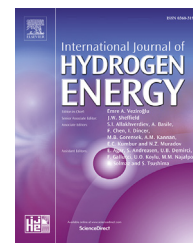




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# A novel long-side-chain sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) membrane for vanadium redox flow battery

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## ABSTRACT

A novel long-side-chain sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (S-L-PPO) membrane was successfully prepared for VRFB applications. The long side chains were introduced onto the PPO backbones by a simple and controllable acylation with 4-fluorobenzoyl chloride and a subsequent condensation with sodium 4-hydroxybenzenesulfonate. The introduction of long side chains drives the formation of a good hydrophilic/hydrophobic micro-phase separation structure, which is evidenced by AFM. The S-L-PPO membrane with a degree of sulfonation (DS) of 51% showed an ultralow vanadium permeability ( $4.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ) and a decent proton conductivity ( $44 \text{ mS cm}^{-1}$ ). As a result, the energy efficiency of VRFB with S-L-PPO-51% membrane was up to 81.8% that was higher than that with Nafion 212 (78.0%) at a current density of  $120 \text{ mA cm}^{-2}$ . In addition, the self-discharge duration of the cell with S-L-PPO-51% membrane was 222 h that was nine times longer than that of Nafion 212 (23 h). All these indicate that the membrane prepared here is promising for the application in VRFB.

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## Introduction

Vanadium redox flow battery (VRFB) has been recognized as a promising energy storage system which has received wide attentions, owing to the long cycle life, high efficiency and energy capacity, good security, rapid response, flexible design, and low cost [1–8]. In VRFB, ion selective membrane is used to separate the vanadium ions at different valence states in positive and negative electrolytes, and also to transport the proton to form an internal circuit [9–11]. An ideal membrane

used in VRFB should have low cost, high proton conductivity, low vanadium ion permeability, and high chemical and mechanical stabilities [12–15].

The perfluorosulfonic acid membranes (etc. DuPont's Nafion series membranes) have been frequently used in VRFB on account of their high proton conductivity and chemical stability [16,17]. Nevertheless, they have drawbacks of high cost and serious vanadium ion permeability [13,18]. Recently, sulfonated aromatic polymers, such as sulfonated poly(sulfone) (SPSf) [19,20], sulfonated poly(ether ether ketone) (SPEEK) [21,22], sulfonated polyimide (SPI) [23], sulfonated

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poly(arylene ether ketone) (SPAEEK) [24], sulfonated poly(phthalazinone ether sulfone) (SPPEs) [25], sulfonated poly(fluorenyl ether ketone) (SPFEK) [26], sulfonated poly(arylene ether sulfone) (SPAES) [27], have been developed as the alternative membrane materials for the applications in VRFB, owing to their low cost and reduced vanadium ion permeability. In general, it is hard for sulfonated aromatic polymer membranes to form a good hydrophilic/hydrophobic micro-phase separation structure due to the poor mobility of the hydrophilic sulfonic acid groups which are directly linked onto the rigid polymer backbone [28]. In order to achieve high proton conductivity, a high ion exchange capacity (IEC) is required to absorb enough water which is necessary for continuous proton transport channels [29,30]. Unfortunately, a large swelling ratio is also induced, which unexpectedly causes reduced mechanical properties and enhanced vanadium ions' crossovers [31,32]. Therefore, a large number of researchers have been focused on increasing proton conductivity of these membranes at low IEC, mainly by introducing sulfonic acid group onto the long side chains of the polymer backbone. The long chain between sulfonic acid and the polymer backbone would increase the mobility of the sulfonic acid groups and thus promote the aggregation of sulfonic acid groups, which could improve the hydrophilic/hydrophobic micro-phase separation structure in the membrane [32–36].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an engineering plastics with excellent performance including good mechanical properties, thermal and chemical stability. To our best knowledge, there are few reports on PPO-based membrane for VRFB application. In this work, a novel long-side-chain sulfonated PPO membrane was prepared. The sulfonic acid terminated long side chains are introduced onto the PPO backbone by the acylation with 4-fluorobenzoyl chloride and the subsequent condensation with sodium 4-hydroxybenzenesulfonate. The introduction of the long side chains between the sulfonic acid groups and polymer backbone would increase the mobility of the sulfonic acid groups, thus promoting their aggregation. It is favorable to the formation of hydrophilic/hydrophobic micro-phase separation structure, increasing the proton conductivity. The properties and cell performances of long-side-chain sulfonated PPO membrane were investigated.

## Experimental

### Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, GFN2-701) was obtained from SABIC Innovative Plastics (USA), with a molecular weight of about 50,000. Aluminum chloride anhydrous, 4-fluorobenzoyl chloride, ethanol, sodium 4-hydroxybenzenesulfonate, potassium carbonate, ethyl acetate, methanol, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and N,N-dimethylacetamide (DMAc) were commercially obtained and used as received without further purification. All the used chemicals in the experiments were analytical grade. Dichloroethane was dried over molecular sieves before use.

### Membrane preparation

The long-side-chain sulfonated PPO (S-L-PPO) was synthesized by the Friedel-Crafts acylation with 4-fluorobenzoyl chloride and the subsequent condensation with sodium 4-hydroxybenzenesulfonate. Firstly, the 4-fluorobenzoylated PPO was synthesized by Friedel-Crafts acylation reaction of PPO and 4-fluorobenzoyl chloride according to the Ref [37]. 3 g PPO was dissolved in 25 ml dichloroethane to form a PPO solution in a 50 ml round-bottom flask under vigorous stirring. 2.4 g of anhydrous aluminum chloride was added into 25 ml dichloroethane with stirring in a three-neck flask under nitrogen. The three-neck flask was placed in an ice/water bath, then 1.83 ml 4-fluorobenzoyl chloride was added dropwise into the stirring solution. After that, the PPO solution was added into the three-neck flask, and the reaction mixture was stirred at 60 °C for 10 h. The final 4-fluorobenzoylated PPO (PPO-COC<sub>6</sub>H<sub>4</sub>-F) was obtained by depositing the reaction solution into ethanol, followed by drying at room temperature under vacuum. Then 1.2 g PPO-COC<sub>6</sub>H<sub>4</sub>-F, 2.25 equiv of sodium 4-hydroxybenzenesulfonate, and 3 equiv of K<sub>2</sub>CO<sub>3</sub> were dissolved into 30 ml NMP with vigorous stirring under nitrogen. The water produced in the reaction was taken away by bubbling, then the solution was heated to 140 °C and kept for 96 h. After cooling to room temperature, the S-L-PPO polymers were obtained by depositing the reaction solution in ethyl acetate and drying at 30 °C under vacuum.

0.2 g S-L-PPO was dissolved into DMSO to form a transparent solution. The solution was cast onto a clean glass plate, and the membranes were peeled off after drying at 60 °C for 48 h. Then the membranes were immersed in 1 M H<sub>2</sub>SO<sub>4</sub> solution for 24 h, and soaked in deionized water for another 24 h to remove the residual acid. The membranes were stored in deionized water prior to test. The membranes were denoted as S-L-PPO-xx%, where xx% was the degree of sulfonation (DS) of S-L-PPO. The membrane synthetic procedures are shown in Fig. 1.

### <sup>1</sup>H NMR

<sup>1</sup>H NMR spectroscopy was used to confirm the acylation and the later sulfonation of PPO; <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III HD 500 spectrometer at a resonance frequency of 500 MHz using CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as the solvent. Tetramethylsilane (TMS) was used as an internal standard in all cases. The degree of acylation (DA) of PPO-COC<sub>6</sub>H<sub>4</sub>-F was calculated from the <sup>1</sup>H NMR peak areas:  $DA = 3A(H_4)/A(H_2)$ , where A(H<sub>4</sub>) and A(H<sub>2</sub>) are the integral area of the H<sub>4</sub> peak and H<sub>2</sub> peak in Fig. 2(a), respectively. The degree of sulfonation (DS) of S-L-PPO was calculated from the <sup>1</sup>H NMR peak areas:  $DS = 3A(H_{4,6})/2A(H_2)$ , where A(H<sub>4,6</sub>) and A(H<sub>2</sub>) are the integral area of the H<sub>4,6</sub> peak and H<sub>2</sub> peak in Fig. 2(b), respectively.

### Ion exchange capacity (IEC)

The IEC of the membrane was tested by titration method. The dry membranes were immersed in the 1 M NaCl solution for 24 h to replace all the fixed H<sup>+</sup> of the membrane into the NaCl solution. This solution was titrated by 0.01 M NaOH standard

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