



Impregnated membranes for direct methanol fuel cells at high methanol concentrations

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ABSTRACT

Sulfonated poly(phthalazinone ether ketone) (SPPEK) impregnated Solupor[®] microporous film (SPPEK–PE) and pure SPPEK membranes with two different ion-exchange capacities (IECs) were prepared and characterized for use in DMFC applications. Swelling, proton conductivity, diffusion and DMFC experiments were performed at various methanol concentrations to understand the effect of impregnation of an ion-conductive polymer membrane to the fuel cell performance.

Impregnating SPPEK into PE decreases swelling degree and methanol permeability of the membranes, but at the same time the proton conductivity. Unlike perfluorinated membranes, SPPEK–PE shows an increase in its DMFC performance at high methanol concentration and that makes it more attractive for mobile DMFC applications where high methanol concentrations are needed to compete with Li-ion batteries.

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1. Introduction

The development of fuel cells has become the focus of intense worldwide R&D activities, which is stimulated by the legislative pollution control in most industrialized countries [1]. Direct methanol fuel cells (DMFCs), which can convert the chemical energy of a fuel directly into electrical energy, have gained attention as candidates for mobile power sources to portable electronic devices [2–6].

The proton exchange membrane is the heart of DMFC. Currently, perfluorosulfonated ionomer (PFSI) membranes, like DuPont's Nafion[®] and Asahi Chemical's Aciplex[®], are used due to their excellent proton conductivity, mechanical strength and thermal and chemical stability [7–11]. However, these materials also have drawbacks like high cost (US\$ 700/m²) due to the expensive fluorination step and high methanol cross-over, especially at high methanol concentrations. In order to compete with Li-ion batteries for portable applications, higher power densities must be achieved. For that reason DMFCs should be operated at high methanol concentrations

[12]. Therefore there is a strong need to develop new membrane materials, which would have low methanol cross-over and high dimensional stability.

To achieve a membrane stable at high methanol concentration, one strategy is the impregnation of a conductive polymer into a porous support [13–16]. In fact, we showed previously that excessive swelling of the membrane can be suppressed by impregnation of Nafion into polyethylene porous support, while the methanol cross-over can be minimized [17]. An alternative strategy to minimize methanol crossover is by using a polymer with low methanol cross-over such as sulfonated poly(phthalazinone ether ketone) (SPPEK). Its low methanol cross-over and reasonable proton conductivity make it attractive for hydrogen and methanol fuel cells [1,17–21]. In this study we combine both strategies, in fact we impregnate SPPEK polymer into a polyethylene support, Solupor[®] microporous film (SPPEK–PE), aiming to decrease the methanol cross-over and cost, and at the same time to increase their dimensional stability and fuel cell performance. The composite membranes are systematically characterized with respect to their swelling degree, proton conductivity, methanol permeability and DMFC performance at various methanol concentrations. For comparison, the performance of Nafion[®] 117 (N117), Nafion impregnated PE (N-PE) and pure SPPEK membranes is also investigated.

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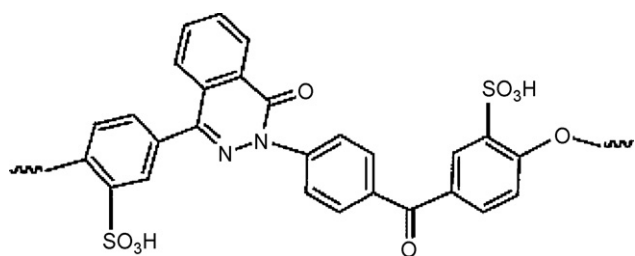


Fig. 1. Chemical structure of SPPEK.

2. Experimental

2.1. Materials and membrane preparation

2.1.1. Materials

SPPEK-polymers (Fig. 1), with two different ion-exchange capacities (IECs) (1.4 and 1.6 mmol/g), were kindly provided by FuMA-Tech GmbH (Germany). For the composite membranes a porous PE film, Solupor[®] microporous UHMWPE (provided by DSM Solutech), with a thickness of 13 μm , mean flow pore size of 0.7 μm , and porosity of 85%, was used. The density of PE is 0.97 g/cm³. N117 membranes (185 μm and 1100 equivalent weight (EW)) were purchased from Aldrich (Germany). *N*-Methyl-2-pyrrolidone (NMP) was purchased from Aldrich (Germany). E-TEK electrodes were purchased from E-TEK DeNora (USA).

2.1.2. Preparation of SPPEK membranes

The SPPEK polymers were dissolved in NMP to obtain 10 wt% solutions. The mixture, SPPEK/NMP, was stirred over night in the fumehood to get a homogenous solution. After dissolving, the solutions were filtered with metal mesh filters first with 40 μm and afterwards with 15 μm pore size to remove undissolved and dirt particles. The solution was cast on a glass plate with a casting knife of 0.5 mm to get dense membranes with a thickness of 50 μm . The membranes were dried in the fumehood for 3 days, and afterwards in an oven for 5 days at 80 °C. To remove the remaining NMP, they were placed in demineralized water for one day; the water was exchanged several times. The membranes were dried for 5 days under vacuum at 30 °C and finally were stored in a dry place at room temperature.

2.1.3. Preparation of SPPEK–PE composite membranes

A 10 wt% SPPEK/NMP solution was used for the impregnation. A PE-film (30 cm \times 15 cm) was fixed on a glass frame with scotch tape. For the impregnation of the PE substrate, an airbrush gun with a 0.5 mm nozzle was used. The gas pressure was set to 2 bar. After filling 20 ml of the solution into the airbrush gun, the PE film was impregnated at a distance of 10 cm from both sides (10 ml solution at each side). The impregnated membranes were dried in the same way as the SPPEK membranes (see earlier).

2.2. Membrane characterization

2.2.1. Scanning electron microscopy (SEM)

Membranes were visualized by a scanning electron microscope (Jeol JSM 5600LV). The membrane samples were sputtered with a thin layer of gold (30 nm) using a Balzers Union SCD 040 sputtering device prior to the SEM observation.

2.2.2. Porosity of the composite membrane

The porosity of the N-PE membrane, φ_p (%), was estimated using the equation [12]:

$$\varphi_p = \left\{ 1 - \frac{(w_{fp}^d / \rho_{fp}) + (w_{sub}^d / \rho_{PE})}{V_{mem}^d} \right\} \times 100 \quad (1)$$

where w_{fp}^d weight of the dry Nafion[®], w_{sub}^d weight of the dry poly(ethylene) substrate, ρ_{fp} the density of Nafion[®], ρ_{PE} the density of PE, and V_{mem}^d is the dry membrane volume estimated from the geometric membrane area (A) and thickness (l).

2.2.3. Swelling degree (SD)

Membranes were dried in the vacuum oven at 30 °C for 1 day and then immersed in ultra pure water or methanol solutions of various concentrations. The weight and the area of the wet (Value_{wet}) and the dry (Value_{dry}) samples were measured. The SD of the membrane was calculated using:

$$SD (\%) = \left(\frac{\text{Value}_{wet} - \text{Value}_{dry}}{\text{Value}_{dry}} \right) \times 100, \quad (2)$$

2.2.4. Methanol permeability

The methanol permeability, P [cm²/s], at 25 °C was measured using a two compartment diffusion cell following the procedure described elsewhere [13].

2.2.5. Proton conductivity

The proton conductivity measurements were performed by impedance spectroscopy in a homemade cell following the procedure described elsewhere [13]. Prior to all experiments, membranes were equilibrated for 24 h in ultra pure water and various methanol solutions (from 1 M to 10 M).

2.3. Fabrication of membrane–electrode assemblies

E-TEK commercial electrodes were used to fabricate the membrane–electrode assemblies (MEAs). Both anode and cathode contain 5 mg/cm² Pt–Ru and Pt, respectively. For both electrodes DE2020 Nafion[®] dispersion was used as a binder layer. The Nafion loading was about 1.2 mg/cm². The geometric area of each electrode was 6.25 cm². The MEAs were prepared by hot pressing of the anode and cathode on both sides of the membrane with a pressure of 10 bar for 5 min at 120 °C.

2.4. Single cell DMFC performance

The performance of the MEAs was evaluated using a DMFC set-up constructed by the Energy Research Centre (ECN, The Netherlands). The MEA was clamped between two graphite blocks. A serpentine flow pattern is etched in each of the graphite blocks to provide fuel to the MEA. Both graphite blocks were connected with electrical wires to an adjustable electrical load. The cell was thermostated with a heating bath and the temperature of the cell was measured with a thermocouple. The methanol solution was fed to the anode at flow rates of 20 ml/min and dry oxygen was fed to the cathode at flow rates of 75 ml/min and back pressure of 2 bar. The temperature of the cell was kept at 80 °C. Polarization curves were measured by applying different currents and measuring the correspondent cell voltages. The current was increased step-by-step till the cell voltage became zero. The equilibration time between the measured points was at least 30 s and the difference between the voltages in the last two seconds of each point was less than 1 mV.

3. Results and discussion

3.1. SEM study of SPPEK–PE composite membrane

Fig. 2 shows SEM images of the cross-section of SPPEK–PE composite membrane. SPPEK–PE membrane consists of an impregnated middle layer of about 13 μm and two layers of pure conductive polymer at the top and bottom (\sim 2–3 μm). The porosity of the pure PE

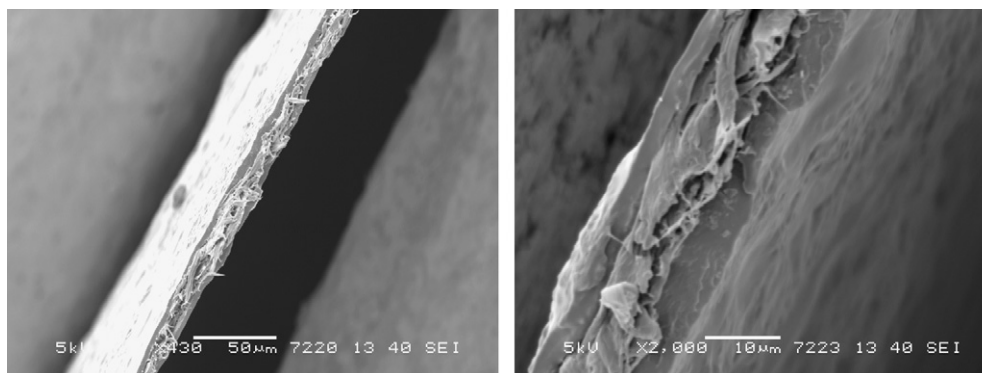


Fig. 2. SEM images of cross-sections of the SPPEK-PE composite membranes.

film is 85% according to the manufacturer. The porosity of the middle layer of the composite membrane was estimated (using Eq. (1)) to be 30%. This indicates that the impregnation is rather incomplete and air might be trapped in the non-filled pores of the substrate. In our previous work [13], we studied commercial Nafion impregnated PE membrane with similar porosity (~27%). Those membranes had superior DMFC performance than N117 membranes.

3.2. Swelling experiments

Fig. 3 shows the swelling degree (SD) of all membranes as a function of time in ultra pure water (Fig. 3a) and 10 M MeOH (Fig. 3b). After 24 h, the swelling degree remains constant. It seems that the membranes soaked the maximum amount of water or methanol within the first day. The swelling of all membranes is higher in 10 M MeOH solution than in ultra pure water. In all cases SPPEK1.6 swells more than SPPEK1.4 due to its higher ion-exchange capacity. The swelling of the impregnated membranes are lower than pure membranes due to the presence of hydrophobic PE substrate.

Fig. 4a and b shows the results of the SD by weight and area, respectively, of all membranes at various methanol concentrations. Swelling by weight of SPPEK1.4 and SPPEK1.6 show a slight increase till 6 M and then increase more sharply up to 10 M methanol concentration (especially, the SPPEK1.6) (Fig. 4a). Swelling by weight of SPPEK1.6 is higher than SPPEK1.4 due to its higher ion-exchange capacity. For comparison, the swelling by weight of N117 and N-PE membranes are much higher than SPPEK and SPPEK-PE mem-

branes at high concentrations and they are in the range of 70% and 50%, respectively [13].

Swelling by weight of both composite membranes (SPPEK1.4-PE and SPPEK1.6-PE) is independent of methanol concentration and almost factor of two lower than the pure SPPEK1.4 and SPPEK1.6 membranes. This is probably due to the suppression of the swelling degree of the composite membranes by the PE substrate.

In Fig. 4b, one can see similar trends concerning the swelling by area of the various membranes. At higher methanol concentrations, the SD by area of the SPPEK1.4 and SPPEK1.6 increases, but of the composite membranes stay constant and most importantly is very low (5–10%). Even at 10 M methanol concentration the dimensional stability of composite membranes is high; the PE support effectively suppresses swelling in the area direction. For comparison, the swelling by area of N117 membrane is much higher than SPPEK and SPPEK-PE membranes at high concentrations and it is in the range of 40%. The N-PE shows a significantly low swelling in the area direction, like SPPEK1.4-PE composite membrane, even at high methanol concentrations and it is about 5% [13].

3.3. Methanol permeability

High methanol crossover from the anode to the cathode is detrimental to the fuel cell performance as it reduces the efficiency and cell voltage. Fig. 5a and b shows methanol permeabilities of pure and composite SPPEK membranes in comparison to N117 and N-PE membranes [13] as a function of methanol concentration.

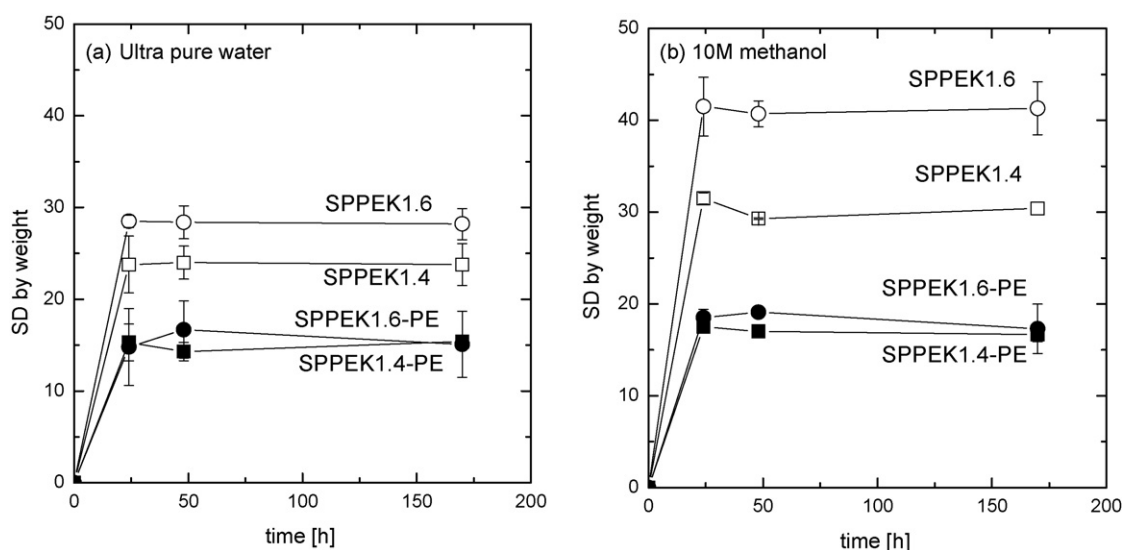


Fig. 3. Swelling degrees by weight in (a) ultra pure water and (b) 10 M methanol solution.

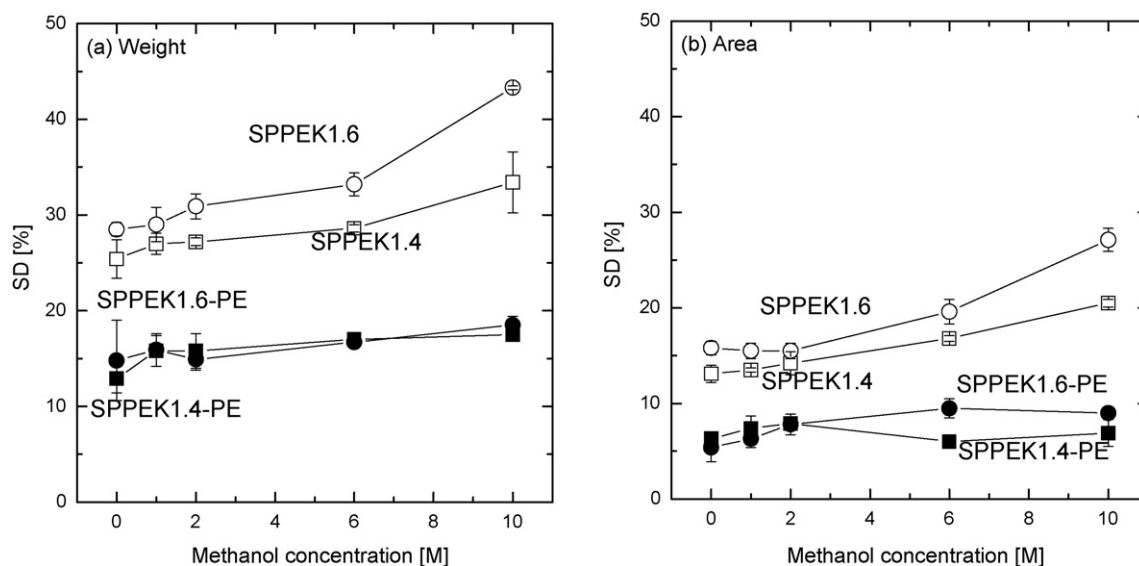


Fig. 4. Swelling degrees (a) by weight and (b) area as a function of methanol concentration.

SPPEK and SPPEK-PE membranes have one order of magnitude lower methanol permeability than N117 and N-PE membranes. This is an advantage of these membranes, because the efficiency losses caused by methanol crossover are expected to be much lower. We think that the difference in methanol transport between the two cases is due to the difference in chemical structures of Nafion and SPPEK polymers. The microstructure of N117 (and generally of perfluorosulfonic polymers) consists of extremely hydrophobic backbone and extremely hydrophilic sulfonic groups. In the presence of water, the hydrophilic sulfonic groups aggregate to form ion clusters, which form the water channels with good connectivity. Compared with Nafion, the backbone of SPPEK is less hydrophobic and the sulfonic groups are less acidic. This results in larger hydrophobic-hydrophilic interface corresponding to highly disperse sulfonic groups and less nano-separation. Thus, the water filled channels in SPPEK are probably more branched with more dead-end pockets compared with those of Nafion. This results in low methanol and water transport and lower proton conductivity (as we see later). In addition to that, the methanol permeability of

SPPEK-PE composite membranes is factor of 2–3 lower than pure SPPEK membranes showing once more that the impregnation to the support is an effective method to lower methanol permeability. The same phenomenon has been reported by Yamaguchi et al. with other filling electrolytes into various supports [12,22].

3.4. Proton conductivity

The proton conductivity of our membranes are generally low and in the range of 0.1×10^{-2} S/cm for the SPPEK1.4-PE and SPPEK1.6-PE and 0.3×10^{-2} S/cm for the SPPEK1.4 and SPPEK1.6 membranes. In general, the values of SPPEK membranes are in the lower range with values reported in literature ($(0.2\text{--}5.0) \times 10^{-2}$ S/cm) [1,17,18,20,23]. Although one should be careful with the experimental conditions used there. Many parameters can influence the proton conductivity, i.e. pre-treatment, casting solvent, etc. For example, in literature *N,N*-dimethylacetamide (DMAc) was often used as a casting solvent [19,21], while our membranes were prepared in NMP.

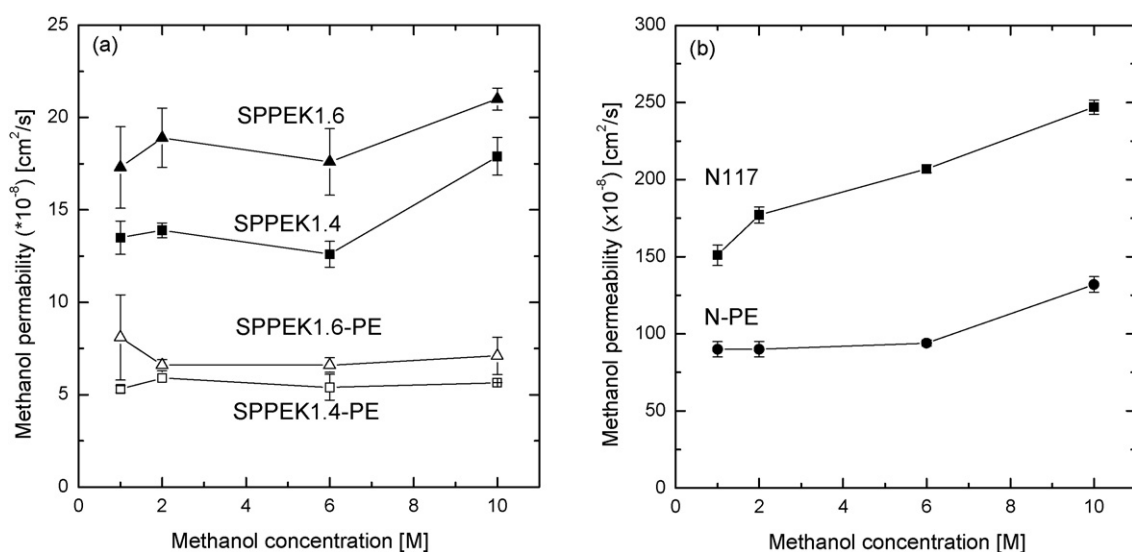


Fig. 5. Methanol permeabilities of (a) SPPEK, (b) N117 and N-PE membranes as a function of methanol concentration (data from N117 and N-PE are replotted from [13]).

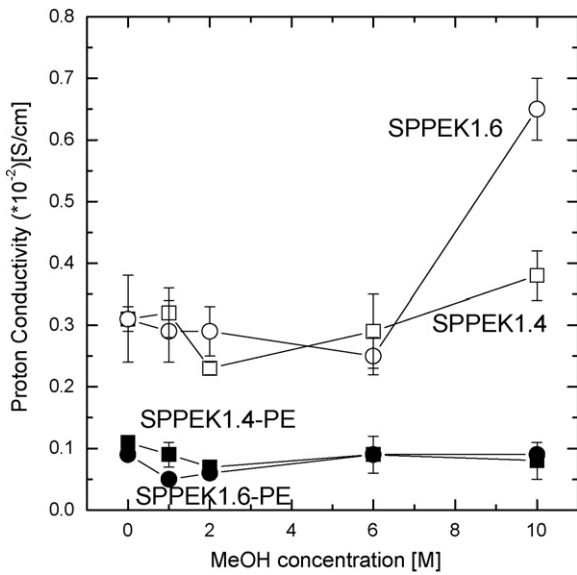


Fig. 6. Proton conductivities of SPPEK membranes as a function of methanol concentration.

Fig. 6 shows the proton conductivities of the membranes as a function of methanol concentration. Proton conductivities of SPPEK1.4 and SPPEK1.6 are in the same range for methanol concentration up to 6 M. At higher methanol concentration, the proton conductivity of SPPEK1.6 increases sharply, whereas increases modestly for SPPEK1.4. SD measurements show the same effect. The rate of increase is smaller for SPPEK1.4 than SPPEK1.6. It seems that there is a threshold for swelling as well as conductivity at ~ 6 M especially for the SPPEK1.6 membrane. This phenomenon is not observed for the SPPEK-PE impregnated membranes. The conductivity of those membranes is independent of the methanol concentration at around 0.1×10^{-2} S/cm (Fig. 6) and a factor 3 lower than pure membranes, due to the presence of the non-conductive PE material. For comparison, the proton conductivities of N117 and N-PE membranes are much higher and they are in the range of $(5-6) \times 10^{-2}$ S/cm and $(0.5-3) \times 10^{-2}$ S/cm, respectively for methanol concentrations of 1–10 M [13].

3.5. Single cell performance

SPPEK1.4 and SPPEK1.4-PE membranes were selected for further tests in the DMFC due to their low swelling and methanol cross-over. MEAs were prepared by hot pressing two E-TEK commercial electrodes on both sides of the membranes at 10 bar. At least two MEAs were prepared and measured for each methanol concentration. Minimum 70 polarization curves were measured for each MEA and the values presented in this work are their average values.

Fig. 7 presents polarization curves of SPPEK1.4 and SPPEK1.4-PE membranes at various methanol concentrations. The open cell voltage (OCV) values of each membrane decreases at higher methanol concentration due to the increasing driving force for the methanol cross-over. In all graphs, there are clear regions of activation, ohmic and concentration polarization. The concentration polarization is significant at 1 M, but becomes lower at 3 M and 6 M. For SPPEK1.4 membrane, it seems that the performance at 6 M is slightly worse than at 3 M. However, for the SPPEK1.4-PE, the performance at 6 M is better than 3 M. In fact, the impregnated membrane can be used up to 1600–1700 mA/cm² at high methanol concentrations. This is also obvious when comparing the power density curves of the membranes at various methanol concentrations (see Fig. 8). SPPEK1.4-PE composite membrane shows superior performance than SPPEK1.4 membrane at every concentration and at low and high current density regions of the curves due to its significantly low methanol cross-over and reasonable proton conductivity. Since the composite membrane has significantly low methanol cross-over, the performance increases with increasing methanol concentration, which is also an advantage over the perfluorinated Nafion-based membranes.

Fig. 9 summarizes the DMFC measurements of this study and compares our results with our previous study for N117 and N-PE membranes [13]. It presents the maximum power densities as a function of methanol concentration at the anode side of the fuel cell (lines are used to guide the eye of the reader and do not correspond to experimental result). The power density of the N117 and N-PE is higher than SPPEK1.4 and SPPEK1.4-PE at 1 M, but decreases sharply at 6 M. The maximum power density of SPPEK1.4 increases with increasing methanol concentration up to 3 M and then shows a slight decrease at 6 M, but the power density at 6 M is still higher than 1 M. The power density of the SPPEK1.4-PE is always higher than SPPEK1.4 and interestingly is independent

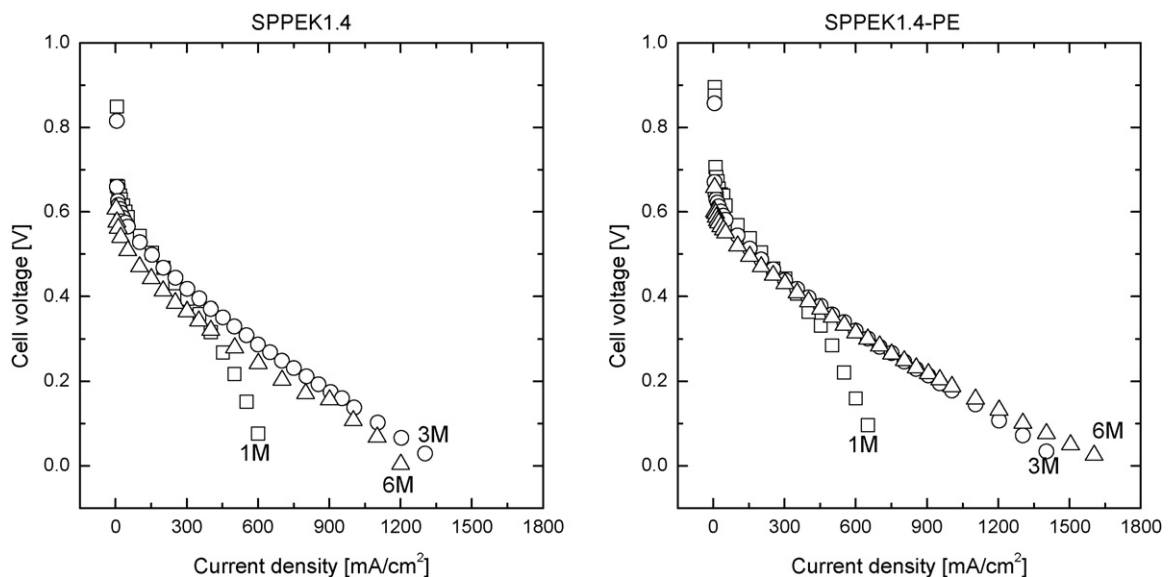


Fig. 7. Polarization curves of SPPEK1.4 and SPPEK1.4-PE membranes at various methanol concentrations.

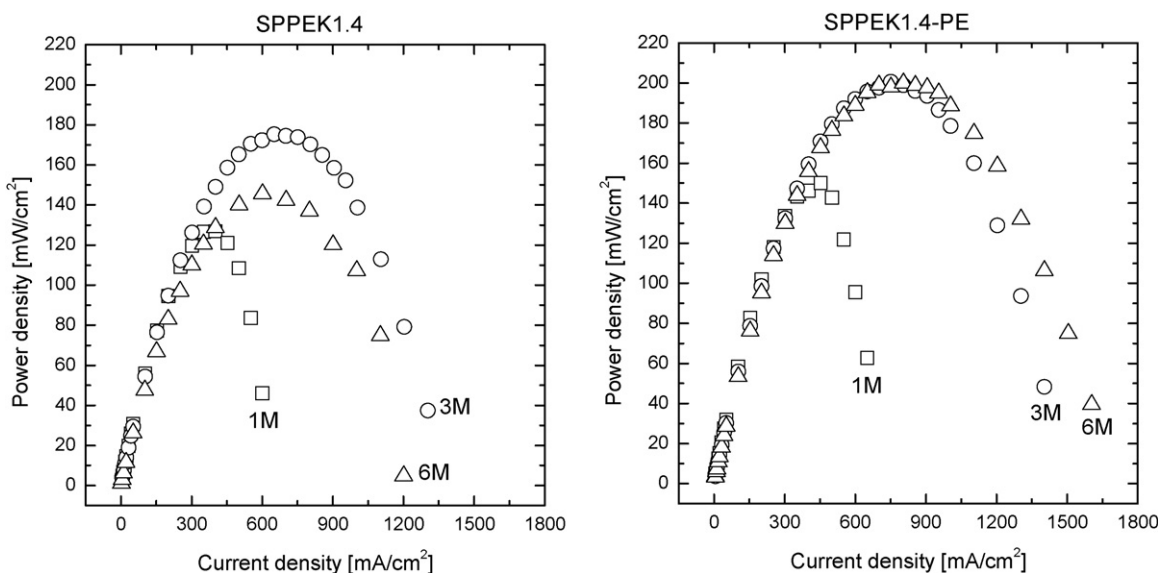


Fig. 8. Power density curves of SPPEK1.4 and SPPEK1.4-PE membranes at various methanol concentrations.

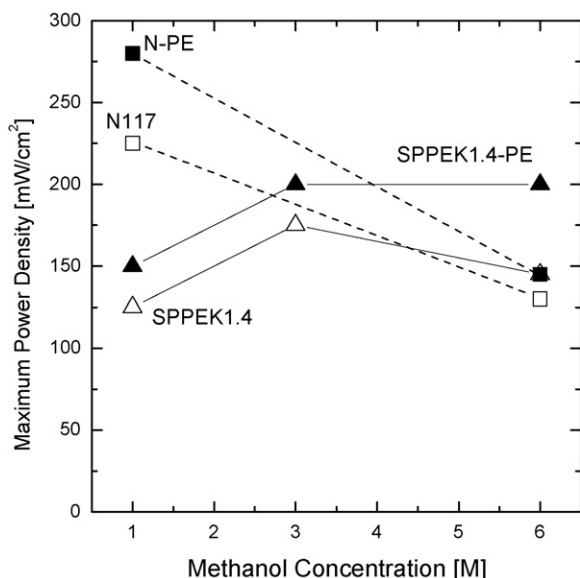


Fig. 9. Maximum power densities of SPPEK1.4 and SPPEK1.4-PE as a function of methanol concentration (data from N117 and N-PE are replotted from [13]).

of methanol concentration above 3 M. The performance of the SPPEK1.4-PE composite membrane at 6 M is higher not only than the pure SPPEK1.4 membrane, but also significantly higher than those results of N117 and N-PE membranes at 6 M. This shows that the SPPEK1.4-PE membrane is a very promising material for DMFC applications at high methanol concentrations. In order to compete with Li-ion batteries, high methanol concentrations should be used as a fuel in DMFCs and SPPEK1.4-PE is the best material at 6 M in comparison to all the other materials we have tested.

4. Conclusions

In the present work, SPPEK and SPPEK-PE membranes, with two different IECs, were prepared and characterized for use in DMFC applications. Swelling, proton conductivity, diffusion and DMFC experiments were performed to understand the effect of impregnation of a conductive polymer into a non-conductive porous substrate.

The swelling of the composite membrane is very low. Diffusion measurements show that the methanol permeability of SPPEK-PE is one order of magnitude lower than Nafion® and N-PE membranes and a factor 2 lower than pure SPPEK membrane. The proton conductivity, however, is rather low at 1 mS/cm². It seems, however, that the substantially low methanol cross-over compensates the low proton conductivity and therefore the composite membrane shows superior performance than SPPEK, N117 and N-PE membranes at high methanol concentrations (6 M). Unlike perfluorinated membranes, SPPEK-PE shows an increase in its DMFC performance with increasing methanol concentration and this makes it more attractive material for mobile DMFC applications where high methanol concentrations are needed to compete with Li-ion batteries.

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