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# Amphoteric ion exchange membrane synthesized by direct polymerization for vanadium redox flow battery application

Yufei Wang<sup>a</sup>, Shuanjin Wang<sup>a,\*</sup>, Min Xiao<sup>a</sup>, Shuqin Song<sup>a</sup>,  
Dongmei Han<sup>a</sup>, Michael A. Hickner<sup>b</sup>, Yuezhong Meng<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Optoelectronic Materials and Technologies/The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen University, Guangzhou 510275, PR China

<sup>b</sup> Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

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## ABSTRACT

Novel sulfonated poly (fluorenyl ether ketone) with pendant quaternary ammonium groups (SPFEKA) was successfully synthesized by one-pot copolymerization of bis(4-fluoro-3-sulfophenyl)sulfone disodium salt, 4,4'-difluorobenzophenone, bisphenol fluorene and 2,2'-dimethylaminemethylene-9,9'-bis(4-hydroxyphenyl) fluorene (DABPF). The chemical structures were confirmed by FT-IR, and <sup>1</sup>H NMR. The thermal properties were fully investigated by TGA. The synthesized copolymers SPFEKAs are soluble in aprotic solvents, and can be cast into membranes on a glass plate from their N,N'-dimethylacetamide (DMAc) solution. A new kind of amphoteric ion exchange membrane (AIEM) was obtained by immersed SPFEKA into 1 M sulfuric acid. The proton conductivities of these membranes are comparable to the most reported sulfonated polymers under the same conditions. The permeability of vanadium ions in vanadium redox flow battery (VRB) was effectively suppressed by introducing quaternary ammonium groups for Donnan exclusion effect. AIEM-20% possess a only 4.4% vanadium ion permeability of Nafion 115. Cell performance tests showed that the VRB assembled with AIEM-20% shows the highest coulombic efficiency (CE) at the current density of 50 mA/cm<sup>2</sup>, because of its lowest VO<sup>2+</sup> permeability. In conclusion, these ionomers could be promising candidates for ion-exchange membranes for VRB applications.

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## Introduction

Since the vanadium redox flow battery (VRB) was proposed by Skyllas-Kazacos and Sum in 1985 as candidates for stationary

energy storage facilities, it has attracted extensive attention for its long cycle, flexibility in design, fast response time, deep-discharge capability and high energy efficiency [1–3]. As one of the most important components of VRB, ion exchange membrane (IEM) should possess high proton conductivity, low

\* Corresponding authors.

E-mail addresses: [wangshj@mail.sysu.edu.cn](mailto:wangshj@mail.sysu.edu.cn) (S. Wang), [mengyzh@mail.sysu.edu.cn](mailto:mengyzh@mail.sysu.edu.cn) (Y. Meng).

vanadium ion permeability, good chemical stability and low cost [4,5]. Consequently, researches on exploiting IEMs with improved properties are of great importance to the large-scale application of VRB. However, some commercial membranes cannot meet all of the requirements. Daramic membrane which chosen for its low cost and reasonable chemical stability exhibits high permeability and low coulombic efficiency [6]. Nafion membrane (DuPont, USA) which used for its high proton conductivity and excellent chemical stability suffers from high permeability of vanadium ions as well as high price [5]. Nowadays, there are many researches on the development of suitable and stable membrane for VRB application.

Cationic exchange membranes exhibit high conductivity and higher energy efficiency but are difficult to prevent the permeation of vanadium ions [7]. Owing to Donnan exclusion effect, anionic exchange membranes exhibit lower vanadium ion permeability but are simultaneously restricted by lower conductivity which results in the sacrifice of voltage efficiency of the battery [5,8]. Therefore, it is necessary to exploit a novel IEM with high conductivity and low vanadium permeability. The amphoteric ion exchange membrane (AIEM) with both cation and anion exchange capabilities has potential applications in many fields since it was first proposed by Sollner in 1932 [9]. Luo et al. coated PEI on Nafion membranes via interfacial polymerization [10]. Zeng et al. reported polypyrrole modified on the surface of Nafion membranes [11]. And Xi et al. used the layer-by-layer self-assembly technique to fabricate a barrier layer onto the surface of Nafion membrane [12]. All these methods can introduce anion exchange groups onto Nafion membrane to reduce permeability of vanadium ions. Zhai's group prepared a series of AIEM via a handy radiation grafting approach to obtain quaternary ammonium salt group and by sulfonation to get sulfonic group [13–16]. It showed that these amphoteric membranes exhibited lower vanadium ion permeability, as well as higher coulombic efficiency and energy efficiency and maintain a rather high conductivity.

In our previous work, many sulfonated aromatic polymers have been synthesized, which demonstrated high proton conductivity and chemical stability [17–19]. In this paper, we report the facile synthesis of amphoteric ion exchange ionomers with pendant quaternary ammonium groups by one-pot direct polymerization method to decrease the vanadium ion permeability. The advantage of this method is the amount of quaternary ammonium groups and sulfonic acid group could be controlled precisely by adjusting the feed ratio of comonomers. The ion exchange capacity (IEC), proton conductivity, water uptake, swelling ratio, thermal stability, oxidative stability,  $\text{VO}^{2+}$  permeability, selectivity (S) of the membranes and cell performance were investigated to illustrate the structure–property relationship of the synthesized polymers and to develop novel AIEM for vanadium redox flow battery application.

## Experimental

### Materials

4,4'-Difluorobenzophenone (purity > 99%) was purchased commercially from Aldrich. Bisphenol fluorene (purity > 98%) was purchased from Tokyo Kasei Kogyo Co. Ltd (TKI).

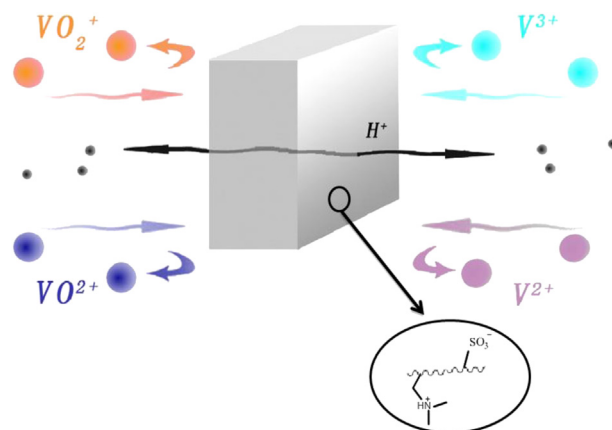
Anhydrous cesium carbonate was purchased from Aladdin.  $\text{VO}_2 \cdot x\text{H}_2\text{O}$  was purchased from Shanghai Luyuan Fine Chemical Plant, China. Dimethyl sulfoxide (DMSO), N,N'-dimethylacetamide (DMAc), N,N'-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), 2-propanol, chloroform ( $\text{CHCl}_3$ ), toluene, methanol, concentrate sulfuric acid (95–98%), hydrochloric acid, sodium hydroxide, magnesium sulfate heptahydrate, ferrous sulfate and aqueous hydrogen peroxide (30%) were obtained from commercial sources. DMSO and toluene were dried with 4 Å molecule sieves and cesium carbonate was dried at 130 °C for 10 h prior to use. Other chemicals were used as received. Bis(4-fluoro-3-sulphophenyl)sulfone disodium salt was synthesized according to a previously reported method [20]. 2,2'-Dimethylaminemethylene-9,9'-bis(4-hydroxyphenyl) fluorene (DABPF) was prepared according to the procedure described in literature [21].

### Synthesis of sulfonated poly (fluorenyl ether ketone) with pendant quaternary ammonium groups (SPFEKA-x)

The typical synthesis procedure of SPFEKA-10% with 10% feed percent of DABPF biphenol is as follows. The synthetic route of SPFEKA-10% is depicted in Scheme 2. To a 50 mL three necked round bottom flask, equipped with a Dean–Stark trap, a nitrogen inlet, a condenser and a magnetic stirrer, 0.4223 g (1 mmol) of bis(4-fluoro-3-sulphophenyl)sulfone disodium salt, 0.2182 g (1 mmol) of 4,4'-difluorobenzophenone, 0.6307 g (1.8 mmol) of bisphenol fluorene, 0.0929 g (0.2 mmol) of DABPF, 0.9774 g (3 mmol) of anhydrous cesium carbonate, 9 mL of DMSO and 10 mL of toluene were introduced. The reaction was first carried out at 120 °C for 3 h to remove the produced water by refluxing toluene. After toluene and water had been distilled off, the temperature was raised to 130 °C and kept at that temperature for 24 h. After cooling down, the resulting viscous mixture was poured into stirred 80 mL methanol/water solution (5:1) to precipitate out the polymer. The yellow fiber-like precipitate was washed with hot water and ethanol several times and dried under vacuum at 80 °C for 24 h. Yield: 94%.

### Membrane preparation and quaternization

The SPFEKA membranes were prepared by casting a viscous solution in N,N'-dimethylacetamide (DMAc) onto a glass plate in a dust-free environment. The thickness of membrane was



Scheme 1 – Schematic principle of AIEM in VRB.

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