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Short communication

Ultra-low vanadium ion diffusion amphoteric ion-exchange membranes for all-vanadium redox flow batteries

J.B. Liao [a, b], M.Z. Lu [a, b], Y.Q. Chu [a, b], J.L. Wang [a, b, *]

[a] State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, PR China
[b] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China

HIGHLIGHTS

- An amphoteric ion-exchange membrane (AIEM) was prepared for VRB.
- A covalently cross-linked AIEM was prepared by addition of a cross-linker.
- AIEMs show impressively low VO^{2+} permeability.
- CE and EE of VRBs with AIEMs are higher than that with Nafion117.

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ABSTRACT

An amphoteric ion-exchange membrane (AIEM) from fluoro-methyl sulfonated poly(arylene ether ketone) bearing content-controlled benzimidazole moiety, was firstly fabricated for vanadium redox flow battery (VRB). The AIEM and its covalently cross-linked membrane (AIEM-c) behave the highly suppressed vanadium-ion crossover and their tested VO^{2+} permeability are about 638 and 1117 times lower than that of Nafion117, respectively. This is further typically verified by the lower VO^{2+} concentration inside AIEM that is less than half of that inside Nafion117 detected by energy dispersive X-ray spectrometry, in addition of the nearly 3 times longer battery self-discharge time. The ultra-low vanadium ion diffusion could be ascribed to the narrower ion transporting channel originated from the acid-base interactions and the rebelling effect between the positively-charged benzimidazole structure and VO^{2+} ions. It is found that, VRB assembled with AIEM exhibits the equal or higher Coulombic efficiency (99.0% *vs.* 96.4%), voltage efficiency (90.7% *vs.* 90.7%) and energy efficiency (89.8% *vs.* 87.4%) than that with Nafion117 and keeps continuous 220 charge–discharge cycles for over 25 days, confirming that the AIEM of this type is a potentially suitable separator for VRB application.

1. Introduction

Sustainable development of the world requires increasing use of renewable energy generated from sources like solar radiation and wind [1]. However, the unstable electricity supply and mismatch between generation and consumption demand large-scale electrical energy storage (EES) system. So far, the most promising large-scale EES technologies are redox-flow batteries (RFBs) that afford to reversibly fulfill the conversion between multi-megawatt-hours (MWhs) of electrical energy and chemical energy [2]. Of the reported RFB systems, the all-vanadium sulfate RFB (VRB) proposed by Skyllas-Kazacos's group is one of the most promising redox systems, for its reduced crossover of active redox species and excellent electro-chemical reversibility et al. [3]. To create a VRB with high energy density, energy efficiency and durability, a high-performance separator is quite required. Up to now, the mostly used separator for VRB is Dupont's Nafion® series,

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* Corresponding author. College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China.
E-mail address: wangjl@zjut.edu.cn (J.L. Wang).

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which features good proton conductivity and long-term chemical stability to the highly oxidative VO_2^+ ions. However, this kind of perfluorinated cation-exchange membranes (CEMs) is high-cost and suffering from a drawback of serious vanadium ion leakage, owing to the facilitating hydrophilic channel assembled by the side sulfonic groups [4]. This cross-contamination of vanadium species between the positive and negative tanks consequently results in the severe capacity decay and an open circle voltage decline of the VRB [2,5].

Currently, alternatives of cost-competitive non-perfluorinated aromatic polymer ion exchange membrane (IEMs) are actively being developed to reduce the vanadium-crossover effect. One important type is the anion-exchange membranes (AEMs) with covalently fixed cationic groups. The key benefit of using AEM is its capacity to highly suppress the permeation rate of vanadium ions for the charge repulsion effect [6]. For example, a recently reported quaternized AEM can achieve the very low vanadium ion diffusion (two orders of magnitude lower than that Nafion115) and Coulombic efficiency (CE) of 98.7–98.9% in VRBs [7]. However, AEM of this type generally shows the intrinsic disadvantage in its conductivity, owing to the fact that the current carriers SO_4^{2-} (or HSO_4^-) ions inside AEM matrix show the much lower mobility than that exclusively H^+ ions in cation-exchange membranes (CEMs) [6,8]. Another type of alternative is the mostly-reported sulfonated aromatic polymer CEMs, which also raises quite high attention due to their desirable proton-conductivity and much lower VO^{2+} permeability than Nafion®. But their resistant capacities to vanadium species and oxidation stability generally cannot be compared to that AEM for the quite different interactions with vanadium species [3]. Amphoteric ion exchange membrane (AIEM), containing both acidic (negative charge) groups and weak basic (positive charge) groups, can be an alternative to achieve an intrinsic conductivity/permeability trade-off [9]. Under VRB operating condition, the positive (basic) groups effectively suppress the positive vanadium species transporting due the Donnan exclusion effect, whereas the negative groups function to provide the desirable proton conductivity [10]. Recently, AIEMs from sulfonated poly(fluorenyl ether ketone)-based or PVDF-based copolymer tethered with quaternary ammonium groups [10,11], and SPEEK/PSf-ABIm or SPEEK/PEI acid-base blends [12,13] have been developed for VRBs. The findings reveal that their VO^{2+} permeability is tens of times lower than that Nafion®, while some of them can achieve the high voltage efficiency (VE) values, which can be compared to or even surpass that Nafion membrane.

In previous work [14–16], we proposed a polyelectrolyte membrane composed of alternating sulfonated poly(arylene ether ketone-benzimidazole) for direct methanol fuel cell (DMFC) application, and found that i) the self-formed acid-base interaction inside an IEM matrix could significantly avoid the micro-phase separation and compact the polymer matrix, thus, greatly hindered the methanol crossover and improved the mechanical, thermal and chemical stability; ii) the base benzimidaole moiety in the backbone avoided the drawbacks of Hoffman degradation [17,18] and the toxic trimethylamine (TMA)-enabled post-quaternization [6,19,20].

In this work, we intend to synthesize the sulfonated fluoromethyl poly(arylene ether ketone)s bearing content-controllable base benzimidazole moieties, and fabricate a desirable AIEM for VRB. Hereof, we can expect an ultra-low vanadium ion diffusion AIEM for its compact structure that originated from the self-assembly ionic cross-linking, in addition of a special interaction with vanadium species in the acid environment provided by the weak base moiety. Meanwhile, it is expected an enhanced chemically and mechanically stable AIEM because of the introduced anti-oxidative $-CF_3$ groups and the repulsion effect between the charged benzimidaozle structure and positive vanadium species. Thus, it is believed that these combined benefits could make the quite remarkable membrane characteristics and stable VRB performance.

2. Experimental

2.1. Materials

4,4′-difluorobenzophenone (DFBP) and 2,2′-bis(4-hydroxyphenyl)hexafluoropropane (6F-BPA) were respectively purchased from Jintan Songsheng Medical and Chemical Co. Ltd. and Sinopharm Chemical Reagent Co. Ltd. Sulfonated 4,4′-difluorobenzophenone in a salted form (SDFBP-Na) was obtained by sulfonation of DFBP in our lab, and 5,5′-bis[2-(4-hydroxyphenyl) benzimidazole] (HPBI) was synthesized according to the literature [14]. $VOSO_4 \cdot nH_2O$ (s), where n = 3.5, was purchased from Shanghai Huating Chemical Co. Ltd. (China). $MgSO_4$ and H_2SO_4 (98%) and some other materials were used as received.

2.2. Polymer synthesis

The synthetic route was according to our previous work [16] and the structure is shown in Fig. 1. For *m*SPAEK-6F-*co*-x%BI, *m* denotes the mole percent of SDFBP-Na with respect to the total amount of difluorobenzophenone monomers (amount of DFBP and SDFBP), while x% is referring to the mole percent of HPBI with respect to the total bisphenols (amount of 6F-BPA and HPBI) in the feed (see Supplementary Data). In this case, *60*SPAEK-6F, *60*SPAEK-6F-*co*-10% BI and *60*SPAEK-6F-*co*-20%BI are synthesized, where *60* is an optimal value that could achieve a desired proton conductivity based on our work the former is used for comparison [13–15,21].

2.3. Membrane preparation

Membrane preparation was according to our previous work [16] and it was detailed in Supplementary Data. Here, typically as shown in Fig. 2, a covalently cross-linked AIEM (*60*SPAEK-6F-*co*-10%BI-*cld*) was prepared from a polymer solution (e.g. 0.5 g *60*SPAEK-6F-*co*-10%BI-Na in 10 mL DMAc) containing 0.0204 g *p*-xylylene dichloride (PXD) by the solvent evaporation method [16]. The weight of cross-linker PXD was calculated according to the amount of benzimidazole moiety in polymer.

2.4. Polymers and membranes characterization

2.4.1. ^1H NMR

Chemical structure of polymer was analyzed by ^1H NMR (Bruker AVANCE 500 MHz) using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethyl silicane (TMS) as standard.

2.4.2. Ion exchange capacity (IEC)

In view of specific interaction between acid and base moieties, the IEC was measured by the method reported by our previous work [16].

2.4.3. Vanadium ion (VO^{2+}) permeability

VO^{2+} permeating through membrane was determined by an in-house diffusion cell that consists of two compartments separated by IEMs. A solution of 1.5 M $VOSO_4$ in 3.0 M H_2SO_4 was filled in right side of the cell, and 1.5 M $MgSO_4$ in 3.0 M H_2SO_4 was added in the left side for balancing the osmotic pressure between the two sides of the IEM. A magnetic stirring was applied in each compartment to ensure uniformity. And the diffusion cell is immersing in the water