



Polyelectrolyte based on tetra-sulfonated poly(arylene ether)s for direct methanol fuel cell

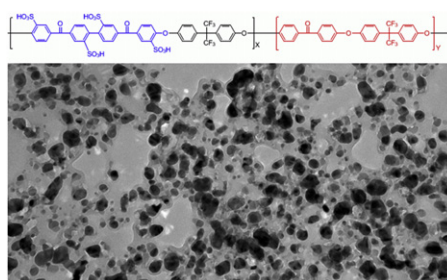
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HIGHLIGHTS

- ▶ We synthesized novel tetra-sulfonated poly(arylene ether ketone)s as PEM materials.
- ▶ The membranes exhibited lower water uptake and swelling ratio than Nafion 117.
- ▶ Combination of considerable proton conductivity and low methanol permeability.
- ▶ The membranes are promising candidate PEM materials for direct methanol fuel cell.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of tetra-sulfonated poly(arylene ether)s are prepared from a new tetra-sulfonated difluoride monomer and commercial 4,4'-difluorobenzophenone and 4,4'-(hexafluoroisopropylidene)diphenol via polycondensation process. With the content of tetra-sulfonated monomer raising from 15% to 35% in difluoride monomer, sulfonated polymers with ion exchange capacity (IEC) ranging from 0.92 to 1.66 mequiv g⁻¹ are obtained. The high thermal stable polymer owns the glass transition temperature higher than 190 °C and onset decomposition temperature higher than 300 °C. The polymers exhibit good solubility in dimethylacetamide (DMAc) and the tough, flexible and transparent films are obtained by solution casting method. These membranes exhibit suitable proton conductivity, low methanol permeability and excellent dimensional stability. The membrane with IEC_E = 1.81 mequiv g⁻¹ shows considerable proton conductivity (84 mS cm⁻¹) and swelling ration (only 8.6%) under fully hydrated state at 100 °C. Their excellent performance is attributed to distinct phase separation between hydrophilic and hydrophobic morphology, which is observed by TEM. This work demonstrates that the strategy of combining locally high densities hydrophilic segment with fluorine-containing hydrophobic segment in a polymer chain can balance on proton conduction and dimensional stability efficiently. Furthermore, these membranes own much lower methanol permeability and higher selectivity than Nafion.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are receiving increasing attention because of their high energy conversion efficiency, low emission of pollutants and low operating temperature [1]. Polymer

electrolyte membranes (PEMs) have attracted considerable attention because they play the key role in PEFCs, acting as a proton transport media and as a separator of fuel and oxidant. Currently, Nafion is the most widely used proton exchange membrane [2]. However, it still shows some serious disadvantages. Hence, modified fluorine-containing membranes and aromatic membranes have been developed as alternative membranes for PEMs, due to their thermal stability, low cost, and low fuel permeability [3–8].

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PEMs usually require high proton conductivity and low methanol permeability, and both factors contribute high selectivity, which shows overall performance of the membrane [9,10]. The aromatic ionomers with high ion exchange capacity (IEC) are widely used to achieve high proton conductivity, but they also have drawbacks such as high water uptake, poor dimensional stability, and increased methanol permeability [11,12]. Therefore, some strategies have been attempted to improve the selectivity under the high methanol concentration condition [13,14]. Besides, the polymers lose their mechanical stability and this limits their practical application in PEFCs. Also there is much research related to improving proton conductivity and mechanical strength by ionic cross-linked ionomer. However, it has drawbacks, such as rapidly decreased proton conductivity [15].

Many researchers have made effort to improve mechanical property and to lower methanol permeability while maintaining higher proton conductivity [16,17]. In general, the acid units of these ionomers have been concentrated to specific side chain or to polymer backbone in order to improve the nanophase separation between hydrophilic and hydrophobic domains. So far, there have been several studies on the application of much concentration sulfonated technology. Hay group reported poly(arylene ether)s ionomers with concentrated sulfonic acid segment or end cap [18–20]. Those ionomers had the same level of IECs (1.16 mequiv g^{-1}) as Nafion 117 (0.91 mequiv g^{-1}) and showed the same level of proton conductivity as Nafion 117. Guiver et al. prepared comb-shaped copoly(arylene ether)s ionomers [21–23], which exhibited organized phase-separated morphology with well-connected nanochannels, thus resulting in a dramatic enhancement in proton conductivity under partially hydrated conditions relative to other hydrocarbon-based PEMs. While Jannasch group prepared the poly(ether sulfone)s with highly sulfonated unit in the backbone or side chain [24,25]. These highly sulfonated ionomers were tailored to acquire enhanced proton conductivity, however the methanol resistance of the membranes was put aside. In addition, when sulfonated aromatic polymers serve as PEM in direct methanol fuel cell (DMFC), their methanol permeability is raised to an indispensable role.

Therefore, we aimed at designing concentrated sulfonated aromatic polymers with considerable conductivity and good methanol resistance. The present work reports the synthesis and properties of sulfonated poly(arylene ether ketone) (SPAEK) containing the nonsulfonated moiety and highly sulfonated moiety. The tetrasulfonic-containing segment can enhance sulfonic acid density in hydrophilic phase, and high fluorine-containing hydrophobic segment increases the dimensional stability of the SPAEK membranes. This approach allows a more uniform distribution of sulfonic acid group better precision with targeted IEC, and better control over the length of the statistical nonsulfonated segments, are favorable for hydrophilic/hydrophobic microphase separation morphology.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), toluene, sulfuric acid fuming ($SO_3 > 30\%$) and 4-fluorobenzoyl

chloride were purchased from Shanghai Chemical Reagent Co., Ltd. 4,4'-(hexafluoroisopropylidene)diphenol (6FBPA), 4,4'-difluorobenzophenone (DFDPK), biphenyl and K_2CO_3 were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Other commercially available materials and solvents were used without further purification.

2.2. Synthesis

2.2.1. Synthesis of 4,4'-bis(4-fluorobenzoyl)diphenyl (1)

To a 100 mL round-bottomed flask were added 4-fluorobenzoyl chloride (17.44 g, 0.11 mol), diphenyl (7.7 g, 0.05 mol), anhydrous aluminum chloride (20 g, 0.15 mol), and *o*-dichlorobenzene (60 mL) with stirring under nitrogen at 0 °C. The suspension was stirred at room temperature for 1 h and at 90 °C for 8 h. The reaction mixture was poured into cold aqueous hydrochloric acid, and then the water was decanted off and the residue was washed with water several times. Next, methanol was added to the oily residue to precipitate the solid. Finally, the crude product was recrystallized from DMAc and dried under vacuum at 100 °C to afford 16.9 g of white crystals (1). Yield: 85%; m.p. 267 °C (by DSC).

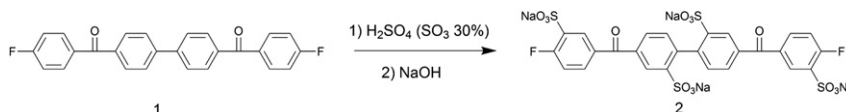
2.2.2. Synthesis of sodium 4,4'-bis(4-fluoro-3-sulfonatobenzoyl)biphenyl-2,2'-disulfonate (SDFDPK)

The synthesis of sulfonated monomer was performed according to a sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) procedure described by Wang et al. [11]. As shown in Scheme 1, 39.8 g (0.1 mol) of 4,4'-bis(4-fluorobenzoyl)diphenyl was dissolved in 30% fuming sulfuric acid (100 mL). The solution was stirred at 110 °C for 6 h, cooled to room temperature, and poured into ice water. Excess NaOH was added to the mixture to neutralize the solution. The mixture was then incubated to room temperature and NaCl was added to precipitate the sulfonated monomer. The sulfonated monomer was finally filtered and dried in an ambient condition. The monomer was then recrystallized for three times using a mixture of ethanol and water. The yield of the sulfonation reaction is around 85%. The chemical structure of sodium 4,4'-bis(4-fluoro-3-sulfonatobenzoyl)biphenyl-2,2'-disulfonate was confirmed by Fourier transform infrared (FT-IR) and 1H NMR spectroscopy. The FT-IR spectrum (KBr substrate, cm^{-1}) shows intense absorption bands at 1646 (C=O stretching), 1033 and 1089 cm^{-1} (asymmetric and symmetric stretching vibrations of sodium sulfonate groups).

The 1H NMR spectrum (500 MHz, DMSO- d_6) shows peaks at $J_{H1} = 8.5$ ppm (d, 8.1 Hz, 2H), $J_{H2} = 8.3$ ppm (d, 1.4 Hz, 2H), $J_{H3} = 8.1$ ppm (m, 8.5 Hz, 4H), $J_{H4} = 7.8$ ppm (m, 2H), and $J_{H5} = 7.4$ ppm (t, 8.6, 9.4 Hz, 2H) where H_1 – H_5 respectively represent the hydrogen atoms of the sulfonated monomer labeled in Fig. 1. These spectroscopic results confirm the formation of the sulfonated monomer.

2.2.3. Synthesis of SPAEK- x

A typical polymerization of SPAEK- x (x is the mole ratio of sulfonated moiety in a molecular chain) is shown in Scheme 2. As an example, the synthesis of SPAEK-20 is described as follows. To a round-bottomed flask equipped with a Dean-Stark trap and mechanical mixture, DFDPK (0.004 mol, 0.8728 g), 6FBPA (0.005 mol, 1.6812 g), SDFDPK (0.001 mol, 0.8066 g), and K_2CO_3 (0.0055 mol, 0.7590 g) were charged. Then DMSO (10 mL) and



Scheme 1. Synthesis of sulfonated monomer (SDFDPK).

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