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Formation and characterization of PEDOT-modified Nafion 117 membranes

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Abstract Nafion 117 membranes were modified with a thin film of poly(3,4-ethylenedioxythiophene) (PEDOT) by a diffusion-controlled polymerization process using a two-compartment cell with the monomer EDOT on one side of the membrane and the oxidizing agent FeCl_3 on the other side. The methanol permeability and ion conductivity of the composite PEDOT/Nafion membranes were measured as a function of temperature and polymerization time by DC and AC polarization measurements in four-electrode technique and permeation experiments in a diaphragm cell. These modified membranes have lower methanol permeability while maintaining adequate conductivity.

Keywords Direct methanol fuel cell · Poly(3,4-ethylenedioxythiophene) · Methanol permeability

Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention due to its simple system design, low operating temperature and convenient fuel storage and supply. The proton exchange membrane (PEM) is one of the most critical components in the DMFC. Generally, PEMs with high-proton conductivity and low-methanol permeability are desirable for efficient DMFC operation. Currently Nafion, a perfluorosulfonate ionomer, is the major membrane material used in polymer electrolyte membrane fuel cells (PEMFC). However, the Nafion membrane is a poor barrier to methanol crossover. In addition, the high cost of perfluorosulfonate membranes prohibits wide commercial application of PEMFC. Therefore, it is important to develop novel PEMs with low methanol permeability at a low cost.

Several new types of membranes have been prepared for use in DMFC. Among them are sulfonated polyetherether ketone [1, 2], sulfonated poly(arylether sulfone) [3, 4], sulfonated or phosphonated polyphosphazenes [5, 6], poly(vinyl alcohol)-crosslinked-polystyrene sulfonic acid [7], acid–base blending membranes [8], and inorganic–organic composite membranes [9, 10].

To decrease methanol crossover in conventional PEMFC membranes, a number of methods of modifying the Nafion membrane were reported, such as substituting part of H^+ in Nafion 117 by Cs^+ ions [11], treating the surface of Nafion membranes using plasma etching and palladium sputtering [12] or in situ polymerizing poly(1-methylpyrrole) [13], polypyrrole [14], and polyaniline [15]. Non-ion exchange polymer support layers [16], laminated structures with nanometer-thick Pd or Pt foils [17, 18], and layers of plasma polymerized hexane [19] have also been used to partially block the methanol crossover. In another approach, some inorganic proton conductors were doped into the Nafion membrane to reduce the methanol permeability [9, 10].

In this paper, we report about the modification of commercial Nafion 117 membranes impregnated with poly(3,4-ethylenedioxythiophene) (PEDOT) by chemical polymerization. The methanol permeability and ionic conductivity of these membranes were investigated.

Experimental

Membrane preparation

Nafion 117 membranes were cleaned by immersion in boiling 3% H_2O_2 and in 1 M H_2SO_4 for 1 h each. The membranes were then rinsed in boiling deionized water for 1 h and the procedure was repeated at least twice to remove sulfuric acid completely. After this purification procedure the membranes were stored in deionized water at room temperature before use.

PEDOT-modified membranes were prepared by the diffusion method [20]. The Nafion membrane was placed

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between the two chambers of a divided glass cell. One chamber contained EDOT monomer dissolved either in water or in 0.1 M NaPSS (sodium polystyrenesulfonate) solution and the other chamber 0.5 M FeCl_3 as oxidizing agent. In the case of EDOT in NaPSS solution, the molar ratio of EDOT to NaPSS was 5:1. The EDOT monomer diffuses to the other side of the Nafion membrane where it is polymerized, forming a thin PEDOT film on the membrane. During polymerization, the compartment containing the EDOT monomer was agitated by a magnetic stirrer. After polymerization, the PEDOT/Nafion composite membranes were treated in boiling 1 M H_2SO_4 for 1 h to replace Fe^{3+} by H^+ and then in boiling de-ionized water for 1 h to remove the sulfuric acid completely. The PEDOT/Nafion composite membrane was black. All samples were stored in deionized water before testing.

Experimental techniques

Methanol permeability was measured using a diaphragm cell [11]. The glass cell consisted of two identical compartments ($V=16$ ml), separated by the test membranes and containing 1 M methanol on one side and deionized water on the other side. Both compartments were magnetically stirred during the permeation experiments. The concentration of permeated methanol was measured by GC (HP 5890 Series II Gas Chromatograph). The permeability was calculated from the slope of the linear plot of methanol concentration vs permeation time. The temperature was controlled thermostatically between 25 and 70 °C.

Ionic conductivity of the membranes was derived from DC measurements using a potentiostatic four-electrode technique [21, 22]. The experimental cell consisting of two identical compartments separated by the test membrane is shown in Fig. 1. Each compartment was filled with 1 M H_2SO_4 solution and contained a Pt and an Ag–AgCl reference electrode with Luggin capillary. The electrodes were connected to the terminals of a potentiostat (EG&G Princeton Applied Research, Model 273 Potentiostat/Galvanostat) as shown in Fig. 1. The ionic current I

through the membrane was measured as a function of the potentiostatically controlled potential difference ΔE between the tips of the Luggin capillaries. Ionic conductivity σ was calculated from the slope of the linear plot I vs ΔE with the relation $\sigma=l/RA$, where $R=\Delta E/I$ is the resistance, l (≈ 200 μm) the thickness, and A (0.78 cm^2) the area of the PEDOT/Nafion composite membranes. To correct for the electrolyte resistance between the membrane and the two Luggin capillaries, measurements were carried out also without a membrane. The temperature was controlled thermostatically between 25 and 80 °C. All PEDOT/Nafion composite membranes were immersed in 1 M H_2SO_4 solution for at least 1 h before the measurements.

Electrochemical impedance spectroscopy, EIS, was also applied using the four-electrode cell connected to a frequency response analyzer (SI 1255, Solartron Schlumberger). Measurements at room temperature were carried out in the frequency range 0.1 $\text{Hz} \leq f \leq 10$ kHz and constant AC-voltage amplitude 5 mV.

The morphology of the membranes was studied by scanning electron microscopy SEM (Philips XL-40).

Results and discussion

The cross-sectional SEM image of the PEDOT/Nafion composite membrane in Fig. 2 shows the thin PEDOT layer on top of the Nafion membrane. The sulfonic acid groups of Nafion may serve as counter-ions in the PEDOT polymerization process so that the polymerization inside the Nafion membrane cannot be excluded. This could not, however, be verified in our experiments.

PEDOT/Nafion composite membranes with different PEDOT loading were prepared by varying of the polymerization time. As the solubility of EDOT in pure water is rather low (2.1 g l^{-1} at 20 °C), its dispersion was very poor even with magnetic stirring. The low concentration of free EDOT monomer in solution is the reason for the observed strongly retarded diffusion and growth of the PEDOT film. The solubility of EDOT can be significantly improved when 0.1 M NaPSS is added to the solution. In this case,

Fig. 1 Schematic diagram of the four-electrode glass cell used for the DC conductivity and AC impedance measurements; W working, S sense, R reference and C counter-electrode terminals

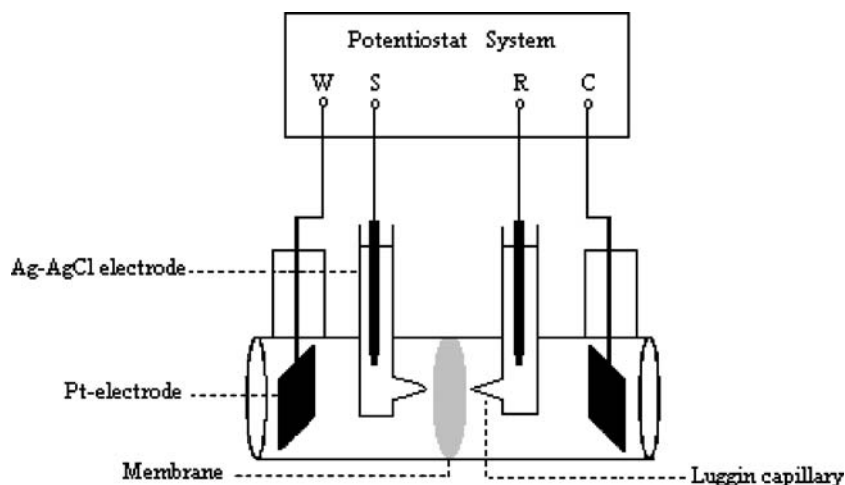
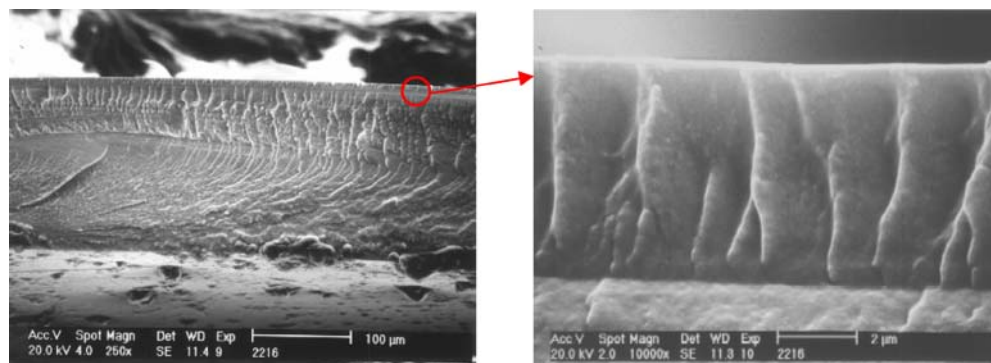


Fig. 2 Cross-sectional SEM image of PEDOT/Nafion composite membrane prepared by polymerization of EDOT (dissolved in water) for 24 h



the polymerization proceeds much faster, which is indicated by the time dependence of the experimental data.

The ionic conductivity σ of PEDOT/Nafion composite membranes as a function of temperature T is shown in Figs. 3 and 4. The measured ionic conductivity of the Nafion 117 membrane was about $5 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. In the case of EDOT in pure water, the ionic conductivity of membranes at room temperature was found to decrease gradually from $2.1 \times 10^{-2} \text{ S cm}^{-1}$ to $1.3 \times 10^{-2} \text{ S cm}^{-1}$ and $9.7 \times 10^{-3} \text{ S cm}^{-1}$ with increasing polymerization time of 24, 30, and 48 h, respectively. This is due to the fact that the ionic conductivity of PEDOT is obviously lower than that of Nafion 117 and the resistance of the membrane increases with the amount of PEDOT. For EDOT in NaPSS solution, the ionic conductivity of the membranes decreased from 2.4×10^{-2} to $1.8 \times 10^{-2} \text{ S cm}^{-1}$ and $1.5 \times 10^{-2} \text{ S cm}^{-1}$ during much shorter polymerization times of 1, 3, and 4 h, respectively. This indicates that the polymerization reaction is faster if EDOT is dissolved in NaPSS solution instead of pure water. From the slope of the Arrhenius plots in Figs. 3 and 4, the apparent activation energy for the migration of protons in the Nafion 117 membrane was found to be 13.7 kJ mol^{-1} , which is in reasonable agreement with the literature value of 13.4 kJ mol^{-1} [23]. Similar values were found for the PEDOT/Nafion composite membranes ranging from 10.5 to 16.4 kJ mol^{-1} . Although the total resistance of the PEDOT/Nafion membranes increases with the amount of PEDOT, the ionic conductivities of the composite membranes remained above the value 0.01 S cm^{-1} over the whole temperature range 25–80 °C studied. These results reveal that PEDOT/Nafion composite membranes maintain adequate conductivity for fuel cell applications.

Figure 5 shows the methanol permeability of PEDOT/Nafion composite membranes as a function of polymerization time at room temperature. It can be seen that methanol permeability decreases with increasing polymerization time. Again, the methanol permeability decreases much faster if EDOT is dissolved in NaPSS solution instead of pure water. Considering both the ionic conductivity and the methanol permeability, the better performance is found for the membranes prepared with EDOT monomer in NaPSS solution after 3- and 4-h polymerization time. The methanol permeability of these two membranes is reduced to 78 and 85% of the value of the Nafion 117 membrane, while the conductivity is decreased to 64 and 70%.

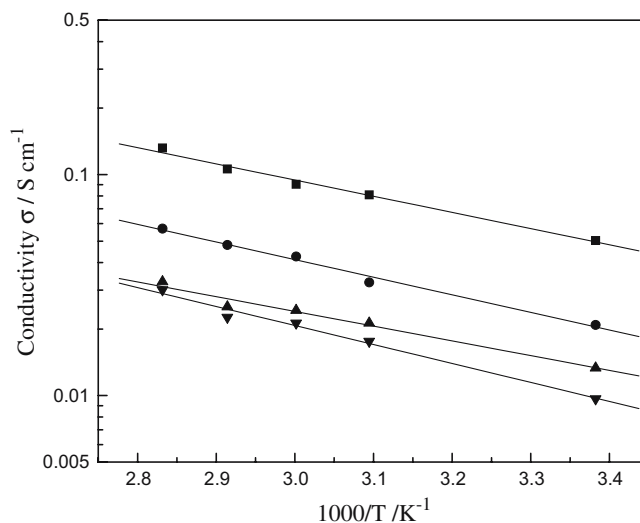


Fig. 3 Arrhenius plots of ionic conductivity of Nafion 117 membrane (■) and PEDOT/Nafion composite membranes prepared by polymerization of EDOT (dissolved in water) for 24 h (●), 30 h (▲) and 48 h (▼)

The temperature dependence of the methanol permeability of PEDOT/Nafion composite membranes prepared

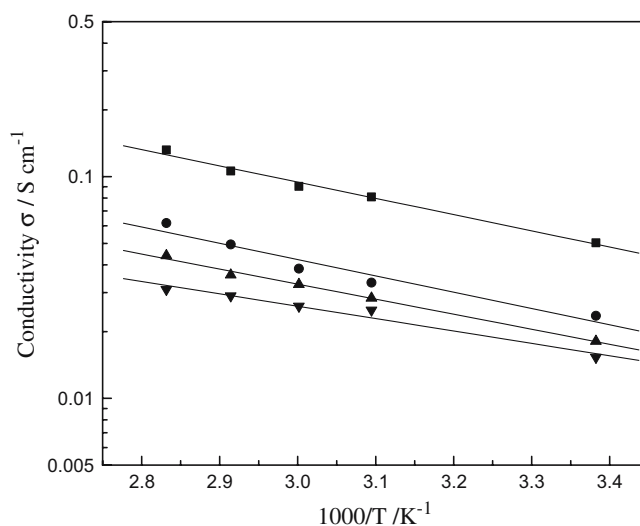


Fig. 4 Arrhenius plots of ionic conductivity of Nafion 117 membrane (■) and PEDOT/Nafion composite membranes prepared by polymerization of EDOT (dissolved in 0.1 M NaPSS solution) for 1 h (●), 3 h (▲) and 4 h (▼)

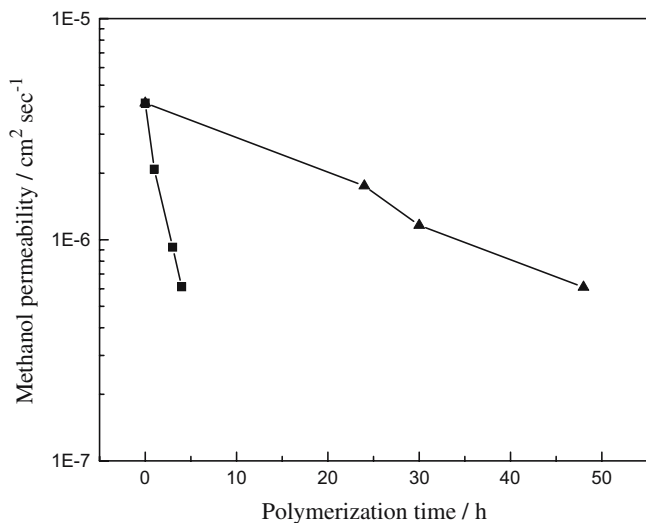


Fig. 5 Methanol permeability of PEDOT/Nafion composite membranes as a function of the polymerization time at room temperature; polymerization of EDOT dissolved in 0.1 M NaPSS solution (■) and pure water (▲)

with EDOT in NaPSS is shown in Fig. 6 together with the respective data of pure Nafion 117 membrane. The Arrhenius-type dependence subsists for all these membranes. The apparent activation energy for methanol permeation in the Nafion 117 membrane is about 16 kJ mol⁻¹, which is in reasonable agreement with the literature value of 17.96 kJ mol⁻¹ [11]. The values for our composite membranes are 23.6 and 21.7 kJ mol⁻¹, respectively, which are slightly higher than that of the Nafion 117 membrane. In addition, it can be observed that the methanol permeability of PEDOT/Nafion composite membranes is as much as 70–80% lower than the Nafion 117 membrane value. This means the PEDOT layer on the surface of Nafion membrane can effectively block the methanol crossover.

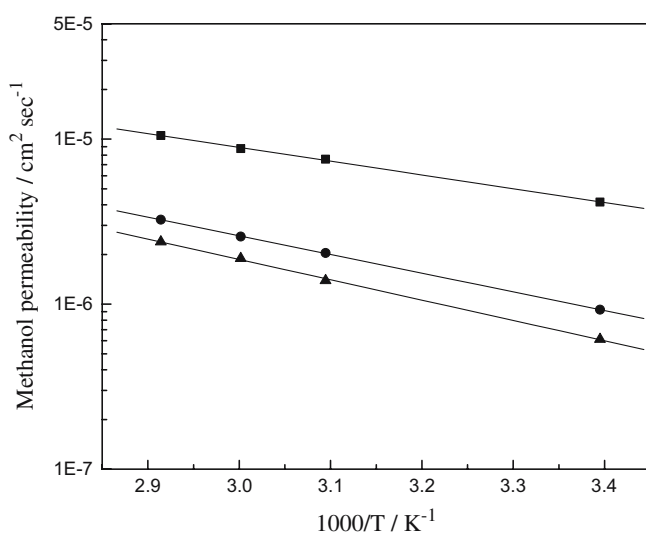


Fig. 6 Arrhenius plots of methanol permeability for Nafion 17 membrane (■) and PEDOT/Nafion composite membranes prepared by polymerization of EDOT (dissolved in 0.1 M NaPSS solution) for 3 h (●) and 4 h (▲)

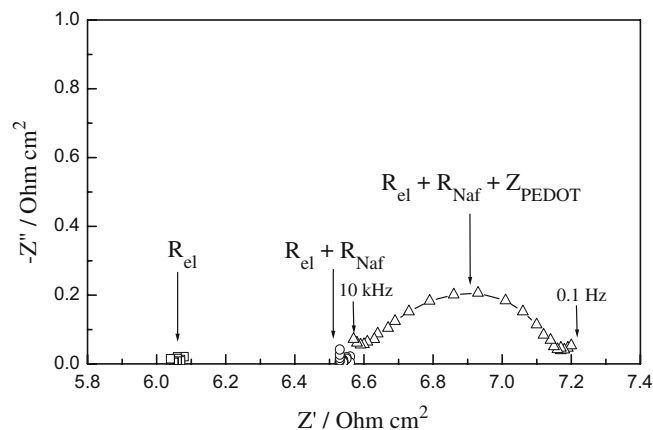


Fig. 7 Nyquist plots of four-electrode impedance spectra obtained in the membrane cell: without membrane (□), with Nafion 117 membrane (○), with PEDOT/Nafion composite membrane prepared by polymerization of EDOT (dissolved in water) for 24 h (Δ). Electrolyte 1 M H₂SO₄; T=298 K

From DC conductivity measurements, it is difficult to separate the contributions of the Nafion membrane from that of the PEDOT film. It will be shown that this is possible in principle by AC impedance technique. Typical diagrams of the complex impedance $Z(j\omega)$

$$Z(j\omega) = Z'(\omega) + jZ''(\omega) \quad (1)$$

are shown in Fig. 7; they were obtained by measurements in the four-electrode cell (A) without a membrane, (B) with the unmodified Nafion 117 membrane, and (C) with the PEDOT/Nafion composite membrane. In Eq. 1, Z' and Z'' are the real and imaginary parts of the complex impedance, $\omega=2\pi f$ is the angular frequency and $j=\sqrt{-1}$. From this

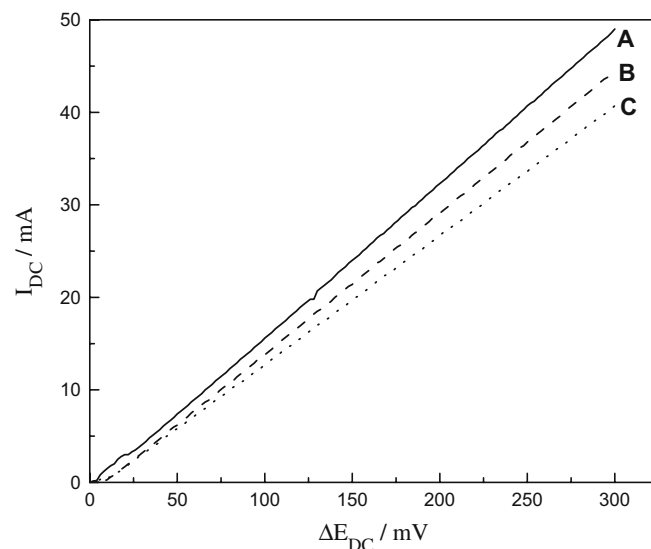
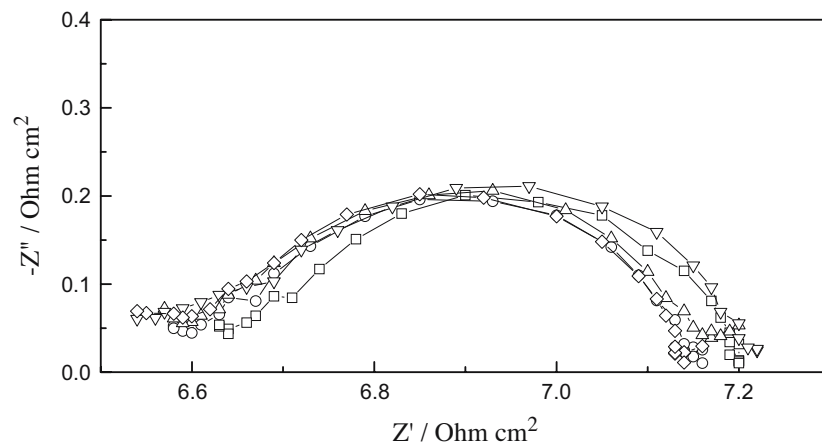


Fig. 8 DC polarization curves obtained in the four-electrode membrane cell. **a** without membrane; **b** with Nafion 117 membrane; **c** with PEDOT/Nafion composite membrane prepared by polymerization of EDOT (dissolved in water) for 24 h. Electrolyte 1 M H₂SO₄; T=298 K

Fig. 9 Nyquist plots of four-electrode AC-impedance spectra obtained at different DC potentials $\Delta E_{DC}/mV$: -80 (\square), -20 (\circ), 0 (\triangle), 50 (∇), 100 (\diamond). The PEDOT/Nafion composite membrane was prepared by polymerization of EDOT (dissolved in water) for 24 h; electrolyte: 1 M H_2SO_4 ; $T=298$ K



measurement, it is evident that the electrolyte resistance R_{el} (A) and the impedance of the Nafion 117 membrane (B) do not exhibit any frequency dependence, whereas, the impedance of the composite membrane (C) shows a well-pronounced frequency-dependence with an imaginary part.

The impedance of the empty cell (A) is described by a pure ohmic electrolyte resistance

$$Z(j\omega) = R_{el} \quad (2)$$

The impedance of the cell with the Nafion 117 membrane (B) is also purely ohmic and consists of the resistances of the electrolyte and the Nafion membrane in series

$$Z(j\omega) = R_{el} + R_{Naf} \quad (3)$$

Whereas, the impedance of the cell with the modified PEDOT/Nafion composite membrane displays a frequency dependent third contribution related to the PEDOT film,

$$Z(j\omega) = R_{el} + R_{Naf} + Z_{PEDOT}(j\omega) \quad (4)$$

The DC conductivity can be obtained from the polarization resistance R_p , defined as the low-frequency limit of the impedance $Z(j\omega)$

$$R_p = \lim_{\omega \rightarrow 0} Z(j\omega), \quad (5)$$

which corresponds to the reciprocal slope of the DC polarization curve I vs ΔE . The DC curves corresponding to the impedance data in Fig. 7 are shown in Fig. 8. The resistances R_{el} , R_{Naf} and $R_{PEDOT/Nafion}$ obtained from the slope of the DC curves are in good agreement with the R_p values of the impedance measurement. As the slope of the DC curves is a constant, the impedance spectra of the PEDOT/Nafion membrane should be independent of the applied DC voltage ΔE and the ionic current I through

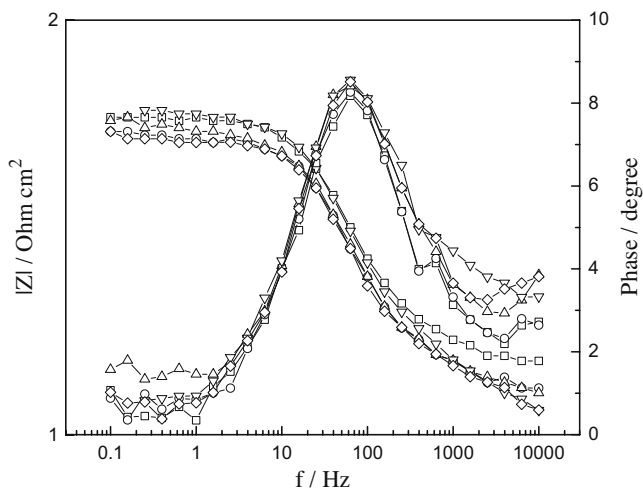


Fig. 10 Bode-plots of four-electrode AC-impedance spectra obtained at different DC potential $\Delta E_{DC}/mV$: -80 (\square), -20 (\circ), 0 (\triangle), 50 (∇), 100 (\diamond). The PEDOT/Nafion composite membrane was prepared by polymerization of EDOT (dissolved in water) for 24 h; electrolyte: 1 M H_2SO_4 ; $T=298$ K

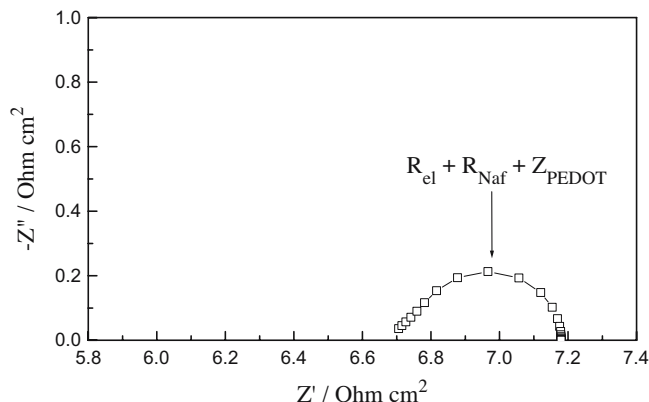


Fig. 11 Simulation of the PEDOT/Nafion membrane impedance using Eq. 4 and the heterogeneous pore model, Eq. 6, with $Z_{PEDOT}=Z_{por}$ and $R_{el}+R_{Naf}=6.6$ Ohm cm^2 , $R^*=0.7$ Ohm cm^2 and $C^*=3.16 \times 10^{-4}$ F cm^2

the membrane. This is depicted in Figs. 9 and 10, where the Nyquist and corresponding Bode plots obtained at different ΔE values are shown.

The observed frequency dependence of Z_{PEDOT} can be explained by the mixed electronic and ionic conductivity of the conducting polymer PEDOT. Impedance models of such conducting polymer films have been discussed in the literature [24–30]. In some of the models, it is assumed that the film is heterogeneous and consists of two separate electron and ion conducting phases [27–30], whereas, other models consider the polymer film as a homogeneous single phase [24, 26]. The most prominent heterogeneous approach is the one-dimensional cylindrical pore model derived by De Levie and Delahay [31], which corresponds to the well-known transmission line for a free-standing membrane with the condition $\sigma_e \gg \sigma_{\text{ion}}$

$$Z_{\text{por}} = R^* \frac{th(\sqrt{j\omega R^* C^*})}{\sqrt{j\omega R^* C^*}}, \quad (6)$$

where R^* is the overall resistance of the ion-conducting phase (pore electrolyte) and C^* is the capacitance at the inner interface between the electron- and ion-conducting phases (pore wall). Figure 11 depicts a simulation of the pore-model impedance using Eq. 6. The shape of the impedance resembles that of the experimental impedance spectra.

Conclusion

Commercial Nafion membranes were impregnated with poly(3,4-ethylenedioxythiophene) PEDOT by chemical polymerization. From the SEM image, it can be found that a thin PEDOT layer is formed on the surface of the membrane. The rate of the polymerization reaction can be increased when the EDOT monomer is dissolved in 0.1 M NaPSS solution due to its higher solubility compared to pure water. An Arrhenius-type dependence of methanol permeability and ionic conductivity was found for all modified membranes. The methanol permeability of the modified membrane was decreased by about 75% compared to Nafion 117, while the ionic conductivity remained at a level of 0.01 S cm^{-1} . Four-electrode impedance measurement on free-standing PEDOT/Nafion membrane allows separation of the ohmic resistance of the Nafion 117 membrane from the frequency-dependent impedance of the conducting polymer PEDOT film.

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