ORIGINAL PAPER

Electro-osmotic drag of methanol in proton exchange membranes

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Abstract A good understanding of the fundamental transport phenomena of water and methanol in PSA (Perfluoro Sulfonic Acid) membranes is one of the keys in developing efficient direct methanol fuel cells (DMFCs). Electro-osmosis, being one of the most important water and methanol transport mechanisms in DMFCs, has been investigated with a number of different proton exchange membranes. Two aspects were of particular interest: firstly, the interdependencies between the electro-osmotic drag coefficient and methanol concentration and temperature, and secondly the interdependence between the electro-osmotic drag coefficient and current density. The results of these investigations are compared to published data.

Keywords Electro-osmosis · Electro-osmotic drag coefficient · Proton exchange membrane · Direct methanol fuel cell · DMFC

1 Introduction

Ion exchange membranes are used in many different applications. A good understanding of the fundamental membrane transport mechanisms as well as a complete set of parameters describing transport rates of ions and solvents for a specific type of membrane is required if

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the membrane is to be operated efficiently for a certain application [1]. Both, the fundamental understanding of the transport mechanisms, as well as the corresponding set of parameters, has been investigated with water and methanol transport in PSA (Perfluoro Sulfonic Acid) membranes under current flow. A theoretical and experimental basis for the characterization of water and methanol transport in PSA (Perfluoro Sulfonic Acid) membranes under current flow is introduced.

The flux of hydrated protons migrating between the anode and the cathode of a PEM fuel cell results in transport of water out of the anode electrode domain into the cathode domain. This effect is called electro-osmotic drag [2, 3]. Electro-osmotic transport of water inevitably occurs in low-temperature fuel cells, where liquid water is present within the volume of the membrane. The membrane of a DMFC, however, does not only hold a significant volume of water, but also a certain fraction of methanol. The solvating envelope of the flux of protons migrating through the membrane therefore not only drags water, but a mixture of water and methanol. This transport of methanol into the cathode electrode domain is commonly referred to as 'methanol crossover' and leads to a significant decrease in fuel cell efficiency [4].

Electro-osmosis is quantified by the electro-osmotic drag coefficients κ_{H_2O} and κ_{MeOH}. The resulting coefficient ($\kappa_{H_2O+MeOH}$) describes the number of water and methanol molecules dragged by each proton in the absence of a water concentration gradient within the membrane:

$$\kappa_{H_2O} = \frac{n_{H_2O}}{n_{H^+}} \tag{1}$$

$$\kappa_{MeOH} = \frac{n_{MeOH}}{n_{H^+}} \tag{2}$$

$$\kappa_{H_2O+MeOH} = \frac{n_{(H_2O+MeOH)}}{n_{H^+}} \tag{3}$$

where n_{H_2O} = number of transported water molecules, n_{MeOH} = number of transported methanol molecules, $n_{(H_2O+MeOH)}$ = number of transported water and methanol molecules n_{H^+} = number of transported protons.

The electro-osmotic drag coefficient is a key parameter in the operation of a proton exchange membrane fuel cell. An increase in fuel cell current density inevitably increases the rate at which water and methanol molecules are carried in the solvating envelope of the ions (protons). In order to be able to operate a DMFC efficiently it is necessary to optimize the methanol supply to the anode electrode as a function of the fuel cell operating conditions. This can be done if key fuel cell parameters are known, with the electro-osmotic drag coefficient being one of these parameters.

Previous research investigating transport characteristics of polymer electrolyte membranes showed that electro-osmosis is a function of temperature and, in particular, of methanol concentration [5]. The electro-osmotic drag coefficient for methanol and water in different Nafion® membranes and a FT-FKH 1400/60 membrane, a membrane based on partially fluorinated super acids (PFPSA) with an equivalent weight of 1,400, was measured as a function of temperature and methanol concentration. The transport rate of water and methanol molecules was examined as a function of current density.
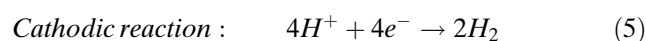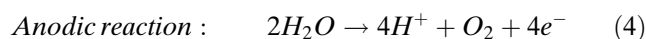
2 Experimental

A custom measuring cell was designed for determining the electro-osmotic drag coefficient in different proton exchange membranes. A similar approach in measuring the electro-osmotic drag coefficient of water was described by Zawodzinski et al. [6]. Verbrugge et al. [1] described the use of radioactive tracers for determining the electro-osmotic drag coefficient. A more common measurement setup for electro-osmotic experiments in aqueous electrolytes was introduced by Harff [7].

The experimental cell was composed of two chambers made of acrylic glass. Each of the two chambers had an internal volume of 25 ml. These two chambers were separated by the investigated proton exchange membrane (cross section surface area of the membrane was 50.3 cm^2). A simplified schematic of the experimental cell is shown in Fig. 1. Each chamber was

equipped with an electrode to allow current flow through the membrane. The current flow through the cell was controlled by a modified potentiostat (MP 75) as shown in Fig. 1. The expression H$^+$ (H$_2$O)$_n$ in Fig. 1 denotes the number of water molecules (n) being transported through the membrane in the solvating envelope of one proton in the direction of the proton flux (labelled with the arrow). H$^+$ (MeOH)$_m$ in Fig. 1 denotes the number of methanol molecules (m) being transported through the membrane in the solvating envelope of one proton.

The following reactions take place at the electrodes in deionized water

$$Anodic\ reaction: \qquad 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{4}$$

$$Cathodic\ reaction: \qquad 4H^+ + 4e^- \rightarrow 2H_2 \tag{5}$$

In order to quantify the electro-osmotic drag coefficient, the pretreated membrane was clamped in the measuring cell and the chambers were filled with a sulfuric acid/water solution and with a sulfuric acid/water/methanol solution of identical concentration, respectively. The low sulfuric acid content (0.35 M) on both sides of the membrane was necessary to provide sufficient conductivity for proton transport in the solution. The measuring cell assembly was accommodated in a thermostatic bath in order to be able to maintain a pre-defined cell temperature throughout the
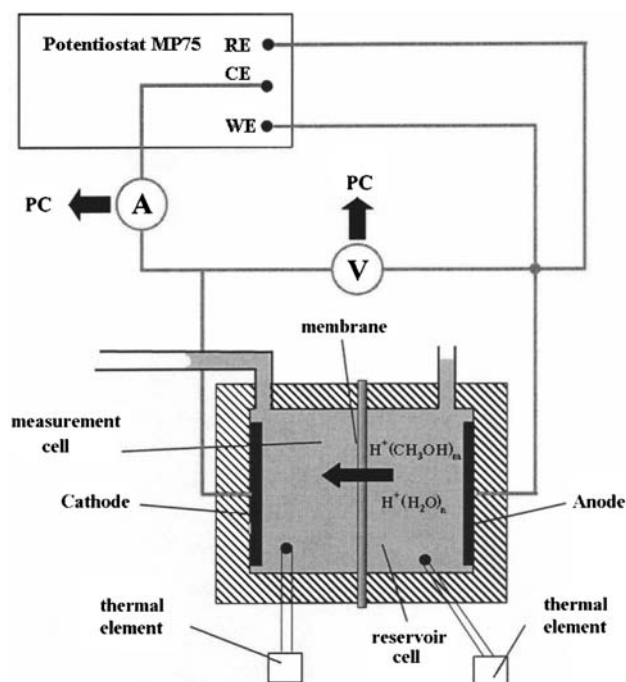
Fig. 1 Measurement setup for determination of the electroosmotic drag coefficient [5]

measurement. The amount of liquid transported through the membrane was measured using a capillary. Samples were taken from both chambers during the measurements. Methanol concentrations in the samples were determined using an improved gas chromatographic method using a headspace sampler and a gas chromatographic system. Transport characteristics of the membrane could thus be identified by comparing the transport rates of methanol and water [8].

The volumes of the cell chambers were small. The measurement setup was thus extremely sensitive to disturbances (e.g. leaks or evolving gas bubbles) caused by changes in volume of the fluids. Even very small losses of liquid lead to measurement uncertainties that cannot be neglected.

Changes in cell temperature during the measurements also lead to changes in the volume of the liquid. It was therefore necessary to ensure constant temperatures throughout the measurements by applying the thermostatic bath. Another contributing factor to a possible change in temperature is the Joule heat produced by the current flow, which causes an increase in temperature and therefore also a volumetric effect. Only very low current densities were used in order to minimize this effect.

It was important that the cell had two identical chambers with each half being filled with exactly the same volume of liquid. A change in volume due to an increase in temperature of the cell materials would therefore have the same effect on both chambers. It was also very important to pay attention to an exact match of the methanol concentrations in both chambers of the cell. Thus, additional transport phenomenon due to an existing concentration gradient could be avoided. Permeation of species due to a pressure gradient induced by evolving gas bubbles in one of the chambers also had to be avoided. This was done by applying the aforementioned restrictions in cell current density as well as by building the cell from transparent material. Visual observation of the measurement cell was thus possible, identifying operating conditions where gas bubbles were generated.

3 Results

3.1 Electro-osmotic drag coefficient—concentration dependence

In Fig. 2, the derived electro-osmotic drag coefficients for fully hydrated Nafion® (112, 115 and 117) membranes and the FT-FKH 1400/60 membrane are shown as a function of methanol concentration at 30 °C.
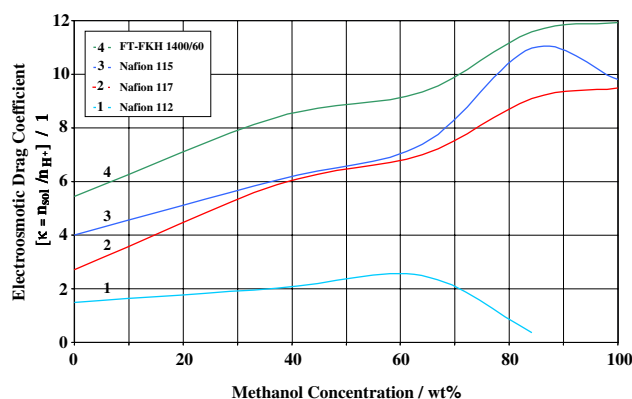
Fig. 2 Electroosmotic drag coefficients for different membrane types (Nafion® 112, 115, 117 and FT-FKH 1400/60) depending on the methanol concentration at 30 °C [5]

The results for the Nafion® 112 membrane do not reflect the electro-osmotic drag correctly, as this very thin membrane (~50 μm) swells considerably in methanol environment, making it very permeable. Other transport phenomena therefore mix with the electro-osmosis in the case Nafion® 112. This leads to the sharp drop in the electro-osmotic drag coefficient at methanol concentrations in excess of 60wt%. Similar characteristics were also derived with the drag coefficients of other membranes operated with very high methanol concentrations. However, the electro-osmotic drag coefficient is only superposed with other transport phenomena at methanol concentrations that are beyond the scope of interest for fuel cell applications.

It is interesting to see that the drag coefficient plots of Nafion® 115 and the 1400/60 FT-FKH membrane are roughly parallel (see Fig. 2). The electro-osmotic drag coefficient for the Nafion® membranes in pure water is between $\kappa_{H_2O} = 1.4$ and $\kappa_{H_2O} = 4$, which corresponds well with other values found in the literature (see below). As expected, the electro-osmotic drag coefficient increases with methanol concentration, as higher methanol concentrations lead to an enlargement of the canal diameters in the membranes and the molecules are carried along in the solvating envelope more easily. In Table 1 the electro-osmotic drag coefficients for different membranes are shown for methanol concentrations up to 20wt%.
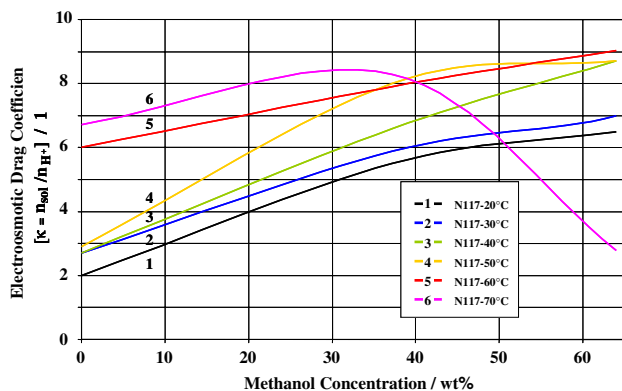
3.2 Electro-osmotic drag coefficient—temperature dependence

The dependence of electro-osmosis on temperature is shown in Fig. 3 and Table 2. The experiment was carried out with entirely hydrated Nafion® 117 membranes exposed to different methanol concentrations,

Table 1 Electroosmotic drag coefficients in methanol surrounding at 30 °C ($\Delta\kappa = \pm 1$) [5]

Methanol concentration			Electroosmotic drag coefficient $\kappa_{H_2O+MeOH} = n_{(H_2O+MeOH)}/n_{H^+}$			
wt%	vol%	M	Nafion® 112	Nafion® 115	Nafion® 117	FT-FKH 1400/60
0	0	0	1.5 [a]	4	2.7	5.4
5	6.3	1.5	1.6 [a]	4.3	3.1	5.8
10	12.4	3	1.6 [a]	4.6	3.6	6.3
15	18.3	4.4	1.7 [a]	4.8	4	6.7
20	24.1	6	1.8 [a]	5.1	4.5	7.1

[a] other transport phenomena dominate the electroosmosis (see text above)

Fig. 3 Electroosmotic drag coefficient for Nafion® 117 for different temperatures depending on the methanol concentration ($\Delta\kappa = \pm 1$)

Table 2 Electroosmotic drag coefficients for Nafion® 117($\Delta\kappa = \pm 1$)

Methanol concentration			Electroosmotic drag coefficient Nafion® 117 $\kappa_{H_2O+MeOH} = n_{(H_2O+MeOH)}/n_{H^+}$					
wt%	vol%	M	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C
0	0	0	2	2.7	2.7	2.9	6	6.7
5	6.3	1.5	2.5	3.1	3.2	3.6	6.2	7
10	12.4	3	3	3.6	3.8	4.4	6.5	7.3
15	18.3	4.4	3.5	4	4.3	5.1	6.8	7.7
20	24.1	6	4	4.5	4.8	5.8	7	8

only. This restriction was made because the measurement is complex and protracted. It is assumed that the two other Nafion® membranes 112 and 115 show a similar dependence because they are made of the same polymer.

The electro-osmotic drag coefficient was observed to rise with temperatures as shown in Fig. 3. The considerable increase in the values between 50 °C and 60 °C is remarkable and may be due to a change in the conductivity mechanisms (reinforced vehicle mechanism instead of Grotthuss mechanism) (see below).

Swelling of the Nafion® membrane becomes apparent at temperatures in excess of 70 °C and methanol concentrations in excess of 30wt%. This can be clearly seen with the curve of Nafion® 117 at 70 °C (the curve labeled 'N117-70 °C in Fig.3), where a strong decrease in the drag coefficient is observed for methanol concentrations in excess of 30wt%.

3.3 Electro-osmotic drag coefficient—current dependence

The relation between electro-osmosis and current was also examined using the same experimental setup. The measurements were carried out with a Nafion® 117 membrane in 42 vol% methanol solution (ratio of water:methanol molecules = 3:1).

A good linear relationship between electro-osmotic transport and current flow was obtained for the range of current densities investigated (Fig. 4). These results are also confirmed by Ötztürk [9].

3.4 Water and methanol—differences in transport phenomena

At methanol concentrations in excess of 40 vol% (> 10 M methanol) no preferential transport was observed. No significant concentration change was measured in either of the two measuring chambers. At a methanol concentration of 1:1 (MeOH:H₂O ratio), the same number of water and methanol molecules are dragged in the solvatic envelope of the protons. At methanol concentrations below 40 vol%, the electro-osmotic transport rate of water molecules is disproportionately high. With a solution consisting of 20 vol% methanol at the anode (electrolyte concentration neglected), more than 80 vol% of water is transported in the solvating envelope. Thus, the methanol concentration increases on the anodic side during operation of
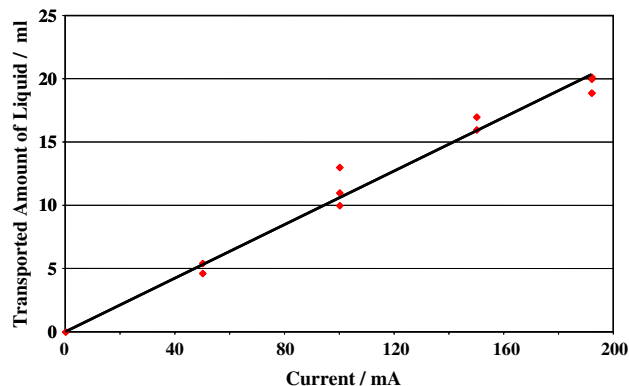
Fig. 4 Dependence of the electroosmotic transported amount of liquid on the current flow

the measurement and decreases on the cathodic side. The difference in transport behavior should, however, be relatively small due to the similarity of the molecules (dipole momentum methanol: 1.70 Debye [10], dipole momentum water: 1.85 Debye [11]).

3.5 Conductivity mechanisms

The proton-water/methanol and the polymer-water/methanol interactions have to be taken into consideration in order to be able to draw conclusions on the conductivity mechanism from the experimental results. Two aspects govern the interactions between protons and water/methanol: firstly, the solvating envelope dragging the latter in the direction of the proton flux. And secondly, the presence of protons and water molecules permits proton transfer reactions where a proton of a H_3O^+-ion is transferred to a neighboring H_2O molecule (Grotthuss mechanism).

The polymer-water/methanol interaction binds water and methanol molecules to the polymer and thereby hinders drag by the protons. The electro-osmotic drag coefficient is influenced by two temperature effects: at low temperatures there are more proton transfer processes which contribute to the proton flux, but not to the water and methanol transport. Secondly the polymer-water interaction becomes stronger, leading to lower values of the electro-osmotic drag at lower temperatures.

In Fig. 3, a strong increase in the drag coefficient can be seen with increase in temperature from 50 to 60 °C. This increase cannot be explained by a temperature-dependent change in membrane porosity or canal structure. This would rather suggest the aforementioned change in the conductivity mechanism (reinforced vehicle mechanism instead of Grotthus mechanism). The number of water molecules dragged per ion depends on the size of the ion and the pore size of the membrane [12]. These investigations have shown that all other ions carry more water molecules than the protons. The experimentally obtained values for the protons lie far under the predictions, an indication of the Grotthuss mechanism, i.e. for jumping (hopping) of the protons from one molecule to another.

4 Comparison with literature values

Helfferich [12] reports that 5 to 50 moles of water are transported per Faraday in typical ion exchange membranes. This results in a value of 5 to 50 molecules of water being dragged with each proton. Springer et al. [13] identified an electro-osmotic drag coefficient for water in an entirely hydrated Nafion® 117 membrane

of $\kappa_{H_2O} = 2.5 \pm 0.2$ at 30 °C and 50 °C. They also found that the electro-osmotic drag coefficient decreases strongly with the membrane water content.

Zawodzinski et al. [14, 15] determined a value of 2.5 to 2.9 for κ_{H_2O} for an entirely hydrated Nafion® 117 membrane with a water content of $\lambda = 22$ H_2O/SO_3H at 30 °C. According to Zawodzinski et al. the Grotthuss mechanism is responsible for the proton conductivity in well hydrated membranes.

Ise [16] investigated the electro-osmotic drag coefficient for water in entirely hydrated Nafion® 117 membranes using electrophoretic nuclear magnetic resonance (ENMR) and determined the electroosmotic drag coefficient $\kappa_{H_2O} = 2.6$ at 300 K ($\lambda \sim 21$ H_2O/SO_3H), $\kappa_{H_2O} = 2.9$ at 317 K ($\lambda \sim 20$ H_2O/SO_3H) and $\kappa_{H_2O} = 3.4$ at 350 K ($\lambda \sim 20$ H_2O/SO_3H).

Paddison et al. [17] determined an electro-osmotic drag coefficient of $\kappa_{H_2O} = 1$ in water vapor equilibrated Nafion® membranes and found the values for κ_{H_2O} to be 2 to 3 in membranes immersed in water. Ren, Henderson and Gottesfeld obtained a value of $\kappa_{H_2O} = 2$ at 150 °C [18] in a direct methanol-fuel cell for entirely hydrated Nafion® 117 membranes. All of these investigations show a very good correspondence with the present values for Nafion® 117.

The temperature dependence of the electro-osmotic drag coefficient was examined by Okada et al. [19]. They observed a small temperature dependence and determined a value of $\kappa_{H_2O} = 3.2$ at 80 °C. An increase in the electro-osmotic drag coefficient was also reported up to $\kappa_{H_2O} = 5.0$ for Nafion® 117 at 120 °C [20]. The values for Nafion® 117 in the present work show a considerably stronger temperature dependence, so the values do not show a good correspondence with the values obtained by Okada et al. However, Okada et al. also confirm an increase of the electro-osmotic drag coefficient with temperature.

It should also be taken into consideration that in a continuously working fuel cell (at least in a PEM fuel cell) the membrane is usually not entirely hydrated (water activity < 1). A concentration gradient is normally observed through the membrane, so the electro-osmotic drag coefficient is smaller than in the experiments described in the present work.

Data for electro-osmotic drag coefficients for swollen membranes in methanol solution could not be found in the literature.

5 Conclusions

A comprehensive investigation of methanol crossover in DMFCs has been made with different membranes

and separators using an improved gas chromatographic method [8]. One of the factors that play a key role in methanol crossover is electro-osmosis. We have investigated electro-osmotic drag from the anode to the cathode of a fuel cell as a function of methanol concentration, temperature and current density. Drag coefficients measured with the electro-osmotic transport of water compare favorably with literature. The set of parameters presented in this work also specifically addressed the variation of the drag coefficients with methanol concentration. This data is inevitably required with a thorough analysis of methanol crossover. Results indicate no preferential transport of methanol or water with methanol concentrations in excess of 40wt%, but a disproportionately high rate of electro-osmotic water transport with smaller methanol concentrations. The experimental setup only failed to deliver drag coefficients with very high methanol concentrations due to swelling of the membranes. This limitation is, however, not considered critical as these very high methanol concentrations are normally not found in normal DMFC operation.

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