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Preparation and DMFC performance of a sulfophenylated poly(arylene ether ketone) polymer electrolyte membrane

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ABSTRACT

A sulfonated poly(aryl ether ether ketone ketone) (PEEKK) having a well-defined rigid homopolymer-like chemical structure was synthesized from a readily prepared PEEKK by post-sulfonation with concentrated sulfuric acid at room temperature within several hours. The polymer electrolyte membrane (PEM) cast from the resulting polymer exhibited an excellent combination of thermal resistance, oxidative and dimensional stability, low methanol fuel permeability and high proton conductivity. Furthermore, membrane electrode assemblies (MEAs) were successfully fabricated and good direct methanol fuel cell (DMFC) performance was observed. At 2 M MeOH feed, the current density at 0.5 V reached 165 mA/cm, which outperformed our reported similarly structured analogues and MEAs derived from comparative Nafion® membranes.

1. Introduction

Direct methanol fuel cells (DMFCs) are currently under intense study for their potential as efficient and clean electrochemical power devices for portable applications such as notebook computers and mobile phones [1,2]. Known for their outstanding chemical, mechanical and oxidative stability and high proton conductivity, perfluorinated sulfonic acid polymers (such as Nafion®) exhibit excellent electrochemical performance as polymer electrolyte membranes (PEMs). To date, only a few PEMs have been reported to possess improved single cell performance over commercial Nafion®-type PEMs [3–7]. As an example, the PEMs based on stretched recast Nafion® were claimed to have better performance than commercial Nafion® in DMFCs [6,7]. Continuing efforts are being made to develop new kinds of hydrocarbon-based membranes as alternatives to Nafion® because of cost, high fuel crossover, complicated synthetic procedure and environmental uncertainty of Nafion® membranes [8,9].

Poly(aryl ether ketone)s (PAEKs) are a class of high-performance polymers known for their excellent combination of chemical and physical properties [10]. Many PEM studies have been based on PAEKs onto which have been introduced sulfonic acid groups to impart proton conductivity. Typically, two approaches have been used to accomplish this. The direct polymerization approach, which is based on the polymerization of sulfonated monomers, has the advantage of well-defined structural repeat units, though the actual copolymer, containing both sulfonated and non-sulfonated repeat units to control the ion exchange capacity (IEC), may be random. However, the monomer synthesis and purification may be a tedious multi-step synthesis, and the reactivity and solubility of the sulfonated monomer may lead to low molecular weight polymers. Post-sulfonation of existing polymers presents an attractive and relatively simple reaction procedure. However, it is sometimes difficult to achieve precise control of the site of sulfonation, especially for more complex chain structures having several potential sulfonation sites. Furthermore, it may be difficult to achieve the target degree of sulfonation. Both these factors may result in a random or less-defined distribution of sulfonic acid groups along the polymer chains [8,11]. In addition, an extended sulfonation reaction period, strong sulfonated reagent and high temperature are often necessary conditions required to prepare the sulfonated polymers using this procedure. For example, it requires many days to prepare SPEEK with high degree of

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sulfonation. Therefore, it is of practical interest to prepare PEM materials by a rapid and mild post-sulfonation method whereby improved control of the site of sulfonation and degree of sulfonation (DS) could be achieved by introducing pendant phenyl groups that are highly susceptible to rapid and site-specific sulfonation.

Several site-controlled post-sulfonated polymers have been reported, wherein it was suggested that polymers bearing sulfonic acids groups on side chains are more stable to thermal degradation, hydrolysis and oxidation [12,13]. Almost all reported sulfonated polymers are derived from a copolymer-type framework comprising sulfonated and non-sulfonated repeat units, which results in the random distribution of hydrophilic blocks and correspondingly undesirable water swelling in comparison with well-defined homopolymers [8,11].

It is obvious that single cell performance is very helpful to study the relationship between PEM structure and electrochemical performance, which offers feedback for the further design and preparation of new PEM materials. Unfortunately, most of the current hydrocarbon-based PEM research has been limited to the polymer synthesis and membrane characterization, and much fewer MEA and cell performance studies of hydrocarbon-based polymers have been conducted [14–17]. In this work, we report the DMFC performance of a new homopolymer-like sulfonated phenylated PAEK that was made by a rapid and site-specific post-sulfonation of a readily prepared PAEK having a rigid molecular chain structure. Furthermore, a careful and systematic comparison of this membrane with its analogues [18] and Nafion® series (Scheme 1 and Table 1) is also made.

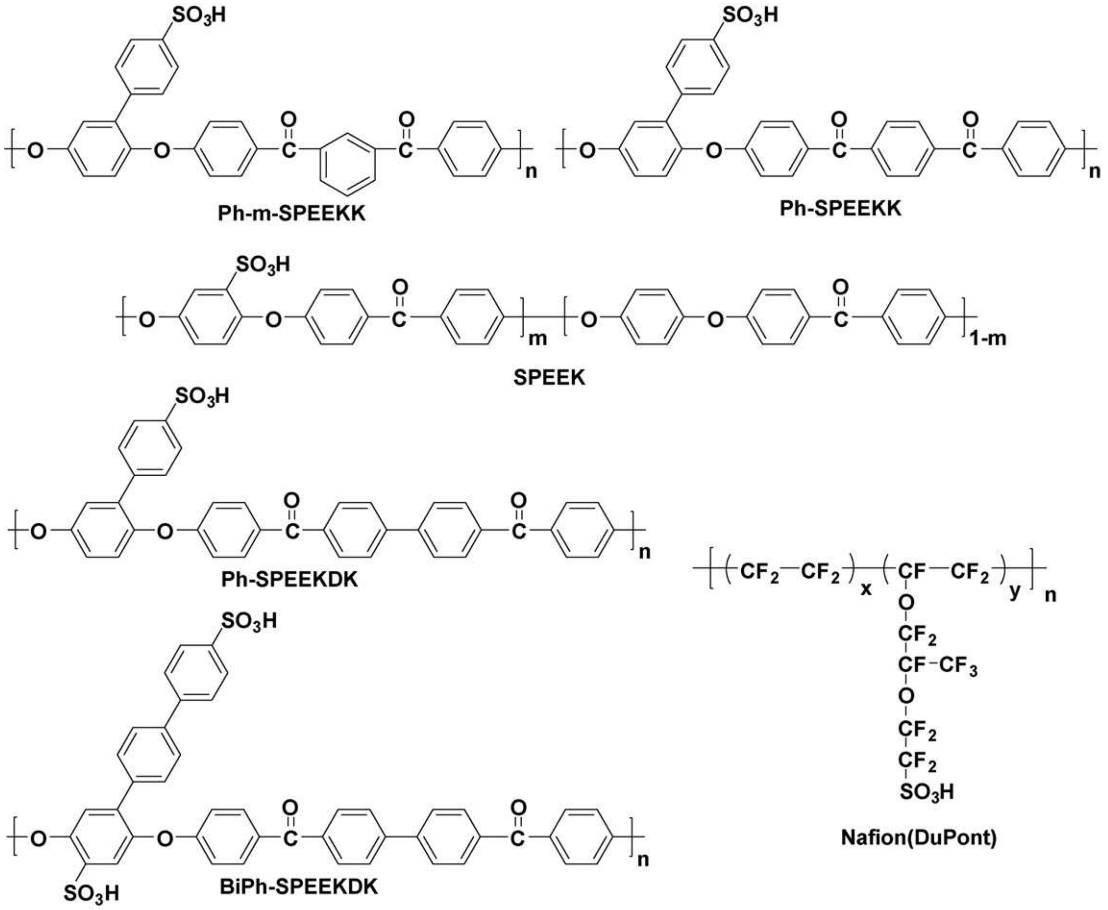
2. Experimental

2.1. Materials

1,3-Bis(4-fluorobenzoyl)benzene and phenylhydroquinone were obtained from Sigma–Aldrich Ltd., and recrystallized from chlorobenzene and toluene, respectively. Potassium carbonate (Sigma–Aldrich Ltd.) was ground into fine powder and kept at 120 °C before use. Concentrated sulfuric acid was commercial grade (95–98%). All other chemicals were obtained from commercial sources, and used without further purification.

2.2. Synthesis of starting polymer

Into a 1 L three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap with a condenser, were added phenylhydroquinone (52.44 g, 0.2 mol), 1,3-bis(4-fluorobenzoyl)benzene (64.68 g, 0.2 mol), anhydrous K_2CO_3 (35.88 g, 0.26 mol), dimethyl acetamide (DMAc) (440 mL) and toluene (100 mL). The mixture was allowed to reflux for 3 h, during which time water was removed, and then heated to 170 °C to remove the toluene. After 8 h, another 100 mL of DMAc was added to dilute the viscous reaction mixture. The polymerization was complete after another 2 h. The viscous solution was slowly poured into 2 L of deionized water. After cooling, the resulting polymer fiber was ground into fine powder by a high-speed blender, and refluxed in deionized water and ethanol several times to remove the salts and solvents, and dried at 120 °C in a vacuum oven for 24 h. Thus, a PAEK having a pendant phenyl on a



Scheme 1. Chemical structures of the PEMs in this study.

poly(arylene ether ether ketone ketone) backbone (Ph-m-PEEKK) was obtained.

2.3. Preparation of sulfonated polymer

To a 1 L flask, 15 g of the dry polymer powder and 500 mL of concentrated sulfuric acid were added. After mechanically stirring at room temperature for 6 h, the clear and homogeneous viscous solution was poured into a mixture of water and ice to precipitate the sulfonated polymer. The obtained fiber was washed with hot water until the wash water had neutral pH. The product (Ph-m-SPEEKK) was dried in a vacuum oven at 100 °C for 24 h.

2.4. Membrane casting

Dry sulfonated polymer (2.0 g) was dissolved in 40 mL of DMAc (5 wt% solution) and filtered using filter paper. The filtrate was then poured onto a carefully leveled glass plate and placed in a self-made casting plate assembly and dried at 50 °C under a constant slow purge of nitrogen for 4–5 days. The resulting flexible membrane was conditioned by immersing it in 1 M H_2SO_4 for 24 h, washed thoroughly and then dried in a vacuum oven at 120 °C for 24 h.

2.5. Characterization

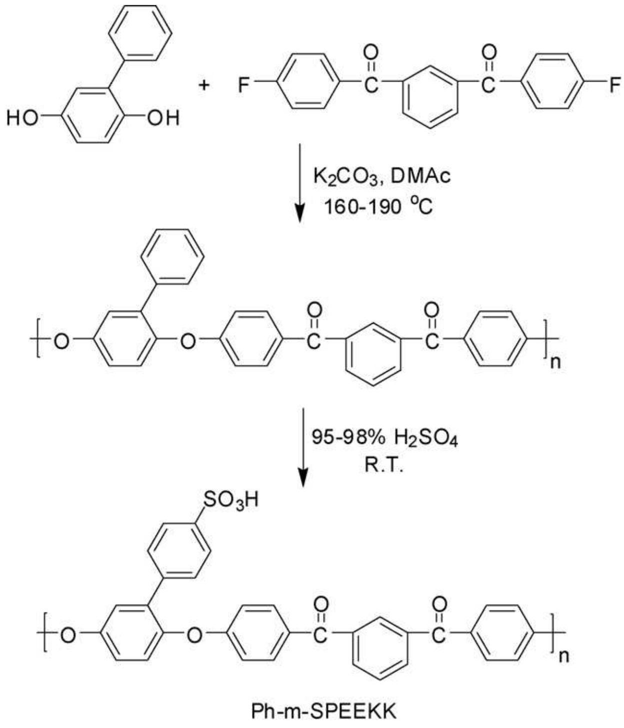
^{1}H and ^{13}C NMR spectra of the sulfonated polymers were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^{1}H and 100.575 MHz for ^{13}C. An indirect detection probe was used for the acquisition of 1D and 2D spectra. Deuterated dimethylsulfoxide (DMSO-d_6) was selected as the solvent and the DMSO signals at 2.50 ppm (^{1}H NMR) and 39.51 ppm (^{13}C NMR) were used as the chemical shift references.

A TA Instruments thermogravimetric analyzer (TGA) instrument (model 2950) was used for evaluating thermal stability of the polymers. Polymer samples for TGA analysis were preheated at 150 °C for 40 min under nitrogen atmosphere to remove moisture. Samples were then heated at 10 °C/min from 50 to 800 °C under air atmosphere.

2.6. MEA fabrication and test

DMFC MEA fabrication and fuel cell operating conditions were conducted according to a reported procedure [3,5]. The anode ink composition was 86 wt% 1:1 platinum–ruthenium (Johnson Matthey) and 14 wt% Nafion®, and the cathode ink composition was 90 wt% platinum black (Johnson Matthey) and 10 wt% Nafion®. Catalyst inks were mixed by sonication for about 90 s and then transferred to a pre-dried membrane in acid form by direct painting at 75 °C. The painted MEA was dried at 75 °C for 20 min on a vacuum plate. The anode and cathode catalyst loading was approximately 8 and 6 mg cm^{-2}, respectively. Single- and double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas diffusion layers, respectively. The geometric active cell area was 5 cm^2.

Cell resistance and polarization curves for single cells were performed using a fuel cell test station (Fuel Cell Technology, Inc.). The cell was held at 80 °C; methanol was fed to the anode with a flow rate of 1.8 mL/min; 90 °C humidified air was fed at 500 sccm without back pressure (high humidification and stoichiometry were used to minimize cathode effects). High-frequency resistance (HFR) was measured by applying a sinusoidal wave perturbation at 2 kHz and 30 mV. Proton conductivity and methanol permeability were measured from HFR and methanol crossover limiting current, respectively.



Scheme 2. Synthetic route to obtain side-group-acid Ph-m-SPEEKK.

3. Results and discussion

3.1. Synthesis and characterization of Ph-m-SPEEKK

In this study, the Ph-m-PEEKK starting material could be readily synthesized in the laboratory at the hundreds of grams scale via a typical nucleophilic polycondensation of commercially available monomers, phenylhydroquinone and 1,3-bis(4-fluorobenzoyl)benzene (Scheme 2). Generally, hydrocarbon-based PEMs have adequately high proton conductivity suitable for fuel cell operation when the IEC values are in the range of 1.5–2.0 mequiv./g. It is of practical interest to introduce sulfonic acid groups onto the specific sites of starting polymers under mild and rapid reaction conditions and a simple procedure, which may facilitate the large-scaled production of the sulfonated polymer. Although the electrophilic sulfonation reaction may sometimes yield complicated products depending on the structure of the polymer, structural design of the starting polymer through arrangement of the types and positions of substituents on aromatic rings allows the control of sites that are attacked by the $^+SO_3H$ cations. In the present study, a phenylated PAEK was sulfonated to yield specifically a (4-sulfonic acid)phenyl substituted poly(arylene ether ether ketone ketone), Ph-m-SPEEKK, under mild sulfonation conditions at room temperature within several hours. Importantly, no degradation was observed during this time, judging by the high inherent viscosity (2.90 dL/g in DMAC solution at a concentration of 0.5 g/dL at 30 °C) of sulfonated polymer. Ph-m-SPEEKK was readily soluble in DMAc, dimethyl formamide (DMF) and DMSO, and tough, flexible and transparent membranes could be prepared by solution casting.

^{1}H and ^{13}C NMR were performed to site specificity and extent of the sulfonation reaction, and the results showed that a new sulfophenylated PEEKK with well-defined homopolymer-like chemical structure was successfully prepared. 2D NMR COSY, HSQC and HMBC were obtained to fully characterize both ^{1}H and ^{13}C NMR spectra shown in Fig. 1.

Table 1
Electrochemical properties of Ph-m-SPEEKK, its analogues and Nafion® 1135 at 80 °C (0.5 M MeOH solution).

Property	Ph-m-SPEEKK	Ph-SPEEKK	Ph-SPEEKDK	BiPh-SPEEKDK	Nafion® 112
Membrane thickness (μm)	62	60	60	53	50
IEC (mequiv./g)[a]	1.82	1.76	1.60	2.32	0.90
σ (mS/cm)[b]	66	85	28	60	77
MP ($\times 10^{-7}$ cm^2/s)[c]	14.3	21	6.0	16.5	49
HFR (mΩ cm^2)[d]	94	71	215	88	75
ξ (mA/cm^2)[e]	68	110	23	90	247
Selectivity (HFR^{-1} ξ^{-1})[f]	156	125	200	126	54

[a] Experimental data by titration.
[b] Proton conductivity calculated from single cell at 80 °C.
[c] Methanol permeability calculated from single cell at 80 °C.
[d] High-frequency resistance (HFR).
[e] ξ is the methanol crossover limiting current.
[f] Selectivity = 1/(HFR × ξ).

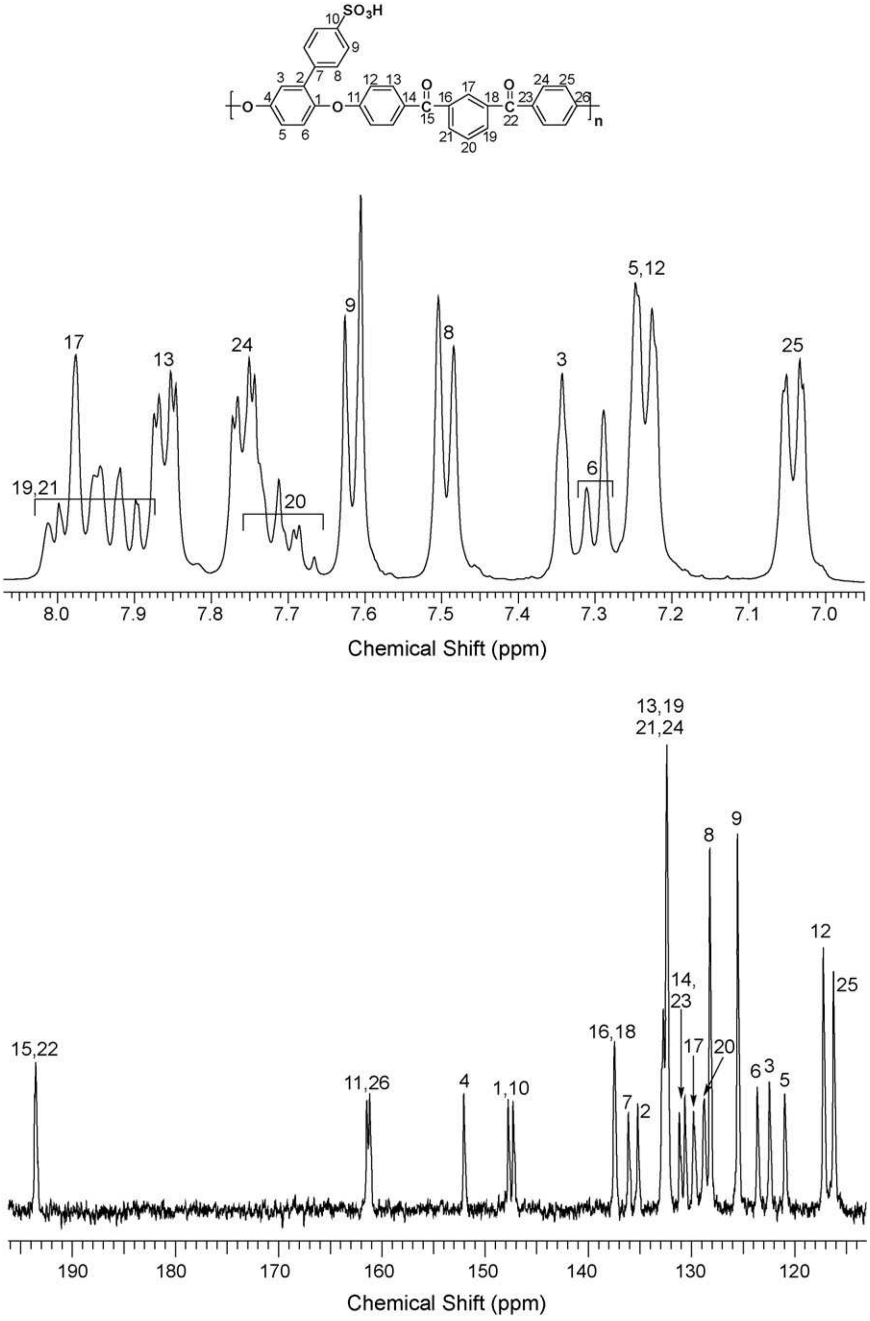


Fig. 1. ^{1}H and ^{13}C NMR spectra of Ph-m-SPEEKK.

3.2. Thermal-oxidative stability and water uptake of Ph-m-SPEEKK

A TGA test of dry membrane showed that no weight loss occurred until 220 °C in air. Good oxidative stability is one of the key parameters for PEMs to operate in fuel cell systems. The oxidative attack by $HO^\bullet$ and $HOO^\bullet$ radicals mainly occurs in the hydrophilic domains to cause the degradation of polymer chains, which leads to the loss of performance [19]. Sulfophenylated polymers are expected to have improved oxidative resistance over main-chain-substituted sulfonic acid polymers [12,13,20], since the hydrophilic site is removed from the vicinity of the main chain. The oxidative stability of Ph-m-SPEEKK was evaluated in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. Ph-m-SPEEKK membrane maintained its shape after 220 min treatment, which suggests comparatively good oxidative stability. It should be pointed out that, after treating a membrane for 30 min in Fenton's reagent, polymer degradation might partly occur, as indicated by above 50% decrease (a part of the decrease may result from the possible reaction of $-SO_3H$ with the Fenton's reagent) in its proton conductivity (45 mS/cm at 80 °C after Fenton's reagent exposure).

To achieve high proton conductivity, the membrane needs to have a relatively high IEC value. For proton conductivity comparable with Nafion® membranes, no less than 1.5 mequiv./g is generally needed for sulfonated PAEK-type PEMs. However, for many hydrocarbon-based PEMs, the high IEC values of membranes are often associated with poor dimensional stability in hot water [11]. For example, although SPEEK membranes with IEC ∼1.7 mequiv./g were reported to exhibit comparable DMFC performance to Nafion®, the operating temperature had to be limited to <65 °C, because excess dimensional swelling occurred at elevated temperature. Even for SPEEK with a lower IEC value of 1.62, there was unacceptably high water uptake (∼140%) [21]. The preparation of the PEMs possessing both high IEC values (high proton conductivity) and low dimensional change due to water swelling is especially of interest. The dimensional swelling ratio may be affected by regularity of chemical structure, interaction of molecular chains and rigidity of backbones [22]. Although the IEC value estimated by titration was 1.82 mequiv./g, this homopolymer-like sulfonated polymer having well-defined chemical structure and rigid backbone exhibited relatively low water uptake (water uptake $= (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$) and swelling ratio (swelling ratio $= (L_{\text{wet}} - L_{\text{dry}})/L_{\text{dry}} \times 100\%$). At 20 °C, water uptake and swelling ratio were 15% and 5%, respectively. At 80 °C, water uptake and selling ratio were less than 60% and 25%, respectively. These values are well in the range suitable for MEA fabrication [5].

3.3. Proton conductivity and methanol permeability of Ph-m-SPEEKK

Proton conductivities and methanol permeability were measured in single cell. High proton conductivity and low methanol permeability of PEMs are a good combination to enhance the DMFC performance of single cell. Fig. 2 shows a plot of HFR versus methanol crossover limiting current of MEAs (measured at 80 °C and 0.5 M methanol feed concentration) in order for comprehensive property comparisons of the selected membranes that used in DMFC testing. Obviously for DMFC, ideal membranes that have low HFR (ohmic losses) and low methanol crossover (cathode overpotential losses) would be located in the lower left corner of the plot of HFR versus methanol crossover limiting current. As shown in Fig. 2, Ph-m-SPEEKK exhibited much lower methanol crossover limiting current in comparison with Nafion® 112, BiPh-SPEEKDK and Ph-SPEEKK, although they had comparable HFR values. In addition, despite its lower methanol permeability, Ph-SPEEKDK had much higher HFR. Fig. 3 converted the HFR and methanol crossover limiting current data to conductivity and methanol permeability, respectively, to evaluating the thickness-independent membrane properties. [5,23]. The methanol permeability of Ph-m-SPEEK was $1.43 \times 10^{-6}\ \text{cm}^2/\text{s}$, which was about three times lower than the $4.9 \times 10^{-6}\ \text{cm}^2/\text{s}$ value of Nafion® 112. The DMFC mode conductivity of Ph-m-SPEEKK membrane was 66 mS/cm at 80 °C, which was slightly lower than that of Nafion® (77 mS/cm). It was also noticed that the stand-alone conductivity of Ph-m-SPEEKK membrane was about 120 mS/cm at 80 °C under 100% relative humidity, which was comparable with that of Nafion®.

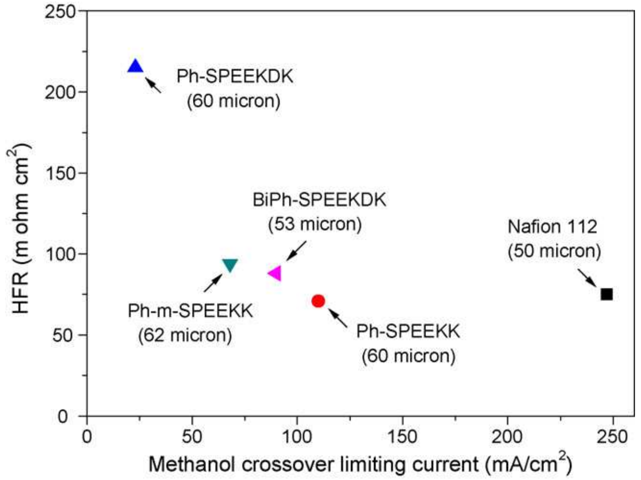


Fig. 2. HFR vs. methanol crossover limiting current of the membranes measured in DMFC mode at 80 °C.

3.4. Performance of single cell

Fig. 4 shows the cell performance of the MEAs using Ph-m-SPEEKK, Ph-SPEEKK [18], Ph-SPEEKDK [18], BiPh-SPEEKDK and Nafion® series at methanol feed concentrations of 0.5, 1 and 2 M. At 0.5 and 1 M methanol feed concentration, MEAs using highly conductive Ph-SPEEKK and Nafion® 112 showed the best DMFC performance among others. At this low methanol feed concentration, it is obvious that the cell resistance is the predominant factor on the polarization behaviors since methanol oxidation reaction

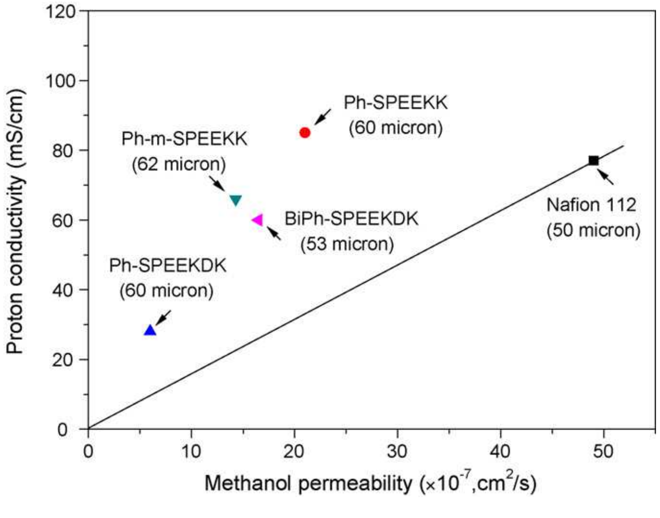


Fig. 3. Proton conductivity vs. methanol permeability of the membranes measured in DMFC mode at 80 °C.

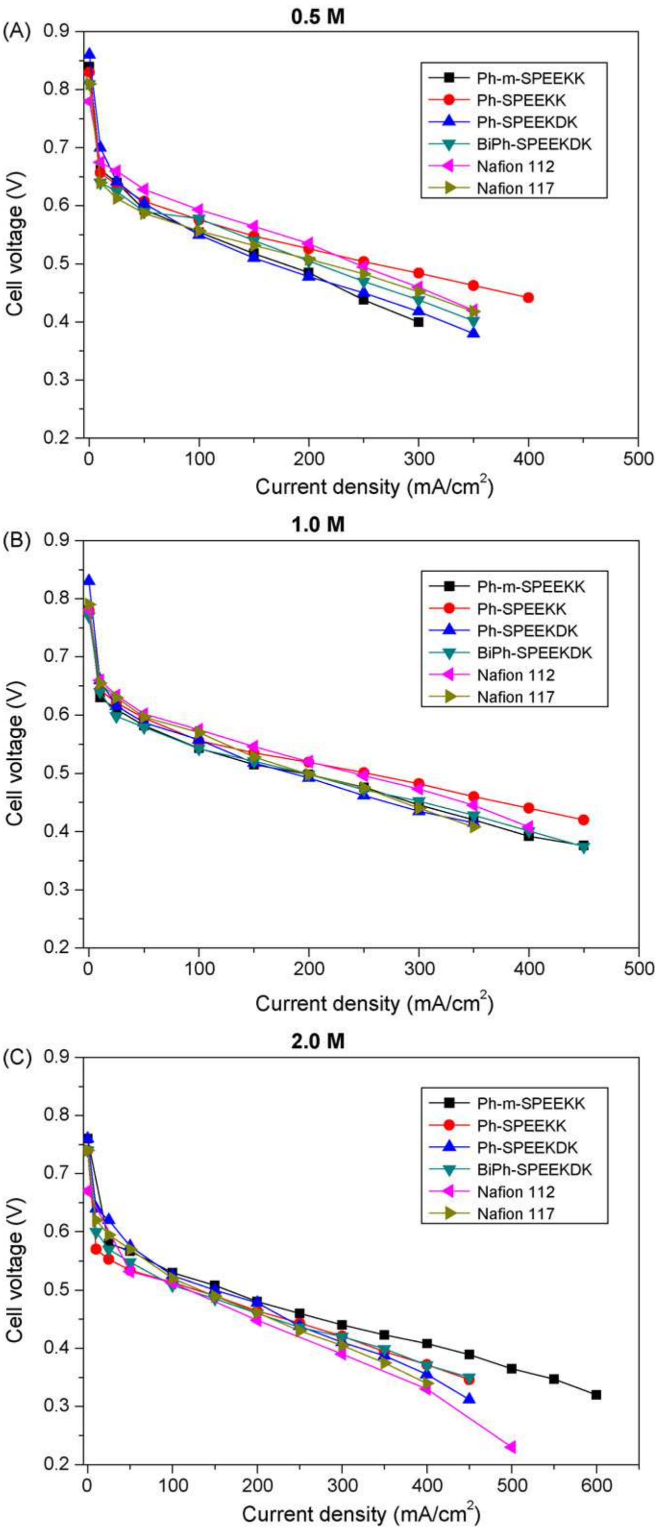


Fig. 4. DMFC performance of the membranes at 0.5 M (A), 1.0 M (B) and 2.0 M (C) methanol feed concentration (cell temperature: 80 °C).

consumes most methanol at the feed. On the other hand, MEA using Ph-m-SPEEKK showed the best performance at 2 M MeOH feed. The current density at 0.5 V reached 165 mA/cm, which outperformed Ph-SPEEKK, Ph-SPEEKDK, BiPh-SPEEKDK and all the comparative Nafion® membranes. This is attributed that methanol crossover effect becomes predominant on the polarization characteristics. This is also consistent with the fact that MEA using thick Nafion® (Nafion® 117) showed better performance than MEA using thin Nafion® 112 at this methanol feed concentration. Obtained high performance at high current density (ca. >500 mA/cm^2) of the MEA using Ph-m-SPEEKK suggests that this cell did not reach mass transfer limit and generate high power density. Another high selective and low methanol permeable membrane, Ph-SPEEKDK, showed relatively poor performance at 2 M methanol feed, probably because significantly low membrane conductivity induced great ohmic loss. These results clearly show the importance of balance of proton conductivity and methanol permeability. Considering the excellent combination of its high DMFC performance and its advantage in synthesis, Ph-m-SPEEKK may be a promising candidate for DMFC applications.

4. Conclusions

A novel sulfophenylated poly(aryl ether ether ketone ketone) with a well-defined homopolymer-like structure was prepared via rapid post-sulfonation of a phenylated starting polymer under mild sulfonation conditions. This PEM material possessed excellent thermal-oxidative and dimensional stability. The plot of HFR versus methanol crossover limiting current indicated this membrane would be promising for DMFC application, and this was well supported by the high DMFC performance of the MEA based on Ph-m-SPEEKK membrane.

Acknowledgments

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