Determination of Electroosmotic Drag Coefficients for Water and Methanol in Membranes for DMFC

T. Tschinder, B. Evers, T. Schaffer,
V. Hacker, J.O. Besenhard
CD-Laboratory for Fuel Cell Systems;
Graz University of Technology
Steyrergasse 21, 8010 Graz, Austria

To improve the performance of a direct-methanol-fuel-cell it is essential to understand the transport phenomena for the water as well as methanol in membranes e.g. perfluoro sulfonic acid membranes like Nafion under current flow. The electroosmosis is quantified by the electroosmotic drag coefficient κ_{H20} and κ_{MeOH}. It describes how many water molecules or methanol molecules per proton are carried along at the vectored proton transport through the membrane, if the gradient of the water concentration disappears through the membrane:

$$\kappa_{H_2O} = \frac{n_{H_2O}}{n_{H^+}}; \kappa_{MeOH} = \frac{n_{MeOH}}{n_{H^+}}$$

κ_{H20} = number of transported water molecules
κ_{MeOH} = number of transported methanol molecules
κ_{H+} = number of transported protons

This molecule transport depends on the current density, as well as on the electrolyte (membrane). The electrioosmotic drag coefficient for methanol and water in different membranes was measured as a function of temperature and methanol concentration. Additional it was examined whether there is a difference between the transport of water molecules and methanol molecules and whether the molecule transport rises linear with the current density.

For the determination of the electroosmotic drag coefficient in different Polymer-electrolyte-membranes, a measuring cell shown in figure 1 was used. The cell consists of two laterally reversed chambers with a volume of 25 ml each, made of acrylic glass. These two chambers are separated by the Polymer-electrolyte-membrane to be examined. The current flow through the cell is set up and regulated by a galvonostatic. To quantify the electroosmotic drag coefficient, both chambers were filled with a sulfuric acid/water solution and with a sulfuric acid/water/methanol solution with identical concentration. The low sulfuric acid content (0.35 M) on both sides is necessary to provide the conductivity for the proton transport in the solution. The measuring cell is held at constant temperatures. After each measurement, probes were taken from both chambers, and the methanol concentrations were determined with the Headspace sampler and a gas chromatography system in order to be able to draw conclusions on the preferential transport of water or methanol.

The concentration dependencies of the electro osmotic drag coefficient found are shown in figure 2. The electro-osmotic drag coefficient for the Nafion® membranes in pure water is between κ_{H20} = 1,4 and κ_{H20} = 4, which corresponds well with other values found in the literature [1,2]. As expected, the electroosmotic drag coefficient increases with rising methanol concentrations, because higher methanol concentrations lead to an enlargement of the canal diameters in the membranes and the molecules can be carried along in the solvating envelope more easily. Both types of membranes Nafion® 115 membrane and 1400/60 FT-FKH behave quite similar.

At higher MeOH-concentrations (or pure methanol) the membranes swell very strongly, get very permeable and other transport phenomena overlay the electroosmosis.

The dependence of electroosmosis from temperature is shown in Figure 3 and was carried out for a entirely hydrated Nafion® 117 membrane and different methanol concentrations. The electroosmotic drag coefficient is observed to rise with higher temperatures. Remarkable is the jump of the values at a temperature change from 50 to 60°Celsius, which could possibly be a tip to a change of the conductivity mechanisms (reinforced vehicle mechanism instead of Groffhuss mechanism)

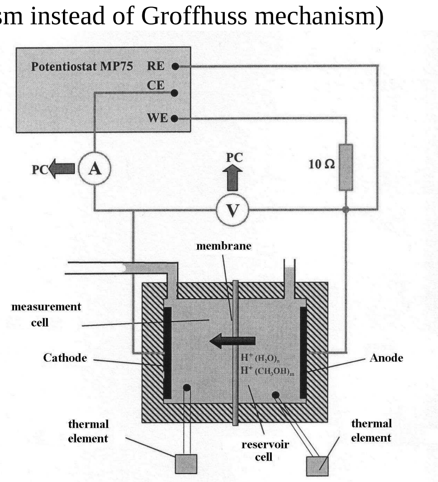

Figure 1 Measurement setup for determination of the electroosmotic drag coefficient [3]

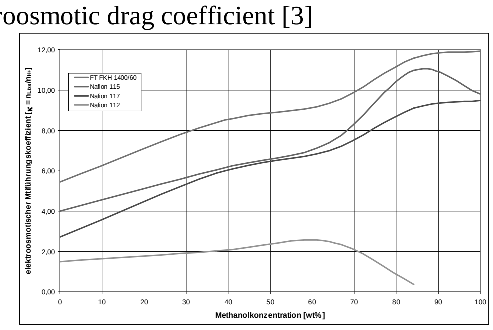

Figure 2 Electroosmotic drag coefficients for different membrane types (Nafion® 112, 115, 117 and FT-FKH 1400/60) depending on the methanol concentration at 30°C

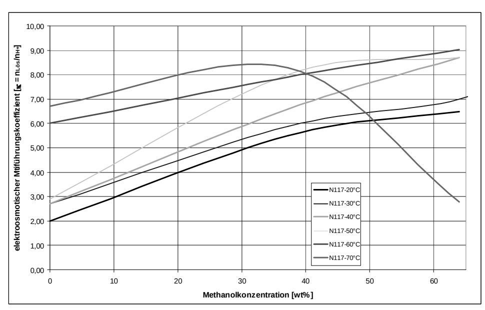

Figure 3 Electroosmotic drag coefficient for Nafion® 117 for different temperatures depending on the methanol concentration ($\Delta\kappa = \pm 1$)

Acknowledgements
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[2] Zawodzinski et al., J. Electrochem. Soc., Vol.140, No.7, July 1993;
[3] T. Tschinder, doctoral thesis, Graz University of Technology, 2004.