INVESTIGATION OF THE PROTON CONDUCTIVITY IN THE DMFC ANODES WITH THIN CATALYST LAYER

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The influence of the Nafion content (5 – 16 wt% or 37 – 60 vol% resp.) on the proton conductivity of DMFC anode catalyst layers based on unsupported Pt/Ru was investigated. Following the theory of a macrohomogeneous model published in /1/, specific proton conductivities were calculated from the slope of the high frequency linear part of impedance spectra and the pseudo double layer capacitance obtained from cyclic voltamograms. It turns out, that the values of the specific proton conductivity are in the order of mS/cm, i.e more than one order of magnitude lower than the bulk conductivity of Nafion under these conditions. This means that the microstructure and tortuosity of the Nafion phase in the catalyst layer significantly influences the proton conductivity. The performance of the DMFC anodes tends to deteriorate with increasing Nafion content. This suggests, that compared to the influence of the mass transport of methanol / CO_2 and the active catalyst surface, the proton conductivity is a less important factor for the performance of the DMFC anode in the scope of the Nafion fractions investigated. This is also true for the electronic conductivity, which is a factor of 1000 higher than the proton conductivity.

Introduction

In order to extend the reaction zone from the membrane / electrode interface into the bulk of the catalyst layer, a proton conducting polymer phase is prepared in the catalyst layer. The addition of the proton conducting phase influences mainly the electrical conductivity. The electrical conductivity of the catalyst layers consists of two kinds of conductivities: the electronic and the ionic conductivity

While the Pt/Ru phase is responsible for the electronic conductivity, the proton conductivity is caused by the proton conducting polymer. The investigation of the overall electrical conductivity is quite trivial measuring procedure, but to separate the electronic conductivity from the polymer conductivity requires special treatments, like performed i.e. authors T.E. Springer et al. /2/ or C. Boyer et al. /3/.

In this work, a new method was performed to determine the proton conductivity of DMFC anode catalyst layers, which doesn't require any preparation of special samples where the Nafion phase must be substituted by silica Springer et al. /2/ , or to apply a inactive 'catalyst layer', like describes C. Boyer et al. /3/. Our method uses a physical model of a modified 'transmission line' equivalent circuit (see Fig. 1). This circuit is commonly used to describe the complex impedance of composite layers with both ionic and electronic conducting phases.

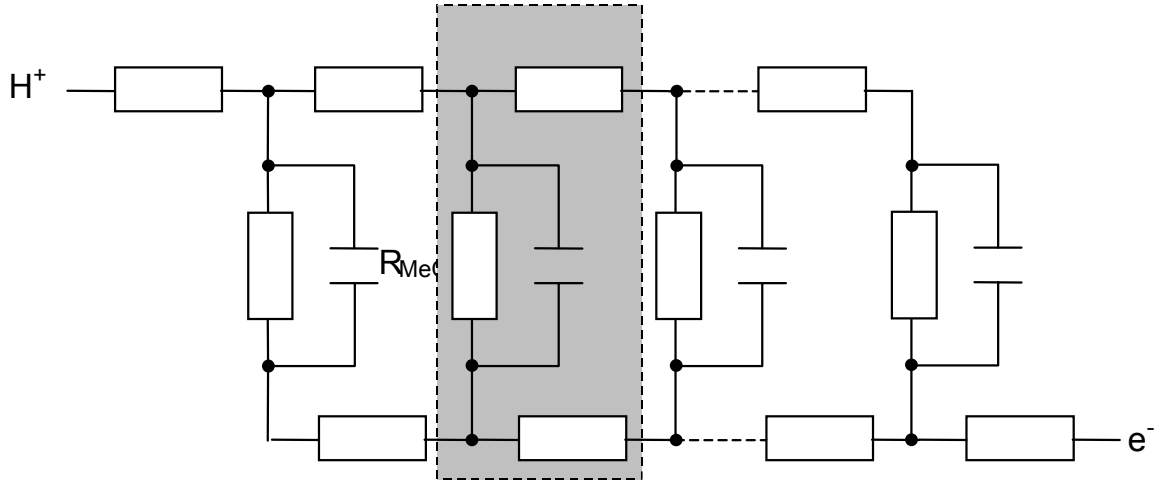

Fig. 1: *Two-dimensional model circuit of a transmission line*

The 'transmission line' is characterised by a complex impedance *Z,* when a harmonic signal ω is applied to electrodes. According to the theory described in /1/, the Nyquist plots of the impedance should feature a linear slope at frequencies higher than the so-called 'characteristic frequency', i.e. $\omega >> \omega_c$. In the case of the methanol oxidation, the characteristic frequency is then defined as

$$\omega_C = \frac{1}{R_{MeOH} \cdot C_{pdl}} \qquad (1)$$

The linear slope can be determined according to

$$Z = \sqrt{\frac{R_p}{C_{pdl}}}\omega^{-1/2}\frac{\sqrt{2}}{2}(1-i) \qquad (2)$$

$$|Z| = \sqrt{\frac{R_p}{C_{pdl}}}\omega^{-1/2} \Rightarrow K = \sqrt{\frac{R_p}{C_{pdl}}} \qquad (3)$$

Z complex impedance [Ω*cm^2]

ω frequency of harmonic signal [Hz]

As can be seen from equation 3, the slope yields the ratio of the protonic resistance and the pseudo double layer capacitance. Hence, the protonic resistance of the catalyst layer can be determined, if the pseudo double layer capacitance is known. The pseudo double layer capacitance can be obtained from the capacitive charging current of cyclic voltamograms of the methanol oxidation, according to

$$C_{PDL} = j_{pdl} \cdot \left(\frac{\Delta E}{\Delta t}\right)^{-1} \qquad (4)$$

j_{pdl} pseudo capacitive charging current

$\Delta E/\Delta t$ scan rate

The specific proton conductivity of the catalyst is calculated from equation (5):

$$\sigma_p = \frac{d}{A \cdot R_p} \quad (5)$$

d average thickness of the catalyst layer (cm)

A geometric surface of the catalyst layer (1.77 cm²)

The knowledge of the proton conductivity is essential for the determination of another important parameter, i.e. the penetration depth, which helps us to suggest an optimal thickness of the catalyst layer and thus the catalyst loading, which plays a significant role in the reduction of the expensive noble metal.

Experimental

Anode catalyst layers:

- Preparation method: spraying onto the backing layer, i.e. carbon cloth with 13 wt% PTFE, 87 wt% carbon black (Vulcan XC72)
- Ink: Pt/Ru (1:1) black (Johnson Matthey), 5% Nafion solution (Aldrich), isopropanol
- Variation of Nafion content: 5, 7, 10, 13 and 16 wt%; Pt/Ru loading: about 2 mg/cm²

Cathode catalyst layers:

- same preparation method as described above, Pt-black, 9 wt% Nafion, cathodes acted as counter (disc) and reference (ring) electrodes (reversible hydrogen electrodes !)

MEA's:

- Electrodes (catalyst layer + backing layer) were hot-pressed (T = 130 °C, p = 0.5 kN*cm^{-2}) onto Nafion 117 membranes

Electrochemical measurements:

- 3-electrode arrangement,
- cyclic voltametry: scan rate: dE/dt = 20mV/s
- quasi-stationary current potential curves: (0.5 mV/s),
- impedance spectra, E = 0.4 V; harm. signal amplitude 10 mV;

Results and discussion

At first, impedance spectra of the methanol oxidation were recorded at anode catalyst layers with different fractions of the Nafion phase.

Our interest is focused on the high frequency part of the impedance spectra. Approximately linear branches of the complex impedance with angles close to the theoretical value of 45° are obtained. The critical frequency, above which a linear behaviour is observed, tends to decrease with increasing Nafion content and ranges from 10 to 80 Hz . These results are in accordance with the calculated impedances presented in /1/. Following the theory of /1/, only capacitive effects and proton transport, but no faradaic processes should influence the impedance at high frequencies. Hence, the high frequency impedance should only slightly depend on the electrode potential. This demand is fulfilled by a fact, that above frequencies of about 1 Hz, the complex impedance is nearly independent on the electrode potential!

According to equation (3), the modulus of the high frequency impedance has to be plotted vs. $1/\omega^{1/2}$, to determine the square root of the ratio of the proton resistance and the pseudo double layer capacitance. The linear regression yields proportionality constants $K = (R_p/C_{pdl})^{1/2}$, which tend to decrease with increasing Nafion content.

The dependence of the specific proton conductivity of the DMFC anode catalyst layers on the Nafion content is shown in Fig.2. As can bee seen, the specific proton conductivity slightly decreases at low Nafion contents and increases pronouncedly at fractions of the Nafion phase higher than 42 vol. %. Regarding the fraction of the Nafion phase in the range of 6 -17 vol.%, and the bulk conductivity of Nafion of 0.12 S/cm at 40 °C, we expect values of the specific proton conductivity of about 0.02 S/cm, if the microstructure of the Nafion phase would be neglectable. This is not the case: the conductivity values are smaller by more than one order of magnitude, i.e. in the range of 10^{-3} S/cm. Hence, the microstructure, e.g. the tortuosity of the Nafion phase has a decisive influence on the specific proton conductivity. Moreover, a change of the microstructure of the Nafion phase at low Nafion contents could explain the unexpected slight increase of the specific conductivity at fractions of the Nafion phase, lower than 40 vol.%. This unexpected increase can be also explained by the substitution of the proton conductivity, provided by the Nafion phase, by the proton conductivity of the ruthenium oxide, as describes Thomas *et al*. /4/.

In addition to the proton conductivity, the specific electrical conductivity of the anode catalyst layers was determined. As seen from Fig. 3, the values of the specific electrical conductivity are about three orders of magnitude higher than the proton conductivities. This means, that the electronic conductivity is dominated by the electrical conductivity. As expected, the electronic conductivity decreases with increasing fraction of Nafion, i.e. decreasing amount of electronically conducting catalyst. This effect could also explain the decrease of the anode performance at Nafion contents higher than 37 vol. % /5/, because the current distribution within the catalyst layer improves with increasing electrical conductivity.

Conclusions

The Nafion fraction affects the electrical conductivity of the catalyst layer. A new method for the determination of the proton conductivity of mixed conducting electrodes was developed, which is based on a theory of M. Eikerling and A. Kornyshev /1/. It turns out, that the specific proton conductivity increases from 0.9 mS/cm for 37 vol.% Nafion to 2.4 mS/cm for 60 vol.% Nafion. Because the current of methanol oxidation decreases with rising proton conductivity, the proton conductivity seems to be less important for the anode performance as compared to other parameters like hydrophobicity of the pores /5/. The specific electronic conductivity of the platinum-ruthenium catalyst was determined by impedance spectroscopy and is about three orders of magnitude higher than the proton conductivity. It decreases from 5.3 $S*cm^{-1}$ (37 vol. Nafion) to 1.1 $S*cm^{-1}$ (60 vol. Nafion).

Acknowledgements

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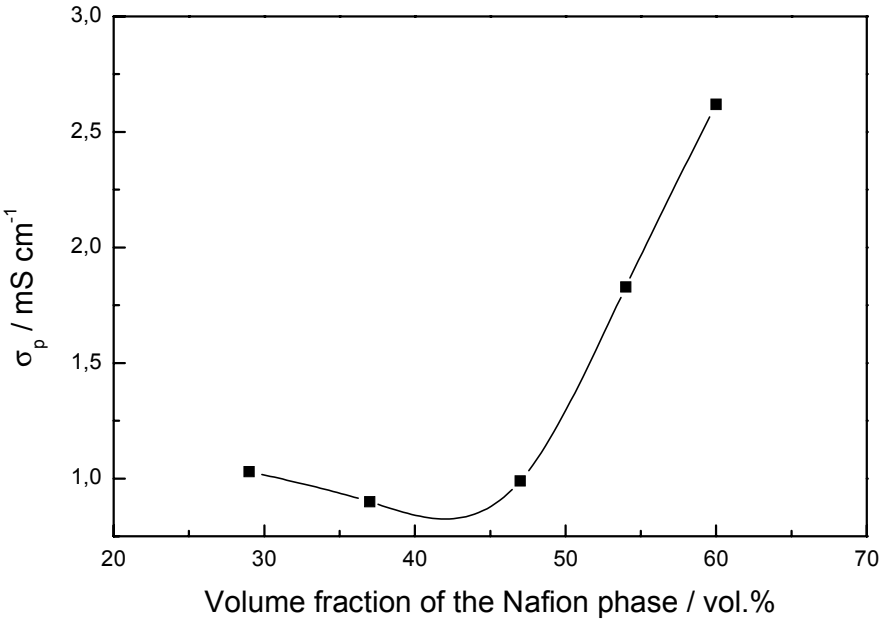

Fig.2: *Specific proton conductivity of DMFC anode catalyst layers as a function of the Nafion fraction*

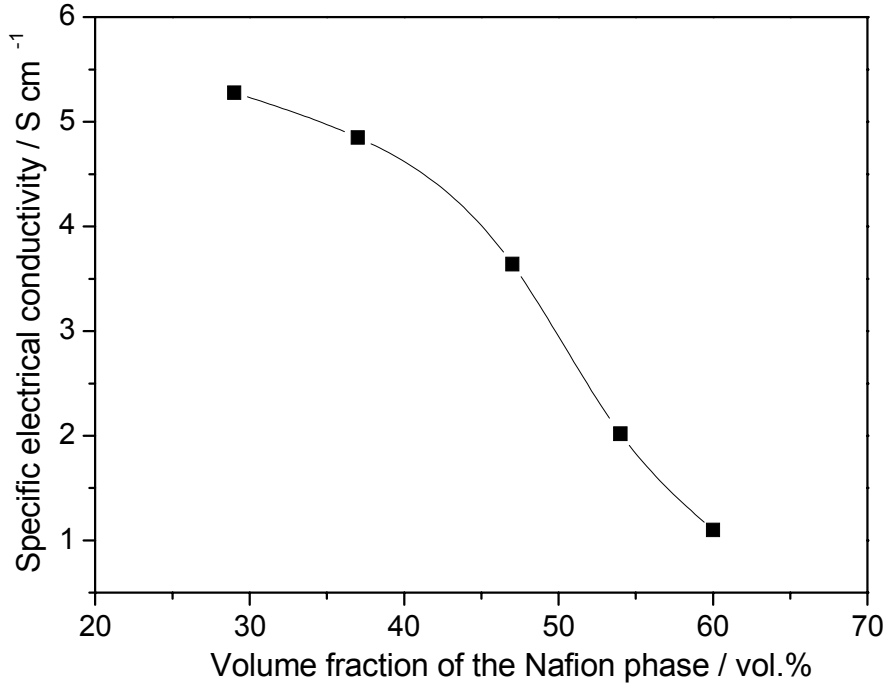

Fig. 3: *Specific electrical conductivity of DMFC anode catalyst layers prepared on PTFE foils as a function of the Nafion content, values obtained from 4 point a.c. measurements*