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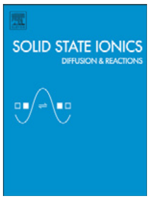

Sulfonated polyimide/chitosan composite membrane for vanadium redox flow battery: Influence of the infiltration time with chitosan solution

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A B S T R A C T

In order to probe the effect of the infiltration time with chitosan solution, a series of sulfonated polyimide/chitosan (SPI/CS) composite membranes with different infiltration time including 6 h, 12 h, 24 h and 36 h were prepared and applied in vanadium redox flow battery (VRB) system. SEM images demonstrate the presence of thin CS layer on the surface of SPI membrane, and the thickness of the CS layer increases with the infiltration time. The proton conductivity and the vanadium ion barrier property of SPI/CS composite membranes increase with the increment of the infiltration time. The SPI/CS-24 and SPI/CS-36 membranes show similar proton selectivity which is over eight times of that of Nafion® 117 membrane. VRB single cell using SPI/CS membrane reveals higher coulombic efficiency (*CE*) and energy efficiency (*EE*) than that using Nafion® 117 membrane. In particular, the *CE* and *EE* for SPI/CS-24 membrane achieve 97.8% and 88.6% respectively. All experimental results indicate that the SPI/CS composite membranes are promising proton conducting membranes for VRB, among which SPI/CS-24 membrane exhibits the best combination property.

1. Introduction

The vanadium redox flow battery (VRB) has attracted considerable attention owing to its long cycle life, flexible design, fast response time, deep discharge capability, low cost and low pollution. Therefore, it has a wide range of applications such as remote area power systems, emergency back-up usage and uninterruptable power sources (UPS) [1,2]. The proton conducting membrane is one of the key components for VRB, which effectively prevents the crossover of catholyte and anolyte and provides a conducting pathway to complete the circuit during the passage of current. An ideal proton conducting membrane for VRB should possess high proton conductivity, low vanadium ion permeability, excellent chemical stability, good mechanical strength and low price [3]. Most early commercial membranes except Nafion® membranes are unsuitable for VRB application due to their poor stability in VO_2^+ solution. However, Nafion® membranes also reveal high vanadium ion permeability and high production cost, which limit their large-scale application in VRB undoubtedly [4,5]. Therefore, developing novel proton conducting membranes with excellent cost performance is significantly important for commercial VRB application [6–8].

In our earlier work (revised for publication in Journal of Applied Polymer Science), the sulfonated polyimide/chitosan (SPI/CS) composite membrane prepared by an infiltration and self-assembly method has been demonstrated to possess low VO^{2+} permeability and reasonable proton conductivity for VRB application, where the time of infiltration with CS solution was set to be 24 h like other composite membranes such as sulfonated polysulfone/chitosan membrane [9] and sulfonated poly(ether ether ketone)/chitosan membrane [10]. However, how the infiltration time affects the performance of SPI/CS composite membrane is still unknown. Such a parameter is necessary to be determined to realize the future industrialization of SPI/CS composite membrane. Therefore, a series of SPI/CS composite membranes with different infiltration time were prepared in this work. The physico-chemical properties and the performances of VRB single cells using these SPI/CS composite membranes were also investigated respectively.

2. Experimental

2.1. Preparation of SPI/CS composite membranes

The SPI/CS composite membranes were prepared by the same infiltration and self-assembly method as that presented in our previous work (revised for publication). First, the random SPI with the sulfonation degree of 50% was synthesized according to C. Genies et al. [11]. Then the SPI was dissolved, coated and heated to be a membrane (in TEA salt form). The membrane in TEA salt form was transferred to be in proton form by soaking it in a 1.0 M H_2SO_4 solution. The structural formula of SPI (in proton form) was shown in Scheme 1.

Second, 2% (w/v) chitosan solution was prepared by dissolving certain chitosan powder in 2% acetic acid solution at 70 °C. After the chitosan powder was dissolved completely, bubbles in the chitosan

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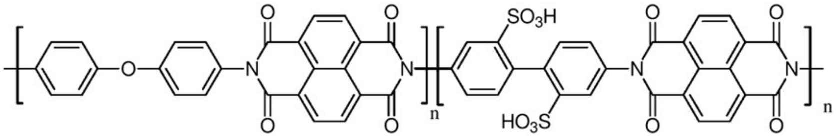


Scheme 1. Structural formula of sulfonated polyimide.

solution were removed, and then the chitosan solution was kept quiescent at room temperature. For preparation of SPI/CS composite membranes, the SPI membranes (in proton form) were immersed respectively in the previously prepared 2% (w/v) chitosan solution for different infiltration time such as 6 h, 12 h, 24 h and 36 h, and then dried at 50 °C for 6 h. Finally, the membranes were crosslinked with sulfuric acid for 10 h. Then these membranes were rinsed repeatedly with deionized water to remove the nonreactive monomers and stored in deionized water for further analysis. Thus, a series of SPI/CS membranes with different infiltration time with CS solution were obtained. Scheme 2 shows the crosslinking between CS and sulfuric acid [12], and Scheme 3 shows the interaction between the SPI and crosslinked CS.

2.2. Characterization of SPI/CS composite membranes

The cross-sectional images of SPI/CS membranes were determined using a FEI scanning electron microscope (SEM). All the membranes were dried, fractured in liquid nitrogen and the cross-sections were sputter-coated with Au prior to SEM measurements.

The thermal stability was determined by thermogravimetric analyzer (TGA) on a SDT Q600 analyzer in 100 mL min^{-1} nitrogen gas atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 700 °C.

The water uptake (*WU*) was defined as the ratio of the weight of absorbed water to that of the dry membrane. The swelling ratio was determined by the dimensional change as linear expansion ratio ($\triangle L$) [13]. The *WU* and swelling ratio were investigated by the methods as presented in the literature [14]. The *WU* and $\triangle L$ were calculated according to Eqs. (1) and (2):

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

$$\Delta L(\%) = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100 \quad (2)$$

where W_{wet} and W_{dry} are the weight of the wet and dry membranes (g), respectively. L_{wet} and L_{dry} are the length of the wet and dry membranes (cm), respectively.

The proton conductivity was determined using four-point-probe electrochemical impedance spectroscopy (EIS) [15,16] with Princeton 2273 electrochemical workstation at galvanostatic mode with ac current amplitude of 5 mA over frequency range from 1.0 Hz to 100 kHz. All the membranes were immersed in deionized water overnight prior to the measurement. The proton conductivity was calculated using Eq. (3):

$$\sigma = \frac{L}{R \times S \times d} \quad (3)$$

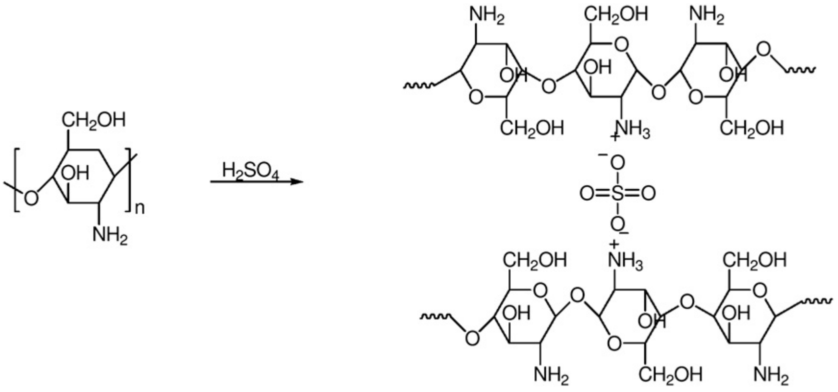
where σ is the proton conductivity (S cm^{-1}), R the obtained membrane resistance (Ω), L the distance between two platinum wires (cm), S and d the width (cm) and thickness ($\times 10^{-4}$ cm) of the membrane, respectively.

The permeability of vanadium ion was investigated by the method as in the literature [17]. 120 mL of 1.0 M $VOSO_4$ in 2.0 M H_2SO_4 solution and 120 mL of 1.0 M $MgSO_4$ in 2.0 M H_2SO_4 solution were filled into the left and right compartments, respectively. The two compartments were separated by the proton conducting membrane, and the effective membrane area was 5.31 cm^2. $MgSO_4$ here was used to balance the ionic strength of two solutions and reduce the osmotic pressure effect. The sample solution was taken out from the right compartment at a regular time and the concentration of VO^{2+} was determined by Ultraviolet–visible spectroscopy (UV-1200). VO^{2+} concentration in the right compartment as a function of time was given by the following Eq. (4):

$$\frac{dC_{\mathrm{R(t)}}}{dt} = \frac{A \cdot P}{V_R \cdot d}\left(C_{\mathrm{L}} - C_{\mathrm{R(t)}}\right) \quad (4)$$

where C_{L} is VO^{2+} concentration in the left compartment (mol L^{-1}), $C_{\mathrm{R}(t)}$ is VO^{2+} concentration (mol L^{-1}) in the right compartment at diffusion time t (min). V_{R} is the volume of the right compartment (cm^3). A (cm^2) and d ($\times 10^{-4}$ cm) are the area and the thickness of the membrane, respectively. P is VO^{2+} permeability coefficient of the membrane (cm^2 min^{-1}). And an assumption that the P is independent of vanadium ion concentration is made here.

The tensile strength was measured at room temperature and relative humidity of 50% by Qingji 201A universal tester. The membrane was cut into a size of 5 mm × 75 mm with dumbbell shape and pulled



Scheme 2. Crosslinking reaction of chitosan with sulfuric acid [12].