Macromol. Symp. ***188,*** *73–89 (2002)*

Electrochemical Characterization of Ionically Conductive Polymer Membranes

K. Richau[1], V. Kůdela[2], J. Schauer[2], R. Mohr[1]*

[1]GKSS Research Centre GmbH, Institute of Chemistry,
Kantstr. 55, D -14513 Teltow, Germany

[2]Institute of Macromolecular Chemistry, Academy of Sciences
of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, The Czech Republic

Summary: Cation conductive membranes, especially highly proton conductive membranes, are of interest not only for chlor-alkali electrolysis but for polymer electrolyte fuel cells as well. The very challenge for electrochemical characterization in this case is the low specific resistance of the polymer required for such applications, which in turn makes resistance measurements a non-trivial problem. We investigate the different possibilities to characterize such membranes. The present part of our work deals with the adequate conditioning and equilibration of membranes designed especially for direct methanol fuel cell applications, with the measurement of the conductivity and with the determination of apparent transport numbers in the membrane. The usefulness of the respective leaching investigations, impedance spectroscopy measurements and concentration potential measurements for the case of membranes made from sulfonated poly(phenylene oxide) is discussed.

1. Introduction

Confronted with the task of electrochemical characterization of free standing membranes designed for application in direct methanol fuel cells, we investigate the different possibilities to characterize such membranes. We recognized that the variety of membranes to be characterized includes highly conductive membranes as well as less conductive samples.

The first problem is the adequate conditioning and equilibration of the membranes, in order to get reliable electrochemical characteristics later on. Therefore we perform leaching experiments. The second task is the choice of appropriate cells for conductivity measurements. We decided to start with cells exposing the membrane to the stimulating electric field in the same way as during the foreseen application. The electrodes were placed apart from the membranes surface, in order to exclude changes of the membrane material during e.g. hot pressing of electrodes onto the membranes surfaces. With that cell design, we have to choose a supporting electrolyte. We decided to use neutral salts (KCl) and acids (HCl, H_2SO_4) as well, because the latter will simulate the situation during the foreseen application better than salts. Also from the cells design, it is clear that frequency range for conductivity measurements is restricted: Above $\approx 10^6$ Hz, the geometric dimensions of cell and wiring becomes comparable with the wavelenght of the stimulating electric field. Therefore, it is not possible to get information exclusively referring to the

CCC 1022-1360/00/$ 17.50+.50/0

intrinsic polymers proton conductivity (that would require measurements in the 10^9 Hz region). Instead, our results include all resistances originating from polarizable interfaces in/at the membrane, besides that of the resistance against proton transport.

Third, we were looking for the apparent transport numbers within the membranes, in order to get additional information concerning the relative contribution of the ions to charge transfer in dependence on the membranes modification.

The present contribution summarizes our first results concerning the usefulness of the respective leaching and swelling investigations, impedance spectroscopy measurements and concentration potential measurements for the case of membranes made from sulfonated poly(phenylene oxide).

2. Experimental Part

2.1 Materials

Aqueous solutions of KCl, HCl and H_2SO_4 (all of p.a. grade) were prepared using bidistilled and filtered water (specific conductivity $\lambda < 1$ µS/cm).

Membrane samples of Nafion 117 (Aldrich; H^+-form) were used as received. Membrane samples of sulphonated poly(phenylene oxide) SPPO (see figure 1) were prepared with different degrees of sulfonation (DS) according to the following procedure: Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was dissolved in 1,2-dichloroethane (45 °C) to a 3 % solution. Different amounts of 1,2-dichloroethane solution (5 %) of chlorosulfonic acid were slowly added with stirring to the PPO solution at 45 °C. The precipitated sulfonated products were removed by filtration, washed thoroughly with distilled water, left to stand in an excess of aqueous ammonia overnight, filtered off, washed with distilled water and dried.

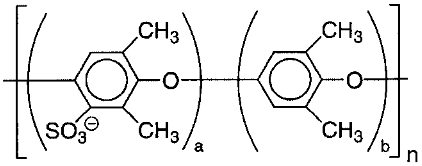

Fig. 1: Sulphonated poly(phenylene oxide). If a = 0 we have DS = 0 %, if b = 0 we have DS = 100 %.

The membranes of SPPO (in the NH_4^+ form) were cast from 15 % DMF solutions onto a glass plate and the solvent was slowly evaporated at 80 °C. The films were removed from the glass plate by immersion into a water bath and the resulting membranes were washed in water for 48 h. The details are described elsewhere [1], some characteristic properties are listed in table 1.

Tab. 1: Initial properties of the membranes prepared.

Sample	29-80	30-65	30-75	37-65	38-45	39-65	40-60	41-45	42-50	43-45
DS [%]	25.4	43.8	44.0	39.9	28.1	23.3	38.7	10.8	18.6	7.2
Counterion	NH_4^+	NH_4^+	NH_4^+	NH_4^+	NH_4^+	NH_4^+	NH_4^+	NH_4^+	NH_4^+	H^+
dry thickness [µm]	80	65	75	65	45	65	60	45	50	45

2.2 Methods

2.2.1 Conditioning and equilibration of the samples

Usually 2 samples 40*50 mm^2 were cut for the impedance investigations and their thickness in the dry state was determined. Thereafter, these samples were shaked together for 24h at 50°C in 100 ml bidistilled water in closed beakers (in the case of Nafion 117: at 80 °C). In parallel, beakers filled with 100 ml bidistilled water only were subjected to the same cycle. After that first cycle, the specific conductivities of the solutions were measured at room temperature using a WTW 3000 conductometer equipped with an electrode (TetraCon 3000) designed for low conductivity liquids with automatic temperature compensation (both from WTW Weilheim, Germany).

From these results, leaching y of ionic species was calculated according to

$$y\,[\%] = \{(\lambda_1 - \lambda_0) / \lambda_0\} * 100, \qquad (1)$$

where

λ_1 is the conductivity of the 100 ml water used for a given sample and

λ_0 is the reference conductivity (measured without samples in the beaker filled with 100 ml H_2O only, usually approx. 1 µS/cm).

That procedure was repeated as long as necessary (see 3.1), using fresh bidistilled water for every cycle.

After conditioning, the lateral dimensions and the thickness of the samples were determined. For the sake of equilibration, the samples were shaked for 24h at room temperature in 50 ml of the desired measuring solution, the solution was refreshed at least 2 times. After equilibration, the lateral dimensions and the thickness of the samples were determined once more. That data were used for calculation of the specific conductivity of the membranes.

Samples for the other electrochemical investigations were treated in parallel in the same way.

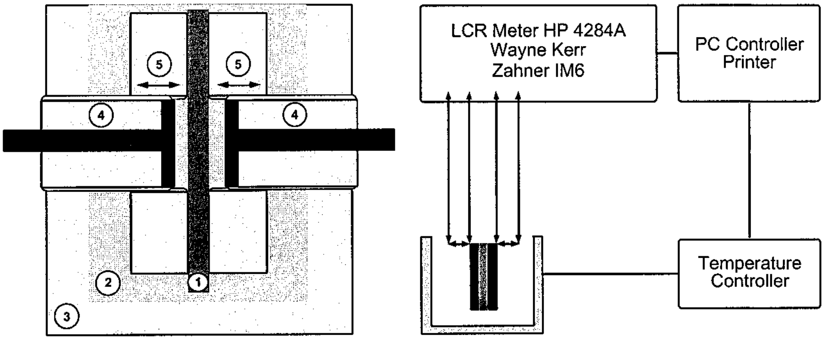

Fig. 2: Schematical cross-section of the cell for impedance measurements (1: membrane; 2: measurement solution; 3: cell body; 4: electrode holders with electrodes and wiring; 5: ring with internal thread) and equipment for impedance measurements.

2.2.2 Impedance spectroscopy

The cells (Labio a.s., Czech Republic) used were made from polycarbonate or polypropylene, a cross section of the design is given in figure 2. The cell constructed by H. Clinton and V. Kudela consists of a cylindrical container (3) in the bases of which cylindrical electrode holders (4) are fixed juxtaposed to each other. Each electrode holder is equipped with a thread and bears a ring (5) with internal thread that can be moved by rotation on the electrode holder. The internal diameter of the rings is nearly equal to that of circular electrodes firmly pasted on the holders. The leads to the electrodes are centered through the holders. By rotation, the rings move and join tightly one to the other. So, a cylindrical chamber is formed ≈ 2.87 cm in diameter and ≈ 1...2 mm thick. The two bases of the chamber are consequently formed by slightly platinized platinum foils – electrodes, the wall is the internal part of the rings (5). For measurement, the container with separated rings is filled with the electrolyte, a membrane strip 40 x 50 mm is inserted between the rings and the rings are tightened together. So, the measuring chamber is insulated from the electrolyte in the rest of the container. Aqueous solutions of KCl, HCl and H_2SO_4 of ionic strenght 0.1 as well as 1.0 mol/l were used.

The whole cell is inserted in an incubator. Various incubators were used, temperature accuracy amounts to ± 0.4 °C in worst cases. If not stated otherwise, the measurements were performed at 25.0 °C.

The cell is joined with the impedance spectrometer by means of Kelvin clamps. The following impedance spectrometers were used:

- LCR Meter HP4284A (Hewlett Packard), frequency range 5 Hz - 1 MHz, Kelvin clamps frequency range up to 100 kHz, temperature up to 50 °C, controlled by WinDeta software (Novocontrol GmbH, Germany);
- Wayne Kerr MultiBridge 6425, frequency range 20 Hz - 300 kHz, controlled by 6425 Analyzer Ver. 1.0 software (Staffordshire University, UK);
- IM6 impedance meter, controlled by THALES software (Zahner electric GmbH, Germany), frequency range 10 μHz - 8 MHz,

A schematic drawing of the equipment shows figure 2.

The Measurement Protocol A used routinely is as follows:

1. Equilibration of the cell filled with fresh pretempered solution and with the membrane inserted for > 2h in the incubator. Usually, that equilibration proceeds overnight.
2. Measuring the modulus of the impedance $|Z_{m+s}|$ with membrane in the cell within an appropriate frequency window. From the Bode - plot one obtains $|{}^1Z_{m+s}|$ at phase angle $\phi = 0$ (see figure 3).
3. Repetition without any changes after 20 minutes. From the Bode - plot one obtains $|{}^2Z_{m+s}|$ at phase angle $\phi = 0$.
4. If $|{}^2Z_{m+s}| - |{}^1Z_{m+s}| \leq 10^{-4}\ \Omega$, the measurement is recognized as stable with respect to leaching (see 3.1) and temperature. Otherwise it is necessary to repeat the procedure once more and evaluate as above. That accuracy is inevitable, because otherwise the error of the (small) difference $|{}^iZ_{m+s}| - |{}^jZ_s|$ can become very high.

5. Removal of the membrane from the cell.

6. Equilibration of the cell filled with the remaining, used solution for ≥ 2h in the incubator.

7. Measuring $|Z_s|$ with used solution in the cell within the appropriate frequency window. From the Bode - plot one gets $|{}^1Z_s|$ at phase angle $\phi = 0$ (see figure 3).

8. Repetition without any changes after 20 minutes. From the Bode - plot we obtain $|{}^2Z_s|$ at phase angle $\phi = 0$.

9. If $|{}^2Z_s| - |{}^1Z_s| \leq 10^{-4}\ \Omega$, the measurement is recognized as stable with respect to temperature. Otherwise repeat once more and evaluate as above.

10. The membrane resistance R_m is calculated according to

$$R_m = |{}^iZ_{m+s}| - |{}^jZ_s| * ((d_e - d_p)/d_e), \qquad (2)$$

whith d_e: electrodes distance, d_p: sample thickness and $i, j \geq 2$.

An illustration of Protocol A is given in figure 3.

Because the phase angle $\phi \approx 0$ is observed in the frequency range from $8 * 10^3$ to $2 * 10^4$ Hz in most cases, as a tool for fast screening the measurement at a fixed frequency $f = 10^4$ Hz (Protocol B) is allowed under our conditions, following the steps described above.

If the phase angle $\phi \approx 0$ is not observed in the high frequency region, impedance spectra covering the whole frequency range available (instead of a frequency window around phase angle $\phi \approx 0$ (Protocol A) or at a fixed frequency (Protocol B)) were recorded with and without membrane in the cell (Protocol C).

The procedure according to Protocol A keeps the error of the single measurement well below

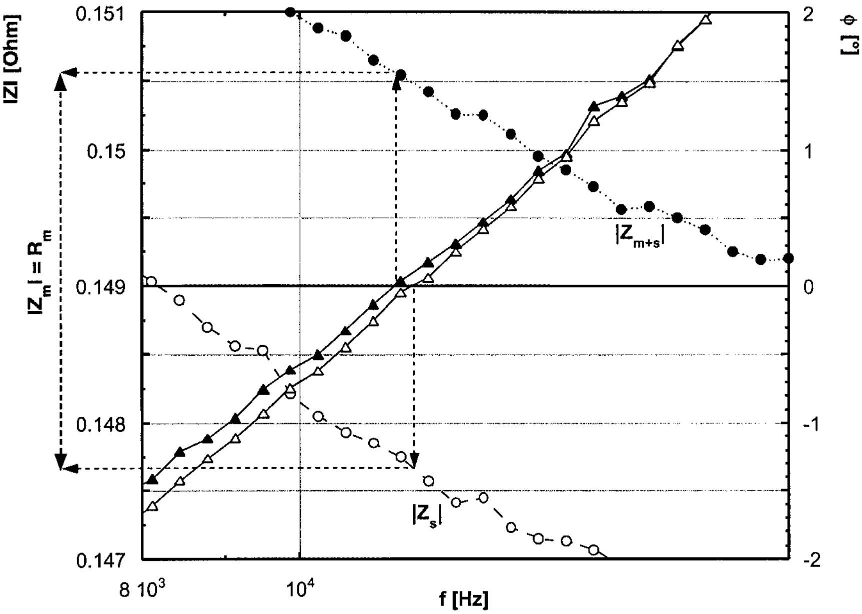

Fig. 3: Example for determination of R_m according to equ. (2) from $|Z_{m+s}|$ (closed circles) and $|Z_s|$ (open circles) at phase angle (triangles) $f = 0$: Bode-Plot for the sample 40-60.

0.1%. The error of the single membrane resistance estimation (equ. 2) amounts to approximately 1%, it is determined mainly by the change of the contact resistance and of the parasitic inductance, difficult to avoid completely during handling of the cell. The reproducibility of the membrane resistance in the case of Nafion 117 amounts to 4% under the conditions described above.

Concerning equation (2), the underlying assumptions are:

1. Membrane and solution act as ohmic resistors in series with a "black box", the latter describing wiring to / within the cell, electrodes properties and electrode - electrolyte interfaces.
2. The „black box" consists of resistances and capacities in parallel in such a way, that at high frequencies the „black box" is short-circuited. At phase angle $\phi = 0$ ohmic contributions only contribute to the filled cells response. Furthermore, only at $\phi = 0$ the complex impedance Z_i may be treated as skalar (i.e. subjected to simple subtraction).

For the verification of these assumptions see the discussion in 3.2.1.

2.2.3 Concentration potential

A universal cell (see figure 4) consisting of two independently thermostatted compartments was used. Any compartment is equipped with three tubes leading through its thermostatting jacket into the electrolyte containing chamber and making possible to insert a standard electrode, a platinum electrode (only for resistance measurements) and a thermometer. A membrane disc is inserted between the compartments. The compartments with the membrane were held tightly together by a metallic cage. They were filled with a pair of differently concentrated solutions of the same electrolyte. Solutions were stirred with rotating magnetic stirrers (1500 revolutions per minute). The membrane was equilibrated in contact with the solutions and after the equilibration, the measurement of voltage drop between the standard electrodes was carried out with fresh pretempered solutions by a high input impedance digital voltmeter. A second value of the voltage drop was read after commuting the standard electrodes in order to take into account their asymmetric potential. The mean value of both measurement was taken as the result.

The standard electrodes (saturated calomel electrodes) used were equipped with external electrolyte bridges filled with saturated KCl solution, thus cancelling out the liquid junction potentials. Dependent on the actual requirements, these cells were made from organic glass or from polycarbonate. The active membrane area varies from 0.12 up to 0.78 cm^2. The samples were equilibrated in advance with the more concentrated solution. Measurements were carried out at 25.0 °C.

3. Results and discussion

3.1 Conditioning and equlilibration

Strictly speaking, any resistance measurement is meaningful only if a steady state between sample and measuring solution is reached at least approximately and the sample is nearly in equilibrium with surrounding solution. For a perfect membrane leaching should be zero, the membrane being in equilibrium with the surrounding solution. For real world membranes leaching

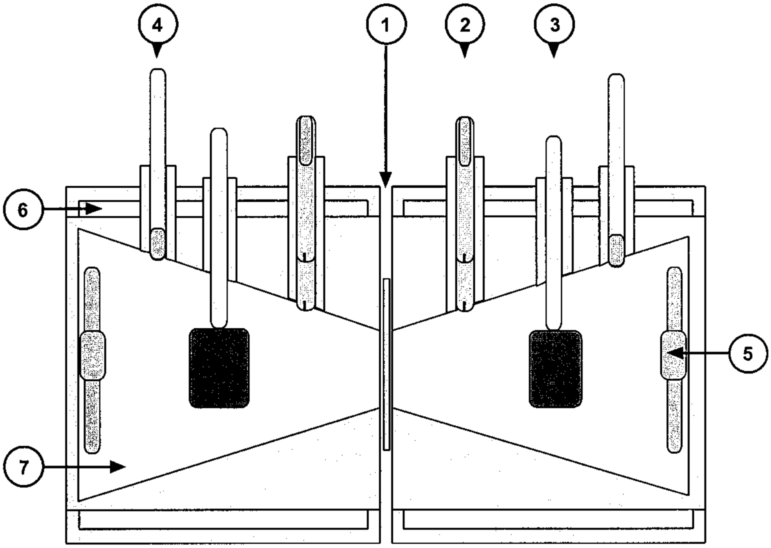

Fig. 4: Schematic cross-section of the two-compartment cell for measurements of DC resistance and concentration potential (1: membrane; 2: SCE with salt bridge; 3: platinized Pt electrode; 4: thermometer; 5: stirrer bars; 6: thermostatting liquid, 7: test solution).

should decrease with time, approaching a value as low as possible and the steady state as fast as possible.

Typical results of our investigations are summarized in figure 5 in terms of power fits leaching $y = M0 * x^{M1}$ vs number of cycle x. Because in many cases the first cycle gives extraordinary high or low leaching (probably due to different finishings during membrane preparation), it was useful to neglect the first cycle. Furthermore, the first derivative dy/dx [% / cycles] = $M0 * M1 * (x^{M1-1})$ (as a measure whether the steady state between sample and solution is reached or not) is given. It turns out that for Nafion 117 the requirements of equilibrium and steady state are fulfilled after 8 cycles. In contrast, for sample 30-75 both criteria are not reached after even after 18 cycles. With sample 38-45, equilibrium is reached after 3 cycles, but establishment of the steady state requires 7 cycles.

Normalizing the results with respect to initial sample volume (see figure 6), the relation between initial value of leaching M0 and DS seems to be approximated by an exponential fit $M0 = M2*e^{M3*DS}$. This gives an indication of the nature of leaching: Besides residual acids from final preparation steps, low molecular constituents with a very high DS are responsible for the leaching observed. The relation between the exponent M1 (characterizing the steepness of the decay of leaching with the number of cycles) and DS seems to be almost linear, there is a tendency of increasing M1 with increasing DS. Taking into account the change of lateral dimensions and thickness in dependence on the actual state of equilibration in water (table 2) as well as in 1/3 m H_2SO_4 (table 3), we see that at highest DS the swelling is extraordinarily high. We can conclude

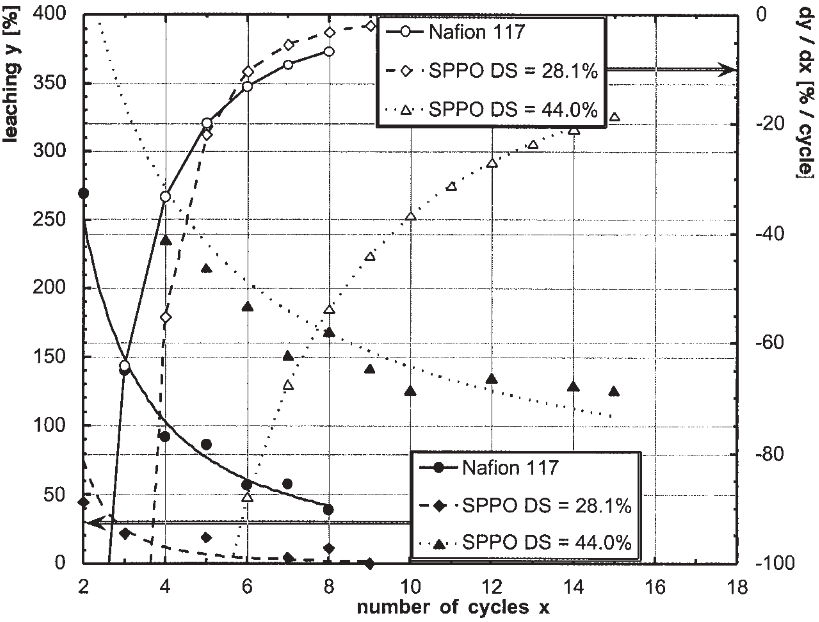

Fig. 5: Leaching and its first derivative vs. number of cycles. Experiments were performed at 80 °C in the case of Nafion 117 and at 50 °C in all other cases, resp.. Results of the first cycle were neglected.

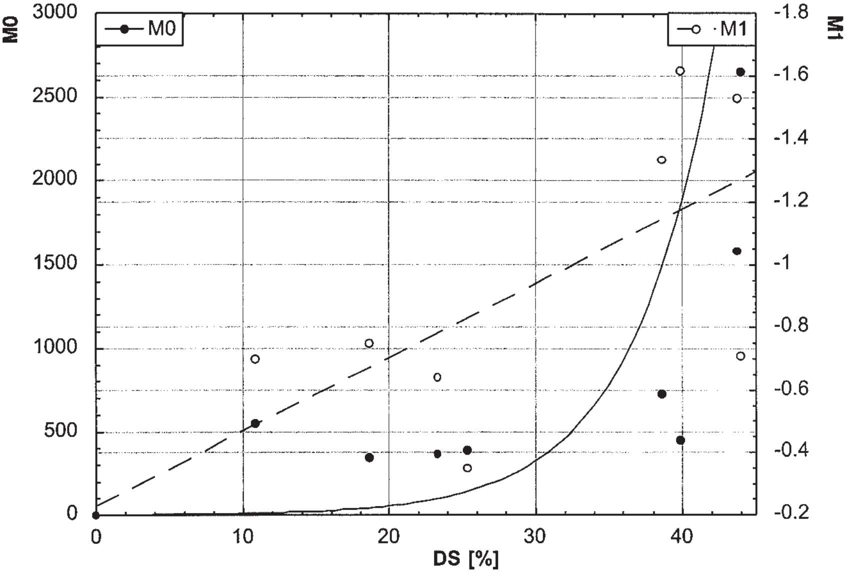

Fig. 6: Coefficients of power fits vs DS: Leaching normalized to initial sample volume 1 cm^3. Samples 29-80 ...43-45 (fits without first cycle; experiments were performed at 50 °C).

that the network is weakened and the mobility of highly charged low molecular constituents becomes higher than at lower DS.

Leaching is a general phenomenon, it is observed not only with our own samples but with Nafion 117 and other sulfonated materials for fuel cell applications, too [2]. Leaching is also a technical problem, because ionic leachates accumulate into the feed loop of DMFC's depressing the systems performance by the decrease of that bypass resistance. Finally, as a consequence of deviations from the requirements mentioned below, a shift of impedance measurement results with time because of instantaneous change of solution and membrane properties was observed in some cases, making impedance investigations meaningless. At present time the steady state seems to be the very precondition for proper impedance measurements. This does not mean an established equilibrium between sample and solution. According to our experience, sufficient conditioning requires to perform leaching cycles until

$dy/dx \leq 10\ \%$ and

$y \leq 30\ \%$ at the same time.

Tab. 2: Change of lateral dimensions and thickness of the membrane samples (in % with respect to the initial dry state) after completion of the leaching course. For the sake of comparison, results from Nafion 117 are given, too.

sample	43-45	41-45	42-50	39-65	29-80	38-45	40-60	37-65	30-65	30-75	Nafion 117
DS [%]	7.2	10.8	18.6	23.3	25.4	28.1	38.7	39.9	43.8	44.0	
thickness		-9	3	-5	42	16	22	16	27	136	23
lenght		2	3	4	12	6	7	5	31	112	5
width		3	0	5	10	6	3	4	31	106	29

Tab. 3: Change of lateral dimensions and thickness of the membrane samples (in % with respect to the initial dry state) after equilibration in 0.333m H_2SO_4. For the sake of comparison, results from Nafion 117 are given, too.

sample	43-45	41-45	42-50	39-65	29-80	38-45	40-60	37-65	30-65	30-75	Nafion 117
DS [%]	7.2	10.8	18.6	23.3	25.4	28.1	38.7	39.9	43.8	44.0	
thickness	7	0	5	-6	47	-14	23	3		160	18
lenght	2	1	4	4	11	5	6	5		76	5
width	-1	2	-1	2	11	6	3	3		77	30

3.2 Impedance spectroscopy

3.2.1 Membrane resistance at phase angle $\phi = 0$

Figure 7 summarizes the results obtained according to Protocol A. We have a clear linear relationship between specific conductivity of the membrane λ and degree of sulfonation DS > 10%: $\lambda = M0 + M1 * DS$ with $M0 = -59.3$; $M1 = 4.38$ and $R = 0.993$. Due to the different thicknesses

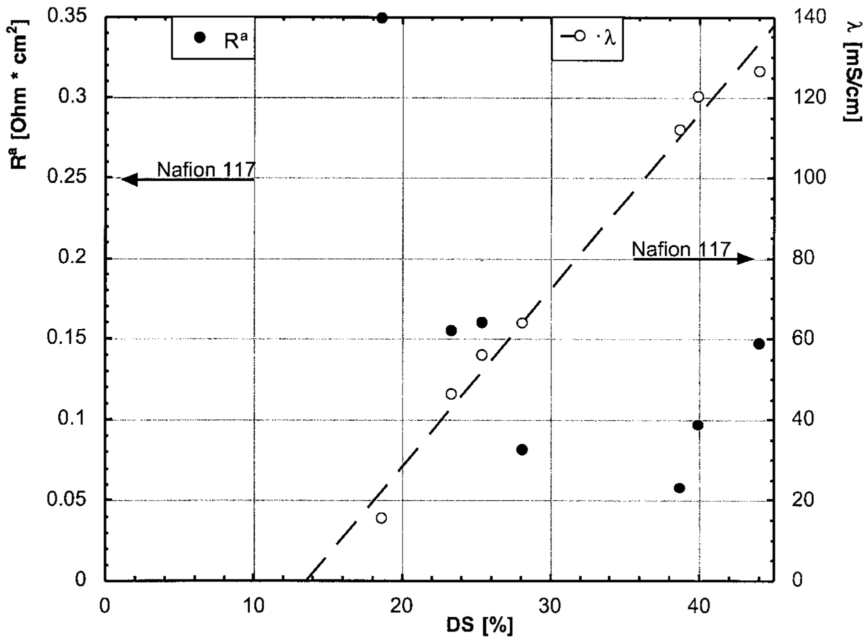

Fig. 7: Areal resistance R^a as well as specific conductivity l vs degree of sulfonation DS: Experiments were performed in 1/3 m H_2SO_4 at 25 °C according to Protocol A. Results obtained with Nafion 117 are indicated for the sake of comparison.

there is more scatter in the expected decrease of the areal resistance R^a with DS. Useful membranes with half the resistance of Nafion 117 are obtained at moderate DS. The results for Nafion 117 agree with those given in the literature [3, 4].

3.2.2 Cell and membrane models from the complete impedance spectrum

In order to enable a deeper analysis, impedance spectra covering the whole frequency range available were recorded in the potentiostatic mode (AC amplitude 10 mV) with membrane ($Z_{m+s} = Re_{m+s} + jX_{m+s}$) and without ($Z_s = Re_s + jX_s$) membrane in the cell (Protocol C). Typical spectra of a highly conductive membrane as well as a low conducting membrane, together with the results of the measuring solution alone, are given in figure 8 in terms of real part Re and imaginary part X vs frequency f. The vector difference

$$Z_m = Z_{m+s} - Z_s = (Re_{m+s} - Re_s) + j(X_{m+s} - X_s) \tag{3}$$

is indicated, too.

Both spectra are quite different. In the first case (Nafion 117), the difference between results with and without membrane is small. The contribution of the membrane is hidden by the response of the solution and the cell. In the second case (sample 43-45), the membrane determines the cells response almost completely, the contribution of the solution is negligible. Therefore, it is appropriate to consider the cell without membrane in terms of an equivalent circuit in a first

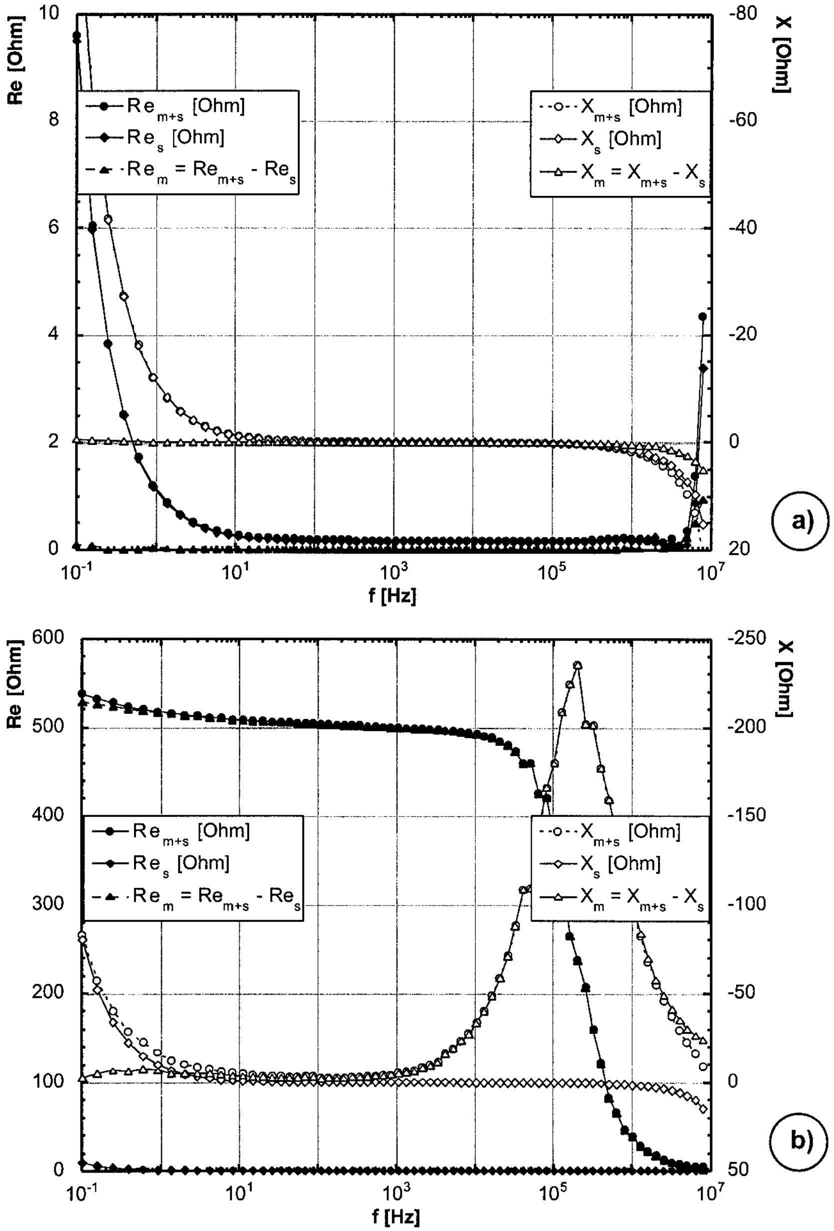

Fig. 8: Real (closed symbols) and imaginary (open symbols) part of impedance vs frequency: a) Results obtained according to Protocol C with Nafion 117 in 1/3 m H_2SO_4 at 25 °C - measurement with (circles) and without (squares) membrane as well as differences (triangles). b) Results obtained according to Protocol C with sample 43-45 in 1/3 m H_2SO_4 at 25 °C - symbols see above.

step. These results concerning the "empty" cell (without membrane but filled with the solution) are given in figure 9 and table 4.

Using the non linear least square fit procedures given by Boukamp [5] as well as by the SIM / THALES software package [6], the model (Fig. 9) fits the experimental data reasonably well. Stray capacitances and parasitic inductances are considered by C_{geom} and L. They are dependent mainly on the kind of external wiring, which can be kept rather constant. Their influence is seen mainly in the high frequency region. C_{geom} accounts for not only the different electrode distance in both cells, but the relative position of the electrodes, too. In parallel, we have the capacitance of the electrolytic double layer Z_{EDL} at the interface between electrodes and solution, and an impedance Z_{fdb} related to the finite (by boundary) diffusion processes at the electrodes surface, sometimes called "blocked diffusion". The resistance of the electrolyte solution R_s obtained according to Protocol C corresponds satisfactorily to the expected value

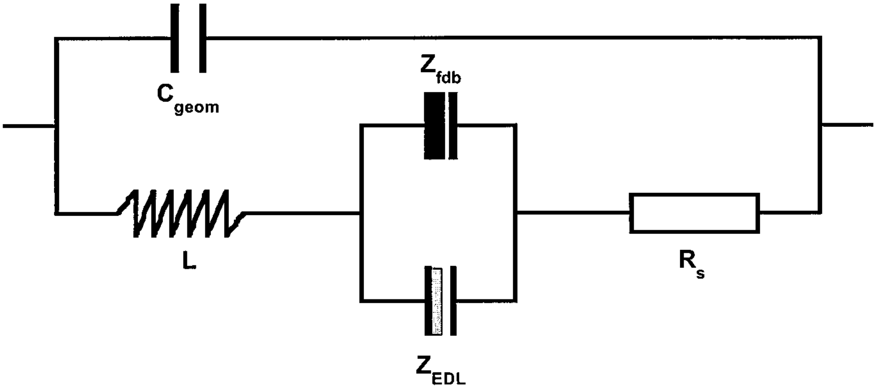

Fig. 9: Equivalent circuit (platinized platinum electrodes, 10 mV): cell filled with 1m HCl or 1/3m H_2SO_4 at 25 °C.

Tab. 4: Elements of the equivalent circuit describing the "empty" cells (Protocol C, fit frequency window 1 Hz – 1 MHz).

Solution	Cell	C_{geom}	L	Z_{fdb}: W_s	Z_{fdb}: k_s	Z_{EDL}: V	Z_{EDL}: α	R_s	R_s^{calc}
		nF	nH	$\Omega * s^{-0.5}$	s^{-1}	mF	-	Ω	Ω
1/3 m H_2SO_4	01/98	2.5	200	6.5	1318	5.8	0.92	0.150	0.132
1/3 m H_2SO_4	03/98	7.3	198	6.5	654	5.6	0.90	0.305	0.231
1 m HCl	01/98	6.4	199	23.3	3323	3.0	0.95	0.075	0.059

We follow the notation of symbols and units used throughout the THALES/SIM data evaluation software [7]:
W_s: accounts for concentration gradient and diffusion coefficient;
k_s: accounts for diffusion coefficient and thickness of the concentration polarization layer;
V: accounts for the (electrolytic double layer) capacity;
α: reflects the fractal dimension of the element (α = 1 for capacitor, α = 0 for resistor).

R_s^{calc}, obtained from geometric dimensions of the cell and known conductivity of the solution. The same holds in the case of solution resistance obtained according to protocol A, therefore the assumption underlying equation (2) (Protocol A) seems justified.

The model (Fig. 9) is valid for different cells (different mainly with respect to electrodes distance and surface) and for different acids of the same ionic strenght. It resembles that proposed in the literature for symmetric “empty” cells [7].

In a second step, an analysis of the Cole-Cole plots $|-X_m|$ vs $|Re_m|$ should give a first idea concerning suitable descriptions of the both membranes representing the extreme cases in our series. The results are given in figure 10 and table 5.

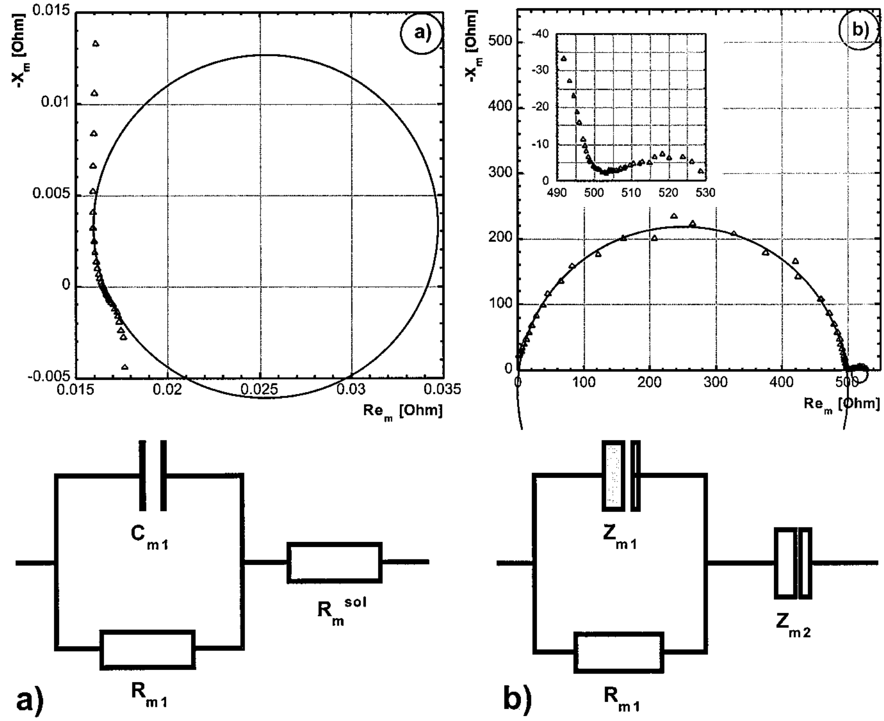

Fig. 10: Cole - Cole plots and equivalent circuits (platinized platinum electrodes, 10 mV): a) Nafion 117; b) sample 43-45; both in 1/3 m H_2SO_4 at 25 °C according to Protocol C, fit frequency window 1 Hz – 1 MHz.

Tab. 5: Elements of the equivalent circuit describing the high (Nafion 117) and low (sample 43-45 and 41-45) conducting membranes (Protocol C, fit frequency window 1 Hz – 1 MHz).

solution	sample	R_{m1}	Z_{m1}: V	Z_{m1}: α	Z_{m2}: V	Z_{m2}: α
		Ω	nF	-	μF	-
1/3 m H_2SO_4	43-45 from ($-X_m$ vs Re_m)	490	2.4	0.93	17.5	0.13
1 m HCl	43-45 from ($-X_m$ vs Re_m)	143	2.0	0.95	39.0	0.17
1/3 m H_2SO_4	43-45 from ($-X_{m+s}$ vs Re_{m+s})	490	2.4	0.75	12.0	0.10
1 m HCl	43-45 from ($-X_{m+s}$ vs Re_{m+s})	143	1.8	0.72	41.1	0.20
1/3 m H_2SO_4	41-45 from ($-X_{m+s}$ vs Re_{m+s})	41	210	0.65	0.012	0.09
1/3 m H_2SO_4	Nafion 117 from ($-X_{m+s}$ vs Re_{m+s})	0.029	5.3	1.00		
1 m HCl	Nafion 117 from ($-X_{m+s}$ vs Re_{m+s})	0.017	6.1	1.00		

It was possible to fit the data for the low conducting membrane 43-45 from the Cole-Cole plot of the vector differences (Fig. 10b) with high accuracy by the model Fig. 10b. The same model is valid in H_2SO_4 and HCl of the same ionic strength.

If we add the model for the membrane (Fig. 10b) to that of the "empty" cell (Fig. 9), it is possible to fit the data directly from the impedance spectrum (Re_{m+s}; X_{m+s} vs frequency f) displayed in figure 8b. With the exception of the exponent α of the capacitance-like element Z_{m1}, the agreement between the results of the complete model (cell with membrane) (Fig. 10b + Fig. 9) and that of the membrane model (Fig. 10b) alone is good. Consequently, without knowledge of the model for the membrane 41-45, that complete model was applied to the data of the impedance spectrum of sample 41-45. The fit was possible with acceptable accuracy.

It was not possible to fit the data for the high conducting membrane Nafion 117 alone (Fig. 10a) in a similar manner. The reason is probably that the impedances to be modelled are very low, so that even minor experimental errors can cause large scatter of the vector differences. But using the complete model described above it was easy to find the description of the high conducting membrane as a parallel arrangement of resistor R_{m1} and capacitor $C_{m1} = Z_{m1}$ with acceptable accuracy in both acids used. There is a reasonable agreement between the result from the fit in H_2SO_4 (29 mΩ) with the results according to Protocol A (39 mΩ at phase angle $\phi = 0$), thus convincing the applicability of Protocol A.

Concerning the nature of the elements describing the different membranes, from the value of α we conclude that Z_{m1} represents a (nonideal) capacitor, whereas Z_{m2} behaves as a (nonideal) resistor. The designation "nonideal" refers to their inhomogeneity. Therefore, we assume that the low conducting membrane 43-45 consists of two types of phases arranged in series: The first one is a relatively conducting phase Z_{m2} (modelling an ohmic resistance instead of Z_{m2} yields $R_{m2} = 1...2\,\Omega$, but the fit becomes worse), probably attributed to agglomerates of highly sulfonated chain segments concentrated in the bulk of the membrane. The second phase is described by a high ohmic resistance R_{m1} in parallel with a small capacitance Z_{m1}. R_{m1} fully determines the membranes behaviour in the low frequency region, where the capacitance Z_{m1} blocks the current. That second phase may be attributed to agglomerates of unsulfonated PPO or to a surface layer of unsulfonated PPO.

Increasing the degree of sulfonation DS from 7% (sample 43-45) up to 11% (sample 41-45), the resistance of the first phase becomes lower than that of sample 43-45, as to be expexted for a higher content of ionic sites inside the membrane. The resistance of the second phase decreases with increasing DS, the capacitance Z_{m1} shifting towards a Warburg impedance ($\alpha \approx 0.5$) at the same time. R_{m1} furthermore fully determines the membranes behaviour in the low frequency region.

Concerning the high conducting Nafion 117, the equivalent circuit reduces to a parallel arrangement of a low resistance with a low ideal capacitance. Phase separation as discussed above is not detectable in the impedance spectrum.

In all cases, the ohmic resistance R_{m1} is lower in HCl as in H_2SO_4, whereas the capacitance Z_{m1} is not influenced by the kind of acid used. Magnitude and nonideality of the resistor Z_{m2} probably depend on the kind of acid used.

3.3 Concentration potential

The permselectivity of the membranes investigated in aqueous solutions of salts and acids is a precondition for the comparison of our results with that from literature obtained with membranes equilibrated in water and measured in cells where the electrodes are in intimate contact with the membrane. Therefore the apparent transport numbers of the counterions within the membrane t^{+}_{app} (see figure 11) were calculated from the results of measurements of concentration potential E_c according to [8]

$$E_c = (t^{+}_{app} - t^{-}_{app}) * (RT / zF) \ln(a'/a''), \qquad (4)$$

$$t^{+}_{app} + t^{-}_{app} = 1.$$

Activity coefficients and transport numbers in free solution were taken from the literature [9].

In KCl at the lowest DS we have counterion transport numbers in the membrane equal to that in free solution. With increasing DS there is a maximum $t^{+}_{app} \approx 1$ around DS = 30%, only the cation contributes to the charge transfer. At higher DS, t^{+}_{app} goes down.This corresponds to the more pronounced swelling of the membrane discussed in 3.1, which obviously enables the coion to penetrate into the membrane, too.

A qualitatively similar dependence is obtained in HCl, with t^{+}_{app} depressed down to 0.85. The counterion dominates the charge transfer through the membrane to the same extend as in free solution.

In the literature, the following reasons for the depression of t^{+}_{app} in HCl as compared to KCl are discussed:

First of all, the equation (3) takes into account the diffusion potential across the membrane, but not the influence of the water transport number t^{W}_{app} according to [10]

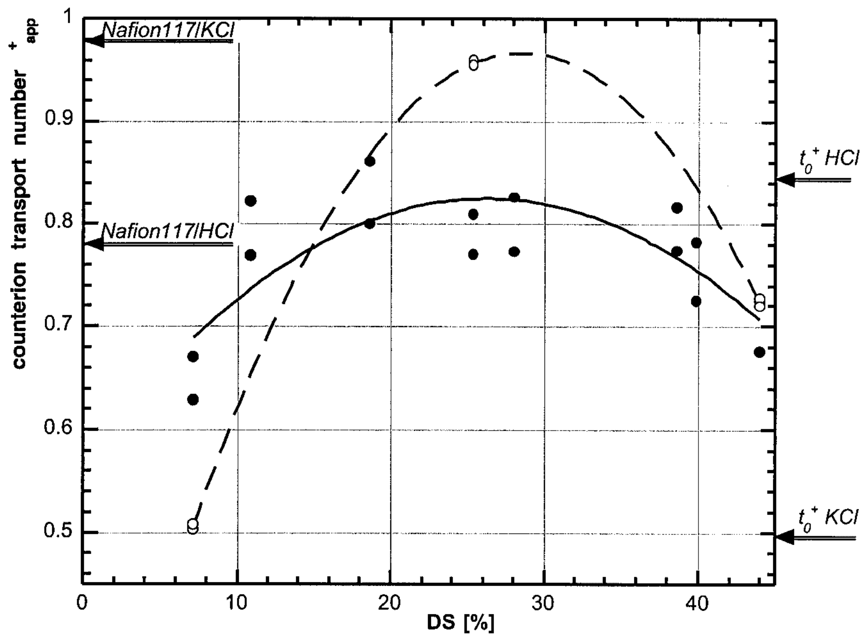

Fig. 11: Apparent transport number of the counterion within the membrane t^+ vs DS in 1.0/0.1 m aqueous KCl (open circles) and HCl (closed circles) solutions. Results with Nafion 117 as well as the cation transport number at 18 °C in solution t_0^+ [9] are indicated for sake of comparison.

$$t^+ = t^+_{app} + 0.018 * m_\pm * t^W_{app} \quad (5)$$

with $m_\pm$ being the mean molality. Under our conditions, that contribution would lead to a true transport number t^+ around 0.88 instead of $t^+_{app} = 0.85$.

Second, the acidity of the sulfonic acid site itself is suspected to be rather low in sulfonated polymers like sulfonated polyether(ether)ketone, sulfonated polyethersulfone and sulfonated polyphenylquinoxaline [11]: The authors report degrees of dissociation lower than 10% in the membrane, thus lowering the effective ion density and conductivity. But according to the authors this should not be the case with Nafion 117, in contrast to our results which show a similar depression of t^+_{app} in HCl.

Having in mind the results of impedance measurements (see Fig. 7), the membranes best suited for DMFC application with respect to low resistance and dominant contribution of the counterion to the charge transfer can be found near the maximum of t^+_{app} vs DS.

4. Conclusions

Using a series of sulfonated poly(phenylene oxide) (SPPO) membranes with degree of sulfonation DS from 7% up to 40%, several characteristics relevant for direct methanol fuel cell (DMFC) application are investigated.

From leaching experiments in water at 50 °C, informations concerning the equilibrium and the steady state of the samples were obtained. Leaching increases with increasing DS. Moreover, criteria to be fulfilled before starting electrochemical investigations are deduced.

For fast screening of the resistance of membranes an adequate impedance Measurement Protocol A was elaborated. That ohmic resistance determination is based on the comparison of the impedance moduli with and without membrane at phase angle $\phi = 0$. These investigations are performed in a cell with layers of acids at both sides of the membrane. Obeying the criteria mentioned above, a linear relationship between DS and specific conductivity in H_2SO_4 is obtained. Useful membranes with half the areal resistance of Nafion 117 are identified at moderate DS. The specific conductivity of Nafion 117 membranes is found in reasonable agreement with literature data.

An analysis of the whole impedance spectrum enabled us to describe the membrane itself in terms of an equivalent circuit. Its structure depends on the DS of the membrane. From the nature of the elements of the equivalent circuit and from its value in dependence on DS, indications concerning the homogeneity of the membrane are deduced.

From the dependence of the apparent counterion transport number in the membrane on the DS, a criterion for the selection of the most useful membranes for i.e. DMFC applications is deduced.

5. Acknowledgements

This work is performed in the framework of the programme "Scientific and technological cooperation between The Czech Republic and Germany". Financial support of the Bundesminister für Bildung und Forschung (project WTZ CZE 028/00) as well as that of The Ministry of Education (project KONTAKT C-N ME 366) is greatly acknowledged.

Thanks are due to Ms. A. Ritschel for excellent technical assistance.

6. References

[1] J. Schauer, W. Albrecht, Th. Weigel, V. Kudela, Z. Pientka, Microporous membranes prepared from blends of polysulfone and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide), J. Appl. Polym. Sci. **2001**, *81*, 134-142.

[2] R. Mohr, K. Richau, in preparation.

[3] R. S. Yeo, in *"Transport processes in electrochemical systems"*, R. S. Yeo, T. Katan, D.-T. Chin (Eds.), The Electrochem. Soc. Softbound Proc. Series **1982**, 178-204.

[4] T. A. Zawodzinski, Jr., M. Neeman, L. O. Sillerud, S. Gottesfeld, Determination of water diffusion coefficients in perfluorosulfonate ionomeric membranes, J. Phys. Chem. **1991**, *95*, 6040-6044.

[5] Ian D. Raistrick, in: *"Impedance Spectroscopy"*, J. Ross Macdonald (Ed.), John Wiley & Sons, New Yorck 1987, p.103.

[6] Bernard A. Boukamp, *"Equivalent Circuit Users Manual"*, University of Twente, The Netherlands, May 1989.

[7] Zahner electric GmbH, *"THALES/IM6 Owner's Manual"*, Kronach, Germany, 2000.

[8] N. Lakshminarayanaiah, *"Transport phenomena in membranes"*, Academic Press, New Yorck and London, 1969, p. 199.

[9] D. Dobos, *"Electrochemical Data"*, Elsevier Scientific Publishing Company, Amsterdam - Oxford - New York 1975.

[10] N. Lakshminarayanaiah, *ibidem*, p. 237 ff.

[11] R. W. Kopitzke, C. A. Linkous, H. R. Anderson, G. L. Nelson, Conductivity and water uptake of aromatic-based proton exchange membrane electrolytes, J. Electrochem. Soc. **2000**, *147(5)*,1677-1681.