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Preparation of covalently cross-linked sulfonated polybenzimidazole membranes for vanadium redox flow battery applications

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ABSTRACT

A series of polybenzimidazole copolymers with varied content of pendant amino groups have been synthesized by condensation polymerization of 4,4'-dicarboxydiphenyl ether (DCDPE), 5-aminoisophthalic acid (APTA) and 3,3'-diaminobenzidine (DAB) in polyphosphoric acid at 190 °C for 20 h. The resulting copolymers undergo post-sulfonation in fuming sulfuric acid at 100 °C yielded the highly sulfonated polybenzimidazoles (**SOPBI-NH₂(x/y)**, 'x/y' refers to the monomer molar ratio of DCDPE to APTA). A series of covalently cross-linked membranes (**CSOPBI-NH₂(x/y)**) with good mechanical properties are fabricated by solution cast technique using bisphenol A epoxy resin as a cross-linker. The CSOPBI membranes show 3–4 orders of magnitude lower VO²⁺ permeability and 6–30 times higher ion diffusion selectivity (proton vs. VO²⁺) than Nafion 117. The charge-discharge behaviors of the vanadium redox flow batteries (VRBs) assembled with the **CSOPBI-NH₂(x/y)** membranes and Nafion 117 are investigated and compared. The VRBs assembled with the CSOPBI membranes exhibit significantly higher columbic efficiency and lower self-discharge rate than that assembled with Nafion 117 owing to the extremely lower vanadium cations crossover of the former. The VRB assembled with the **CSOPBI-NH₂(9/1)** membrane exhibits fairly high energy efficiency (~85% at 60 mA cm⁻²) and little decay in performance is observed after 300 charge-discharge cycles.

1. Introduction

Since the discovery of vanadium redox flow batteries (VRB) by Sklyllas-Kazacos and co-workers [1,2] in 1985, the VRB has attracted increasing attention owing to its promising applications in medium- and large-scale energy storage. In 1997, a 200 kW VRB stack built by Kashima-Kita was successfully interconnected to the company's power plant grid system [3]. A separator is one of the key components of a VRB system. From viewpoint of practical applications, a separator must meet the requirements of high proton conductivity, little vanadium crossover, good mechanical properties and excellent chemical stability. At present, the most widely used separator in the VRB is DuPont's Nafion[®], a sulfonated perfluorinated polymer membrane which has been widely used in chlor-alkali industry in the past decades. It has the merits of high proton conductivity and excellent chemical stability. However, the high cost and high vanadium permeability which causes serious self-discharge problem restrict their further applications in VRB. It is generally recognized that Nafion[®] possesses perfect nanophase-separated morphology consisting of ionic channels

(1 nm in diameter) interconnecting ionic clusters (4 nm in diameter) which facilitate ionic (protons, vanadium cations, etc.) transport, while the highly hydrophobic Teflon backbone provides Nafion[®] with excellent chemical stability and good mechanical properties [4–6]. To reduce vanadium crossover of Nafion[®], many modification approaches have been developed such as incorporation of amino-silica [6] or layered silicate [7] into Nafion[®] matrix, preparation of composite membrane using porous poly(tetrafluoroethylene) substrate [8,9], blend with other polymers [10,11], modification with polypyrrole [12] and interfacial graft copolymerization [13,14]. These modification approaches are indeed effective for reduction of vanadium crossover. However, since Nafion[®] is very expensive, cost seems to be still a major concern associated with these modified membranes. Besides Nafion[®], in the past decade many cost-effective and high performance hydrocarbon polymer membranes have been attempted as alternative for VRBs such as sulfonated poly(aryl ether ketone)s [15–22], sulfonated poly(aryl ether sulfone)s [23–25], branched sulfonated poly(fluorenyl ether ketone sulfone)s [26], sulfonated polyimides [27–30], sulfonated Diels Alder poly(phenylene) [31], poly(vinyl difluoride)-*g*-poly(styrene-

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4-sulfonic acid-co-maleic anhydride) [32], and various anion exchange polymer membranes [33–42]. Unlike Nafion[®], hydrocarbon polymer membranes generally exhibit low vanadium cation permeability when their ion exchange capacities (IECs) are controlled at an appropriate level. This is because they lack perfect ionic channels as observed in Nafion[®] to facilitate vanadium cation transport. For example, Sankir and coworkers reported that the sulfonated poly(aryl ether sulfone) membrane (BPSH 35) displayed one order of magnitude lower vanadium permeability but even higher proton conductivity than Nafion 212 [23]. Very recently Zhang and co-workers reported that the VRB assembled with a cross-linked anion exchange membranes derived from chloromethylated polysulfone and 4,4'-bipyridine exhibit very high energy efficiencies (88.3–81.8%) in the current density range of 80–140 mA cm⁻² which are superior to those (83.2–76.1%) assembled with Nafion 115 in the same current range owing to the high ionic conductivity and low vanadium crossover of the former [33]. The very low vanadium permeability of the anion exchange membranes is ascribed to the Donnan exclusion effect and the cross-linking network [33].

Because hydrocarbon polymers are generally less stable to oxidation than perfluorinated polymers, chemical stability in highly oxidative environment is an important concern to most hydrocarbon polymer membranes for use in VRBs (VO₂⁺ is highly oxidative in acidic solution). To achieve long-term durability of VRBs, it is very crucial to select polymers with highly stable backbones. Heterocyclic polymers, in particular, polybenzimidazoles (PBIs), are known for their excellent chemical stability to oxidation [43–45]. However, up to date, quite few publications on PBI-based separators are reported. Zhou et al. reported that the commercial PBI membrane showed only 2.9% weight loss after soaking testing in 1 M VO₂⁺ at room temperature for 120 days which is comparable to that of Nafion[®] [46]. The VBR assembled with the PBI membrane exhibited a substantially higher coulombic efficiency of up to 99% at current densities ranging from 20 mA cm⁻² to 80 mA cm⁻² due to very low vanadium cation permeability of the PBI membrane. Liao et al. reported that the benzimidazole groups-containing sulfonated poly(aryl ether ketone) membranes exhibit ultra-low vanadium ion diffusion due to the acid-base interaction (ionic cross-linking) and the exclusion effect between the positively-charged (protonated) benzimidazole groups and vanadium cations [15]. The VRBs assembled with their membranes exhibit little performance decay after 200 charge-discharge cycles.

Herein, for the first time we report on the preparation of covalently cross-linked sulfonated polybenzimidazole (CSOPBI) membranes and their VBR performance. The highly inert PBI backbones is expected to ensure excellent chemical stability to the highly oxidative electrolyte (VO₂⁺). The covalent cross-linking network in combination with Donnan exclusive effect resulting from the protonated imidazole groups and vanadium cations are favorable for prohibiting vanadium cation crossover, while the sulfonic acid groups are responsible for proton transport.

2. Experimental

2.1. Materials

4,4'-Dicarboxydiphenyl ether (DCDPE), 3,3'-Diaminobenzidine (DAB) and 5-aminoisophthalic acid (APTA) were purchased from Acros and used without further purification. Polyphosphoric acid (PPA), bisphenol A diglycidyl ether (BADGE) and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). APTA was dried at 80 °C in vacuum for 10 h before use. DMSO was directly dried over 4A molecular sieves prior to use. Other materials were used as received.

2.2. Synthesis of polybenzimidazole copolymers

The synthetic procedures are described as follows using the copolybenzimidazole comprising DCDPE and APTA moieties at the molar ratio of 9:1 (the copolymer is denoted as OPBI-NH₂(9/1) as an example.

To a 250 mL dry three-neck flask were added 2.32 g (9.0 mmol) of DCDPE, 0.181 g of (1.0 mmol) APTA, 2.14 g (10.0 mmol) of 3,3'-diaminobenzidine (DAB) and 60 g of PPA under nitrogen flow. The reaction mixture was mechanically stirred and slowly heated to 150 °C and kept at this temperature for 2 h. The reaction temperature was further raised to 190 °C and maintained for another 20 h. While hot the resulting solution mixture was slowly poured into 300 g of ice water with stirring. The precipitated product was first washed with deionized water for three times and then soaked in 5 wt% sodium bicarbonate solution for 24 h. The solid was thoroughly washed with deionized water till pH neutral and dried in vacuum at 60 °C for 20 h.

The same procedures were followed to synthesize other polybenzimidazole copolymers comprising of DCDPE and APTA moieties at the molar ratio of 5:1, 4:1 and 3:1, respectively (the copolymers are denoted as OPBI-NH₂(5/1), OPBI-NH₂(4/1), OPBI-NH₂(3/1), respectively).

2.3. Post-sulfonation

To a 100 mL dry three-neck flask were added 2.0 g of a polybenzimidazole copolymer and 20 mL of fuming sulfuric acid (20% SO₃) under nitrogen flow. The mixture was mechanically stirred at room temperature for 0.5 h and then slowly heated to 100 °C and kept at this temperature for 12 h. After cooling to room temperature, the highly viscous solution mixture was slowly poured into 200 mL of ice water with stirring. The precipitate was collected by filtration, soaked in 5 wt % sodium bicarbonate solution for 24 h and finally washed with deionized water till pH neutral. The solid was dried in vacuum at 60 °C for 20 h. The resulting sulfonated polybenzimidazole copolymers are denoted as SOPBI-NH₂(x/y). Here, x/y refers to the molar ratio of DCDPE to APTA (9/1, 5/1, 4/1 and 3/1).

2.4. Membrane formation and proton exchange treatment

The sulfonated polybenzimidazoles were dissolved in DMSO to give 5 w/v% solutions. Then stoichiometric amount of the cross-linker BADGE was added to the solutions (the molar ratio of the BADGE to the APTA moiety of the sulfonated polybenzimidazoles was controlled at 1:1). The solution mixtures was filtered and subsequently cast onto clean glass plates and dried in an air oven at 80 °C for 8 h. The resulting membranes were peeled off from glass plates and further dried in vacuum at 120 °C for 10 h. They are denoted as CSOPBI-NH₂(x/y). Here, x/y refers to the same meaning as foregoing mentioned.

Proton exchange treatment was performed by immersing the membranes in 1.0 M H₂SO₄ solution at room temperature for 3 days. Then the membrane was thoroughly washed with deionized water until the rinsed water became pH neutral. Finally the membranes were dried at 120 °C for 10 h in vacuum.

2.5. Characterization of membranes

FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. ¹H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument. Thermogravimetric analysis (TGA) was performed in air with a TGA2050 instrument at a heating rate of 10 °C min⁻¹. Elemental analysis test was performed with a Vario EL Cube instrument (Elementar, Germany).

Ion exchange capacity (IEC) was measured by titration method. The dry membranes (0.2–0.3 g per sheet) were cut into small pieces and

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