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A novel amphoteric ion exchange membrane synthesized by radiation-induced grafting α-methylstyrene and *N*,*N*-dimethylaminoethyl methacrylate for vanadium redox flow battery application

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ABSTRACT

A novel amphoteric ion exchange membrane (AIEM) was synthesized by radiation-induced grafting α-methyl styrene (AMS) and dimethylaminoethyl methacrylate (DMAEMA) into poly(vinylidenedifluoride) (PVDF) films, followed by sulfonation and protonation processes. The monomer AMS could be co-grafted successfully with DMAEMA in the presence of $AlCl_3$ although it was difficult for AMS to be grafted solely into PVDF films. The grafting yield (*GY*) increased with absorbed dose up to about 40 kGy. It was found that the ratio of DMAEMA to AMS in the poly(DMAEMA-*co*-AMS) grafts changed slightly with various monomer ratio of DMAEMA to AMS in the feed by elemental analysis. The Micro-FTIR and XPS analyzes testified that the AIEM had been prepared as designed. The AIEM with a *GY* of 40% showed similar conductivity, higher IEC and lower permeability of vanadium ions compared with Nafion117 membrane. The vanadium redox flow battery (VRFB) assembled with the AIEM of 41.1% *GY* maintained an open circuit voltage higher than 1.4 V after placed for 60 h, which was much longer than that with the Nafion117 membrane. Therefore, it is expected to be excellent candidate for the application of VRFB.

1. Introduction

In recent years, vanadium redox flow battery (VRFB) has attracted more and more attention as energy storage system due to its long cycle life, deep discharge ability, high energy efficiency and low cost [1]. Ion exchange membrane (IEM) is one of the key components of the VRFB which is used to prevent the crossover of vanadium ions, and meanwhile allow the transport of ions to complete the conducting circuit. The ideal IEM should be designed with low permeability of vanadium ions, high conductivity, excellent chemical stability and low cost [2]. However, some commercial membranes such as Daramic and Selemion CMV membrane had poor stability in the V (V) electrolyte [3]. Nafion and Selemion AMV showed good chemical stability in V (V) solution, but the high cost limited the commercial application of them in VRFB [3]. Therefore, study on exploiting new IEMs with excellent chemical stability, low permeability of vanadium ions and high conductivity is of great importance to the successful commercial development of VRFB.

Modification of low-cost membranes by radiation grafting technology is a kind of effective method to prepare IEMs for electrochemical applications [4–6]. This technique exhibits obvious advantages, i.e. the properties of the membrane can be easily controlled by applying appropriate grafting conditions. Various hydrocarbon and fluorocarbon films have been employed as base films to prepare IEMs for fuel cell or VRFB. Poly(vinylidene difluoride) (PVDF) film combined with hydrocarbon and fluorocarbon structures is a kind of membrane with suitable mechanical properties, high chemical and thermal stability and high resistance to radiation [7–9]. The radiation-induced grafting of styrene (St), dimethylaminoethyl methacrylate (DMAEMA) and other monomers into PVDF films has been used to prepare IEMs for fuel cell and VRFB [10–12]. Nevertheless, the application of these IEMs including cation exchange membranes (CEMs) and anion exchange membranes (AEMs) in VRFB is still limited due to respective shortcomings. For example, the conductivity of CEMs is usually high but CEMs exhibit high permeability of vanadium ions [13], in contrast, AEMs can effectively suppress the crossover of vanadium ions but the conductivity of AEMs is relatively lower [14]. Therefore, it is necessary to prepare a novel IEM which possesses suitable conductivity and permeability of vanadium ions for the industrialization of VRFB. Amphoteric ion exchange membrane (AIEM) can

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effectively suppress vanadium ions crossover and meanwhile it possesses excellent conductivity performance [11].

The radiation-induced grafting of styrene (St) into base films and subsequent sulfonation has been widely used to prepare IEMs [15,16]. Moreover, it has been reported that a kind of AIEM grafted with St and DMAEMA was prepared and the VRFB charge-discharge test with the AIEM was performed [11,17]. However, the St sulfonic acid showed poor chemical stability because the tertiary hydrogen (α-hydrogen) of St is susceptible to chemical attack by the oxidative radicals [18,19]. It was found that the membranes prepared using a ring substituted St were more stable than polystyrene membranes under oxidative conditions [6,20]. One of the most stable substituted styrenic derivatives is α-H substituted St such as alpha-methyl styrene (AMS). It has been found that the polymerized AMS in which α position is protected by methyl group shows superior stability to polystyrene [21]. Moreover, AMS has an unmodified aromatic ring which makes AMS grafted chains to be sulfonated easily and its cost is low. However, AMS is very difficult to be grafted into the films alone because of the steric hindrance of the α-methyl group and the low ceiling temperature. Therefore, the co-grafting of AMS with other monomers is a more practical way [22–24].

In this work, AMS and DMAEMA were grafted into PVDF film for the first time via simultaneous irradiation technique, and with subsequent sulfonation and protonation, a novel AIEM was prepared. The parameters of the preparation procedure, such as initial monomer ratio of DMAEMA to AMS, and absorbed dose were investigated. Micro-FTIR, elemental analysis and XPS analysis were used to testify the successful grafting of AMS and DMAEMA into the base film. The properties of the resulting AIEM were also investigated, and the test of the AIEM in the VRFB system was performed to evaluate the prospect for its application in VRFB.

2. Experimental

2.1. Materials

PVDF film with a thickness of 25 μm was supplied by Kureha Company (Japan) and used as the base film. DMAEMA, AMS and St (99% purity) was purchased from Acros and used without further purification. Chlorosulfonic acid was purchased from Beijing Yili Fine Chemical Co. Ltd. Acetone and toluene (analytical reagent) were supplied by Beijing Chemical Regents Company. Hydrogen peroxide (30%) was purchased from Beijing Chemical Works. $VOSO_4 \cdot 5H_2O$ (analytical reagent) was supplied by Shanghai LvYuan Fine Chemical Plant. Aluminum trichloride ($AlCl_3$) was supplied by Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of the AIEM

The preparation route of the AIEM is shown in Scheme 1. A piece of PVDF film was washed with acetone to remove impurity on its surface and dried at 50 °C under vacuum for 24 h. Then the film with known weight was immersed into monomer solution. Three monomer solutions with DMAEMA/AMS molar ratios of 3, 0.75 and 0.18 in the total concentration of 30 (wt.%) were used, and the solvent was toluene. However, the obtained grafting yield (*GY*) was low because of the severe radiation-induced homopolymerization of the monomers. To increase the *GY*, 5 mg $AlCl_3$ powder was added into 100 ml monomer solution. After bubbling with nitrogen for about 15 min and sealed, the sample was subjected to γ-ray irradiation from a ^{60}Co source (Peking University). After irradiation with certain absorbed dose at a dose rate of 35 Gy/min, the film was placed in a Soxhlet's extractor to remove the non-grafted monomers, homopolymers and copolymers by toluene for 24 h, and the temperature of extraction was 110.8 °C which was the boiling point of toluene. Then the grafted film was dried at 50 °C under vacuum for 24 h. The *GY* was calculated as follows:

$$GY(\%) = \frac{W_a - W_b}{W_b} \times 100 \tag{1}$$

where W_a and W_b are weights of the film after and before grafting, respectively.

The grafted films (PVDF-*g*-PDMAEMA-*co*-PAMS) were sulfonated in a solution (0.2 M) of chlorosulfonic acid in dichloromethane at 50 °C for 8 h, and then hydrolyzed with distilled water at 60 °C overnight. Consequently, the dried films were protonated in 1 M HCl for 6 h, and then the resulting AIEMs (PVDF-*g*-PMAOEDMAC-*co*-PAMSSA) were kept in distilled water at room temperature before further use.

2.3. Characterization of the grafted film

Micro-FTIR analysis was performed on a Nicolet (NICOLET In10MX) spectrometer. The spectra were measured in absorbance mode in a wave number range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1} and 64 times of scanning. The detector is mercury cadmium telluride (MCT), and the beam-splitter is KBr/Ge. The membrane samples were flattened by diamond plates and then analyzed. Micro-FTIR analyzes were performed in reflected mode.

To determine the content of DMAEMA and AMS, the grafted film was subjected to elemental analysis using an Elementar Vario MICRO CUBE (Germany). The molar ratio of DMAEMA to AMS (n_{DMAEMA}/n_{AMS}) in poly(DMAEMA-*co*-AMS) grafts was determined according to the following equation:

$$\frac{n_{DMAEMA}}{n_{AMS}} = \frac{118.17 \times (100 + GY) \times P_N}{14 \times GY - (100 + GY) \times P_N \times 157.21} \tag{2}$$

where P_N is the content of nitrogen (wt.%); 14, 118.17 and 157.21 are molar mass of nitrogen, AMS and DMAEMA, respectively.

In order to study the amount of AMS in poly(DMAEMA-*co*-AMS) grafts of the grafted film, the mass ratio of DMAEMA to AMS of 4:1 was chosen to calculate. And the amount of AMS grafted into PVDF film was calculated according to Eq. (3):

$$\text{Amount of AMS}\,(\%) = \frac{118.17GY}{157.21 \times (n_{DMAEMA}/n_{AMS}) + 118.17} \tag{3}$$

where *GY* is the total *GY* of DMAEMA and AMS into PVDF base film, and n_{DMAEMA}/n_{AMS} is the molar ratio of DMAEMA to AMS in the grafts of the grafted film.

The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at a binding energy (*BE*) of 284.8 eV. The data were converted into VAMAS file format and imported into Casa XPS software package for manipulation and curve fitting.

2.4. IEC, ion conductivity and water uptake of the AIEM

The IEC (ion exchange capacity) of the AIEM was determined by acid-base titration. To measure the cation exchange capacity, a piece of dried AIEM with certain weight was immersed into 0.05 M NaOH overnight and stirred intermittently. The AIEM was washed by deionized water for several times, and the water was poured into the NaOH solution. Then the NaOH solution was back titrated with 0.05 M HCl to be neutral. IEC (mmol g^{-1}) was calculated as follows:

$$IEC = \frac{V_{NaOH}C_{NaOH} - V_{HCl}C_{HCl}}{W} \tag{4}$$