

Introduction of an improved gas chromatographic analysis and comparison of methods to determine methanol crossover in DMFCs

T. Schaffer^{a,*}, V. Hacker^a, T. Hejze^a, T. Tschinder^a, J.O. Besenhard^a, P. Prenninger^b

^a Institute for Chemistry and Technology of Inorganic Materials, CD-Laboratory for Fuel Cell Systems, Graz University of Technology, Steyrergasse 21, 8010 Graz, Austria

^b AVL List GmbH, Fuel Cell Systems, Powertrain Engineering, Hans-List-Platz 1, 8020 Graz, Austria

Accepted 12 November 2004

Available online 1 June 2005

Abstract

Direct methanol fuel cells (DMFCs) are capable of utilising a liquid fuel directly in the fuel cell and they are therefore an interesting option for a variety of mobile and portable applications. Still there are several barriers which have to be overcome before DMFCs are able to compete with conventional technologies. A major restriction in reaching high efficiencies with DMFCs is methanol crossover from anode to cathode. This work discusses several methods to characterise the methanol crossover and introduces a newly developed measurement method which allows an exact determination of methanol crossover in DMFCs with liquid and solid electrolytes.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Direct methanol fuel cell; Methanol crossover; Methanol barriers; Polymer electrolyte membrane; Gas chromatography

1. Introduction

Fuel crossover occurs to some degree in all low temperature fuel cells. Particularly in direct methanol fuel cells (DMFCs), however, it causes problems which influence the performance of the cell considerably. Methanol crossover in the DMFC does not only result in additional fuel consumption of the cell, but it also reduces the cell voltage by the so called “mixed potential”. Therefore, methanol crossover from anode to cathode through the electrolyte is the main technical barrier for a high efficiency of DMFCs, besides the slow catalytic rate of methanol oxidation at the anode electrode [1,2].

The loss of methanol due to fuel crossover effects is often described via an *equivalent current* in order to directly relate the crossover to the current density in the cell. This is the current which would be produced by the methanol, if it had reacted electrochemically at the fuel anode. Based

on this current, the *fuel utilisation* as a descriptive figure for methanol crossover in a DMFC is calculated and shown. The described fuel utilisation coefficient gives the ratio of the fuel that is usefully converted at the anode (cell current) to the total fuel consumed at the anode (cell current plus equivalent current). The values of fuel utilisation therefore not only provide information about the maximum efficiency of different cell assemblies, but the values also show the operating “window” (range of current density) in which a fuel cell should be operated in its application.

Fig. 1 shows fuel utilisation curves for different DMFCs at different temperatures and pressures with a methanol concentration of up to 1 M. A single cell operated at different temperatures (B, F, G, H, J) leads to very high power densities of more than 250 mW cm^{-2} at operation temperatures above 100°C (at the low voltage of 0.5 V) [5]. In order to reach a high efficiency, the single cell should be operated with low current density. At low current densities, however, the fuel utilisation becomes small as the measurement curve at $T = 120^\circ\text{C}$ (J) shows. Even at current densities around 250 mA cm^{-2} , the fuel utilisation is only approx.

* Corresponding author.

E-mail address: thomas.schaffer@tugraz.at (T. Schaffer).

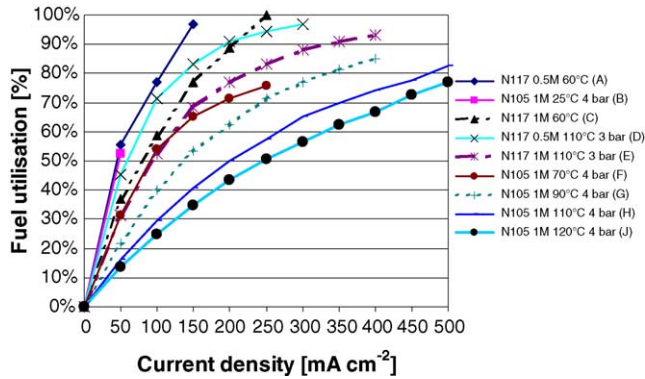


Fig. 1. Fuel utilisation curves for different DMFCs at different temperatures and pressures with a methanol concentration of up to 1 M: (A and C) [3] Nafion 117 membranes, E-Tek carbon cloth as gas diffusion and fuel diffusion electrodes and as catalyst Pt–Ru black for the anode (4 mg cm^{-2}) and Pt black for the cathode (4 mg cm^{-2}). MeOH/O₂; (D and E) [4] Nafion 117, 4 mg cm^{-2} PtRuC anode, mg cm^{-2} PtC cathode, 110°C , 3 bar, oxygen $300 \text{ mN l min}^{-1}$; (B, F, G, H and J) [5] Nafion 105, cathode flow 4.1 min^{-1} air, anode: unsupported 5.4 mg cm^{-2} Pt–Ru, 2.5 bar pressure (outlet). Cathode: unsupported 6.3 mg cm^{-2} Pt, 4 bar pressure (outlet).

50%, implying that the methanol loss due to permeation is as high as the cell current density. In order to reduce methanol crossover you have to operate the cell with even higher current densities, as the array of curves shows, that for low methanol concentrations the permeation through the MEA decreases with increasing current densities. However, for the operation window it has to be considered, that at higher current densities the cell efficiency is strongly reduced by the Faradaic efficiency.

Fig. 2 shows the influence of the methanol concentration on the methanol permeation through a cell with methanol concentrations at the anode above 1 M. Most of the operated cells do not even reach a fuel utilisation of 80%.

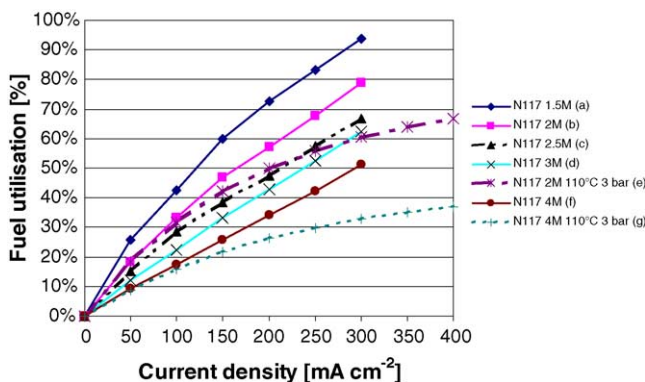


Fig. 2. Fuel utilisation curves for different DMFCs at different temperatures and pressures with methanol concentrations above 1 M: (a–d and f) [3] Nafion 117 membranes, E-Tek carbon cloth as gas diffusion and fuel diffusion electrodes and as catalyst Pt–Ru black for the anode (4 mg cm^{-2}) and Pt black for the cathode (4 mg cm^{-2}). MeOH/O₂; (e and g) [4] Nafion 117, 4 mg cm^{-2} PtRuC anode, 4 mg cm^{-2} PtC cathode, 110°C , 3 bar, oxygen $300 \text{ mN l min}^{-1}$.

2. Determination of methanol crossover during operation

The commonly used method to determine methanol crossover in an assembled DMFC is to monitor the CO₂ content in the cathode exhaust gas flux. The CO₂ level in the cathode exhaust gas flux is determined by using an optical infrared sensor, by gas chromatographic analysis, or by mass spectrometry [6–8]. These measurements imply, that the methanol transported through the electrolyte is completely oxidised at the cathode. If an infrared analysis is performed, a catalytic burner is sometimes used to convert the remaining methanol in the gas outlet to CO₂. It has to be considered that, depending on the current density, CO₂ is produced at the anode and also permeates to the cathode along with the methanol. It was found that the fraction of CO₂ permeating the membrane at the cathodic side is in the range of 20% at room temperature and OCV, rising to 25% at higher current densities [9]. Under special circumstances (low methanol concentration, high current density), the amount of CO₂ passing from the anode to the cathode can be even higher than the amount of CO₂ formed at the cathode by methanol oxidation [10]. For the determination of the carbon dioxide crossover different methods were developed.

The carbon dioxide flux can be approximately determined by half-cell measurements, where carbon dioxide is produced at the anode and passes together with methanol through the membrane to the cathode. The cathode itself gets flushed with nitrogen gas. The carbon dioxide flux through the membrane can be determined, since the methanol is not oxidised at the cathode.

Another method uses methanol-tolerant catalysts at the cathode, which do not oxidise the permeating methanol. The amount of CO₂ permeated to the cathode could also be calculated from the missing CO₂ fraction in the anode exhaust. For exact measurement, a method of gravimetric determination of BaCO₃ to analyse is reported ($\text{Ba}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O}$) [11].

2.1. Methods examined for methanol crossover reduction

Two different approaches for methanol crossover reduction are examined at Graz University of Technology. One approach investigates a pumped liquid electrolyte that washes out the permeating methanol, and the second proposed solution uses a barrier layer on the membrane to reduce the methanol crossover.

2.1.1. Barrier layers on polymer electrolyte membranes for methanol crossover suppression

A very promising strategy for the suppression of methanol crossover in DMFCs is the introduction of functional layers as a methanol barrier. These can be either a substitute for existing and widely used polymer electrolytes – like Nafion – or be deposited as an additional layer onto these electrolytes,

thus combining the good ion conductivity of the substrate with the methanol blocking ability of the coating. Two main directions can be spotted:

- new types of polymer electrolytes,
- layers of metals which exhibit a certain permeability for hydrogen.

Phenyl phosphonic acid functionalized poly[aryloxy-phosphazene] and sulfonated polyphosphazene membranes [26,12] are candidates of the first group. Their diffusion coefficient for methanol is significantly lower compared to Nafion and if their ionic conductivity can be increased, an improvement of polymer electrolyte technology will be achieved.

The other strategy, the use of metallic layers is schematically shown in Fig. 3. It takes advantage of the fact that some metals – mainly palladium, but tantalum and its alloys or niobium and its alloys are also considered [13] – are permeable for hydrogen.

The charge transport in a fuel cell takes place primarily by hydrogen ions. These can be reduced on the surface of the metallic layer which faces the anode, cross the metallic layer in their atomic state and finally be oxidised on the surface of the metallic layer facing the cathode. Thus, formally an electric compensation current crosses the metallic layer diametrically opposed to the hydrogen flow. Methanol, which is dissolved in the electrolyte between the anode and the metallic layer does not react at the metallic surface and will not penetrate, provided the layer contains no defects. It is clear that such an assembly will not be loss-free and the losses contribute to a reduction of the (hypothetical) cell voltage. The reasons for this are:

- electrochemical charge transfer overpotentials on the metal surfaces,
- overpotential from limited hydrogen diffusion through the metal,
- ohmic losses from the compensation current.

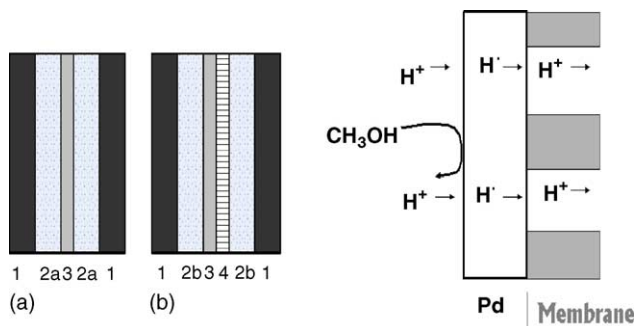


Fig. 3. The introduction of a metallic layer into a DMFC (a) with polymer electrolyte (b) with liquid electrolyte. Right side: working principle of the metallic layer: hydrogen is reduced at the side facing the anode, moves through the metal in its atomic state and is oxidised at the side facing the anode. (1) Electrodes; (2a) polymer electrolyte; (2b) liquid electrolyte; (3) hydrogen permeable metallic layer; (4) carrier layers.

The charge transfer overpotentials could be minimised by improving the hydrogen reduction/oxidation kinetics of the metal surfaces relying on well known fuel cell technology. Concerning diffusion resistance and compensation current ohmic losses it will be necessary to reduce the thickness of the metallic layer to a minimum. Nevertheless it is believed that the benefit from the elimination of methanol crossover will overwhelm these losses.

The first application of this strategy was reported by Pu et al. [14], who demonstrated the complete suppression of methanol crossover at the price of reduced electrode performance. They used a 25 μm palladium foil for their experiments between two layers of Nafion, suggesting the use of thinner Pd layers. A significant reduction of the layer thickness is possible by means of coating technology. The application of sputtering [15–17] or wet chemical technology [18–20] is reported in the literature.

Choi and coworkers [15] investigated composites consisting of 20 nm Pd sputtered on Nafion 117. They found a slight decrease in methanol permeation and a significant increase in cell performance compared to uncoated Nafion. Yoon et al. [16] came to a different result with layers of 10–100 nm on both Nafion 117 and Nafion 115. The methanol permeability was shown to decrease with the Pd-layer thickness, but the conductivity was reduced as well. The authors did not find a gain of performance for Pd-coated Nafion and explained this as a trade-off between protonic conductivity and methanol crossover. Ma et al. [17] sputtered Pd–Ag alloys in the range of 0.1–1 μm . They demonstrated a significant reduction of methanol crossover.

However Using sputtering technology has a major drawback: Ultrahigh vacuum is required for the sputtering process. The metal is thus sputtered on dry Nafion. The inevitable humidification thereafter leads to an expansion of the polymer electrolyte, to mechanical stress on the Pd layer and finally to cracks.

The use of electroless plating could be a solution to avoid cracks in the Pd layer because no shrinkage or swelling needs to happen between metal deposition and cell assembling. The membrane is pre-treated the same way as pre-treatment for uncoated Nafion is done and the metal deposition takes place in aqueous solutions. The current densities reported so far [20] are rather low because of the special test cell the authors used for electrochemical experiments and methanol concentration monitoring at the same time, but the comparative results between coated and uncoated Nafion show an increase of cell performance and a decrease of methanol transport through the electrolyte.

A test cell according to Fig. 3 with usage of a liquid electrolyte was constructed. In the case of bare Nafion, a quick rise of the methanol concentration in the electrolyte used at the cathodic side is found. With the Pd/Nafion composite, the methanol concentration in the cathode compartment remains quite constant at a low level. Presumably, the deposited Pd layers were not completely free of defects, since some methanol was still detectable reaching the electrolyte at the

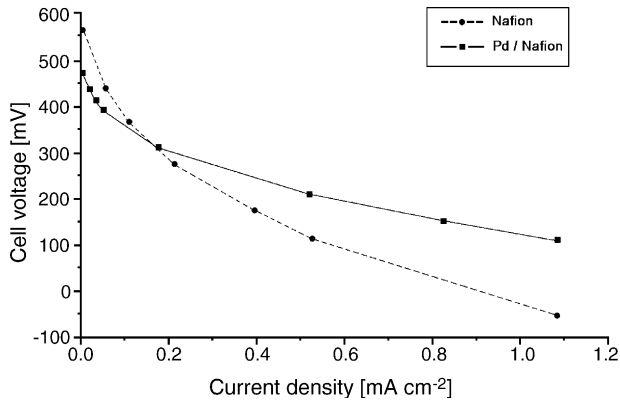


Fig. 4. Dependence of cell voltage on current density of the test cell with ELAT electrodes, for bare and Pd-coated Nafion at 338 K, $E_{Pd} = 0.450$ V vs. DHE [20].

cathodic side. With this measurement setup it is possible to gain information about the methanol crossover as well as knowledge about effects on the overall cell performance.

Fig. 4 shows the dependence of the cell voltage on current densities up to 1.1 mA cm^{-2} of the used test cell with ELAT electrodes at 338 K for bare and Pd-coated Nafion. The potential of the Pd layer was kept at 450 mV versus DHE (dynamic hydrogen electrode).

Although slightly higher cell voltages were measured with bare Nafion at current densities less than 0.2 mA cm^{-2} , the series done with Pd-coated Nafion in the range of $0.2\text{--}1.1 \text{ mA cm}^{-2}$ showed significantly better performance because of the reduction of methanol crossover. It is suggested that the lower cell voltages observed for the palladium-coated Nafion at very small current densities are due to an additional activation barrier for the hydrogen transport through the palladium layer.

For constant current experiments with ELAT electrodes at 0.53 mA cm^{-2} and 338 K with bare Nafion no stable cell voltage could be achieved, consequently the experiments were stopped after 180 min. In contrast, the values for Pd-coated Nafion were found to be stable for more than 480 min. With further improvements palladium coating technology

could be a key to methanol crossover free commercial fuel cells.

2.1.2. Pumped liquid electrolyte for crossover reduction

The main advantage of a circulating electrolyte is the possibility to remove the methanol before it reaches the cathode [21,22], where it causes polarization losses. Bipolar designs for a DMFC with a pumped liquid electrolyte for methanol crossover reduction have been investigated. A so-called spacer (separator) material has to be applied which is inert in a sulphuric acid/methanol surrounding. This material has to be porous so that the liquid electrolyte can be pumped through it. Swelling characteristics as well as variation of material properties with temperature and pressure have been investigated with several materials [33]. It is essential to minimise the internal cell resistance mainly through reduction of the electrolyte channel thickness in order to achieve a good performance of the direct methanol fuel cell.

The measurements are carried out at 333K with an electrolyte pumping velocity of 7 ml min^{-1} (in the case of liquid electrolyte) and the pumping velocity of the 2M methanol feed is 10 ml min^{-1} . The thickness of the spacer layer could be reduced to 0.5 mm, where a double layer of the polyvinylidene difluoride (PVDF) grid is used as matrix for the electrolyte canal to pump the sulphuric acid through.

To allow a certain methanol crossover, the pumped electrolyte was stopped for 20 min and the methanol level was determined by using the improved gas chromatographic method. The loss in cathodic potential due to the allowed methanol crossover is observed and displayed as the lower curve in Fig. 5. The measured level of methanol concentration in the electrolyte is about 0.8 vol%. The methanol concentration due to the crossover measured is comparable to that observed under identical conditions with other cell designs.

To evaluate the advantages of introducing a liquid electrolyte assembly independent from the overall performance of the fuel cell, it is necessary to design a polymer electrolyte membrane-direct methanol fuel cell (PEM-DMFC) made

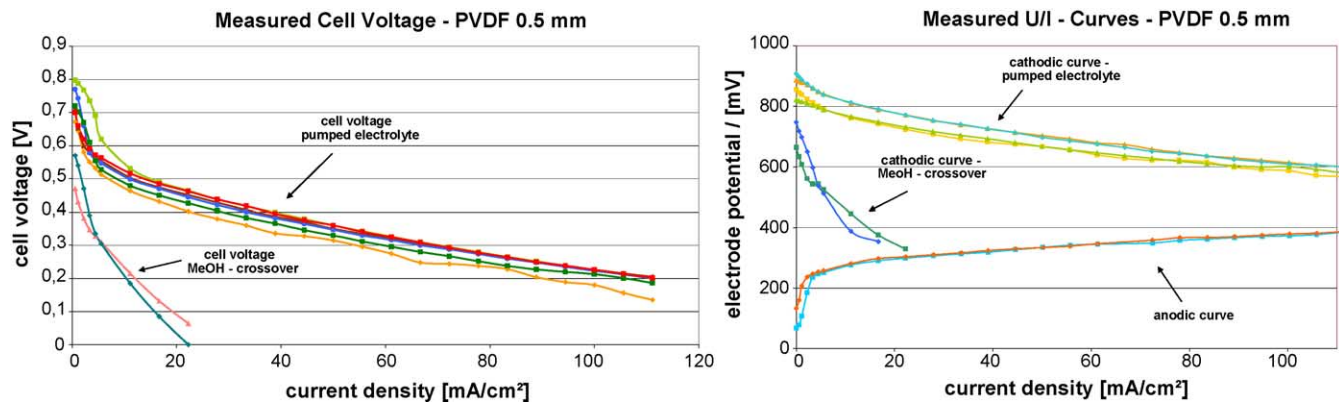


Fig. 5. Measured total cell voltage curves and measured polarization curves of cathodes and anodes (spacer layer 0.5 mm).

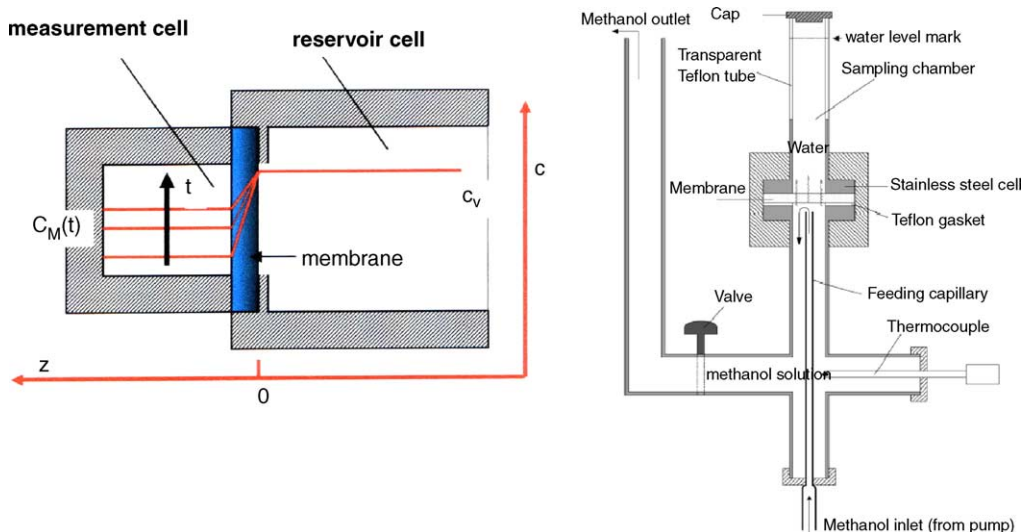


Fig. 6. Schematic view of measurement setup for the determination of methanol diffusion coefficients.

of the same components used in the liquid electrolyte fuel cell.

Comparing the measured curves derived from the measurements with the DMFC operated with a pumped liquid electrolyte to the power maximum or the cell voltage of a PEM-DMFC a significant improvement in power is derived [23].

3. Determination of methanol crossover through polymer electrolyte membranes

Methanol crossover rates are commonly determined in experimental mountings like the one described below. An electrochemical cell with two compartments of the same volume is used. The membrane to be tested is mounted between these two chambers [24–27]. One chamber gets filled with a defined methanol solution. The other side gets filled with deionized water and the permeation of methanol is measured as a function of time. Diffusion coefficients of methanol are determined from a dynamic model based on Fick's law of diffusion [9,24].

A different form of measurement cell for a stationary measurement was introduced by Navarra et al. [25]. The cell used is U-shaped with the membrane in the middle of one of the two compartments filled up to the same liquid level, thus pressure effects cannot develop (shown in Fig. 6). A stationary measurement method uses two chambers of fixed volume, in this case 15 ml each. The initial methanol concentration at the starting point is 1 M methanol in one chamber.

The solution in the compartment containing deionized water at the beginning gets stirred slowly to prevent an occurrence of a concentration gradient towards the membrane in the cell compartment.

The measurement setup used for the investigations on methanol crossover equals a system shown in Fig. 7. Pressure

effects can be avoided by designing the drain as a communicating vessel. The results obtained are shown in comparison to other groups in the following section.

3.1. Electrochemical analysis

The following methods are reported to measure methanol permeation through a membrane. A potentiometric method was introduced by Munichandraiah et al. [28]. A two compartment measuring cell divided by the membrane is used, where one side contains the methanol solution of the given concentration, and the second part is filled with deionized water. 0.2 M H_2SO_4 is applied as electrolyte on both sides. The potential of a PtRu/C electrode in the supporting electrolyte is measured versus time during methanol crossover. It has been shown that the slope (dE/dt) of this curve is proportional to the crossover rate. Methanol crossover rates can be derived from the time required to reach the equilibrium concentration of CH_3OH on either side of the polymer electrolyte membrane.

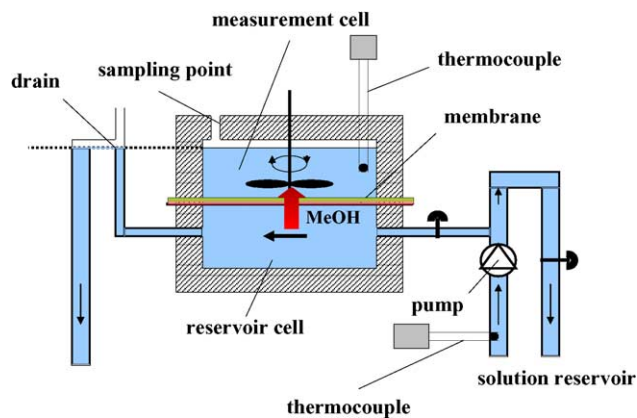


Fig. 7. Measurement setups for a non-stationary methanol diffusion measurement cell [9,11].

Another cyclic voltammetric (CV) method to analyse the methanol permeation is commonly used. A two compartment cell divided by the membrane being investigated is filled either with equal concentrations of electrolyte (usually 0.5 M H_2SO_4) or the measurement cell contains half the electrolyte concentration [29,30]. A plain platinum electrode (working electrode) is used at the side where the solution of defined methanol concentration is added, a platinum mesh electrode (as counter electrode) is used at the side where the crossover through the membrane is measured. It was observed that the methanol oxidation potential at these electrodes is nearly independent of the methanol concentration. Calomel electrodes are used as reference electrodes. Calibration is done filling equal known solutions of methanol in both compartments and obtaining the cyclic voltammograms (CVs). The methanol oxidation current peak is a reference for the methanol concentration on the permeated side. The variation of results lies usually in the range of approximately 5%. It is observed that the current peak shows a non-linear correlation to the methanol concentration [31].

3.2. Gas chromatographic analysis

A second method commonly used is a measurement system shown in Fig. 7. At the methanol permeated side, samples of the water/methanol concentration are measured using gas chromatographic methods after a certain permeation time. Normally a capillary column in combination with a flame-ionization detector (FID) is used.

3.3. Improved gas chromatographic analysis

The developed method was used to determine the methanol concentration in a measurement cell containing 0.5 M H_2SO_4 as electrolyte and a permeated concentration of methanol as found in measurement cells to determine the electroosmotic drag coefficient of the membrane [9,32] or in DMFCs with liquid electrolytes [33].

Methanol concentration in aggressive media such as sulphuric acid cannot be directly analysed in the gas chromatograph (GC). Therefore, the following measurement system was designed. A HP-Innowax capillary column inserted in a GC using a FID is used to measure the methanol concentration. Two millilitres of the electrolyte/methanol solution are filled in a small probe (vial). It gets heated in a headspace sampler with a defined temperature slope for a certain time (equilibration time). After this time, the equilibrium between gas phase and liquid phase is obtained. Setting adequate conditions, the acid remains fully in the liquid phase according to the boiling curve shown in Fig. 8 [34]. The vial is set under pressure by helium gas and a defined vapour volume is taken via the sample loop. A preheated transfer line injects this gas volume into the gas splitting inlet of the GC, where the detection volume is again divided into an outlet gas volume and detection gas volume transferred into the FID.

The vial total volume is about 20 ml, but it was found that 2 ml of the methanol solution is a sufficient amount of liquid for the methanol detection. The equilibration time of about 15 min together with the detection time of the GC leads

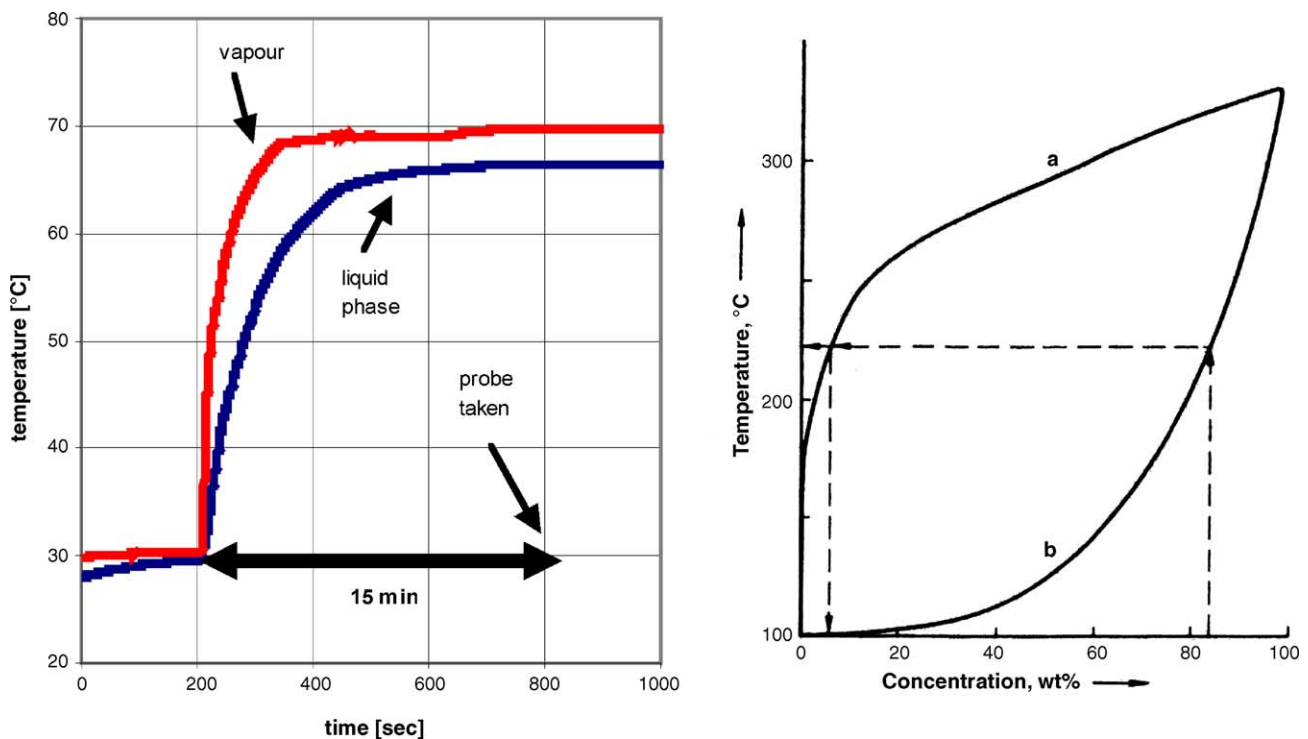


Fig. 8. Temperature in vial (2 ml, 20 vol% MeOH in water), measured in headspace sampler for temperature set to 338 K and (right side): boiling curve of H_2SO_4 at 1013 mbar. (a) Vapour, (b) liquid [31].

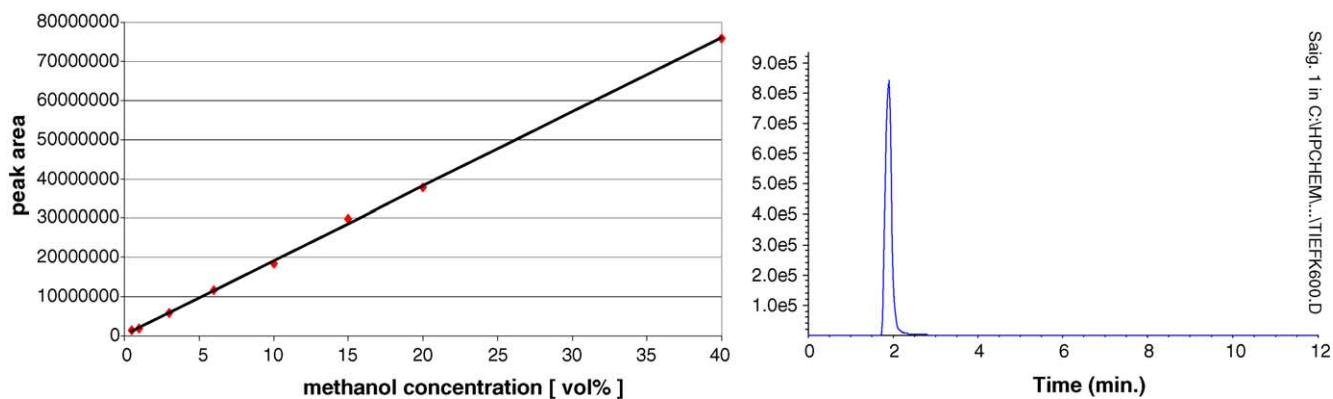


Fig. 9. Calibration curve for different H_2SO_4 /methanol solutions and (right side): calibration peak area of a H_2SO_4 /methanol solution with a methanol concentration of 6 vol%.

to an overall measurement time of 28 min, which is quite reasonable. It is possible to run 12 measurements in parallel, which reduces the overall measurement time to about 18 min per probe taken. This method also gives the opportunity to measure the same probe several times, which leads to a very good statistical value, because only a very small amount of vapour is taken for detection, and the methanol concentration in the probe is almost unaffected by the measurement.

3.3.1. Calibration

After system adjustment, the retention time and the peak area of a given methanol solution was reproducibly measured, and a calibration for different methanol contents was performed. Sulphuric acid/methanol solutions from 0.01 vol% up to 69 vol% were prepared and the peak area for these measurement points were obtained. The derivation of the peak area correlated to the methanol content is less than 3% obtained at several repeated measurements for a single probe (Fig. 9).

The headspace sampler gets heated to 338 K, whereas the starting oven temperature of the GC is set to 323 K. After 4 min a temperature ramp with an increase of 10 K min^{-1} until the final temperature of 423 K is started. For the main methanol peak a retention time of approx. 1.85 min is found. The calibration solutions used are pure water/methanol solutions as well as H_2SO_4 /methanol solutions with 1 M H_2SO_4 and 3.9 M H_2SO_4 (1st conductive maximum) where no difference in the detected methanol concentration could be found.

3.3.2. Impurities and background suppression

Besides the methanol peak some weak peaks resulting from the water in the solution were found. The measurement system is also used to determine methanol oxidation intermediates. To ensure that the peaks from the water are not interfering with these, the following peak analysis is performed to correct the measurement background. The measurements are carried out according to the temperature profile and system parameters already described in Section 3.3.1 (Fig. 10).

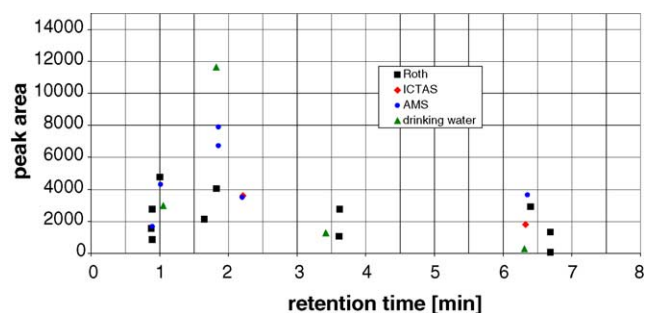


Fig. 10. Peak area over retention time for different types of deionized water. Roth: ROTIPURAN[®], Carl Roth GmbH&Co, Karlsruhe; ICTAS: Institute for Chemical Technology of Inorganic Materials, TU Graz; AMS: AMS Austria Microsystems, Unterpennstatten, Graz; drinking water from the laboratory water supply, Graz.

3.3.3. Measurement results

This adopted measurement method was used to obtain the values found for the diffusion coefficients of different membranes [9] the hydrodynamic permeability of these membranes and the electroosmotic drag coefficients [9,24]. In addition, the methanol crossover in a running DMFC with liquid electrolyte [30] and the occurrence of the methanol oxidation intermediates and their proportions could be measured.

3.4. Diffusion coefficients

Methanol diffusion coefficients measured using the above described improved gas chromatographic method are shown in Fig. 11. Already published values for Nafion[®] [11,24,35–38] could be achieved. No literature values are given for the other investigated membranes and the separator SP800/40. Small values of the effective diffusion coefficient could be measured at the FT-FKH950/30MF and PK12CE/714 membrane.

The separator SP800/40A showed a very high permeability for methanol (and water). The solution contained in the reservoir cell (see Fig. 7) penetrated through the separator

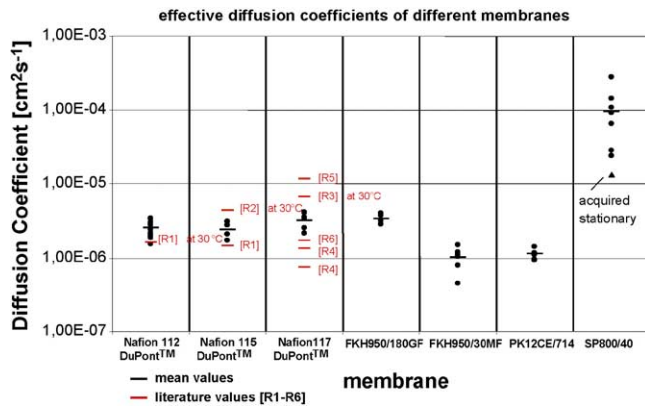


Fig. 11. Measured effective methanol diffusion coefficients for different membranes and separators in comparison to literature values. (R1) Öztürk [35]; (R4) Fedkin et al. [26]; (R2) Gottesfeld and Zawodzinski [36]; (R5) Verbrugge [38]; (R3) Ren et al. [37]; (R6) Scott et al. [27].

within seconds, which made an alternation of the measurement method (stationary measurement as described in [9]) necessary. Other separators got tested in short examinations, but showed a similar high permeability.

3.5. Electroosmotic drag coefficients

For the determination of the electroosmotic drag coefficient in different polymer electrolyte membranes, a measuring cell was constructed. Similar methods to measure the electroosmotic drag coefficient of water are described at Zawodzinski et al. [39] and Verbrugge and Hill [40], where the second source describes the use of radioactive tracers for the determination of the electroosmotic drag coefficient. A more common measurement setup for electroosmotic experiments in aqueous electrolytes is shown in an article of Harif [41]. The developed experimental cell made of acrylic glass is assembled from two laterally reversed chambers with a volume of 25 ml each. These two chambers are separated by the polymer electrolyte membrane to be examined. Both chambers got filled with a sulphuric acid/water solution of identical concentration. Methanol was added to the side of the reservoir cell. The low sulphuric acid content (0.35 M) on both sides is necessary to provide the necessary conductivity for the proton transport in the solution. Each chamber

contains a platinum grid electrode that allows the current flow through the membrane. The membrane cross section surface is 50.3 cm². The current flow through the cell is set up and regulated by a galvanostat (MP 75).

The whole measuring cell is accommodated in a thermostatic bath, that holds the chosen cell temperature at the selected level. The amount of liquid transported through the membrane is measured with a capillary. After each measurement a probe from both chambers is taken and the methanol concentration is determined with the improved gas chromatography method in order to be able to draw conclusions on the preferential transport of water or methanol.

The results of the determination of the electroosmotic drag coefficients for totally hydrated Nafion[®] (112, 115 and 117) membranes and the FT-FKH 1400/60 membrane as a function of methanol concentration at 303 K, as a function of temperature and a function of current flow is shown in [42] (Table 1).

Comparable data for electroosmotic drag coefficients in methanol solutions for swelled membranes could not be found in the literature, all other investigations show a very good correspondence with our values found for Nafion[®] 117 [36,43–48].

3.6. Methanol oxidation peaks

In order to detect the methanol intermediates, it was necessary to calibrate the measurement system. Calibration was done as described before, whereas instead of methanol/water other prepared solutions, e.g. methyl formate/water are used (Fig. 12).

3.7. Methanol crossover measurements in DMFC electrolyte

A power decrease over time due to methanol crossover into the electrolyte in a DMFC with pumped liquid electrolyte was investigated [30]. The improved GC method was used to determine the methanol concentration after an operation of the DMFC with a constant load. A power drop is observed after some time of operation and probes of the electrolyte are taken. Afterwards the electrolyte gets renewed and the power level is restored to the initial value (Fig. 13).

Table 1
Electroosmotic drag coefficients in methanol surrounding at 303 K ($\Delta\kappa = \pm 1$) [39]

| 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 ⁻¹) | 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 overlay the electroosmosis, measurement data are not valid for determination of electroosmotic drag coefficient.

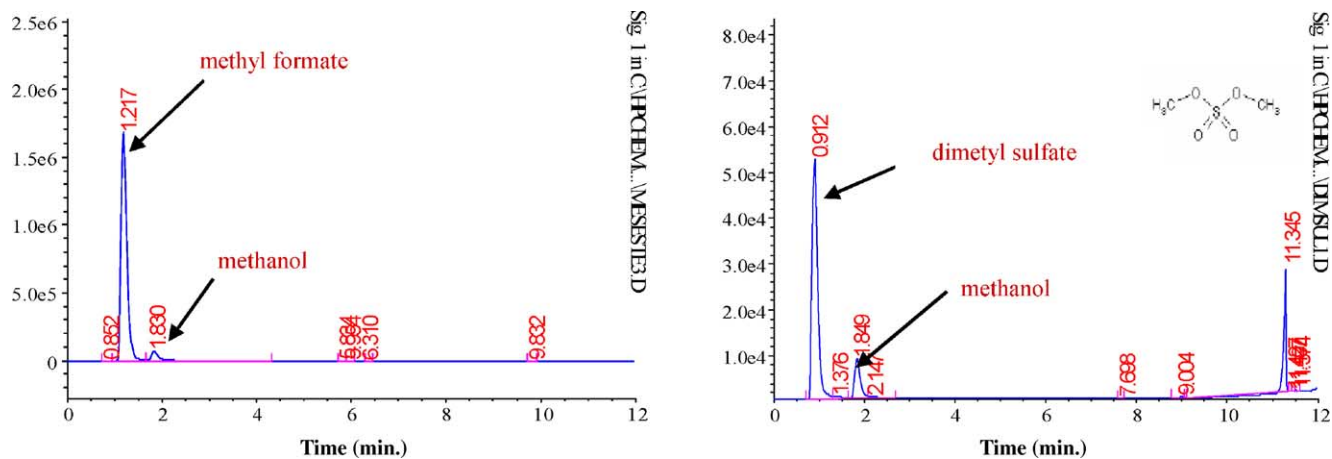


Fig. 12. Calibration curve for methyl formate/ H_2SO_4 /methanol solution and (right side): calibration curve for dimethyl sulfate/ H_2SO_4 /methanol solution.

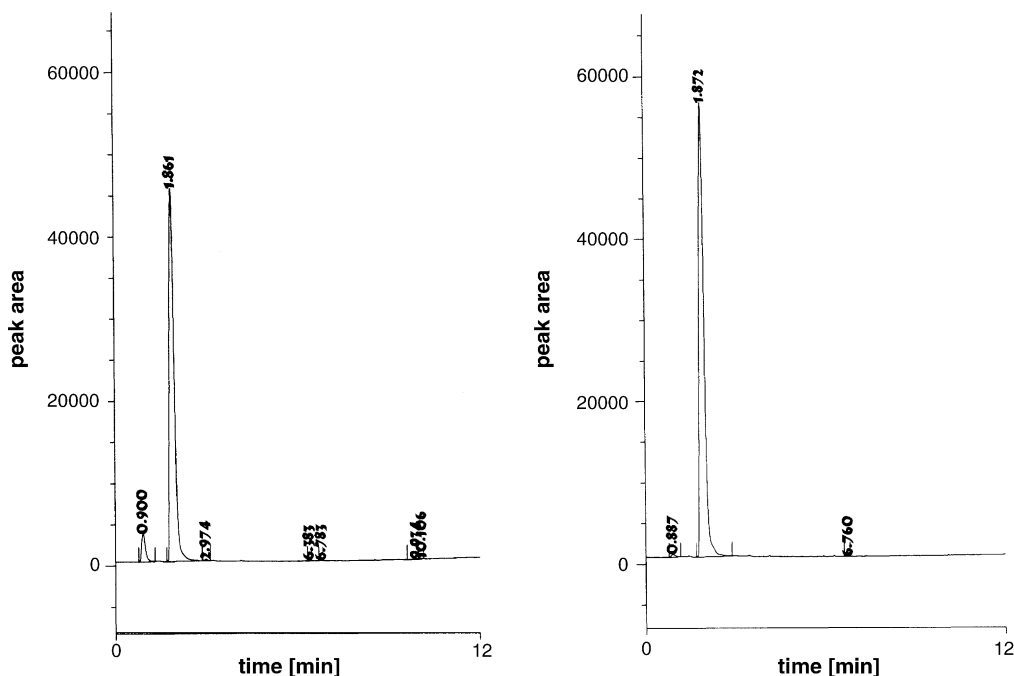


Fig. 13. Methanol crossover and intermediates in 1 M H_2SO_4 electrolyte in DMFC after 165 min running on constant load and (right side): methanol crossover and intermediates in 1 M H_2SO_4 electrolyte in DMFC after 230 min running on constant load.

4. Conclusion

The improved gas chromatographic analysis method has shown to be a fast and reliable method to determine methanol concentrations in a variety of solutions and aggressive electrolytes, e.g. sulphuric acid. With the presented test equipment, this method offers a valuable option to measure methanol crossover rates, the diffusion coefficient and the electroosmotic drag coefficients for DMFCs with liquid and solid electrolytes. The results obtained showed good correspondence with literature values. In addition, by-products and intermediate reaction products can be detected and analysed with this method. The development

of the measurement method led also to the investigation of two techniques to minimise methanol crossover. Firstly, to circulate a liquid electrolyte and wash permeating methanol out of the cell and secondly, to use barrier layers attached to the membrane surface to lower the methanol crossover. Both fundamental investigations led to promising results.

Acknowledgements

The authors appreciate the cooperation and support of the Christian Doppler Society (CDG), Vienna and of AVL List GmbH, Graz, for this project.

References

- [1] V. Hacker, Brennstoffzellensysteme, Habilitation, TU Graz, Faculty of Chemical Engineering, Graz, 2004.
- [2] J. Larminie, A. Dicks, Fuel Cell Systems Explained, second ed., Wiley, West Sussex, England, 2003.
- [3] R. Jiang, D. Chu, Comparative studies of methanol crossover and cell performance for a DMFC, *Electrochem. Soc.* 151 (1) (2004) A69–A76.
- [4] H. Dohle, Entwicklung und Modellierung von Direkt-Methanol-Brennstoffzellen, FZ Jülich, Jül 3752, März 2000, p. 56.
- [5] V. Gogel, T. Frey, Z. Yongsheng, K. Friedrich, L. Jörissen, J. Garche, Performance and methanol permeation of direct methanol fuel cells, *J. Power Sources* 127 (2004) 172–180.
- [6] H. Dohle, Entwicklung und Modellierung von Direkt-Methanol-Brennstoffzellen, FZ Jülich, Jül 3752, März 2000, p. 50.
- [7] J. Kallo, W. Lehnert, R.V. Helmolt, Conductance and methanol crossover investigation of Nafion membranes in a vapour-fed DMFC, *J. Electrochem. Soc.* 150 (6) (2004) A765–A769.
- [8] L. Jörissen, V. Gogel, J. Kerres, J. Garche, New membranes for direct methanol fuel cells, *J. Power Sources* 105 (2002) 267–273.
- [9] J.A. Drake, W. Wilson, K. Killeen, Evaluation of the experimental model for methanol crossover in DMFCs, *J. Electrochem. Soc.* 151 (3) (2004) A413–A417.
- [10] H. Dohle, J. Divisek, J. Mergel, H.F. Oetjen, C. Zingler, D. Stolten, Recent developments of the measurement of the methanol permeation in a direct methanol fuel cell, *J. Power Sources* 105 (2) (2002) 274–282.
- [11] R. Jiang, D. Chu, Comparative studies of methanol crossover and cell performance for a DMFC, *J. Electrochem. Soc.* 151 (1) (2004) A69–A76.
- [12] R. Carter, R. Wycisk, H. Yoo, P.N. Pintauro, Blended polyphosphazene/polyacrylonitrile membranes for direct methanol fuel cells, *Electrochem. Solid-State Lett.* 5 (2002) A195–A197.
- [13] H. Dohle, DE19803132 (C1) (1999).
- [14] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, A methanol impermeable proton conducting composite electrolyte system, *J. Electrochem. Soc.* 142 (7) (1995) L119.
- [15] S.I. Woo, W.C. Choi, J.D. Kim, Modification of proton conducting membrane for reducing methanol crossover in a direct-methanol fuel cell, *J. Power Sources* 96 (2) (2001) 411.
- [16] S.R. Yoon, G.H. Hwang, et al., Modification of polymer electrolyte membranes for DMFCs by using Pd films formed by sputtering, *J. Power Sources* 106 (1–2) (2002) 215.
- [17] Z.Q. Ma, P. Cheng, T.S. Zhao, A palladium–alloy deposited Nafion membrane for direct methanol fuel cells, *J. Membr. Sci.* 215 (1–2) (2003) 327.
- [18] T. Hejze, G.A. Koscher, B.R. Gollas, F. Hofer, K. Kordes, J.O. Besenhard, Recent progress in methanol crossover reduction using palladium coated Nafion, in: J. Reiter, J. Vondrak, V. Novak (Eds.), 5th ABA, 70. Brno University of Technology, Faculty of Electrical Engineering and Communication, Department of Electrotechnology, 2004.
- [19] T. Hejze, R.K. Sauerbrey, B.R. Gollas, M. Schmied, F. Hofer, J.O. Besenhard, Fortschritte bei der Unterdrückung von Methanol-Crossover in Direkt-Methanol-Brennstoffzellen, GDCh Jahrestagung – Kurzreferate – Jahrestagung der Fachgruppe Angewandte Elektrochemie GDCh, 51 (2003).
- [20] T. Hejze, B.R. Gollas, R.K. Sauerbrey, M. Schmied, F. Hofer, J.O. Besenhard, *J. Power Sources*, in press.
- [21] P. Enzinger, T. Tschinder, B. Evers, I. Schneider, S. Fraser, J.O. Besenhard, Advantages of liquid electrolytes in direct methanol fuel cells, *Fuel Cells Science & Technology 2002*, Amsterdam, Abstract, 25–26 September 2002.
- [22] P. Enzinger, V. Hacker, I. Schneider, S. Fraser, J.O. Besenhard, DMFC with liquid electrolyte, in: *Fuel Cell Seminar 2002*, Palm Springs, USA, November 18–21, 2002.
- [23] T. Schaffer, V. Hacker, J. Besenhard, Innovative system designs for DMFC, in: *Extended Abstract of the Battery and Fuel Cell Materials Symposium, Graz (Austria)*, April 8–22, 2004.
- [24] T. Schaffer, T. Tschinder, V. Hacker, J. Besenhard, Determination of methanol diffusion and electroosmotic drag coefficients in proton-exchange-membranes for DMFC, *J. Power Sources*, submitted for publication.
- [25] M.A. Navarra, S. Materazzi, S. Panero, B. Scrosati, PVdF-based membranes for DMFC applications, *J. Electrochem. Soc.* 150 (11) (2003) A1528–A1532.
- [26] M.V. Fedkin, X. Zhou, M.A. Hofmann, E. Chalkova, J.A. Weston, H.R. Allcock, S.N. Lvov, Evaluation of methanol crossover in proton-conducting polyphosphazene membranes, *Mater. Lett.* 52 (2002) 192–196.
- [27] K. Scott, W.M. Taama, P. Argyropoulos, Performance of the direct methanol fuel cell with radiation-grafted polymer membranes, *J. Membr. Sci.* 171 (2000) 119–130.
- [28] N. Munichandraiah, K. McGrath, G.K. Surya Prakash, R. Aniszfeld, G.A. Olah, A potentiometric method of monitoring methanol crossover through polymer electrolyte membranes of direct methanol fuel cells, *J. Power Sources* 117 (2003) 98–101.
- [29] K. Ramaya, K.S. Dhathathreyan, Direct methanol fuel cells: determination of fuel crossover in a polymer electrolyte membrane, *J. Electroanal. Chem.* 542 (2003) 109–115.
- [30] J. Ling, O. Savadogo, Comparison of methanol crossover among four types of Nafion membranes, *J. Electrochem. Soc.* 151 (10) (2004) A1604–A1610.
- [31] H.A. Gasteiger, N. Markovic, P.N. Ross Jr., E.J. Cairns, *J. Phys. Chem.* 97 (1993) 12020.
- [32] T. Tschinder, T. Schaffer, V. Hacker, J. Besenhard, Determination of electroosmotic drag coefficients in proton-exchange-membranes for DMFC, in: *Extended Abstract of the Battery and Fuel Cell Materials Symposium, Graz (Austria)*, April 8–22, 2004.
- [33] T. Schaffer, V. Hacker, J. Besenhard, Innovative system designs for DMFC, *J. Power Sources*, submitted for publication.
- [34] Ullmann, *Encyclopaedia of Industrial Chemistry*, VCH, vol. A25, 1994, p. 638.
- [35] N. Öztürk, Ionische Leitfähigkeit und Massenspektrometrische Bestimmung der Methanol-Diffusion und des “Electroosmotic Drag” an protonenleitenden Membranen für die Direkt-Methanol-Brennstoffzelle (DMFC), Frauenhofer Institut Chemische Technologie, 2001.
- [36] S. Gottesfeld, T.A. Zawodzinski, Polymer electrolyte fuel cells, in: R.C. Alkire, H. Gerischer, D.M. Kolb, C.W. Tobias (Eds.), *Advances in Electrochemical Science and Engineering*, vol. 5, Wiley-VCH, Weinheim, 1997.
- [37] X. Ren, T.A. Zawodzinski, F. Uribe, H. Dai, S. Gottesfeld, Methanol crossover in direct methanol fuel cells, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton Conducting Membrane Fuel Cells I*, PV 95-23, The Electrochemical Society Proceedings Series, Pennington, NJ, 1995, pp. 284–298.
- [38] M.W. Verbrugge, *J. Electrochem. Soc.* 136 (1989) 417.
- [39] Zawodzinski, et al., *J. Electrochem. Soc.* 140 (4) (1993).
- [40] M.W. Verbrugge, R.F. Hill, *J. Electrochem. Soc.* 137 (4) (1990).
- [41] K. Harif, *Elektroosmose bei wässrigen Elektrolytlösungen*, Dissertation, Technische Hochschule Aachen, 1982.
- [42] T. Tschinder, T. Schaffer, V. Hacker, Investigation of methanol diffusion due to electroosmotic drag in proton-exchange-membranes for DMFC, *J. Electrochem. Soc.*, submitted for publication.
- [43] F. Helfferich, *Ionen austauscher*, Bd. 1, Verlag Chemie, Weinheim, 1959.
- [44] T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, *J. Electrochem. Soc.* 138 (8) (1991).
- [45] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, The water content dependence of electro-osmotic drag in proton-conducting polymer electrolytes, *Electrochim. Acta* 40 (1995) 297–302.

- [46] M. Ise, *Polymer-Elektrolyt-Membranen: Untersuchungen zur Mikrostruktur und zu den Transporteigenschaften für Protonen und Wasser*, Max-Planck-Institut für Festkörperforschung, Stuttgart, 2000.
- [47] S.J. Paddison, R. Paul, T.A. Zawodzinski, Ion and Water Transport in a Nafion Membrane Pore: A Statistical Mechanical Model with Molecular Structure, *The Electrochemical Society Proceedings Series*, PV 98–27, NJ (1999), p. 106.
- [48] X. Ren, W. Henderson, S. Gottesfeld, Electroosmotic drag of water in ionomeric membranes, *J. Electrochem Soc.* 144 (9) (1997) L267.