimental techniques. On the other hand, much membrane characterisation can be done ex situ in an early state of development. Various materials and electrochemical characterisation techniques were used to study membrane properties such as gas permeation, proton conductivity and long-term durability. Also studies on gas diffusion electrode characteristics having different Nafion contents and the influence of water transport in the membrane on the anode characteristics have been performed. Much work has been focused on methodology and on adjusting experimental equipment and techniques to suit the experimental evaluation and model fitting. Mathematical modelling extends the possibilities of interpretation and extraction of parameters not possible to determine from experimental data alone and has been a useful tool in this work.
2 EXPERIMENTAL

2.1 Materials and experimental equipment

2.1.1 Membranes
In paper I, a series of the sulfonic acid-functionalised polymer having different degrees of substitution was synthesised. The ionomer was functionalised by end-capping the hydroxy groups of poly(3-ethyl-3-(hydroxymethyl)oxetane), PTMPO, with 1,4-butanesultone. PTMPO was synthesised following the procedure according to Magnusson et al. [164]. Proton conducting membranes were prepared by a) mixing the partly sulfonated PTMPO with hexamethoxymethyl melamine (HMMM) and cross-linking by ether formation between the methylol groups on HMMM and the hydroxy groups on the hyperbranched polyether or b) using the sulfonated PTMPO in conjunction with PSU-pyridine, supplied by Polymer Science and Engineering, Lund University (LTH), to produce acid-base blend membranes.

In papers II, IV and V, Nafion 117 or 1035 was used as membranes. The Nafion membranes were pre-treated by boiling for 1 h in 0.5 M H$_2$SO$_4$ and a solution of 3 % H$_2$O$_2$ and distilled water, consecutively. Prior to the MEA fabrication, the membranes were dried and flattened.

In paper III, the degradation of PVDF-based radiation grafted PSSA membranes with different degrees of grafting was studied. These membranes were supplied by the Laboratory of Polymer Chemistry, Helsinki University, and used as received except boiling in MilliQ-water. After the long-term fuel cell tests, the membranes were characterised by Raman spectroscopy at the Department of Experimental Physics, Chalmers University of Technology, Göteborg.

2.1.2 Electrodes and Membrane Electrode Assemblies (MEA)
Commercially available gas diffusion electrodes with gas backing (Elat/HL/DS/V2) and in-house fabricated thin-film electrodes were used in papers II, III, V and papers III-IV, respectively. The thin-film electrodes were prepared by spraying the catalyst ink directly onto the pre-treated membrane. For small electrodes an airbrush was used as spraying equipment, but for larger electrodes or when preparing several identical electrodes simultaneously a semi-automatic fabrication unit consisting of a programmable positioning and sequence control unit and an air-mix spray gun was used. The ink mixture, made of the catalyst carbon, 20 wt % Pt on Vulcan XC-72, and a solution containing 5 wt % Nafion ($EW$ 1100) was mixed using ultrasound for 2 h. The weight percentage of dry Nafion to the total weight (Pt/C + dry Nafion) was varied from 10 to 70 wt %. The membrane was heated to 70 ºC during spraying in order to evaporate the solvents. The device and procedure for spraying have been described in detail by Lundblad [112]. Materials characterisation of the thin-film electrodes includes porosimetry measurements, scanning electron microscopy (SEM, instrument JEOL/JSM 840) equipped with an energy dispersive X-ray analyzer (EDX, instrument Link AN-10000), scanning transmission electron microscopy (STEM, instrument JEOL, JEM-2000 EX) having also an X-ray analyser,
conductivity measurements using the Van der Pauw method and electrochemical impedance spectroscopy (EIS).

2.1.3 Fuel cell hardware

The employed in-house PEFC used in paper III was described earlier by Ihonen et al. [136]. In papers IV-V, the area of the current collectors was increased from 2 to 7 cm$^2$ in order to improve the heat removal. A photograph of this cell is presented in Figure 3. The clamping pressure applied between the cylindrical current collectors, controlled with a spring screw or pneumatic control, was kept at a constant value, typically 10 bar. The current collectors were in stainless steel (paper IV), or in graphite (paper V). Instead of gas channels, a stainless steel foam (90 % porosity) and a backing (Carbon A cloth, 40 wt % PTFE, E-TEK) were used, paper IV, to distribute the gases evenly over the surface of the electrodes. In paper V, a SGL 10 BA gas backing was used for the same purpose. The cell also had a reversible hydrogen electrode (RHE) on the anode side. The test bench comprised control of the cell temperature ($T_{\text{cell}}$), of the H$_2$ and O$_2$ humidification temperatures ($T_{\text{hum,a}}$ and $T_{\text{hum,c}}$), and of the temperature of the pipe linking the humidification bottles to the cell ($T_{\text{pipe}}$).

![Figure 3: Photograph of the in-house single cell fixture](image)
2.2 Electrochemical characterisation techniques

2.2.1 Chronoamperometric measurements
In paper II, gas permeation of hydrogen and oxygen in Nafion membranes was investigated using a cylindrical microelectrode. Mass-transport information was obtained from cyclic voltammetry and chronoamperometric measurements. The chronoamperometric measurements of the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR), respectively, were performed by stepping the potential from its open circuit value to a potential where the reaction was mass-transport limited as judged from the cyclic voltammograms, paper II. The potential was controlled using an EG&G, 237A, potentiostat and the current response was sampled using a Nicolet 410 transient recorder. Each chronoamperometric curve evaluated was an average of 25 measurements.

2.2.2 Reference electrodes
Conventional PEFC RHEs were used in paper IV and in the hydrogen permeation studies in paper II. An oxygen pseudo-reference electrode was also used in paper II to obtain oxygen transport information. In paper V, another concept, based on thin-film pseudo-references placed in the centre of the MEA, was utilised for EIS investigations of the membrane and anode impedance responses.

2.2.3 Steady-state polarisation experiments
In papers IV and V, the steady-state polarisation curves of the anode or cathode potential versus the reference electrode were recorded and corrected for iR drop by using the current-interruption method. The experimental procedure is described in detail in the thesis of Jaouen [147]. The current interrupt measurements were performed by using the EG&G, 237A, potentiostat and the Nicolet 410 transient recorder.

2.2.4 Electrochemical impedance spectroscopy (EIS)
Electrochemical impedance spectroscopy (EIS) was used in paper I to determine membrane proton conductivity, in paper III to measure iR drop and finally in papers IV-V in combination with mathematical modelling to investigate the membrane and electrode characteristics more thoroughly. In general, the PEFC impedance measurements were carried out at a given current. Prior to the impedance measurement, the cell was run galvanostatically for 1 h. The amplitude of the ac current was always 5 % of the dc current density (Solartron FRA 1255 and potentiostat 1287). The frequency of the perturbation was typically varied from 50 kHz to 10 mHz. In paper IV, the cell voltage, instead of the cathode potential vs. the RHE, was recorded since the latter gave rise to an inductive loop at high frequency. Using anodes with a fixed composition ensures that the differences between the cell spectra arise only because of the change in cathode composition.
3 RESULTS AND DISCUSSION

3.1 A new type of proton conducting membranes for PEFC?

Dendritic polymers are highly branched polymers based on ABₙ-monomers introducing potential branching points in every repeating unit. The possibility to obtain tailored barrier properties, as well as introduce cross-linking points and other functional groups to a dendritic polymer by end-group modification, suggest that they have potential as polymer electrolyte fuel cell membrane components. However, only very few papers have been published on dendritic polymers as proton conducting membranes in PEFC [165-168]. The molecular architecture of dendritic polymers makes it possible to introduce various amounts of functional groups and cross-linking points by end-group modification and, as a consequence, to control the properties of the membrane. The purpose of this study was to demonstrate the potential use of dendritic polymers as the acidic components in proton conducting membranes, paper I.

3.1.1 Synthesis and Characterisation of sPTMPO

Sulfonated PTMPOs with different ion exchange capacities (S1-S3) were synthesised according to Scheme 1, and are listed in Table 1.

1H-NMR spectroscopy was found to be a versatile characterisation tool. Figure 4 presents the 1H-NMR spectrum of sample S2 after purification by precipitation and subsequent ion exchange. By comparing the integrals originating from the two middle methylene groups (peaks g and h) remaining from the 1,4-butane sultone with the integrals emanating from the ethyl group in the repeating unit in PTMPO (peak a or b) it was possible to assess the degree of substitution (DS).

![Scheme 1: Sulfonation of PTMPO by end-capping with 1,4-butane sultone](image-url)
RESULTS AND DISCUSSION

Figure 4: $^1$H-NMR spectrum of sPTMPO (in DMSO-$d_6$)

Since the number of repeating units ($n$) in PTMPO and the number of functional groups ($n+1$) were assumed to be equal, the ion exchange capacity ($IEC$), of the sulfonated PTMPO can be expressed as:

$$IEC = \frac{DS \cdot 10^3}{M_w, \text{repeating unit poly-TMPO} + DS \cdot M_w, \text{1,4-butanesultone}}$$

(1)

As a comparison, the degree of substitution determined from $^1$H-NMR and from titration is presented in Table 1. A good agreement between the outcome of these two methods was obtained. However, due to uncertainties in the $^1$H-NMR integration and the assumption $n \approx n+1$, the $IEC$ data acquired from the titrations were utilised for the membrane preparation.

Table 1: $IEC$, $DS$ obtained from titration and theoretically calculated $DS$ obtained from $^1$H-NMR spectroscopy for sulfonated PTMPO (S1-S3)

<table>
<thead>
<tr>
<th>sPTMPO</th>
<th>$IEC$ / meq g$^{-1}$</th>
<th>$DS$ titration</th>
<th>$DS$ $^1$H-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.2</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>S2</td>
<td>2.3</td>
<td>0.39</td>
<td>0.33</td>
</tr>
<tr>
<td>S3</td>
<td>2.6</td>
<td>0.46</td>
<td>0.47</td>
</tr>
</tbody>
</table>
3.1.2 Membrane preparation

The proton conductivity in sulfonated membranes is favoured by a high concentration of sulfonic acid groups and increasing water content. A high IEC will increase the conductivity, but at the same time the mechanical strength is reduced due to high water uptake and swelling. The molecular structure of the polymer backbone and phase separation due to hydrophobic and hydrophilic groups strongly affect the water uptake and the proton conductivity. In dendritic polymers, the water uptake has to be controlled by cross-linking or by introduction of grafts by end-group modification due to the globular shape and lack of entanglements. The material properties are greatly dependent on the nature of the numerous end-groups. The sulfonated PTMPOs were highly water soluble, which complicated the membrane preparation. To investigate whether or not it was possible to prepare membranes with sufficient mechanical properties, two different approaches were explored - chemical and physical cross-linking.

3.1.2.1 Chemical cross-linking

Membranes consisting of sPTMPO (S1 and S3) and HMMM as cross-linking agent were prepared, Table 2. It was difficult to find a polymer / cross-linker ratio giving a membrane with a good balance in the mechanical properties. A concentration of 10 wt % HMMM was found to give acceptable mechanical properties while still retaining a high concentration of proton conducting sulfonic acid groups in the membrane. The membranes exhibited poor mechanical properties in the humidified state and became brittle when dried.

The proton conductivity of the chemically cross-linked membranes (M1-M2) is presented in Figure 5 as a function of relative humidity, RH. As a reference, the conductivity of Nafion 117 (R) at 20 °C is included using a polynomial equation fitted to experimental data presented by Sone et al. [81]. The proton conductivity was, as expected, found to be proportional to the IEC and strongly dependent on relative humidity. At a relative humidity of 80%, the conductivity for both membranes (M1-M2) was comparable to that of Nafion 117. At higher RHs, the conductivity exceeded the conductivity of Nafion. At relative humidities below 80%, Nafion exhibited superior conductivity properties. The same trend has also been observed for other kinds of alternative membranes, e.g. sPEEK and PVDF-g-PSSA [37, 77] related to a higher self-diffusion coefficient of water and proton mobility due to the better hydrophobic / hydrophilic separation in Nafion [77].

<table>
<thead>
<tr>
<th>membrane</th>
<th>sPTMPO</th>
<th>cross-linker</th>
<th>( x_{cross-linker} )</th>
<th>( l )</th>
<th>IEC / meq g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>S1</td>
<td>HMMM</td>
<td>10</td>
<td>160</td>
<td>2.0</td>
</tr>
<tr>
<td>M2</td>
<td>S3</td>
<td>HMMM</td>
<td>10</td>
<td>100</td>
<td>2.3</td>
</tr>
<tr>
<td>M3</td>
<td>S2</td>
<td>PSU-pyridine</td>
<td>33</td>
<td>240</td>
<td>1.0</td>
</tr>
<tr>
<td>M4</td>
<td>S2</td>
<td>PSU-pyridine</td>
<td>24</td>
<td>130</td>
<td>1.3</td>
</tr>
<tr>
<td>M5</td>
<td>S2</td>
<td>PSU-pyridine</td>
<td>19</td>
<td>150</td>
<td>1.6</td>
</tr>
</tbody>
</table>
3.1.2.2 Physical cross-linking (blends)

Acid/base blend membranes having ion exchange capacities ranging from 1.0 to 1.6 meq/g were prepared, Table 2. The ion exchange capacity of the acidic and basic components was 2.3 meq/g (S2) and 1.6 meq/g (PSU-pyridine), respectively. The blends of the PSU-pyridine and the water-soluble acidic polymer resulted in water-insoluble proton conducting membranes with a strong interaction between the basic and the acidic compounds. Water uptake and proton conductivity as function of IEC at a temperature of 25 °C are presented in Figure 6. The water uptake in these membranes had the range from $\lambda = 45-177 \text{ mH}_{2}\text{O} / \text{SO}_{3}\text{H}$. This is far too high even for the 1.0 meq/g membrane (M3) and further improvement on reduced swelling is necessary, e.g. by reducing the degree of substitution. In spite of the high water uptake, the membranes showed relatively good mechanical properties in the wet state up to 1.3 meq/g (M4). However, when reaching IECs of 1.6 meq/g for the membrane (M5), the high water uptake and swelling of the membrane strongly reduced its mechanical strength. All membranes were found to be brittle when dry, especially at low IEC. The brittleness can be explained by the strong physical cross-linking introduced by the interactions between the acid and base functional groups. The brittleness decreased noticeably when the amount of sulfonated PTMPO was increased. Membrane M4 showed sufficiently good mechanical stability both in the dry state and when soaked in water. Consequently, a membrane ion exchange capacity of 1.3 meq/g was found to be a good balance between the amount of sPTMPO and PSU-pyridine. The proton conductivity was in the range between 0.01-0.04 S/cm for the membranes M3-M5. To improve on these acid/base blend membranes, it is important to maintain the high proton conductivity and reduce the water uptake and brittleness to reasonable levels.
RESULTS AND DISCUSSION

![Graph showing proton conductivity and water uptake of acid/base blend membranes based on sPTMPO and PSU-pyridine (M3-M5) as a function of IEC](image)

The durability of PTMPO-based membranes is still an open question but most probably an increased chemically stability is needed to obtain a long-term durability in PEFC applications. The PTMPO backbone consists of secondary $\alpha$-hydrogens, which are relatively sensitive to hydrolysis and hydroxy radicals produced in the fuel cell environment. The investigated membranes in this study are therefore addressed as model materials. On the other hand, PVDF-g-PSSA membranes, known to have poor chemical stability due to the tertiary $\alpha$-hydrogens in the polystyrene grafts, have received attention from several research groups and have been demonstrated to last thousands of hours of operation in fuel cells [22, 23, 39]. In order to increase the long-term durability, there are several hyperbranched polymers having perflourinated or other thermally stable backbones that can be utilised. The hyperbranched poly(ethersulfone), HPES, presented by Takeuchi et al. [168, 169] is an example of such a promising structure of this type.

Besides the water uptake and proton conductivity, transport properties are also influenced by the molecular structure and morphology. An example is permeation of oxygen in the heterogeneous structure of perflourinated membranes. Dissolution of oxygen in Nafion was shown to take place in the hydrophobic regions whereas the diffusion is mainly pronounced in the hydrophilic clusters [65]. Since the PEFC membrane acts as a gas diffusion barrier between anode and cathode, investigations of mass-transport parameters in the polymer electrolyte are of crucial importance.
3.2 Gas permeability measurements using a cylindrical microelectrode

There are various techniques to measure gas permeability in membranes. One example is micro-disc electrode investigations. Using a micro-disc electrode, transport properties of hydrogen and oxygen in proton conducting membranes can be studied electrochemically. A small well-defined area of the electrode is of crucial importance to obtain a well-defined diffusion field. However, the small area will result in low currents and cause experimental difficulties especially at high temperatures and low relative humidities. In such systems it can be advantageous to use micro-cylinder electrodes, which are easy to place inside the PEMFC, because it is possible to increase the electrode area, i.e. increase the length of the wire, without foregoing a well-defined diffusion field. Micro-cylinder electrodes have earlier been studied by Aoki et al. [170, 171] and Mesaros et al. [172]. The focus of this work was to develop an in-situ method that can easily provide reliable transport and kinetic data for PEMFC models, paper II.

Semi-infinite diffusion of oxygen or hydrogen, using cylindrical microelectrodes, can be described by Fick’s first and second laws in cylindrical coordinates. A numerical model describing the chronoamperometric current response, including mass transport and kinetics for the reaction, $R \leftrightarrow O + n \, e^-$, was utilised:

\[
\frac{\partial C}{\partial \tau} = \left( \frac{\partial^2 C}{\partial \chi^2} + \frac{1}{x} \frac{\partial C}{\partial \chi} \right)
\]

\[\chi = \frac{r}{r_s}; \quad C = \frac{c}{c_{bulk}}; \quad \tau = \frac{Dt}{r_s^2}\]

\[
\left( \frac{\partial C}{\partial \chi} \right)_{\chi=1} = C_{\chi=1} \frac{i_q r_s}{\nu n F D c_{bulk}} \exp\left( \pm \frac{\alpha F}{RT} \eta \right)
\]

using the initial and boundary conditions:

\[C(x, \tau = 0) = 1\]

\[C(x_, \tau) = 0\]

The concentration ($c$) is the solubility of either hydrogen or oxygen, $r_s$ is the radius of the micro-cylinder electrode and $\nu = +1$ (HOR) or $-1$ (ORR); $i$ refers to the current density at the cylindrical microelectrode.
An empirical expression describing the chronoamperometric curve obtained with a cylindrical microelectrode was earlier presented by Aoki et al. [171], Equation (7).

\[
i = \frac{nFDC_{\text{bulk}}}{\nu r_s} \left[ (\pi \varphi)^{-1/2} + 0.422 - 0.0675 \log(\varphi) \pm 0.0058 (\log(\varphi) - 1.47^2) \right]
\] (7)

The results obtained from the numerical model were in good agreement with Equation (7) and the chronoamperometric measurements were evaluated numerically by fitting both Equation (7) and the numerical model to the same sets of experimental results. The fitted parameters using the numerical model were \( D \), \( c_{\text{bulk}} \) and \( i_0 \). By doing this, it was shown that the kinetics has no influence on the permeability results obtained in this system. It was also shown experimentally that the current response was independent of the applied potential step in the mass transport-limited region. The values of \( D \) and \( c_{\text{bulk}} \) were obtained from the fit and the calculated current responses agree well with experimental data even at high temperatures and low relative humidities. Chronoamperometric results of the oxygen reduction reaction, and modelled current responses at a temperature of 60 °C and at a range of relative humidities are shown in Figure 7.

![Figure 7: Chronoamperometric current response and numerically fitted results of the ORR at 60 °C: (a) \( RH = 35\% \), (b) \( RH = 57\% \), (c) \( RH = 94\% \)](image_url)
RESULTS AND DISCUSSION

Linear sweep voltammograms of the Pt/Nafion interface were recorded regularly at different temperatures and relative humidities. Figure 8 shows examples of voltammetry measurements in oxygen at a temperature of 60 °C. The value of the limiting current is strongly affected by the change of relative humidity and is in line with the measured permeability properties presented below.

Evaluated experimental results for oxygen obtained from three different cylindrical microelectrodes are listed in Table 3. The microelectrodes were hot pressed in the same MEA and the measurements were carried out at the same conditions ($RH = 56\%$ and $T = 25 °C$). The results show a good agreement between the wires for both the solubility and the diffusion coefficient. The same results were obtained when repeating the measurement under the same conditions after changes in relative humidity and temperature had been made.

![Figure 8: Linear sweep voltammograms of the cylindrical microelectrode equilibrated in oxygen at 60 °C, rate=10 mV/s; (a) $RH = 35\%$, (b) $RH = 57\%$, (c) $RH = 75\%$, (d) $RH = 94\%$](image)

Table 3: Solubility, diffusion coefficient and permeability of oxygen in Nafion 117 at 56% relative humidity and 25 °C measured using three different cylindrical microelectrodes ($r = 12.5 \mu m$, 1) $l = 11$ mm, 2) $l = 8.5$ mm, 3) $l = 9$ mm. The microelectrodes were hot pressed in the same MEA.

<table>
<thead>
<tr>
<th>microelectrode</th>
<th>$10^6 c_{bulk}$ / mol cm$^{-3}$</th>
<th>$10^6 D$ / cm$^2$ s$^{-1}$</th>
<th>$10^{12} P$ / mol cm$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.2</td>
<td>0.56</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>5.1</td>
<td>0.56</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>5.4</td>
<td>0.56</td>
<td>3.0</td>
</tr>
</tbody>
</table>
In Table 4 (a) and (b), solubility and diffusion coefficients of oxygen and hydrogen are listed. The diffusion coefficients increase with increasing water content in the membrane, which is probably due to water acting as a softener in the polymer resulting in a higher mobility of the polymer chains. However, the solubility of both gases decreases with increasing water content at all temperature studied. As opposed to the water dependence of $D$ increasing the water content seems to have an adverse effect on the solubility. The gas diffusion and the solubility are dependent on the Nafion properties, temperature and relative humidity. In general, the solubility of gases in polymers increases with temperature, but the gas transport properties in a membrane vary greatly with the water content. The contribution of water therefore makes it difficult to predict the dependence of solubility and diffusion coefficient on temperature and relative humidity.

Table 4: Solubility, diffusion coefficient and permeability:

a) oxygen in Nafion 117 at different relative humidities and temperatures

<table>
<thead>
<tr>
<th>T / °C</th>
<th>RH / %</th>
<th>$10^6 c_{bulk}$ / mol cm$^{-3}$</th>
<th>$10^6 D$ / cm$^2$ s$^{-1}$</th>
<th>$10^{12} P$ / mol cm$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>30</td>
<td>5.2</td>
<td>0.33</td>
<td>1.7</td>
</tr>
<tr>
<td>56</td>
<td></td>
<td>5.1</td>
<td>0.56</td>
<td>2.8</td>
</tr>
<tr>
<td>82</td>
<td></td>
<td>4.0</td>
<td>1.1</td>
<td>4.2</td>
</tr>
<tr>
<td>60</td>
<td>35</td>
<td>4.6</td>
<td>1.1</td>
<td>4.9</td>
</tr>
<tr>
<td>56</td>
<td></td>
<td>4.1</td>
<td>1.4</td>
<td>5.7</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>4.0</td>
<td>1.5</td>
<td>5.9</td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>3.8</td>
<td>1.7</td>
<td>6.7</td>
</tr>
</tbody>
</table>

b) hydrogen in Nafion 117 at different relative humidities and $T = 60$ °C

<table>
<thead>
<tr>
<th>T / °C</th>
<th>RH / %</th>
<th>$10^6 c_{bulk}$ / mol cm$^{-3}$</th>
<th>$10^6 D$ / cm$^2$ s$^{-1}$</th>
<th>$10^{12} P$ / mol cm$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>43</td>
<td>4.2</td>
<td>2.2</td>
<td>9.2</td>
</tr>
<tr>
<td>53</td>
<td></td>
<td>2.7</td>
<td>4.4</td>
<td>12</td>
</tr>
<tr>
<td>76</td>
<td></td>
<td>2.0</td>
<td>7.1</td>
<td>14</td>
</tr>
<tr>
<td>87</td>
<td></td>
<td>1.7</td>
<td>10</td>
<td>17</td>
</tr>
</tbody>
</table>
The permeability, \( P = D \times c_{\text{bulk}} \, \text{mol/(cm s)} \), as a function of relative humidity and temperature is presented in Figure 9. In general, the permeability increases with increasing temperature and relative humidity. The variation in permeability between different Nafion samples can clearly be seen when comparing (b) and (c). Differences in methodology and conditions make it difficult to compare the results to literature data. Over all, the results are in line with data obtained by other methods, Table 1 in paper II.

In the direct methanol fuel cell (DMFC), the crossover of methanol from the anode to the cathode is obviously due to high solubility of methanol and one of the major challenges to overcome. At standard operating conditions, the high crossover will cause loss of fuel and mixed potential at the cathode corresponding to several tenths of mA/cm\(^2\) parasitic load. In the PEFC, gas crossover is not critical in the same sense as in the DMFC [96]. The permeability of hydrogen or oxygen in conventional membranes is much lower than for methanol and, even if the open circuit potential (OCP) is decreased several mV, the gas crossover corresponds to currents smaller than 1 mA/cm\(^2\). On the other hand, gas permeability in PEFC membranes has been discussed as a possible cause of increased membrane degradation due to radical formation when mixing hydrogen and oxygen [22].

Figure 9: Permeability of oxygen and hydrogen in Nafion 117 as a function of relative humidity: (a) hydrogen, \( T = 60^\circ C \) (MEA1), (b) oxygen, \( T = 60^\circ C \) (MEA1), (c) oxygen, \( T = 60^\circ C \) (MEA2), (d) oxygen, \( T = 25^\circ C \) (MEA2)
3.3 Membrane durability

In order to increase the understanding of the degradation processes of importance at fuel cell operating conditions, the degradation of PVDF-based radiation grafted PSSA membranes with different degrees of grafting (dog) was studied, Table 5.

Table 5: Investigated model membranes: matrix, degree of grafting (dog), thickness (l), water uptake (WU) and ion exchange capacity (IEC)

<table>
<thead>
<tr>
<th>membrane</th>
<th>matrix</th>
<th>dog / %</th>
<th>l(dry) / µm</th>
<th>l (wet) / µm</th>
<th>WU / g g⁻¹</th>
<th>IEC / mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>PVDF (50 µm)</td>
<td>25</td>
<td>66</td>
<td>88</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>X2</td>
<td>PVDF-co-HFP(6%) (50 µm)</td>
<td>35</td>
<td>90</td>
<td>130</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>X3</td>
<td>PVDF (40 µm)</td>
<td>43</td>
<td>55</td>
<td>70</td>
<td>1.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

3.3.1 Long-term fuel cell tests

One way to study membrane degradation in operating fuel cells is to monitor the change in membrane resistance as a function of time, i.e. the loss of sulfonic acid groups during operation. This can be done by measuring the iR drop using the current interrupt technique, or by measuring the high frequency intercept of the cell impedance. In paper III, the degradation was studied in situ by a combination of galvanostatic steady-state and impedance measurements. Since these methods measure the cell resistance, all other resistances except the membrane resistance should remain constant. However, an experimental difficulty was to fabricate high-performing MEAs. The Nafion-containing electrodes were not fully compatible with the PVDF-g-PSSA membranes. It was therefore difficult to establish a stable interfacial contact between the electrodes and the membrane, especially when using thin-film electrodes fabricated by spraying catalyst ink on the membrane surface. When using thin-film electrodes, cracking and delamination of the MEA was obtained. All presented experimental data in paper III concerning degradation of PVDF-g-PSSA membranes were obtained from MEAs with Elat electrodes. As can be seen in Figure 10, in which the results of a 100 hour constant current test with membrane X2 are presented, it takes some 30 hours before the contacts between the electrodes and membrane have stabilised and the high and low frequency impedances reach a stable rate of increase.
In Figure 11, the EIS data as a function of time are presented in the Nyquist plane. The large increase of the high frequency intercept in the beginning of the experiment is due to increasing interfacial resistance between the membrane and the electrode. Furthermore, the difference in magnitude between the EIS curves reflects changes in the electrode kinetics. At longer times the size of the EIS curves is more constant and the increasing resistance is due to loss of sulfonic-acid groups in the membrane.

Figure 11: Nyquist diagram presentation of the total impedance spectra obtained from the long-term fuel cell experiment presented in Figure 10 (membrane X2); measured after 0, 1, 10, 30, 60 and 90 hours
RESULTS AND DISCUSSION

A second experimental problem was that the durability of these membranes was only about 400 h. The main reason was mechanical failure due to pinhole formation. Since a large gas crossover is known to increase the degradation rate, the OCP was readily monitored and the experiments were stopped before pinholes were formed in order to save the samples for post-mortem analysis. Galvanostatic long-term experiments provide important information concerning the degradation rate of sulfonic acid groups, especially in combination with post-mortem analysis. Using this method for evaluation of membranes with longer durability than the investigated ones could probably provide a good interpretation of the degradation rate.

As a conclusion, interfacial contact and cracking of the electrode are important factors to take into account when studying membrane degradation by means of resistance changes. It is also of advantage to monitor the complete impedance spectrum to assure that no changes in electrode kinetics will affect the long-term results. In addition, formation of pinholes can substantially accelerate the membrane degradation due to increasing gas crossover. Therefore, it is of importance to be assured that no pinhole has been formed during the long-term experiment, when evaluating the degradation process with complementary post-mortem analyses such as micro-Raman spectroscopy.

3.3.2 Post-mortem analysis

Raman spectra of the membranes were obtained after the fuel cell tests in order to ascertain the occurrence of degradation. Micro-Raman spectroscopy turned out to be ideally suited for post-mortem analysis, because it gives information about local changes in the membrane structure. In Figure 12 depth profiles of the relative PSSA concentration of membrane X1 before and after long-term fuel cell test are shown as an example. The other membranes show a similar loss of PSSA. This loss is higher at the cathode side of the membrane and is in line with results earlier reported by Ericson et al. [30].

![Figure 12: A depth profile of the relative PSSA concentration of a reference sample, upper curve, and membrane X1, lower curve, measured by micro-Raman spectroscopy in the middle of the active area after the fuel cell test.](image-url)
The most remarkable results were obtained when surface scans of the membranes were performed. The MEA consisted of a circular ELAT electrode surrounded by an inactive gas backing, Figure 13. A surface scan of the membrane (X1) shows that there was a large degradation of the membrane at the edges of the electrodes where there was poor mechanical support. Moreover, Figure 13 shows that there is significant degradation at the interface between the gas backing and the PTFE sealing, at 4-6 and 37-38 mm, in the area far from the electrochemically active surface. In the regions 5-10 and 30-37 mm, where the membrane contacts the inactive part of the electrode, there was also some degradation. Wang and Capuano [73], who also used radiation-grafted partially fluorinated membranes, have reported degradation outside the active surface.

Figure 13: Schematic presentation of the measurement set-up and surface profile of the relative PSSA concentration of membrane X1 as obtained by micro-Raman spectroscopy after the fuel cell test.
The region at the interface between gas backing and sealing, where localised accelerated degradation could occasionally be observed visually is also a region where membranes sometimes cracked in our fuel cell experiments. Mechanical failure in this region was usually the limiting factor for lifetime in the fuel cell when membranes such as X3 (with degrees of grafting above ~35 %) were tested. Neither of the membranes X1 and X2, which had lower degrees of grafting and lower water uptakes, broke during tests. This behaviour is most certainly connected with the fact that membranes with low water uptake show less dimensional changes and mechanical stress is induced in particular by uneven swelling and shrinking; the membrane changes dimension more in the interface sealing-gas backing region than beneath the electrodes.

Measurement of the IEC was used to study membrane durability at open circuit in a fuel cell. The experiments were done with membrane X3, as this was found most susceptible to degradation. For each membrane sample, the IEC in the inactive and active regions, i.e. beneath the PTFE-sealing and the electrodes, was measured. Typical results of such experiments where the anode and cathode sides of the fuel cell have been flushed with different gas combinations are given in Table 6 for the case when catalyst-loaded ELAT® electrodes were used. (For reference the changes in IEC for membrane X3 when the cell was under load are also included.)

As revealed, the changes in ion exchange capacity of the membranes were quite within experimental error even when the membranes were exposed to hydrogen and/or oxygen. After 100 h at open circuit potential (OCP), the ion exchange capacity remained almost the same as in the reference sample, the pristine membrane. As expected, degradation neither occurred when the experiments were done using only gas backing. In addition, the membrane was remarkably degraded when the fuel cell had been under load for about the same amount of time. These experiments show that membrane durability is quite good at open circuit conditions contrary to the case when the fuel cell is under load. However, these experiments were not complemented with micro-Raman measurements, and therefore no conclusions about localised

<table>
<thead>
<tr>
<th>gases used:</th>
<th>sampled from</th>
<th>Test time / h</th>
<th>IEC / meq g(^{-1})</th>
<th>IEC / % of pristine membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)/N(_2)</td>
<td>inactive area</td>
<td>93</td>
<td>2.3</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>active area</td>
<td>1.9</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>H(_2)/O(_2)</td>
<td>inactive area</td>
<td>96</td>
<td>2.4</td>
<td>102</td>
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<tr>
<td></td>
<td>active area</td>
<td>2.3</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>N(_2)/O(_2)</td>
<td>inactive area</td>
<td>98</td>
<td>2.3</td>
<td>101</td>
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<tr>
<td></td>
<td>active area</td>
<td>2.4</td>
<td></td>
<td>103</td>
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<tr>
<td>fuel cell test</td>
<td>inactive area</td>
<td>72</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>active area</td>
<td>0.65</td>
<td></td>
<td>32</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

degradation can be made. The water transport is obvious in an operating fuel cell; low molecular fractions of degraded PSSA can easily be removed from the membrane as opposed to the OCP experiments where no water gradient is present. With this taken into account, all the membranes were thoroughly washed in distilled water for three days before the IEC measurements.

3.3.3 Accelerated membrane degradation

Ex-situ hydrogen peroxide tests were carried out for all three model membranes at the same temperature as in the fuel cell tests in order to study the influence of the degree of grafting on the degradation rate. Initial tests with hydrogen peroxide showed that the PVDF and PVDF-co-HFP (6%)-matrix films used for membrane preparation suffered no degradation during the time scale of our experiments. The results for the model membranes are therefore presented as the remaining mass of the grafted PSSA fraction as a function of time, Figure 14. In the hydrogen peroxide solution, the membrane X3, which has the highest degree of grafting, is initially degraded slowly but the rate of degradation increases rapidly after approximately 200 minutes. Membranes X1 and X2 show a better resistance to hydrogen peroxide. These results are correlated to the water uptake in the membranes, Table 5. The degradation rate in Fenton’s solution, however, was for all membranes very high and considerable mass loss occurred very rapidly. At least for the type of membranes used in this study Fenton’s reagent is therefore less suitable for evaluation of differences in membrane durability. When judging these hydrogen peroxide measurements one has to remember that a difference from the fuel cell tests is that no mechanical stress is present. Still it seems that hydrogen peroxide testing could be used as a fairly quick indicator of the durability of a fuel cell membrane. A significant weight loss over a period of 5-7 h, such as that shown by membrane X3, means that the membrane probably is not suitable for fuel cell use.

![Figure 14: Accelerated chemical degradation of membrane X1 (Δ), X2 (□) and X3 (O) in 3% H2O2 as a function of time (T=68 °C). The degradation is presented as the loss of PSSA groups in relative wt %.]
3.4 Electrode characterisation

The objective of this study, paper IV, was to investigate the effect of the Nafion content in the PEFC cathode on its structure and electrochemical behaviour in order to test the validity region of the agglomerate-based model [122, 124] and to understand which mass-transport processes limit the cathode performance. The cathodes, having a Nafion content spanning from 10 to 70 wt %, were formed on a Nafion membrane by the spray method and using 20 wt % Pt on Vulcan (E-TEK). The investigated electrodes are presented in Table 7.

<table>
<thead>
<tr>
<th>Nafion content / wt %</th>
<th>Pt loading / mg cm(^{-2})</th>
<th>(L) / (\mu m)</th>
<th>(10^2 \varepsilon_2) / %</th>
<th>(d) (SEM) / nm</th>
<th>(d) (BET) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.05</td>
<td>3.4</td>
<td>63.5</td>
<td>159</td>
<td>95</td>
</tr>
<tr>
<td>30</td>
<td>0.11</td>
<td>7.6</td>
<td>52.0</td>
<td>172</td>
<td>211</td>
</tr>
<tr>
<td>36</td>
<td>0.14</td>
<td>7.7</td>
<td>31.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>43</td>
<td>0.12</td>
<td>7.4</td>
<td>31.9</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.11</td>
<td>6.1</td>
<td>13.4</td>
<td>234</td>
<td>256</td>
</tr>
<tr>
<td>70</td>
<td>0.11</td>
<td>9.8</td>
<td>9.7</td>
<td>263</td>
<td>--</td>
</tr>
</tbody>
</table>

3.4.1 Materials characterisation

The volume fractions of Pt/C, Nafion and gas pores are presented in Figure 15. The porosity, \(\varepsilon_2\), decreases only slightly when increasing the polymer content from 10 to 30 wt %, whereas it decreases dramatically from 30 to 50 wt %. At a Nafion content of 70 wt %, the cathode has a porosity of only 10 %.

![Figure 15: Volume fractions of gas pores, Nafion and Pt/carbon in the electrode as a function of the Nafion content](image-url)
The agglomerate size, $d$, determined from SEM micrographs, Figure 16, or BET area increases with increasing Nafion content, Table 7. Furthermore, the agreement between the SEM and BET agglomerate sizes sustains that the agglomerates detected in the SEM images are nonporous. However, there is a discrepancy in the agglomerate diameter determined by SEM and BET at a content of 10 wt % Nafion. This can be explained by values for the areas coming from gas porosimetry, Table 8.

At 10 wt % Nafion, the Pt/C powder is not entirely covered by Nafion, thus the BET area not only reflects the outer surface of agglomerates but to some extent also the high surface area of the Pt/C. This yields a BET area larger than that of the other samples and thus underestimates the agglomerate size.

Table 8: Specific surface areas obtained from gas porosimetry, in m$^2$ per gram carbon; 0 wt % Nafion corresponds to the blank Pt/C powder.

<table>
<thead>
<tr>
<th>Nafion content / wt %</th>
<th>Area imparted by pores &lt; 10 nm / m$^2$ g$^{-1}$</th>
<th>Area imparted by pores &gt; 10 nm / m$^2$ g$^{-1}$</th>
<th>BET area / m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88</td>
<td>52</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>24</td>
<td>56</td>
<td>80</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>12</td>
<td>13</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

In order to investigate the repartition of fluorine and platinum, fragments of the cathodes were peeled off and investigated by STEM. Fluorine indicates how the Nafion polymer is distributed in the agglomerates, whereas platinum gives the location of the catalyst particles, and de facto of the carbon particles as well. Thus the micrographs in Figure 17 show that the distribution of Nafion and catalyst is quite even over the agglomerates. It is emphasised that this holds also for a Nafion loading of only 10 wt %.

Double layer capacitance and ion exchange capacity measurements, presented in detail in paper IV, suggest that that only 1/10 to 1/5 of the Pt/C surface in the 10 wt %-Nafion cathode is wetted by Nafion. At the other extreme, Pt/C in the 70 wt %-Nafion cathode seems to have its surface completely wetted, while the Pt/C percolating network could simultaneously be maintained throughout the porous electrode. One can also look at how the BET surface evolves as a function of the Nafion content. The high BET area at 10 wt % Nafion, Table 8, is explained by Pt/C particles being uncovered by Nafion, which is congruent with a low value of the double layer capacitance. The dramatic decrease of BET area and increase of double layer capacitance from 10 to 30 wt % is due to the covering of the Pt/C powder by Nafion. This covering can also be observed visually in the STEM micrographs presented in Figure 17.

![Figure 17: STEM micrographs and element mapping (fluorine and platinum) of fragments of electrodes. Nafion content of the electrodes indicated on the left.](image-url)
RESULTS AND DISCUSSION

Beside reduced mechanical strength of the membrane, the water uptake / swelling also affects the performance of the electrodes. At dry conditions, the electron conductivity of any of the investigated cathodes in paper IV lies above 80 S/m, Figure 18. Such values are by far sufficient to keep the electric potential uniform in the Pt/C phase. However, the electron conductivity is likely to decrease with increasing relative humidity owing to the Nafion expansion upon wetting. Recently, Saab et al. measured a decrease of electron conductivity from about 130 to 3-6 S/m upon wetting of an electrode containing 33 wt % Nafion [118]. Clearly, this shows that more attention should be given to measuring electron conductivity under PEFC conditions than has been done in the past. The electron and ion conductivities of the 70 wt % electrode were therefore measured using the method presented by Saab et al. At dry and wet conditions the electrode exhibited an electron conductivity of 78 and 28 S m\(^{-1}\), respectively. The efficient proton conductivity was about 0.7 S/m at wet conditions, which is reasonable comparing with conductivity data obtained from model fitting presented in paper IV, Figure 11. Obviously, the decrease in electron conductivity of these investigated electrodes is not as drastic as been reported by others. Morphological aspects due to different preparation methods are a possible explanation.

![Figure 18](image-url)

**Figure 18:** Electron conductivity (○) and volume fraction of carbon (■) of the electrodes as a function of their Nafion content

3.4.2 Electrochemical characterisation

Figure 19 shows the iR-corrected polarisation curves of each cathode, in a semi-logarithmic plot. The curves were normalised for a Pt loading of 0.1 mg/cm\(^2\). An immediate conclusion is that, at high current density, the performance of the cathode is very dependent on its Nafion content. The 36 and 43 wt %-Nafion cathodes display a single/double Tafel slope, which was proven to be caused by slow diffusion of O\(_2\) in the agglomerates. On the contrary, the other cathodes have a sharper decrease of their potential with increasing current. The cathode with 10 wt % Nafion seems to display a
quadruple Tafel slope of -460 mV/dec., which can be interpreted as a combined limitation by diffusion and proton migration. For the other cathodes, it is too questionable to propose any explanation for their performance only on the basis of the polarisation curves. Further insights will be given by EIS and by drawing parallels between the electrochemical results and the outcomes of the materials characterisation. Figure 19 shows also that, at low current density, there is no noticeable difference between the various cathodes, but for the one containing 10 wt % Nafion.

The impedance experiments were analysed by fitting the EIS model developed by Jaouen et al. [124] to the curves. This model is based on the same geometry as the steady-state model [122]. It takes into account the kinetics of the ORR (Tafel law), O$_2$ diffusion in the agglomerates and proton migration throughout the porous cathode. No polymer or water film around the agglomerates is considered. The fitting parameters are the double layer capacitance per unit volume of Pt/C, $A_{dl}C_{dl}$, the Tafel slope, $b$, the O$_2$ solubility in Nafion, $c^*$, the parameter group $D_{eff}/\lambda^2$ where $D_{eff}$ is the effective diffusion coefficient of O$_2$ in the agglomerates and $\lambda$ the agglomerate radius, and finally the effective conductivity for protons throughout the cathode, $\sigma_{efl}$. The fitting procedure and the parameters obtained are described in detail and tabled in paper IV.

The structure of the investigated electrodes is built up of spherical homogenous agglomerates consisting of catalyst carbon and Nafion. As a consequence, the gas is restricted to diffuse in the polymer phase. Diffusion in the agglomerate can therefore be described by using the efficient diffusion coefficient, $D_{efg}$. Furthermore, $D_{efg}$ can empirically be expressed as $D\varepsilon_i^a$, where $D$ is the true diffusion coefficient in Nafion,
RESULTS AND DISCUSSION

ε₁, the volume fraction of Naftion in the agglomerates, and \( a \) is the tortuosity factor. In Figure 20, the group \( \varepsilon _1 ^{2/3} / d^2 \), with the agglomerate diameter, \( d \), obtained from SEM micrographs, is presented (right hand-side axis) as a function of Naftion content. The overall porosity of the cathode is also displayed (left hand-side axis). The group \( \varepsilon _1 ^{2/3} / d^2 \) increases steadily with the Naftion content because the increase in agglomerate size is more than compensated for by the increasing content of Naftion in the agglomerates. In Figure 20, the values of \( D_{\text{eff}} / (2 \lambda)^2 \) obtained from EIS are compared with the values of the group \( \varepsilon _1 ^{2/3} / d^2 \). The results show similar trends up to intermediate Naftion contents. Only results within the validity region of the agglomerate model are included in the figure. The EIS agglomerate model does not apply for Naftion contents equal to or larger than 50 wt % due to a change in the electrode structure - the pore system may not be percolating any longer.

For the cathodes containing 10-43 wt % Naftion, the reliability of the parameters obtained from EIS and materials characterisation was tested using them as input data for the steady-state agglomerate model, and comparing the calculated polarisation curves to the experimental ones, Figure 21. The agreement is good for the 10 wt %-Naftion cathode, very good for the 36 and 43 wt %-Naftion cathodes.

**Figure 20:** Diffusion properties in the agglomerates as a function of the Naftion content. Right hand-side axes: (A) values of \( \varepsilon _1 ^{2/3} / d^2 \), where \( \varepsilon _1 \) is the volume fraction of Naftion in the agglomerates and \( d \) is the agglomerate diameter obtained from SEM micrographs; (B) values of \( D_{\text{eff}} / (2 \lambda)^2 \) obtained from the fitting of the model to EIS data, where \( D_{\text{eff}} \) is the effective \( \text{O}_2 \) diffusion coefficient in the agglomerates and \( 2 \lambda \) is the agglomerate diameter. Assuming \( D_{\text{eff}} = D \varepsilon _1 ^{2/3} \), the scale factor between scale A and B is simply equal to \( D \), the true \( \text{O}_2 \) diffusion coefficient in Naftion.
As a conclusion, the performance of cathodes with low Nafion content (<30 wt %) is limited by poor kinetics owing to incomplete wetting of Pt by Nafion, by proton migration throughout the cathode as well as by O₂ diffusion in the agglomerates. At medium Nafion contents (35<x<45 wt %), the wetting of Pt by Nafion is almost complete and the mass-transport limitation is essentially due to O₂ diffusion in the agglomerates. At large Nafion content (>45 wt %), the overall porosity and average pore size decrease dramatically; consequently the cathode becomes limited by diffusion of O₂ both in the agglomerates and throughout the cathode. Probably, the pore system does not percolate any more, forcing O₂ to diffuse partly in Nafion and partly in the gas phase. Since the model does not take this into account, the values of the parameter group $D_{eff}/\lambda^2$ and the proton conductivity obtained from the fitting was tuned down in order to fit somehow the experimental data. The steady state model takes gas-phase diffusion into account and a better prediction was obtained by reducing the gas-phase diffusion coefficient by a factor of $10^3$-10⁴. Overall, future research on the investigated kind of electrodes should focus on how to improve the mass-transport properties.
3.5 Influence of water transport on membrane and anode characteristics

In paper V, the influence of water transport on the membrane and anode characteristics was modelled and investigated experimentally with focus on low frequency impedance characteristics. Models for the membrane and the hydrogen electrode were developed. The membrane model was based on dilute electrolyte theory and the electrode model was taking varying water content into account.

3.5.1 Modelling results

Water transport in the membrane was described one-dimensionally by diffusion and water drag. The water diffusion coefficient, $D_{H,O}$, was assumed to be constant irrespective of water concentration and the water drag coefficient, $t_{H,O}$, as well as the effective conductivity, $\sigma_e$, were assumed to be linearly dependent on water concentration. In the hydrogen electrode model, the surface coverage of adsorbed hydrogen and the water concentration were taken into consideration and a Langmuir isotherm was assumed. The electrode performance was assumed to be influenced by the water drag in the membrane. A drying out of the anode could result in a decrease in proton conductivity, a change in kinetics or a change in active area due to changes in wetting angle. In the present study, it was investigated whether a change in proton conductivity or kinetics with water concentration can result in a low frequency loop in EIS. The models were constructed to describe the steady-state and EIS response of the membrane and the hydrogen electrode. Further information concerning the modelling part of this study is presented in paper V.

The EIS model for the membrane gives a semicircle when there is a net current and the resistance changes with current density. This semicircle appears at a characteristic frequency proportional to the water diffusion coefficient and inversely proportional to the square of the membrane thickness, $D/L^2$. The high frequency intercept is equal to the membrane resistance, $R$, and the low frequency intercept is equal to the slope of the potential drop over the membrane, $d\Delta\phi/di$. Therefore, the size of the loop is $idR/di$ according to Equation 8. The loop can be either capacitive or inductive, depending on whether the resistance increases or decreases with current density.

$$\frac{d\Delta\phi}{di} = \frac{d}{di}(i \cdot R) = \frac{i}{di} \frac{dR}{di} + R$$  \hspace{1cm} (8)

The results obtained from the membrane and the hydrogen electrode models, put in series, are presented in Figures 22 and 23. The water concentration is introduced in the hydrogen reaction as presented in Equation 12, paper V. The modelled anode overpotential and iR drop, as well as the expressions for the slopes of the polarisation curves are shown in Figure 22. The expressions are also included in Figure 23, where the anode impedance, curve (a), and the sum of the anode and the membrane impedance, curve (b), are presented. As expected, the high frequency intercept is
equal to the resistance, $R$, and the distance between the high and low frequency intercept of the anode impedance is equal to the slope of the iR-corrected polarisation curve. Furthermore, the low frequency intercept of the total impedance is equal to the slope of the non-iR corrected polarisation curve, $dE/di$, including the term $idR/di$.

The anode contributes with three semicircles to the impedance plot, curve (a), Figure 23. The small high frequency semicircle is assigned to the relaxation of the double layer capacitance through the Volmer reaction and the medium frequency semicircle is assigned to the pseudo capacitance resulting from the adsorbed hydrogen. When the anode kinetics is coupled to water transport in the membrane, the third semicircle appears at low frequencies. This semicircle has a 45° branch and results from the changes in kinetics with water concentration; note that the membrane impedance gives a pure semicircle. The only difference between the anode impedance response, curve (a), and the total impedance response, curve (b), is the enlargement of the low frequency loop, since the anode and the membrane impedance overlap at the same frequency.

Taking changes in proton conductivity into account or introducing water dependent rate constants in the Volmer step will result in a low frequency loop in the same way as the modified Volmer step does. It can, therefore, not be concluded whether an obtained low frequency semicircle is a result of the influence of the water concentration on the Volmer step, the proton conductivity or a combination.
The results obtained using the modified Volmer step have been presented, since the magnitude of the obtained semicircles correlates well with experimental data. Notice that the water dependence of the hydrogen electrode kinetics is not fully elucidated and the proposed mechanisms need to be further investigated. It can, however, be concluded that a change in water concentration in the anode gives rise to a semicircle with the same characteristic frequency as the membrane.

3.5.2 Experimental results

In order to validate the models experimentally, a new reference electrode approach had to be introduced. To avoid geometrical difficulties with reference electrodes, discussed previously, a four-electrode setup consisting of two sprayed thin-film electrodes, as references, located between the membranes in a three-membrane MEA was developed; see paper V for more details. The concept with porous reference electrodes was utilised to achieve an even current distribution and a large surface area. The large surface area was desired to get a good stability even at low frequencies. The electrodes are pseudo-references, resulting very useful for this work. Examples of
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Experimentally obtained parameters confirming the modelled predictions are $R, d\eta_a/di, idR/di$ and $dE/di$, presented in Table 9. It is seen that the sum of the first three parameters corresponds well with $dE/di$, and that the term $idR/di$ cannot be neglected. The derivatives were estimated from a polynomial fit (third order) to the experimental steady-state data presented in paper V, Figure 8. Also, a good correlation between $dE/di$ and the magnitude of the impedance was achieved.

Table 9: Parameters calculated from experimental steady-state data: current density in mA/cm$^2$, all other parameters in mOhm cm$^2$

<table>
<thead>
<tr>
<th>$i$</th>
<th>$R$</th>
<th>$d\eta_a/di$</th>
<th>$i\frac{dR}{di}$</th>
<th>$d\eta_a + i\frac{dR}{di} + R$</th>
<th>$dE/di$</th>
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<td>240</td>
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In Figure 24, EIS curves for the hydrogen electrode versus the reference electrode at current densities ranging from 240 to –240 mA/cm$^2$ are presented. The current was defined positive when the working electrode was acting as an anode. The low frequency semicircle increases with increasing positive currents, while the medium semicircle decreases. At negative currents the low frequency semicircle decreases and eventually becomes increasingly inductive. The characteristic frequency was, however, constant.

The effect of membrane thickness was studied by comparing the cell impedance of MEAs without potential probes, MEA2 and MEA3. MEA2 consisted of three membranes to get the same thickness as the reference electrode MEA, whereas MEA3 consisted of one membrane. The low frequency semicircle from MEA3 is much smaller and shifted in frequency compared to the three-membrane MEA2, Figure 25. The decrease in size can be explained by higher water content in the anode and a smaller change in membrane resistance due to enhanced back transport of water in the thinner membrane. The shift in frequency corresponds well to $D/L^2$. For the increase of the membrane thickness with a factor of three the characteristic frequency is nine times lower for both modelled and experimental data. The experimental EIS curves correspond well in appearance and frequency with the modelled semicircles at medium and low frequency, i.e. adsorption of hydrogen and influence of water transport, respectively. The high frequency semicircle obtained from the model appears at a frequency higher than experimentally measurable.
RESULTS AND DISCUSSION

Figure 24: EIS measurements of the hydrogen electrode and a Nafion membrane (1035) vs. reference as a function of current density, $T_{cell}=50 \, ^\circ C$, $T_{dew}=47 \, ^\circ C$; (a) 240 mA/cm$^2$, (b) 120 mA/cm$^2$, (c) 40 mA/cm$^2$, (d) –40 mA/cm$^2$, (e) –120 mA/cm$^2$, (f) –240 mA/cm$^2$

Figure 25: Influence of membrane thickness on the characteristic frequency in EIS, $i=120 \, mA/cm^2$, $T_{cell}=50 \, ^\circ C$, $T_{dew}=47 \, ^\circ C$; (a) MEA2, three stacked Nafion 1035 membranes, (b) MEA3, one Nafion 1035 membrane
4 CONCLUDING REMARKS

In general, materials development is labour intensive and time consuming. Behind the several novel PEFC-membranes presented during the past few years there are thousands of hours of hard work and perseverance. Overall, the path from polymer synthesis of a novel ionomer to a high-performing MEA is long and narrow. As has been discussed in earlier sections, the evaluation of membrane and electrode performance in operating fuel cells is a complicated issue, time consuming and often including several experimental techniques. On the other hand, much membrane characterisation can be done in an early state of development. Proton conductivity, water uptake and gas permeability are examples of properties that have to, or with advantage, can be investigated ex situ. However, in some aspects it is desirable to relatively early obtain a first indication about the material’s capability in its real operating environment. Long-term durability is one property that is really difficult to study ex situ. There are some examples in the literature of membranes that suffer from rapid degradation ex situ in Fenton’s solution but function excellently in the fuel cell environment [21]. Unfortunately, there is a tendency to forego the important aspects of in-situ membrane evaluation and, instead, fuel cell tests of novel membranes are often presented with a certain focus on obtained current density and power performance. Often, the discussion concerning important questions such as MEA performance and membrane durability is weak. From a more cynical point of view, steady-state polarisation curves collected after a few hours of operation say more about the success in the MEA preparation, the cell-equipment and operating conditions than the potential of the novel fuel cell membrane presented.

Mathematical modelling is a useful tool in order to obtain a deeper understanding of the membrane properties and the limiting processes in the electrodes. The models to some extent need experimentally determined input parameters obtained from materials and electrochemical characterisation. Fitting of models to experimental data will extend the possibilities of interpretation and extraction of parameters not possible to determine from experimental data alone. Modelling and experimental work are in that way closely connected. Model validation is important since the models are limited in what they describe. One way to validate the models is by prediction and comparison of experimental results at various experimental conditions. Even though there is a certain risk of, by mistake, neglecting a non-expected process, not included in the model, when interpreting experimental data. An estimation of the reasonability of data is therefore of crucial importance.

The work presented in this thesis ranges from polymer synthesis to electrochemical characterisation of the MEA performance. Various materials and electrochemical characterisation techniques were used to study membrane properties such as water uptake, gas permeation, proton conductivity and long-term durability. The effect of composition on the cathode’s electrochemical characteristics was studied as well as the effect of water transport in the membrane on the anode performance. The broad selection of experimental techniques in combination with mathematical modelling is a useful tool in future investigations of new membranes and materials for PEFC applications.
5 FURTHER RESEARCH ON THE TOPICS OF THIS THESIS

Dendritic polymers are interesting materials due to the globular shape and properties greatly dependent on the structure of the numerous end-groups. However, much work has to be done in order to optimise the investigated sPTMPO to obtain mechanically stable membranes. In future work, the reduction of water uptake and swelling should be in focus. The effect of the cross-linking level, the nature of the cross-linkers and the composition of the blend membranes are also of crucial importance. Furthermore, the architecture of sulfonated dendritic polymers having extensive branching and numerous end-groups, i.e. the surface location of sulfonic acid groups, is interesting from a morphological perspective. Regarding chemical stability, the PTMPO was the most stable dendritic polymer available when this study was initiated. The durability of PTMPO-based membranes is still an open question but probably a more chemically stable backbone structure is desired in some applications. The material is therefore currently introduced more as a model membrane.

In many fuel cell applications it is of advantage to run the fuel cell close to the power maximum. It is therefore of interest to study the electrode performance at relatively high current density. The in-house fabricated electrodes presented in paper IV are mainly limited by mass-transport in the agglomerates or in the gas pores throughout the electrode. Since this kind of limitations dominate at high current density, further work on MEA preparation should be focused on improving the mass-transport properties. The experimental techniques also need to be further improved. At high current density, the polarisation of the anode will be significant and the need of a stable reference electrode without influences of potential gradients is obvious in order to study the cathode characteristics.

Another interesting and challenging topic is the evaluation of new membranes and MEAs for high-temperature applications. This is a focus of the recent activities in the MISTRA research programme. Currently, new fabrication methods of MEAs and thorough evaluation of high-temperature membranes based on the methodology and the techniques developed in this thesis are in progress at Applied Electrochemistry, KTH.
6 CONCLUSIONS

The work presented in this thesis is ranges from polymer synthesis to electrochemical characterisation of the fuel cell performance. The synthesis of a novel hyperbranched acid-functionalised polymer was presented. However, the main focus of this thesis is on proton conducting membrane properties and characteristics. Various materials and electrochemical characterisation techniques were used to study membrane properties such as degree of sulfonation, water uptake, proton conductivity, long-term durability but also the electrochemical response of cathodes containing varying amounts of Nafion and the influence of water transport in the membrane on the anode characteristics.

The results can be summarised as follows:

The use of sulfonated PTMPO as the acidic component in proton conducting membranes was demonstrated.

- A series of the sulfonic acid-functionalised polymer having different degrees of substitution was successfully synthesised by end-capping the hydroxy groups of poly(3-ethyl-3-(hydroxymethyl)oxetane), PTMPO, with 1,4-butane sultone. A good correlation between ion exchange capacity data determined from $^1$H-NMR and titration was obtained. Proton conducting membranes were prepared by mixing the partly sulfonated PTMPO with HMMM and cross-linking by ether formation between the methylol groups on HMMM and the hydroxyl groups on the hyperbranched polyether or using the sulfonated PTMPO in conjunction with PSU-pyridine to produce acid-base blend membranes. All membranes showed reasonably high proton conductivity, comparable to Nafion. The main challenge was to obtain good mechanical properties in both the dry and wet state. The membranes exhibited poor mechanical properties in the humidified state and were brittle when dried. The acid/base blend membranes were found to have more flexible and promising mechanical properties than the chemically cross-linked membranes.

- The molecular architecture makes it possible to introduce various amounts of functional groups and cross-linking points by end-group modification and, as a consequence, to control the properties of the membrane. Dendritic polymers could be useful in various membrane approaches such as chemically and physically cross-linked membranes or in a combination of these two. To maintain the high proton conductivity and reduce the water uptake, the presented membranes have to be further optimised.
A new in-situ method to measure gas permeability in proton conducting membranes based on a cylindrical microelectrode was presented. An advantage of this method is that the measurements can be carried out at elevated temperature and a wide range of relative humidities.

- The reproducibility of data was excellent when measuring with different microelectrodes on the same membrane sample but, as expected, greater variations in the results were found when measuring on different samples. The diffusion coefficient and the solubility of oxygen and hydrogen are strongly affected by the water content. The oxygen and hydrogen diffusion coefficients increase with increasing relative humidity. The solubility however, decreases with increasing relative humidity.

The durability of PVDF-based radiation grafted membranes for use in a polymer electrolyte fuel cell (PEFC) has been studied in situ by a combination of galvanostatic steady-state and impedance measurements.

- The fuel cell experiments show that the behaviour of a membrane in the fuel cell is very dependent on cell design and the fabrication of the membrane-electrode assembly. The accelerated chemical testing with hydrogen peroxide, combined with determination of weight loss and IEC, seems to be a method that can be used for fast screening of membrane durability, even if the final test must be its performance in a fuel cell. It is of importance to look at structural changes in membranes. For this purpose micro-Raman spectroscopy is ideally suited, because it also gives information about local changes in the membrane structure. In addition the micro-Raman measurements reveal that proper mechanical support for the membrane in the fuel cell is very important. Repeating swelling and shrinking of the membrane might result in mechanical failure and degradation of the membrane.

The influence of Nafion content on the structure and electrochemical characteristics of PEFC cathodes was demonstrated. The electrodes were thoroughly investigated using various materials and electrochemical characterisation techniques.

- The performance of cathodes with low Nafion content (\(<30\) wt %) is limited by poor kinetics owing to incomplete wetting of Pt by Nafion, by proton migration throughout the cathode as well as by \(O_2\) diffusion in the agglomerates. At medium Nafion contents (\(35<x<45\) wt %), the wetting of Pt by Nafion is almost complete and the mass-transport limitation is essentially due to \(O_2\) diffusion in the agglomerates. At large Nafion content (\(>45\) wt %), the overall porosity and average pore size decrease dramatically; consequently the cathode becomes limited by diffusion of \(O_2\) both in the agglomerates and throughout the cathode. Probably, the pore system does not percolate any more, forcing \(O_2\) to diffuse partly in Nafion and partly in the gas phase. On the contrary, the network of Pt/C particles still provides a good utilisation of Pt and sufficient electron conductivity up to 70 wt % Nafion as measured in the dry state.
• A comparison between the mass-transport parameters obtained from model fitting to experimental data and the bulk diffusion coefficient in Nafion, determined by using the cylindrical microelectrode, raises the question of whether gas-phase diffusion is involved even in electrodes of Nafion content less than 50 wt %.

The influence of water transport on the membrane and anode performance was modelled and investigated experimentally. A new experimental approach based on porous pseudo-reference electrodes in a four-electrode setup has been demonstrated in order to validate the models experimentally. Data obtained with the experiments were in good agreement with and confirmed the model predictions.

• The membrane resistance was shown to be a function of current density, as a consequence of water drag. Due to the varying resistance, the membrane gave rise to a semicircle in EIS. When taking the influence of water concentration into account, the hydrogen electrode EIS model gave a low frequency semicircle attributed to changes in reaction rate with water concentration. The low frequency semicircle appears at the same characteristic frequency as the membrane semicircle. Therefore, the membrane impedance and the anode low frequency semicircle will overlap.

• Experimental EIS data confirmed the modelled results. The magnitude of the measured impedance could only be explained by taking the membrane impedance into account. The change in resistance with current density was also necessary to include when calculating the slope of the polarisation curves obtained from current interrupt measurements.

This work shows some of the complexity and the multi-disciplinary broadness in the field of proton conducting membrane development and the implementation of the membranes in the fuel cell application. It also shows the great value of using several experimental techniques and evaluation methods in order to obtain a deeper understanding of the processes limiting the performance and durability of the fuel cell. Fitting of models to experimental data will extend the possibilities of interpretation and extraction of parameters not possible to determine from experimental data alone. Validation of models by prediction and comparison of experimental results at various experimental conditions is of crucial importance. A close connection between modelling and experimental work is therefore of great importance.
REFERENCES


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