



Preparing alkaline anion exchange membrane with enhanced hydroxide conductivity *via* blending imidazolium-functionalized and sulfonated poly(ether ether ketone)



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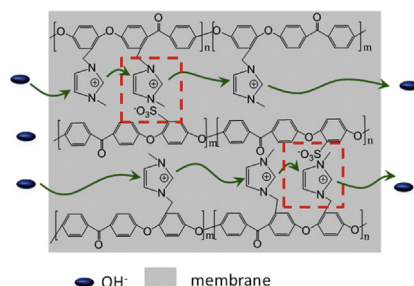
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HIGHLIGHTS

- Alkaline anion exchange membranes were prepared by blending ImPEEK and SPEEK.
- IEC of the alkaline anion exchange membranes with was up to 3.15 mmol g⁻¹.
- Hydroxide conductivity up to 31.59 mS cm⁻¹ was obtained at 30 °C.
- Physical, thermal and alkaline stabilities of membranes are elevated.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of alkaline anion exchange membrane (AEM) with both high ion conductivity and stabilities is of great significance for fuel cell applications. In this study, a facile acid-base blending method is designed to improve AEM performances. Basic imidazolium-functionalized poly(ether ether ketone) with a high functionalization degree is employed as polymer matrix to pursue high ion-exchange capacity (IEC) as well as high hydroxide conductivity, meanwhile acidic sulfonated poly(ether ether ketone) (SPEEK) is employed as the cross-linking agent to enhance the stabilities of the blend membranes. Particularly, an *in-situ* Menshutkin/crosslinking method is exploited to prevent the flocculation in the preparation process of blend membranes. As a result, dense and defect-free blend membranes are obtained. The blend membranes exhibit high level of IEC up to 3.15 mmol g⁻¹, and consequently possess elevated hydroxide conductivity up to 31.59 mS cm⁻¹ at 30 °C. In addition, benefiting from the strong electrostatic interaction introduced by the acid-base blending, the stabilities and methanol resistance of blend membranes are enhanced.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are considered as promising candidates of clean energy for many situations because of

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their excellent properties, like high efficiency, low pollution and so forth [1–4]. Till now, majority of efforts have been devoted to the development of PEFCs based on proton exchange membranes (PEMs) [5–7]. However, because of the strong acidic operating conditions of PEMs, only some noble metal-based catalysts are stable in these acidic operating conditions, which hamper the broad commercialization of PEFCs. As an alternative solution, alkaline anion exchange membrane fuel cells (AEMFCs) have been developed and drawn enormous attention in recent years [8–10]. Owing to the alkaline operating condition, AEMFCs can get rid of the dependency on noble metal-based catalysts [11]. Alkaline anion exchange membrane (AEM), is the heart of AEMFC, and its development faces the following two challenges: 1) the ion conductivity of AEM is lower than that of PEM duo to the low inherent hydroxide ion mobility ratio; 2) the alkaline stability of AEM in alkaline condition are often poor [12–14].

The ion conductivity of AEM is usually governed by three factors: 1) the amount of charge carriers in unit volume (the ion-exchange capacity, IEC); 2) the ionic mobility of charge carriers; and 3) the morphology of ion channels [15,16]. Increasing the IEC of membrane has been demonstrated as a feasible way to enhance the hydroxide conductivity of AEMs. When utilized as the matrix of AEMs, most of functional polymers exhibited a positive correlation between IEC and hydroxide conductivity [3,17–19]. The high IEC can be easily acquired from high functionalization degree (FD) of polymers. However, high FD usually accompany with the worse stability, e.g. excessive area swelling, dissolution in water environment [20,21]. Therefore, it is crucial to explore a facile and practical strategy to simultaneously solve the above problems. Acid–base blending should be an appropriate choice considering its successful application in PEMs and the similarity between AEMs and PEMs [22–24]. Benefiting from the electrostatic interaction brought by the acid–base blending, the intermolecular forces of polymer chains are enhanced, and the stabilities of membranes can be improved significantly. Besides, the electrostatic attractions within the anion–cation pairs can induce an optimum orientation of water networks, which contributes to the formation of hydrogen-bonding networks for the facile immigration of proton and hydroxide ion [25,26].

In this study, AEMs with high IEC and stabilities were prepared by blending basic imidazolium-functionalized poly(ether ether ketone) (ImPEEK) and acid sulfonated PEEKs (SPEEK) via an *in-situ* Menshutkin/crosslinking method. The interaction between ImPEEK and SPEEK and the structure of the blend membranes were characterized by X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and differential scanning calorimetry (DSC). Subsequently, the blend membranes were evaluated in terms of hydroxide conductivity, methanol permeability, and chemical and physical stabilities. Meanwhile, for estimating the performances improvements offered by this study, control membranes consisted of ImPEEK with 94% FD was fabricated as comparison.

2. Experimental

2.1. Materials

1-methylimidazole (analytical reagent, 99.9 wt %) and dimethyl formamide (DMF, analytical reagent, 99.9 wt %) were purchased from J&K Scientific Ltd. N-octyl alcohol (analytical reagent, 99.9 wt %), paraformaldehyde (analytical reagent, 99.9 wt %), and N-methyl-2-pyrrolidone (NMP, analytical reagent, 99.9 wt %) were purchased from Shanghai Aladdin-reagent Ltd. Concentrated sulfuric acid (analytical reagent, 98.2 wt %), standard aqueous hydrochloric acid (analytical reagent, 0.1 mol L⁻¹) and standard

aqueous sodium hydroxide (analytical reagent, 0.01 mol L⁻¹) were purchased from Tianjin Jiangtian Chemical Scientific Ltd. Poly ether ether ketone (PEEK, 450PF) was produced by Victrex[®] England and sold by Guangdong Suangfu Plastic Ltd. All of the aforementioned reagents were used as received, without further purification. All the reagents not mentioned were commercially available with analytical pure degree and used as received and all water was deionized.

2.2. Sulfonation of PEEK

28 g PEEK was dissolved sufficiently in 200 mL concentrated sulfuric acid at 0 °C. Then, the temperature was raised to 50 °C for a certain time to obtained desired degree of sulfonation (DS). The SPEEKs were precipitated by pouring the reaction solutions into abundant water, purified by flowing water until neutral pH and dried under vacuum.

2.3. Chloromethylation of PEEK

PEEK was chloromethylated using chloromethyl octyl ether (CMOS) as chloromethylation reagent based on Blanc-chloromethylation reaction. The CMOS was prepared by bubbling hydrogen chloride into the mixture of paraformaldehyde, n-octanol, and chloroform, as reported in literature [27]. 8 g PEEK was sufficiently dissolved in 480 mL concentrated sulfuric acid at –10 °C. Then, 40 mL fresh CMOS was added and the temperature was raised to 0 °C. The reaction lasted a certain time to obtain specified FD [17]. Chloromethylated PEEK (CMPEEK) was precipitated by pouring the reaction solution into abundant water, and subsequently washed by ethanol (EtOH) until no sulfonated acid and octanol left. For further purification, the raw CMPEEK was redissolved in methyl-2-pyrrolidinone (NMP) to obtain a 10 wt. % solution and reprecipitated in cold EtOH. The purified CMPEEK was dried at room temperature under vacuum until constant weight was achieved and stored at –10 °C, which was designated as CMPEEK-X, where X is the FD of polymers. Similarly, the corresponding ImPEEK was designated as ImPEEK-X, as shown in Scheme 1 and Table 1.

2.4. Preparation of blend membranes

Because the basic ImPEEK and acid SPEEK bears opposite charges in their chains, serious flocculation will occur when we directly mix them with each other, which make the mixture unsuitable for fabricating membrane. Thus, to solve this problem, an *in-situ* Menshutkin/crosslinking method was designed.

A certain amount of CMPEEK was dissolved in 4.25 mL dimethyl formamide (DMF), and a certain amount of SPEEK was dissolved in 4 mL 1-methylimidazole. Then, these two solutions were mixed quickly under vigorous stirring and cast onto glass plates. The mixtures were firstly placed at 40 °C for 2 h and 60 °C for 24 h. During this period, CMPEEK could react with 1-methylimidazole to form ImPEEK based on Menshutkin reaction, and the produced ImPEEK could be cross-linked by SPEEK. Next, the temperature was raised to 80 °C for another 24 h to volatilize the residual DMF and 1-methylimidazole, and blend membranes were presented, which were subsequently peeled off, soaked in 1 mol L⁻¹ aqueous KOH for 48 h to replace Cl⁻ with OH⁻, washed by flowing water for 24 h to remove the residual KOH and dried at room temperature under vacuum. The blend membranes were designated as Im/SPEEK-X-Y, where X represented the type of SPEEK (Table 1 in Results and discussion section), and Y referred to the weight percentage of SPEEK to the blend membrane. The control membrane was formed by ImPEEK with an FD of 94%, and was prepared in the same process. The membrane preparation process was shown in Scheme 1.

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