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Sulfonated poly(ether ether ketone)/sulfonated graphene oxide hybrid membrane for vanadium redox flow battery

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A B S T R A C T

In this paper, a series of sulfonated poly(ether ether ketone) (SPEEK) hybrid membrane doped by the different amount of sulfonated graphene oxide (SGO) nanosheets are prepared by solution-casting method. The membrane structure, physicochemical property and cell performance of vanadium redox flow battery (VRB) have been characterized through FT-IR, SEM, XPS, and single-cell test system, *etc*. The incorporation of SGO in SPEEK improves the water uptake, ion exchange capacity and proton conductivity of the hybrid membrane, and effectively reduces the swelling degree and the vanadium ion permeability. In the single cell performance test, the energy efficiency of the SPEEK/SGO-3 hybrid membrane is 81.1%, which is higher than that of SPEEK (76.0%) and Nafion 117 membrane (73.8%). And, a longer self-discharge time (56.6 h) against Nafion 117 (23.5 h) and SPEEK (32.8 h) membrane is shown. In addition, the incorporated SGO nanofillers don't improve the chemical stability of SPEEK membrane soaked by 1.5 M V^{5+} solution although they block the vanadium ion permeation. Then, the durability for SPEEK/SGO hybrid membranes should be further explored for VRB system.

1. Introduction

Increased energy consumption and pollution are presenting major problems for the development of a sustainable society. An alternative energy strategy to find a green and clean energy source is getting more and more attentions in recently years [1–6]. Since the discovery of vanadium redox flow battery (VRB) by Skyllas-Kazacos et al., the exploration of VRB system and its application are underway from the industrial and academic interests [7,8]. However, the practical engineering application of VRB system needs to be solved these aspects such as the structure of VRB system, life cycle and the cost of proton exchange membrane, *etc* [4,9–11].

Typically, PEM applied for VRB system should have high proton conductivity, low vanadium ion permeability, excellent chemical stability and low cost [12–17]. Commercial Nafion series' membranes show an obvious advantage over the proton conductivity and the chemical stability as compared with other sulfonated polymers. However, their high cost and vanadium ion permeability limit the engineering application [18–20]. Aromatic polymers as PEM have been extensively studied such as sulfonated polyimide (SPI) [21,22], sulfonated poly(sulfone) [23,24], sulfonated poly(phthalazinone ether ketone) [25–27], sulfonated polybenzimidazole [28,29], sulfonated poly(ether ether ketone) (SPEEK) [16,30–34]. For these sulfonated aromatic polymers, the higher the degree of sulfonation (DS) is, the worse the mechanical property and the appearance stability of membrane [35]. So, organic or inorganic nanofillers are used to enhance the proton conduction ability [36–41]. Graphene oxide (GO) as a new kind of carbon material, exhibits many applications in the aspects of sensor [42], energy storage [43], display screen [44], semiconductor materials [45] and biomedical field [46]. Due to GO having a unique two-dimensional layered structure and high surface area, the increased water uptake and proton transport channels can be achieved [30,47–50]. In our previous studies, the 2D nanosheets, *i.e.*, $g-C_3N_4$, graphene oxide (GO) and amine-functionalized GO had been introduced into SPEEK and SPI membrane, which exhibit the good physicochemical properties of proton conductivity and vanadium ion selectivity, as well as VRB single-cell performance. SPEEK/$g-C_3N_4$ [34], SPEEK/PPD-GO [51] and SPI/amine-functionalized GO [21,52] hybrid membranes demonstrate an

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enhanced proton conductivity and ion selectivity for these PEMs, and the VRB performance also show an obvious enhancement as compared with Nafion membrane. This possible formed acid-base interfacial interaction between -NH_2 and -SO_3H improves the proton transport and constitutes a stable proton channel, and then decreases the vanadium permeability through the membrane. Chien et al. reports Nafion/sulfonated GO (SGO) hybrid membranes for direct methanol fuel cells, and an improved proton conductivity and extremely high methanol selectivity is demonstrated due to the SGO nanofillers creating much more interconnected transfer channels in membrane matrix [53]. Owing to the existed -SO_3H groups onto the surface of SGO nanofillers, the proton conductivity of PEM is enhanced, and the proton network based on the ion clusters is also strengthened. Therefore, keeping an optimal balance between the proton conductivity and the structure stability of PEM is a prerequisite for VRB application.

Herein, in this paper, by selecting SGO nanosheets as the interfacial modifiers, SPEEK/SGO hybrid membranes have been fabricated. Through controlling the physicochemical properties such as proton conductivity, ion selectivity, and IEC value, the SPEEK/SGO hybrid membrane is used for VRB system. The VRB single cell performance and chemical stability of hybrid membranes is characterized, and the energy efficiency is also compared with the Nafion 117 membrane. The VRB cell performance of SPEEK/SGO hybrid membrane is further discussed from the aspects of proton transport mechanism and synergistic effect.

2. Experimental

2.1. Materials

Natural graphite powders (NGP) (325 mesh) are kindly provided by Qingdao Laixi Graphite Co., Ltd. 3-Aminobenzene sulfonic acid is purchased from J&K Scientific Co., Ltd. Sodium nitrite, concentrated H_2SO_4 (98%) and N, N-dimethyl formamide (DMF) are purchased from Tianjin Guangfu Fine Chemical Research Institute. Poly(ether ether ketone) is provided by Panjin zhongruntesu Co., Ltd. (China), and sulfonated poly(ether ether ketone) (SPEEK) with IEC 1.75 ± 0.1 mmol g^{-1} and sulfonated degree 58.6% have been reported in our previous studies [34]. The Nafion 117 membrane is purchased from Dupont company.

2.2. Preparation of GO and SGO

GO nanosheets can be prepared by chemical technique [21,51,52,54,55] and electrochemical method [56], respectively, and here it is not introduced again. The details of SGO preparation are described as follows [57]. Firstly, 3-aminobenzene sulfonic acid, H_2SO_4 and $NaNO_2$ are added to a three-necked flask containing 1 mg/mL of GO solution at a ratio of 1: 3: 2.5, respectively, and keep at 0 °C for 1 h. After that, the solution is reheated to 60 °C for 4 h, and then the raw product is centrifuged and washed several time until reach the neutral state. Finally, the SGO is freeze-dried to the constant weight.

2.3. Preparation of SPEEK/SGO hybrid membranes

SPEEK and SGO are dispersed into DMF solution, and a transparent and homogeneous solution is obtained. The hybrid membrane is fabricated by pouring the solution into homemade mold at 80 °C, and keeps for 24 h to obtain a dry membrane. The hybrid membrane is marked as SPEEK/SGO-X, where X represents the weight ratio (wt%) of SGO, where the SGO contents change from 1 to 4 wt%.

2.4. Characterization of SPEEK/SGO hybrid membranes

X-ray photoelectron spectroscopy (XPS) (GENESIS EDAX, US) with Al Kα radiation (hν = 1486.4 eV) and Fourier Transform Infrared spectrometer (FTIR, Nicolet IS5, US) in the range of 4000-500 cm^{-1} at 4 cm^{-1}resolution are used to analyze the structure and chemical composition of ODA-AN-GO. The morphology of GO, SGO and SPEEK/SGO membranes is observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800, Japan) with an accelerating voltage of 10 kV.

2.4.1. Water uptake (WU), electrolyte uptake (EU) and swelling ratio (SR)

SPEEK/SGO hybrid membranes are vacuum dried at 80 °C for 24 h, and then the hybrid membranes are immersed into deionized water at room temperature for another 24 h. The excess water onto membrane surface is removed and weighted immediately. The water uptake (WU) is calculated by equation (1):

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{1}$$

Similarly, the electrolyte uptake (EU) is analyzed through soaking into the electrolyte of 1.0 mol L^{-1} $VOSO_4$ in 2.0 mol L^{-1} H_2SO_4. The EU is calculated by equation (2):

$$EU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{2}$$

where, W_{dry} and W_{wet} are the weight of membrane in wet and dry state, respectively.

Swelling ratio (SR) is calculated according to equation (3), where L_{wet} and L_{dry} are the length of wet and dry membrane, respectively.

$$SR = \frac{Lwet - Ldry}{Ldry} \times 100\% \tag{3}$$

2.4.2. Ion exchange capacity (IEC) and proton conductivity

IEC is determined by the typical titration method [58]. Hybrid membrane is immersed into a saturated NaCl solution for 24 h, and then the H^+ concentration of solution is titrated with 0.01 mol L^{-1}NaOH solution. The IEC is calculated by equation (3a):

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{W_{dry}} \tag{3a}$$

where C_{NaOH} and V_{NaOH} are the concentration and the volume of NaOH solution, respectively, and $Wdry$ is the weight of dry membrane.

Proton conductivity is mainly depended upon the membrane resistance, which can be characterized by a steady state linear sweep galvanodynamic technique [59,60] and electrochemical impedance spectroscopy. In this paper, the membrane is soaked in a solution of 1.0 mol L^{-1} $VOSO_4$/2.0 mol L^{-1} H_2SO_4 for 24 h. The conductivity cell is separated into two parts, filled with 1.0 mol L^{-1} $VOSO_4$/2.0 mol L^{-1} H_2SO_4. The electrical resistances of the conductivity cell with membrane (r_1) and without membrane (r_2) are measured by electrochemical impedance spectroscopy (EIS) with frequency ranging from 1 MHz to 1 Hz using an electrochemical workstation (CHI604E, China) at room temperature. The effective membrane area (S) of the cell is 7.065 cm^2. The area resistance of membrane (R) is calculated by equation (4) [58]:

$$R = (r_1 - r_2) \times S \tag{4}$$