



A novel imidazolium-based amphoteric membrane for high-performance vanadium redox flow battery



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ABSTRACT

A novel amphoteric membrane was prepared using imidazolium-functionalized polysulfone (ImPSf) as the base polymer and sulfonated poly (ether ether ketone) (SPEEK) as the acid polymer for vanadium flow battery applications. The introduction of the ImPSf effectively resists the migration of vanadium ions owing to the Donnan repelling effect of the imidazolium cations on the vanadium ions and the low swelling ratio of the amphoteric membranes due to the ionic cross-linked interactions between the imidazolium and sulfonic groups. The amphoteric membrane with an ImPSf mass ratio of 17% shows a vanadium permeability of $1.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ that is much lower than that of Nafion212 ($21 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$). Having a high IEC of 2.04 mmol g^{-1} , it also exhibits a low area resistance of $0.48 \Omega \text{ cm}^{-2}$ that is comparable to that of Nafion212 membrane ($0.41 \Omega \text{ cm}^{-2}$). As a result, the VFB cell with the amphoteric membrane exhibits high performances even at high current densities, i.e. at a current density of 200 mA cm^{-2} , and the amphoteric membrane achieves a coulombic efficiency of 97.5% and an energy efficiency of 77.3%, both of which are higher than those of Nafion212 (92.4% and 73.4%). These results indicate that the ImPSf/SPEEK amphoteric membrane is promising for VFB applications.

1. Introduction

All-vanadium flow battery (VFB) pioneered by M.Skylas-Kazacos [1] is one of the most promising energy storage technologies owing to the flexible design, long life cycle, high efficiency, satisfied safety and environmental benignity [2,3]. As a critical component, the ion-selective membrane separates active species in the positive and negative components and meanwhile allows the transport of H^+ , HSO_4^- or SO_4^{2-} ions to maintain electrical neutrality. An ideal membrane in a VFB should possess low vanadium ion permeability, high conductivity, good chemical stability, and low cost [4,5].

Dupont's Nafion® membranes have been frequently employed in VFBs, on account of the high proton conductivity and excellent chemical stability [6]. Nevertheless, their extremely high cost and serious migration of vanadium ions obstructs the large-scale commercialization of VFB [7,8]. The sulfonated non-fluorinated aromatic polymers, such as sulfonated poly (ether ether ketone) (SPEEK) [9–12], sulfonated polyimide (SPI) [13–15], and sulfonated polysulfone (SPSF) [16,17], have attracted many interests due to the low cost, easy preparation and good electrochemical activity in VFB. However, to satisfy high proton conductivity particularly at high current density, the high degree of

sulfonation (DS) was required for sulfonated non-fluorinated aromatic polymer membranes, which usually caused excessive swelling [18]. Thus the vanadium permeability increased, and the VFB performance and the stability decreased [19,20].

The anion exchange membranes (AEMs) with immobilized cations usually have low vanadium ion permeabilities due to the Donnan repelling effect on positive vanadium ions [21,22]. Proton having a very small diameter could penetrate the AEMs, but the proton conductivity is low due to the cations' repelling effect [23]. The cations could promote the transports of the negative HSO_4^- or SO_4^{2-} ions, but their conductivities were also low because of their large dimensions. Thus the low ionic conductivity of AEMs caused low voltage efficiency and energy efficiency of VFBs [24,25]. Recently, the amphoteric membranes with acid-base composite structures have been indicated to have the potential to achieve high conductivity and low swelling ratio [26–28]. In addition, the positively charged base groups in the amphoteric membranes theoretically have the repelling effects on the vanadium ions. The amphoteric membranes with the amine groups (i.e. $-\text{NH}_2$ and $-\text{N}(\text{CH}_3)_2$) as the base groups showed improved VFB performances [29–36]. It seems that the amphoteric membrane would be a promising candidate for the application in the VFB.

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Herein, a novel ImPSf/SPEEK amphoteric membrane was prepared for the VFB by an in-situ Menshutkin/ionic cross-linking method. Compared to the frequently used amine groups, the imidazolium cation could have a stronger ionic cross-linked interaction with sulfonic group which would reduce the swelling ratio of the membrane more efficiently, and also have a higher Donnan repelling effect on the vanadium ions. The swelling ratio, vanadium ions permeability, chemical stability and battery performance of ImPSf/SPEEK amphoteric membranes were comprehensively investigated. The introduction of ImPSf effectively resists the migration of vanadium ions, leading to low vanadium permeability. In addition, ImPSf/SPEEK amphoteric membrane shows high ionic conductivity owing to the existence of abundant free sulfonic acid groups. As a result, the ImPSf/SPEEK amphoteric membrane exhibits high battery performance even at high current densities.

2. Experimental

2.1. Materials

Poly (ether ether ketone) (VESTAKEEP® 4000P) powder and Udel P3500 polysulfone (PSf) were obtained from Evonik Degussa (China) Co. Ltd. Chloromethyl octylether (CMOE) was synthesized according to the Ref [37]. Concentrated sulfuric acid (analytical reagent, 98 wt%), 1-methylimidazole (MIm), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), ethyl acetate, ethyl alcohol and chloroform were purchased commercially and used as received without further purification. All the chemicals used were analytical purity grade.

2.2. Sulfonation of PEEK

7.5 g PEEK was dried overnight in a vacuum oven at 60 °C. The oven-dried PEEK was added into 150 mL concentrated sulfuric acid at room temperature. After the complete dissolution, the temperature was

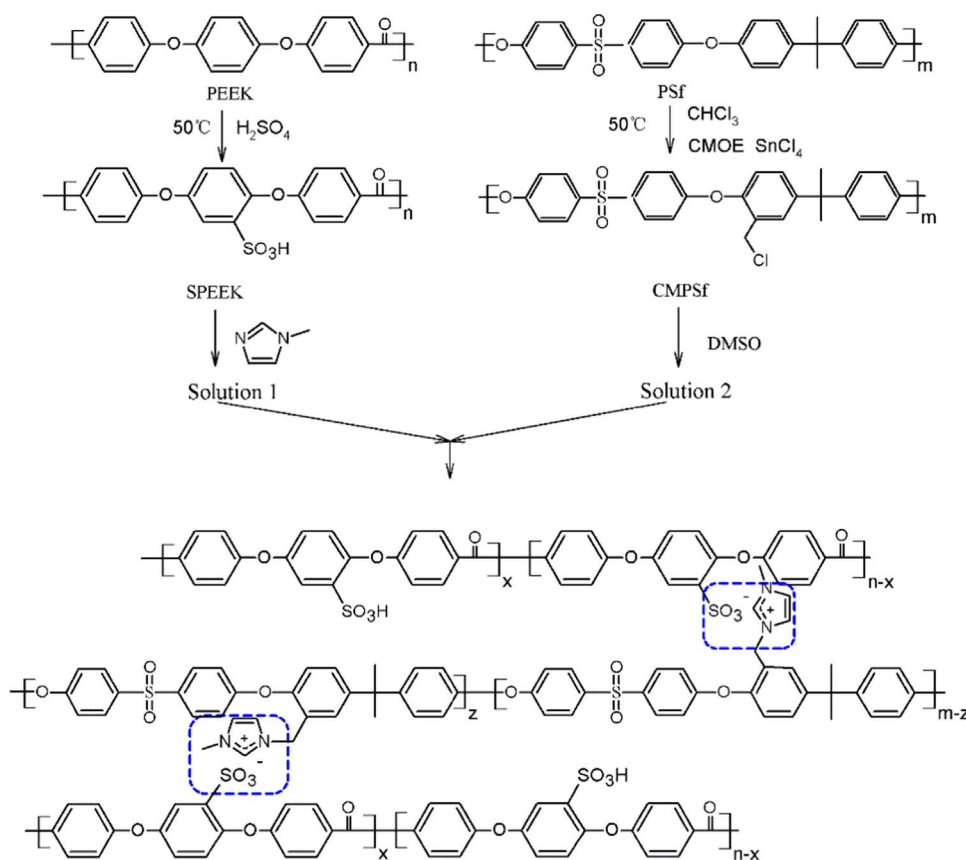
raised to 50 °C and kept for a certain time. The product polymer, SPEEK, was precipitated by pouring the reaction solution into ice-water, and then washed repeatedly until neutral. The solid SPEEK was obtained by drying at 80 °C for 24 h.

2.3. Chloromethylation of PSf

The chloromethylated polysulfone was synthesized using the CMOE as chloromethylating agent, stannic chloride as catalyst, and chloroform as solvent. Specifically, 1 g PSf was dissolved in 50 mL chloroform at 50 °C with stirring, and then 6 mL freshly synthesized CMOE and 0.3 mL stannic chloride was added. The reaction was kept at 50 °C for a certain time. After that, the product polymer, CMPSf, was obtained by precipitation in ethanol, filtration and washing with ethanol several times, and then drying in vacuum at 50 °C for 24 h. The chemical structure and synthetic process of the CMPSf are shown in Scheme 1.

2.4. Preparation of amphoteric membranes

Different mass ratio CMPSf and SPEEK (total mass: 0.2 g) were dissolved in 3 mL dimethyl sulfoxide (DMSO) and 4 mL 1-methylimidazole, respectively. Then, these two solutions were mixed together under vigorous stirring and cast the mixed solution onto a glass plate. The mixture was placed at 60 °C for the first 24 h to conduct the Menshutkin reaction of CMPSf and 1-methylimidazole according to the work [38]. Next, the temperature was raised to 80 °C for another 24 h to volatilize the residual DMSO and 1-methylimidazole. The dried membrane was peeled off from the substrates, soaked in 1 mol L⁻¹ H₂SO₄ aqueous solution for 24 h, and then immersed in deionized water for 24 h to remove the residual H₂SO₄. The membrane preparation procedure is shown in Scheme 1.



Scheme 1. Preparation procedure of amphoteric membranes.

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