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Novel acid-base hybrid membrane based on amine-functionalized reduced graphene oxide and sulfonated polyimide for vanadium redox flow battery

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ABSTRACT

A series of novel acid-base hybrid membranes (SPI/PEI-rGO) based on sulfonated polyimide (SPI) with polyethyleneimine-functionalized reduced graphene oxide (PEI-rGO) are prepared by a solution-casting method for vanadium redox flow battery (VRB). FT-IR and XPS results prove the successful fabrication of PEI-rGO and SPI/PEI-rGO hybrid membranes, which show a dense and homogeneous structure observed by SEM. The physicochemical properties such as water uptake, swelling ratio, ion exchange capacity, proton conductivity and vanadium ion permeability are well controlled by the incorporated PEI-rGO fillers. The interfacial-formed acid-base pairs between PEI-rGO and SPI matrix effectively reduce the swelling ratio and vanadium ion permeability, increasing the stability performance of the hybrid membranes. SPI/PEI-rGO-2 hybrid membrane exhibits a higher coulombic efficiency (CE, 95%) and energy efficiency (EE, 75.6%) at 40 mA cm^{-2}, as compared with Nafion 117 membrane (CE, 91% and EE, 66.8%). The self-discharge time of the VRB with SPI/PEI-rGO-2 hybrid membrane (80 h) is longer than that of Nafion 117 membrane (26 h), demonstrating the excellent blocking ability for vanadium ion. After 100 charge-discharge cycles, SPI/PEI-rGO-2 membrane exhibits the good stability under strong oxidizing and acid condition, proving that SPI/PEI-rGO acid-base hybrid membranes could be used as the promising candidates for VRB applications.

1. Introduction

Vanadium redox flow battery (VRB), as one type of energy storage systems, developed by M. Skyllas-Kazacos et al. in 1985 [1–3], has been widely explored based on its long cycle life, high energy efficiency and low cost. For VRB, the ion exchange membrane is a crucial component, which controls the perspective of commercial application [4–6]. Nafion membrane, produced by DuPont company, has been used in VRB system due to its high proton conductivity and good chemical stability [7–13]. However, low proton/vanadium ion selectivity and high cost of Nafion membrane obviously limit the practical applications. Therefore, a promising membrane with the low cost and high performance is necessary to push the commercial development of VRB [14–19].

Recently, the alternative membranes for VRB application has been developed by the pore-filling method [8,20], polymer blending [12,21] and the inorganic nanofiller doping technique [10,11,22]. Sulfonated polymeric membranes are proved as an alternative for VRB applications, such as sulfonated poly(ether ether ketone) (SPEEK) [6,21], sulfonated poly(phthalazinone ether ketone) (SPPEK) [19,22] and sulfonated polyimide (SPI) [23–25], etc. High requirement of sulfonated groups (degree of sulfonation) onto polymeric backbone, accompanied with the weakened mechanical property, affects the proton conductivity and vanadium ion permeability in VRB system, and also it brings a hard issue to balance the relationship between the property and structure of sulfonated polymer. Thus, incorporation of functional inorganic filler into sulfonated polymer matrix provides another choice to obtain the hybrid membranes with the determined high performance. Li et al. prepared SPEEK/mesoporous silica hybrid membranes, which show a low vanadium ion permeability and a good oxidation stability because of the formed hydrogen bond [21]. Enhancement in VRB performance is also realized by using TiO_2 [23], tungstophosphoric acid (TPA) [19] or AlOOH [25] in polymer membranes. Recently, graphene and its derivatives have been widely investigated for VRB application owing to their unique properties [26,27]. By incorporating graphene into SPEEK, Dai et al. fabricated SPEEK/GO hybrid membranes, which show a good single

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cell performance and a high cell efficiency of VRB, demonstrating the role of proton donor for GO [16,28–30]. He et al. designed GO-based proton exchange membrane for fuel cell (PEMFC) via the acid-base pairs' interaction, demonstrating the proton conductivity can be increased from SPEEK hybrid membranes with polydopamine-modified GO [31]. In other words, the hybrid membranes based on the sulfonated polymers and the basic groups such as NH_2-functionalized GO can effectively enhance the proton conductivity through the acid-base pairs. Besides, Li et al. prepared a polymer acid-base blend membrane based on SPEEK and polyacrylonitrile for VRB application [32]. The acid-base blend membrane exhibits low vanadium ion permeability and swelling ratio, which leads to high efficiency (CE, 96.2%, EE, 83.5%) and stable performance of VRB. A similar good performance of VRB was also achieved by using a SPEEK/polyetherimide acid-base blend membrane developed by Liu et al. [33]. Therefore, it is reasonable for acid-base membranes used in VRB system. Moreover, the appeared basic groups such as NH_2—GO further provide the positive charge, and a Donnan exclusion effect on the vanadium ions is also expected. Lots of studies on the acid-base pairs are found for PEMFC system, however, few study reports the graphene-based acid-base hybrid membranes for VRB, especially for combining sulfonated polymers and NH_2-functionalized GO in VRB system.

Herein, in this paper a novel acid-base hybrid membrane based on NH_2-functionalized reduced graphene oxide with polyethyleneimine (PEI-rGO) and sulfonated polyimide (SPI) is prepared and used in VRB system. The swelling ratio, water uptake, proton conductivity and vanadium ions permeability of the hybrid membrane are investigated. The effect of electrostatic interaction between $-NH_2$ and $-SO_3H$ on the proton transport and the vanadium ion permeation is detailed analyzed and compared. The single cell performance of VRB with the hybrid membranes is carefully detected, and the effect of acid-base pairs on VRB performance is further discussed.

2. Experimental

2.1. Materials

Natural graphite powders (NGP) (325 mesh) are kindly provided by Qingdao Laixi Graphite Co., Ltd. 4, 4'-Oxydianiline (ODA) and 1, 4, 5, 8-Naphthalenetetracarboxylic dianhydride (NTDA) are purchased from Sinopharm Chemical Reagent Co., Ltd. and are purified by vacuo sublimation. 2, 2'-benzidinedisulfonic acid (BDSA) is provided by J&K Scientific Ltd. and dried at 100 °C for 12 h before use. Polyethyleneimine (PEI) is purchased from Sigma-Aldrich Co. Ltd and used as received. Concentrated H_2SO_4 (98%), $KMnO_4$, $NaNO_3$, H_2O_2 (30%), HCl (37%), m-cresol, triethylamine and benzoic acid are provided by Tianjin Guangfu fine Chemical Research Institute and used as received. Nafion 117 membrane with a thickness of 200 μm is purchased from DuPont (Beijing, China).

2.2. Preparation of GO and PEI-rGO

Graphite oxide powder is prepared from natural graphite powder (325 mesh) through a modified Hummers method, as reported in our previous work [34].

For PEI-rGO, 0.5 g PEI is firstly dissolved in 50 mL deionic water and 100 mg GO powder is re-dispersed into PEI solution by ultrasonication. And then, PEI-rGO solution is refluxed at 100 °C for 12 h under N_2. The black solid is isolated by centrifugation and washed with deionic water for 5 times to remove the residual PEI. The obtained PEI-rGO is dried at 80 °C for 12 h in vacuum oven.

2.3. Preparation of sulfonated polyimide (SPI)/PEI-rGO membranes

SPI with a 50% sulfonation degree is prepared according to the study of C. Genies et al. [35]. SPI/PEI-rGO membranes with different contents of PEI-rGO are prepared by a solution-casting method. First, the predetermined weight of PEI-rGO is dispersed in m-cresol by ultrasonication for 30 min, and then SPI is dropped and stirred at 60 °C. The homogenous solution is cast on a clean glass plate, which is firstly dried at 60 °C for 12 h, and then at 100 °C for 12 h in vacuum to remove the solvent. The SPI/PEI-rGO membranes are peeled off through the immersion of deionized water, and then continue to put in 2 mol L^{-1} H_2SO_4 for 48 h to acidify. Finally, SPI/PEI-rGO membranes are washed with deionized water to remove excess H_2SO_4 solution, and stored in deionized water before use. SPI/GO hybrid membranes are also prepared by the same procedure. The SPI/PEI-rGO membranes with various contents of PEI-rGO are termed as SPI/PEI-rGO-X, where X is the mass ratio of PEI-rGO to SPI. For example, SPI/PEI-rGO-1 is a membrane with 1 wt% of PEI-rGO and 99 wt% of SPI. The thickness of SPI/PEI-rGO membrane is ca. 50 μm. Nafion 117 membrane is pretreated according to the literature [6].

2.4. Characterization of PEI-rGO and SPI/PEI-rGO membranes

The chemical compositions of PEI-rGO and SPI/PEI-rGO membranes are characterized by a Fourier Transform Infrared (FT-IR, Bruker Vector 22) in the range of 4000-600 cm^{-1} at room temperature. X-ray photoelectron spectroscopy (XPS) is conducted on a 60 (GENESIS EDAX, US) with Al Kα radiation ($h\nu$ = 1486.4 eV). Raman spectra for GO, PEI-rGO powders and SPI/PEI-rGO hybrid membranes are analyzed using a Renishaw 1000 Raman microprobe system (Renishaw, UK) with an Argon ion laser of wavelength 532 nm. The surface and cross-section of SPI/PEI-rGO membranes is observed by field-emission scanning electron microscopy (FE-SEM, S4800Hitachi, Japan) with an accelerating voltage of 10 kV. The thermal property of SPI/PEI-rGO membranes is analyzed by thermogravimetric analysis (TGA, NETZSCH STA 409, Germany) under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 800 °C. The mechanical property of SPI/PEI-rGO membranes is detected by a mechanical tester (SANS-20 kN, China) with a crosshead speed of 5 mm min^{-1} at room temperature.

2.4.1. Water uptake (WU) and swelling ratio (SR)

SPI/PEI-rGO membranes are dried under vacuum at 80 °C for 24 h, and then weighed. After the membrane is immersed into deionized water for 24 h, the excess water on membranes surface is removed and weighed immediately. The water uptake (WU) of the membrane is calculated by the following equation:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

Where, W_{wet} and W_{dry} are the weight of membranes before and after water absorption, respectively.

Swelling ratio (SR) is measured according to the change of length ratio for membrane. The length of the vacuum-dried membranes is firstly measured, and then the length of the soaked membrane in deionized water is measured again. SR of membrane is calculated according to the following equation:

$$SR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

Where L_{wet} and L_{dry} are the length of the soaked membrane and the dry membrane, respectively.