

Utilization of Nafion[®]/conducting polymer composite in the PEM type fuel cells

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Abstract

The present study focuses on the problem of using conducting polymers (CPs) in proton exchange membrane fuel cell technology. It covers the electrocatalytic properties of the CP/Pt composite, permeability of the CP film for H₂, fixation of the compact CP film on the top of the Nafion[®] membrane and first results of its utilization in a fuel cell. The present results did not confirm a previously reported increase in CP/Pt composite electrocatalytic activity when compared to the commercially available carbon supported catalysts. The main reason seems to be the very low permeability of the compact CP film for the fuel. This may be an advantage with respect to the minimization of fuel cross-over, which is a serious problem in the direct methanol fuel cell. On the other hand, it represents a serious danger in water management of the fuel cell. This fact has been recognized and alternative solutions are presented.

List of symbols

a area (m²)
c molar concentration (mol m⁻³)
C solubility of H₂ (mol m⁻³)
D diffusion coefficient (m² s⁻¹)
F Faraday number (C mol⁻¹)
j current density (A m⁻²)
k permeability (m² s⁻¹)
n molar amount (mol)
z number of electrons exchanged
V volume (m³)

*c*_{MeOH}[∞] function of the bulk methanol concentration
τ time
ads adsorption
comp composite
CP conducting polymer
dif diffusional
EQCN electrochemical quartz crystal nanobalance
ext extrapolated
film polymer film
GC glassy carbon
GDL gas diffusion layer
kin reaction kinetics
MeOH methanol
Naf Nafion[®] membrane
PAni polyaniline film
PPy polypyrrole film
RDE rotating disc electrode
synth synthesis

Greek symbols

δ thickness (m)
τ time (s)
ω angular rotation rate (rad s⁻¹)

Indices and abbreviations

0 bulk concentration
1, 2 reservoir number

1. Introduction

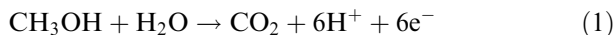
The state of the art of proton exchange membrane fuel cell (PEMFC) technology suffers from several serious problems. The most important ones are: (i) low catalyst utilization, (ii) catalyst sensitivity to CO chemisorption and (iii) membrane permeability to fuel [1].

Several ways of solving these problems have been proposed [1], one of them being the application of conducting polymers (CPs). The application of CPs in low temperature fuel cell (FC) technology has been studied mainly with respect to utilization as a catalyst support [2]. This concept allows solution of the above-mentioned problems with regard to the following three aspects:

(i) increased availability of three-phase contact [2]

- (ii) enhancement of catalyst resistivity to CO poisoning [3]
- (iii) reduced fuel permeation through the membrane [4].

These individual aspects will be briefly discussed in the context of the direct methanol fuel cell (DMFC). The overall reaction taking place in DMFC is:



The place where fuel, proton and electron conductor are in contact is called the three-phase interface. The limited occurrence of such sites is responsible for low catalyst utilization. The state of the art is shown in Figure 1A. The carbon support plays the role of electronic conductor removing electrons; the Nafion[®] membrane conducts the protons to the cathode side of the cell. Nowadays, Nafion[®] is commonly added to a suspension of carbon supported catalyst during electrode preparation in order to increase the number of particles contacted and thus to improve the Pt utilization (Figure 1A).

The alternative approach is shown in Figure 1B. According to this concept the Nafion[®] membrane is covered by CP film serving as a Pt catalyst support. Due to the mixed electronic and ionic conductivity of CPs the electrons and protons can diffuse out of the reaction zone and three-phase contact no longer represents a serious problem [2].

The application of a CP layer also reduces the extent of the fuel crossover [4, 5]. This is caused by the more rigorous structure of the CP film and lower methanol solubility in these polymers when compared to the swollen Nafion[®] membrane. Some authors also claim enhanced Pt resistivity to poisoning by chemisorbed CO caused by a closely unspecified synergistic effect originating from the contact of Pt and CP [3].

The studies published so far have focused mainly on the electrocatalytic properties of Pt modified CP film synthesized on the surface of the solid electrode, typically a glassy carbon (GC) rotating disk electrode (RDE) [6]. So far no serious attention has been paid to the subsequent step of the application of CP in FC technology – the fixation of CP on the membrane surface, i.e., membrane electrode assembly (MEA) construction. Studies [2, 7, 8] represent a few exceptions. Qi et al. [2] proposed hot-pressing of the

polypyrrole (PPy) particles, modified by Pt nanoparticles and bonded by Teflon[®] and Nafion[®] on the top of the membrane. Similarly Lamy et al. [7] used the gas diffusion layer on which polyaniline (PAni) was electrochemically synthesized and subsequently modified by the cathodically deposited catalyst. This electrode was also fixed on the top of the membrane by hot-pressing. Lee et al. [8] chose a different approach. The Nafion[®] membrane was impregnated with FeCl₃ and subsequently exposed to the monomer solution. Pt was deposited on its surface by chemical reduction. All authors report satisfactory activity of the MEAs prepared. The only problem mentioned is the guarantee of stable contact between the catalyst particles and the CP support.

A diffusion method for synthesis of CP directly on the PEM surface was proposed as an alternative approach [9] based on the work of Hsu [10]. A broader characterization of these composites is still missing.

The present paper describes results obtained on the application of CPs as a catalyst support in PEMFCs, compares them with published theories and discusses the use of these composite materials with special attention to FCs.

2. Theory of experimental permeability data evaluation

2.1. CP film permeability for hydrogen

In this study a modification of the RDE method developed in [11] was chosen to evaluate CP film permeability for H₂ dissolved in electrolyte solution. It is based on the study of H₂ oxidation kinetics on the surface of a Pt RDE covered by a CP film of known thickness. A description of the method was given previously [12]. Only the main principles and resulting equations are presented here.

In order to analyze the potentiostatic polarization curves the consecutive steps influencing the kinetics of the overall process of H₂ oxidation on a CP modified Pt RDE must be distinguished. These are as follows: (i) diffusion of H₂ from the bulk solution to the CP film surface, (ii) diffusion of H₂ through the CP film, (iii) adsorption of H₂ on the Pt electrode surface and finally (iv) oxidation of H₂ on the Pt surface to

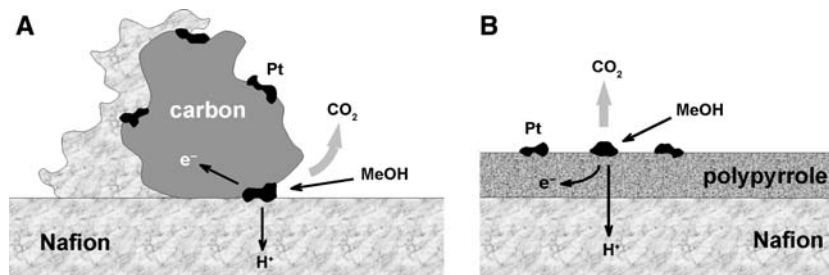


Fig. 1. Concept of FC catalyst support; (A) state of the art, (B) alternative solution using conducting polymer.

H^+ . Thus, the current density at the working electrode is given by:

$$\frac{1}{j} = \frac{1}{j_{\text{dif}}} + \frac{1}{j_{\text{film}}} + \frac{1}{j_{\text{ads}}} + \frac{1}{j_{\text{kin}}} \quad (2)$$

where the individual terms on the right-hand side are related to points (i) to (iv), respectively.

At overvoltages higher than 100 mV the kinetic term $1/j_{\text{kin}}$ becomes negligible [11]. The value of j_{dif} is dependent on the electrode rotation rate and can be described by the Levich equation. It can be neglected when the electrode rotation rate is extrapolated to infinity using Koutecky–Levich analysis. It remains to distinguish between the diffusional (j_{film}) and adsorptive (j_{ads}) contributions in Equation (2). The diffusion of H_2 through the PPy film can be described by a modified Fick's law as follows:

$$j_{\text{film}} = -zFD_{\text{film}} \frac{C_{\text{film}}}{\delta_{\text{film}}} \quad (3)$$

where C_{film} is the solubility of H_2 in the CP film and δ_{film} is the film thickness. The permeability k_{film} is defined by:

$$k_{\text{film}} = \frac{D_{\text{film}} C_{\text{film}}}{C_0} \quad (4)$$

where $C_0 = 5.9 \times 10^{-4} \text{ mol dm}^{-3}$ is the H_2 solubility in the electrolyte (0.5 M H_2SO_4 solution, 25 °C [13]). Now:

$$\frac{1}{j_{\text{ext}}} = \frac{\delta_{\text{film}}}{zFk_{\text{film}}c_0} + \frac{1}{j_{\text{ads}}} \quad (5)$$

If data for different PPy film thickness δ_{film} are available, the values of $1/j_{\text{ext}}$ obtained by Koutecky–Levich analysis may be plotted against thickness δ_{film} . A linear dependence, which intercepts the abscissa at $1/j_{\text{ads}}$, is obtained. The slope of the regression line permits the determination of permeability k_{film} , see Equation (5) and Figure (7), inset.

2.2. Permeability for methanol

The classical method of a separator permeability determination in the case of an electroneutral compound consists in placing demineralized water and solution of the compound studied into reservoirs separated by the sample under study. Transport across the separator is assumed to be the rate determining step.

2.2.1. Nafion[®] membrane permeability

For a homogeneous separator consisting of only a single layer (in the present case a free-standing Nafion[®] membrane) an expression for the increase in the molar amount of methanol passing through the separator may be derived from Fick's law and the methanol molar balance. After integration and simple rearrangement an expression for Nafion[®] permeability for methanol can be obtained,

$$k_{\text{MeOH}}^{\text{Naf}} = -\frac{\delta_{\text{Naf}} V_1}{a_{\text{Naf}} \left(\frac{V_1}{V_2} + 1\right) \tau} \ln \left[1 - \frac{n_{\text{MeOH},1}^{\tau} \left(\frac{V_1}{V_2} + 1\right)}{V_1 c_{\text{MeOH},2}^{\tau=0}} \right] \quad (6)$$

where subscript 1 indicates the compartment containing demineralized water and subscript 2 the compartment containing the methanol solution at the beginning of the experiment.

2.2.2. Nafion[®]/CP composite permeability

The case of determining the permeability of CP fixed on the composite represents a more complex problem. This is because CP forms one of the two composite layers with significantly different properties. The expression for its permeability is again derived from Fick's law and methanol molar balance. An assumption of the methanol flux continuity on the Nafion[®]-CP interface is used. Under this condition the following expression can be obtained.

$$k_{\text{MeOH}}^{\text{CP}} = \frac{\frac{V_1 V_2}{V_1 + V_2} k_{\text{MeOH}}^{\text{Naf}} \delta_{\text{CP}} \ln \left(\frac{c_{\text{MeOH},2}^{\tau=0}}{c_{\text{MeOH},2}^{\tau=0} - \frac{V_1 + V_2}{V_1 V_2} n_{\text{MeOH},1}^{\tau}} \right)}{k_{\text{MeOH}}^{\text{Naf}} a_{\text{comp}} \tau - \frac{V_1 V_2}{V_1 + V_2} \delta_{\text{Naf}} \ln \left(\frac{c_{\text{MeOH},2}^{\tau=0}}{c_{\text{MeOH},2}^{\tau=0} - \frac{V_1 + V_2}{V_1 V_2} n_{\text{MeOH},1}^{\tau}} \right)} \quad (7)$$

Using Equations (6) and (7) the permeability can be calculated for the free-standing Nafion[®] membrane and for CP film embedded on its surface on the basis of the experimentally determined amount of methanol permeated from reservoir 2 to reservoir 1.

3. Experimental

3.1. Determination of the electrocatalytic activity

The electrochemical experiments were performed using a HEKA potentiostat-galvanostat PG310. Typically a three-electrode configuration in a gas-tight glass cell was used. A PINE rotating disk electrode (RDE) with a geometric area of 0.196 cm² served as a working electrode. A smooth Pt foil was used as a counter-electrode. All potentials are referred to a saturated calomel electrode (SCE).

GC was used as an electrode material for electrocatalytic and Pt for permeability measurements. Both electrode materials were carefully cleaned before each experiment using standard procedures.

During all electrocatalytic activity and permeability determination experiments PPy was used as a model CP. It was synthesized potentiostatically at 0.75 V. A 0.1 M aqueous solution of pyrrole (Py) in 0.1 M supporting electrolyte was used. Sodium salts of the following counter-ions were applied as supporting electrolytes: Cl^- , SO_4^{2-} , tosylate (Tos^-) and poly(styrenesulphonate) (PSS^{n-} ; concentration related to the monomer unit). In the case of Nafion[®] counter-ion the synthesis solutions

were prepared by mixing a given volume of commercial 5 wt.% solution of Nafion[®] in isopropyl alcohol with an aqueous solution of Py. The thickness of the film was controlled by the charge passed during electropolymerization. A charge of 100 mC cm⁻² was considered to correspond to the film thickness of 0.19–0.30 μm, depending on the counter-ion [12]. For the electrocatalytic activity study the PPy films synthesized on the top of GC RDE were modified by Pt particles deposited from 1 mM solution of K₂[PtCl₄] in 0.5 M H₂SO₄ by potentiostatic reduction at -45 mV.

For the comparative experiments employing commercially available carbon supported catalysts GC electrodes were used. The catalyst was fixed on their surface using the thin film technique developed by Schmidt et al. [14].

The polarization curves of H₂ oxidation were measured in 0.5 M H₂SO₄ solution saturated with H₂ (5.0 purity grade, SIAD) with different RDE rotation rates. For ignition potential determination H₂ was used in a mixture with 4 vol.% of CO. During all experiments the temperature was kept constant at 20 °C.

3.2. Nafion[®]/CP composite synthesis and characterization

The Nafion[®]/CP composite was synthesized by the diffusion method described in [9]. The synthesis of Nafion[®]/PPy was conducted at the room temperature. On the monomer side 0.1 M Py solution was used. In the case of the Nafion[®]/PAni composite the temperature of 30 °C was identified as the optimum. An 0.1 M aniline (Ani) solution in 0.5 M H₂SO₄ was placed into the monomer compartment. In both cases 0.1 M Na₂S₂O₈ was used as oxidant.

After careful washing of the composite in demineralized water the same experimental arrangement was used for the diffusion experiments and electrocatalytic activity testing [4]. In the later case the PTFE sealing ring placed between the glass pieces was equipped on its perimeter with a Pt wire providing an electrical contact.

A Knauer differential refractometer model 2025/50 was used to determine the concentration of methanol in the diluate compartment during the experiments. SEM pictures were recorded using a Hitachi S4700 field emission microscope.

3.3. Fuel cell experiments

A H₂/O₂ FC made in-house was used for the evaluation of the prepared Nafion[®]/CP composites. The active area of the cell was 6.25 cm². Commercial ELAT (E-TEK) electrodes with Pt loading of 5 g m⁻² were used as both anode and cathode. Gases were supplied to the cell through mass flow controllers (Aalborg). The anodic gas stream was humidified using a tempered bubble humidifier; the cathodic gas stream was humidified in selected cases in the same way. The experiments were

performed at a temperature of 30 °C. A flow rate of 20 cm³ min⁻¹ was used for both gas streams.

All the chemicals were of analytical purity grade and used as received, except for Py and Ani, which were redistilled before use. A commercially available 5 wt.% solution of Nafion[®] received from Ion Power and Nafion[®] 117 membranes from Aldrich were used. All solutions were prepared from demineralized water with conductivity of 1.0 μS cm⁻¹ or lower.

4. Results and discussion

4.1. CP/Pt composite electrocatalytic activity

In this part of the study the main focus was on PPy as the model CP. This is largely because of its easy and reproducible synthesis. Later attention shifted to PAni as a representative of CP materials suitable for the strongly acidic environment typical of the PEMFC.

In the previous work [15] the different methods of PPy modification by Pt were compared with respect to the electrocatalytic activity of the resulting polymer for H₂ oxidation. Three methods were studied: (i) cathodic deposition from the aqueous solution of Pt salt, (ii) incorporation of [PtCl₄]²⁻ into the PPy film during the synthesis as a counter-ion and (iii) incorporation of the Pt colloidal particles into the PPy film during synthesis.

Methods (ii) and (iii) were claimed to provide homogeneous distribution of Pt inside the PPy film. The XPS results, however, indicate that the form of Pt present in the PPy bulk and partly also on the CP film surface is electrocatalytically inactive Pt²⁺ [15, 16]. Nevertheless, by using a suitable preparation procedure, a composite with relatively high electrocatalytic activity can be obtained in the case of method (ii) [16]. The activity obtained is in the best case comparable with the composite prepared by method (i) having Pt particles only on the surface of the PPy film. This indicates that only the surface of the composite is electrocatalytically active. The reason for such behavior consists either in the absence of electrocatalytically active Pt particles in the film interior or in the low composite permeability for fuel.

In order to prove the influence of CP fuel permeability an additional experiment was performed using structured “sandwich” composites, consisting of multiple PPy/Pt layers. No influence of the increased number of cathodically deposited Pt layers covered by PPy (and thus Pt loading) was observed. This result confirms the theory of the low permeability of PPy film for fuel.

Beside the homogeneous distribution of Pt particles in the CP film high specific activity and resistivity to CO poisoning were claimed in the literature [3]. An experiment was performed comparing specific electrocatalytic activity of the Pt modified PPy film with a commercially available carbon supported catalyst. Typical results obtained are shown in Figure 2.

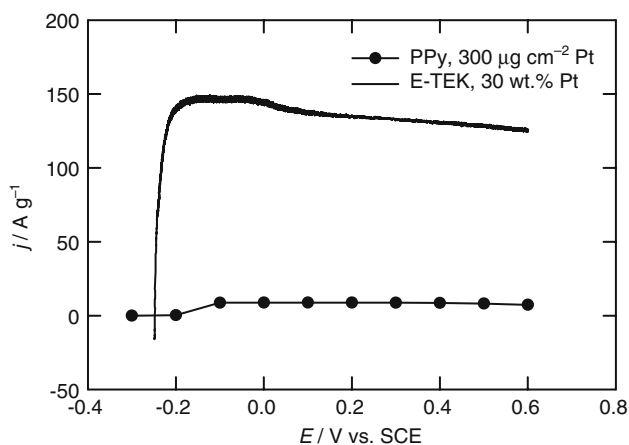


Fig. 2. Comparison of specific electrocatalytic activity of PPy/Pt composite and commercially available catalyst E-TEK, 30 wt.% Pt supported on Vulcan X-72 for H_2 oxidation reaction; H_2 saturated 0.5 M H_2SO_4 at 20 °C, 1600 rpm.

The result corresponds to the specific surface of Pt particles. Whereas in the case of the carbon supported commercial catalyst the diameter of the Pt particles is in the order of units of nanometers (Figure 3A), in the case of PPy/Pt composite it typically reaches hundreds of nanometers (Figure 3B). For higher Pt loadings the particles grow together, forming a compact Pt layer (Figure 3C). Both the increased particle size and the formation of a compact Pt layer result in a reduced catalyst specific surface. An additional aspect is the increase in the number of active sites on the surface of the particles in the nanometer scale [17]. Both these aspects result in superior behavior of the commercial catalyst compared to the PPy/Pt composite.

An important parameter characterizing the resistivity of the catalyst to poisoning by CO is the ignition potential. In the present case the 0.5 M H_2SO_4 solution was saturated by a mixture of 4 vol.% of CO in H_2 under otherwise identical conditions. In this case the bulk Pt electrode was included in the comparison also (in contrast to specific electrocatalytic activity a relative comparison of ignition potentials with the composite electrodes is possible for the Pt bulk electrode). A comparison of the behavior of the materials tested is provided in Figure 4.

These results are in contradiction to the data presented so far. It follows from the polarization curves given, that the resistivity of the PPy/Pt catalyst is comparable to the bulk Pt. This is probably given by the presence of Pt in the form of a compact layer on the top of PPy film. Any interaction of the PPy with Pt and/or CO is thus prohibited. Nevertheless, experiments with lower Pt content did not show any change in behavior. An alternative explanation is the contamination of the Pt surface by Cl^- ions from the solution used for the Pt deposition. The Cl^- ions are strongly adsorbed on the Pt surface and deteriorate its catalytic activity [18].

4.2. Nafion[®]/CP composite synthesis

For the synthesis of CP on the surface of the Nafion[®] membrane the diffusion method has been selected [9]. It allows simple and reproducible synthesis of compact, well adhesive CP film on the PEM surface. At the same

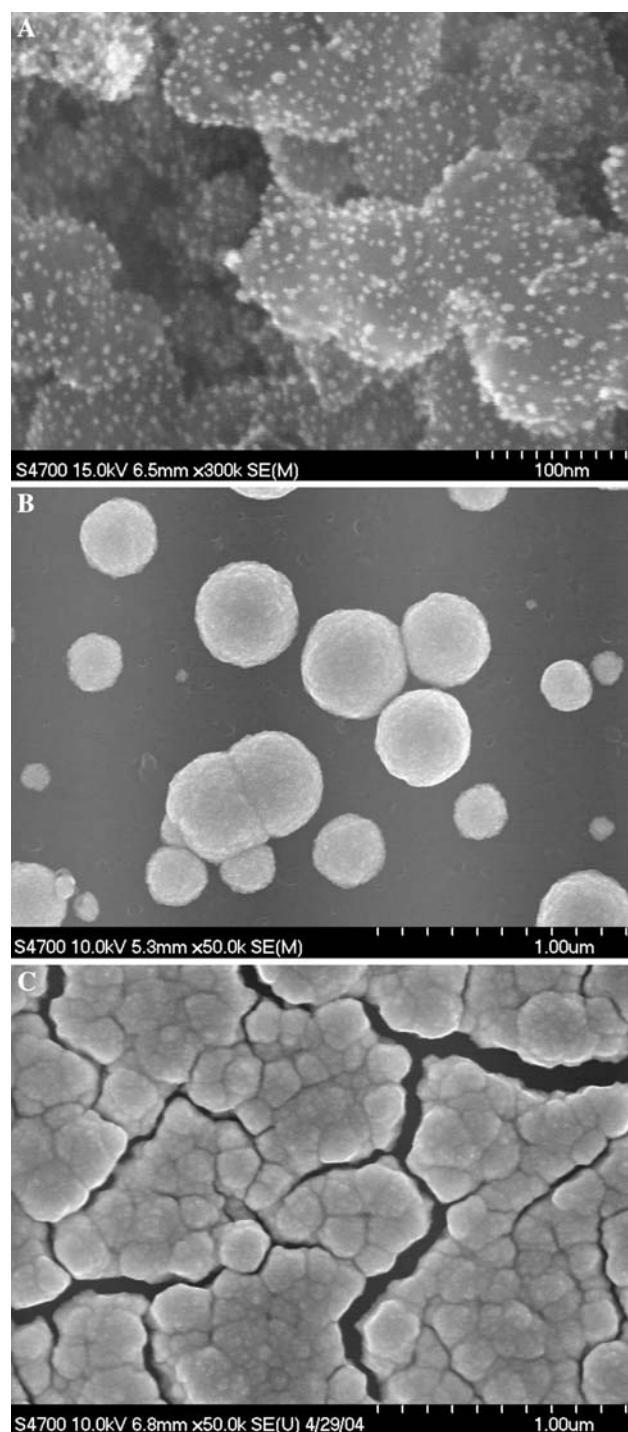


Fig. 3. SEM microphotography of (A) commercial catalyst E-TEK, 30 wt.% Pt supported on Vulcan X-72; (B) PAni/Pt composite, $\delta_{PAni} = 0.1 \mu m$, Pt loading $100 \mu g cm^{-2}$, cathodically deposited at $E_{const} = 0 mV$; (C) PPy/Pt composite, $\delta_{PPy} = 2 \mu m$, Pt loading $300 \mu g cm^{-2}$, cathodically deposited at $E_{const} = -45 mV$ (the cracks are the result of composite drying).

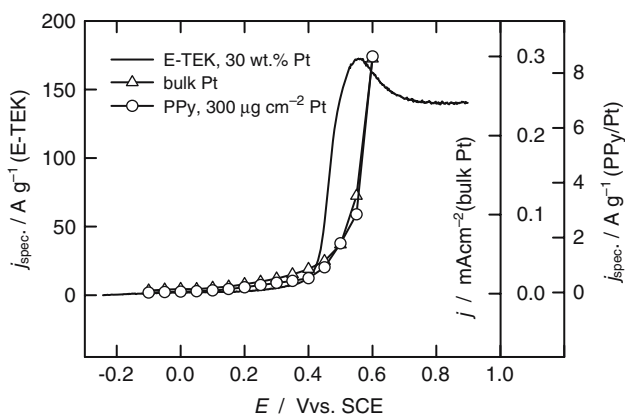


Fig. 4. Comparison of ignition potential for oxidation of H_2 contaminated by 4 vol.% of CO for PPy/Pt composite, commercially available catalyst E-TEK, 30 wt.% Pt supported on carbon and bulk Pt; 0.5 M H_2SO_4 saturated with H_2/CO mixture at 20 °C.

time CP does not penetrate deep into the membrane structure, (see Figure 5). This is caused mainly by Donnan exclusion. If the concentration of the negatively charged oxidant ions in the solution is sufficiently low,

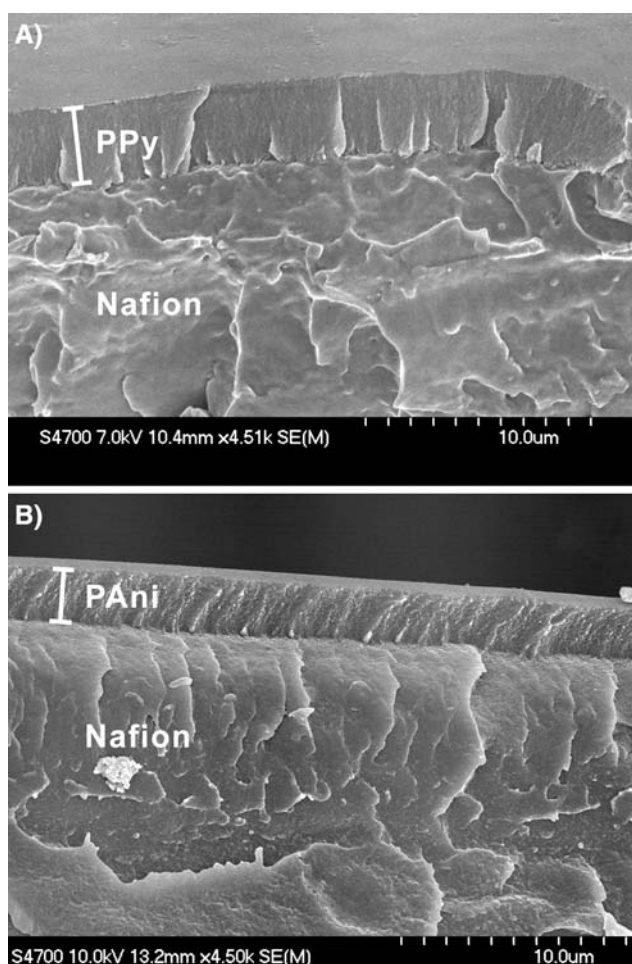


Fig. 5. SEM microphotography of (A) Nafion®/PPy composite, synthesis conditions: 0.1 M Py, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, $\tau_{\text{synth}} = 30$ min at 22 °C; (B) Nafion®/PAni composite, synthesis conditions: 0.1 M Ani in 0.5 M H_2SO_4 , 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, $\tau_{\text{synth}} = 90$ min at 30 °C.

they are prevented from penetrating into the cation selective membrane, i.e., Nafion®, interior. This is fully true for the synthesis of PPy (see Figure 5A). In the case of PAni a limited transition layer on the top of the Nafion® membrane is clearly filled by polymer formed in the membrane pores. This is in contradiction to the previous statement about Donnan exclusion. The explanation lies in the electronic conductivity of the CP film formed on the membrane surface. In the oxidized state it may act as an electrode and mediate transfer of the electrons from Ani oxidized in the membrane interior to the top of the film. Here they reduce the oxidizing agent. The thickness of such a transition film is limited because of the transport of suitable counter-ion to the reaction zone. It can be transported either from the oxidant solution or from the sulphuric acid present in the Ani solution. In the later case proton has to be transferred across the CP film in order to maintain electroneutrality.

The films produced are electrochemically active. This is an important factor with respect to the further electrochemical treatment of the composite, e.g. CP modification by the Pt catalyst using cathodic deposition or electrochemical synthesis of an additional CP layer. At the same time it is a necessary prerequisite for the successful action of the CP as a catalyst support. The electrocatalytic activity of the film is documented by the cyclic voltammetric polarization curves shown in Figure 6. It was found that a charge corresponding to the redox processes in the PPy film increased linearly with its thickness [9]. This offers an opportunity for a fast, nondestructive, *in situ* rough estimate of the synthesized film thickness. In the case of the PAni film the situation was different. Here the charge increased with film thickness up to approximately 8 μm . For thicker films a sharp decrease was observed. Possible explanation is the oxidative degradation of PAni by prolonged contact with the oxidant solution during synthesis.

4.3. CP film permeability

The crucial parameter in utilizing compact CP film as a catalyst support is its permeability for the fuel. Only sufficiently permeable material will allow penetration of the fuel into its bulk and the efficient utilization of a possibly three dimensionally (3D) distributed catalyst. No factual evidence was found in the literature that the structure of this type of composite is porous. Therefore the permeability of PPy film with various counter-ions was investigated.

4.3.1. CP film permeability for hydrogen

The influence of the nature of the counter-ion incorporated into the PPy film during its synthesis on its permeability for H_2 was first investigated using the RDE technique. Typical results are shown in Figure 7. The results obtained are summarized in Table 1.

The permeability determined attained a similar value for the majority of counter-ions. There were two exceptions: SO_4^{2-} and Nafion® as a counter-ion.

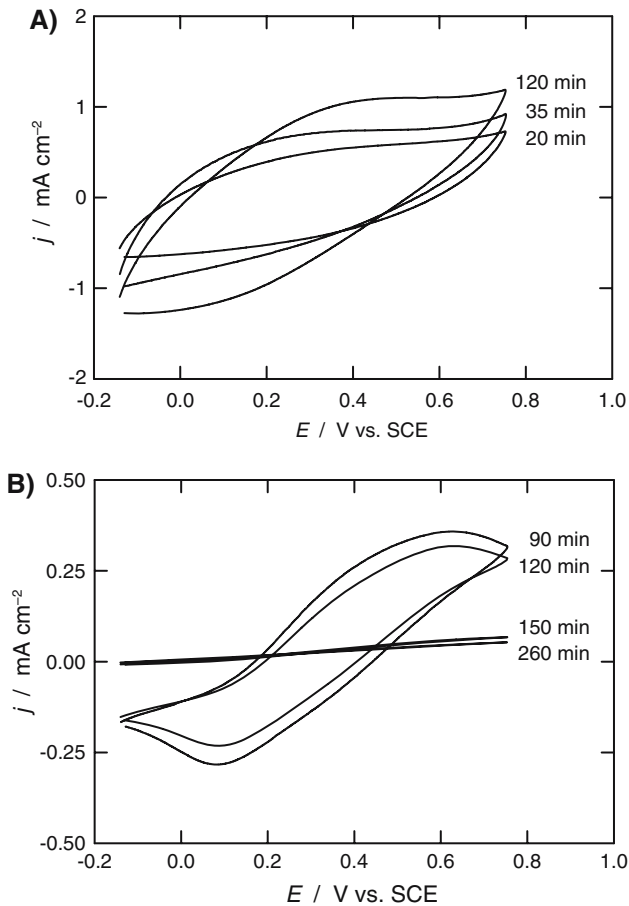


Fig. 6. Cyclic voltammograms of the Nafion[®]/CP composites: (A) Nafion[®]/PPy, (B) Nafion[®]/PANI (see also caption of Figure 5); potential scan rate 20 mV s⁻¹, 0.5 M H₂SO₄, the times indicated correspond to the synthesis duration of the particular sample.

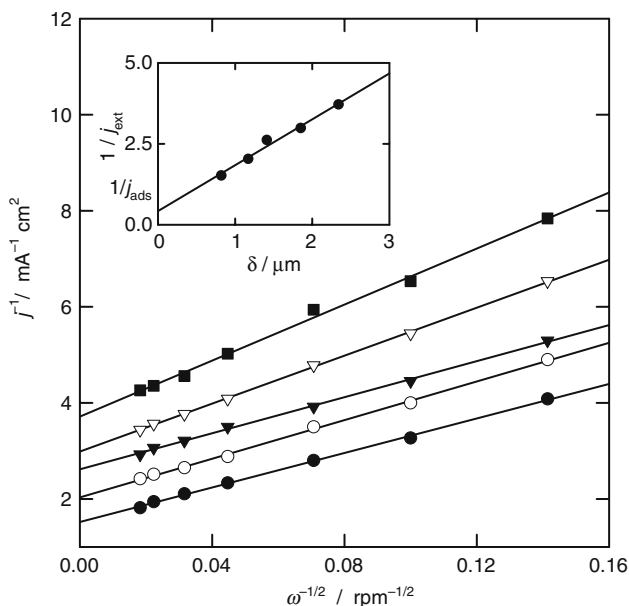


Fig. 7. Koutecky–Levich plots for PPy(PSSⁿ⁻) modified Pt RDE in 0.5 M H₂SO₄ saturated with H₂, δ_{film} : ● 0.82 μm , ○ 1.17 μm , ▼ 1.41 μm , ▽ 1.85 μm , ■ 2.34 μm , Inset: linear regression of $1/j_{\text{ext}}$ as a function of thickness.

Table 1. Dependence of PPy film permeability to H₂ on counter-ion incorporation

Counter-ion type	$10^{11} \times K_{\text{film}}/\text{m}^2 \text{ s}^{-1}$
Cl ⁻	7.1
SO ₄ ²⁻	2.9
Tos ⁻	9.5
PSS ⁿ⁻	6.2
Nafion [®] , 70%	14.5
Nafion [®] (pure) [19]	207

The PPy(SO₄²⁻) film exhibited the lowest permeability. At the same time its density was the highest of all the samples studied [12]. This can be explained by the fact that a sulphate anion is a relatively small, divalent ion. Due to electrostatic interactions in the oxidized state the film shrinks in its presence. This leads to a more compact structure, higher density and lower permeability.

The permeability of PPy(Nafion[®]) film prepared from a solution containing 70 vol.% of Nafion[®] solution is about twice that of PPy(Cl⁻). The reason is not the polymeric character of the Nafion[®] anion, as experiments with PSSⁿ⁻ confirm. This increase can be explained by the structure of Nafion[®]. This polymer consists of two domains – hydrophilic and hydrophobic. The hydrophilic domain is formed by highly polar and hydrated sulphonic moieties, the hydrophobic domains are spread along the perfluorinated chains of the polymer backbone. The incorporation of hydrophobic chains thus improves the permeation of molecular hydrogen and the presence of hydrophilic areas facilitates the conduction of protons [12].

A pure Nafion[®] polymer exhibits a permeability of $2.07 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [19]. The permeability of PPy film for H₂ is thus two orders of magnitude lower than that of Nafion[®]. This confirms the theory that limited CP permeability can result in limited utilization of 3D-distributed catalyst particles. In fact, on the basis of the present data it might be expected that the electrode in the present configuration acts two-dimensionally.

4.3.2. Nafion[®]/CP composite permeability for methanol

The availability of a reproducible method of compact CP film synthesis on the top of the Nafion[®] membrane also allowed us to study its permeability for methanol. This compound was chosen because it is assumed to be one of the most promising fuels for PEMFCs. Since methanol is an electroneutral compound, a simple diffusion experiment provides reliable permeability data. Permeability of the self-standing Nafion[®] membrane was determined by an independent diffusion experiment using Equation (6). The permeability value obtained was used as an input parameter for Equation (7) during evaluation of the CP film permeability.

As found during this series of experiments, in the case of methanol, too, the CP film represents an efficient barrier. The permeability of the Nafion[®] membrane was evaluated as $9.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. For the PPy film as part of the Nafion[®]/PPy composite, the permeability to

methanol attained an average value of $2.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. In the case of PANi the permeability achieved a value of $5.7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. This result is consistent with the PPy film permeability to H_2 reported in the previous section. It is a very important finding in relation to the perspective utilization of the CPs in the DMFC where it can play the role of a highly effective barrier to methanol permeation. On the other hand, permeability lower by 2 orders of magnitude than that of Nafion[®] can result in a serious disturbance of FC water management. A deterioration of the FC efficiency may also be caused by the limited accessibility of the 3D catalyst structure for the fuel.

As found during this study, a possible solution of this problem is the incorporation of Nafion[®] chains into the CP film as a counter-ion. The permeability of PPy to methanol can be increased 20-fold in this way compared to sulphate as the counter-ion. This is in qualitative agreement with the RDE study. So far, the question whether this is sufficient remains open.

4.4. Preliminary fuel cell tests

MEA on the basis of a Nafion[®] membrane modified on both sides by a PPy layer with cathodically deposited Pt was tested in the laboratory FC. The power density obtained was three orders of magnitude lower compared to the classical MEA with commercial ELAT electrodes. The reason for this was the absence of the GDL in the cell arrangement and mainly the disturbance of the FC water management. This explanation was confirmed by experiments utilizing Nafion[®] with one side covered by PANi as a PEM with ELAT electrodes. In this case, too, the power density of the cell was reduced compared to the cell based on the pure Nafion[®] membrane. The explanation consists in the low permeability of the compact CP layer for water. This results in the drying out of the membrane and decrease in FC efficiency.

To confirm this explanation, the CP layer was firstly placed on the cathode side and a H_2 gas stream was humidified at the operating temperature of the FC. Despite this arrangement a gradual deterioration of the cell performance was observed, as shown in Figure 8. If the PANi layer was located on the anode side, the deterioration of the power density was clearly more significant. The humidification of the oxygen stream did not achieve any noticeable improvement. Similar behavior was also observed for PPy films.

These results disagree with those of Lee et al. [8] who reported enhanced catalyst utilization and approximately three orders of magnitude higher current densities compared to the present results, i.e., current densities typical for commercial electrodes. In the present case the application of commercial ELAT type electrodes circumvents the influence of catalyst preparation. Therefore the discrepancy between these results can only be explained by the CP film properties. In contrast to the present study, Lee et al. [8] used a different method of Nafion[®] modification by CP.

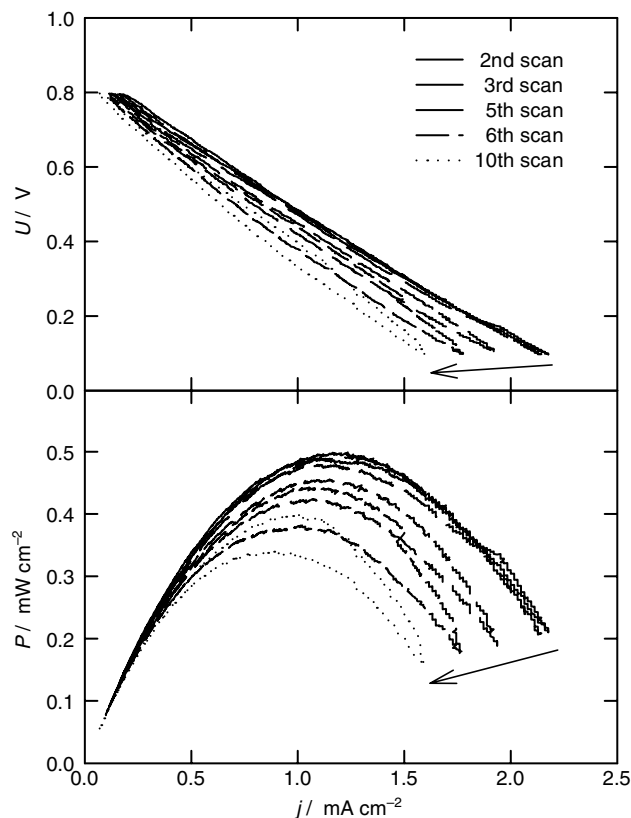


Fig. 8. H_2/O_2 FC voltage and performance against current load. Subsequent scans at scan rate of 2 mV s^{-1} are presented. Electrodes: commercial ELAT GDE Pt load 5 g m^{-2} ; PEM: Nafion[®] 117 with PANi layer ($\delta_{\text{PANi}} = 6 \mu\text{m}$) on cathode side; flow rates: H_2 , $20 \text{ cm}^3 \text{ min}^{-1}$; O_2 , $20 \text{ cm}^3 \text{ min}^{-1}$; atmospheric pressure; operational temperature $30 \text{ }^\circ\text{C}$.

The synthesis procedure used resulted, according to our previous results [9], in PPy polymerization in the bulk of the membrane. No compact layer on the top of the membrane disturbing the FC water management was probably formed. Pt particles produced by reduction of $\text{H}_2[\text{PtCl}_6]$ using NaBH_4 are deposited mainly on the surface of bare Nafion[®] membrane. According to SEM pictures [8] the catalyst has higher specific surface area when compared to the present study.

5. Conclusion

The application of compact CP film as catalyst support shows no advantage over commercially available carbon supported catalysts for the H_2/O_2 FC. The main reasons are the low permeability of CPs for fuel and water. This limits the electrode utilization on its surface and disturbs FC water management. Another problem is the relatively large size of Pt catalyst particles. The utilization of CP particles modified by nano-sized catalyst represents a possible solution of this problem. This allows synergism between Pt particles and CP and at the same time reduces drawbacks of the low CP film permeability.

On the other hand the main advantage of the present method consists in the fact that CPs can be easily

deposited on the Nafion[®] membrane surface, where they form an efficient barrier to methanol penetration. However, further research is needed to overcome the problem of disturbed water management. Modification of the CP film permeability to water seems to be a promising way forward.

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