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Novel sulfonated poly (ether ether keton)/polyetherimide acid-base blend membranes for vanadium redox flow battery applications

Shuai Liu[a,b], Lihua Wang[a,*], Yue Ding[c], Biqian Liu[a], Xutong Han[c], Yanlin Song[a]

[a] Key laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P.R. China
[b] University of Chinese Academy of Sciences, 100049, P.R. China
[c] School of materials science and engineering, Tianjin Polytechnic University, Tianjin, 300387, P. R. China

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ABSTRACT

Novel acid-base blend membranes composed of sulfonated poly (ether ether ketone) (SPEEK) and polyetherimide (PEI) were prepared for vanadium redox flow battery (VRB). The blend membranes were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electronic microscopy (SEM). The ion exchange capacity (IEC), proton conductivity, water uptake, vanadium ion permeability and mechanical properties were measured. As a result, the acid-base blend membranes exhibit higher water uptake, IEC and lower vanadium ion permeability compared to Nafion117 membranes and all these properties decrease with the increase of PEI. In VRB single cell test, the VRB with blend membranes shows lower charge capacity loss, higher coulombic efficiency (CE) and energy efficiency (EE) than Nafion117 membrane. Furthermore, the acid-base blend membranes present stable performance up to 50 cycles with no significant decline in CE and EE. All experimental results indicate that the SPEEK/PEI (S/P) acid-base blend membranes show promising prospects for VRB.

1. Introduction

The vanadium redox flow battery (VRB) was pioneered by Skyllas-kazacos in 1985 [1–3] and has attracted considerable attention as a large-scale energy storage system due to its high energy efficiency, long cycle life, fast response time and flexible design. In a VRB system, the ion exchange membrane is one of the key materials, which effectively separates the anode and cathode electrolytes while allowing the transport of protons to complete the circuit. The ideal membranes used for VRB should exhibit high proton conductivity, low permeability for vanadium ions, and possess high chemical and mechanical stability [4]. The membranes traditionally used in VRB are perflurosulfonic acid membranes such as DuPont Nafion membranes. Even though the Nafion membranes show high chemical stability and proton conductivity, the high vanadium ion permeability and cost have limited their further application [5,6]. In addition, modification Nafion, modification polyvinylidene fluoride, and non-fluorinated membranes were also investigated and used in VRB [7–9]. These membranes exhibited lower vanadium ion permeability and good mechanical stability. However, the costs of these membranes are still higher as a result of the complexity of modification process.

Recently, several sulfonated aromatic polymers, such as sulfonated poly(ether ether keton)(SPEEK), sulfonated polyimide(SPI), and sulfonated polysulfone(SPSF) have been widely investigated as candidates in direct methanol fuel cells (DMFC) or vanadium redox flow batteries due to their lower costs, outstanding mechanical and chemical stabilities [10–15]. Among them, SPEEK has been widely studied as proton exchange membrane materials for its good mechanical property, low methanol and vanadium ions crossover, and thermal stability. In order to maximize the proton conductivity, the high degree of sulfonation is desired, which often causes high swelling and poor mechanical stability.

Blending is a facile way to improve the comprehensive properties of a matrix [16–18]. Among many types of blend membranes, the acid-base blend membranes show many attractive properties. Acid-base blend membranes described as organic-organic blend membranes are new class of interesting materials that exhibit improved proton conductivity and reduced methanol permeability when applied in DMFC [19–22]. Kerres and co-workers reported several acid-base blends based on SPEEK and some N-base polymers [23–28]. In this kind of acid-base blend membranes, the polymer chains cross-linked by the ionic interactions between sulfonic acid groups and N-containing groups, which reduced swelling and improved stability of the membranes. Besides, polymer

* Corresponding author. Tel.: +86 10 6265 0812; fax: +86 10 6255 9373.
E-mail address: wanglh@iccas.ac.cn (L. Wang).

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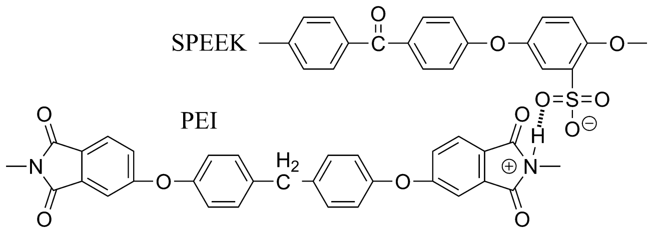

Fig. 1. Schematic of the interactions between SPEEK and PEI.

blending is an effective method to improve the mechanical and chemical stability via addition of another more stable component. Commercially available polyetherimide (PEI) has several important advantages, such as good chemical, thermal stability and low resistance [29–31]. The introduction of PEI (as a base polymer) in the SPEEK (as an acid polymer) membrane is an effective way to prepare a new kind of acid-base blend membranes applied in VRB. As seen in Fig. 1, the interactions between acid and base polymers, such as ionic cross-linking and hydrogen bond, contributed to control the swelling of membranes. Therefore, the acid-base blend membranes may have many advantages in VRB application, such as high proton conductivity, reduced vanadium ions crossover, good mechanical flexibility and chemical stability [32,33].

In this paper, S/P acid-base blend membranes were fabricated with different mass ratios. The microstructure and mechanical properties of the membranes were observed. Water uptake, ion exchange capacity, swelling ratio, proton conductivity and vanadium ion permeability were investigated. Compared to Nafion117 membranes, the acid-base blend membranes exhibited higher water uptake, IEC and lower vanadium ion permeability. In the VRB single cell performance, 50 charge-discharge cycles were also discussed and the corresponding coulombic, energy and voltage efficiencies were obtained.

2. Experimental

2.1. Materials

Nafion117 membrane was purchased from DuPont Co. PEEK was obtained from Changchun JIDA plastic engineering co. Ltd. PEI (Ultem® 1000) was provided from Dongguan BAIFU plastic technology co. Ltd. PEI and PEEK were used as received without further purification. Carbon felt and graphite felt were purchased from Beijing Jixing sheng'an Industry&Trade Co. Ltd., 99.999%; 1-methyl-2-pyrrolidone (NMP), NaCl, NaOH, $MgSO_4$ and H_2SO_4 were obtained from Beijing chemical reagent co. Ltd. All of them were used as received without further purification. All water was deionized.

2.2. Preparation of blend membranes

SPEEK were prepared as the following procedure: 12 g PEEK were added into H_2SO_4 (98%, 200 mL) at 25 °C with stirring under 200 rpm for 25 h. Subsequently, the solution was poured into ice-cold water under mechanical agitation for 3 h. The solution was stored overnight, followed by thorough washing with deionized water. Finally, the SPEEK was dried at 80 °C for 10 h.

S/P blend membranes were prepared with six different mass ratios: 100:0(S/P-0), 95:5 (S/P-1), 90:10(S/P-2), 85:15(S/P-3), 80:20(S/P-4) and 75:25(S/P-5). SPEEK and PEI were simultaneously dissolved in NMP to form 10wt% solutions with stirring at 60 °C for 12 h. After cooled to room temperature, the resulting polymer solutions were cast on glass plates and dried in a vacuum oven at 80 °C for 6 h, and then at 100 °C for 12 h. The dried membranes were peeled off from the substrates and kept in deionized water before using.

2.3. Characterization of S/P blend membranes

FT-IR spectra of the membranes were measured by BRUKERTENSOR-27 in the range of 4000-600 cm^{-1}. The samples were dried at 80 °C for 1 h before measurement.

The cross-section morphology of the blend membranes were examined with a Hitachi S4800 field emission scanning electron microscope. All the samples for cross-sectional view were fracture in liquid nitrogen.

The mechanical properties of the blend membranes were measured using a tensile machine (Instron 5567, TA Instruments Co.) at room temperature. The samples were tested at elongation rate of 5.0 mm min^{-1}. All membranes were tested five times to obtain an average value.

2.4. Water uptake and swelling ratio

The membranes were dried at 80 °C under vacuum for 24 h and the dry weights of the samples were weighed. Subsequently, the membranes were immersed in deionized water for 24 h at room temperature. After quickly wiping off the water adhered to the surface of the membranes, the weights and dimensions of wet membranes were measured. The water uptake and swelling ratio could be determined according to the following equations:

$$water\ uptake = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

Where W_{wet} and W_{dry} are the weights of membranes in wet and dry state, respectively.

$$swelling\ ratio = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (2)$$

Where L_{wet} and L_{dry} are the lengths of membranes in wet and dry state, respectively.

2.5. Ion exchange capacity (IEC)

The IEC of membranes was obtained by titration method. The dry membranes were immersed in the 1 mol L^{-1} NaCl solution for 24 h. This solution was titrated by 0.01 mol L^{-1} NaOH with phenolphthalein as the indicator. The IEC of the samples was calculated by following equation:

$$IEC = \frac{V_{NaOH} C_{NaOH}}{W_d} \quad (3)$$

Where V_{NaOH} is the volume of consumed NaOH solution, C_{NaOH} is the concentration of NaOH solution and W_d is the weight of the dry membrane.Proton conductivity (δ) and Vanadium ion permeability (P)

The area resistance of the membranes was measured by the method as described in literature [9,34]. The measurement was performed with a bi-compartmental device which consists of two cells separated by the membrane. Both compartments were filled with 1 mol L^{-1} H_2SO_4. The effective area of the membrane was 0.785 cm^2. The electric resistance was measured by electrochemical impedance spectroscopy (EIS) (Zahner Zennium) over a frequency range from 100 kHz to 100 MHz [35]. The resistance value associated with the membrane conductance was determined from a high-frequency intercept of the impedance with the real axis. The area resistance R can be calculated by the following expressions:

$$R = (r_1 - r_2)S \quad (4)$$