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A novel Nafion-g-PSBMA membrane prepared by grafting zwitterionic SBMA onto Nafion via SI-ATRP for vanadium redox flow battery application

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ABSTRACT

A novel N115-g-PSBMA membrane containing zwitterionic groups was successfully prepared by grafting the zwitterionic SBMA (sulfobetaine methacrylate) onto Nafion 115 (N115) via SI-ATRP (surface-initiated atom transfer radical polymerization) technique. The N115-g-PSBMA membrane has shown higher hydrophilicity, lower vanadium permeability, higher coulombic efficiency and energy efficiency than that of commercial N115 membrane for VRB (vanadium redox flow battery) application. At the current density of 40–80 mA cm^{-2}, the average energy efficiency of the VRB with N115-g-PSBMA membrane has reached up to 87.3%, which is 2.6% higher than that of the VRB with N115 membrane at the same current densities. The method is expected to present a new direction to prepare novel separators with both excellent performances and low cost for VRB application.

1. Introduction

Recently, the reliable and large scale energy storage system (EES) has generated considerable interests for renewable energy, smart grid and distributed power generation development [1]. To date, different technologies have been pioneered to meet the energy storage demands including pumped hydro, compressed air energy storage, flywheels, Ni-metal batteries, Li-ion batteries, sodium-sulfur batteries, redox flow batteries and etc. [2] Among these EESs, all vanadium redox flow battery (VRB) invented by M. Skyllas-Kazacos et. al. [3] is now considered to be one of the most promising electrochemical storage technologies due to its large capacity, flexible design, long cycle life and high efficiency [4]. Membrane is one of the most critical components in VRB. The ideal membrane should possess high chemical and mechanical stability, high proton conductivity and low vanadium permeability as well as low cost [5,6]. So far, both ion exchange and non-ion exchange membranes have been developed for VRB application. Ion exchange membranes, especially cation exchange membranes (CEMs) have been widely applied in VRB due to the good proton conductivity. However, they often suffer from relatively higher vanadium permeability at the same time. On the other hand, due to Donnan exclusion effect, anion exchange membranes (AEMs) often exhibit low vanadium permeability in VRB. However, they often suffer from relatively lower ionic conductivity due to the lower anion mobility than that of protons [5,6]. In recent years, membranes with both cationic and anionic exchange groups in a single polymer matrix have shown great potential in VRB application, such as different kinds of amphoteric ion exchange membranes (AIEMs) [7]. The potential advantages of such membranes are that they possess both high proton conductivity and low vanadium permeability if appropriate molecular structures are designed. However, seldom studies have been referred to perfluorosulfonic acid (PFSA) polymers due to the high chemical stability of PFSA membrane and it is difficult for zwitterionic groups to be introduced into PFSA matrix by broking the high stable C–F bonds. Nafion is one of the most widely used PFSA membranes in VRB due to its high chemical and mechanical stability as well as good proton conductivity [8]. Nevertheless, Nafion often suffers from the relatively higher vanadium permeability and higher cost, which limits its further application in VRB [9]. Traditionally, sol-gel and solution casting methods are commonly used to modify Nafion in order to improve its selectivity. Very recently, the group of Ying-Ling Liu [10–12] has first discovered that the C-F groups and main-chain CF_2 groups of Nafion can be employed as the active sites to initiate atom transfer radical addition/polymerization (ATRA/ATRP). The exciting discovery provides a totally new and wide window for designing PFSA based polymers due to that ATRP is such a powerful and simple method to prepare for diverse polymer assemblies [13]. Following the research, Feng et al. [14] have prepared a series of Nafion-*co*-poly(1-vinylimidazole) (Nafion-PVIm) membranes with greatly enhanced proton conductivity and methanol resistivity for fuel cell application. Zwitterionic polymer such as sulfobetaine methacrylate (SBMA) is widely used as a monomer via ATRP to prepare membranes with better antifouling property and blood compatibility in the

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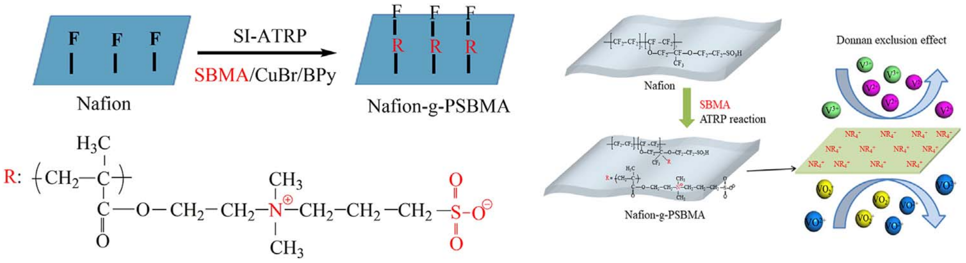

Scheme 1. Illustration of the Nafion-g-PSBMA membrane for VRB application.

field of biomedical applications [15]. However, to the best of our knowledge, there are no reports on the Nafion based membranes containing zwitterionic groups for VRB application via ATRP technique. Therefore, in this paper, the Nafion 115 membrane (N115) which exhibits the best comprehensive performance in VRB [16] is chosen as the ATRP initiator and reacts with SBMA to prepare a novel Nafion-based membrane containing both positive and negative groups for VRB application (Scheme 1).

In this design, the Nafion-g-PSBMA membrane is aimed to have both the high stability of Nafion and low vanadium permeability induced by Donnan exclusion effect of NR_4^+ groups in SBMA. Moreover, SO_3^- groups in SBMA are expected to remain the good voltage efficiency of modified Nafion membrane.

2. Experimental

2.1. Main materials

Nafion 115 (N115) was purchased from DuPont Company (USA). CuBr and 2,2′-dipyridyl (Bpy) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). SBMA was synthesized and confirmed by ^{1}H NMR according to the literature [17].

2.2. Preparation of N115-g-PSBMA membrane

A piece of N115 membrane was first treated according to the literature [18] and stored in deionized water before use. ATRP reaction of Nafion 115 with SBMA was referred to the literature [10,14]. MeOH/water solution, 2,2′-dipyridyl (Bpy), and CuBr were used as solvent, ligand and catalyst, respectively. SBMA was first mixed with 2,2′-dipyridyl in methanol/deionized water with thoroughly agitation to form a settled solution. After then, the pretreated Nafion membrane and CuBr were put into it and the system was kept at 60 °C and reacted for 48 h to make the SI-ATRP reaction fully conducted. All the process was conducted under Ar protection by vacuuming and filling the system with Ar for several times. After reaction, the Nafion-g-PSBMA membranes were drawn out and treated by H_2O_2 and H_2SO_4 and then stored in deionized water for further measurement. The prepared membraes were denoted as N115-g-PSBMA. The amount of SBMA grafted on the Nafion is 8.0% determined by weighting the pristine and grafted Nafion membranes after drying them at 80 °C for 24 h in a vacuum oven.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) of the samples were taken by using a Themo-Nicolet 380 (USA) spectrometer. ATR (attenuated total reflection) method was used with a diamond accessory as sample holder and the resolution was set as 4 cm^{-1}. SEM (scanning electro microscopy) images of the samples were obtained by using a Zeiss field emission scanning electron microscopy (Germany). All the SEM samples were pretreated by gold-spraying before test in order to enhance the conductivity. Surface elemental analysis of the samples was conducted using a Thermo Scientific ESCALAB250Xi X-ray photoelectron spectrometer (XPS) Instrument (USA) with the Al Kα as excitation radiation (1486.68 eV). Thermogravimetric analysis (TGA) of the samples were performed with a NETZSCH STA 449F5 analyzer (Germany). For each measurement, the sample was put into an Al_2O_3 pan and heated at a rate of 10 K min^{-1} under N_2 flow rate of 20 mL min^{-1}. All the samples were dried in a vacuum oven before test to remove any residue water on the membrane surface. Water contact angles (WCAs) test were performed using sessile drop method with a JGW-360 instrument (Chengde Chenghui, China). 2 μL of distilled water was dropped on the surface of the membranes at room temperature for each measurement. Three spots were chosen and tested for each sample of a given surface.

2.4. Physico-chemical properties

Cation exchange capacity (CEC) of all the membranes were determined by titration method. Samples were first dried at 80 °C for 24 h in a vacuum oven and weighed to obtain their dry mass (m_{dry}). After then, the samples were immersed into 2 mol L^{-1} NaCl solution for overnight to exchange all H^+ with Na^+. The solution was then analyzed with a standardized NaOH solution by using phenolphthalein as the indicator. The CEC value was then calculated with the formula (1).

$$\mathrm{CEC} = \frac{V_{\mathrm{iNaOH}} C_{\mathrm{NaOH}} - V_{\mathrm{eNaOH}} C_{\mathrm{NaOH}}}{m_{\mathrm{dry}}} \tag{1}$$

where C_{NaOH} is the molar concentration of NaOH, V_{iNaOH} and V_{eNaOH} is the initial and end volume of NaOH before and after titration, respectively, and m_{dry} is the mass of dry samples.

Water uptake (WU) and swelling ratio (SR) of the samples was obtained by the following procedures. Samples were first put into a vacuum oven under 80 °C for 24 h to get the dry mass (m_{dry}) and dry thickness (d_{dry}). After then, the dried membranes were soaked in deionized water at room temperature for 24 h to fully hydrate the membranes. Finally, the membranes were taken out, removing the water on their surface and quickly being weighted to obtain the wet mass (m_{wet}) and wet thickness (d_{wet}). The water uptake and swelling ratio were calculated by formula (2) and (3).

$$\text{Water uptake}\ (\%) = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \times 100\% \tag{2}$$

$$\text{Swelling ratio}\ (\%) = \frac{d_{\mathrm{wet}} - d_{\mathrm{dry}}}{d_{\mathrm{dry}}} \times 100\% \tag{3}$$

Ionic conductivity of deionized water fully hydrated membranes were acquired by using EIS (electrochemical impedance spectroscopy) technique. An electrochemical workstation CHI 660c (Shanghai Chenhua Instruments, China) with the frequency adjusted from 1 Hz to 100 kHz and the amplitude of 10 mV was used to conduct the analysis. The ionic conductivity of the samples was obtained by formula (4).

$$\sigma = \frac{L}{RA} \tag{4}$$

where σ is the ionic proton conductivity, L is the distance between two Pt electrodes, R is the membrane resistance obtained from EIS curves, and A refers to the area of the membrane.

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