PERMEABILITY OF POLYPYRROLE FILM FOR PYRROLE AND METHANOL

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Introduction

Conducting polymers (CPs) represent a class of materials possessing unusual properties, of which the most important is electronic conductivity. It makes them promising for the broad field of applications. Catalyst support for the PEM type Fuel Cells represents one of them. The reasons for replacement of classical carbon catalyst support by CPs are mainly enhancement of the three-phase contact appearance probability and higher Pt-CP composite resistivity against CO poisoning [1]. In our study we have focused on the problem of polypyrrole (PPy) film embedding on the Nafion[®] surface, which has not been solved so far. We have used a diffusion method to prepare CP/ion selective membrane composite. The experimental set-up consisted of two compartments containing monomer and oxidant solution respectively separated by the membrane to be modified. Diffusion method has been chosen as the most appropriate one providing well-defined kinetics of the PPy film growth on the membrane surface. The advantage of this method consists also in the fact that PPy does not seem to penetrate deep into the Nafion[®] membrane structure. At the same time the PPy film retains its electrochemical activity. In the first stage our effort has focused on verifying results published so far on the ion selective membrane modification by PPy [2]. The attention was paid mainly to the mechanical and electrochemical properties of the composite prepared, as well as to the simplicity and reproducibility of the modification method. The present study intends to contribute to characterisation of the novel Nafion[®]/PPy (NP) composite, especially from the point of view of composite permeability for small organic molecules, especially for pyrrole (Py) and methanol.

Theory of Nafion-Polypyrrole composite permeability evaluation

Kinetics of PPy film growth

According the study of kinetics of the PPy film growth on the membrane surface, we may assume that the synthesis rate-determining step is the monomer diffusion through the PPy film formed. Since large excess of the oxidant is used, this is a reasonable assumption. Therefore we may assume the monomer concentration on the PPy/oxidant solution interface $c_{Py}^{out} = 0 \text{ mol.dm}^{-3}$. The next assumption is continuity of the flux through the interface between the two layers of the composite $(J_{Py}^{Naf} = J_{Py}^{PPy})$, where *J* indicates molar flux. Under these assumptions expression for the dependence of the PPy film thickness on

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the time of synthesis can be obtained.

$$\frac{k_{Py}^{Naf}}{2}\delta_{PPy}^{2} + k_{Py}^{Naf}\delta_{Naf}\delta_{PPy} - \frac{M_{Py}}{\rho_{PPy}}k_{Py}^{Naf}k_{Py}^{PPy}c_{Py}^{0,Naf}\tau = 0$$
(1)

where δ_{PPy} and δ_{Naf} are thickness of PPy film and Nafion[®] membrane respectively, M_{Py} molar weight and ρ_{Py} density of pyrrole, $c_{Py}^{0,Naf}$ molar concentration of pyrrole in Nafion[®] membrane and τ indicates time.

Permeabilities of Py in the Nafion[®] membrane k_{Py}^{Naf} and PPy film k_{Py}^{PPy} can be obtained by optimising values of these parameters in Eq. (1) according to the experimentally obtained dependence of the PPy film thickness on the synthesis duration.

The parameters values were obtained by the minimisation of the deviations squares sum performed using the library procedure DEQNF [3].

Nafion[®] – PPy composite permeability

Classical method of permeability determination in the case of electroneutral species consists in placement of demineralised water and solution of followed specie in the demineralised water in reservoirs separated by the sample under study. Transport between the bulk of the solution and separator surface may be neglected in comparison to the transport across the separator. The concentrations of compound A in the both compartments are interconnected through the molar balance. For a homogeneous separator consisting of only single layer (in a present case self-standing Nafion[®] membrane) an expression for k_A in form of Eq. (2) is obtained.

$$\delta_{Naf} V_{1} ln \left[1 - \frac{n_{A,1}^{\tau} \left(\frac{V_{1}}{V_{2}} + 1 \right)}{V_{1} c_{A,2}^{\tau=0}} \right]$$

$$k_{A}^{Naf} = - \frac{1}{a_{Naf} \left(\frac{V_{1}}{V_{2}} + 1 \right) \tau}$$
(2)

where V_1 and V_2 are volume of two reservoirs, $n_{A,1}^r$ molar amount of specie A in the reservoir 1 in dependence on the time, $c_{A,2}^{r=0}$ initial molar concentration of specie A in the reservoir 2 and a_{Naf} is surface area of the Nafion[®] membrane.

In the case of NP composite permeability determination we face more complicated problem. This is because composite consists of two layers with significantly different properties. The evaluation of the diffusion coefficient has to account for this fact. Afterwards value of permeability of the PPy film in form of Eq. (3) can be expressed as

$$k_{A}^{PPy} = \frac{\frac{V_{1}V_{2}}{V_{1} + V_{2}} ln \left(\frac{c_{A,2}^{\tau=0}}{c_{A,2}^{\tau=0} - \frac{V_{1} + V_{2}}{V_{1}V_{2}} n_{A,1}^{\tau}} \right) k_{A}^{Naf} \delta_{PPy}}{k_{A}^{Naf} a_{NP} \tau - \frac{V_{1}V_{2}}{V_{1} + V_{2}} \delta_{Naf} ln \left(\frac{c_{A,2}^{\tau=0}}{c_{A,2}^{\tau=0} - \frac{V_{1} + V_{2}}{V_{1}V_{2}} n_{A,1}^{\tau}} \right)}$$
(3)

where a_{NP} is surface area of the NP composite.

Using Eqs. (2) and (3) value of diffusion coefficient can be calculated for self-standing Nafion[®] membrane and for PPy film embedded on the surface of Nafion[®] membrane respectively on the base of the experimentally determined number of moles of compound A transported from the reservoir 2 to the reservoir 1 across separator.

Experimental

NP composite synthesis

Diffusion method of the Nafion[®]/PPy synthesis has been used in this study. Membrane sample was squeezed between two reservoirs, one of them being filled with 0.1 M Py solution and the second one with 0.1 M $Na_2S_2O_8$ solution. The polymerisation lasted for the defined time interval. Afterwards solutions were discharged and sample thoroughly washed in demineralised water.

Characterisation of Nafion[®] membrane and NP composite

Following parameters were determined for the NP composite prepared: PPy film morphology and thickness, kinetics of the growth, permeability for Py and methanol. As a last parameter PPy film electrochemical activity was followed.

Scanning electron microscopy (SEM) was used to determine ex-situ samples morphology and PPy film thickness in dependence on the time of synthesis.

Nafion[®] membrane or NP composite permeability was determined using glass diffusion cell identical with this used for the sample synthesis. It has contained originally 0.1 M Py or 1.0 M methanol solution in demineralised water on one side of the sample and pure demineralised water on the opposite side. Both solutions were deaerated in order to prevent changes in the composite properties. The gradual concentration increase in the later chamber was followed spectrophotometrically and using differential refractometry for the Py and methanol permeation experiments respectively.

Electrochemical activity was tested using three-electrode arrangement employing saturated argentchloride electrode (SAE).

Results and Discussion

Permeability of NP composite for Py

Permeability represents from more points of view an important characteristic of the composite synthesised. In this study the attention has turned to the permeability for monomer and methanol. As it has been discussed in the Theory of PPy film growth chapter, composite permeability for monomer represents limiting parameter for the kinetics of the PPy film growth.

Two methods were used to determine composite permeability for monomer: (i) kinetics of the PPy film growth and (ii) diffusion through the presynthesised composite in the deaerated demineralised water. The advantage of method (i) based on the kinetics of the PPy film growth consists in the fact it is determined directly during synthesis. Therefore it is not influenced by the composite changes induced by the post-synthesis exposure to the monomer solution and provides thus more relevant data. The later method, on the other hand, allows direct evaluation of the data and thus reduces error introduced by the subsequent mathematical treatment of experimental results and by the assumptions made. Experimental points shown in Fig. 1 have been used for the coefficients evaluation. Permeability evaluation delivers following values: $k_{Py}^{Naf} = 5.20 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and

 k_{Py}^{PPy} = 3.67x10⁻¹³ m² s⁻¹. The line shown in the figure represents values of PPy thickness calculated using Eq. (1) with optimised values of coefficients.

Typical monomer concentration courses vs. time of penetration used for the permeability evaluation from the diffusional flux are for the Nafion[®] and NP composite shown in Fig. 2. As it was expected, both dependencies show logarithmic shape. They indicate serious decelerating effect of membrane modification by PPy on the composite permeability. Diffusion coefficient of Py in the Nafion[®] membrane was evaluated using Eq. (2) as 2.82x10⁻¹¹ m² s⁻¹. As it was expected, this value is by almost 6 orders of magnitude lower than diffusivity evaluated from the kinetics of PPy film growth. It is much more realistic value and has been therefore used to evaluate PPy permeability for the Py using Eq. (3).

The results are for different PPy film thicknesses summarised in Table 1. These data show several interesting aspects: (i) much lower value of permeability for Py when compared with self-standing Nafion[®] membrane, (ii) value lower than this evaluated from the kinetics of PPy film growth and (iii) value increasing with the thickness of the film.

Present results have confirmed lower composite permeability for Py when compared to the self-standing Nafion[®] membrane. PPy permeability is approximately by 3 orders of magnitude lower. This is a very interesting finding with respect to application especially in the DMFC, where high Nafion[®] permeability for methanol as a fuel plays a serious negative role. Application of PPy film(s) would allow minimising this problem. The reason for PPy low permeability consists in its rigorous structure with much smaller pores than these of Nafion[®].

There are two possible reasons for PPy permeability for Py evaluated from the PPy film growth kinetics being by an order of magnitude higher than this from the diffusional experiments. The first one consists in the continuing polymerisation process during the permeation study. Py is very sensitive to the oxidation and polymerisation is initiated easily. This explanation, however, doesn't seems to be very probable. The more probable explanation consists in different behaviour of the PPy film during its growth when compared with the consolidated film stored in demineralised water overnight.

Different question represents variation of the PPy film permeability with its thickness documented by Table 1. Monotonous growth of the permeability with the film thickness is accelerated at its higher values. This indicates reason being the increasing probability of film defects occurrence with the increasing thickness.

Despite the differences in the Py permeability through Nafion[®] and PPy determined by the above two methods it is clear, that diffusion of the monomer through the PPy film formed on the membrane surface is a rate determining step of the PPy growth. By the primary film formation on the membrane surface initial period is sufficiently fast. Nevertheless, thickness of the film, which can be obtained in a realistic polymerisation time of units of hours, is strongly limited by the decelerating effect of already formed film on the Py transport to the reaction zone. This at the same time confirms the theory about the rate-determining step during the PPy film formation introduced above.

Even more detrimental effect has this fact on the secondary PPy film formation on the opposite membrane side. Here the film growth has to be initiated already by the Py flux density corresponding to the thick primary PPy film. This may represent a problem during the nucleation phase. After the first compact layer of the secondary PPy film is formed, further PPy growth kinetics will be reduced practically to zero. This is consistent with the experimentally obtained results. An attempt was made to synthesize secondary PPy film on the bare side of the Nafion[®] membrane covered primary on the opposite side by the 3.8 µm thick PPy film. After 15 h of polymerisation almost negligible amount of PPy has been formed (δ_{PPv} < 0.3 µm). It further confirms the above given explanation of the changes in the PPy film permeability for Py during storage after completed synthesis. Whereas primary PPy 4 µm thick would growth by additional at least 2 to 3 µm during 15 hours exposure to the synthesis solutions, secondary PPy film does reach during the same time thickness lower than 0.3 µm, *i.e.* by 1 order of magnitude lower. This is in a good agreement with PPy film permeability decline during consolidation. Therefore it is possible to conclude, that purely chemical synthesis is not suitable to form entire thickness of the secondary PPy film. A viable alternative has to be found. This will be discussed in the following section.

Electrochemical modification of NP composite

As it has been shown in the previous study [2], PPy film chemically synthesised on the Nafion[®] membrane surface possesses electrochemical activity comparable with electrosynthesised PPy films. It is therefore straightforward, that electrochemical modification represents a viable option to solve problem of the slow synthesis kinetics for thicker PPy films, or synthesis of PPy film on the second membrane side.

Cyclovoltammetric polarisation curve has been used for rapid characterisation of the changes of the PPy film thickness on the Nafion membrane. These curves document clearly that after electropolymerisation step amount of PPy deposited on the both membrane sides is comparable. There remains a danger, that during electropolymerisation PPy was formed mainly on the current feeder and little or no PPy was formed in the sample center. This suspicion was refuted by means of SEM. Microphotography of the sample center cross-section is shown in Fig. 3. In this case the sample was analysed with PPy electropolymerised on the top of the primary layer. Identical results were obtained for the electrochemical modified secondary layer.

Permeability of Nafion[®] and NP composite for methanol

As already mentioned, reduction of the Nafion[®] membrane permeability for methanol would represent an important advantage for the DMFC construction. In order to quantify influence of PPy on the NP composite permeability for this compound similar experiments like for Py were performed for the methanol solution.

Since methanol permeation through the composite is not connected with the changes in its structure, application of the later method based on the permeation of one component from the concentrate side to the diluate is the most appropriate one. Typical course of the moles number of methanol permeated through the composite on the time of diffusion is shown in Fig. 4. It is evident, that also in the case of methanol PPy film represents an efficient barrier against organic molecules penetration. The permeability of Nafion[®] membrane was evaluated as 9.70x10⁻¹¹ m².s⁻¹. For the NP composite the permeability for methanol determined is summarised in Table 1.

Table 1 Nafion[®] membrane and Nafion[®]/polypyrrole composite permeability for pyrrole and methanol evaluated on the basis of experiments with the diffusion cell. Diffusion coefficient of pyrrole and methanol in the Nafion[®] membrane was determined as $2.82 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $2.04 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ respectively.

PPy film thickness	permeability [m ² .s ⁻¹]	
[µm]	pyrrole	methanol
0	2.82x10 ⁻¹¹	9.70x10 ⁻¹¹
2.35	1.20x10 ⁻¹⁴	1.98x10 ⁻¹³
3.85	1.24x10 ⁻¹⁴	4.45x10 ⁻¹³
4.52	3.13x10 ⁻¹⁴	2.06x10 ⁻¹³

Conclusions

Diffusion method has been proved to be a viable method of PPy fixation on the Nafion[®] membrane surface. NP composites prepared have shown homogeneous morphology, very good adherence to the membrane surface and high electrochemical activity. As it was found, PPy represents an efficient barrier against methanol permeation through the composite. Its permeability for Py as well as for methanol is approximately two orders of magnitude lower when compared to the self standing Nafion[®] membrane. This may represent a serious problem during polymerisation of the secondary PPy layer. It has been solved by means of electropolymerisation of PPy film of necessary thickness on the top of chemically presynthesised sublayer.

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Fig. 1 Kinetics of the PPy film growth on the surface of Nafion[®] membrane. The line indicates the kinetics calculated using model with optimised Py diffusion coefficient in Nafion and PPy permeability for monomer.



Fig. 2 Time course of Py content in the diluate chamber of the diffusion cell for O - Nafion membrane and ∇ - NP composite (thickness of the PPy film 4.52 µm); area of the separator 9.08x10⁻⁴ m², Py initial concentration in the concentrate chamber 0.1 M.



Fig. 3 SEM microphotography of the cross-section of NP composite with PPy layer electropolymerised ($2.3 \mu m$) on the top of chemically synthesised primary PPy layer ($2.3 \mu m$). Electrical charge used for the electropolymerisation reached 1.28 C.m⁻².



Fig. 4 Time course of methanol content in the diluate chamber of the diffusion cell for O - Nafion membrane and ∇ - NP composite (thickness of the PPy film 3.85 µm); area of the separator 9.08x10⁻⁴ m², methanol initial concentration in the concentrate chamber 1 M.

Figures