



Highly stable pyridinium-functionalized cross-linked anion exchange membranes for all vanadium redox flow batteries



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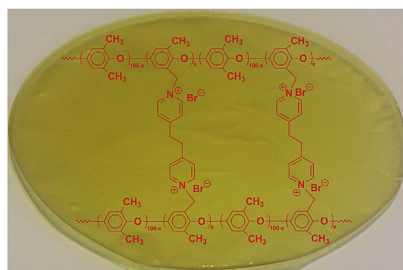
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HIGHLIGHTS

- Pyridinium-functionalized cross-linked BrPPO were fabricated for VRFBs.
- The AEMs exhibited a low vanadium permeability and an acceptable conductivity.
- The AEMs exhibited a superior chemical stability in an *ex situ* immersion test.
- The VRFBs cycled over 537 cycles with a capacity decay rate of 0.037% cycle⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

It has recently been demonstrated that the use of anion exchange membranes (AEMs) in vanadium redox flow batteries (VRFBs) can reduce the migration of vanadium ions through the membrane due to the Donnan exclusion effect among the positively charged functional groups and vanadium ions. However, AEMs are plagued by low chemical stability in harsh chemical environments. Here we propose and fabricate a pyridinium-functionalized cross-linked AEM for VRFBs. The pyridinium-functionalized bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) exhibits a superior chemical stability as a result of the strengthened internal cross-linking networks and the chemical inertness of the polymer backbone. Therefore, the membrane exhibits little decay in a harsh environment for 20 days during the course of an *ex situ* immersion test. A cycling test also demonstrates that the VRFB assembled with the membrane enable to retain 80% of the initial discharge capacity over 537 cycles with a capacity decay rate of 0.037% cycle⁻¹. Meanwhile, the membrane also shows a low vanadium permeability and a reasonably high conductivity in supporting electrolytes. Hence, all the measurements and performance tests reported in this work suggest that the membrane is a promising AEM for redox flow batteries to achieve excellent cycling stability and superior cell performance.

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1. Introduction

Electrical energy storage (EES) systems are indispensable for the application of future renewable energies as a result of their intermittent and distributed nature [1–4]. Among several categories of EES systems, redox flow batteries (RFBs), which employ metal salts

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[5] or organic components [6,7] with different oxidation states, have been widely investigated due to their significant merits, including flexibility in configuration and operation, long cycle life and high reliability. Among these RFBs, vanadium redox flow batteries (VRFBs) invented by Skyllas-Kazacos in the 1980s have been comprehensively investigated [3]. VRFBs, employing the same vanadium element in four different oxidation states as the redox couples, possess additional merits, such as reduced cross-contamination, high electrochemical activity and suitable polarization potential [8–10].

However, the commercialization of VRFBs has been partially hampered by the ion exchange membranes, which not only preclude the intermixing of positive electrolytes and negative electrolytes, but also allow the transport of ions (typically protons) to complete the internal circuit in VRFBs [11,12]. Notwithstanding, the extensively used perfluorinated membranes (Nafion) possess most of the properties desired for VRFBs, their application has been limited by two issues: the severe migration issue of vanadium ions and the high cost [13,14]. On one hand, due to the particular structure of perfluorinated membranes, microphase separated and hydrated ionic aggregate clusters are well established. Normally, the microphase separation is beneficial for ionic migration. However, due to the large size of hydrophilic ionic clusters (4 nm–5 nm) [15], the ion selectivity of perfluorinated membranes is extremely low. That is, the vanadium ions with different oxidation states, which should be maintained in the separated electrolyte reservoirs, also migrate through the membrane accompanying the transport of protons as well as water molecules [16,17]. The severe migration of vanadium ions not only significantly reduces the utilization of electrolytes, but also causes a severe self-discharge process that decreases the energy efficiencies of the total flow battery system. On the other hand, the fabrication of perfluorinated membranes is complicated and time-consuming, leading to a high cost (500–700 dollar m^{-2}) [18]. More importantly, thick perfluorinated membranes are required for real applications to avoid the severe intermixing of vanadium ions. Based on the cost analysis made by Department of Energy (DOE) of America, the membrane cost was the main component of the total system cost (44% for 0.25 MWh and 27% for 4 MWh) [19,20].

To address these issues, alternative membranes, including hydrocarbon-based proton exchange membranes (PEMs) [21–23], anion exchange membranes (AEMs) [24–26] and nanofiltration membranes (NFs) [27,28], have been gradually applied in VRFBs. Among these membranes, AEMs have received considerable attention for application in VRFBs due to their low vanadium permeability, which results from the Donnan exclusion effect among the positively charged functional groups and vanadium ions [29–31]. Though attractive, AEMs are plagued by low chemical stability of functional groups in harsh acid environments. AEMs with traditional quaternary ammonium groups have been applied in VRFBs. However, the quaternary ammonium groups were demonstrated to be easily degraded in the harsh environments (high concentration of supporting electrolyte (H_2SO_4) and high oxidative reactive species (VO_2^+)) [31–33]. Recently, AEMs containing pyridinium groups have been applied in VRFBs owing to their promotion of proton transport due to acid-base interactions and their extended cycling life in VRFBs [34–36]. Moreover, an internal cross-linking network, created by reacting 4, 4'-bipyridine with the halomethyl on the modified polymer backbone, provided the AEMs with enhanced stability [14]. Nevertheless, subsequent research work demonstrated that the pyridinium groups still suffered severe degradation due to the introduction of hydrophilic carbon in the benzene ring during the course of the grafting process [37]. The induced hydrophilic carbon center was attacked by the lone pair electron of VO_2^+ , which caused not only the deterioration

of the mechanical properties, but also the high internal resistance of VRFBs.

Herein, in the present work, we report a novel and durable AEM for VRFBs. Contrary to the backbone structure containing the electron-donating alkyl groups, we chose bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BrPPO) as the starting polymer to graft the pyridinium functional groups. More importantly, the bromomethyl groups can be cross-linked by the bipyridine during the course of thermal treatment. Hence, the chemical stability was improved that was ascribed to the internal cross-linking networks and the chemical inertness of polymer backbone. In addition, the bromomethylation process, which avoided the usage of the highly toxic and carcinogenic reagents (chloromethylether and trimethylamine), was more environmentally friendly. After the fabrication, we then evaluated the cell performance of the VRFBs assembled with the BrPPO/Py membranes and compared to the battery with perfluorinated membranes (Nafion 212). It was demonstrated that VRFBs with BrPPO/Py exhibited superior cell performance and excellent cycling stability. These results confirm that the BrPPO/Py membranes are the promising AEMs for redox flow batteries.

2. Experimental

2.1. Materials

1,2-bis(4-pyridyl)ethane (BisPE), *N*-bromosuccinimide (NBS), 2,2'-Azo-bis-isobutyronitrile (AIBN), dimethylformamide (DMF) and sulfuric acid (95 wt%) were purchased from Sigma-Aldrich. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a molecular weight of 350,000 $g\ mol^{-1}$ was obtained from SABIC Innovative Plastics (PPO6130). A Nylon membrane (pore size: 0.22 μm ; OSMONICS Inc.) was used for the filtration process. ELAT[®] hydrophilic plain cloths and vanadyl sulfate ($VOSO_4 \cdot 3H_2O$, $\geq 99\%$) were purchased from FuelCellsEtc and Shenyang Haizhongtian Fine Chemical Factory, respectively. AIBN was twice recrystallized from methanol. All other chemicals were used as received without any further purification. Deionized (DI) water with resistivity not less than 18.2 M Ω (Millipore) was prepared for all aqueous solutions.

2.2. Synthesis of BrPPO/Py

The preparation process of the bromomethylated PPO (BrPPO) with different degrees of bromomethylation (DOB, α) was achieved by controlling the ratio between the PPO and NBS, as reported elsewhere [38,39]. Generally, PPO (40 mmol) was dissolved in 200 mL chlorobenzene at 50 °C to obtain a light yellow solution. The solution was then added into a three-neck flask equipped with a water-cooling condenser and heated in an oil bath at 145 °C while magnetically stirred. The reaction was held at this temperature for 24 h after a desired mole of NBS and 4 mmol AIBN were successively added. Once the reaction was complete, the mixture was cooled down to room temperature. The resulting deep red solution was poured slowly into 1000 mL methanol to precipitate the brown polymer. The polymer was then filtrated, carefully rinsed with methanol several times, and subsequently dissolved in chloroform and re-precipitated in the hot methanol solution. The polymer was then dried overnight in a vacuum oven at 80 °C.

The as-prepared BrPPO was dissolved into DMF to form a 5 wt% solution. A predetermined amount of BisPE was then added. The mixture was stirred at room temperature for 12 h. The polymer solution was subsequently cast on a clean glass plate using a micrometer adjustable film applicator. The plate was then placed inside a forced convection oven. To completely evaporate the solvents, the oven temperature was maintained at 100 °C for 12 h and

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