



Comparison of homogeneously and heterogeneously sulfonated polyetheretherketone membranes in preparation, properties and cell performance

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ABSTRACT

For application in direct methanol fuel cells, polyetheretherketone (PEEK) membranes with different degrees of sulfonation (40–80%) are prepared by both homogeneous and heterogeneous methods. Sulfonation and its degree are identified by means of Fourier transform infrared (FT-IR) spectroscopy and a back-titration method, respectively. Thermal analysis shows that an increase in the sulfonation degree increases the glass-transition temperature and enhances the thermal stability. The room-temperature ion conductivity of the homogeneously sulfonated PEEK (sPEEK) membrane with a 68% degree of sulfonation is higher than that of Nafion[®] 117, while its methanol permeability is lower. The tensile strength of the sPEEK membrane is comparable with that of Nafion[®] 117 at the equilibrium water swollen state. Various properties of sPEEK membranes prepared by two methods are compared. Overall, the ion conductivity of the homogeneous system is higher than that of the heterogeneous counterpart, but there is little difference in methanol permeability. The cell performance of the homogeneously sulfonated PEEK (homo-sPEEK) membrane is much better than that of the heterogeneously sulfonated PEEK (hetero-sPEEK) and Nafion[®] 117 membranes.

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1. Introduction

The proton-exchange membrane is one of the main components in the fuel cell system. The electrolyte material frequently used in direct methanol fuel cells (DMFCs) is a Teflon-based sulfonated polymer. DuPont electrolytes are marketed under the generic brand name Nafion[®], and the specific type used most often is membrane No. 117. Nafion[®] membranes exhibit exceptional chemical and thermal stability they are also stable against strong bases, oxidants, and reducing acids such as H₂O₂, Cl₂, H₂, and O₂ at temperatures up to 125 °C [1]. This type of membrane possesses both high hydrophobicity associated with the perfluorinated backbone and high hydrophilicity associated with the sulfonic acid groups [2]. Aggregation of hydrophilic domains (nanoseparation) takes place readily in the presence of water in the hydrophobic matrix [2], and their connection, so-called percolation, induces easy transport of water and methanol [3,4]. This methanol permeation through the membrane is a critical drawback in DMFC application, as it reduces the cell efficiency down to 35% [4]. In addition, the high water per-

meability can cause flooding in the cathode side and thus lowers cathode performance [3].

In order to improve the performance of DMFC, it is necessary to develop a new membrane that reduces methanol crossover without a considerable decrease of proton conductivity [5]. Non-fluorinated polymers based on poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) or polyetheretherketone (PEEK) have been presented as base materials with excellent chemical and mechanical resistance [6–9]. Hydrophilicity is possibly provided by the sulfonation where its degree can be controlled by the reaction conditions. The degree of sulfonation controls the hydrophobic–hydrophilic balance and thus a variety of properties that include both the transport properties such as proton conductivity and methanol permeability and the bulk properties, such as thermal, mechanical and chemical resistance [10]. Sulfonated PEEK (sPEEK) was found to exhibit obvious differences in phase separation behaviour and morphology from perfluorosulfonic polymers [2]. Hydrophilic/hydrophobic phase separation is less distinctive due to a smaller hydrophobic backbone, fewer acidic functional groups linked to the aromatic ring, and a less-flexible polymer chain [7]. It has also been reported [2] that the water channels developed in hydrated sulfonated poly-aryletherketone membranes are relatively narrow and highly branched to result in dead-end

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channels [2]. Thus, the permeation coefficient and electro-osmotic drag of the sulfonated poly-aryletherketone polymers have been found to be lower than those of Nafion® [2]. In addition, the preparation of sPEEK membrane allows direct casting from organic solutions and is therefore less expensive than perfluorosulfonic membranes.

There have been many studies on the preparation of sPEEK membranes. In most cases, the PEEK was sulfonated directly by concentrated sulfuric acid solution. At room temperature, the methanol permeability of a sPEEK membrane prepared by this method, namely, 2.71×10^{-7} to 1.54×10^{-6} [11] or 1×10^{-8} to 1×10^{-7} $\text{cm}^2 \text{s}^{-1}$ [12], was much lower than that of Nafion® membrane, viz., size 1.77×10^{-6} $\text{cm}^2 \text{s}^{-1}$. The ion conductivity was, however, also much lower than that of the Nafion® membrane, 1.2×10^{-1} S cm^{-1} as follows: 4.1×10^{-3} to 9.3×10^{-3} S cm^{-1} for a degree of sulfonation of 0.59–0.93 [11]; 1×10^{-3} to 5×10^{-3} S cm^{-1} [12]; 2.2×10^{-2} to 1.1×10^{-1} S cm^{-1} for the degree of sulfonation of 0.69–0.96 [13] and others [14–17].

The degree of sulfonation PEEK can be controlled by the time in the acidic concentration ranging from 30 to 100%. It was reported [18] that the formation of sulfone and its induced crosslinking increased in the order: 97.4% H_2SO_4 solution < 100% H_2SO_4 « HSO_3Cl [18,19]. Formation of sulfone in 97.4% H_2SO_4 aqueous solution was negligible because water decomposed the intermediate substances required for its formation, but when water is absent, it could occur. From hence, the sulfonation of PEEK in H_2SO_4 solution is essentially free of degradation and crosslinking when the concentration of the acid is kept around 97–98% [19–21]. A disadvantage of the direct sulfonation method is that it cannot produce truly random copolymers because dissolution and sulfonation of PEEK occur concurrently in sulfuric acid, leading to the heterogeneous product [22] (Thus, it is called the heterogeneous sulfonation method). According to Bailly and collaborators [22], truly random copolymers can be produced by the homogeneous when PEEK is dissolved completely in a solvent, and then H_2SO_4 is added for its sulfonation. The sulfonation reaction proceeds in a homogeneous environment in this case (Thus, it is called the homogeneous method). In this work, both homogeneous and heterogeneous sulfonation methods are utilized to prepare PEEK membranes for their application in DMFCs. Comparison of the synthesis and properties between the two sPEEK membrane systems, homogeneous and heterogeneous, is conducted together with those of Nafion® 117.

2. Experimental

2.1. Materials

The PEEK samples were Vitrex® 450PF purchased from the ICI Company (Rotherham, UK) with a molecular weight of $100\,000 \text{ g mol}^{-1}$. The particle size was $100 \mu\text{m}$, relative density 1.32 g cm^{-3} , the melting temperature 340°C , and the glass-transition temperature 143°C , respectively. Sulfuric acid (analyzed ACS Reagent) was obtained from Mallinckrodt Baker (Phillipsburg, NJ, USA), methylsulfonic acid (MSA) from Acros Organics (New Jersey, USA) and *N,N*-dimethyl acetamide (DMAC) from Fluka Chemie AG (CH-9470 Buchs, Switzerland). In order to prepare the membrane electrode assembly, carbon black (Vulcan XC-72), carbon paper (Toray, thickness $220 \mu\text{m}$) and catalyst (60 wt.% HP Pt on Vulcan XC-72R and 60 wt.% HP Pt:Ru Alloy (1:1 a/o) on Vulcan XC-72R) were purchased from E-Tek Inc. (Somerset, NJ, USA). 2-Propanol anhydrous (99.9%) and glycerol (Reagent Plus 99.0%, Sigma–Aldrich, St. Louis, MO, USA) were used as solvents for mixing carbon black and Teflon emulsion (PTFE 30, Fuel Cell Scientific, Stoneham, MA, USA).

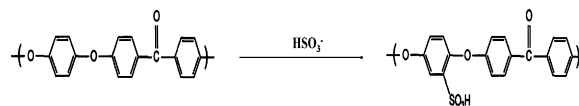


Fig. 1. Chemical synthesis of sPEEK from PEEK.

2.2. Sulfonation of polymers

PEEK particles were dried in a vacuum oven at 100°C for 24 h. For homogeneous sulfonation, 20 g of each PEEK sample was gradually dissolved in 100 ml of MSA under vigorous stirring for 24 h at room temperature. The solution was diluted with 800 ml of 97% sulfuric acid in a three-neck flask under a nitrogen atmosphere to sulfonate the PEEK. For the heterogeneous method, 40 g of PEEK were dissolved directly in 800 ml of 97% sulfuric acid. Both reactions were performed at room temperature (see Fig. 1). After a prescribed time, the sulfonated polymers were recovered by precipitation in a large excess of ice water. The polymers were filtered and washed repeatedly with distilled water. The recovered sPEEKs were dried at room temperature for 24 h, ground into smaller particles, and then kept in vacuum at 60 – 100°C for at least 1 day.

2.3. Characterization of sPEEK polymers

2.3.1. Sulfonation degrees and ion-exchange capacity (IEC)

The degree of sulfonation was determined using a back-titration method. The sPEEK particles (0.1 g) were placed in 20 ml of 0.05 M NaOH aqueous solution and kept for 3 days. The solution was then titrated with 0.05 M HCl aqueous solution using a pH meter (Orion 420+, Waltham, MA, USA). The calculation of sulfonation degree and IEC value has been reported elsewhere [23].

2.3.2. FT-IR

Samples for Fourier transform infrared spectroscopy analysis (Mattson 5000 FT-IR spectrometer, GL-5020, Unicam, UK) were prepared by blending 200 mg of IR spectroscopic grade KBr and 2 mg of polymer.

2.3.3. Size and morphology of sPEEK

Scanning electron microscopy (SEM, Hitachi S-3000H, Tokyo, Japan) was used to investigate the size and shape of the two types of sPEEK particle. Each sample was placed on a holder and coated with platinum for 120 s before SEM analysis.

2.3.4. Thermal properties of sPEEK

Differential scanning calorimetry (DSC 2910, PerkinElmer, Morwalk, CT, USA) was employed to measure the thermal transition properties of sPEEK samples. The samples ($\sim 8 \text{ mg}$) were heated from 30 to 300°C at a scanning rate of $10^\circ\text{C min}^{-1}$. A thermogravimetric analyzer (TGA7, PerkinElmer, Norwalk, CT, USA) was used to investigate the thermal degradation behaviour of sPEEK samples. The samples ($\sim 30 \text{ mg}$) were heated from 25 to 800°C at a scanning rate of $40^\circ\text{C min}^{-1}$ in a nitrogen atmosphere.

2.4. Membrane preparation

The dry sPEEK particles were dissolved to give a 3–5 wt.% concentration in DMAC. The solution was cast on a flat-roll glass plate, and then dried in a vacuum oven at 25 – 140°C for a few days. The sPEEK membranes were peeled from the glass plates, rinsed, and

kept in distilled water before characterization. The thickness of the membranes was in the range of 80–120 μm .

2.5. Characterization of sPEEK membranes

2.5.1. Water uptake

All membranes were kept in desiccators for a week at room temperature. After each dry membrane was weighed, it was immersed in distilled water at room temperature for 48 h. The weight of the water-absorbed membrane was periodically measured to determine the water uptake see Eq. (1). Before each weighing, the membrane surface was quickly wiped with soft tissues to remove water

$$\% \text{Water uptake} = \frac{(m_{\text{wet}} - m_{\text{dry}}) \times 100}{m_{\text{dry}}} \quad (1)$$

where m_{wet} and m_{dry} indicate the weight of dry and wet membranes, respectively.

2.5.2. Methanol permeability measurement

Methanol permeability was measured using a glass diffusion cell. An aqueous solution containing 50 ml of 2M methanol, was placed in the left side of the diffusion cell and 50 ml pure water on the other side. A magnetic stirrer was used in each compartment to ensure uniform concentration. The methanol concentration in the water compartment was continuously monitored by a detector (RI750F, Young Lin, Korea) at room temperature.

2.5.3. Proton conductivity measurement

The fully hydrated membranes were kept in 1 M H_2SO_4 solution for 2 days. Proton conductivity was measured with electrochemical instrumentation (Pastat 2263, Princeton Applied Research, Oak Ridge, TN, USA) over a frequency range of 1– 10^5 Hz at 50 mV. All measurements were conducted in a transverse direction across the membrane. The advantages and limitations of the technique have been discussed elsewhere [10]. The conductivity, σ , of the sample in the transverse direction was calculated from the impedance data, using the relation $\sigma = d/RS$ where d and S are the thickness and face area of the sample, respectively. The value of R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re (Z) axis.

2.5.4. Mechanical properties measurement

The tensile strength and Young's modulus of each hydrated membrane were measured using a universal tensile machine (UTM-model 5565, Lloyd, Fareham, UK). The 20 mm (W) \times 50 mm (L) samples were stretched with a 250 N load cell.

2.5.5. DMFC performance test

TGP-H-120 carbon paper with a thickness of 220 μm was used as gas-diffusion media. A paste of 6 g carbon black and 20 wt.% PTFE in isopropanol and glycerol solution was spread on the carbon paper and heat-treated for 6 h at 160 $^\circ\text{C}$, respectively. This carbon paper was used as a gas-diffusion layer (GDL). The electrodes were loaded with 0.3 mg cm^{-2} of catalyst using 60 wt.% Pt:Ru alloy on Vulcan XC-72 for the anode and 60 wt.% Pt on Vulcan XC-72 for the cathode. A mixture of catalyst and 5 wt.% Nafion[®] ionomer in isopropanol, 1-propanol and distilled water was coated on the side of the GDL by spraying. A solution of 68% DS homo-sPEEK was overlaid on the catalyst layer as binder to membrane. The membrane electrode assembly (MEA) was prepared by hot pressing at 100 $^\circ\text{C}$ and 6.9 MPa for 3 min. A DMFC with the prepared MEA (6.25 cm^2) was operated with 2 M methanol solution (5 $\text{cm}^3 \text{min}^{-1}$) on the anode side and oxygen (100 $\text{cm}^3 \text{min}^{-1}$) on the cathode side.

The temperature of the cell was set at 35, 50 and 80 $^\circ\text{C}$, respectively.

3. Results and discussion

3.1. Sulfonation kinetics

PEEK was sulfonated for different times from 0 to 220 h to provide different degrees of sulfonation (DS). In Fig. 2, the DS of the sPEEK increases monotonically with increasing reaction time. There are, however, some differences between the curves (a) and (b). In the initial sulfonation period from 0 to 24 h, the rate of sulfonation for the homogeneous system (Fig. 2(b)) is higher than that for the heterogeneous counterpart (Fig. 2(a)). This is because dissolution and sulfonation occur simultaneously in the heterogeneous system but only sulfonation for the homogeneous system. Part of the PEEK particles is not dissolved even after 24 h for heterogeneous system, but all particles have been completely dissolved to establish higher DS for homogeneous system. After 24 h, the equilibrium DS for the heterogeneous system is higher than that for the homogeneous one, as the concentration of H_2SO_4 (97% for heterogeneous system) is much higher than that of the homogeneous system (88%), due to the presence of MSA solvent. The MSA affects the rate of reaction in at least two ways: (i) dilution of the sulfonating species and their precursors, and (ii) solvation and reaction with part of the SO_3 , further decreasing the concentration of active species [22].

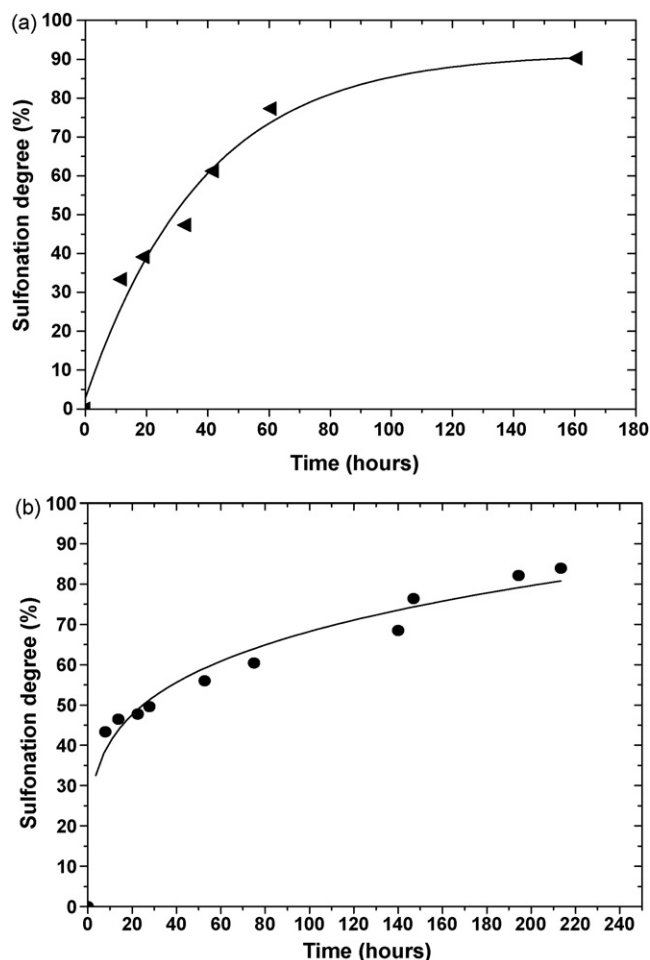


Fig. 2. Sulfonation kinetics of PEEK at room temperature by (a) heterogeneous and (b) homogeneous methods, respectively.

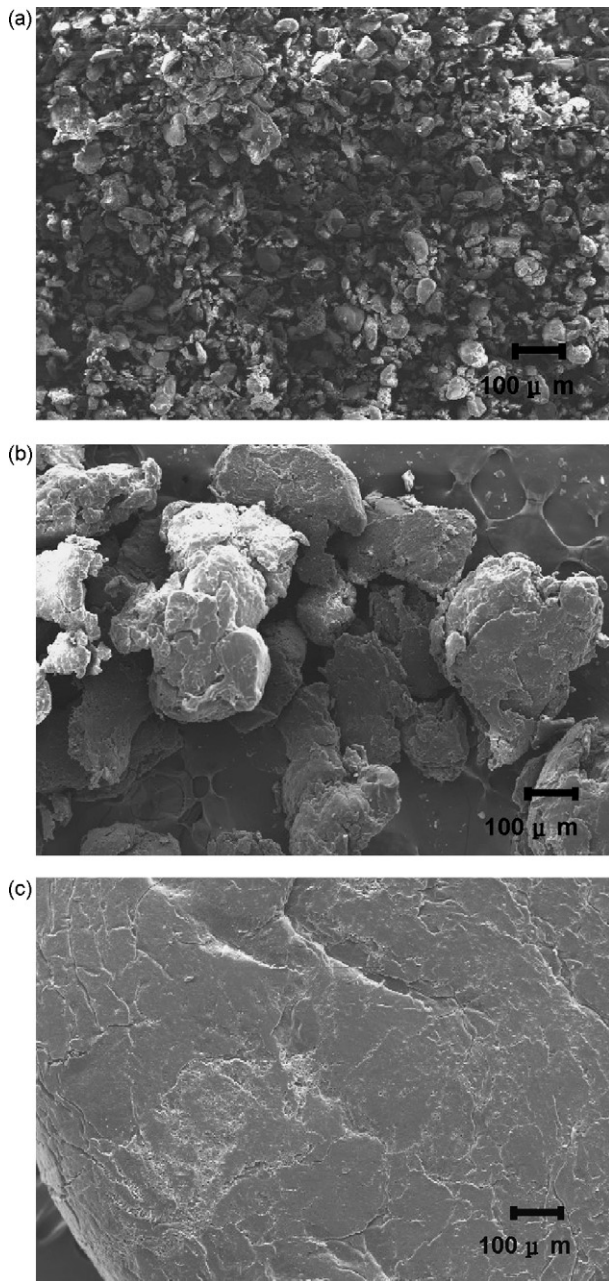


Fig. 3. Scanning electron microphotographs of (a) PEEK, (b) homo-sPEEK, and (c) hetero-sPEEK, respectively.

3.2. Particle size

The particle sizes of pure PEEK and sPEEK prepared via homogeneous and heterogeneous methods are shown in Fig. 3(a)–(c), respectively. The average size of sPEEK particles is larger than that of pure ones due to the aggregation of particles during sulfonation. The particle size of homogeneously sulfonated PEEK (homo-sPEEK) is smaller than that of heterogeneously sulfonated PEEK (hetero-sPEEK) because the presence of solvent weakens the aggregation of polymer particles.

3.3. Chemical identification of PEEK and sPEEK

Based on the information about the sulfonation kinetics, four samples were prepared by each method to have the DS from 50

Table 1
Transition temperature of sPEEK samples

Homo-samples	IEC (mequiv. g ⁻¹)	T _g (°C)	Hetero-samples	IEC (mequiv. g ⁻¹)	T _g (°C)
PEEK		143	PEEK		143
sPEEK-48%	1.49	187.20	sPEEK-45%	1.4	188.82
sPEEK-60%	1.79	192.00	sPEEK-59%	1.75	200.72
sPEEK-68%	1.99	192.00	sPEEK-71%	2.07	201.61
sPEEK-83%	2.36	207.76	sPEEK-80%	2.25	205.53

to 85% and IEC from 1.4 to 2.4 mequiv. g⁻¹, respectively, as shown in Table 1. The FT-IR spectra of PEEK and sPEEK with different DS are shown in Fig. 4. The new absorption peak at 1078 cm⁻¹ in the spectra of sPEEK samples (Fig. 4a) is from the O=S=O group. In order to track the quantitative change of SO₃ group, the ratio A:B is calculated (Fig. 4b), where A is the area of the SO₃ peak at 1078 cm⁻¹ and B is the area of the reference (unchanging) PEEK peak at 1150 cm⁻¹. The result proves that sulfonic functional groups are gradually introduced to the PEEK polymer.

3.4. Thermal properties of sPEEK

The PEEK is a highly thermo-stable polymer with a glass transition temperature (T_g) of 143 °C. In Table 1, the DSC results show that the transition temperatures of sPEEK are in the range of 188–207 °C depending on the DS of samples. The increasing behaviour of T_g values with DS is a typical observation for ionomers that arise from strong polar interaction.

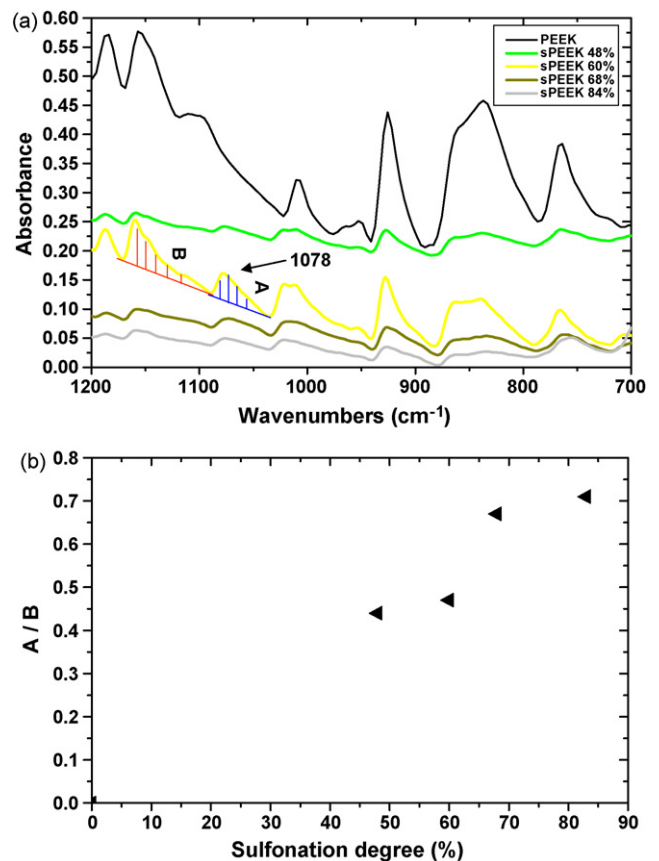


Fig. 4. FT-IR spectra of sulfonated PEEK samples with (a) different DS of 0, 48, 60, 68 and 84% (from top to bottom) and (b) A/B area ratio as function of sulfonation degree.

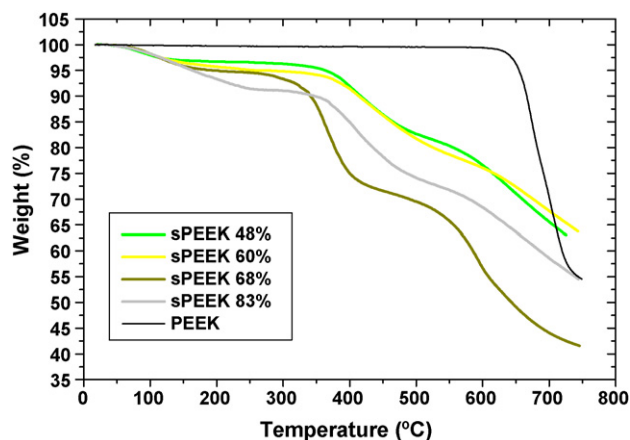


Fig. 5. TGA results for sPEEK samples with different DS of 0, 48, 60, 68 and 83%.

The Victrex® 450 PF PEEK starts to degrade at around 600 °C. In comparison with pure PEEK, sPEEK has three distinct degradation regions [8,24] as shown in Fig. 5. In the range of 90–110 °C, a small weight loss occurs due to the evaporation of water. While the second weight loss in the range of 250–280 °C is mainly due to debonding of the sulfonic groups, the third weight loss in the range of 400–580 °C is caused by decomposition of the main chain of PEEK. The degradation temperature for sPEEK is lower than that for PEEK because of the catalytic degradation of the polymer chain caused by SO_3H [15].

3.5. Water uptake of sPEEK membranes

Water absorption can facilitate proton transport in the membrane, but too much water absorption results in a mechanically unstable membrane [11]. As shown in Fig. 6, the water uptake increases with increasing DS due to the introduction of hydrophilic SO_3H groups. There is a small sharp increase in water uptake at DS around 70%. This is perhaps due to a percolation phenomenon. When the SO_3H group content is high enough, the dispersed SO_3H hydrophilic ion clusters are connected together to cause more water uptake [11]. It is shown that the water uptake of the

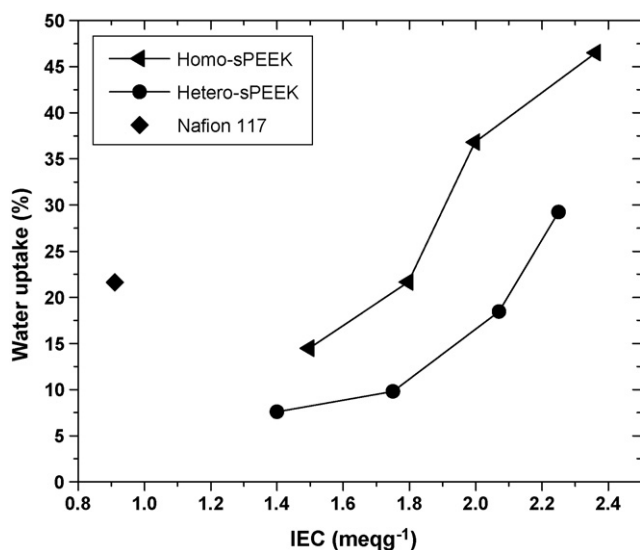


Fig. 6. Water uptake of homo- (◄) and hetero- (●) sPEEK membranes at room temperature as function of IEC. Symbol (◆) indicates Nafion® 117.

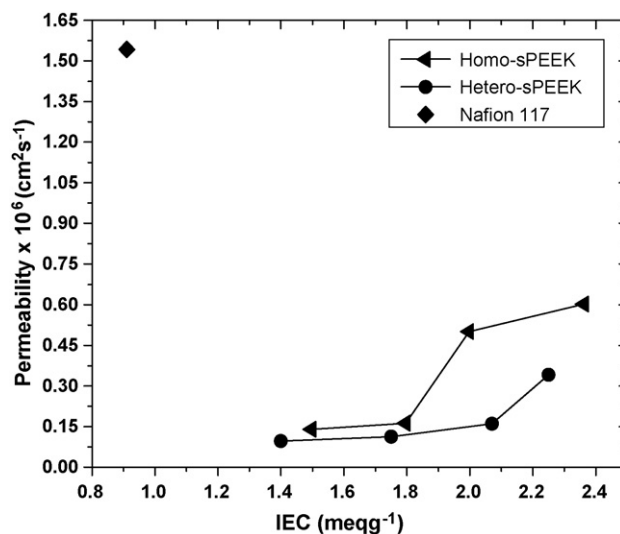


Fig. 7. Methanol permeability of homo- (◄) and hetero- (●) sPEEK membranes, respectively. Symbol (◆) indicates Nafion® 117.

homo-sPEEK membrane is much higher than that of the hetero-sPEEK counterpart, or even Nafion® 117 when its DS is higher than 60%.

3.6. MeOH permeability

All membranes were soaked in water to be hydrated before measurement of methanol permeability. The methanol permeability of two sPEEK membrane systems at room temperature is presented in Fig. 7. The methanol permeability of the Nafion® 117 membrane is $1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The methanol permeability of the sPEEK membrane increases with DS, but is still lower than that of Nafion® 117 in this experimental range. The methanol permeability of homo-sPEEK membranes is a little higher than that of hetero-sPEEK ones. It has been reported that the hetero-sPEEK membranes form narrower water channels with 'dead-end pockets' [2]. As the polymer backbone is not randomly sulfonated in the hydrated state for hetero-sPEEK, the ion clusters formed by aggregation of the hydrophilic SO_3H groups hardly have non-uniform size and structure. On the other hand, the distribution of SO_3H groups in homo-sPEEK membranes is much more random, whereas much more uniform clusters are expected. As the water channels in sPEEK are reported to be narrower than in Nafion®, a comparatively lower methanol permeability is observed.

3.7. Proton conductivity

As shown in Fig. 8, the proton conductivities increase with increasing DS for both membranes. The dependence is more prominent for the homo-sPEEK membrane, as the values are comparable with the use for Nafion® 117 membranes ($1.1 \times 10^{-1} \text{ S cm}^{-1}$) measured under the same conditions. The proton conductivity of the homo-sPEEK membrane is much higher than that of hetero-sPEEK membrane. The proton conductivity becomes higher at higher water uptake in a continuous water channel.

3.8. Mechanical properties

The tensile strength of fully hydrated homo-sPEEK membranes is given in Fig. 9. The tensile strength decreases, but water uptake

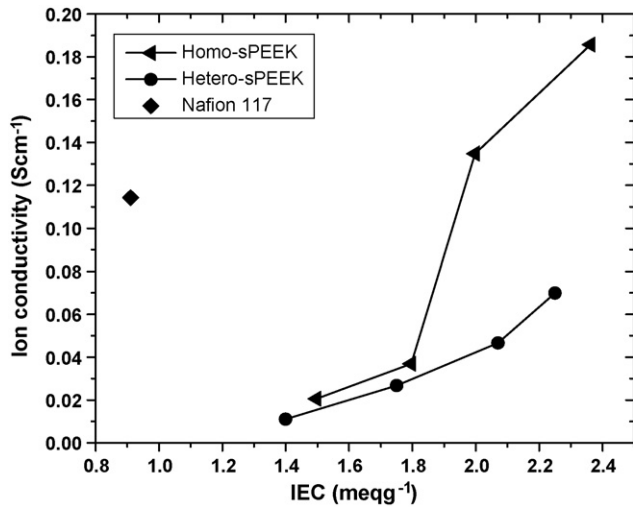


Fig. 8. Proton conductivity of homo- (▲) and hetero- (●) sPEEK membranes, respectively. Symbol (♦) indicates Nafion® 117.

increases with the increment of DS. The mechanical property is progressively deteriorated with the content of water by a plasticization effect. In the presence of water, the polymer chain becomes more flexible, which leads to lower values of the tensile strength. The tensile strength of sPEEK is comparable with that of Nafion® at an IEC value of 1.95 where the water uptake is even higher than that of Nafion®.

3.9. Characteristic factor

The characteristic factor, CF, is the ratio of proton conductivity to methanol permeability and indicates the membrane performance in a DMFC application. As shown in Fig. 10, the CF increases with DS from 48 to 68%, but decreases at DS 83%. At very high DS, the membrane is not useful for DMFC applications, as it is swollen too much in water and thereby give rise to excessive methanol permeability.

It is of important to note that both types of membrane have CF values much higher than Nafion® 117 and those of the homo-sPEEK membranes even higher than for hetero-sPEEK membranes. A comparison between the homo-sPEEK membrane and Nafion®

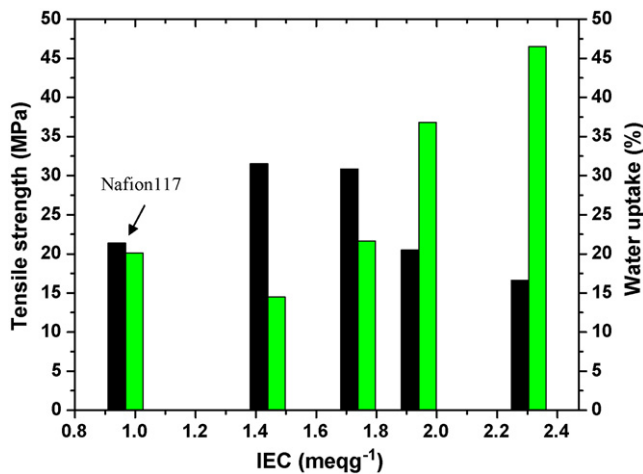


Fig. 9. Tensile strength of water absorbed homo-sPEEK membranes with different IEC values. Left bars indicate Nafion®.

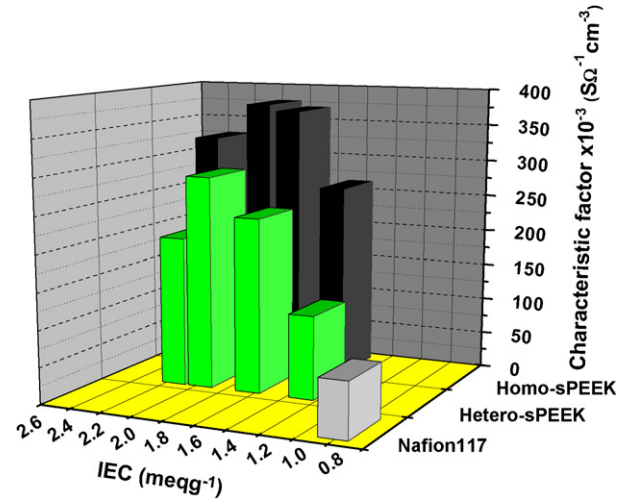


Fig. 10. Characteristic factors of homo- and hetero-sPEEK membranes.

117 membrane is shown in more detail in Fig. 11. The homo-sPEEK membrane with 68% DS appears to give the best performance when considering relevant properties such as ion conductivity, methanol permeability, and mechanical strength in combination.

3.10. DMFC performance

The relationship between power density and current density for MEAs composed of 65% homo-sPEEK membranes at different temperatures is presented in Fig. 12. Increasing temperature raises the power density, as the oxidation/reduction reaction kinetics improve with temperature. At a fixed temperature of 80 °C, power densities are compared for two MEAs composed of different sPEEK membrane systems (see Fig. 13). The effect of sulfonation degree on cell performance is distinguishable between the two membranes. While the power density increases in the order of DS from 60 to 80% for hetero-sPEEK membranes, a maximum is observed at 65% DS for homo counterparts. In both cases, the power densities of membranes with 60% DS are too low because of poor ion conductivity. For DS >80%, the hetero-sPEEK membrane shows a higher

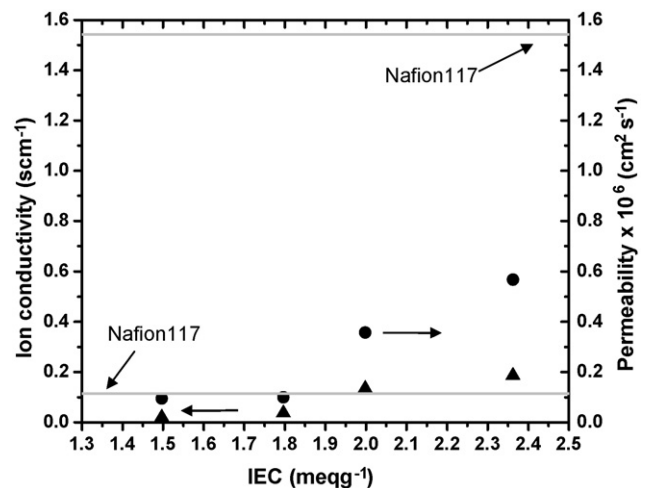


Fig. 11. Comparison of ion conductivity (▲) and permeability (●) of homo-sPEEK membranes with those of Nafion® 117 membrane according to IEC.

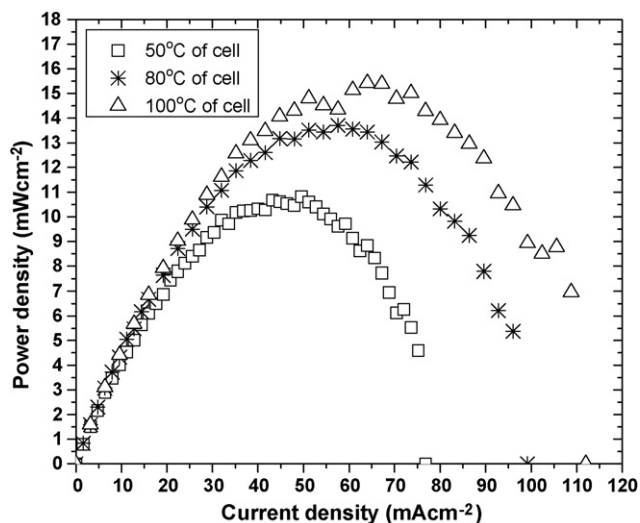


Fig. 12. Cell performance of 65% DS homo-sPEEK membrane at different temperatures of 35 °C (□), 50 °C (*) and 80 °C (Δ), respectively.

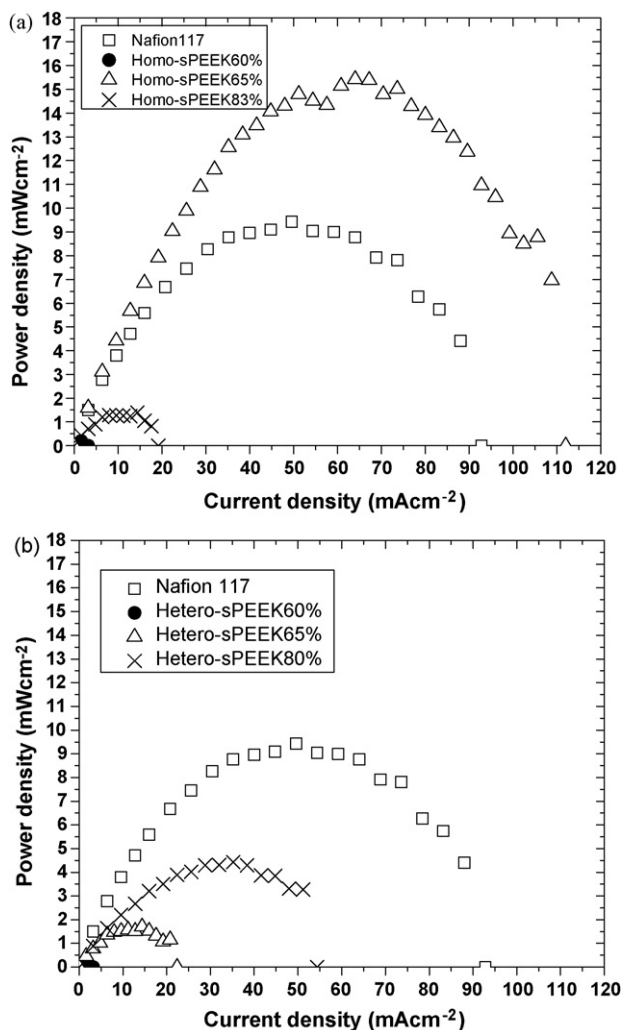


Fig. 13. Cell performance of (a) homo-sPEEK membranes with different sulfonation degrees of 60% (●), 65% (Δ), and 83% (×) and (b) hetero-sPEEK membranes with different sulfonation degrees of 60% (●), 65% (Δ), and 80% (×), respectively, at 80 °C. Symbol (□) indicates Nafion® membrane.

cell performance than the homo version. This is because a 83% DS homo-sPEEK membrane has too high a water uptake (~47%), that leads to unstable and poor performance. In summary, 65% DS homo-sPEEK membrane shows the highest power density among the present samples, even higher than Nafion® 117 membrane.

4. Conclusions

PEEK has been sulfonated via the two different methods—homogeneous and heterogeneous. The particle size of homo-sPEEK is smaller than that of hetero-sPEEK, because the aggregation of polymer particles in homogeneous phase is weakened by the presence of solvent. Bulk properties such as thermal, mechanical and equilibrium water uptake are quite different between the two sPEEK membranes, due to the difference in random copolymer structure. Some homo-sPEEK membranes show comparable or better ion conductivity but lower methanol permeability to/than the Nafion® 117 membrane. This has not been achieved for hetero-sPEEK membranes. Evaluating all bulk and transport properties including thermal, mechanical, ion conducting and permeable properties, a homo-sPEEK membrane with 68% DS gives the best results for DMFC applications. In particular, its methanol permeability, $0.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, is much lower than that of a Nafion® 117 membrane, $1.55 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, while the ion conductivity is still high, $1.35 \times 10^{-1} \text{ S cm}^{-1}$. Around this DS, the homo-sPEEK membrane produces a power density that is much higher than that of a heterogeneous one, and is even higher than for a Nafion® 117 membrane.

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