Journal of Power Sources 257 (2014) 221–229

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Sulfonated poly(ether ether ketone)/mesoporous silica hybrid membrane for high performance vanadium redox flow battery

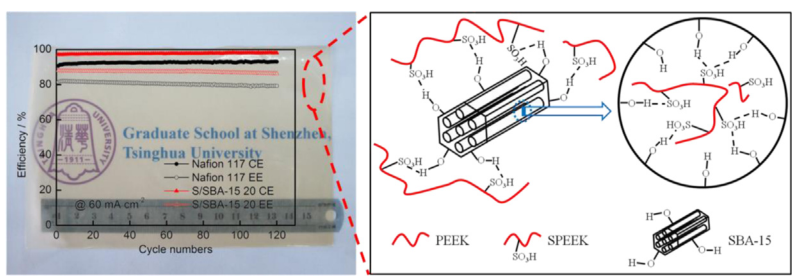
Zhaohua Li [a,b], Wenjing Dai [a], Lihong Yu [c], Jingyu Xi [a,*], Xinping Qiu [a,b,**], Liquan Chen [a,b]

[a] Lab of Advanced Power Sources, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China
[b] Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China
[c] Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

HIGHLIGHTS

- SPEEK/SBA-15 (S/SBA-15) hybrid membranes are used in vanadium redox flow battery.
- S/SBA-15 hybrid membranes are dense and homogeneous with no visible hole.
- Membranes show good property trends for the interaction between SPEEK and SBA-15.
- S/SBA-15 20 membrane shows highest efficiency and highly stable cycle performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form
17 January 2014
Accepted 28 January 2014
Available online 8 February 2014

Keywords:
Vanadium redox flow battery
Sulfonated poly(ether ether ketone)
Mesoporous silica
Hybrid membrane

ABSTRACT

Hybrid membranes of sulfonated poly(ether ether ketone) (SPEEK) and mesoporous silica SBA-15 are prepared with various mass ratios for vanadium redox flow battery (VRB) application and investigated in detail. The hybrid membranes are dense and homogeneous with no visible hole as the SEM and EDX images shown. With the increasing of SBA-15 mass ratio, the physicochemical property, VO^{2+} permeability, mechanical property and thermal stability of hybrid membranes exhibit good trends, which can be attributed to the interaction between SPEEK and SBA-15. The hybrid membrane with 20 wt.% SBA-15 (termed as S/SBA-15 20) shows the VRB single cell performance of CE 96.3% and EE 88.1% at 60 mA cm^{-2} due to its good balance of proton conductivity and VO^{2+} permeability, while Nafion 117 membrane shows the cell performance of CE 92.2% and EE 81.0%. Besides, the S/SBA-15 20 membrane shows stable cell performance of highly stable efficiency and slower discharge capacity decline during 120 cycles at 60 mA cm^{-2}. Therefore, the SPEEK/SBA-15 hybrid membranes with optimized mass ratio and excellent VRB performance can be achieved, exhibiting good potential usage in VRB systems.

1. Introduction

To fulfill the rapid increasing of global usage of renewable energy such as wind and solar energy, it is urgent to develop a safe and effective electrical energy storage (EES) to surmount the instability and intermittence natures of the renewable energy [1,2]. As a sort of rechargeable battery, vanadium redox flow battery (VRB), which is pioneered and developed by M. Skyllas-Kazacos et al. [3–6], has been considered to be a promising candidate for

* Corresponding author. Tel.: +86 755 2603 6436; fax: +86 755 2603 6181.
** Corresponding author. Lab of Advanced Power Sources, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China. Tel./fax: +86 10 6279 4234.
E-mail addresses: xijingyu@gmail.com (J. Xi), qiuxp@tsinghua.edu.cn (X. Qiu).

http://dx.doi.org/10.1016/j.jpowsour.2014.01.127
0378-7753/

stationary EES due to its features like long cycle life, low cost, flexible design and high energy efficiency [7–9]. The conventional VRB, with the standard open circuit cell voltage of 1.26 V, employs VO^{2+}/VO_2^+ and V^{2+}/V^{3+} dissolved in sulfuric acid as the positive and negative electrolytes respectively, carbon materials as the electrodes, and ion exchange membranes (IEMs) as the separators [10,11]. To date, many progresses have been reported in high concentration and stability electrolytes, high activity electrodes, high performance membranes, monitoring, modeling, etc [12–20]. However, the lack of low-cost membrane accompanied with low vanadium ion permeability and high VRB performance is limiting the commercialization of VRB.

The commonly used IEMs in VRB are perfluorosulfonic polymer such as Nafion membranes (DuPont) owing to their high proton conductivity and excellent chemical, electrochemical stability. However, the Nafion membranes possess high vanadium ion permeability accompanied with corresponding problems like low efficiency and fast capacity decline [21]. Though great deal of modified Nafion membranes with improving VRB performances have been prepared and researched [22–29], the costs of these membranes for large-scale VRB systems are still extremely high. The modified Nafion membranes are not suitable for the commercialization of VRB systems. Therefore, alternative low-cost membrane with high performance is imminently required for the widely usage of VRB.

Owing to the feature of low cost, the nonionic porous membranes have been researched for VRB applications recently [30–32]. The porous membrane could separate vanadium ions from protons via pore size exclusion due to the differences in stokes radius, causing low vanadium ion permeability and relatively high VRB performance. However, it is hard to control the uniform morphology of porous membrane, and the heterogeneous morphology would highly affect the VRB performance. Further optimization should be proposed to make homogeneous morphology of porous membrane and higher VRB performance.

In recent years several research groups have tried to develop anion exchange membranes (AEMs) as alternative low-cost materials for VRB application [33–36]. The low vanadium ion permeability of AEM can be due to the Donnan exclusion effect between cationic groups in AEM and vanadium ions. Furthermore, the decrease of VO_2^+ adsorbed in AEM could be postulated to reduce the chemical degradation of membrane. However, the much lower ionic conductivity of AEM, which is owing to the slower mobility of sulfate anion served as the major charge carrier, would lead to lower voltage efficiency and energy efficiency, making AEM unsuitable for VRB high current density application. Therefore, the cation exchange membranes (CEMs) are still drawing considerable attention for the widely usability in VRB systems.

As one kind of CEMs, the sulfonated poly aromatic membranes have been assessed in VRB systems as candidates for the substitution of Nafion membranes [37–41]. In these sulfonated poly aromatic membranes, the sulfonated poly(ether ether ketone) (SPEEK) membrane has received more attention due to its easy preparation and high VRB performance. However, high degree of sulfonation (DS) SPEEK membrane would cause high vanadium ion permeability, low membrane stability and VRB performance, which are limiting its further application in VRB. Thus the inorganic doping [40] or polymer blending [17] modification of high DS SPEEK membrane could be used to prepare composite membranes with high VRB performance.

The mesoporous silica SBA-15 could be used in many fields due to its ordered mesoporous pore structure and high mechanical, thermal stability [42,43]. As excellent inorganic filler, SBA-15 modified with high DS SPEEK hybrid membranes would possess low vanadium ion permeability and high membrane stability by the postulate of hydrogen bond formed between $-SO_3H$ group from SPEEK and $-OH$ group on SBA-15, resulting in low-cost and high performance membranes for VRB. In this work, the SPEEK/SBA-15 hybrid membranes were prepared by solution casting method. The morphology, physicochemical property, VO^{2+} permeability, mechanical property, thermal stability and VRB single cell performance of the hybrid membranes were investigated and discussed in detail. The interaction mechanism between SPEEK and SBA-15 was also proposed.

2. Experimental

2.1. Materials and membrane preparation

Poly(ether ether ketone) (PEEK) (Victrex, PEEK 450P) was washed and then dried. Sulfonated poly(ether ether ketone) (SPEEK) with ion exchange capacity (IEC) of 2.12 mmol g^{-1} (DS = 0.74) was prepared according to our previous report [17], and its chemical structure was shown in Scheme 1. Mesoporous silica SBA-15 (Pore Diameter: 9 ∼ 10 nm; BET: 800 $m^2\ g^{-1}$) was purchased from China Nanjing XFNano Material Tech Co., Ltd. Nafion 117 membrane was purchased from Dupont company. Other reagents were all analytical grade and used without further purification.

The SPEEK/SBA-15 hybrid membranes were prepared by solution casting method as following procedures. First, predetermined weight of SBA-15 was added in 10 mL *N*,*N*-Dimethylformamide (DMF) to make a homogeneous suspension via 30 min of ultrasonic dispersion. Then the corresponding weight of SPEEK was added in the SBA-15 homogeneous suspension and magnetic stirred for 24 h to form a 15 wt./vol.% homogeneous casting solution. The casting solution was cast on a clean plate glass and dried at 60 °C over night, then dried at 80 °C for 24 h in vacuum. The membrane was peeled off from the plate glass by immersing the plate glass into deionized water. Finally, the membrane was immersed in 1 mol L^{-1} H_2SO_4 solution for 24 h, then immersed in deionized water for 48 h to remove the residual acid solution, and stored in deionized water.

The SPEEK/SBA-15 hybrid membranes with various SBA-15 mass ratios are termed as S/SBA-15 *X*, where *X* is the SBA-15 mass ratio. For example, the S/SBA-15 20 is a membrane with 20 wt.% SBA-15 and 80 wt.% SPEEK. Besides, the Nafion 117 membrane served as reference membrane was pretreated by the standard method according to our previous report [17].

2.2. Membrane characterization

2.2.1. Morphology

The morphology and EDX of membrane cross-section were confirmed by SEM (Hitachi S-4800, Japan). The sample membrane prepared for the morphology observation was obtained by breaking the sample membrane in liquid nitrogen and then coating it with gold.

2.2.2. Physicochemical property

The residual water on the surface of sample membrane was wiped off with filter papers, following with the quick measurements of size and weight. Then the sample membrane was dried at 100 °C in vacuum for 12 h and measured as soon as possible. The above-mentioned procedures were repeated at least three times to gain a good data reproducibility. The water uptake and swelling ratio of sample membrane were calculated by following equations:

$$\text{Water uptake }(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{1}$$

$$\text{Swelling ratio }(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \tag{2}$$