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Preparation of a novel composite material based on a Nafion® membrane and polypyrrole for potential application in a PEM fuel cell

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Abstract

The process of embedding polypyrrole (PPy) on the surface of a Nafion® membrane was studied. Three methods of PPy synthesis directly on the membrane surface were compared. The diffusion method based on the separation of monomer and oxidant (peroxidisulphate) solutions by the membrane to be modified is proposed as the most promising one. The monomer diffuses through the membrane to the oxidant side, where it is polymerized. In this case sulphate is incorporated into the film as a counter-ion. PPy film prepared in this way adheres well to the Nafion® surface and shows promising electrochemical activity. The permeability of the composite for monomer in comparison to self-standing Nafion® film is reduced significantly. This may be important for the potential application of this composite, especially in a direct methanol fuel cell, as an alternative membrane-electrode assembly (MEA), particularly with regard to the currently used MEA's permeability for fuel.

1. Introduction

Conducting polymers (CPs) have attracted intensive attention by numerous research groups for decades [1]. This is due mainly to their unique properties, of which the most important is electronic conductivity. Numerous applications for CPs have been proposed. Those reported most often include charge storage [2], sensors [3], anticorrosion coatings [4] and electrochromic displays [5]. It is considered that CPs may also play an important role in the development of proton exchange membrane (PEM) type fuel cells. The reasons for this are, among others, their parallel ionic and electronic conductivity and enhancement of Pt–CP composite resistivity to CO poisoning when compared with bare Pt or Pt particles on a carbon support [6]. Numerous studies have been performed on methods of CP modification by Pt catalyst, e.g. [7–16], and on assessment of their electrocatalytic activity [6–15].

For the application of CP-based electrodes in PEM fuel cells it is, however, necessary to develop a simple and reproducible method of embedding the electrode on the surface of the polymer electrolyte, thus preparing MEA. Nowadays Nafion® type membranes are almost exclusively used as polymer electrolytes for this type of application. In this case we face a different situation regarding the number of studies published to date. Only one method has been proposed for the preparation of MEA using CP as a component of the catalyst support, namely hot pressing of polystyrene sulphonate-doped PPy particles impregnated with Pt particles and bonded by Teflon on the Nafion® membrane surface [17]. Although the electrocatalytic activity of this electrode has been proved, the negative influence of high temperatures on the properties of PPy particles must be considered. Therefore it is of interest to verify the possibility of an alternative method of CP embedding on the membrane surface. As follows from the literature data, synthesis directly on the membrane surface is a promising method [18–29]. These studies were motivated by various interests. Most often the membranes were synthesised with respect to their possible utilisation in electrodialysis [18–22]. It is thought that the modification of an ion selective polymer with a second polymer characterised by a rigid structure may help to increase the selectivity of the membrane to the required ions, while at the same time maintaining reasonably high permeability. A small group of studies has declared its interest in the production of a new type of separation membrane [23, 24], a slightly larger group in the preparation of a new type of functionalised materials [25–29]. Recently, a study was published on the preparation and characterisation of a Nafion/PPy composite for application in direct methanol fuel cells (DMFC), especially with respect to its permeability for methanol [30]. A typical oxidant used for chemical polymerisation is $FeCl_3$ [18, 20–26, 29] or $Fe(NO_3)_3$ [30]. Only in rare cases were $Na_2S_2O_8$ [18, 19, 27] or H_2O_2 [30] used. Whereas, according to Sata [18], during modification of an anion selective membrane the application of $FeCl_3$ results in the formation of CP film on the membrane surface, $Na_2S_2O_8$ also allows the formation of CP inside the ion selective film. This is probably caused by the polarity of the oxidising ion and that of the membrane. On the basis of this finding it may be expected that the converse situation (surface CP film formation during oxidation by $Na_2S_2O_8$ and polymerisation in the bulk of the membrane by $FeCl_3$) will arise during modification of the cation selective membrane material. The electroneutral H_2O_2 molecule should thus allow formation of the CP film inside the ion selective membrane regardless of its polarity.

A typical polymerisation procedure follows the scenario of membrane equilibration with the monomer and its subsequent plunging into the oxidant solution [18, 19, 23, 29]. The inverse method (equilibration with the oxidant and plunging into the monomer solution) has also been proposed [21, 22, 25, 26]. Ermolaev et al. [24] and Hsu [31] are the exceptions. They used a diffusion cell where two compartments, containing a monomer and an oxidant solution respectively, are separated by the membrane to be modified. According to [24] both Fe^{3+} and pyrrole (Py) diffuse through the membrane. Thus, polymerisation takes place mainly inside the membrane film where both components come into contact. Hsu [31] also indicates that both the protonised aniline and the oxidant ($FeCl_3$ or $(NH_4)_2S_2O_8$) diffuse through the Nafion® film. According to his results polymerisation takes place both on the film surface on the oxidant side as well as inside the film, but not through its entire thickness. It is, however, doubtful whether $S_2O_8^{2-}$ can easily diffuse into the Nafion® membrane in sufficient quantities to initiate polymerisation inside the membrane.

As follows from the above, the application of the diffusion method (i.e. two compartments containing a monomer and an oxidant solution respectively) represents a promising method for Nafion® membrane modification by CP. Since Nafion® is a cation exchange membrane, $Na_2S_2O_8$ is a promising oxidising agent permitting synthesis of CP on the surface of the membrane without deep penetration into the membrane interior. The latter would entail the danger of the cell short-circuiting. The aim of this study is to verify this assumption and to characterise a composite material produced with a view to of its possible future utilisation in a DMFC.

2. Experimental

2.1. *Nafion®/polypyrrole composite synthesis*

Three methods of PPy synthesis directly on the surface of or inside the Nafion® membrane were compared. They are briefly described in the following.

Method I denotes the procedure consisting of equilibration of the membrane with an oxidant solution, i.e. in the present case $Na_2S_2O_8$. A membrane sample was stored for 1 h in 0.1 or 1.0 M $Na_2S_2O_8$ solution. Droplets of the oxidant solution were than carefully removed from the surface of the membrane with cellulose wadding and it was plunged into the 0.1 or 1.0 M Py solution for 3 h. Finally, the sample was washed in demineralised water.

Method II differs from Method I in the sequence. In this case the membrane sample was stored for 1 h in 0.1 or 1.0 M Py solution. The membrane equilibrated with Py solution was removed from the solution, droplets of monomer were carefully removed with cellulose wadding from the membrane surface and it was plunged into 0.1 or 1.0 M $Na_2S_2O_8$ solution for 3 h. Finally, the sample was washed in demineralised water.

Method III is sometimes also called the diffusion method. The membrane sample (active area 9.1 cm^2) was squeezed between two reservoirs (volume 42 cm^3), one of them filled with 0.1 M Py solution and the other with 0.1 M $Na_2S_2O_8$ solution. A schematic sketch of the diffusion cell is shown in Figure 1(a). The polymerisation lasted for a defined time. Subsequently the solutions

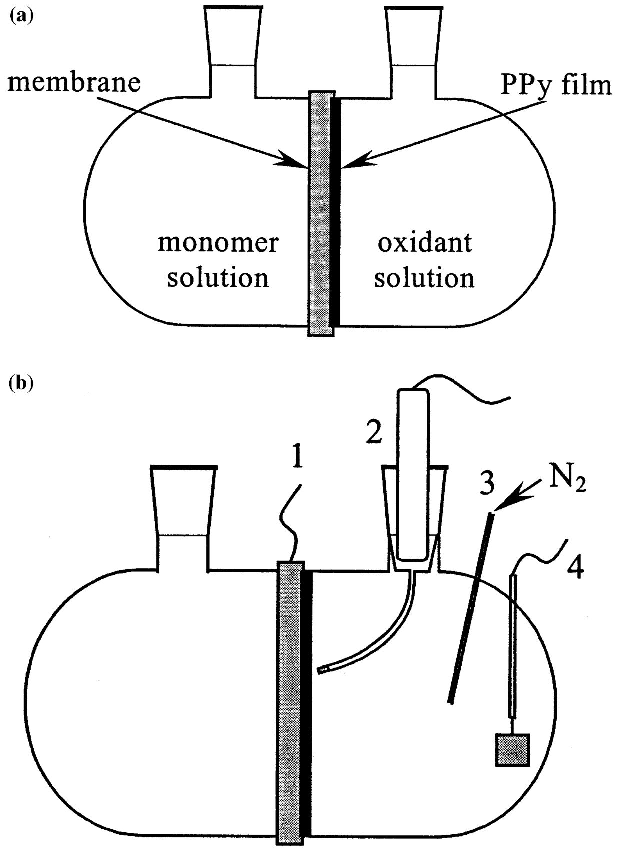

Fig. 1. (a) Schematic sketch of the diffusion cell used for Nafion®/PPy composite synthesis by Method III. Active membrane area 9.1 cm^2, volume of each compartment 42 cm^3. (b) Schematic sketch of the cell used for testing the electrochemical activity of the composite prepared. The numbers indicate: 1 – working electrode (area of 7.1 cm^2), 2 – reference electrode, 3 – inlet of nitrogen, 4 – Pt counter electrode. Volume of each compartment 42 cm^3.

were discharged and the sample was thoroughly washed in demineralised water.

2.2. *Characterisation of the Nafion®/polypyrrole composite*

The following parameters were determined for the Nafion®/polypyrrole (NP) composite prepared: PPy film morphology, penetration of PPy into the Nafion® membrane, kinetics of PPy film growth on the membrane surface and its electrochemical activity.

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

The electrochemical activity was tested using a three-electrode arrangement employing a saturated silver-silver chloride electrode (SSCE). The electrochemical cell used is shown in Figure 1(b). The compartments volume is identical to the diffusion cell. The active sample area comprises 7.1 cm^2.

2.3. *Apparatus*

The cell used for the synthesis and characterisation of the NP composite was described in chapters 2.1 and 2.2. SEM pictures were recorded using a Hitachi S4700 Field Emission Microscope. For the electrocatalytic activity testing a HEKA potentiostat – galvanostat PG310 (Germany) was used.

2.4. *Chemicals*

All chemicals used were of analytical purity or higher grade. The Py used was freshly purified by vacuum distillation. The Nafion® 117 membrane was purchased from Sigma-Aldrich; it was purified prior to each experiment by the following procedure: storage for 60 min in demineralised water at a temperature of 80 °C, followed by leaching in 30% H_2O_2 for 25 min at 60 °C, protonisation in 0.05 M H_2SO_4 for 25 min at 60 °C and washing in demineralised water for 120 min at 60 °C.

3. Results and discussion

3.1. *NP composite synthesis*

The three methods used for NP composite preparation were applied. *Method I* was tested in the first trial using synthesis solutions with a concentration of 0.1 M. In this case PPy formation was observed neither in the solution nor on the Nafion® sample. This can be explained in terms of Donnan exclusion. Since $S_2O_8^{2-}$ used as an oxidant is charged negatively, it is practically excluded within a certain concentration limit from diffusion into the cation selective membrane. Therefore there is no oxidant present in the sample. This is the reason why no PPy is produced during subsequent plunging of the sample into the monomer solution. This problem may be avoided by increasing the oxidant concentration. In the present case 1 M $S_2O_8^{2-}$ solution was used. Under these conditions once the sample comes into contact with the 1 M Py solution, PPy formation starts immediately. This can be observed visually because the colourless Nafion® membrane sample becomes dark. A typical cross-section of the sample prepared in this way is shown in Figure 2(a). A similar experiment was performed with 0.1 M monomer solution, the concentration of the oxidant being the same. A SEM microphotograph of a cross-section of this sample is shown in Figure 2(b). Whereas the composite prepared from 1 M monomer solution shows a well-defined surface layer of PPy approximately 17 μm thick, the application of 0.1 M monomer solution results in the composite showing no well-defined PPy film. On the other hand, the cross-section shown in Figure 2(b) indicates PPy formation in the bulk of the Nafion® membrane. A similar problem, however, can also be detected in the composite prepared from 1 M monomer solution. As is visible in Figure 2(a), below the PPy surface film, part of the Nafion® membrane approximately 13 μm deep shows different structural properties, indicating possible PPy formation in the membrane pores, too. This is, however, not so well pronounced as in the case of Method II discussed later and it still remains to be proved.

As already discussed, polymerisation inside the membrane represents a hazard for application in a PEM fuel cell due to the possible short-circuiting of the cell. 0.1 M monomer solution is, therefore, not suitable for this type of application. In the case of 1 M monomer solution, a thick PPy film forms with good adherence to the surface. But the danger of the cell short-circuiting is again not completely eliminated. Additionally, it is difficult to control the amount of PPy deposited on top of the composite. Therefore, this method is generally assumed not to be suitable for MEA preparation.

Method II did result in PPy formation even when applying 0.1 M oxidant solution. This confirms the explanation given above concerning the absence of PPy formation when applying 0.1 M oxidant solution in Method I. In the present case, where the electroneutral monomer Py is soaked into the membrane and it is subsequently plunged into the oxidant solution, Donnan exclusion no longer plays an important role and polymerisation can take place. A typical SEM microphotograph of a sample prepared in this way is shown in Figure 2(c). This picture illustrates one interesting phenomenon: formally, a layer of PPy is present on the top of the membrane; a closer look, however, reveals that it is not a separate PPy layer, but either a layer of Nafion® membrane with pores filled with PPy, or a PPy layer forming on top of the membrane and continuing into its pores to a certain depth. Since the existence of such a well distinguishable interface between two Nafion® phases, differing in the degree the pores are filled by PPy, is not realistic, the latter option seems more probable. By increasing the concentration of monomer to 1 M, a

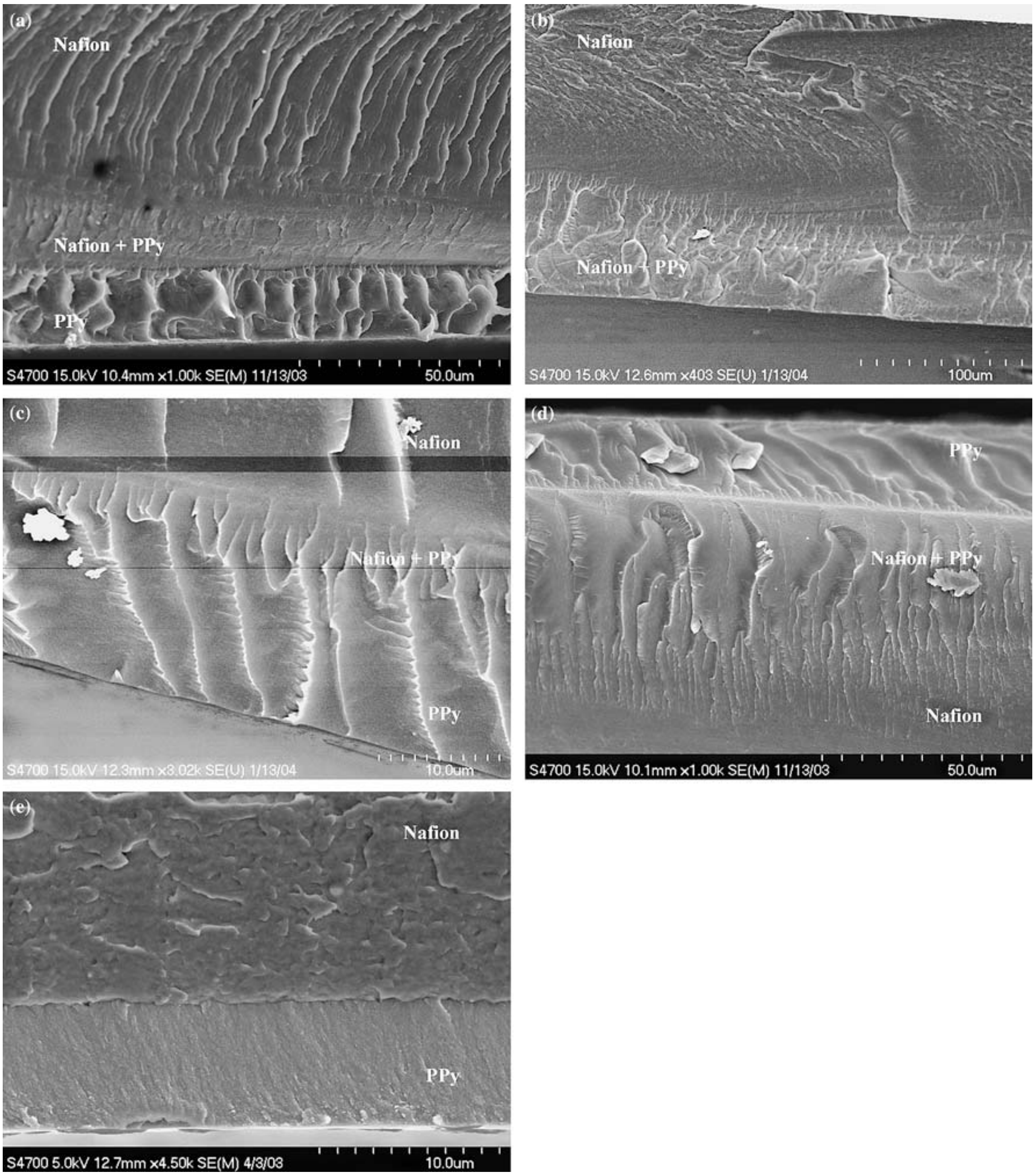

Fig. 2. (a) SEM microphotograph of the cross-section of the NP composite prepared by Method I. Synthesis conditions: 1.0 M $Na_2S_2O_8$, 1.0 M Py, soaking time in $Na_2S_2O_8$ solution 1 h, polymerisation in Py solution 3 h. (b) SEM microphotograph of the cross-section of NP composite prepared by Method I. Synthesis conditions: 1.0 M $Na_2S_2O_8$, 0.1 M Py, soaking time in $Na_2S_2O_8$ solution 1 h, polymerisation in Py solution 3 h. (c) SEM microphotograph of the cross-section of NP composite prepared by Method II. Synthesis conditions: 0.1 M Py, 0.1 M $Na_2S_2O_8$, soaking time in Py solution 1 h, polymerisation in $Na_2S_2O_8$ solution 3 h. (d) SEM microphotograph of the cross-section of NP composite prepared by Method II. Synthesis conditions: 1.0 M Py, 1.0 M $Na_2S_2O_8$, soaking time in Py solution 1 h, polymerisation in $Na_2S_2O_8$ solution 3 h. (e) SEM microphotograph of the cross-section of NP composite prepared by Method III. Synthesis conditions: 0.1 M Py, 0.1 M $Na_2S_2O_8$, polymerisation time 1 h.

highly irregular PPy layer with a very rough surface formed. Otherwise no distinct difference to the previous case was observed. The penetration of PPy into the membrane interior still occurs.

In the last step the concentration of oxidant was also increased to 1 M. A typical cross-section of the resulting film is given in Figure 2(d). A relatively thick layer on top of the Nafion® membrane has formed. In this case, too, it is difficult to distinguish whether it is PPy film or the Nafion® matrix highly doped by PPy. When compared with Figure 2(c), the option of PPy film on top of the membrane and penetrating into its interior again seems more probable. An important part of the membrane below this primary layer contains a significant amount of PPy.

Another interesting question is the mechanism of PPy formation in the membrane pores. It is obvious that the first portion of PPy forms on the membrane surface where the monomer and the oxidant come into contact for the first time. One would expect Py to diffuse more easily from the membrane interior to the surface than peroxodisulphate ion into the membrane through the PPy film that has formed. This process would, however, result in the growth of a distinct PPy layer only on the top of the membrane. As has just been shown, a substantial part of PPy forms on the membrane surface, a significant amount also forms in the pores of the membrane. The most probable explanation is the analogy to electrochemical polymerisation. The surface of the PPy film in contact with the $S_2O_8^{2-}$ solution is oxidised. This positively charged film acts oxidatively on the opposite side, i.e. on the membrane – PPy interface or in the interior of the membrane and causes PPy formation inside the membrane pores. Protons produced by the polymerisation reaction are transported much more easily through the PPy film to the surface of the composite, thus compensating negative charge of the SO_4^{2-} ions formed during the reaction. What remains unclear is the problem of doping of the film by the counter-ions. To date there are two possible explanations: (i) migration of SO_4^{2-} ions into the film initiated by the local excess of positive charges in the polymerisation zone or (ii) compensation of the PPy positive charge by the Nafion® sulpho groups. Excessive protons present at the beginning of the experiment in the membrane as the counter-ions easily diffuse into the bulk of the surrounding solution. The indirect evidence supporting this explanation of PPy formation inside the pores is clearly the lower penetration of PPy into the membrane interior when lower reactant concentrations are used.

It can be concluded that the application of Method II does not ensure the formation of homogeneous reproducible CP film on the surface of the membrane without danger of the cell short-circuiting. From this point of view it is not suitable for MEA preparation and another alternative has to be sought.

As previously mentioned, *Method III* represents a modification of Method II. It is based on the fact that the monomer diffuses relatively easily through the cation selective Nafion® membrane, whereas $S_2O_8^{2-}$ is excluded from transport through this barrier. In this part of the study only 0.1 M monomer and oxidant solutions were used in order to minimise the risk of penetration of the oxidant into the membrane. Another advantage of this method is that both monomer and oxidant can be continuously fed to the reaction zone. This permits control of the thickness of PPy film produced within a certain range. A typical picture of the NP composite cross-section is shown in Figure 2(e). When compared with the previous pictures, it is clearly evident that PPy film forms exclusively on the membrane surface. No penetration into the membrane pores is evident on the microphotographs. This suggests low adherence of the CP to the membrane surface. Nevertheless, the composite remains elastic and PPy does not peel off the membrane even during freezing and breaking of the composite in liquid nitrogen. Method III has proved to have good potential for preparation of NP samples for potential future application as MEAs in low temperature fuel cells. This is due to the fact that, besides the good adhesion of CP to the membrane, it also permits control of the thickness of the PPy film and that it avoids PPy formation in the interior of the membrane. These are very important parameters and for these reasons, therefore, this method was chosen for further studies.

3.2. *Kinetics of PPy film growth on top of the Nafion® membrane*

It is difficult to follow the kinetics of PPy film growth *in situ*. *In situ* UV–Vis spectrophotometry is a viable alternative. This method, however, only allows qualitative analysis of the development of film thickness vs synthesis time. This is mainly because it is difficult to determine the content of the polaron and bipolaron states in the PPy film during its growth and thus the sample-specific absorbance coefficient. Such an experiment, therefore, only provides qualitative information on film growth. Thus it was necessary to use an *ex situ* technique capable of providing an exact film thickness value. SEM was chosen for this work as it can be used to determine CP film thickness and morphology at the same time. Since this technique uses high vacuum, PPy has to be dried prior to insertion to the analysis. This represents the main source of inaccuracy of this method. It was proved experimentally that, during drying, electrochemically synthesised PPy film loses less than 1% of its weight. This is due to the relatively rigid structure of PPy. It can, therefore, be assumed that the error in determining film thickness *ex situ* is negligible. The dependency obtained is shown in Figure 3. The curve is characterised by a hyperbolic shape. This indicates that the synthesis is limited neither by the kinetics of Py oxidation nor by Py transport through the Nafion® membrane. The rate-determining step seems to

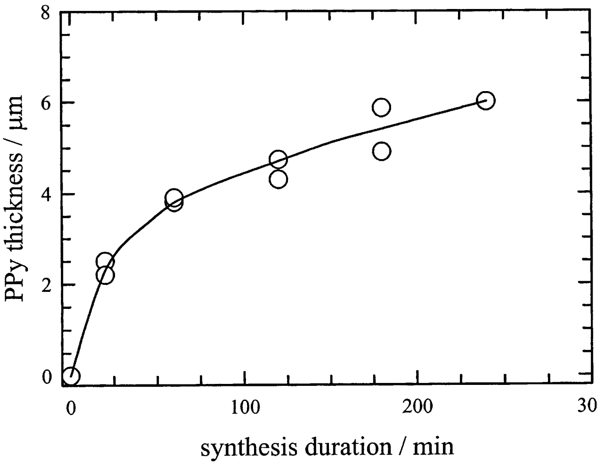

Fig. 3. Kinetics of PPy film growth on the surface of a Nafion® membrane determined from SEM microphotographs of cross-sections of NP composites.

be transport of the monomer through the PPy film formed. This phenomenon may be of great importance for various reasons. The two most important are the kinetics and extent of PPy film growth and the low permeability for organic molecules, i.e., among others, probably also for methanol. Further analysis of this process is necessary to obtain sufficient evidence to prove this theory.

The induction period was observed during the composite synthesis both visually and by UV–Vis spectrophotometry. Synthesis of PPy film was first initiated 2 min after the experiment started. This can be explained either by the delay caused by monomer diffusion through the Nafion® membrane or by the initial nucleation period. As is known from the literature [32], nucleation is a critical step in PPy formation. The washing of oligomers formed from the reaction zone is often the main reason for inhibition of PPy formation. Since no oligomer formation was indicated spectrophotometrically in this case, the explanation can be assumed to be monomer diffusion through the membrane.

3.3. *NP composite electrochemical activity*

Electrochemical activity is an important characteristic of PPy film. It is a prerequisite for its envisaged application in fuel cell technology. Moreover it opens up a much greater possibility of modification of the PPy support by the Pt catalyst. Therefore the electrochemical activity of the PPy films deposited was tested each time.

A typical polarisation curve of the PPy covering the membrane surface recorded for two films after different synthesis times is shown in Figure 4. Both films show a typical PPy polarisation curve. Characteristic anodic and cathodic current peaks corresponding to the charging and discharging of the PPy layer are in this case not so well defined as it is characteristic for the films deposited directly on the electrode surface. This is probably caused by slower charge propagation through the PPy film contacted to the current feeder just by the Pt wire localised on the perimeter of the sample. Nevertheless, the increase in the curve hysteresis corresponds well to the increase in synthesis time and thus to the increase in film thickness. This is in accordance with the fact, that increasing amount of PPy has to be charged and discharged. A linear dependence between the film thickness and electrical charge used for its charging and discharging during the potential cycling was observed, as it is shown in Figure 5. This indicates that the whole volume of PPy is electrochemically active. The electrochemical activity of the film is high enough to permit its subsequent electrochemical treatment.

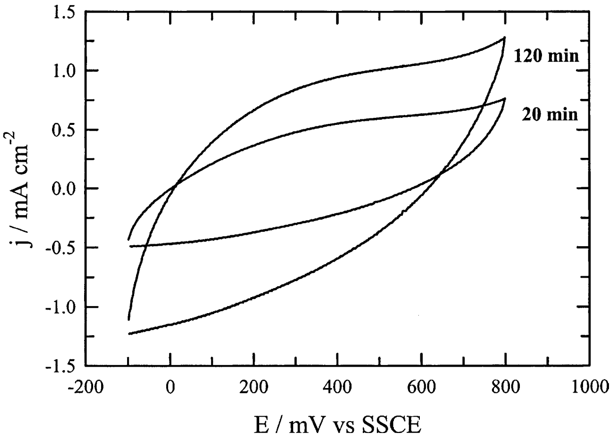

Fig. 4. Cyclic voltammogram of the PPy film synthesised on top of the Nafion® membrane. Potential scan rate 20 mV s^{-1}, the times indicated inside the graph correspond to the synthesis duration of the particular sample.

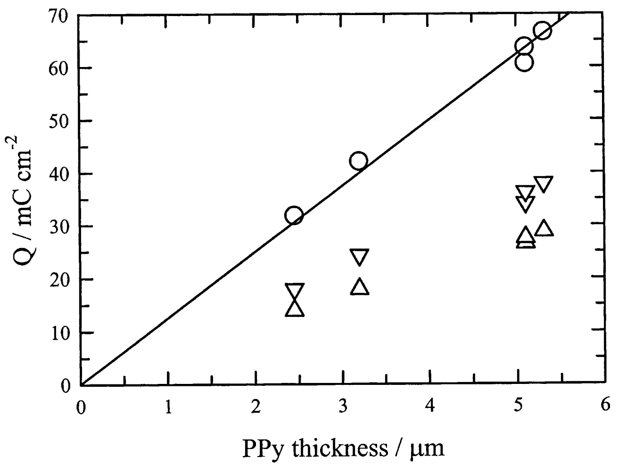

Fig. 5. Dependence of the electrical charge passed during the cyclic voltammetric polarisation of PPy film synthesised on top of the Nafion® membrane in dependence on the film thickness: O – total charge, ∇ – anodic charge and Δ – cathodic charge. Potential scan rate 20 mV s^{-1}.

4. Conclusions

Chemical synthesis was proved to be a viable method of PPy fixation on the surface of a Nafion® membrane. The diffusion method was selected as the most appropriate one due to its advantageous properties as compared to the alternatives studied. The composite prepared showed homogeneous morphology, very good adherence to the membrane surface and high electrochemical activity. It is also interesting to note that PPy seems to act as an efficient barrier to Py permeation, which is the rate-determining step during polymerisation of the secondary PPy layer. This offers an interesting opportunity to produce MEA with strongly reduced permeability for methanol as a fuel in the direct methanol fuel cell.

Acknowledgements

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