Mass Transport in Proton Conducting Membranes for the Direct
Methanol Fuel Cell

Thomas Vernersson

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KTH- Royal Institute of Technology
Department of Chemical Engineering and Technology
Applied electrochemistry
SE-100 44 Stockholm, Sweden
Abstract

Direct methanol fuel cells, DMFC, are considered a promising and suitable power source for increasingly energy demanding portable electronics. Performance is hampered by methanol crossing the electrolyte, causing power loss from the mixed potential that arises, and worse fuel economy. Methanol crossover is necessarily investigated for new types of membranes in order to appreciate their suitability for use in DMFC. For existing membranes such as Nafion, which is extensively used in DMFC due to the lack of better alternatives and because of the extensive characterisation of other properties, the methanol crossover is analysed with the aim of improving performance.

A steady state model for multicomponent mass transport was derived for the direct methanol fuel cell membrane. Data for and validation of the model was taken both from experiment and literature. The experimental data was collected in a polarisation cell, where mass transport of methanol across the electrolyte was measured through a potentiostatic method. The results from modelling and experiments showed good agreement. The model was capable of describing the non-linear response in mass transport to increased methanol feed concentration. From the model transport equations, it was also possible to derive some characteristic transport parameters, namely the membrane conductivity, electro osmotic drag of both water and methanol, diffusive drag of water and methanol, and effective, concentration dependent diffusion coefficients for methanol and water.

A SulfoPhenylated polysulfone, carrying 0.8 sulfonic acid units per repeating unit of the polymer, was evaluated as membrane electrolyte in a DMFC. The water and methanol uptake, methanol transport characteristics, electrolyte conductivity and the fuel cell performance were measured. The methanol transport and DMFC performance results were compared to those of Nafion 117, a well characterised and frequently used electrolyte material in DMFC research. The results showed that solvent uptake is approximately one third that of Nafion 117. The investigated PSU-sph membrane showed superior qualities when it comes to methanol crossover, and the methanol permeability of the PSU-sph membrane was approximately 25% compared to that of Nafion. Proton conductivity of the PSU-sph was significantly lower than that of Nafion. The conductivity of PSU-sph was measured to be 2.0 S m$^{-1}$, approximately 15% compared to that of Nafion, measured to be 13 S m$^{-1}$ at the chosen operating conditions of 343 K and 1 M methanol feed concentration. The performance of a fuel cell using PSU-sph was compared to that of a cell using Nafion 117. The open circuit potential of the PSU-sph cell was higher for the investigated feed concentrations, a consequence of the lower methanol permeability, but the performance under load rapidly diminished due to much higher cell resistance. The lower methanol permeability is not enough to compensate for the high internal resistance of the cell. It was concluded that although the stability of the PSU-sph electrolyte cell was good and the mass transport properties of the PSU-sph membrane were superior, the investigated PSU-sph sample could not match the performance of Nafion 117 in a DMFC application. It must be kept in mind however that the membrane electrode assembly was not optimised and that the electrodes used were developed for use in conjunction with Nafion membranes. Also, a higher degree of sulfonation may have a strong positive effect on cell performance, as the ohmic losses would decrease with an increased ion exchange capacity in the membrane.
Sammanfattning
Direktmetanolbränsleceller, DMFC, anses vara en lovande och passande energikälla för bärbar elektronik, som blir alltmer energikrävande. DMFCs prestanda besväras av att bränslelackage genom elektrolyten dels orsakar effektförstörningar då en blandpotential uppstår på katoden, dels försvårar bränsleekonomin. Metanollackage är en viktig faktor att undersöka då nya membrantyper utvärderas som elektrolyt i DMFC. För redan befintliga och använda membran, t.ex. Nafion, en mycket vanligt förekommande elektrolyt i DMFC då det visat sig ge acceptabel prestanda och är väl karaktäriserad m.a.p andra viktiga parametrar, kartläggs och analyseras metanolflödet i avsikt att förbättra cellens prestanda.


List of papers


Contribution to the different papers by other researchers

In paper II, the polymer synthesis was performed by Benoît Lafitte at the Department of Polymer Science and Technology, Lund University, as was the water and methanol uptake measurements and conductivity measurements.
Acknowledgements

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1. Introduction

1.1 Operation & Performance

Fuel cells are similar to batteries in that they both yield electricity by converting chemical into electrical energy through a separated electrochemical reaction. However, while a battery has a limited lifetime before the reactive electrode materials are consumed and it is completely discharged, a fuel cell offers the possibility of continuous operation. This is because the catalyst layer of the electrodes only acts as an active surface for the reaction to take place upon and the fuel, the actual reactant, is supplied from an external source. The fuel cell technology is often praised as an important step towards more environmentally friendly and sustainable energy production. The high efficiency and combined heat and power production makes it an interesting candidate for both integrated, stand alone, and traction applications.

This work focuses on the direct methanol fuel cell (DMFC) primarily considered a promising and suitable power source for the increasingly demanding, in terms of energy at least, portable electronics. The DMFC is fed with a water/methanol solution to the anode, and air or pure oxygen to the cathode. Methanol is oxidised on a noble metal catalyst and protons migrate through the electrolyte, a proton conducting polymer membrane, to the cathode, where a reaction takes place with oxygen to form water. The principle of DMFC operation is shown in Figure 1.

![Figure 1. Schematic of a DMFC.](image)

The liquid fuel is an important advantage of the DMFC compared to for instance the H₂/O₂ polymer electrolyte fuel cell, using gaseous fuel. The liquid alcohol fuel carries a high energy density per unit volume and makes fuel handling easier and facilitates the supply infrastructure. A liquid fuel also has effects on fuel cell operation since it reduces the risk of drying out the electrolyte, which is beneficial since the electrolyte conductivity is dependent on water content. On the other hand, the DMFC suffers from a couple of other drawbacks when it comes to performance. The standard potential of the DMFC is 1.21 V (at 25 °C),
which is very close to that of the hydrogen/oxygen fuel cell (1.23 V). The cell output voltage is much lower however, due to a number of factors [1-4].

One of the reasons for the poor DMFC performance is the slow reaction kinetics of methanol oxidation on the anode. The potential loss from anode reaction overpotential at 343 K is estimated to about \( \eta_a = 0.2 - 0.25 \) V [1]. Reaction kinetics is greatly enhanced by an increase in temperature, but the thermal stability of the membrane limits the operating temperature. An improved electrolyte material could reduce this problem. Another obstacle due to the slow reaction kinetics is the demand for a high platinum catalyst loading (0.5 - 4 mg cm\(^{-2}\) is usually applied). Platinum is a scarce metal and is rather costly. Consequently, this makes the fuel cells expensive. It has also been concluded that the restricted supply of platinum, in currently exploited deposits together with known reserves, limits the possibilities of using DMFC [5]. This problem will only be solved if fuel cell performance can be maintained either with a different, preferably less expensive, type of catalyst or with a drastically lower catalyst loading. Reaching high fuel cell performance with low catalyst loading could possibly be achieved either through a modified electrode structure or through enabling higher operating temperature. Another problem is the methanol permeability of currently available electrolyte membranes. Methanol crossover to the cathode leads to a mixed potential at this electrode, and as a consequence to considerable losses in cell potential. The loss in cathode potential from methanol crossover under normal operating conditions has been estimated to be directly proportional to the crossover flow [2]. There are also some indications that crossing of methanol results in poisoning of the catalyst active sites for oxygen reduction [6]. Finally, methanol crossover also means a reduction in fuel economy, since fuel is lost through the cathode exhaust.

The most obvious way of significantly reducing methanol crossover in the fuel cell is to develop membranes that offer good stability and proton conductivity, whilst having low methanol permeability. However, a proton exchange electrolyte will most likely never be completely impermeable to methanol. So even for an improved electrolyte with reduced methanol permeability, there is a need for transport parameter characterisation and optimisation of the cell operating conditions. Operating at a high cathode pressure, thus creating a pressure gradient that counters the driving force of diffusion has been shown to reduce the crossover [7]. Another possibility is to avoid the problems of electrochemical short-circuiting by using a methanol resistant cathode (or one that is much more selective towards oxygen reduction).

1.2 Membranes

The proton exchange membrane constitutes the electrolyte in the fuel cell, and the properties of the membrane are of crucial importance to fuel cell performance. Factors that need to be considered are the chemical, mechanical and thermal stability, proton conductivity, and mass transport properties for water and methanol. Nafion, which is the mostly used membrane for H\(_2\)/O\(_2\)-fuel cells, and some other modified types of perfluorated sulfonic acid membranes, together with acid doped polybenzimidazole (PBI) are the membrane types that have been most extensively investigated for DMFC application.

1.3 Conductivity

The membrane conductivity has an obvious impact on cell performance. The membrane water content, or level of membrane hydration, is of major importance. This is true at least for Nafion and other perfluorosulfonic acid type membranes, where at DMFC operating conditions the main mechanism of proton conductivity is one of vehicular motion, protons
moving associated to water molecules. Conductivity has been investigated and discussed by [8-13]. The significance of water content for water transport and proton conductivity in Nafion and other perfluorosulphonic acid type membranes was investigated by [9, 12-17]. Another factor that greatly influences the conductivity of polymer electrolytes is the temperature, since the ion transport is a process that demands activation energy.

1.4 Uptake and transport of water and methanol

The problem of water balance, maintaining a level of membrane hydration that enables good conductivity while avoiding flooding of the electrodes, in the hydrogen polymer electrolyte fuel cell (PEFC) is present, if not to the same extent, in DMFC as well. Having a liquid methanol solution in contact with the membrane on the anode side ensures good hydration from that end. The transport of water with the protons, the water drag, together with the water production at the cathode, are perhaps more likely to cause flooding, at least for higher current densities. On the other hand, using dry air feed at the cathode and a low current density, the evaporation of water from the membrane could have a diminishing effect on the membrane proton conductivity and cause temperature gradients in the system. Also, perhaps more important, changes in water content could cause changes in membrane swelling that would reduce the contact between the membrane electrode assembly, the MEA, and current collector and thus greatly reduce the performance of the cell. The water transport is hence of importance for a complete modelling and understanding of the transport mechanisms in the membrane. Much work has been done on characterising membranes, especially Nafion, and their water uptake and transport, both through diffusion and electro-osmotic drag. Water uptake is easily measured by soaking a dry membrane in water and then determining water uptake through weight increase. This method has also been used to measure water and methanol uptake from methanol solutions [18-19]. The effect of water content on conductivity is then determined by measuring the membrane conductivity at controlled water content.

As mentioned, methanol crossover has negative effects on fuel cell performance. Methanol crossover is necessarily investigated for new types of membranes in order to appreciate their suitability for use in DMFC. For existing membranes such as Nafion, which is extensively used in DMFC due to the lack of better alternatives and because of the extensive characterisation of other properties, the methanol crossover is analysed with the aim of improving performance. Many groups have investigated methanol crossover in order to determine the detrimental effect on cell performance and to find optimal operating conditions in terms of temperature, current densities and methanol feed concentration. [11-12, 17-31]

For instance, Ren et al. [19] measured electrochemically the limiting current when methanol that crossed the membrane in a reversed cell was oxidised. Measurements were carried out both on Nafion 117 and Nafion 120. This limiting current was corrected for electro-osmotic drag and expressed as a crossover current. Nafion 120, being a higher equivalent weight and thereby denser membrane, showed lower methanol crossover compared to the Nafion 117. Generally, with Nafion 120, methanol crossover for the same feed concentration was less than 50% of that measured with Nafion 117. The cell performance when using a Nafion 117 membrane show some dependence on methanol feed concentration for low current densities, lower methanol concentration being favourable, but for higher current densities the polarisation curves for the different feed concentrations becomes rather difficult to distinguish from one another. The main difference in cell performance was the slightly higher open cell voltage obtained with a Nafion 120. The performance at higher current densities improved noticeably and the feed concentration seemed to have a greater influence on the obtained cell voltage over the range of current densities run. The improved performance seen with the denser membrane is obtained in spite of the higher resistance
(about 100% higher) of that membrane, emphasising the importance of hindering methanol crossover.

The aim of this thesis is both to investigate methanol crossover in the DMFC in order to develop a multicomponent model that does not treat the mass transport as two separate fluxes of diffusive and hydrodynamic character. Furthermore, a novel electrolyte membrane is characterised with regards to applicability in the DMFC. Relevant parameters are investigated and the material evaluated.
2. Theory

As part of this thesis, a mass transport model for the DMFC was developed. Modelling is used to improve the understanding of the mass transport processes that occur and to gain insight in system optimisation with the materials presently used. The modelling work done on mass transport in DMFC electrolyte so far mainly focuses on the transport processes as being of diffusive and convective character, following Fick’s law with a correction for the electro osmotic drag [25-26, 29-38]. However, findings imply that a strictly linear relation between feed concentration and crossover flow does not describe the transport properly, for example, the change in methanol swelling with methanol concentration [11, 18-19, 22] together with the results obtained by [27].

In this work, a multicomponent model, based on the Stefan-Maxwell equations for concentrated electrolyte theory is therefore proposed. This approach has been discussed in [42-45], and has been used to describe mass transport in DMFC electrolyte membranes by Meyers & Newman [46-48] and Weber & Newman [49-51], and also in other electrolytes [15, 52-54]. Multicomponent theory offers a versatility and detailed analysis that is not encountered in linear models. The mathematical model was validated using methanol transport data obtained by an experimental method described by Ren et al. [27]. The model was used to predict the fluxes of water and methanol under DMFC operation, as well as to define the electro osmotic drag coefficients of water and methanol respectively. The effect of methanol concentration on the electrical conductivity of the membrane was also modelled. The results of the model calculations were finally compared to other experimental and modelling results.

To take into account the coupling in the diffusion fluxes caused by interactions between species, and describe mass transport in the electrolyte without assuming ideal conditions or dilute solution, concentrated electrolyte theory was used. In this model, the membrane is considered as one homogeneous phase through which all the other species are transported and the gradient in electrochemical potential acts as driving force for mass transport. The one dimensional transport equation for an isothermal and isobaric system, using the notation of Newman [42], in its general form relates the driving force and the sum of friction forces.

\[
c_i \nabla \mu_i = \sum_j M_{ij} (v_j - v_i)
\]

(1)

Where

\[
M_{ij} = K_{ij}\quad \text{for} \quad i \neq j
\]

\[
M_{ij} = K_{ij} - \sum_k K_{jk}\quad \text{for} \quad i = j
\]

\[
K_{ij} = \frac{c_i c_j}{c_i D_{ij}}
\]

In these equations \( c \) is the concentration, \( \mu \) is the electrochemical potential, \( v \) is the velocity, \( c_i \) is the sum of all concentrations and \( D_{ij} \) is the binary diffusion coefficient that expresses the level of interaction between two species in the concentrated electrolyte. The sum of driving forces, \( \sum_{i=1}^{n} c_i \nabla \mu_i \), must be zero, as stated by the Gibbs – Duhamel relation, and this results in three independent equations describing mass transport in a system made up of the four species - water, methanol, protons and sulphonic acid groups (\( R=SO_3^- \)), the polymer
backbone). In the transport equations, the frictional interactions between the different species are described through binary diffusion coefficients. The movement of the three mobile species, water, methanol and protons, is expressed in the simplest manner, relative to the velocity of sulphonic acid groups in the membrane backbone \( R - SO_3^- \), which is zero, since these are immobile.

The electrochemical potential is stated to be the driving force for mass transport in the multicomponent theory. This is defined as

\[
\mu_i = \mu_i^0 + RT \ln(a_i) + z_i F \phi
\]  

(2)

Here, \( R \) is the gas constant, \( T \) the temperature, the activity for a species “i” is defined as \( a_i = f_i c_i \), where \( f \) is the activity factor. \( z \) is the electrical charge of a species, \( F \) is the Faraday number, and \( \phi \) the potential. For a neutral species, the third term in the expression, \( z_i F \phi \), is zero. Consequently, the electrical state, the potential, is only of interest for one species, namely the protons. Since the choice of reference is arbitrary, the protons are also chosen as reference species for defining the potential in the system [42]. Taking the gradient of (2) and combining it with equation (1) while assuming that the activity coefficients are independent of concentration, the transport equation is written as

\[
\nabla c_i = \sum_j \frac{c_i c_j}{c_j D_{ij}} (v_j - v_i) - \frac{c_i z_i F}{RT} \nabla \phi
\]  

(3)

Seeing that in the expressions for the two neutral species, water and methanol, the term relating to electric potential is zero, the gradient in electric potential is obtained from the transport equation of the protons.
3. Experimental

The experimental methods that have been used for the first part of this work are methanol transport measurements to characterise the methanol transport in the DMFC electrolyte membrane. For the second part, the water and methanol uptake measurements and conductivity measurements were carried out at LTH in Lund, the transport measurements and DMFC performance study was conducted at KTH, with the objective to characterise a novel polymer material for use as electrolyte in DMFC. The methods, materials, and the operating conditions used in the experimental work performed at KTH are summarily described. Information on the experimental methods used for the water and methanol uptake measurements and conductivity measurements are given in the article “A sulfophenyalted PSU as electrolyte membrane in the DMFC – an evaluation of methanol permeability and cell performance”.

3.1 Transport measurements

Methanol transport data was obtained from a limiting current method described by Ren et al. [19,27]. In these measurements, the methanol is fed to a permeation cell, a cell with a controlled reversed polarisation compared to a normal DMFC, where the anode and the methanol feed channel is located on opposite side of the membrane. In this configuration, methanol is oxidised after passing through the electrolyte membrane and hydrogen is produced at the cathode, on the methanol feed side. At a high enough potential, the observed current will be controlled by the rate of mass transport through the membrane and will serve as a measure on the permeability of the electrolyte. Thus, the limiting current is a measure of both the proton and the methanol transport, and the methanol concentration on the electrode surface on both anode and cathode side is known. As anode material, an E-Tek developmental gas diffusion electrode for DMFC was used. Pt-Ru (1:1) noble metal loading was 5 mg cm\(^{-2}\). For the cathode, an E-Tek Eta electrode with 30 % Pt on Vulcan XC-72 was used. Noble metal loading was 0.5 mg cm\(^{-2}\). The electrodes and the membrane were assembled in a 2.25 cm\(^2\) cell, using a clamping pressure of 3 bar. The experiments were carried out at 343 K. Methanol solution was fed to the cathode side of the permeation cell, and nitrogen gas saturated with water was fed to the anode side. The potential of the permeation cell was gradually increased until a limiting current of methanol oxidation on the anode could be observed. The potential was controlled and the current recorded with a PAR 263A potentiostat, and data acquisition was made using Corrware\(^\text{®}\) software.

3.2 DMFC performance

The performance of a DMFC using the PSU-sph and Nafion 117 membranes was tested and evaluated using the same cell and electrode materials as above. Operating temperature was 343 K and measurements were made at methanol feed concentrations 0.1 and 1.0 M. Air at atmospheric pressure, humidified to saturation with milli-Q deionised water, was fed to the cathode. Polarisation curves were registered, and each electrode potential was monitored using a hydrogen reference electrode. The results were compared to those of a cell using Nafion 117 as electrolyte membrane. Performance degradation was also measured over a period of 72 h, using a methanol feed concentration of 1.0 M, under a constant current load of 300 A cm\(^{-2}\).
4. Results & Discussion

4.1 Solvent uptake in PSU-sph

The total water and methanol uptake, $\lambda$, and the membrane weight increase due to uptake, $w$, at different methanol concentrations are shown in Table 1. It can be noted that the total water and methanol uptake of the PSU-sph is about one third compared to that of Nafion 117 [18].

Table 1. Solvent uptake and relative mass increase of PSU-sph in its proton form after 48h equilibration.

<table>
<thead>
<tr>
<th>$c$ [M]</th>
<th>$w$ [%]</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M</td>
<td>21</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10 M</td>
<td>22</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50 M</td>
<td>22</td>
<td>7.0</td>
</tr>
<tr>
<td>1.00 M</td>
<td>23</td>
<td>7.2</td>
</tr>
<tr>
<td>2.00 M</td>
<td>24</td>
<td>7.4</td>
</tr>
<tr>
<td>4.00 M</td>
<td>25</td>
<td>7.5</td>
</tr>
</tbody>
</table>

4.2 Conductivity measurements

The results from the conductivity measurements on PSU-sph and Nafion 117 at concentrations 0.1 M and 1.0 M are shown in Figure 2. The conductivity is shown to be slightly lower in a membrane equilibrated with a methanol solution of 1.0 M concentration, than in one equilibrated with 0.1 M methanol solution. This decrease of the conductivity at increasing methanol concentrations is also observed for Nafion 117, as is clearly seen in Figure 2, where conductivity of Nafion 117 is displayed for methanol concentrations up to 8 M. The effect on conductivity caused by increasing methanol equilibration concentrations is expected due to the inferior ion conduction properties of methanol compared to water. The difference in conductivity is likely not large enough to have any significant impact on fuel cell performance however, considering the positive effect a higher feed concentration has on anode kinetics and the reduction of transport limitations in the anode.
Figure 2. Arrhenius plot showing conductivity, $\kappa$ [S m$^{-1}$], of electrolyte membranes. Conductivity of Nafion 117 was measured for methanol concentrations 0.10, 1.0, 2.0, 4.0, and 8.0 M. Conductivity of the PSU-sph membrane was measured for methanol concentrations 0.10 and 1.0 M.

It is seen in Figure 2 that the conductivity of PSU-sph is significantly lower than that of Nafion 117. At an operating temperature of 343 K, the conductivity of the PSU-sph membrane is approximately 15% of the conductivity of Nafion 117.
4.3 Transport measurements with Nafion 117 and PSU-sph

Results from the limiting current measurements are displayed in Figures 3 and 4. It is evident from the results obtained using Nafion 117 as electrolyte membrane that the limiting current is not a linear function of methanol feed concentration and hence does not follow Fick’s law over the entire range of methanol concentrations, as is assumed in many models of methanol transport [28-29, 31-40]. When using PSU-sph, the same effect is not as noticeable, possibly because the concentration interval is too narrow.

It is seen in Figures 3 and 4 that limiting current from methanol crossover through PSU-sph is approximately half of that through Nafion 117. When evaluating these results, it is necessary to take into account the different thicknesses of the two membranes. The thickness of the fully swollen PSU-sph membrane is approximately 100 μm, and the Nafion 117 is about 200 μm in its swollen state. In summary, this indicates that the methanol permeability of the PSU-sph membrane is approximately 25% that of Nafion having an equivalent weight of 1100 g mol⁻¹.

![Figure 3](image)

*Figure 3. Three series of limiting current from methanol crossover through Nafion 117 at 343 K, at different feed concentrations of methanol.*

The reported limiting current flux of methanol through the PSU-sph membrane is partly explained by the lower solvent uptake. Nafion 117 is reported by Ren *et al.* to have a total solvent uptake in pure water of $\lambda = 21$, and in 4 M methanol of $\lambda = 22$ [19]. The uptake of water and methanol in PSU-sph is then approximately one third of that in Nafion having an equivalent weight of 1100 g mol⁻¹.
4.4 Cell performance

Polarisation curves of a DMFC using a 0.1 M methanol feed concentration of methanol are displayed in Figure 5. Polarisation curves and electrode potential curves of a DMFC with PSU-sph electrolyte are displayed in Figure 6. The iR-corrected polarisation curves from one cell using Nafion 117 and one using the PSU-sph membrane, with a methanol feed concentration of 1 M, are compared in Figure 7.

The potential curves at the methanol feed concentration 0.1 M give a very weak indication of the difference in cell resistance. Mass transport limitations in the anode occur at a rather low current density when using such a low feed concentration, causing the curves to bend and making interpretation difficult. At higher feed concentrations the difference in cell resistance becomes more obvious, as higher current can be drawn from the cell. At a feed concentration of 1.0 M, the polarisation curves disclose a significant difference in cell resistance, as shown by the steeper slope of the ohmic plateau region of the polarisation curve. The cell resistance of the DMFC using PSU-sph is high, to some extent because of the problems of achieving good contact in the membrane electrode interface, and partly because of higher membrane resistance. In-situ measurements of cell resistance, using the current interrupt mode of the potentiostat, showed a ten times higher cell resistance of the PSU-sph cell, in comparison to the Nafion cell. Comparing this to the membrane resistance in Figure 2, it becomes obvious that there also is a significant contact resistance between the electrode and electrolyte in the cell, using the PSU-sph membrane.
Figure 5. Polarisation curves at 343 K, and 0.1 M methanol feed concentration.

Figure 6. Electrode and cell potential curves for a cell operating at 343 K, using PSU-sph and a feed concentration of 1.0 M.
Looking at the methanol transport data together with the measured electric conductivity of these materials, and bearing in mind the results obtained by Hikita et al. [2], one would expect the performance of a DMFC using the PSU-spī membrane to be significantly lower than that of a cell using a Nafion 117 membrane as electrolyte, except perhaps when a low current density is drawn from the cell. As seen in Figure 8, a higher open circuit potential, and higher potential at low current density, is evident at both feed concentrations for the PSU-spī cell, than for the cell using Nafion 117 as electrolyte. The cell performance results are hence in good agreement with the results obtained in the transport measurements and conductivity measurements.

The polarisation behaviour at low current densities is, however, somewhat puzzling. It appears that a mass transport limiting phenomena occurs at low current densities as well. Looking at the electrode and cell polarisation curves in Figure 6, this appears to take place on the anode side of the cell. One possible explanation for this is carbon dioxide formation. The adhesion between electrodes and electrolyte is poor already from the beginning and gas formation may worsen the contact between electrode and membrane surface further. This might cause carbon dioxide leakage into the membrane and or make part of the anode unavailable for proton conduction and hence also for methanol oxidation. This explanation seems plausible considering the fact that the effect is more severe in the PSU-spī cell, as seen in the iR-corrected cell polarisation curves. In this cell, adhesion between electrode and electrolyte is lower due to the higher degree of incompatibility between the materials, the electrodes being developed for use in combination with Nafion membranes. Consequently, this implies that the performance measurements alone are a rather uncertain method of analysing a novel membrane material’s applicability as fuel cell membrane. It also implies that one must carefully consider material choices in fuel cell experiments, to avoid negative influence of material incompatibility.
4.5 Modelling of mass transport in Nafion 117

The experimental data was used to determine the binary diffusion coefficients by solving the transport equations for the transport data in multiple data points. The resulting binary diffusion coefficients, shown in Table 2, were then used to calculate limiting currents in a permeation cell. The model’s ability to predict the transport of methanol across the electrolyte membrane is displayed in Figure 8. The accuracy of the multicomponent model was compared to that of a linear model in the examined concentration interval and the results are displayed in Figure 8 and Figure 9.

Table 2. Binary diffusion coefficients at 343 K, fitted in the methanol concentration interval 0.5 – 2.5 M.

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{H}_2\text{O}/\text{CH}_3\text{OH}}$</th>
<th>$D_{\text{H}_2\text{O}/\text{H}^+}$</th>
<th>$D_{\text{H}_2\text{O}/\text{SO}_3^-}$</th>
<th>$D_{\text{CH}_3\text{OH}/\text{H}^+}$</th>
<th>$D_{\text{CH}_3\text{OH}/\text{SO}_3^-}$</th>
<th>$D_{\text{H}^+/\text{SO}_3^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.0 \cdot 10^{-9}$</td>
<td>3.6 $\cdot 10^{-9}$</td>
<td>5.9 $\cdot 10^{-10}$</td>
<td>6.2 $\cdot 10^{-9}$</td>
<td>2.9 $\cdot 10^{-11}$</td>
<td>2.4 $\cdot 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

It is evident that the concentrated solution model offers reasonably good accuracy and is superior to a linear model over the investigated concentration interval. The deviations at low methanol concentrations are rather large in both model approaches. This can be due to the fact that the uncertainty in the measured values of limiting current is relatively large at these low concentrations, as the fitting process was discovered to be sensible to disturbances in limiting current data in the percentage range.

Figure 8. Measured and calculated limiting current through Nafion 117 at 343 K, at different feed concentrations of methanol.
The multicomponent theory enables the distinction of a few characteristic transport parameters from the model results, parameters that are more informing than merely the binary diffusion coefficients when it comes to understanding of the transport processes and system behaviour. These are the electro osmotic drag coefficients, electric conductivity, and apparent Fick diffusion coefficients. The electro osmotic drag, the number of solute molecules transported with each proton under fuel cell operation, can be defined for both water, $\alpha_{\text{H,0}}$, and methanol, $\alpha_{\text{CH,OH}}$. Under conditions of $\nabla c_i = 0$, the following expressions are obtained.

$$
\alpha_{\text{H,0}} = \frac{\frac{c_1}{D_3} + \frac{c_1 c_2}{D_{12} D_{23}} \left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{23}} + \frac{c_4}{D_{34}} \right)}{\frac{c_2 + c_3 + c_4}{D_{12} D_{23} D_{34}}} - \frac{\frac{c_2}{D_3} - \frac{c_1 c_2}{D_{12}^2} \left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{23}} + \frac{c_4}{D_{34}} \right)}{D_{12}^2} \left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{23}} + \frac{c_4}{D_{34}} \right)
$$

(12)
\[
\alpha_{\text{CH,OH}} = \frac{\frac{c_{21}}{D_{23}} \bigg( \frac{c_{2} c_{2}}{D_{22} D_{23}} + \frac{c_{3} c_{3}}{D_{23} D_{24}} + \frac{c_{4} c_{4}}{D_{23} D_{24}} \bigg) - \frac{1}{D_{23}} \bigg( \frac{c_{2} c_{2}}{D_{22} D_{23}} + \frac{c_{3} c_{3}}{D_{23} D_{24}} + \frac{c_{4} c_{4}}{D_{23} D_{24}} \bigg)\bigg) - \frac{1}{D_{23}} \bigg( \frac{c_{2} c_{2}}{D_{22} D_{23}} + \frac{c_{3} c_{3}}{D_{23} D_{24}} + \frac{c_{4} c_{4}}{D_{23} D_{24}} \bigg)\bigg)}{D_{22} + D_{24}}
\]

(13)

Calculated values of water and methanol electro osmotic drag, for changing methanol concentration in the membrane, are displayed in Figure 10. The electro osmotic water drag in a membrane equilibrated with pure water was calculated to 2.9, and the electro osmotic methanol drag under conditions of pure methanol was calculated to 0.4. The fact that the model predicts different values of water and methanol drag coefficients is not in line with the notion that the drag is a hydrodynamic flow and the drag of methanol relative to that of water follows the relative concentration. On the other hand, the relative size of the interaction parameters of water/proton and methanol/proton suggest that the calculated drag should decrease with methanol concentration. One must also consider that interactions with the surrounding polymer have some effect on the electro osmotic drag. According to the modelling results, it appears that total electro osmotic drag is not constant over the entire range of methanol concentration, as can be seen in Figure 10, and not even over the smaller concentration interval, in which limiting current measurements are performed.

![Graph](image)

_Figure 10. Electro osmotic drag of water and methanol in the DMFC electrolyte._
Similarly, the number of water molecules transported with each methanol molecule, $\alpha_{H,O/CH,OH}$, and vice versa, $\alpha_{CH,OH/H,O}$, can also be analytically derived from the transport equations. This can be described as a diffusive drag, and is defined under open circuit, $N_2 = 0$, and under absence of driving force for diffusion. The diffusive drag of water, $\alpha_{H,O/CH,OH}$, is defined from equation (4), when $Vc_1 \to 0$. Correspondingly, $\alpha_{CH,OH/H,O}$ is defined from equation (5), when $Vc_2 \to 0$. The diffusive drag coefficients were calculated for changing methanol concentration in the membrane and are displayed in Figure 11.

\[
\alpha_{H,O/CH,OH} = \frac{c_1}{c_2 + \frac{c_3}{D_{12}} + \frac{c_4}{D_{14}}} 
\]

\[
\alpha_{CH,OH/H,O} = \frac{c_2}{c_1 + \frac{c_3}{D_{12}} + \frac{c_4}{D_{14}}} 
\]

*Figure 11. Diffusvie drag of water and methanol in the DMFC electrolyte.*
The value for the diffusive drag of water with methanol obtained from the model was 5.2, in a membrane saturated with pure water. For methanol with water, the diffusive drag was calculated to 1.1, in a membrane saturated with methanol. It is reasonable to think there should be some coefficient linking water and methanol drag, since this too could be thought of as a hydrodynamic transport phenomenon, similar to electro osmotic drag. This could then be interpreted as a measure of the coupling of diffusive fluxes. These coupling effects are indeed proposed by, and in effect the reason for using, the multicomponent transport theory, and they can thus be identified and quantified under special conditions. Instinctively one might expect the diffusive drag coefficients for water and methanol to be of the same magnitude, since there exist a binary diffusion coefficient expressing to some extent the strength of the interaction between them. However, they also interact with the surrounding polymer membrane, containing both acidic groups and their counter ions. Since these interactions can differ between water and methanol, the diffusive drag can also differ.

The conductivity of the methanol and water filled membrane can be calculated from the transport equations [42]. In this case there is only one charged species carrying the current.

\[
\kappa = -F^2 c_j^2 \frac{M_{11} M_{22} - M_{12}^2}{\text{det}(M^o)}
\]  

(16)

\(M^o\) is the transport matrix containing all the elements \(M_{ij}\) from equation (1).

\[
M^o = \begin{bmatrix}
M_{11} & M_{12} & M_{13} \\
M_{12} & M_{22} & M_{23} \\
M_{13} & M_{23} & M_{33}
\end{bmatrix}
\]

The model corresponds well to the experimental data [55] of conductivity of the methanol and water filled membrane, and the concentration dependence of the conductivity, as shown in Figure 12. The variation with concentration has not been fully investigated, but Edmondson [56] has reported a decrease in conductivity by one order of magnitude, with a membrane fully saturated with methanol compared to one fully saturated with water. Conductivity calculated using the multicomponent model agrees with values reported by Tricoli et al. [20] and Ren et al. [27], and the decrease is similar in its magnitude to what was reported by [56].
Figure 12. Conductivity of a Nafion 117 membrane obtained from the multicomponent model.

Comparing the multicomponent model to a linear model, one can define the measurable, apparent Fick diffusion coefficient of water or methanol in a membrane of a certain methanol concentration. Using Fick’s law together with equations (4) and (5), under open circuit, the following expressions are obtained.

$$D_{H,0} = \frac{1 + \frac{c_1}{D_{12}} \frac{\partial g}{\partial c_2} \left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{23}} + \frac{c_4}{D_{24}} \right)}{c_1 c_2 \left( \frac{c_1}{D_{12}} + \frac{c_1}{D_{23}} + \frac{c_4}{D_{24}} \right) D_T c_T} \left( \frac{c_1}{D_{12}} + \frac{c_1}{D_{23}} + \frac{c_4}{D_{24}} \right) c_T$$

(17)
\[
D_{CH\textsubscript{2}OH} = -\frac{\left(1 + \frac{\partial g}{\partial c_2} \frac{c_2}{D_{12} \left( \frac{c_2}{D_{12}} + \frac{c_3}{D_{13}} + \frac{c_4}{D_{14}} \right)} \right)}{D_{12}^2 \left( \frac{c_2}{D_{12}} + \frac{c_3}{D_{13}} + \frac{c_4}{D_{14}} \right) c_T - \frac{\frac{c_1}{D_{12}} + \frac{c_3}{D_{23}} + \frac{c_4}{D_{24}}}{c_T}}
\]

(18)

The apparent Fick water diffusion coefficient is displayed as a function of the methanol concentration in the membrane in Figure 13. Comparing the calculated \(D_{H_2O}\) with measured values of the diffusion coefficient of water in Nafion 117 at the relevant temperature, yields mixed results. It is seen that the value calculated using this model differs significantly from the diffusion coefficient published by Scott et al. [29] but is close to that of Verbrugge [16]. Motupally et al. [30] calculated the temperature dependence of the water diffusion coefficient, based on the works of three other authors, and reached three very different results. The discrepancy in previously published results makes it difficult to evaluate the accuracy of the proposed expression for \(D_{H_2O}\).

Figure 13. Modelled Fick diffusion coefficient of water in the Nafion 117 membrane.
Similarly, the apparent Fick methanol diffusion coefficient was calculated and is displayed as a function of methanol concentration in Figure 14. The $D_{\text{CH}_3\text{OH}}$ calculated by the model compares reasonably well with measured values of the diffusion coefficient of methanol at low concentrations. The model predicts a diffusion coefficient of about $5 \cdot 10^{-10}$ m$^2$ s$^{-1}$ at near zero concentration, which is very close to the value reported by Kauranen & Skou [23]. Ren et al. [27] and Tricoli et al. [20] reported slightly lower values but still in the same order of magnitude.

![Figure 14. Modelled Fick diffusion coefficient of methanol in the Nafion 117 membrane.](image)

The behaviour of $D_{\text{CH}_3\text{OH}}$ at higher methanol concentration seems erroneous at first glance, since it takes a negative value at concentrations of $c_{\text{CH}_3\text{OH}} > 13$M. However, similar results have been obtained for other systems through modelling, and verified experimentally by Krishna & Wesselingh [45]. The fact that the model predicts a negative apparent Fick diffusion coefficient can be explained by the faster water transport and the coupling in the diffusion fluxes, the diffusive drag, and it is thus obvious that a multicomponent model is capable of predicting and describing this behaviour.

The fitting of the six binary diffusion coefficients reveals that they have a very vague connection to the measured transport data. The fitted binary coefficient can deviate from the initial guess by an order of magnitude. This may seem an error in the model, but when analysing the transport equations a little closer, the actual meaning of the diffusion
coefficients becomes more apparent. The conclusion is that the measurable diffusion coefficient is a function of concentrations and binary diffusion coefficients. This notion is further supported by the fact that the results obtained in this work from fitting the $D_{ij}$ are generally smaller than those obtained by Meyers & Newman [46-48]. Their work was performed at a slightly higher temperature, which can partially explain the difference, but the deviation is not consistent with a similar temperature dependence for all the $D_{ij}$. The results of Dannenberg [53], obtained using data from a H2/O2 PEFC, also differs significantly. Examining the sensitivity in the fitting process also imply that there is no real value of the $D_{ij}$, but what is of greater importance is the magnitude of the $D_{ij}$ relative to each other. One possible source of this apparent instability is the relatively small amount of data that the model was based upon. The fact that the water flux is not measured directly, but rather expressed as a function of methanol concentration and flux also reduces the number of data for which to solve the model equations. Other methods of measuring the fluxes could be used that also gives the water flux, for example mass spectrometry, but this method has proven difficult and unstable as well. One further possibility that would be very helpful in increasing the exactness of the fitting procedure would be to have concentration profiles measured in situ, something that is being looked into for future work.
5. Conclusions

In the first part of this work, limiting current from methanol transport through a Nafion 117 membrane was measured. The rate of methanol transport through the electrolyte membrane was shown not to follow Fick’s law. A significant concentration dependence could be observed in the measured limiting current from methanol flux in the permeation cell. A mass transport model based on multicomponent theory was used to describe the mass transport, and this model performed well under a wide range of methanol feed concentration. It showed superior capacity to predict the permeation flux of methanol through the cell electrolyte, compared to a linear model. The model also accurately described the conductivity of the Nafion membrane at different methanol concentrations.

Characteristic transport parameters were derived from the model equations, describing some of the transport phenomena in the electrolyte. The coupling in fluxes of water and methanol, the diffusive drag, was characterised and expressed as a concentration dependent parameter, as was the electro osmotic drag of both water and methanol. Apparent Fick diffusion coefficients and the membrane’s electric conductivity were calculated as functions of concentration and \( D_p \). These parameters and their concentration dependence cannot be obtained from a linear model, a fact that further emphasises the versatility of the multicomponent model.

In the second part, the applicability of a novel membrane material, PSU-sph, was investigated and evaluated. The material was characterised with respect to important parameters such as solvent uptake, proton conductivity, and methanol transport. Following this characterisation, the overall fuel cell performance was investigated, when using PSU-sph as electrolyte membrane. The initial evaluation showed interesting results. The investigated PSU-sph membrane showed superior qualities when it came to methanol crossover, with a methanol permeation of only 25% of that through Nafion 117 at similar conditions. However, a competitive cell performance was not achieved in this preliminary study. The polarisation curve of the cell with the PSU-sph electrolyte displayed a higher open circuit voltage, consistent with the lower methanol crossover, but a rapidly decreasing performance at higher loads. The ohmic losses in this cell set-up were too high for the lower methanol permeability to compensate. In part, these losses are explained by a significantly lower conductivity, measured to be approximately 15% compared to that of Nafion at the chosen operating conditions of 343 K and 1 M methanol feed concentration. However, this could not account for the difference in the internal resistance of the cell, implying that the contact resistance between the electrodes and electrolyte was higher when PSU-sph was used. It must be kept in mind that the membrane electrode assembly was not optimised and that the electrodes used were developed for use in conjunction with Nafion membranes. In summary, the results are interesting and open up for further investigations. As mentioned above, improved methods for MEA formation, and thus reduction of contact resistance, should be considered. Also, a higher degree of sulfonation of PSU-sph should have a strongly positive effect on the cell performance, as the ohmic losses would decrease with an increased ion exchange capacity in the membrane. A study of the conductivity and methanol permeation at various degrees of sulfonation would be very interesting for this material.
6. List of symbols

$\eta_i$ - Anodic overpotential [V]
$c_i$ - Concentration of species “i” [mol m$^{-3}$]
$c_1$ - Concentration of water [mol m$^{-3}$]
$c_2$ - Concentration of methanol [mol m$^{-3}$]
$c_3$ - Concentration of protons [mol m$^{-3}$]
$c_4$ - Concentration of sulphonlic acid groups [mol m$^{-3}$]
$c_r$ - Sum of all concentrations [mol m$^{-3}$]
$\mu_i$ - Electrochemical potential of species “i” [J mol$^{-1}$]
$\mu_i^0$ - Electrochemical potential of species “i” at reference state [J mol$^{-1}$]
$v_i$ - Velocity of reference species [m s$^{-1}$]
$v_i^0$ - Velocity of species “i” [m s$^{-1}$]
$R$ - Gas constant [J mol$^{-1}$ K$^{-1}$]
$T$ - Temperature [K]
$F$ - Faraday’s constant [As mol$^{-1}$]
$a_i$ - Activity of species “i”
$f_i$ - Activity coefficient of species “i” [mol$^{-1}$]
$z_i$ - Electrical charge of species “i”
$\phi$ - Potential [V]
$D_{ij}$ - Binary diffusion coefficient of species “i” and “j” [m$^2$ s$^{-1}$]
$D_{12}$ - Binary diffusion coefficient of water and methanol [m$^2$ s$^{-1}$]
$D_{13}$ - Binary diffusion coefficient of water and protons [m$^2$ s$^{-1}$]
$D_{14}$ - Binary diffusion coefficient of water and sulphonlic acid groups [m$^2$ s$^{-1}$]
$D_{23}$ - Binary diffusion coefficient of methanol and protons [m$^2$ s$^{-1}$]
$D_{24}$ - Binary diffusion coefficient of methanol and sulphonlic acid groups [m$^2$ s$^{-1}$]
$D_{34}$ - Binary diffusion coefficient of protons and sulphonlic acid groups [m$^2$ s$^{-1}$]
$N_i$ - Flux of species “i” [mol m$^{-1}$ s$^{-1}$]
$N_1$ - Flux of water [mol m$^{-1}$ s$^{-1}$]
$N_2$ - Flux of methanol [mol m$^{-1}$ s$^{-1}$]
$N_3$ - Flux of protons [mol m$^{-1}$ s$^{-1}$]
$\kappa$ - Conductivity [S m$^{-1}$]
$\alpha_{H,0}$ - Electro osmotic drag of water
$\alpha_{CH,OH}$ - Electro osmotic drag of methanol
$\alpha_{H,0}/CH,OH$ - Diffusive drag of water with methanol
$\alpha_{CH,OH}/H,0$ - Diffusive drag of methanol with water
$D_{H,0}$ - Fick diffusion coefficient of water [m$^2$ s$^{-1}$]
$D_{CH,OH}$ - Fick diffusion coefficient of methanol [m$^2$ s$^{-1}$]
References
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