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**Charakterisierung von  
PEM-Membranen für  
Direkt-Methanol-Brennstoffzellen  
mit Online-Massenspektrometrie**

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## Characterization of PEM membranes for direct methanol fuel cells with online mass spectrometry

The development and characterization of polymer electrolyte membranes (PEM) used in direct methanol fuel cells (DMFC) require low methanol permeability and high proton conductivity. Methanol diffusing through the membranes decreases the performance of the fuel cells. An online mass spectrometric measuring procedure allows the determination of the parameters needed for membrane characterization.

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### Fuel cells with ion-conductive solid electrolyte (PEM) membranes

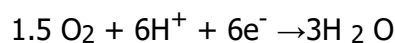
Intensive efforts are currently being made to commercialize fuel cells for various applications. In today's hydrogen-air/oxygen fuel cells, mostly Nafion is used as a solid electrolyte membrane. Nafion has a high ionic conductivity (approx.  $50\text{-}100\text{ mS}\cdot\text{cm}^{-1}$ ) and ensures charge equilibrium in the current supplying anodes or cathode reactions. Nafion is not electrically conductive and therefore also serves as separator for the two half cells in the fuel cell. Membranes with thicknesses of  $50\text{-}175\text{ }\mu\text{m}$  (Nafion 112-117) are used depending on the application. The design of the direct methanol fuel cell (DMFC) is very similar to the hydrogen air/oxygen fuel cell that appears to be more advantageous due to various technical aspects. For example, methanol could be used directly as an energy source. The chemical transformation process that is used today to produce hydrogen from methanol and the necessary humidification of the process gases to prevent the membrane from drying out could be omitted. However, two factors are currently preventing the use of DMFC: Firstly, a reaction intermediate (CO) poisons the electrode surface and secondly, Nafion is permeable to methanol and leads to a drop in system performance due to the reaction at the cathode [1]. In the DMFC, the anode side is supplied with a methanol-water mixture at an operating pressure of approx. 2-3 bar, while the cathode side carries air/oxygen under atmospheric pressure.

The following reactions can be observed at the electrodes:

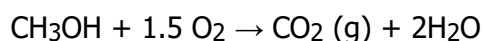
Anode:



Cathode:



Total reaction:



Proton conduction through the Nafion membrane occurs through hydrate shells formed at the sulfonic acid groups in the membrane. Water molecules in the hydrate shell are partially substituted with methanol molecules in the DMFC. According to the methanol concentration gradient, methanol constantly diffuses through the Nafion membrane to the cathode side. The increased diffusion under pressure (2-3 bar) is called methanol permeation.

Besides pure diffusion or permeation through the membrane, the so-called "electroosmotic drag" leads to further methanol transport through the membrane [2,3]. When the DMFC is loaded, i.e. under current flow, protons of the sulfonic acid groups of the membrane and thus

substituted methanol in its hydrate shells migrate to the cathode side [4,5] to equilibrate the charge. Overall, all methanol transport processes lead to undesired mixed potential formation and thus to a drop in the performance of the DMFC. The aim of worldwide work today is to reduce the methanol permeability in new membrane materials. In addition to the development of new materials, "barrier layers" are also applied to commercial membranes to suppress methanol transport. Testing the membranes is usually very time-consuming and not done in real-time. On the cathode side, the sample is collected and examined for methanol by gas chromatography [3]. Important parameters for characterization are:

- proton conductivity
- methanol diffusion
- methanol permeation
- electroosmotic drag

The alternate measurement method presented below allows a simple and fast characterization of proton-conducting PEM membranes. All four parameters can furthermore be determined as a function of temperature when the membrane to be investigated is placed into a measuring cell once.

### Membrane test cell using online mass spectrometry

The structure of the membrane test cell in Figure 1 corresponds to that of a material exchanger based on the countercurrent principle. The two flow channels are separated by the membrane to be investigated. Platinum-plated electrodes are embedded in the flow channels. One channel is connected via the so-called Luggin capillary to a reference electrode (BE) e.g. calomel electrode (SCE). With this three-electrode arrangement, potentiostatic, galvanostatic and potentiodynamic investigations can be carried out [7].

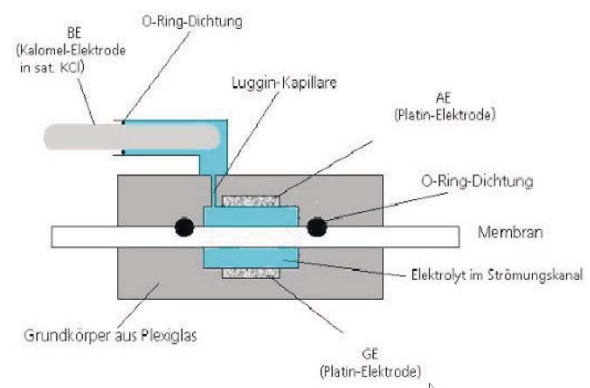


Fig. 1: Diagram of the membrane test cell with three-electrode arrangement

A conventional conductivity meter connected to the platinum electrodes measures the ionic conductivity and determines this way the proton conductivity of the membrane. A known electrolyte standard (e.g. 0.02 m H<sub>2</sub>SO<sub>4</sub>) is pumped through both channels, which provides the measuring arrangement with sufficient basic conductivity between electrodes and membrane and allows to determine the proton conductivity of the membrane as constant value. For the determination of methanol diffusion and methanol permeation, one channel pumps the methanol-water mixture while pure water is pumped in reverse flow through the other channel. Methanol diffusing through the membrane is absorbed by the water and transferred directly into the online mass spectrometer for quantitative analysis. A porous, liquid impermeable but gas permeable Teflon membrane thermostated at 20°C serves as gas inlet system. It allows the mass spectrometric online determination of dissolved volatile compounds from aqueous solutions [8]. The mass spectrometer is calibrated with a separate methanol standard.

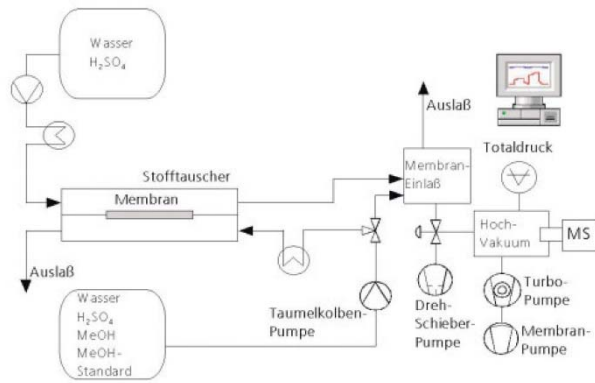


Fig. 2: Overall measurement setup with flow diagram of the test cell

To determine the "Electroosmotic Drag", a methanol-water mixture with standard electrolyte is pumped through the channel of the working electrode (AE) while pure standard electrolyte is guided to the counter electrode (GE). By setting a defined voltage between AE and GE, additional methanol is transported to the water side through proton migration that results from the electrical current flow. In order to investigate the influence of temperature on the individual parameters, the entire cell is placed in a temperature-controlled water bath.

Figure 2 shows the flow diagram of the entire measurement setup.

### Measurements on Nafion 112 and plasma-coated Nafion 115

The influence of temperature on methanol diffusion and ionic conductivity for a Nafion 112 membrane (thickness: 50  $\mu\text{m}$ ) is shown in Figure 3. With flow rates of 3 ml/min, the conductivity is measured on both sides with 0.02 mol/l  $\text{H}_2\text{SO}_4$  and the methanol diffusion with 2 mol/l MeOH in distilled water versus pure distilled water. The calibration of the mass spectrometer for methanol was done with 0.01 mol/l MeOH. As the temperature rises, both the ionic conductivity and the methanol diffusion of the Nafion 112 membrane increase. Table 1 shows the specific methanol diffusion coefficients  $D$  and ionic conductivity  $\kappa$  for Nafion 112 calculated from the measurements as a function of temperature.

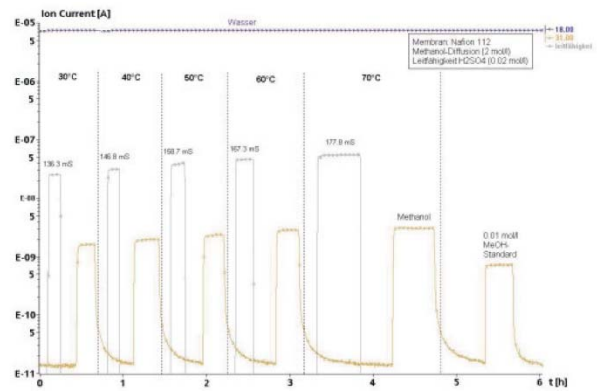


Fig. 3: Methanol diffusion and ionic conductivity as a function of temperature with Nafion 112

In addition to the development of new membrane materials, barrier layers are applied to commercial membranes to reduce methanol diffusion while maintaining ion conductivity. One approach is to use microwave plasma to apply a highly cross-linked, Nafion-like plasma polymer to Nafion membranes [9]. To determine the remaining "electroosmotic drag" for methanol, a defined voltage is specified at the platinum electrodes in the test cell with three-electrode circuit and the resulting current and methanol diffusion are measured online.

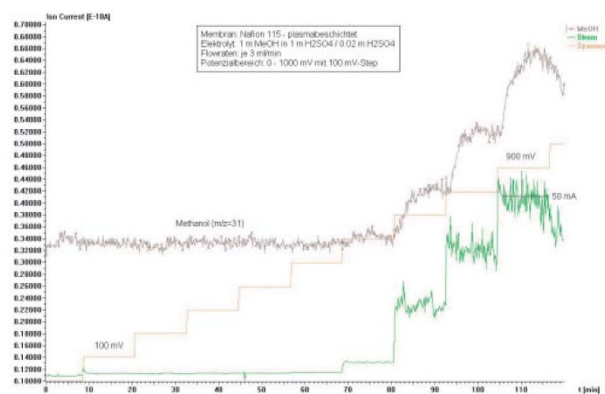


Fig. 4: Electroosmotic drag on a plasma-coated Nafion 115-Membrane at room temperature

Figure 4 shows the "Electroosmotic Drag" at room temperature for methanol on a plasma-coated Nafion 115 membrane (thickness: 125  $\mu\text{m}$ ) in the potential range 0-1000 mV. The total amount of methanol, which combines diffusion and electroosmotic drag, increases proportionally to the current  $it$

flow or proton transport in the membrane. The specific Electroosmotic Drag coefficient  $\xi$  indicates the number of methanol molecules per migrated proton. In Figure 4, the drag coefficient can be calculated as  $\xi = 0.023$  ( $\text{CH}_3\text{OH}/\text{H}^+$ ) from the number of protons transported at 50 mA and at a potential difference of 900 mV and the increased methanol transport by "Electroosmotic Drag" for plasma-coated Nafion 115. The comparison with the value for uncoated Nafion 117 (thickness: 175  $\mu\text{m}$ ) obtained by Cruickshank et al. with  $\xi = 0.164$  ( $\text{CH}_3\text{OH}/\text{H}^+$ ) shows that the electroosmotic drag for methanol is noticeably reduced by the application of a plasma polymerized barrier layer [3]. Methanol diffusion and ion conductivity with plasma-coated Nafion 115 at room temperature are  $D=3.05\text{E-}08$  [ $\text{cm}^2\cdot\text{s}^{-1}$ ] and  $\kappa=0.92$  [ $\text{mS}\cdot\text{cm}^{-1}$ ]. Thus the methanol diffusion is also reduced by more than a decade compared to an uncoated membrane. However, the ionic conductivity also decreases to the same extent.

Temperatur [°C]	Methanol-Diffusionskoeffizient D [ $\text{cm}^2\cdot\text{s}^{-1}$ ]	Ionenleitfähigkeit $\kappa$ [ $\text{mS}\cdot\text{cm}^{-1}$ ]
30	1.61E-06	77.1
40	1.99E-06	90.9
50	2.77E-06	131.2
60	2.95E-06	138.6
70	3.12E-06	147.8

Table 1: Methanol diffusion coefficient D and ionic conductivity  $\kappa$  for Nafion112 as a function of temperature

## Summary

Online mass spectrometry is well suited to quickly and easily determine the parameters that are important for the characterization of PEM membranes. The measuring method is currently being further developed to determine methanol permeation even at a defined pressure.

## Acknowledgement

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