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A sulfonated poly(aryl ether ether ketone ketone) ionomer: synthesis and DMFC performance

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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 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 analogues and eveluated Nafion membranes.

Keywords: Poly(aryl ether ketone)s; polymer electrolyte membrane; Fuel cells; Membrane electrode assemblies; Direct methanol fuel cells

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 Nafion-type PEM [3-5]. Continuous 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 [6,7].

Poly(aryl ether ketone)s (PAEKs) are a class of high-performance polymers known for their excellent combination of chemical and physical properties [8]. 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 for more complex chain structures having several potential sulfonation sites. Especially, 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 [6,9]. In addition, long sulfonation reaction period, strong sulfonated reagent and high temperature are often necessary conditions to prepare the sulfonated polymers using this procedure. For example, it must take many days to prepare SPEEK with high sulfonation level. 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 [10]. 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 [6,11].

It is obvious that single cell performance is very helpful to study the relationship between PEM structure and electrochemical performance, which will offer 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 [12-15]. 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 [16] and Nafion series (Scheme 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 and an 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). The filtrate was obtained through a filter-paper, and then poured onto a horizontal glass plate in a self-made casting assembly and dried at 50 °C under a constant slow purge of nitrogen for 4~5 days. The flexible membrane after immersing in 1 M H_2SO_4 for 24 h was dried in a vacuum oven at 120 °C for 24 h.

2.5. Characterization

^1H 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 ^1H 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 (^1H 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 °C 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 [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 10 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.

3. Results and discussion

3.1. Synthesis and characterization of Ph-m-SPEEKK

In this study, the starting material, Ph-m-PEEKK, could be readily synthesized in the laboratory at the hundreds of grams level 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 FC 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(aryl ether ether ketone ketone), Ph-m-SPEEKK, under a 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.

^{1}H and ^{13}C NMR were performed to site specificity and extent of the sulfonation reaction, and the results showed that a new side-chain-acid 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 Figure 1.

3.2. Basic properties of Ph-m-SPEEKK and its membrane

Since Ph-m-SPEEKK was readily soluble in DMAc, dimethyl formamide (DMF) and DMSO, the polymer could be processed by solution casting to yield strong, flexible and transparent membrane. 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● and HOO● radicals mainly occurs in the hydrophilic domains to cause the degradation of polymer chains, which leads to the loss of performance [17]. Side-chain-acid polymers are expected to have improved oxidative resistance over main-chain-substituted sulfonic acid polymers, 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 ^oC. Ph-m-SPEEKK membrane maintained its shape and flexibility after 220 min treatment, which suggests comparatively good oxidative stability.

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 [9]. For example, although SPEEK membranes with IEC ~ 1.7 mequiv./g exhibited comparable DMFC performance to Nafion, the operating temperature had to be limited to <65 ^oC, 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%) [18]. 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 [19]. 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 and swelling ratio. 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].

Proton conductivities and methanol permeability were measured in single cell. High proton conductivity and low methanol permeability of PEMs is a good combination to enhance the DMFC performance of single cell. The methanol permeability of Ph-m-SPEEK was 1.43×10^{-6} cm^2/s, which was significantly three times lower than the 4.9×10^{-6} cm^2/s value of Nafion 112. The proton conductivity of Ph-m-SPEEKK membrane was 66 mS/cm at 80 °C.

3.3. Performance of single cell

Figure 2 shows a plot of HFR versus methanol crossover limiting current of MEAs using the selected membranes, and their chemical structures are shown in Scheme 1. This considers the combine effects of methanol crossover and ohmic loss, and was used to evaluate the DMFC performance potential. This MEA comparison may be considered as similar to selectivity that is the ratio of proton conductivity to methanol permeability (Figure 3), which is useful in evaluating the quality of PEMs in DMFC [5,20]. Obviously for DMFC, ideal membranes that have low HFR (ohmic losses) and low methanol crossover (low crossover losses) would be located in the lower left corner of the plot of HFR versus methanol crossover limiting current. As shown in Figure 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.

Figure 4 shows the cell performance of the MEAs using Ph-m-SPEEKK, Ph-SPEEKK [16], Ph-SPEEKDK [16], BiPh-SPEEKDK and Nafion series at methanol feed concentrations of 0.5, 1 and 2 M. At 0.5 M methanol feed concentration, MEAs using Ph-SPEEKK and Nafion 112 showed 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 consumes most methanol at the feed. On the other hand, MEA using Ph-m-SPEEKK showed the best performance (The current density at 0.5 V reached 165 mA/cm, which outperformed Ph-SPEEKK, Ph-SPEEKDK, BiPh-SPEEKDK and all Nafion membranes.) at 2 M MeOH feed as methanol crossover effect becomes prominent even at high current density. This is also consistent with the fact that MEA using thick Nafion (Nafion 117) showed better performance than MEA using thin Nafion 112. Particularly good performance of MEA using Ph-m-SPEEKK at high current density suggests that this cell did not reach mass transfer limit and generate high power density. Another high selective 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 benefits of using Ph-m-SPEEKK which has good balance of proton conductivity and methanol permeability. Further increase of proton conductivity maintaining good methanol barrier property will make Ph-m-SPEEKK for ideal DMFC membranes in a wider range of methanol feed concentration. Considering the excellent combination of its high DMFC performance and its advantage in synthesis, Ph-m-SPEEKK may be a promising candidate for fuel cell applications.

4. Conclusions

A novel side-chain-acid 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 a 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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Figure Captions

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

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

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

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

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).

Table 1

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

Property	Ph-m-SPEEKK	Ph-SPEEKK	Ph-SPEEKDK	BiPh-SPEEKDK	Nafion 112
Membrane thickness (μm)	62	60	60	53	50
IEC (meq./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 ($m\Omega\ cm^2$) [d]	94	71	215	88	75
ξ (mA/cm^2) [e]	68	110	23	90	247
Selectivity ($HFR^{-1}\ \xi^{-1}$) [f]	156	125	200	126	54

[a] experimental data by titration;

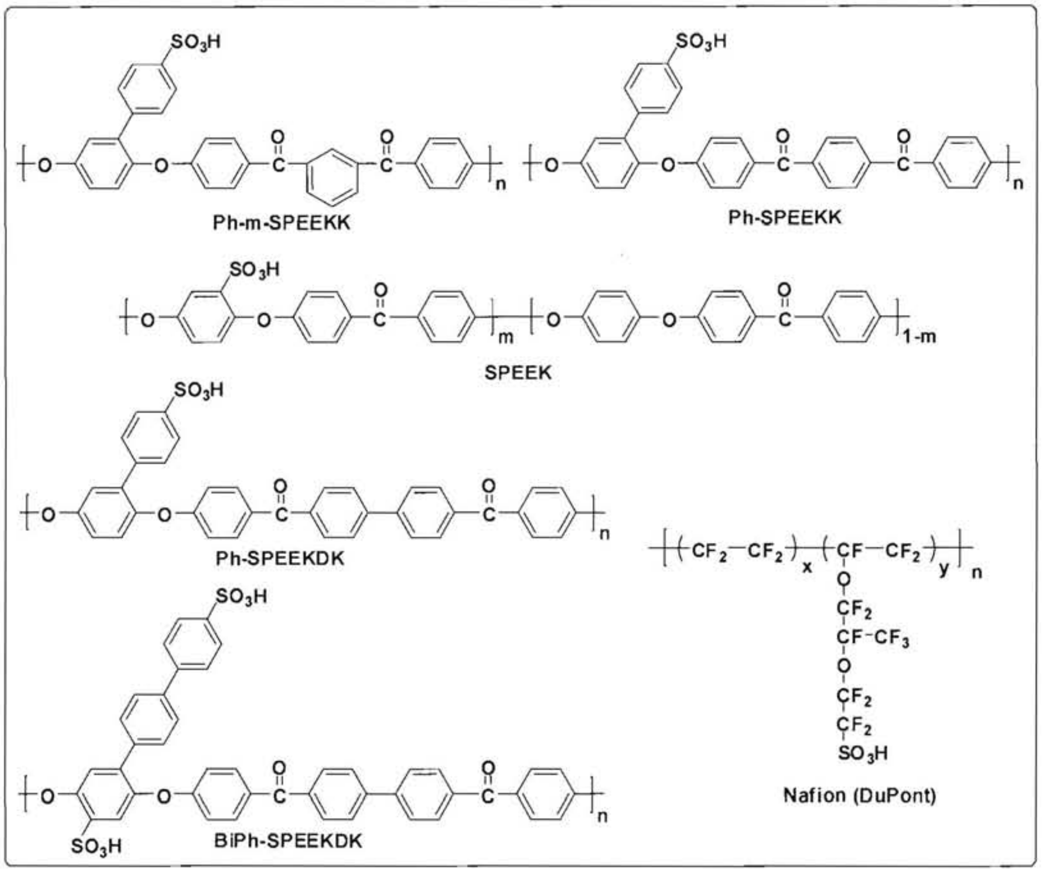
[b] proton conductivity calculated from single cell at 80 °C;

[c] methanol permeability calculated from single cell at 80 °C;

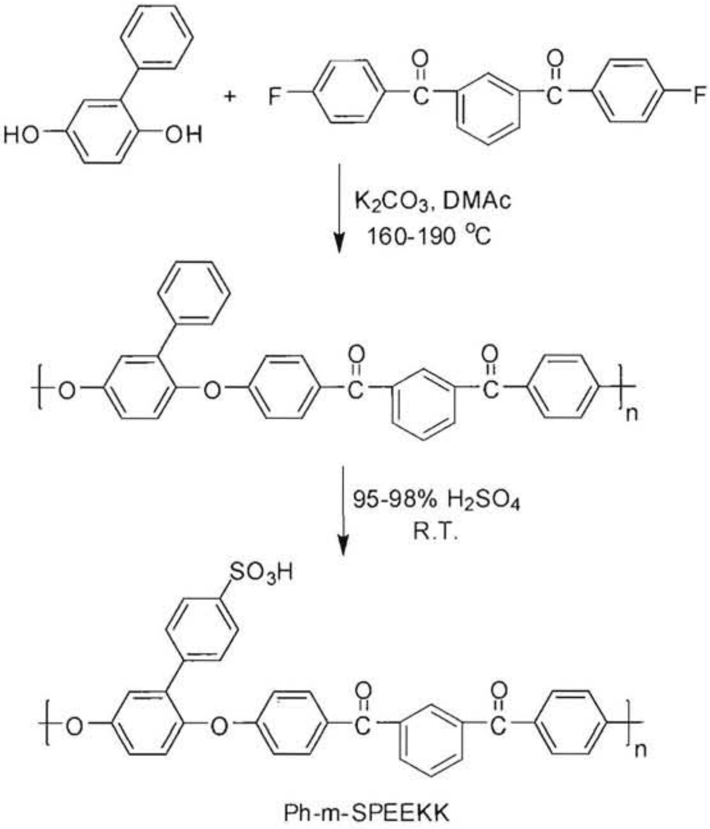
[d] high frequency resistance (HFR);

[e] ξ is methanol crossover limiting current;

[f] selectivity=1/(HFR × ξ).



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



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

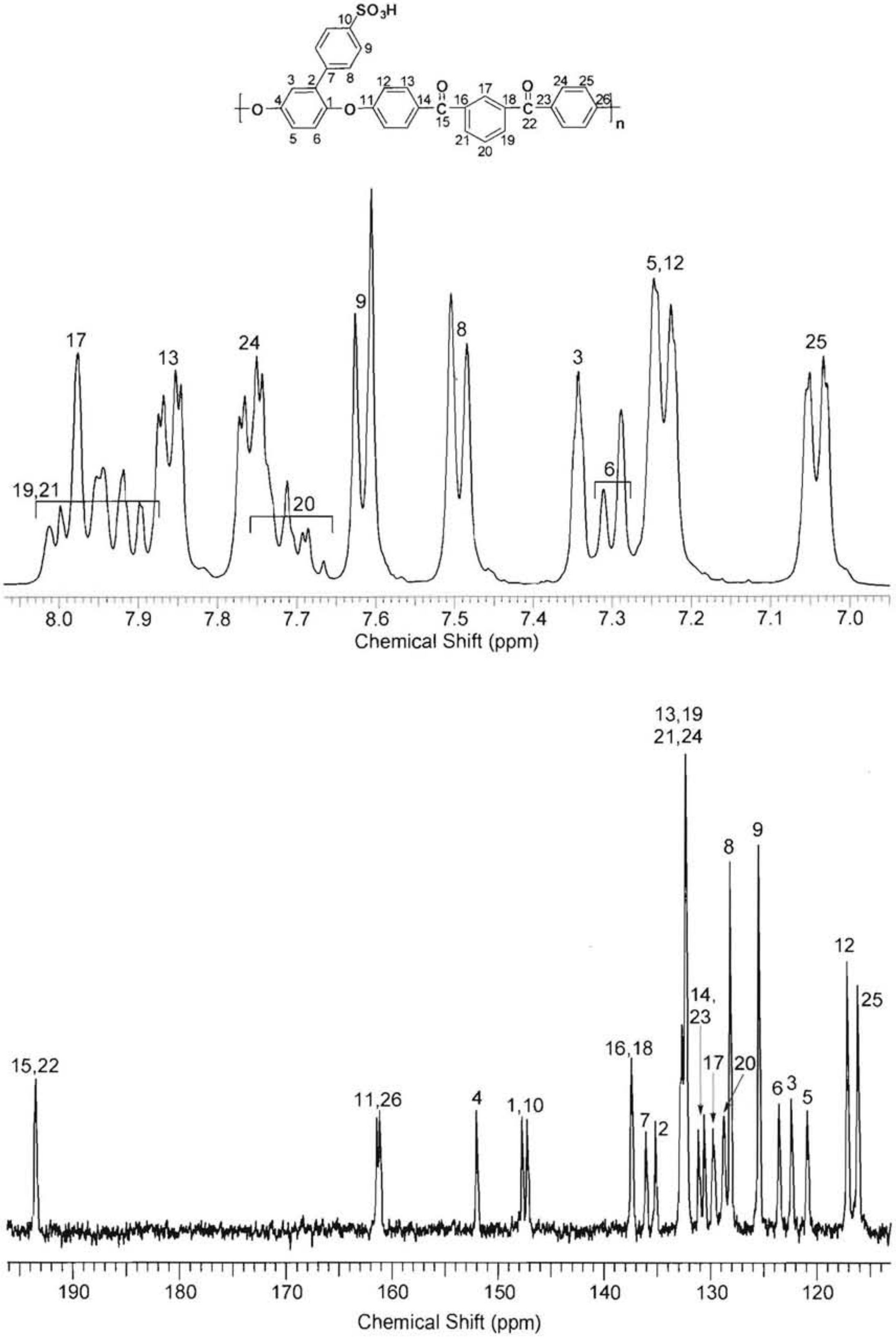


Fig. 1. ^{1}H and ^{13}C NMR spectra of Ph-m-SPEEKK.

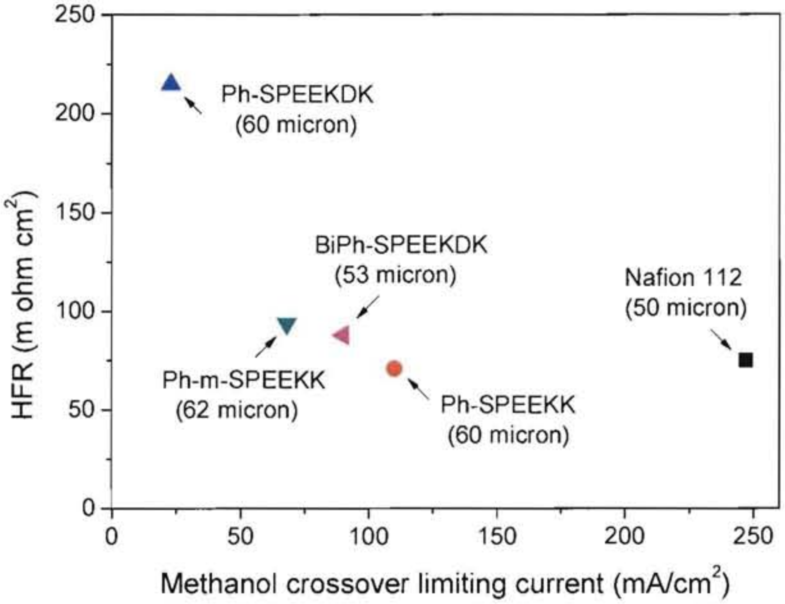


Fig. 2. HFR vs. methanol crossover limiting current of the membranes measured in DMFC mode at 80 °C.

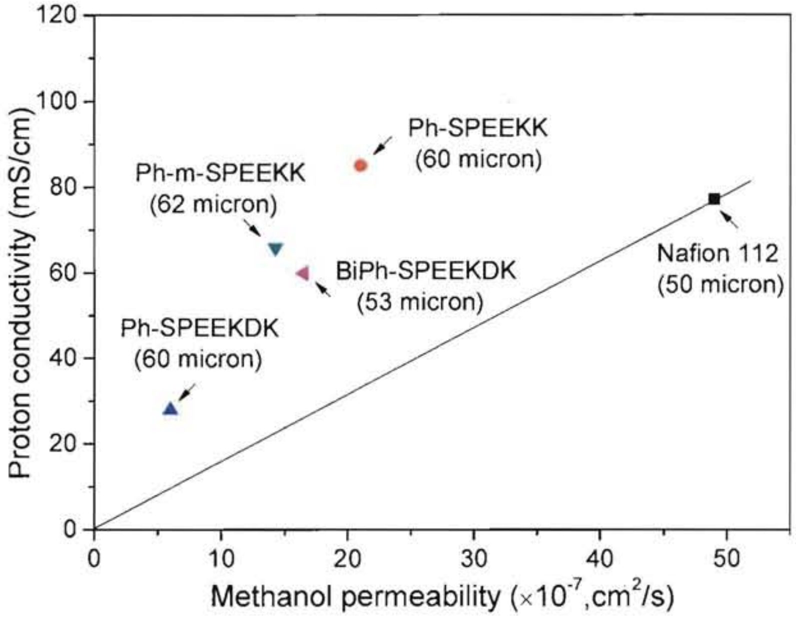


Fig. 3. Proton conductivity vs. methanol permeability of the membranes measured in DMFC mode at 80 °C.

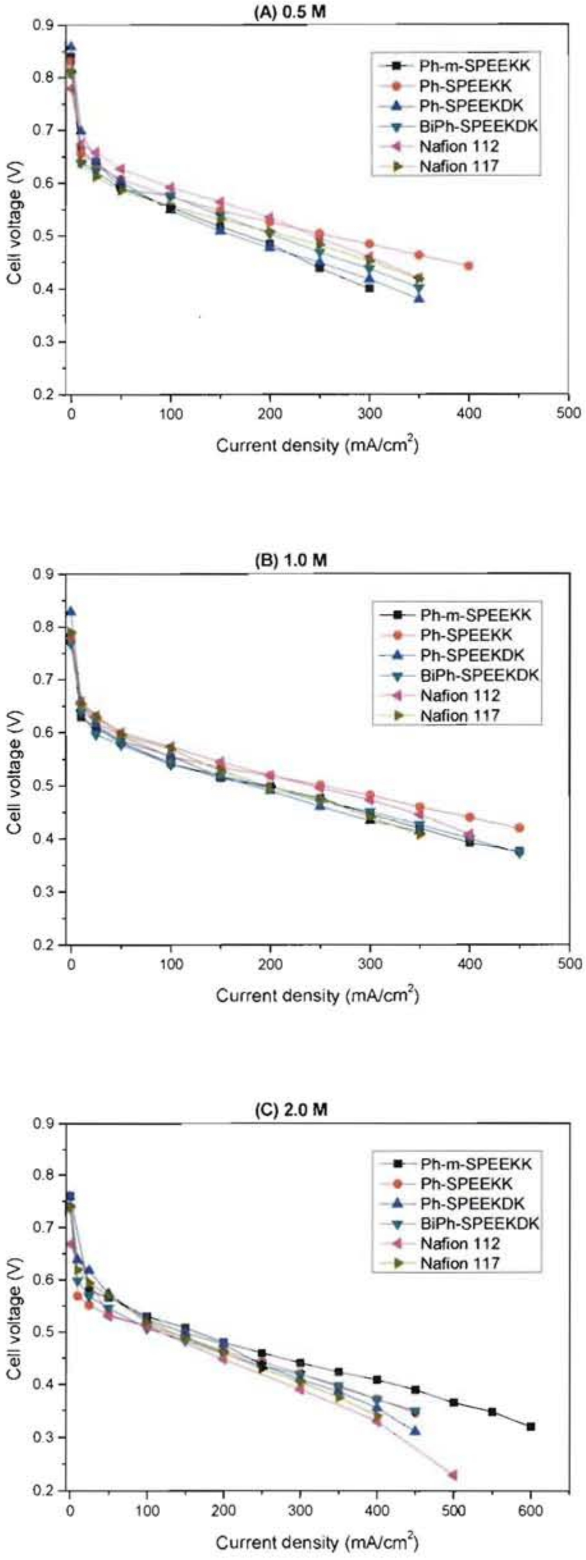


Fig. 4. DMFC performance of the membranes at 0.5 M (A), 1.0 M (B) and 2.0 M (C) methanol feed concentration (Cell temperature: 80 °C).