Azide-assisted cross-linked sulfonated poly(ether sulfone)s as stable and highly conductive membranes with low methanol diffusion coefficients†

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Received (in Cambridge, UK) 7th January 2008, Accepted 1st February 2008
First published as an Advance Article on the web 25th February 2008
DOI: 10.1039/b800064f

Novel cross-linked sulfonated poly(ether sulfone)s, prepared by azide-assisted thermal irradiation, show not only low methanol permeability but also exceptionally high proton conductivity with oxidative and hydrolytic stability.

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising power sources for the future due to their high energy efficiency and being environmentally friendly.[1,2] One of the most important components in a PEMFC is the proton exchange membrane (PEM), for which several specific and demanding properties are required: high proton conductivity, hydrolysis resistance, oxidative stability, and low methanol crossover.[3] Currently, perfluorinated copolymers such as Nafion® are the most commonly used PEMs because of their high proton conductivity and excellent chemical resistance. However, they have some drawbacks such as low proton conductivity at increased temperature, high methanol diffusion, and high manufacturing cost.[4] At elevated temperature, perfluorosulfonic acid polymers suffer from lowered conductivity due to the loss of water, and this is accompanied by considerable deterioration in the mechanical strength. Furthermore, the high methanol crossover of the Nafion®-based membranes causes not only catalyst poisoning but also a decrease in fuel efficiency, and hence the entire cell performance.

Much progress has been made to develop new proton exchange membranes,[5,6] and in some cases, either high proton conductivity[7] or low methanol crossover[8–10] was achieved. Nevertheless, few membranes have satisfied both high conductivity (especially at high temperature) and low methanol crossover with enhanced oxidative and hydrolytic stability. Sulfonated aromatic polymers have been studied as one of the alternatives to Nafion® due to their good physical properties and high proton conductivity.[5,11] These properties have been shown to depend on the degree of sulfonation of the aromatic polymer: a high degree of sulfonation degrades the physical properties of humidified polymers together with an increase in methanol diffusion, whereas an improved proton conductivity under high humidity conditions was obtained.

We were interested in developing highly proton conductive polymers without loss of the structural integrity, and report herein a cross-linked network structure of the sulfonated poly(ether sulfone)s (PESs) with high proton conductivity, oxidative and hydrolytic stability, and low methanol diffusion coefficient.

Our approach to solve the typical limitation of polymer electrolyte membranes (good conductivity by high degree of sulfonation at the expense of structural integrity), was to make a homogeneous arrangement of the conductive sites in the rigid rod poly(ether sulfone) backbone structure and to infer a balanced hydrophobic nature by cross-linking.[12]

To this end we prepared the allyl-terminated telechelic sulfonated sulfone polymers, which were then transformed to the network membranes by *in situ* thermal cross-linking in the presence of a bis-azide compound (Scheme 1). The cross-linked membrane showed a high conductivity of 0.79 S cm^{-1} at 100 °C and relative humidity (RH) with a methanol diffusion coefficient of 3.3×10^{-7} cm^2 s^{-1}, which is only 17% of that of Nafion®.

The hydroxy-terminated sulfonated PESs **1** were first synthesized using hydroquinone 2-potassium sulfonate (HPS) and bis-phenol A (BPA) with fluorophenyl sulfone (FPS). A slight excess of BPA was used to obtain the terminal hydroxy groups, and PESs with different mol% of hydrophilic groups were prepared by changing the mole ratio of HPS in the copolymerization reaction. The copolymer composition ($x : y$) was confirmed by the relative ^{1}H-NMR absorption peak areas between H^a and H^b illustrated in Scheme 1. The properties of the sulfonated PES with 60% hydrophilic portion ($x : y = 6 : 4$; PES-60) will be focused on in this communication.[13] The terminal hydroxy groups of the prepared sulfonated PES-60 were then end-capped with allyl groups using allyl bromide in the presence of sodium hydride as a base to produce the polymer **2**. Under these reaction conditions, about 15% of the sulfonate group was also allylated. The conversion was calculated by comparing integrals of the allyl groups in the polymer **2** with those in the base-treated polymer **3** having the corresponding sulfonate sodium salt and terminal allyl ethers.[14] The film prepared from polymer **2** offered more uniformity in appearance and toughness than the base-treated polymer **3**. The presence of more hydrophobic allyl groups in the sulfonate ester resulted in good-quality films and uniform distribution of the conductive ionic sites over the bulk membrane, thus inhibiting ionic cluster formation even after the allyl sulfonate ester was exchanged to the highly dissociable sulfonic acid form. We further hoped that the interaction among the polymer chains could be enhanced by cross-linking,

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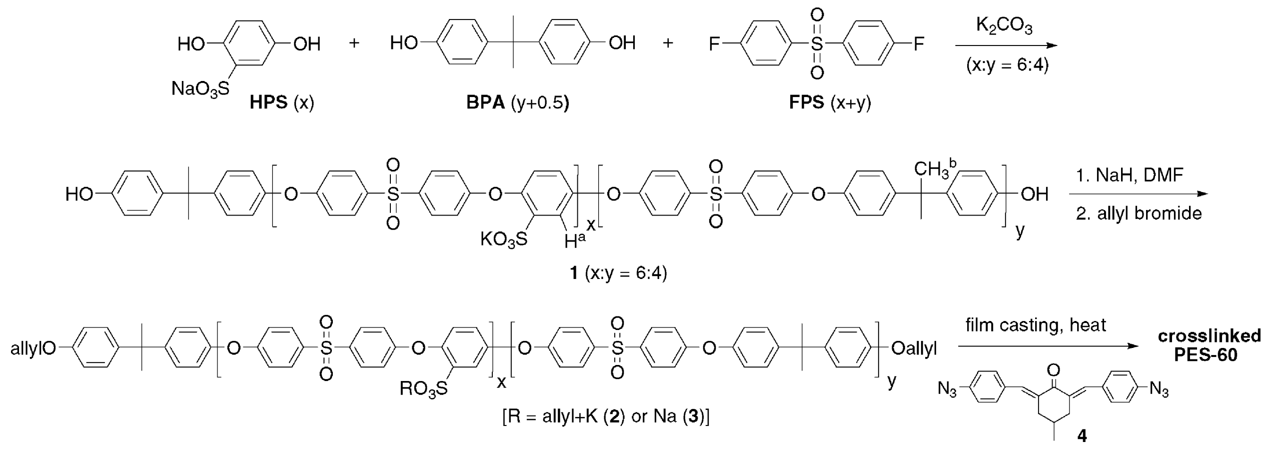
† Electronic supplementary information (ESI) available: Details of experimental procedures. See DOI: 10.1039/b800064f



Scheme 1 Schematic representation of the preparation of the cross-linked poly(ether sulfone) PES-60 with an $x : y$ ratio of 6 : 4.

leading to an enforced mechanical strength and an increased hydrophobicity for the prepared membrane.

To obtain the network structure, a DMF solution of the allyl-terminated PES-60 (**2**) was cast into films in the presence of bis-azide (30 wt% compared to **2**) onto the glass plate, and vacuum-dried at 180 °C for 18 h. During the drying process, the reactive allyl groups in polymer **2** were cross-linked by thermal irradiation to form a polymer network (Scheme 1). The aromatic bis-azide **4** was chosen as a cross-linker since thermolysis or photolysis was known to result in a nitrogen loss to produce the nitrene. It is this highly reactive nitrene intermediate which is then reacted with mainly the double bonds in the exclusion of oxygen.[15]

The thermally cured PES-60 film was then base-treated to deallylate the sulfonate ester, followed by acidification to obtain the sulfonated form of the cross-linked PES-60 membrane. For comparison, sulfonated PES-60n membrane was also prepared using the same method except the addition of the bis-azide during the film casting. It was known that the allyl groups were partially cross-linked during thermal curing in the absence of the cross-linking agent.[8] The membrane prepared from sulfonated PES-60 was not soluble in most organic solvents including DMF and DMSO, whereas the sulfonated PES-60n film was slowly dissolved under the same conditions.

The IR spectra of the films before and after thermal curing of the sulfonated PES-60 were compared, and showed a complete absence of the absorption peak assigned to the azide groups at 2100 cm^{-1} and the allyl peaks at 910 and 990 cm^{-1}, while other characteristic peaks remained identical after thermal treatment. This confirmed that the bis-azide **4** was effectively incorporated into the allyl-terminated PES-60 **2** to form the network structure.

The hydrolytic stability was evaluated by treating the membrane samples at 100 °C and 100% RH for 24 h for an accelerated testing. The PES-60n membrane withstands the condition up to 12 h, after which time it started to decompose, whereas the fully cross-linked membrane PES-60 did not display any changes in appearance (color, toughness and flexibility). Since no changes were observed in the IR spectra of the cross-linked membrane, the sulfonic acid groups were believed to remain intact during the treatment. The prepared membranes were then subjected to Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. More than 3 h was required before the polymer started to dissolve (or decompose) for the PES-60n and the azide-assisted cross-linked membrane (PES-60) withstands the solution up to 4 h. This oxidation stability is, indeed, very high for a polymer electrolyte material based on a non-fluorinated hydrocarbon skeleton. Partial cross-linking of the allyl group, as previously mentioned, can account for the relatively stable membrane formation of PES-60n.

Thermogravimetric analyses (TGA) showed two-step weight loss for both membranes. The first loss from 20 to 170 °C is ascribed to the loss of absorbed water and the second above 265 °C represents decomposition of the polymers, presumably *via* loss of the sulfonic acid groups. The decomposition temperature is almost as high as that of Nafion®, and an increase in the second decomposition temperature was observed for the fully cross-linked membrane (287 °C for PES-60 and 265 °C for PES-60n), indicating that the acid groups were more tightly held for PES-60.

Proton conductivity measurements were performed using the method developed by Sumner *et al.*[16] The film samples were placed in a closed cell to keep the relative humidity at 100%. Both PES-60 and PES-60n membranes displayed proton conductivity over 0.06 S cm^{-1} at 20 °C, and showed a positive temperature–conductivity dependency (Fig. 1). At 100 °C, the fully cross-linked membrane (PES-60) showed high conductivity of 0.79 S cm^{-1}, which was much higher than that of Nafion (0.49 S cm^{-1}) under the same conditions. To the best of our knowledge, this is the highest proton conductivity reported for the cross-linked membrane. The minimized network structure by having the reactive cross-linkable site mainly at the terminus is believed to be responsible for the high conductivity of our system. It has been reported that these highly hydrophobic films had conductivity usually below 0.1 S cm^{-1} even at higher temperatures.[17] In addition, both membranes exhibited more significant increase in proton conductivity with increasing temperature, compared with Nafion®, and this was more pronounced for the PES-60 membrane than PES-60n (Fig. 1). Homogeneous distribution of the conductive sites over the well-defined rigid rod structure and suppressed ionic cluster formation can account for these results (*vide supra*). The more strongly-bound sulfonic acid groups of the PES-60, compared with PES-60n, are another reason for the higher conductivity at higher temperatures.

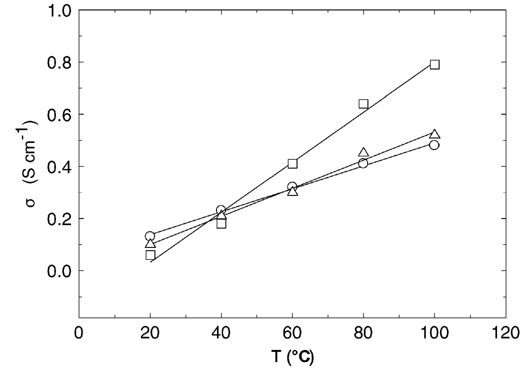


Fig. 1 Temperature dependence of the proton conductivity for the cross-linked PES-60 (□), partially cross-linked PES-60n (△) and Nafion®-112 (○) at 100% RH.

The methanol diffusion coefficient was measured using a glass diffusion cell. The cell consisted of two compartments that were separated by a vertical membrane. Methanol and water were placed on two sides of the diffusion cell, respectively, and each compartment was stirred to ensure uniformity during the measurement. The increases of methanol concentration in the water compartment with time were measured using a digital refractometer at room temperature. The results showed lower methanol diffusion coefficients for both PES-60 and PES-60n membranes than Nafion®, with a much lower value for the more hydrophobic PES-60, as expected (Fig. 2). The methanol permeability of the sulfonated PES-60 is only 17% of that of Nafion® under the same conditions (3.3×10^{-7} cm^2 s^{-1} for PES-60 and 1.9×10^{-6} cm^2 s^{-1} for Nafion-112).

In conclusion, we have prepared cross-linked sulfonated poly(ether sulfone)s (PESs) by thermal irradiation of the allyl-terminated PESs using an azide. Having both a uniform distribution of the hydrophilic conductive sites and a controlled hydrophobic nature by minimized cross-linking over the rigid rod poly(ether sulfone) backbone, our cross-linked polymer (PES-60) membrane offered high proton conductivity at high temperatures without loss of structural integrity. In addition, a much lower methanol permeability than for Nafion® was observed. We believe these preliminary results have proved its potential as an electrolyte for both high temperature PEMFC and direct methanol fuel cells (DMFC).

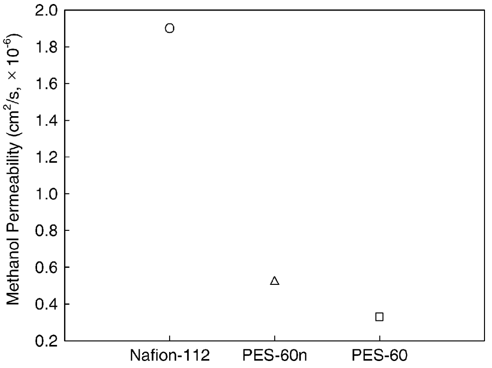


Fig. 2 Methanol diffusion coefficients for the cross-linked PES-60 (□), partially cross-linked PES-60n (△) and Nafion®-112 (○) at 20 °C.

This work was supported by a grant from the Korea Institute of Science and Technology as a part of the "Development of Fuel Cell Power-packs for Portable Power Generation" program in 2008.

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12 Crosslinking is an efficient means to limit methanol diffusion and also to enhance physical properties of the membranes, but the increased hydrophobicity due to the network structure results in inherently lower conductivity of the membranes.

13 The effect of the hydrophilic portion of the sulfonated PES copolymers on the physical and electrical properties of the corresponding membranes will be discussed in a full paper.

14 Selective deallylation of the more reactive sulfonate ester in NaOH solution to its corresponding sodium salt whilst preserving the terminal allyl ethers was confirmed by the comparative spectroscopic analysis using a model counterpart having both allyl ether and allyl sulfonate ester groups. This will also be detailed elsewhere.

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17 Crosslinked SPEEK/AMPS blend membranes having conductivities as high as 0.15 S cm^{-1} at 85 °C with a methanol diffusion coefficient of 8.9×10^{-7} cm^2 s^{-1} were recently reported. See ref. 9.