

# Determination of methanol diffusion and electroosmotic drag coefficients in proton-exchange-membranes for DMFC

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## Abstract

Methanol diffusion and electroosmotic drag coefficients for different polymer–electrolyte-membranes have been investigated. It is essential to understand the transport phenomena of water and methanol transport in perfluoro sulfonic acid (PSA) membranes under different methanol concentrations and current densities in order to optimize cell performance and operation. The dependence of the methanol diffusion coefficient as well as the electroosmotic drag coefficient on methanol concentration and current density were observed. The results are discussed in comparison to measured values obtained by other scientific groups.

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## 1. Introduction

A key performance limiting factor in operation of a DMFC fuel cell is methanol transport through the electrolyte from anode to cathode electrode, known as methanol crossover. It is essential to investigate the mechanisms of the methanol transport through the electrolyte in order to gain a better understanding of the crossover mechanism.

Methanol diffuses due to a gradient in concentration, pressure and electroosmosis through the electrolyte.

Knowledge of transport rates of ions and solvents in ionic exchanging membranes is necessary for intelligent designs in various different systems [1,2]. These types of membrane are also used in a variety of areas in the field of medicine and biology, not only in fuel cell technology. In this article, the results for investigations on the methanol diffusion coefficient of different polymer–electrolyte-membranes are presented, and the theoretical and experimental information is discussed that is required for a characterization of water and methanol transport in perfluoro sulfonic acid (PSA) membranes under current flow.

The proton flux through a PEM leads to a water transport in the same direction due to the hydration of the protons. In a DMFC, this leads to water and an additional methanol transport through the membrane. This effect is called electroosmotic drag (electroosmosis) [3]. In direct hydrogen PEM fuel cells, this leads to a decrease of water concentrations at the anode electrode, and eventually even to a dehydration of the polymer–electrolyte-membrane under worst case conditions, so that the resistance of the membrane is increased and the efficiency of the fuel cell is decreased.

## 2. Methanol diffusion coefficient

In order to obtain the methanol diffusion coefficient of different membranes two different measurement methods are used, a stationary and a non-stationary measurement setup.

The main principle for a diffusion measurement under stationary conditions is shown in Fig. 1a. A reservoir cell contains a methanol solution of constant concentration  $c_V$ . Methanol diffuses through the membrane in a measurement cell, where a constant volume flow is selected. The deionized water flowing into the cell is mixed with the diffused methanol in the measurement cell. The outgoing flux contains the methanol concentration  $c_M$ , which is measured.

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The effective diffusion coefficient  $D_{\text{eff}}$  in a stationary measurement setup can be obtained from the mass balance of the convective and diffusive transport of methanol.

The number of methanol molecules flowing out of the measurement cell equals the number of methanol molecules diffusing through the membrane:

$$c_M \dot{V} = AD_{\text{eff}} \frac{c_V - c_M}{L} \quad (1)$$

where  $c_M$  is the methanol concentration at measurement cell outlet (mol m<sup>-3</sup>) or (vol.%);  $\dot{V}$  the volume flowing through measurement cell (m<sup>3</sup> s<sup>-1</sup>);  $A$  the membrane area (m<sup>2</sup>);  $D_{\text{eff}}$  the effective methanol diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>);  $c_V$  the methanol concentration in reservoir cell (constant) (mol m<sup>-3</sup>) or (vol.%) and  $L$  is the membrane thickness (m).

$c_M$  is measured, while all other parameters are already known or measured in prior examinations, thus the effective methanol diffusion coefficient can be obtained:

$$D_{\text{eff}} = \frac{c_M \dot{V} L}{A(c_V - c_M)} \quad (2)$$

The volume of the measurement cell should be very small to be able to minimize the time until a stationary condition can be observed.

The second method applied is a measurement setup with non-stationary conditions in the measurement cell. From a reservoir cell containing a solution with a constant methanol concentration  $c_V$ , methanol diffuses through the membrane into the measurement cell (as shown in Fig. 1b). The measurement cell is filled with deionized water, where the level of the methanol concentration  $c_M(t)$  is slowly rising.

Under non-stationary conditions, Fick's second law of diffusion mathematically describes the diffusion occurring in the measurement cell. The mass balance at a differential cross-section of the membrane is:

$$\frac{\partial c}{\partial t} = D_{\text{eff}} \frac{\partial^2 c}{\partial z^2} \quad (3)$$

Under the conditions:

- $t = 0, c(z) = 0; z > 0$  (at the beginning of the examination the methanol concentration in the measurement cell is zero),

- $c(0) = c_V$  (the methanol concentration at the membrane surface on the reservoir cell side remains constant), and
- $z = 0, c(t) = c_V$ .

$$-D_{\text{eff}} A \frac{\partial c}{\partial z} \Big|_L = V_M \frac{\partial c_M}{\partial t} \Big|_L \quad (\text{mass balance}), \quad z = L \quad (4)$$

where  $V_M$  is the total volume of the measurement cell (m<sup>3</sup>).

The solution of this problem is solved numerically.

Another method used for determining  $D_{\text{eff}}$  takes a “nearly stationary” condition into account, which is achieved after a certain measurement time  $t_1$ . The concentration profile established through the membrane cross-section shows an almost linear behavior. With increasing measurement time only a change of its gradient (shown in Fig. 1b) can be observed. It is possible to use this as a “nearly stationary” condition, so it is not necessary to use Fick's second law of diffusion for further diffusion analysis.

After a certain time  $t_1$ , the “nearly stationary” condition is setup. An almost linear concentration profile is observed, where only the gradient changes in time, thus the mass balance in both cells can be described as:

$$\frac{\partial c_V}{\partial t} = \frac{1}{V_V} \left( AD_{\text{eff}} \frac{c_M - c_V}{L} \right) = 0 \quad (5)$$

where  $V_V$  is the total volume of the reservoir cell (m<sup>3</sup>).

It is assumed, that the reservoir cell contains a constant methanol concentration, because the methanol solution is steadily renewed.

The measurement cell is described through:

$$\frac{\partial c_M}{\partial t} = -\frac{1}{V_M} \left( AD_{\text{eff}} \frac{c_M - c_V}{L} \right) \quad (6)$$

Solving this equation the separation of parameters method is used:

$$\ln(c_M - c_V) \Big|_{c_M(t_1)}^{c_M(t_2)} = -\frac{1}{V_M} \left( \frac{AD_{\text{eff}}}{L} \right) \Big|_{t_1}^{t_2} \quad (7)$$

$$\ln \left( \frac{c_M(t_2) - c_V}{c_M(t_1) - c_V} \right) = -D_{\text{eff}} \frac{A}{V_M L} (t_2 - t_1) \quad (8)$$

where  $c_M(t_1)$  and  $c_M(t_2)$  are the methanol concentrations in the measurement cell at the time  $t_1$  and  $t_2$  ( $t_2 > t_1$ ).

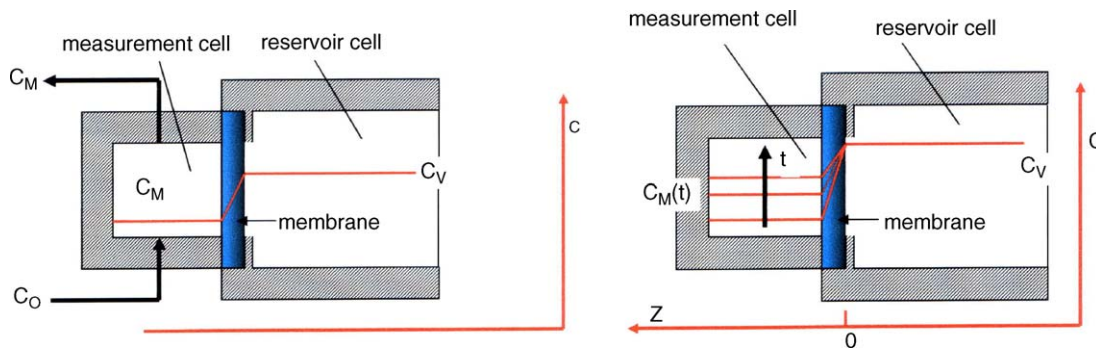


Fig. 1. Measurement setup for (a) stationary methanol diffusion measurement cell and (b) non-stationary methanol diffusion measurement cell.

Now the effective methanol diffusion coefficient can be obtained using Eq. (8):

$$D_{\text{eff}} = -\frac{V_M L}{A(t_2 - t_1)} \ln \left( \frac{c_M(t_1) - c_V}{c_M(t_2) - c_V} \right) \quad (9)$$

2.1. Measurement setup

In order to measure diffusion of methanol through a polymer–electrolyte-membrane as well as other membranes and separators, a non-stationary measurement cell made of acrylic glass is used. By implementing an additional pump, this measurement setup can be altered to a stationary measurement setup. In order to keep methanol consumption low, this was only used with separators with large diffusion coefficients (e.g. SP800/40).

A water/methanol solution (1:1 mol) is pumped out of a storage tank and a special valve was constructed to be sure that most of the gas bubbles and of the pumped volume gets back into that tank. Thus it is assured that no gas bubbles can reach the membrane during the examinations. Only a small amount of liquid (approximately 9 ml min<sup>-1</sup>) flows into the measurement cell. A certain number of methanol molecules diffuses through the membrane into the measurement cell, which is again filled with deionized water, where a continuous rise in the methanol concentration can be detected. A slowly rotating stirrer was implemented to have a good balance in concentration throughout the whole measurement cell. After pre-defined time steps, probes are taken from the measurement cell and replaced by deionized water, which was considered with the analysis. To assure that the hydrostatic pressure is constant throughout the cell, the outlet is at the same height as the liquid level in the measurement cell. The temperature is observed using thermal elements (Fig. 2).

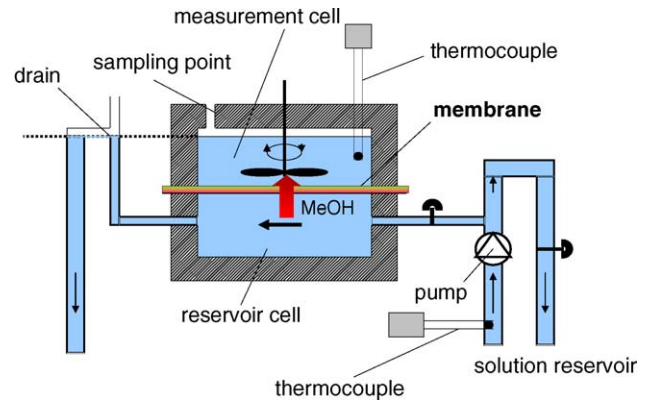


Fig. 2. Schematic view of measurement setup for the determination of methanol diffusion coefficients.

The probes taken are examined using a gas chromatograph and the effective methanol diffusion coefficient is determined using Eq. (9), considering the changes in concentration due to the taken probes as mentioned before.

2.2. Results

Methanol diffusion coefficients obtained are shown in Fig. 3 and listed in Table 1. A good correspondence to values already published for Nafion® could be achieved. No literature values are known for the other membranes and the separator SP800/40, which is a non-woven polypropylene separator of 150 μm thickness. Small values of the effective diffusion coefficient could be measured at the FT-FKH950/30MF and PK12CE/714 membranes, which are polymer–electrolyte-membranes produced by an industrial partner not commercially available yet.

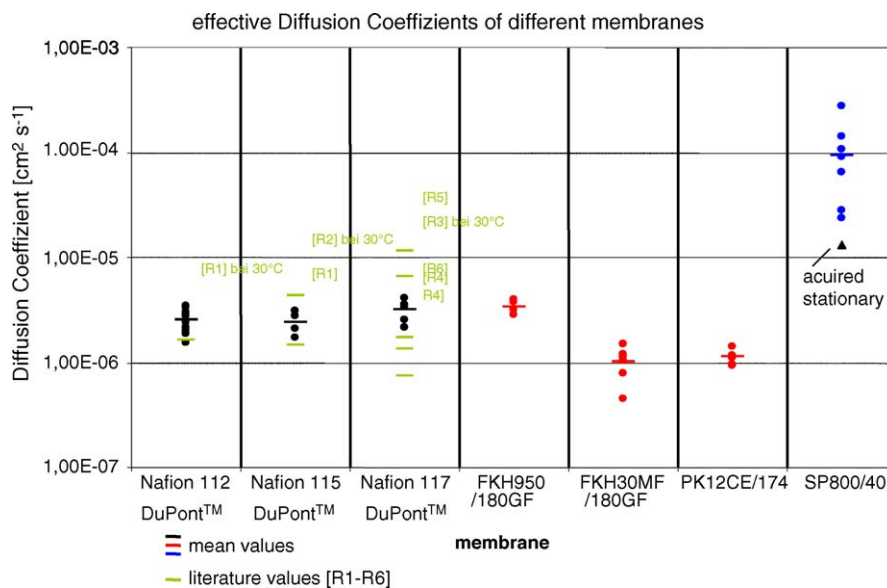


Fig. 3. Measured effective methanol diffusion coefficients for different membranes and separators in comparison to literature values. [R1] Ref. [17]; [R4] Ref. [20]; [R2] Ref. [18]; [R5] Ref. [21]; [R3] Ref. [19]; [R6] Ref. [22].

Table 1  
Values of measured effective methanol diffusion coefficients for different membranes and separators at 23 °C

Membrane	Mean value for effective methanol diffusion coefficient (cm <sup>2</sup> s <sup>-1</sup> )
Nafion® 112 DuPont™	$2.51 \times 10^{-6}$
Nafion® 115 DuPont™	$2.40 \times 10^{-6}$
Nafion® 117 DuPont™	$3.15 \times 10^{-6}$
FKH950/180GF	$3.40 \times 10^{-6}$
FKH950/30MF	$1.02 \times 10^{-6}$
PK12CE/714	$1.12 \times 10^{-6}$
SP800/40	$9.35 \times 10^{-6}$

An estimation of uncertainties on the experimental data was done by an error propagation using the remainder theorem of Gauss and showed results in the range of  $\pm 30\%$ .

A large permeability for methanol (and water) is observed with the separator SP800/40. The whole liquid of the reservoir cell penetrated the separator within seconds due to its high porosity, which made an alternation of the measurement method necessary. In this case a measurement setup for a stationary methanol diffusion measurement cell was used. The measurement cell gets permanently spilled with deionized water (shown in Fig. 1a). The methanol content is examined with a headspace gas chromatography system described in [4]. Other separators got tested in short examinations, but showed a similar high permeability.

### 3. Electroosmotic drag coefficient

Electroosmosis is quantified by the electroosmotic drag coefficients  $\kappa_{\text{H}_2\text{O}}$  and  $\kappa_{\text{MeOH}}$ . These coefficients describe how many water and/or methanol molecules are carried along with each proton at the vectored proton transport path through the membrane, assuming that the gradient of the water concentration is negligible small through the whole membrane

$$\kappa_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}^+}} \quad (10)$$

$$\kappa_{\text{MeOH}} = \frac{n_{\text{MeOH}}}{n_{\text{H}^+}} \quad (11)$$

$$\kappa_{\text{H}_2\text{O}+\text{MeOH}} = \frac{n_{\text{H}_2\text{O}+\text{MeOH}}}{n_{\text{H}^+}} \quad (12)$$

where  $n_{\text{H}_2\text{O}}$  is the number of transported water molecules;  $n_{\text{MeOH}}$  the number of transported methanol molecules;  $n_{\text{H}_2\text{O}+\text{MeOH}}$  the number of transported water and methanol molecules and  $n_{\text{H}^+}$  is the number of transported protons.

More water and methanol molecules are carried along in the solvating envelope of the ions (protons) as higher currents flow through the fuel cell. Hence, it is important to determine the electroosmotic drag coefficient in order to be able to adjust the water and methanol concentrations in the fuel cell membrane.

This transport mechanism depends on the current density, as well as on the electrolyte (membrane). Trans-

port characteristics of the membrane change with the methanol concentration, thus in this investigation the electroosmotic drag coefficient for methanol and water in different Nafion® membranes and a FT-FKH 1400/60 membrane are measured as a function of methanol concentration. Additionally, it is examined whether there is a difference between the transport of water molecules and methanol molecules.

#### 3.1. Measurement setup

A measuring cell for the determination of the electroosmotic drag coefficient in different polymer–electrolyte-membranes was constructed. Zawodzinski et al. [5] and Verbrugge and Hill [2] described similar methods to measure the electroosmotic drag coefficient of water. The latter used radioactive tracers to determine the electroosmotic drag coefficient. A common measurement setup for electroosmotic experiments in aqueous electrolytes is presented in an article of Harif [6].

Two chambers with a volume of 25 ml each are combined to form a experimental cell made of acrylic glass and separated by the polymer–electrolyte-membrane as described in [7] (schematic view in Fig. 4). An electrode mounted in each chamber allows the current flow through the membrane with a membrane cross-section area of 50.3 cm<sup>2</sup>. The current flow through the cell was controlled by a potentiostat (MP 75). This instrument was altered to a Galvanostat by taking a high accuracy resistance of 10 Ω to set the current flow to a constant up to a maximum of 200 mA.

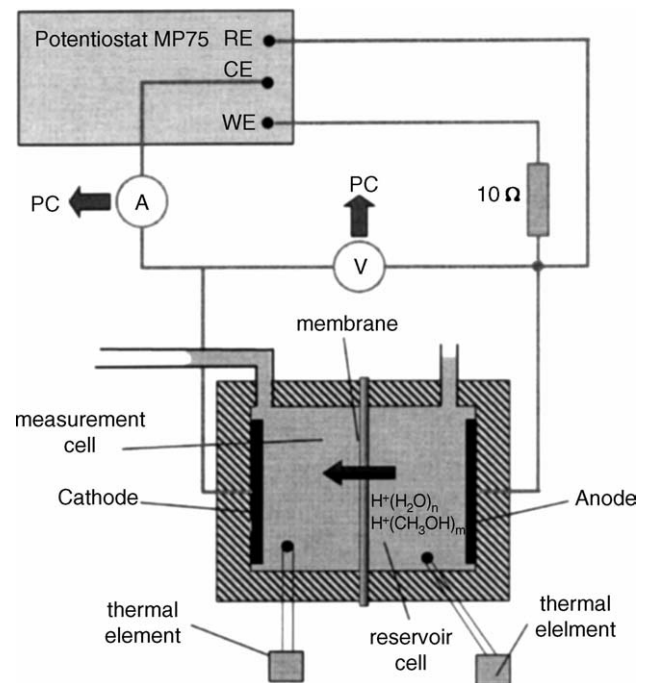
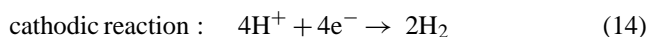
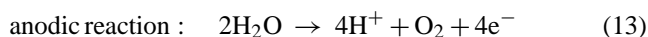


Fig. 4. Measurement setup for determination of the electroosmotic drag coefficient.

The following reactions occur at the electrodes when used in pure water:



In order to quantify the electroosmotic drag coefficient, the pretreated membrane is clamped in the measuring cell, and both sides of the cell are filled with a sulfuric acid/water solution and with a sulfuric acid/water/methanol solution with identical concentration, respectively. A low sulfuric acid content (0.35 M) on both sides is necessary to provide the required conductivity for the proton transport. The cell temperature is kept at the selected level by accommodation in a thermostatic bath. A capillary is used to determine the amount of liquid transported through the membrane. Probes are taken from both chambers after each measurement, and the methanol concentration is determined with a headspace sampler and a gas chromatography system in order to be able to draw conclusions on the preferential transport of water or methanol.

Due to the small volumes involved, slightest variations of operating conditions (e.g. temperatures) or effects influencing the measurements (e.g. leaks, gas bubbles) must be avoided at all times. Temperatures are thus observed at all times in order to avoid any variations of liquid volume due to thermal expansion. Joule heat which is generated as soon as a current flows inside the cell has to be minimized by applying only small current densities.

The measurement cells have to be built with the identical internal volume. Thus, variations of liquid volume due to temperature effects cancel out.

Both sides of the cell are filled with a solution of identical methanol concentration prior to the measurements in order to avoid the generation of a concentration gradient which would

add an additional mechanism of methanol transport through the cell.

### 3.2. Electroosmotic drag coefficient—concentration dependence

In Fig. 5, the acquired electroosmotic drag coefficients for totally hydrated Nafion<sup>®</sup> (112, 115 and 117) membranes and the FT-FKH 1400/60 membrane are shown as a function of methanol concentration at 30 °C.

The results for the Nafion<sup>®</sup> 112 membrane cannot be referred to as realistic results, because this very thin membrane (~50 μm) swells very strongly in methanol surroundings by which this membrane gets very permeable and other transport phenomena overlay the electroosmosis. The electroosmotic drag coefficient could thus not be measured for Nafion<sup>®</sup> 112 in pure methanol. At higher MeOH-concentrations (or pure methanol) this effect becomes also apparent with other membranes increasingly—which leads to a turning point in the measured curve. It is not possible to determine the electroosmotic drag coefficient separated from other transport phenomena. However, this phenomenon occurs only at very high methanol concentrations which are not suitable for the application in fuel cells, anyway.

It is very interesting to see the roughly parallel curves for the Nafion<sup>®</sup> 115 membrane and the membrane FT-FKH 1400/60. The electroosmotic drag coefficient for the Nafion<sup>®</sup> membranes in pure water is between  $\kappa_{\text{H}_2\text{O}} = 1.4$  and 4, which corresponds to other values found in literature (see below). As expected, the electroosmotic drag coefficient increases with rising methanol concentrations, because higher methanol concentrations lead to an increase of the canal diameters in the membranes and the molecules can be carried along in the solvating envelope more easily. In Table 2, the electroosmotic drag coefficients for different membranes are shown for

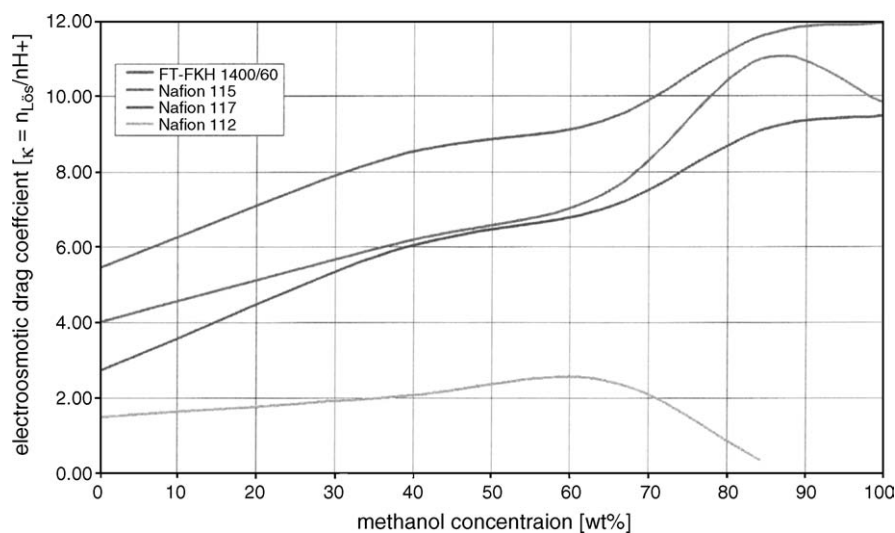


Fig. 5. Electroosmotic drag coefficients for different membrane types (Nafion<sup>®</sup> 112, 115, 117 and FT-FKH 1400/60) depending on the methanol concentration at 30 °C ( $\Delta\kappa = \pm 1$ ) [7].



Table 2  
Electroosmotic drag coefficients in methanol surrounding at 30 °C ( $\Delta\kappa = \pm 1$ )

Methanol concentration			Electroosmotic drag coefficient, $\kappa_{\text{H}_2\text{O}+\text{MeOH}} = n_{\text{H}_2\text{O}+\text{MeOH}}/n_{\text{H}^+}$			
wt.%	vol.%	$M$ (mol l <sup>-1</sup> )	Nafion® 112	Nafion® 115	Nafion® 117	FT-FKH 1400/60
0	0	0	1.5 <sup>a</sup>	4	2.7	5.4
5	6.3	1.5	1.6 <sup>a</sup>	4.3	3.1	5.8
10	12.4	3	1.6 <sup>a</sup>	4.6	3.6	6.3
15	18.3	4.4	1.7 <sup>a</sup>	4.8	4	6.7
20	24.1	6	1.8 <sup>a</sup>	5.1	4.5	7.1

<sup>a</sup> Other transport phenomena overlay the electroosmosis.

methanol concentrations up to 20 wt.% (24 vol.%; 6 M). Measurement uncertainties are quite high ( $\Delta\kappa = \pm 0.8$ –1) mainly due to the large measurement cell dimensions, which will be reduced for further measurements.

### 3.3. Difference in transport phenomena for water and methanol

The question whether methanol or water is preferably transported through the electrolyte is critical for DMFC operation. At high methanol concentrations with more than 40 vol.% (>10 M MeOH), no preferential transport of a molecule species could be derived. This implies that no significant change in concentrations could be measured in the two measuring chambers of the experimental setup. At methanol concentrations of 1 MeOH:1 H<sub>2</sub>O, equal numbers of water molecules and methanol molecules are carried along in the solvatic envelope. At methanol concentrations under 40 vol.%, more water molecules are carried along than implied by the methanol concentrations present. If, for instance, there are 20% of methanol molecules and 80% of water molecules on the anodic side (electrolyte concentration neglected) present, then not 80% of water molecules are carried along in the solvatic envelope, but more. So the methanol concentration rises at the anodic side and decreases at the cathodic side. The measurement results show a big dispersion so that, unfortunately, this observation could not be quantified. The difference in transport behavior should be relatively low, due to the similarity of molecules (dipole momentum methanol: 1.70 D [8], dipole momentum water: 1.85 D [9]).

### 3.4. Comparison with literature values

Helferich [10] reports that in typical ionic exchange membranes 5–50 mol water are transported per Faraday. Five to 50 molecules water are thus carried per proton. Some data are also found especially for Nafion® membranes. Springer et al. [11] identified an electroosmotic drag coefficient for water in an entirely hydrated Nafion® 117 membrane of  $2.5 \pm 0.2$  at 30 and 50 °C. It was determined that the electroosmotic drag coefficient decreases strongly with the water content of the membrane.

Zawodzinski et al. [12,13] determined a value from 2.5 to 2.9 for an entirely hydrated Nafion® 117 membrane with

a water content of  $\lambda = 22$  H<sub>2</sub>O/SO<sub>3</sub>H at 30 °C. It is suggested that the Grotthuss mechanism is responsible for the proton conductivity in well-hydrated membranes, however, in a smaller magnitude compared to aqueous solutions.

Ise [14] investigated the electroosmotic drag coefficient for water in entirely hydrated Nafion® 117 membranes using electrophoretic nuclear magnetic resonance (ENMR) and determined the electroosmotic drag coefficient  $\kappa_{\text{H}_2\text{O}} = 2.6$  at 300 K ( $\lambda \sim 21$  H<sub>2</sub>O/SO<sub>3</sub>H),  $\kappa_{\text{H}_2\text{O}} = 2.9$  at 317 K ( $\lambda \sim 20$  H<sub>2</sub>O/SO<sub>3</sub>H) and  $\kappa_{\text{H}_2\text{O}} = 3.4$  at 350 K ( $\lambda \sim 20$  H<sub>2</sub>O/SO<sub>3</sub>H).

Paddison et al. [15] determined an electroosmotic drag coefficient of 1 for in water vapor equilibrated Nafion® membranes and found the values 2–3 for in water immersed membranes. Ren et al. [16] obtained a value of 2 at 150 °C in a direct methanol-fuel cell for entirely hydrated Nafion® 117 membranes. All these investigations show a very good correspondence with our values found for Nafion® 117.

It should be also taken into consideration that in a continuously working fuel cell (at least in a PEM) the membrane usually is not entirely hydrated (water activity < 1) when comparing the data derived in the measurements with reference data gained from literature. There is a concentration gradient through the membrane, so the electroosmotic drag coefficient is smaller than in the experiments carried out with the experimental setup described.

Data for an electroosmotic drag coefficient in methanol solutions for swelled membranes could not be found in literature.

## 4. Conclusions

To improve the performance of a DMFC fuel cell it is necessary to reduce the methanol crossover through the electrolyte. It is essential to determine the fractions of the different types of methanol transport and their dependence on temperature, concentration and pressure in order to minimize the total crossover effect.

With the investigated measurement setup it is possible to accurately determine these different types of methanol transport and their dependence on temperature, concentration and pressure. These measurements are used to build a semi-empirical model of methanol crossover for direct methanol fuel cells, which is used to evaluate different types of electrolytes.

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