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Sulfonated Poly(Ether Ether Ketone)/Functionalized Carbon Nanotube Composite Membrane for Vanadium Redox Flow Battery Applications

Chuankun Jia *, Yuanhang Cheng, Xiao Ling, Guanjie Wei, Jianguo Liu, Chuanwei Yan *

Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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A novel sulfonated poly(ether ether ketone) (SPEEK) membrane embedded with the short-carboxylic multi-walled carbon nanotube (we name it as SPEEK/SCCT membrane) for vanadium redox flow battery (VRB) has been prepared with low capacity loss, low cost and high energy efficiency. The mechanical strength, vanadium ions permeability and performance of the membrane in the VRB single cell were characterized. Results showed that the SPEEK/SCCT membrane possessed low permeability of vanadium ions, accompanied by higher mechanical strength than the Nafion 212 membrane. The VRB single cell with SPEEK/SCCT membrane showed 7% higher coulombic efficiency (CE), 6% higher energy efficiency (EE) but lower capacity loss in comparison with the one with Nafion 212. The good cell performance, low capacity loss and high vanadium ions barrier properties of the blend membrane is of significant interest for VRB applications.

1. Introduction

Vanadium redox flow battery (VRB) as a large-scale electrochemical energy storage system possessing high storage capacity, flexible design and long cycle life, is one of the most promising systems used to solve the intermittence of wind and solar energy [1–3]. In a VRB, the proton exchange membrane is a critical component that separates the anode and cathode electrolytes while allowing the transport of ions. Up to now, Nafion membranes have been the reference membrane for VRB because of the good chemical stability and high proton conductivity [4]. However, Nafion membranes used in VRB suffer from high vanadium ions crossover, which leads to an increase in the self-discharge and consequently results in low columbic efficiency. In addition, the main limitation of Nafion membranes is the high cost [5,6]. In this regard, sulfonated aromatic membranes like sulfonated poly (sulfone) and poly(ether ether ketone) have been widely investigated as alternative materials for VRB applications owing to their low vanadium ions permeability and low cost [7–9]. It has been reported that the sulfonated poly(ether ether ketone) (SPEEK) membrane exhibits good performances for VRB application such as low vanadium ions crossover and low cost. However, the mechanical properties of a SPEEK membrane with high degree of sulfonation (DS) tend to deteriorate, which lower the long time stability for VRB application. Furthermore, increasing the number of ion exchange groups leads to high swelling and excessive vanadium crossover, and thus affects the battery performances [10].

Functional carbon nanotubes (CNTs)-modified Nafion and SPEEK membranes have been reported and shown low methanol crossover and enhanced mechanical properties [11,12]. Very recently, Dai et al. have reported SPEEK/Graphene membrane applied in VRB with enhanced performance, such as: increased proton conductivity, higher mechanical property and chemical stability, and relatively low vanadium ion permeability [13]. However, until now, to the best of our knowledge, there is no report about such membranes for VRB application. Moreover, in our previous work, we studied the short-carboxylic multi-walled carbon nanotube (SCCT) modified carbon felt electrode [14]. The results show that the modified carbon felt electrode exhibit excellent electrochemical activity and durability. In order to combine the reinforcement effects of SPEEK and the excellent electro-catalytic activity of SCCT, in this study, a novel SPEEK/short-carboxylic multi-walled carbon nanotubes nanocomposite membrane was prepared and used in the VRB for the first time. There are some potential advantages of using CNTs embedded in SPEEK as a proton exchange membrane for VRB application such as high mechanical strength, high surface area, high electro-catalytic activity and low vanadium ions crossover, which can improve the performance of VRB.

* Corresponding author. Tel.: +86 24 2399 8320, fax: +86 24 2388 0201.
E-mail addresses: jack2012ding@gmail.com (C. Jia), cwyan@imr.ac.cn (C. Yan).

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2. Experimental Details

2.1. Chemicals

Poly(ether ether ketone) (Victrex, PEEK 450 PF). short-carboxylic multi-walled carbon nanotubes (length: 0.5–2 μm, diameter <8 nm, Purity >95%, -COOH content 3.86 wt.%) were obtained from Nanjing XFNANO Materials Tech Co. Ltd. Dimethylsulfoxide (DMSO) and sulfuric acid (98 wt.%). All chemicals were used as received.

2.2. Preparation of SPEEK/SCCT membrane

SPEEK was prepared as description in reference [15]. The degree of sulfonation of the SPEEK was determined by titration methods [16]. 1.00 g SPEEK was inmersed into 50 mL NaCl solution (0.5 M) for 24 h to fully replaced the H^+ in the–SO_3H group into the Na^+. The resulting solution was titrated by 0.01 M NaOH standard solution with phenolphthalein as indicator. The DS of the prepared SPEEK is 50.2%. For preparation of nanocomposite membrane, 1.7 g SPEEK was dissolved in 40 mL DMSO to form a solution under magnetic stirring and SCCT (12 mg) was then added to the solution. The resulting mixture was stirred for about 5 h and further sonicated for 10 min at ambient temperature. The mixture was cast into a purpose-made grooved glass plate and heated at 100 °C for 12–15 h to remove solvents. For comparison, SPEEK blank membrane was prepared under the same conditions. The DMSO/SCCT and DMSO/SPEEK/SCCT ink were also prepared as described in supporting information to compare the dispersion of CNT.

2.3. Characterization of the membrane

2.3.1. Scanning electron microscopy

The as prepared membrane was cut using freeze-fractured in liquid nitrogen, and the cross-section of it was observed by a ZEISS scanning electron microscopy (SEM). The accelerating voltage was 15.00 kV, and the magnification was 5000x and 10,000x respectively.

2.3.2. Atomic force microscopy

Atomic Force Microscopy (AFM) was performed with Picoscan^{TM} 2500 (Agilent) in tapping mode at the ambient temperature to study the morphology of membranes. The scan area was 2000 nm × 2000 nm.

2.3.3. Mechanical strength

The mechanical strength of the membranes was measured by CMT 6502 tension tester (Shenzhen Instron Corporation China) at room temperature with a strain rate of 5 mm min^{-1}.

The mechanical strength of SPEEK/SCCT membrane is calculated as follows:

Mechanical strength = $F_m/(W \times L)$

Where F_m is the maximum strength, W is the width of the sample for mechanical measurement and L is thickness of the membrane.

2.4. Vanadium ions permeability and single cell performance

The vanadium ions permeability and cell performances of VRB with different membranes were determined as described in our previous work at room temperature [17]. The carbon felt served as electrodes while the conductive plastic plates served as current collectors, the active area of the electrode was 28 cm^2.

In order to test the vanadium ion permeability, 70 mL of 1.5 M $VOSO_4$ in 2.0 M H_2SO_4 solution was kept in one reservior and 1.5 M $MgSO_4$ in 2.0 M H_2SO_4 solution in the other. Then, 1 mL sample was taken from the MgSO4 reservoir at regular intervals. UV–vs spectrometer was used to determine the concentration of vanadium ions in the sample solution. The permeability of vanadium ions (P) was calculated by the following equation [18]

$$V_B \frac{dc_B(t)}{dt} = A\frac{P}{L}(c_A - c_B(t))$$

Where V_B is the solution volume of $MgSO_4$ reservoir, c_A is the concentration of VO_2^+ ions in $VOSO_4$ reservoir, $c_B(t)$ is the concentration of VO_2^+ ions in the $MgSO_4$ reservoir. A and L is the active area and the thickness of the membrane, respectively.

In the single cell performance, 1.5 M $VOSO_4$ + 2 M H_2SO_4 served as both catholyte (160 mL) and anolyte (80 mL), and were kept separately in two reservoirs. The resistances of VRB single cell with and without the membrane were measured by DME-20 Battery Internal Resistance Tester, respectively. And the area resistance (R) and the conductivity (σ) of the membrane in a VRB cell were calculated as following equations:

$$R = (R_1 - R_0) \times A \text{and} \sigma = L/R$$

Where, R_0 refers to the resistance of single cell without membrane, R_1 is the resistance of single cell with membrane, A is the active area as mentioned above and L is the thickness of the membrane. The short circuit of SPEEK/SCCT membrane is also investigated by the digital multimeter (See the supporting information, Fig. S1 a-e)

The VRB single cell with membrane was charged and discharged at a constant current density of 50 mA cm^{-2} with the voltage range from 0.75 to 1.65 V.

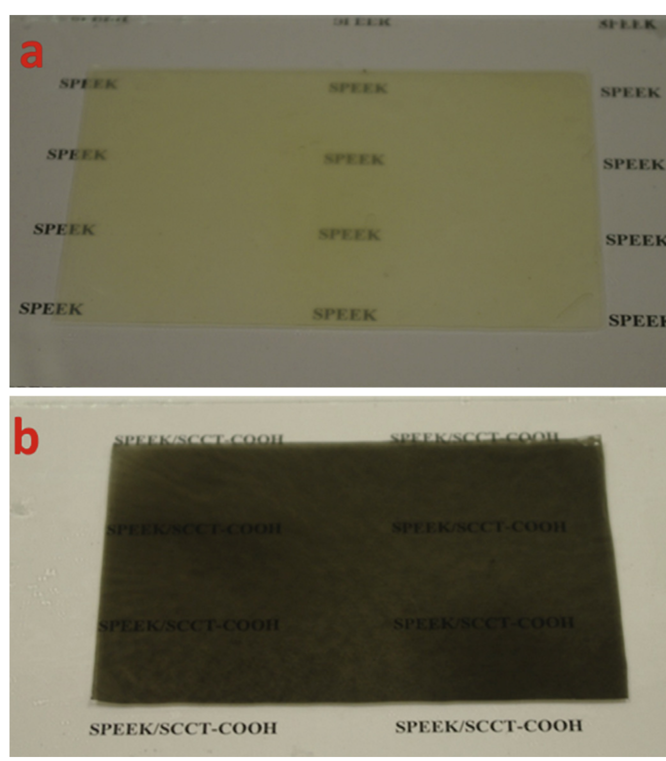

Fig. 1. Visual image: (a) SPEEK membrane, (b) SPEEK/SCCT membrane.