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Sulfonated poly(phthalazinone ether ketone) for proton exchange membranes in direct methanol fuel cells

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Abstract

Sulfonated poly(phthalazinone ether ketone) (SPPEK) membranes were cast from *N*,*N*-dimethylacetamide (DMAc) solution and tested for their application as proton exchange membranes (PEMs) in direct methanol fuel cells (DMFCs). The methanol and water swelling uptake and several permeation tests indicated that SPPEK had a lower affinity to methanol than Nafion and was less permeable than Nafion. In a single cell DMFC test at 70 °C with the membrane electrode assembly (MEA) made of SPPEK, the maximum power density was 55 mW/cm^2 as the current density was 276 mA/cm^2 and the ultimate (limiting) current density was 360 mA/cm^2. The lower permeability of SPPEK compared with Nafion resulted in lower methanol crossover. Consequently, the optimal concentration of aqueous feed methanol (3 M) for the SPPEK MEA was higher than that of Nafion (2 M) under the same operation conditions.

Keywords: Direct methanol fuel cell; Permeation; Swelling; Proton exchange membrane; Polarization curve

1. Introduction

Direct methanol fuel cell (DMFC) is one of the most attractive future power sources for use in such vast application areas as road transportation, power generation and portable electronics. DMFCs are particularly attractive for their use in road transportation because their low operating temperatures allow short start-up times and the infrastructure of the fuelling stations already exist if methanol is used as fuel [1,2]. Other areas of significant DMFC application interests are portable and micro-fuel cells for consumer electronics, such as laptop computers and cell phones. In these applications, FCs offer outstanding advantages over existing technology, such as high efficiencies, long user-times and refuelling in the order of a few minutes or less. For example, a FC powered cellular phone is expected to have a standby time of 50–100 days rather than 5–10 days, and a refuel time of a few seconds.

PEMs are one of the key components for successful DMFC fabrication. The required properties for PEMs are high proton conductivity, low methanol crossover, long-term stability and low cost. So far Nafion is the dominant material in the PEMs for the hydrogen FC because of its high proton conductivity and superb chemical stability. However, its practical application in DMFC is limited due to its high methanol permeability [3–6]. In addition, the current cost of Nafion membrane is high due to its perfluorinated nature. The search for a non-fluorinated PEM with low methanol permeability and high proton conductivity to replace Nafion is a most intensely studied research area in FC [2,3].

In our previous work, sulfonated derivatives of poly(phthalazinone ether ketone) (PPEK) thermoplastics were

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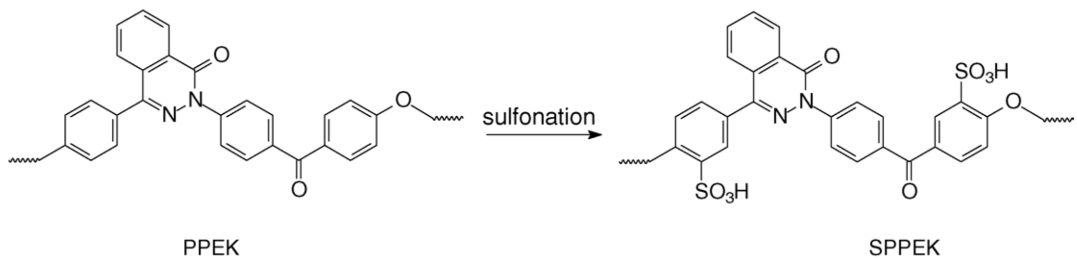


Scheme 1.

developed as the base materials for PEM fabrication. Our preliminary results on this polymer for PEM-FCs suggest this class of thermoplastics to be promising. For example, PPEK has a very high T_g of 263 °C (∼120 °C more than PEEK), excellent thermal stability and many other favorable physical properties. A method of controlled sulfonation of PPEK to produce SPPEK (Scheme 1) was developed and an initial series of polymers with different degree of sulfonation (DS) were produced and several physical properties determined. Initial proton conductivity measurements of the higher DS derivatives showed room-temperature conductivities >10^{-2} S/cm, i.e., well in the acceptable range. Detailed information about the synthesis, chemical structure identification, thermal stability and proton conductivity measurement can be found elsewhere [7].

In this communication, the characterization of the swelling and permeation properties of a SPPEK membrane with a DS of 1.09 is reported. Furthermore, a single cell DMFC test with a MEA made from SPPEK PEM has been conducted. The results are compared with those obtained with a Nafion membrane.

2. Experimental

2.1. Materials

Poly(phthalazinone ether ketone) (PPEK) was obtained from the Dalian Polymer New Material Co., PR China [8,9]. Sulfonated PPEK (SPPEK) was prepared according to a procedure reported previously [7]. The DS of SPPEK was determined by ^{1}H NMR, and the one used in this study was 1.09. All other chemicals obtained commercially were reagent-grade and were used as received. Nafion-117 membranes were obtained from Du Pont and used directly.

2.2. SPPEK membrane preparation

A sample of SPPEK (1 g) was dissolved in 16 g of *N*,*N*-dimethylacetamide (DMAc). The polymer solution was degassed and filtered, and then poured on a glass plate. The thickness of the solution was controlled with a casting knife. The cast membrane was dried at 40 °C for about 2 days. The residual solvent was further evaporated at 120 °C in vacuum for 2 days. The membrane was removed from the glass plate by soaking it in water. A tough and flexible yellowish membrane was obtained after air-dried at ambient temperature. The thickness was determined from a 10-point measurement by a digital micrometer (Mitutoyo, IDF-112).

2.3. Measurement of 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 water or methanol uptake content was determined as follows:

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

where W_s and W_d are the weights of swollen and dried samples, respectively.

2.4. Gas and vapor permeation studies

The permeabilities of oxygen, hydrogen, and methanol vapor through SPPEK or Nafion membranes were determined by a classical constant-volume variable-pressure permeation method. A detailed description of the procedures has been reported previously [10]. The permeation apparatus is comprised of a membrane cell, an upstream gas or vapor supply and a downstream buffer volume. Initially, the downstream volume was evacuated. When the upstream volume was filled with gas or vapor and maintained at a constant pressure, the gas or vapor permeated through the membrane and the downstream pressure increased. By taking a mass balance over the downstream volume, we have

$$J = \frac{22400V}{ART}\frac{\mathrm{d}p_2}{\mathrm{d}t} = P\frac{p_1 - p_2}{l} \qquad (2)$$

where J is the volumetric flux of the gas or vapor though the membrane (cm^3 (STP)/(cm^2 s)), V the downstream volume (cm^3), A the membrane area (cm^2), R the gas constant, T the experimental temperature (K), p_1 and p_2 the pressures of the upstream and the downstream (Pa or cmHg), respectively, l the membrane thickness (cm) and P is the permeability coefficient (barrer = 10^{-10} cm^3 (STP)/(cm^2 s cmHg) or $7.5005 \times 10^{-18}\,m^2\,s^{-1}\,Pa^{-1}$). The permeation apparatus was enclosed in a constant temperature chamber. Baratron-type pressure transducers (1.333 kPa (10 Torr) range, MKS 121A and 122A) were used to monitor the pressure variation. The upstream pressure (p_1) was maintained at 101.3 kPa (76 cmHg) for permanent gas and maintained at the saturated vapor pressure for methanol or water at test temperature. The measuring range of the downstream pressure (p_2) was from 0 to 1.333 kPa (1 cmHg). By integrating Eq. (2), the following equation can be obtained:

$$\ln\left(\frac{p_1}{p_1 - p_2}\right) = P\frac{ART}{22400Vl}t \quad (3)$$

In each run, the permeability can be calculated from the quasi-steady state slope in a plot of $\ln\left(\frac{p_1}{p_1-p_2}\right)$ versus time.

2.5. Membrane pervaporation with aqueous methanol solution

Standard pervaporation experiments were carried out to study the simultaneous permeation of methanol and water through SPPEK or Nafion membranes. The concentration of methanol was varied from 1 to 5 M and the experimental temperature was at 70 °C. The feed solution was circulated using a reciprocating piston pump. The permeate stream was evacuated by a vacuum pump and the permeate mixture was collected alternately by two liquid nitrogen traps. The effective area of the membrane in contact with the feed stream was $12.56 \times 10^{-4}\,m^2$. The total flux was determined by weighing the trapped permeate at predetermined time intervals and the composition of permeate was analyzer by GC.

2.6. Side-by-side permeation study

The methanol permeation through SPPEK or Nafion membranes was studied using a side-by-side two-compartment device [11,12]. A membrane clamped between two compartments had an effective membrane area available for permeation of $4.91 \times 10^{-4}\,m^2$. Each compartment had a 30 ml capacity for solution, which was stirred magnetically to provide agitation. The stirring speed was maintained at 8.33 Hz (500 rpm) so that the boundary layer mass transfer resistance could be considered negligible [12] according to a procedure proposed by Smith et al. [13] and Tojo et al. [14]. The experimental temperature was maintained at 70 °C by circulating thermostated fluid through the outside water jackets. A membrane was preswollen in pure water for 2 days. At the beginning of each experiment, 30 ml of pure water was poured into the receptor compartment, and 30 ml of aqueous methanol solution (1, 3 and 5 M) was added to the donor component. Methanol can permeate through the membrane due to the concentration difference. The solution in the receptor compartment was sampled at various time intervals to determine the methanol concentration using GC.

2.7. 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 PtRu 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) on the anode and humidified O_2 (150 ml/min) on the cathode side. The single cell performance of MEAs was evaluated by using a fuel cell test station (FCT-2000, ElectoChem). The electrical characteristics of the MEAs and the operating conditions were monitored with software provided by Scribner Assoc. Co.

3. Results and discussion

The swelling properties of the PEM directly affect the proton conductivity as well as gas permeability. On the one hand, the swelling should be minimized to maintain the membrane mechanical and dimensional stability; on the other hand, an adequate degree water uptake is desired to maintain good proton conductivity. Fig. 1a shows the water uptake in SPPEK and Nafion membranes as a function of temperature. The uptake of water in Nafion is relatively stable and less dependent of temperature. The uptake of water in SPPEK is higher than that in Nafion and it increases with temperature. There is a sharp increase for the water uptake in SPPEK between 60 and 80 °C. This indicates that the DS of 1.09 of the SPPEK sample studied may be too high, such that at elevated temperatures, a continuous percolation structure is formed when the PEM is immersed in water. In this case, the hydrophobic domains cannot provide adequate mechanical strength due to the excessive water uptake. Fig. 1b shows the uptake of methanol in SPPEK and Nafion membranes as a function of temperature. Both of the uptakes increase with temperature and the uptake of methanol in Nafion is higher than that in SPPEK. The results suggest that SPPEK has less affinity to methanol than Nafion and it may be advantageous to use SPPEK to reduce methanol crossover.

Permeability of fuel or gas through the PEM, which is related to the physical properties of the material, will affect the performance of a DMFC. A membrane with higher permeability to fuel will result in problems of crossover. It is presumed that lower fuel or gas permeability will favor the reduction of crossover. Several methods were used to identify the permeation properties of the membranes for gases, vapors and liquids. Although none of these measurement methods operate in exactly the same way as that in a DMFC operation, the results provide an insight and an indication of the membrane permeation properties toward fuel or oxygen during use in practical DMFC applications.

A classical constant-volume variable-pressure permeation method was adopted for pure gas permeability determination. The hydrogen, oxygen, methanol vapor and water vapor

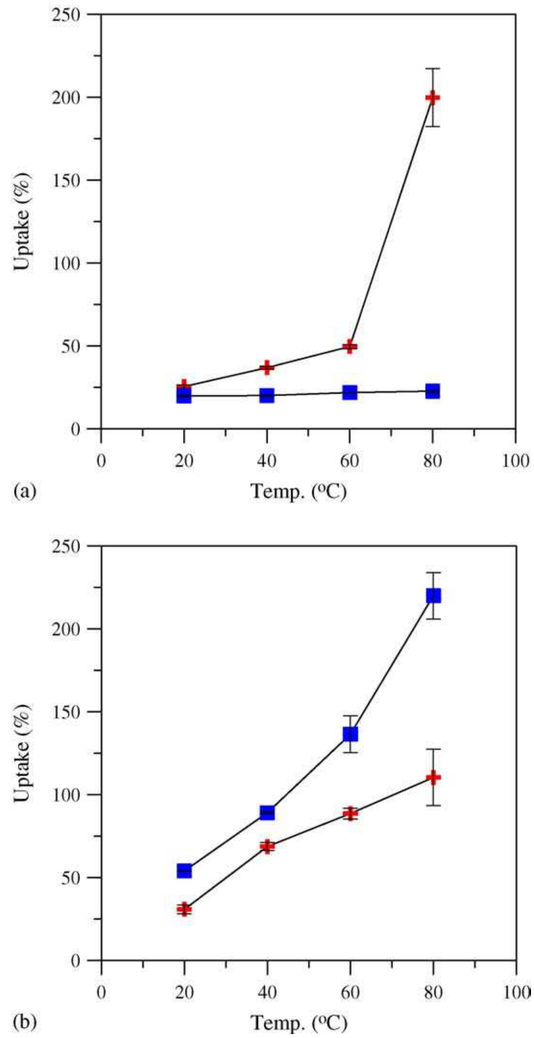


Fig. 1. The swelling ratios of SPPEK and Nafion membranes in (a) water and (b) methanol at various temperatures; (+) SPPEK, (■) Nafion.

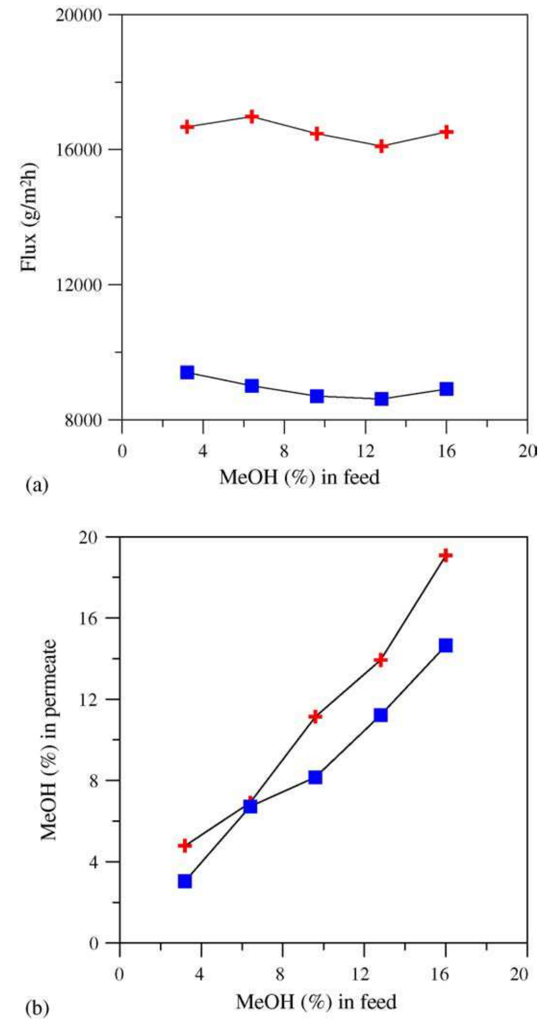


Fig. 2. Pervaporation of aqueous methanol solution through the SPPEK and Nafion membranes at 70 °C. (a) Flux as a function of feed composition and (b) methanol concentration in permeate as a function of feed composition; (+) SPPEK, (■) Nafion. The membrane thickness is 19 and 187 μm for SPPEK and Nafion, respectively.

permeability are shown in Table 1. The results indicate that Nafion is much more permeable toward hydrogen, oxygen, methanol and water than SPPEK. From this data, SPPEK appears to perform better as a gas barrier for retardation of fuel crossover.

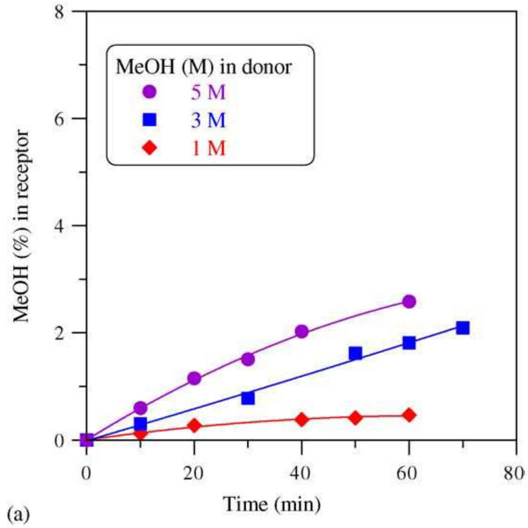
The pervaporation permeation test probably bears the closest similarity to a practical DMFC operation. An aqueous methanol solution was fed on the upstream of a permeation cell, and permeated vapor was removed by vacuum from the downstream. The situation closely resembles the case in DMFC except no vacuum is applied there. Fig. 2 shows the results. Although the thickness of the SPPEK membrane was only about one-tenth of that of a Nafion membrane, the flux of permeate through the SPPEK membrane was only twice that of the Nafion membrane (Fig. 2a). If the flux is normalized to thickness, the barrier property of SPPEK is much superior to that of Nafion. The composition of the permeate was about the same as that of the feed (Fig. 2b). It is possibly due to the high degree of swelling (uptake of MeOH solutions) of both kinds of membranes. The net flux through the membrane is very high in comparison with a lot of membranes for separation purpose. The solution of both methanol and water can easily permeate through the membrane without much resistance; therefore, no significant permselectivity was observed.

Table 1
Gas or vapor permeability ($\times 7.5005 \times 10^{-18}\ m^2\ s^{-1}\ Pa^{-1}$ (barrer)) through SPPEK or Nafion membrane

Gas or vapor	Permeability ($\times 7.5005 \times 10^{-18}\ m^2\ s^{-1}\ Pa^{-1}$ (barrer))	
	SPPEK	Nafion
Oxygen[a]	0.37	1.96
Hydrogen[a]	2.18	9.30
Methanol[b]	10.3	70
Water[b]	18.7	57

[a] 25 °C.
[b] 40 °C.

A side-by-side methanol permeation test has been applied to characterize the net flux of methanol through the PEM.



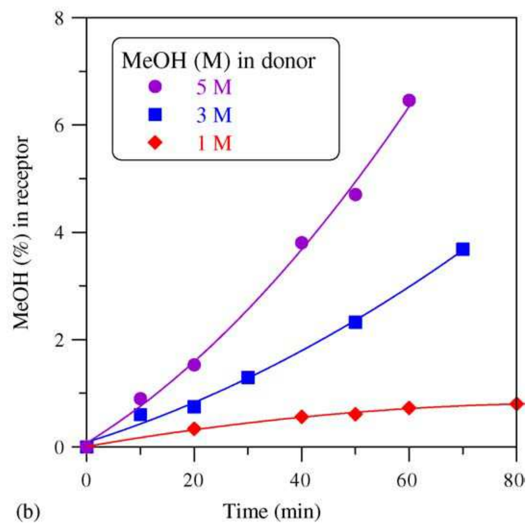


Fig. 3. Side-by-side permeation test, the donor contains MeOH aqueous solution and the receptor initially contains pure water only: (a) SPPEK and (b) Nafion. Membrane thickness: SPPEK, 30 μm; Nafion, 187 μm; temperature, 70 °C. The results shown here are normalized to membrane thickness of 100 μm for comparison purpose.

Fig. 3 shows the accumulated concentration of methanol in the receptor during tests with various methanol concentrations in the donor. The results were normalized to an equivalent thickness of 100 μm for both SPPEK and Nafion membranes. It is clear that methanol has a lower permeation rate through the SPPEK membrane than through the Nafion membrane. Based on these results and the results from gas and vapor permeability measurement and pervaporation test, SPPEK is a less permeable membrane material than Nafion so that crossover can be largely reduced.

Single cell DMFC tests with various methanol concentrations in feed were performed with SPPEK fabricated membrane electrode assembly (MEA). The cell potential versus current density gives the cell polarization curve at each feed concentration as shown in Fig. 4. There are clear regions of activation polarization, Ohmic polarization and concentration polarization on those curves. Concentration polarization is quite significant at lower methanol concentrations and becomes weaker as the methanol concentration increases. It indicates that fuel (methanol) supply is insufficient at the anode and thus a lower ultimate (limiting) current density is resulted at lower methanol concentration. The single cell performance was improved as the methanol concentration increased up to 3 M [15–17]. The ultimate current density increased with the concentration of methanol in feed, reached a maximum of 361 mA/cm^2 when the methanol in feed was 3 M, and then decreased again when methanol concentration increased. This suggests that the methanol concentration is high enough to create a high driving force for methanol permeation and results in significant fuel crossover, and the performance of DMFC cannot be further improved with increasing of methanol concentration in feed [15–19]. Therefore, there is an optimal methanol concentration in feed in a DMFC operation. The optimal concentration is around 3 M in the present case of SPPEK.

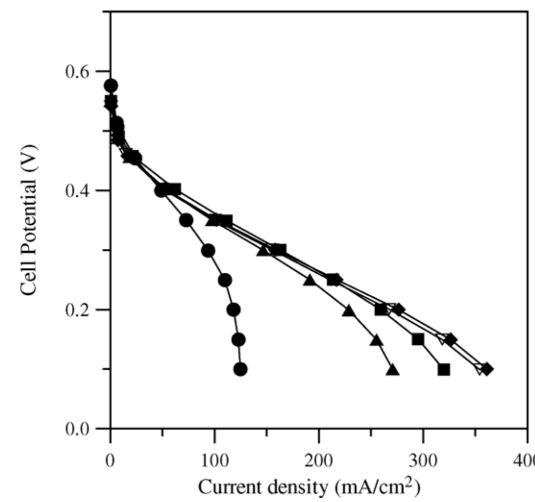


Fig. 4. The polarization curves of single cell DMFC tests for SPPEK MEA with various methanol concentrations in feed: (●) 1 M, (▲) 2 M, (■) 2.5 M, (♦) 3 M and (▽) 4 M 70 °C; $MeOH_{(aq)}$ feeding rate, 2 ml/min; rate of humidified O_2, 150 ml/min.

The open cell voltage (OCV) decreased with the concentration of methanol in feed as shown in Fig. 5. The results are similar to those reported previously for a Nafion PEM in DMFC operation [15,16]. It has been interpreted that the open cell potential of the DMFC at higher methanol concentrations is attributed to the higher methanol crossover than that at the lower methanol concentration.

The power density is also another criterion to evaluate the performance of a DMFC cell. Since the cell potential always decreases with current density, the power density will increase with current density first, reach a maximum and then decrease with current density. The power density curve is related to the methanol concentration in feed. The best performance also occurred at the optimal methanol concentration (3 M). The maximum power density was 55 mW/cm^2 when the current density was 276 mA/cm^2 (Fig. 6).

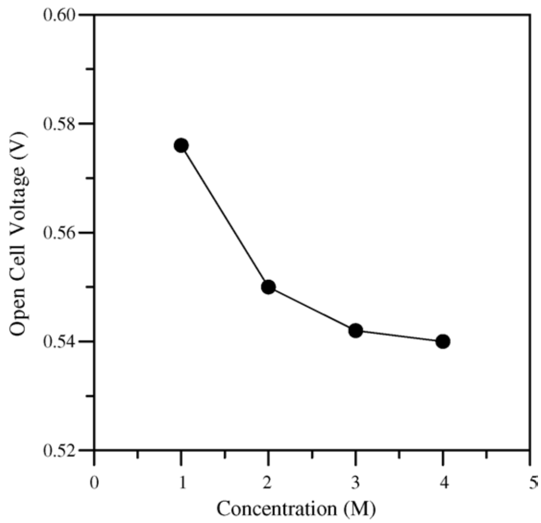


Fig. 5. The open cell potential as a function of the methanol concentration in feed in single cell DMFC tests for SPPEK MEA: 70 °C; $MeOH_{(aq)}$ feeding rate, 2 ml/min; rate of humidified O_2, 150 ml/min.

The performance of the single cell tests with MEA made of SPPEK was compared with that of Nafion-117 (Fig. 7). A MEA with Nafion-117 as the PEM was fabricated under the same conditions as the MEA with SPPEK. The performance of Nafion MEA was similar to that of SPPEK MEA except that the optimum methanol concentration occurred at 2 M. This result is consistent with the result reported in literature (e.g., [17–18]).

It is noted that the OCV of Nafion MEA has a much higher value (0.77 V) than that of SPPEK MEA. However, the cell voltage of Nafion MEA dropped sharply when the current density increased due to the activation polarization. Similar results were found in literature [19]. The measurement of

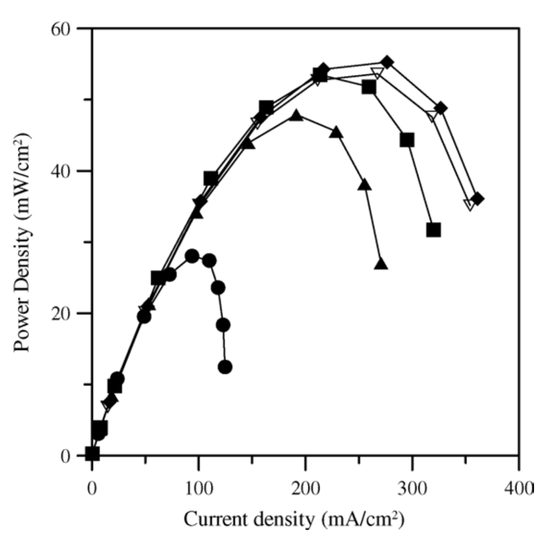


Fig. 6. The relationship of power density and current density in single cell DMFC tests for SPPEK MEA with various methanol concentrations in feed: (●) 1 M, (▲) 2 M, (■) 2.5 M, (♦) 3 M and (▽) 4 M; 70 °C; $MeOH_{(aq)}$ feeding rate, 2 ml/min; rate of humidified O_2, 150 ml/min.

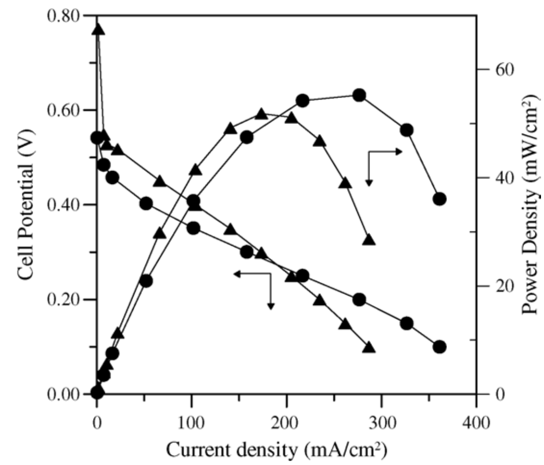


Fig. 7. A comparison of the optimal single cell performance with SPPEK and Nafion as the proton exchange membrane: (●) MeOH at 3 M for SPPEK (membrane thickness = 30 μm) cell and (▲) MeOH at 2 M for Nafion (membrane thickness = 187 μm) cell; 70 °C; $MeOH_{(aq)}$ feeding rate, 2 ml/min; rate of humidified O_2, 150 ml/min.

exact OCV could be very different in such a pre-stabilized region for a different system. Scattered OCV data may be resulted. The comparison of OCV data may not be meaningful for two different systems. Our comparison is based on the more stabilized region (Ohmic polarization region) of the *V–I* curves.

For the Nafion MEA, the ultimate current density was 287 mA/cm^2 and the maximum power density was 52 mW/cm^2 when the current density was 175 mA/cm^2 (Fig. 7). At a higher methanol concentration, the single cell with Nafion may encounter the problem of fuel crossover. The optimum methanol concentration for Nafion MEA is lower than that for SPPEK MEA probably due to the higher methanol permeability in Nafion than that in SPPEK. The single cell with SPPEK at 2 M methanol concentration had slightly inferior performance than the single cell with Nafion at 2 M. However, the best performance of SPPEK cell (methanol concentration at 3 M) is superior to that of Nafion cell (methanol concentration at 2 M) (Fig. 7). The results indicated that DMFC with SPPEK could be operated at higher feed methanol concentration than DMFC with Nafion. The higher the methanol concentration is, the higher the energy density is in the feed solution. The utilization of the energy from fuel to create electricity is more efficient with fuel of higher energy density. SPPEK may be a preferred material than Nafion in fabrication of MEA for the application in DMFC. However, it is likely that the DS of SPPEK needs to be optimized.

4. Conclusion

Sulfonated poly(phthalazinone ether ketone) (SPPEK) is a non-fluorinated polyelectrolyte material. Its non-fluorinated nature, good thermal stability, reasonable proton conductivity and potentially low cost make it attractive to be used as the proton exchange membranes (PEMs) in the fabrication of membrane electrode assemblies for DMFC. The single cell test results indicated that SPPEK performed better than Nafion in terms of higher power density, higher ultimate current density and higher optimal operating concentration of methanol in feed. The lower permeability of SPPEK compared with Nafion limited the crossover of methanol; therefore, the optimal feed methanol concentration in SPPEK cell was higher than that in Nafion cell. However, a long-term stability of SPPEK in DMFC operation should be evaluated since the methanol and water uptake tests indicated that the particular DS 1.09 of SPPEK membrane used in this study might swell excessively at higher temperatures. An optimization of DS is necessary to balance adequate proton conductivity with water and methanol uptake.

Acknowledgements

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