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Quaternized membranes bearing zwitterionic groups for vanadium redox flow battery through a green route

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ABSTRACT

Novel quaternized membranes with zwitterionic groups applied in all-vanadium redox flow battery (VRB) have been prepared using a solvent free strategy, which is environmentally-friendly and different from traditional methods using organic solvents as reaction media. It was performed by dissolving cardopolyetherketone (PEK-C) in monomers mixture of 4-vinylbenzyl chloride (VBC) and divinylbenzene (DVB), and then *in situ* polymerization to incorporate PEK-C into the network of poly (VBC–DVB). The resulting copolymer was immersed in dimethylamine (DMA) followed by 1,3-propane sultone (PS) aqueous solution to obtain the target quaternized membranes bearing zwitterionic groups ($[-\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-]$), which greatly enhance the chain packing density, and consequently improve membrane stability. The optimized quaternized membrane with zwitterionic groups showed a 20% decrease in vanadium ion permeability as compared to the benchmark quaternized membrane without zwitterionic groups. It also possesses good mechanical strength even after immersion in VO^{2+} solution for as long as 20 days. Comparing the commercial Nafion117 with the optimized membrane, the vanadium ion permeability sharply decreased from $10.80 \times 10^{-5} \text{ cm min}^{-1}$ to $0.21 \times 10^{-5} \text{ cm min}^{-1}$ while the coulombic and energy efficiency increased from 89.7% and 68.3% to 97.1% and 73.4% at 50 mA cm^{-2} , respectively. The present quaternized membrane with zwitterionic groups shows good characteristics for application in VRBs.

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1. Introduction

The all-vanadium redox flow battery (VRB) can potentially bridge the gap between power generations and demand. Hence inexpensive and yet-abundant solar/wind power can be efficiently reaped by using such large-scale power conversion system [1,2]. VRB has recently attracted considerable research interest because of several attractive features including long lifetime, simple design, and capability to withstand fluctuating power supply. Most importantly, it employs four different oxidation states to form two redox couples separated by ion exchange membranes (IEMs) with only one active element. This configuration results in significant mitigation of cross-over contamination [3,4]. Despite its compelling merits, commercialization of VRBs is still hampered by technical and economic barriers (e.g., long-term operation stability and low cost), and both of these challenges are largely associated with IEMs [5–7], which are always required to possess high ionic conductivity, low vanadium ion permeability and good chemical stability.

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Until now, commercial cation exchange membranes, like Dupont's Nafion®, have been widely used as the state-of-the-art IEMs for VRB. However, the extremely high cost and relatively high vanadium ion permeability have limited commercialization of VRB [8]. To reduce the permeability of vanadium ion through the membrane, researchers have pay attention to anion exchange membranes (AEMs) as they exhibit lower vanadium permeability due to the Donnan exclusion effect. Among them, quaternized hydrocarbon membranes containing quaternary ammonium groups are the most representative polyelectrolyte for VRB [9–13]. Even though the vanadium ion permeability can be effectively reduced; the conflict between high ionic conductivity and adequate stability of ion exchange membranes is still difficult to overcome. That is, membranes with large concentrations of ion exchange groups normally show poor stability because of excessive swelling caused by water absorption [14].

Zwitterionic polymers containing both anionic and cationic groups in the same repeat unit are specific ion exchange materials. Initially, most studies of zwitterionic polymers focused on their biocompatibility and applications as porous membranes [15,16]. It is found that the two different charged groups can create a large dipole moment and show good stability over a wide range of temperatures because of the enhanced chain–chain interactions and decreased fractional free volume. Recently, zwitterionic polymers

have been investigated for application as polyelectrolytes. MacFarlane et al. reported a zwitterionic ionic liquid system with Li^+ conductivities up to seven times larger than the pure polyelectrolyte [17]. Zhang and co-workers prepared a new class of sulfonated poly (aryl ether sulfone)s with zwitterionic groups by copolycondensation [18]. The copolymer membranes for fuel cell demonstrated better oxidative stability and higher proton conductivity than the side-chain-type sulfonated polymer membranes. It seems that the presence of zwitterionic groups may effectively overcome the contradiction between high ionic conductivity and good stability of ion exchange membranes.

However, for the existing methods for zwitterionic polymers preparation, toxic organic solvents such as N,N-Dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) [19,20] are typically employed, causing a potential threat to the environment and human body. However, a novel solvent-free strategy reported herein is adopted to prepare a series of quaternized membranes bearing zwitterionic groups based on a green environmentally friendly route. The system is composed of cardopolyetherketone (PEK-C, polymer) solubilized in vinylbenzylchloride (VBC, monomer), divinylbenzene (DVB, monomer) and tetraethylenepentamine (TEPA, crosslinker between VBC and PEK-C) [21]. Specifically, this strategy involves first the dissolution of PEK-C in VBC, DVB and TEPA, followed by *in situ* polymerization to get flexible base membranes, which were immersed in dimethylamine (DMA) and 1,3-propane sultone (PS) aqueous solution in turn. The resulting series of novel quaternized membranes bearing zwitterionic groups were obtained, characterized, and utilized in VRB application. The physicochemical properties and morphologies of the membranes and their performances in VRB single cell test were investigated. The introduction of zwitterionic groups into quaternized membranes appears to be a promising approach to achieve not only low vanadium crossover, but also chemical stability and high ionic conductivity.

2. Experiment

2.1. Materials

Cardopolyetherketone (PEK-C) ($M_w=115,000$) was purchased from Xuzhou Engineering Plastic Factory (China). 4-Vinylbenzyl chloride (VBC) and divinylbenzene (DVB) were purchased from Aldrich (Milwaukee, WI, USA.). The thermal initiator benzoyl peroxide (BPO) was purchased from China National Medicines Co. Ltd. All of them were purified before use according to our previous work [21]. Vanadyl sulfate (VO_2SO_4) was obtained from Shanghai Huating Chemicals Factory Co., Ltd. China; carbon felts and graphite plates were obtained from Gansu Haoshi Carbon Fiber Factory Co., Ltd. China; the other analytical reagent, including dimethylamine (DMA), 1,3-propane sultone (PS), H_2SO_4 , NaCl, NaOH, MgSO_4 , and tetraethylenepentamine (TEPA) were purchased from common commercial suppliers and used without further purification. Flat sheet PETEX woven screening fibers (thickness: 45 μm , SEFAR) were used as reinforcing materials and Nafion117 membrane was purchased from Dupont Company.

2.2. Membrane preparation

For base membrane fabrication, a blended casting solution composed of PEK-C (polymer), VBC and DVB (monomer) and TEPA (crosslinker) was first prepared [21]: 15 g PEK-C and 0.015 mol BPO was dissolved in the mixture of 0.4 mol VBC and 0.02 mol DVB monomer solution, and then 0.01 mol TEPA was added followed by ultrasonic treatment for about 30 min. The final solution was cast onto PETEX support and sandwiched between two PVC sheets. This assembly was sealed with aluminum tape to avoid monomer volatilization. Then *in situ* bulk polymerizations were carried out at 80 °C for 8 h; the

resulting base membrane with a thickness of about 80 μm was designated as PPT membrane (Poly (VBC-co-DVB)+PEK-C+TEPA).

To obtain the target quaternized membranes with zwitterionic groups (see Fig. 1), PPT membrane was firstly immersed in 1 M DMA aqueous solution at 60 °C for a certain time, some tertiary amine (TA) hydrochloride (from the reaction of 1 DMA and 1 $-\text{CH}_2\text{Cl}$) and quaternary ammonium (QA) (from the reaction of 1 DMA and 2 $-\text{CH}_2\text{Cl}$) groups would be introduced into the membrane matrix. After immersing in 1 M NaOH aqueous solution for 12 h to neutralize acid, the membranes were then immersed in 10 wt% PS aqueous solution and some sulfonic acid groups were formed (from the reaction of 1 TA and 1 PS). The final quaternized membranes bearing zwitterionic groups were designed as ZPPT membrane (see Fig. 1). A series of ZPPT membranes obtained from different reaction times in the first step are designed as ZPPT-X (X: 1, 2, 3, 4, 5, and 6 for 1 h, 4 h, 8 h, 12 h, 16 h, and 24 h, respectively). For the sake of comparison, the benchmark quaternized membrane without zwitterionic groups prepared by only soaking the base membrane in the DMA solution was designed as QPPT membrane.

2.3. Membrane characterization

2.3.1. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS)

FT-IR spectra were measured using a Bruker Vector 22 FT-IR spectrophotometer. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MK II with Al $K\alpha$ as the excitation source.

2.3.2. Morphological evaluation

Scanning electronic microscopy was employed to observe the surface and cross-section morphology of the ZPPT-6 membrane before and after stability test. Cross section morphology of the membrane, which was quenched in liquid nitrogen and fractured in frozen state, was analyzed using a field emission scanning electron microscope (FE-SEM, SIRION200, FEI), and the distributions of the S and V elements in the thickness direction were evaluated by EDX analysis. In order to analysis cross-section morphology clearly, and quenched of the membrane easily, the ZPPT-6 membrane without PETEX fiber was used.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry analysis of the membrane was performed under nitrogen atmosphere through the heating-cooling-heating cycle from -50 to 250 °C at 20 °C/min heat/cool with a DSC Q2000 V24.10 build 122.

2.3.4. Water uptake (WU) and linear expansion ratios (LER)

A sample of membrane (size: 1 cm \times 4 cm) was firstly immersed in deionized water at a given temperature for 48 h to reach swelling equilibrium. After this hydration step, the wet mass (W_{wet}) and wet length (L_{wet}) of sample membrane were measured after quickly wiping off the excess water on the surface of the sample membrane with filter papers. The sample membrane was subsequently dried at 60 °C and then the dry mass (W_{dry}) and dry length (L_{dry}) of the sample were recorded. The water uptake (WU) and the linear expansion ratio (LER) of membrane sample were calculated according to the following equations:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

$$LER = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (2)$$

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