



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A novel branched side-chain-type sulfonated polyimide membrane with flexible sulfoalkyl pendants and trifluoromethyl groups for vanadium redox flow batteries

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HIGHLIGHTS

- A branched side-chain-type sulfonated polyimide membrane (6F-s-bSPI) is prepared.
- The 6F-s-bSPI membrane possesses a very low vanadium ion permeability.
- The 6F-s-bSPI membrane shows excellent proton selectivity and chemical stability.
- The VRFB assembled with the 6F-s-bSPI membrane exhibits high efficiencies.
- The 6F-s-bSPI membrane maintains a stable cycle performance in VRFB applications.

ARTICLE INFO

Article history:

Received 30 September 2016

Received in revised form

11 February 2017

Accepted 14 February 2017

Keywords:

Branched side-chain-type sulfonated polyimide
Membrane
Proton selectivity
Trifluoromethyl
Vanadium redox flow battery

ABSTRACT

A novel branched side-chain-type sulfonated polyimide (6F-s-bSPI) membrane with accessible branching agents of melamine, hydrophobic trifluoromethyl groups ($-\text{CF}_3$), and flexible sulfoalkyl pendants is prepared by a high-temperature polycondensation and post-sulfonation method for use in vanadium redox flow batteries (VRFBs). The chemical structure of the 6F-s-bSPI membrane is confirmed by ATR-FTIR and ^1H NMR spectra. The physico-chemical properties of the as-prepared 6F-s-bSPI membrane are systematically investigated and found to be strongly related to the specially designed structure. The 6F-s-bSPI membrane offers a reduced cost and possesses a significantly lowered vanadium ion permeability ($1.18 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) compared to the linear SPI ($2.25 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) and commercial Nafion 115 ($1.36 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$) membranes, prolonging the self-discharge duration of the VRFBs. In addition, the VRFB assembled with a 6F-s-bSPI membrane shows higher coulombic (98.3%–99.7%) and energy efficiencies (88.4%–66.12%) than that with a SPI or Nafion 115 membrane under current densities ranging from 20 to 100 mA cm^{-2} . Moreover, the VRFB with a 6F-s-bSPI membrane delivers a stable cycling performance over 100 cycles with no decline in coulombic and energy efficiencies. These results show that the branched side-chain-type structure is a promising design to prepare excellent proton conductive membranes.

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1. Introduction

The vanadium redox flow battery (VRFB) with the attractive features of long cycle life, high safety and reliability, excellent efficiencies, and environmental friendliness has become one of the most promising techniques for large-scale energy storage [1–4]. As

a critical component of VRFBs, the proton conductive membrane provides a barrier against the crossover between positive and negative electrolytes and maintains the charge balance during the operation of VRFBs [5,6]. Although the perfluorosulfonic membranes (such as Nafion membranes) have superior chemical stability and high proton conductivity [7–9], the low proton selectivity and unaffordable cost (e.g., \$500–\$700 m^{-2} for Nafion membranes) have hampered their widespread commercial application in VRFBs [10]. Over the past decade, many kinds of sulfonated aromatic polymer membranes have been prepared and

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studied, such as sulfonated poly(ether ether ketone) (SPEEK) [11], sulfonated poly(arylene ether ketone) (SPAEEK) [12], sulfonated poly(phenylsulfone) (S-Radel) [13], sulfonated polyimide (SPI) [14], and sulfonated poly(phthalazinone ether sulfone) (SPPEs) [15]. Among these sulfonated aromatic polymer membranes, the SPI membranes are considered as a promising candidate for VRFB applications because of their lower vanadium ion permeability, better proton selectivity and thermal stability, excellent VRFB performance, and lower cost compared with the Nafion membranes [14,16]. However, the relatively low chemical stability of the SPI membranes is a major obstacle for their commercial application in VRFBs. Therefore, the effective improvement of the chemical stability of SPI membranes is eagerly pursued. In previous work, a series of SPI membranes with different molecular structures was synthesized by a one-step high-temperature polycondensation reaction from the dianhydride monomers, sulfonated diamine monomers, and non-sulfonated diamine monomers [14]. These linear SPI membranes with high water uptake and electron density would absorb a large amount of VO_2^+ ions from the electrolytes of VRFBs, accelerating their deterioration. This can be attributed to the direct attachment of the hydrophilic $-\text{SO}_3\text{H}$ groups on the polymer main chain and the absence of strong electron-withdrawing groups in these SPI membranes. Therefore, designing a suitable molecular structure to decrease the water uptake and electron density of the main chain could be an effective route to enhance the chemical stability of the SPI membranes.

As is well known, the chemical stability of the sulfonated aromatic polymer membranes may be improved by branching and/or incorporation of the hydrophobic groups [17,18]. However, the mechanical properties (i.e., tensile strength, elongation at break, and Young's modulus) of the branched membranes are notably decreased and cannot satisfy the requirements of VRFBs. A viable strategy for overcoming the mechanical disadvantages is to introduce flexible side chains into the branched membranes, which could help to improve their mechanical properties by increasing the entanglement of the polymer chains. To date, a variety of branched and/or side-chain-type sulfonated polymer membranes with excellent chemical stability have been reported. B. Yin et al. [19] synthesized a highly branched sulfonated poly(flourenyl ether ketone sulfone)s (HSPAEEK) membrane with a degree of branched (DB) value of 8% by the introduction of 1, 3, 5-tris (4-(4-fluorophenyl sulfonyl) phenyl) benzene as a branching agent. The HSPAEEK membrane exhibited an excellent proton conductivity (33.4 mS cm^{-1}) and chemical stability, but the breaking strength and elongation percentage were only 27.4 MPa and 8%, respectively. Y. Zhang et al. [20] reported a series of branched sulfonated polyimide (bSPI) membranes through adjusting the DB values. They found that the optimum DB was 8% to obtain the bSPI-8 membrane with a superior chemical stability than the linear SPI membrane. However, the vanadium ion permeability of the bSPI-8 membrane ($6.27 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) was slightly higher than the linear SPI membrane ($2.37 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$). H. Xie's group [21] reported that the branched star-shaped sulfonated block poly(arylene ether sulfone)s (SPAES) with sulfoalkyl pendant groups was obtained by a post-sulfonation reaction. N. Asano and coworkers [22] synthesized novel SPI membranes containing aliphatic groups both in the main chain and side chains. They found that the hydrolytic stability of these SPI membranes was effectively improved.

In this study, we have designed and synthesized a branched side-chain-type sulfonated polyimide (6F-s-bSPI) membrane with a novel structure (in Scheme 1) that combines the accessible and inexpensive melamine (as a branching agent), hydrophobic $-\text{CF}_3$ groups (as functional electron-withdrawing groups), and flexible sulfoalkyl pendants (as aliphatic side chains) together. To the best of our knowledge, this novel 6F-s-bSPI structure has not been

reported and is expected to improve the chemical stability and mechanical properties, as well as reduce the vanadium ion permeability of the membrane. The flexible aliphatic side chains could help to increase the entanglement of the polymer chains, and thus improve the mechanical properties of the branched membranes. Besides, the introduction of the hydrophobic groups and branching agents into the polymer main chains could decrease the hydrophilicity and electron density, and thus improve the chemical stability of the 6F-s-bSPI membrane. Compared with other aromatic polymer membranes fabricated via post-sulfonation, a distinctive feature of the 6F-s-bSPI membrane is that half of the $-\text{SO}_3\text{H}$ groups are attached on the main chain of the 6F-s-bSPI by a one-step high-temperature polycondensation reaction, whereas the other half of the $-\text{SO}_3\text{H}$ groups are located at the ends of the aliphatic side chains by the post-sulfonation technique. This 6F-s-bSPI membrane with two kinds of $-\text{SO}_3\text{H}$ groups shows a vanadium ion permeability ($1.18 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) over 10 times lower and an ion exchange capacity (1.54 meq g^{-1}) over 2 times higher compared to Nafion 115 membrane ($1.36 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ & 0.74 meq g^{-1}). The proton selectivity (as a critical parameter of membrane properties) of the 6F-s-bSPI membrane ($1.75 \times 10^5 \text{ S min cm}^{-3}$) is also much higher than both the SPI ($1.01 \times 10^5 \text{ S min cm}^{-3}$) and Nafion 115 ($0.44 \times 10^5 \text{ S min cm}^{-3}$) membranes, resulting in higher efficiencies of the VRFB assembled with the 6F-s-bSPI membrane. Other physico-chemical properties of the 6F-s-bSPI membrane and VRFB single cell performances are also investigated in detail and compared with the linear SPI and commercial Nafion 115 membranes (see Table A.1 in the Appendix for the overall comparison of the SPI, 6F-s-bSPI, and Nafion 115 membranes).

2. Experimental

2.1. Materials

The 1, 4, 5, 8-naphthalenetetra-carboxylic dianhydride (NTDA) was purchased from Beijing Multi. Tech., China. The 4, 4'-diaminobiphenyl 2, 2'-disulphonic acid (BDSA) was bought from Energy Chemical. Co., China. The 4, 4'-oxydianiline (ODA) was from Beshine Chem. Co., China. The 2, 2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (APAF) was from Changzhou Sunlight Pharmaceutical Co., Ltd, China. The 1, 3-propane sultone was bought from Shanghai Aladdin Industry Co., China. The vanadyl sulfate was purchased from Shanghai Huating Chem. Plant, China. The *m*-cresol was obtained from J&K Scientific Ltd, China. The triethylamine (TEA), benzoic acid, dimethyl sulfoxide (DMSO), and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd, China. The Nafion 115 membrane with an original thickness of 125 μm was supplied from DuPont Co., USA. Initially, the Nafion 115 membrane was pretreated in 3.0 wt% H_2O_2 solution at 70 °C for 0.5 h and then taken out and washed with deionized water (D. I. water). Afterwards, the Nafion 115 membrane was immersed in 0.05 mol L^{-1} H_2SO_4 solution at 70 °C for 0.5 h and then taken out and washed with D. I. water [20]. Finally, the pretreated Nafion 115 membrane with a thickness of 120 μm was stored in D. I. water for further use.

2.2. Synthesis of branched sulfonated polyimide (6F-bSPI-OH) polymer

The branched sulfonated polyimide polymer containing branching agents of melamine, $-\text{CF}_3$ groups, and $-\text{OH}$ groups was synthesized through a typical high temperature polycondensation reaction (Scheme 1) [14]. The preparation process is described as follows. 0.6887 g (2.0 mmol) of BDSA, 55.0 mL of *m*-cresol, and

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