Using silica nanoparticles for modifying sulfonated poly(phthalazinone ether ketone) membrane for direct methanol fuel cell: A significant improvement on cell performance

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Abstract

Sulfonated poly(phthalazinone ether ketone) (sPPEK) with a degree of sulfonation of 1.23 was mixed with silica nanoparticles to form hybrid materials for using as proton exchange membranes. The nanoparticles were found homogeneously dispersed in the polymer matrix and a high 30 phr (parts per hundred resin) loading of silica nanoparticles can be achieved. The hybrid membranes exhibited improved swelling behavior, thermal stability, and mechanical properties. The methanol crossover behavior of the membrane was also depressed such that these membranes are suitable for a high methanol concentration in feed (3 M) in cell test. The membrane with 5 phr silica nanoparticles showed an open cell potential of 0.6 V and an optimum power density of 52.9 mW cm^{-2} at a current density of 264.6 mA cm^{-2}, which is better than the performance of the pristine sPPEK membrane and Nafion® 117.
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1. Introduction

Two attractive kinds of fuel cells, proton-exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC), employ the proton exchange membranes (PEM). Perfluorinated sulfonated ionomers like Nafion® membranes show some attractive properties for using as PEMs in DMFC. However, the high methanol permeability of about 10^{-6} cm^2 s^{-1} of Nafion® reduces its performance in fuel cell application [1]. Another drawback of Nafion® is its high cost. Therefore, cheap and qualified alternatives of Nafion® are being sought for using as PEMs in DMFC.

One attractive class of alternatives for Nafion® is sulfonated high performance condensation polymers, including poly(arylene ether ketones) [2–5], poly(arylene ether) [6,7], poly(arylene ether sulfones) [8–10], and polyimides [11–14]. These polymers were prepared from both direct polymerization of sulfonated monomers and post-sulfonation on polymer chains. Developments in molecular designs and synthetic techniques have made great progress in structure control and properties enhancement for these polymers. High density of sulfonic acid groups is desired for the polymers to increase their proton conductivity as well as cell performance in application. However, high degree of swelling (poor dimensional stability) in methanol solution and high methanol permeability (methanol crossover) are usually encountered with the polymers possessing very high contents of sulfonic acid

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groups (high degree of sulfonation), to offset the excellences of the polymers. Stabilization of sulfonated polymers is therefore critical to improve their performance. Cross-linking on the polymers is one of the most studied approaches [15]. Another workable method is formation of organic–inorganic nanocomposite membranes [16–21]. Silica is a widely used inorganic reinforcement for the nanocomposites through sol–gel processes. Both cross-linking and sol–gel techniques involve additional chemical reaction and complicated process in preparation of proton exchange membranes. Usages of silica particles were thus considered to replace the sol–gel process. Antonucci et al. [22] reported a composite Nafion®-silica electrolyte for DMFC. The cell could be operated at a relatively high temperature of 140 °C to show improved cell performance. In our previous work [23,24] colloidal silica nanoparticles showed great compatibility with organic polymers, and the particles could be directly added into the polymer solutions for casting membranes. No alternation in the membrane preparation process is needed with the addition of silica nanoparticles. Therefore, silica nanoparticles are utilized for preparation of organic-inorganic nanocomposite proton exchange membranes in this work. Sulfonated poly(phthalazinone ether ketone) (sPPEK) with a high content of sulfonic acid groups is utilized as the proton conducting material [2]. Although possessing high ionic conductivity, the pristine polymer did not exhibit satisfactory performance owing to its high methanol and water affinity. The properties of the prepared nanocomposite PEMs and the single cell performance are examined and discussed. A significant improvement in the cell performance is observed with using the sPPEK-silica nanocomposite PEMs.

2. Experimental

2.1. Materials

Sulfonated poly(phthalazinone ether ketone) (sPPEK) with a degree of sulfonation of 1.23 (equivalent weight of sulfonated group = 514 g mol^{-1}) was obtained from direct sulfonation on poly(phthalazinone ether ketone) [2]. Silica nanoparticle with a size of 10–20 nm was purchased from Nissan Chemical Company. The product coded MIBK-ST was used after a solvent exchange from methylisobutylketone (MIBK) to N,N-dimethylacetamide (DMAc).

2.2. Preparation of nanocomposite membranes

sPPEK (1 g, Fig. 1) was dissolved in 12 ml of N,N-dimethylacetamide (DMAc) and filtered. A certain amount of MIBK-ST (5–30 phr, parts per hundred resin) was added into the solution and stirred for 1 day to result in a homogeneous solution. The solution was then poured onto a glass plate and dried at 40 °C for 2 days. The residual solvent was evaporated at 120 °C in vacuo for another 2 days. The membrane was removed from the glass plate by soaking it in water.
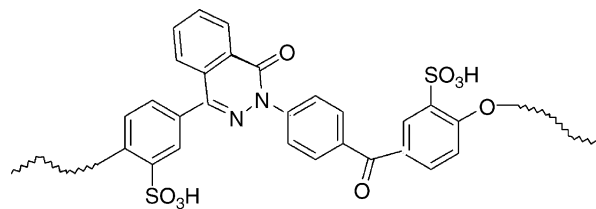

Fig. 1. The chemical structure of sPPEK.

A tough and flexible yellowish membrane was obtained after air-drying at ambient temperature.

2.3. Measurements

2.3.1. Instrumental analysis

Thermogravimetric analysis was conducted with a Perkin-Elmer TGA-7. Polymer samples for TGA were preheated to 150 °C at 10 °C min^{-1} under a nitrogen atmosphere, held isothermally for 60 min, equilibrated at 80 °C, and then heated to 800 °C at 10 °C min^{-1} according to a procedure reported previously. Scanning electron micrographs were observed with a Hitachi S-3000N Hi-SEM. Energy dispersive X-ray (EDX) measurements were conducted with a Horiba ES-320 energy dispersive X-ray microanalyzer.

2.3.2. Water and methanol uptake

The membrane samples were vacuum-dried at 120 °C before the testing. The sample films were soaked in deionized water until swelling equilibrium was attained at predetermined temperatures. The dry weight and the equilibrated swollen weight of the membranes were determined. Swollen membranes were blotted dry with tissue paper before weight measurements. The apparent water or methanol uptake content of the membranes were determined as follows:

$$\text{Uptake content}\,(\%) = \frac{W_s - W_d}{W_d} \times 100\% \qquad (1)$$

where W_s and W_d are the weights of swollen and dried samples, respectively. Moreover, the apparent uptake contents from above were normalized by the sPPEK contents of the membranes to estimate the true uptake content of sPPEK polymer in the nanocomposite membranes.

2.3.3. Methanol permeation measurement by pervaporation process

The experiment is carried out according to the reported process [25]. The feed solution is in direct contact with membrane, in pervaporation apparatus. The effective membrane area is 6.7 cm^2 and the experiments were conducted at a 50 °C feed solution. The permeation rate was determined by measuring the weight of permeate. The compositions of feed solution and permeate were analyzed by a gas chromatography (GC China chromatography 8700 T). The separation factor of water/alcohol ($\alpha_{W/A}$) was calculated from:

$$\alpha_{W/A} = (Y_W/Y_A)/(X_W/X_A)$$

where X_W, X_A, Y_W, Y_A are the weight fraction of water and alcohol in the feed and permeate, respectively.

2.3.4. Proton conductivity

The proton conductivity was measured by alternating current impedance spectroscopy over a frequency range of 1–10^7 Hz with an oscillating voltage of 50–500 mV with a system based on a Solartron 1280 gain phase analyzer. A sample with a diameter of 3.5 mm was placed in an open, temperature-controlled cell, in which it was clamped between two blocking stainless steel electrodes with a permanent pressure of about 3 kg cm^{-2}. Specimens were soaked in de-ionized water before the test. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, with the relation $\sigma = d/RS$, where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersection of the high frequency semicircle on a complex impedance plane with the $Re\ (z)$ axis.

2.3.5. Single cell DMFC test

DMFC tests on SPPEK and Nafion® membranes were carried out in a 25 cm^2 single cell (EFC25-01SP, ElectroChem) at 70 °C. Membrane samples were thermal pressed with E-tek electrodes (anode: 2 mg cm^{-2} Pt–Ru on carbon; cathode: 1 mg cm^{-2} Pt on carbon). Membrane electrode assemblies were tested with various concentrations of MeOH feed solution (2 ml min^{-1}) on the anode and humidified O$_2$ (150 ml min^{-1}) on the cathode side. The single cell was connected with a gas distribution unit (FCT-2000, ElectoChem) for gas flow control. The electrical characteristics of the MEAs were monitored with software provided by Scirbner Assoc. Co.

3. Results and discussion

sPPEK-silica nanocomposite membranes containing 5–30 phr of silica nanoparticles were prepared (SPNM-5, SPNM-10, SPNM-20, and SPNM-30). All samples showed transparent appearance to indicate that the silica nanoparticles did not aggregate in the polymer. The compatibility between sPPEK and silica nanoparticles were directly observed with a scanning electronic microscopy (SEM). Smooth surface and cross-section surfaces were observed. The contribution of silica particles in the membranes was recorded with a energy dispersive X-ray spectroscopy (EDS). Fig. 2 showed the SEM-EDS silicon mapping on the pristine sPPEK membrane and its nanocomposites. No silica signals appeared with pristine sPPEK membrane, and the silicon signals for SPNM samples increased with increasing the amounts of silica particles. The homogeneous distribution of the silicon signals in the observation area indicated that the silica nanoparticles homogeneously distribute in the sPPEK matrix. As above-mentioned, no silica aggregation
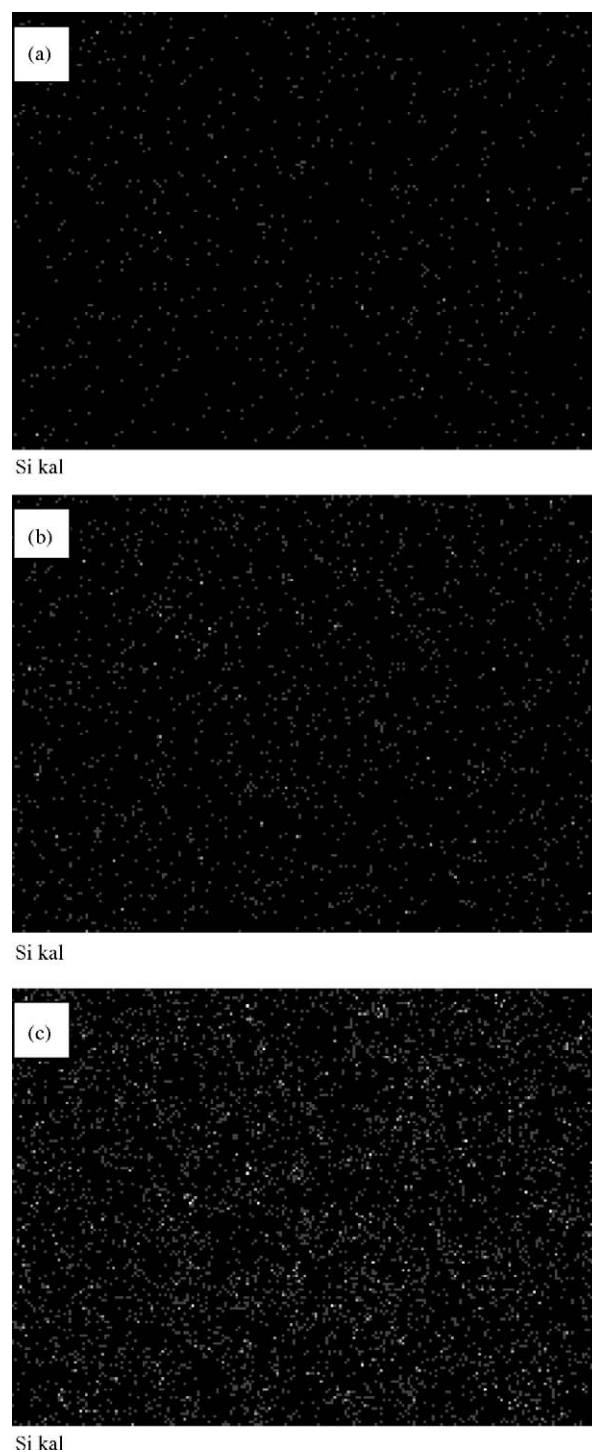

Fig. 2. SEM-EDS Si-mapping on the prepared membranes: (a) pristine sPPEK; (b) SPNM-5; (c) SPNM-20.

and phase separation occurred in the SPNM membranes. The thermal stability of the membranes was examined with a thermogravimetric analyzer and the results were shown in Fig. 3. The initial weight loss temperature and degradation pattern of the pristine sPPEK membrane were similar to those of the sPPEK-silica nanocomposite membranes. Therefore, the added silica particles might neither alter nor be involved in
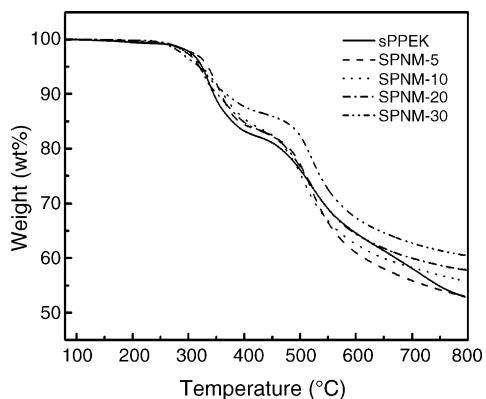
Fig. 3. TGA thermograms of prepared membranes.

the degradation reactions of sPPEK polymer. Similar results were also observed with other polymer-silica nanocomposites [24,26].

Fig. 4 shows the water and methanol absorption properties of the membranes at various temperatures. Miyake et al. [27] reported that Nafion®-silica hybrid membrane from sol–gel process had higher water contents than pristine Nafion® membrane owing to the hygroscopic effect of silica. Similar results were also reported with other silica-modified membranes from sol–gel process [28]. Sol–gel process performed at relatively low temperatures (<300 °C) might limit the gel reaction conversions to result in silica possessing high contents of silanol groups. These retained silanol groups contribute to the high hygroscopic character of the formed silica. Using preformed silica nanoparticles could avoid the hygroscopic effect, which was encountered with sol–gel silica. Therefore, reduced apparent water-uptake and methanol-uptake values were observed with the SPNM membranes (Fig. 4a and c) to demonstrate that formation of sPPEK-silica nanocomposites could result in membranes with improved water and fuel absorption properties. Furthermore, the apparent water and methanol uptake values were normalized with the sPPEK contents of the membranes to probe the true water and methanol absorption properties of the polymer in the nanocomposite membranes. From the plots c and d of Fig. 4, it could be observed that the normalized water and methanol uptake values were smaller than the values of pristine sPPEK membrane. It was further demonstrated that addition of silica with sPPEK might depress the
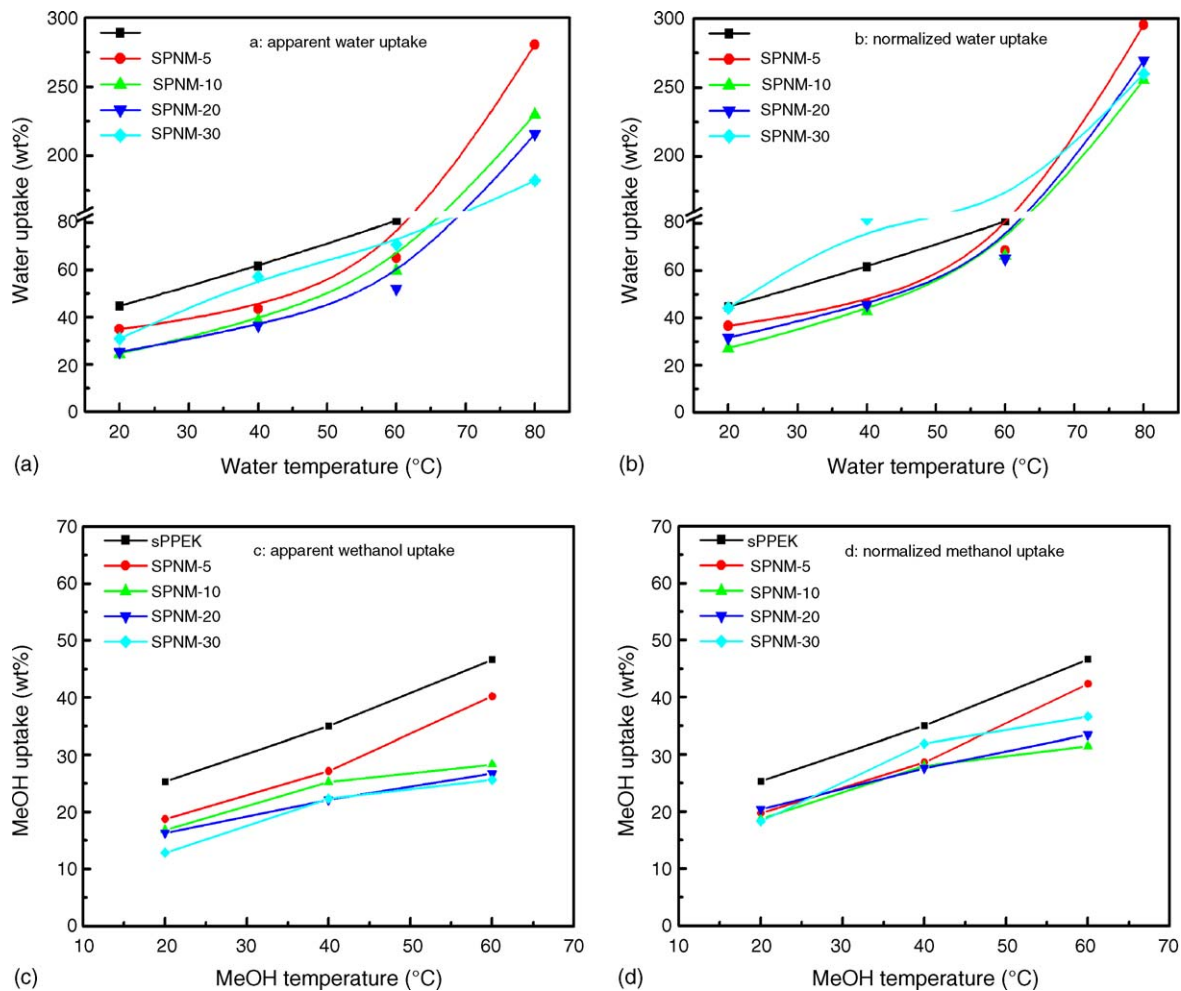

Fig. 4. Apparent and normalized water uptake and methanol uptake measured on the prepared membranes at various temperatures.
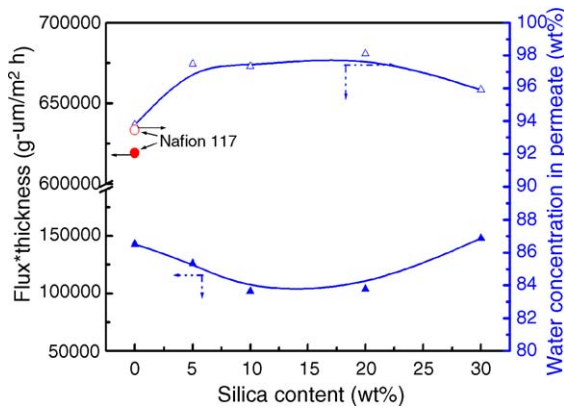
Fig. 5. Methanol permeability of sPPEK based membranes and data obtained with Nafion® 117.

Fig. 6. Proton conductivity measured on the prepared membranes.

water and methanol absorption properties of sPPEK polymer. In addition, the pristine sPPEK membrane dissolved in water at 80 °C, owing to its high sulfonic acid group contents and hydrophilicity. With addition of silica nanoparticles, the nanocomposite membranes become stable and capable of operation at 80 °C. Formation of hydrogen bonding between the $-SO_3H$ groups of sPPEK and the Si–OH groups of silica contributes to stabilizing the nanocomposites membranes [29]. However, the SPNM membranes dissolved in DMAc to indicate that no covalent bonding and cross-linked network formed between silica and sPPEK polymer chains. In addition, the sustainability of membranes at high temperatures is an attractive property for the membranes using in fuel cells.

On the other hand, low methanol uptake of SPNM membranes indicates their low affinity with methanol. A low methanol crossover is thus expected for the SPNM membranes. Fig. 5 shows the methanol permeability of the membranes with a pervaporation test, in which an aqueous solution containing about 9 wt.% methanol (a 3 M methanol solution) was fed. The permeation selectivity of pristine sPPEK membrane is similar to that of Nafion® 117. This means that these two membranes possess similar methanol affinity and diffusion property. Adding silica nanoparticles resulted in a significant depression in methanol permeation crossing the membranes, as increased water concentration in permeate were observed. Since the nanocomposite membranes showed low total permeate flux, both the permeation of water and methanol through the membranes were depressed with silica nanoparticles, and the depressing effect on methanol is especially significant. However, the high permeation flux of SPNM-30 indicates that excess amounts of silica provide extra free-volume in the membrane to increase the permeation rate [23]. It is noticeable that all the sPPEK based membranes showed lower methanol crossover than did Nafion® 117, and SPNM-10 exhibited the optimum properties.

The proton conductivity of the membranes measured at various temperatures is shown in Fig. 6. The membranes showed high proton conductivities at high temperatures. Since SPNM membranes are more stable at high tempera-
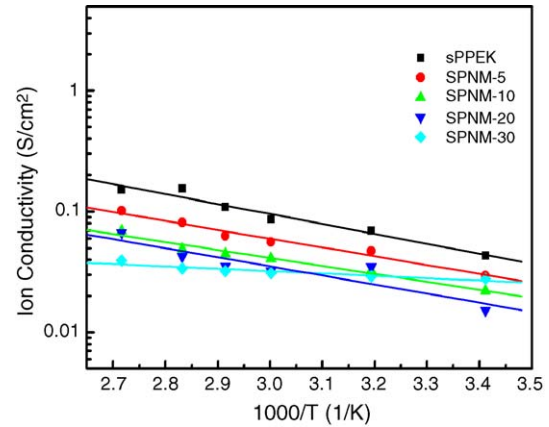
tures than sPPEK membrane, the improvement of silica on the proton conductivity of the membranes could be expected. On the other hand, at same temperatures the nanocomposite membranes showed relatively low proton conductivity compared with the pristine sPPEK membrane. This decrease of proton conductivities of nanocomposite membranes was due to the reduced density of sulfonic acid groups in the nanocomposite membranes. Similar results were also reported in the literature [27]. However, Miyake et al. [27] pointed out that fuel cell performance might also be affected with other effects than simply the membrane conductivity. The low proton conductivity of SPNM membranes does not imply their poor outcome in fuel cell performance. Further examination was made with a single cell test. Fig. 7 shows the cell performance of sPPEK and nanocomposite membranes in various concentrations of methanol in feed. For the polarization curves, concentration polarization is quite significant at low methanol concentrations, to indicate that methanol supply is insufficient at the anode. With high methanol concentration this concentration polarization becomes weaker. Adding silica nanoparticles exhibits certain depression on the polarization effect. Fig. 7b is the plots of the open cell potentials (OCP) versus the concentration of methanol in feed. Generally the open cell potentials decreased with increasing the methanol concentration in feed owing to high methanol crossover at high methanol concentration [30,31]. However, this decrease in the cell potentials is not so significant for the SPNM membranes, further demonstrating the low methanol crossover property of these membranes. In addition to methanol crossover, other factors such as membrane material and modification, membrane thickness, air-flow rate, and membrane ohmic resistance might also be significant influences on OCP values [32,33]. The low open cell potentials observed for SPNM-30 might be due to its relatively high methanol permeation. Moreover, the ohmic resistance of SPNM membranes might increase a lot with the amount of inorganic incorporation. Consequently, the low OCP value of SPNM-30 could be from its high silica content and high ohmic resistance [34]. On the other hand, comparison of the
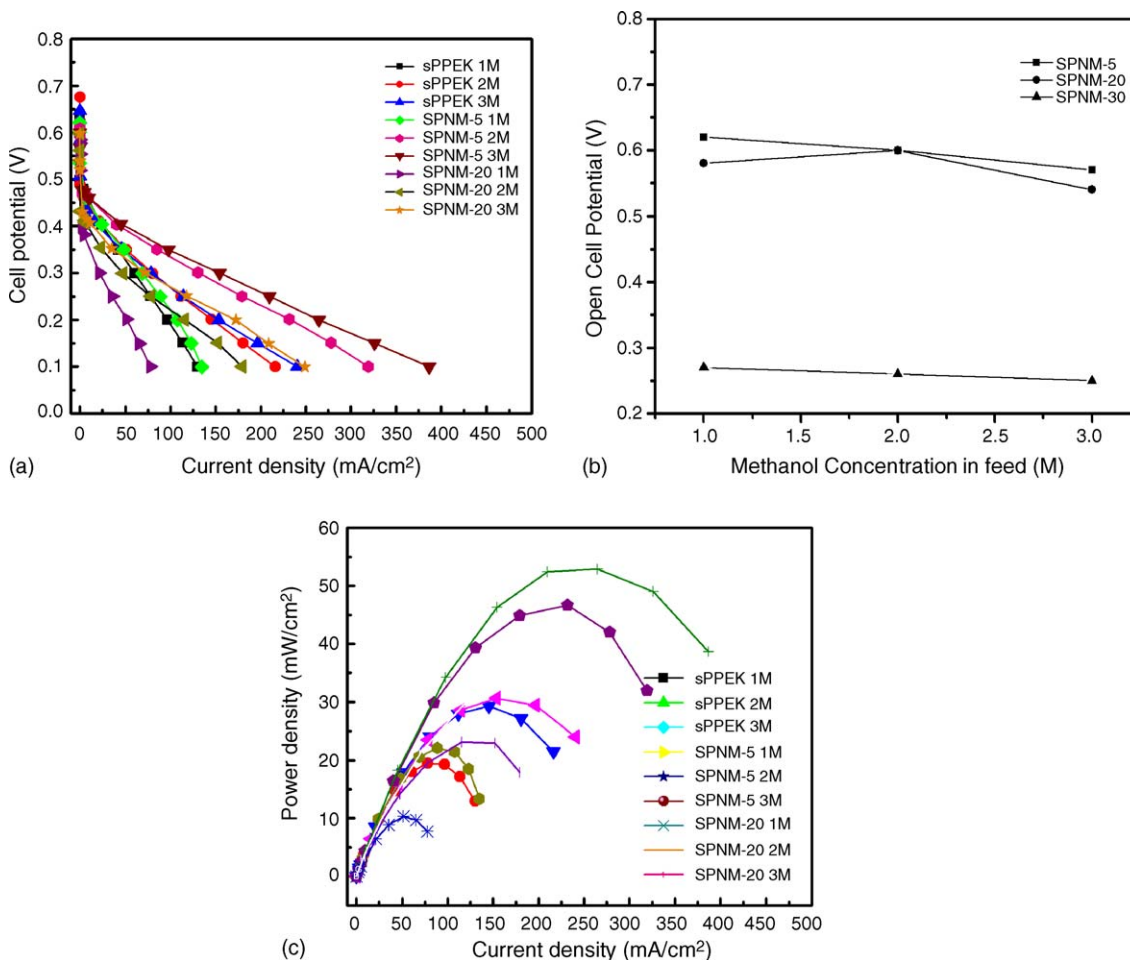
Fig. 7. DMFC performance with various concentration of methanol in feed: (a) polarization curves; (b) the relationship of open cell potentials and methanol concentration in feed; and (c) the relationship between power density and current density.

OCP values of Nafion® 117 and the sPPEK-based membrane could only be a reference in this work, since the methanol concentration in operation were different. From Fig. 7c, the ultimate current density of the cell increased with increasing the concentration of methanol in feed, and reached a maximum at 3 M methanol in feed. The optimum methanol concentration for SPNM based cell was 3 M, which is higher than that for Nafion® 117 (2 M). This could be due to the
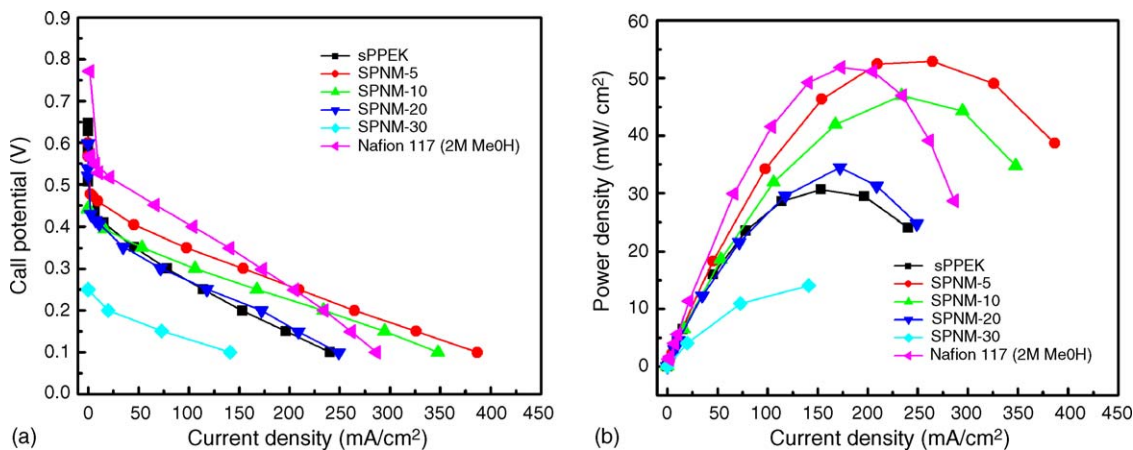

Fig. 8. DMFC performance of using various membranes with 3 M methanol in feed: (a) polarization curves; and (b) the relationship of power density and current density.

Table 1
Cell performance of the tested membranes from MEA measurement

Membrane	Open cell potential (V)	Current density (mA cm^{-2})	Optimum power density (mW cm^{-2})
sPPEK	0.65	153.6	30.6
SPNM-5	0.60	264.6	52.9
SPNM-10	0.44	234.1	47.0
SPNM-20	0.54	172.3	34.4
SPNM-30	0.25	–	–
Nafion® 117[a]	0.75	175.0	52.0

[a] Data obtained at a 2 M methanol in feed.

low methanol permeability of SPNM membranes. The SPNM nanocomposite membranes showed better cell performance than did the pristine sPPEK membrane, to demonstrate that using silica nanoparticles to modify sPPEK membrane is effective in enhancing cell performance. This result also directly responds to the account that low proton conductivities do not indicate low cell performance for composite membranes. Fig. 8 collects the cell performance plots of the tested membranes and Nafion® 117, and some values are shown in Table 1. Excepting SPNM-30, SPNM membranes showed better cell performance than did sPPEK membrane. The poor cell performance of SPNM-30 might be due to its high methanol permeability. On the other hand, SPNM-5 showed the best cell performance among the tested membranes with an optimum power density of 52.9 mW cm^{-2} at a current density of 264.6 mA cm^{-2}. It is concluded that formation of sPPEK-silica nanocomposite membrane bring about a significant improvement to fuel cell performance, and the cell performance is comparable to that of Nafion® 117. Extending the present work of using sulfonated silica nanoparticles for further improving the performance of the nanocomposite membranes is under study.

4. Conclusion

Formation of polymer-silica nanocomposite membranes is a convenient and effective approach to improve the properties of highly sulfonated polymers used as PEMs in direct methanol fuel cell. Not only physical properties of the membrane, but also the cell performance are enhanced. This work certainly extends the workable range of sulfonated high performance polymers using as PEMs in fuel cells.

Acknowledgement

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