Journal of Membrane Science 539 (2017) 197–205

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Highly selective sulfonated poly(ether ether ketone)/titanium oxide composite membranes for vanadium redox flow batteries

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ARTICLE INFO

Keywords:
Vanadium redox flow batteries
Sulfonated poly(ether ether ketone)
Titanium oxide nanoparticles
Composite membranes

ABSTRACT

To lower the cost and enhance the selectivity of membranes used in vanadium redox flow batteries (VRFBs), sulfonated poly(ether ether ketone) (SPEEK)/ titanium oxide (TiO_2) composite membranes with different degrees of sulfonation (DS) (prepared at different time durations of 3 h, 5 h and 7 h) and various TiO_2 nanoparticles loadings (3%, 5% and 7%) were prepared. Optimum DS and TiO_2 nanoparticles loading were confirmed by different characterization techniques including ^{1}H NMR, scanning electron microscopy, water uptake, swelling ratio, proton conductivity, vanadium ion permeability and thermal stability. Results show that 5 h SPEEK/5% TiO_2 composite membrane possessed comprehensive merits, especially high ion selectivity (72.55×10^3 S min cm^{-3}) due to the blocking effect of TiO_2 nanoparticles and good proton conductivity. TiO_2 nanoparticles combined very well with SPEEK due to strong interaction, as deduced from flux tests. The chemical and oxidative stability were sufficiently good for applications of VRFB. The VRFB single cell with 5 h SPEEK/5% TiO_2 composite membrane exhibited excellent performance including high coulombic efficiency (98.3%), high energy efficiency (82.9%), long self-discharge time and low capacity loss compared to Nafion 117. Hence, SPEEK/TiO_2 composite membranes can potentially be promising substitute for Nafion in VRFBs.

1. Introduction

The demand for electric energy is growing due to increasing population and industrialization [1]. Current electrical energy comes from large fossil-fuel, nuclear and hydroelectric power plants [2]. However, rapid consumption of limited fossil resources emits massive greenhouse gas leading to global warming and climate change [3]. To reduce the carbon footprint and environmental impact of electricity generation, renewable energy such as wind and solar energy draws much attention globally [4]. Thus, large-scale energy storage systems with good stability are required as a result of the intermittency of renewable sources. These systems are able to match supply and consumption demand [5]. So far, the most promising large-scale energy storage systems are redox flow batteries (RFBs) which offers many advantages including durability, high round-trip efficiency, flexible design, rapid response, safety and reasonable capital costs [6]. A typical redox flow battery uses reversible electrochemical couples on two electrodes to store chemical energy, whose reactants are dissolved in two electrolyte solutions and stored in external tanks, which separates power and energy [7]. Among various RFB technologies, the vanadium redox flow batteries (VRFBs) pioneered at the University of New South Wales (UNSW) by Maria Skyllas Kazacos and co-workers are the most widely used and commercialized flow batteries [8]. VRFBs have four different oxidation states of vanadium ions as two redox couples separated by the ion exchange membrane, which do not generate any toxic gases, have a low risk of explosion and very little environmental impact [9,10].

Ion exchange membrane (IEM) preventing positive and negative electrolyte from cross-mixing while transporting protons is a key component of the VRFBs. The most commonly used IEM is Dupont's Nafion® with high chemical stability and excellent proton conductivity. But the expensive cost and low ion selectivity due to water channel with 4.0 nm diameter of Nafion membrane have restricted its further commercialization [11,12]. Therefore, alternative membranes development are needed. An idea membrane is with high proton conductivity, low active ion permeation, low resistance, good chemical stability and low cost [13]. To date, there are many kinds of alternative membranes being studied such as polyvinylidene fluoride (PVDF), sulfonated polysulfone (SPSF), sulfonated poly (fluorenyl ether ketone sulfone) (SPAEK), polybenzimidazole (PBI) and sulfonated poly(ether ether ketone) (SPEEK) [14–18]. Poly(ether ether ketone) (PEEK) polymer has good chemical, thermal and mechanical stability. Proton conductive SPEEK membrane with smaller water channel is a good alternative of

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http://dx.doi.org/10.1016/j.memsci.2017.06.015
Received 12 July 2016; Received in revised form 16 May 2017; Accepted 5 June 2017
Available online 08 June 2017
0376-7388/

Nafion®, which performs well in VRFBs with easy preparation, low ion crossover and low cost [19,20]. However, SPEEK with high degree of sulfonation has relatively low mechanical stability due to swelling and high vanadium ions crossover due to relatively wide water channel in SPEEK [17]. In previous literatures, inorganic particles had been incorporated into Nafion membranes to reduce the size of the water channel, thereby reducing vanadium ion permeability across the membrane [21–23]. Inspired by these previous studies, incorporating inorganic particles into SPEEK as a barrier was performed to reduce vanadium ion permeability. Another advantage of incorporating inorganic particles into SPEEK is attributed to the inorganic particles' ability to increase the mechanical stability of the membrane due to the hydrogen bond formed between the -SO_3H group from SPEEK and the –OH group from the inorganic particles [24]. There is a literature which incorporates three kinds of nano oxides into SPEEK backbone using N-methyl-2-pyrrolidone (NMP) as solvent without optimization of balance between DS and ratio of nano oxides [25].

In this work, titanium oxide (TiO_2) was used as the inorganic filler of SPEEK polymer with the expectation to enhance the properties of SPEEK/TiO_2 composite membrane and the performance of VRFB. The schematic illustration of the membrane is shown in Fig. 1A. Carbon felt was used as the electrode of VRFB due to its excellent stability and high active surface area [26]. Thermal activation of electrodes was performed to improve VRFB kinetic performance [27]. In this study, highly selective SPEEK/TiO_2 composite membranes optimized with different DS and various TiO_2 loading were prepared by solution casting method using dimethyl sulfoxide (DMSO) as solvent causing more uniform composite membranes. The fabricated composite membranes would have higher selectivity and better RFB performance compared to the literature mentioned above [25]. Characterizations of SPEEK/TiO_2 composite membrane including water uptake, ion exchange capacity, swelling ratio, thermal analysis, proton conductivity, vanadium ions permeability and cycling performance of VRFB were implemented. All the measurements were also carried out on Nafion® as comparison.

2. Experimental

2.1. Materials

Vanadium (IV) oxide sulfate hydrate $VOSO_4{\cdot}nH_2O$ (97%, n = 3), PEEK and TiO_2 (21 nm nanopowder) were purchased from Sigma-Aldrich (Singapore). PEEK was dried in the vacuum oven at 100 °C overnight before use. $MgSO_4$, NaOH, NaCl, dimethyl sulfoxide (DMSO) and H_2SO_4 (98%) were used as received.

2.2. Membrane preparation

50 mL of concentrated sulfuric acid was added into dried PEEK (5.0 g). The reaction mixture was heated up to 50 °C and stirred for 3, 5 or 7 h to make SPEEK with different degrees of sulfonation. After which, the reaction was quenched by pouring the reaction mixture into ice water while stirring. The mixture was stored in a refrigerator overnight and washed with cold water until pH became 7. The synthesized SPEEK was left to dry in air for 2 h and then dried in an oven at 60 °C overnight. SPEEK/TiO_2 membrane was fabricated according to a previously reported procedure [28]. In detail, dried SPEEK (1.5 g) was sonicated for 1 h in 10 mL of DMSO to dissolve it. After which, the mixture was stirred for 1 h while 3%, 5% or 7% of TiO_2 by weight was dissolved in 4 mL DMSO and the solution was sonicated for 1 h. The TiO_2 suspension was then poured into the SPEEK/DMSO mixture and stirred vigorously with a magnetic stirrer. The resultant mixture was cast onto a flat clean glass. The membranes were dried at 80 °C for 2 days and peeled off from the glass in deionized water. The membranes were then soaked in 1 M H_2SO_4 for 1 day and then immersed in deionized water for 1 day to remove excess acid. The SPEEK/TiO_2 membrane was finally stored in deionized water for further use.

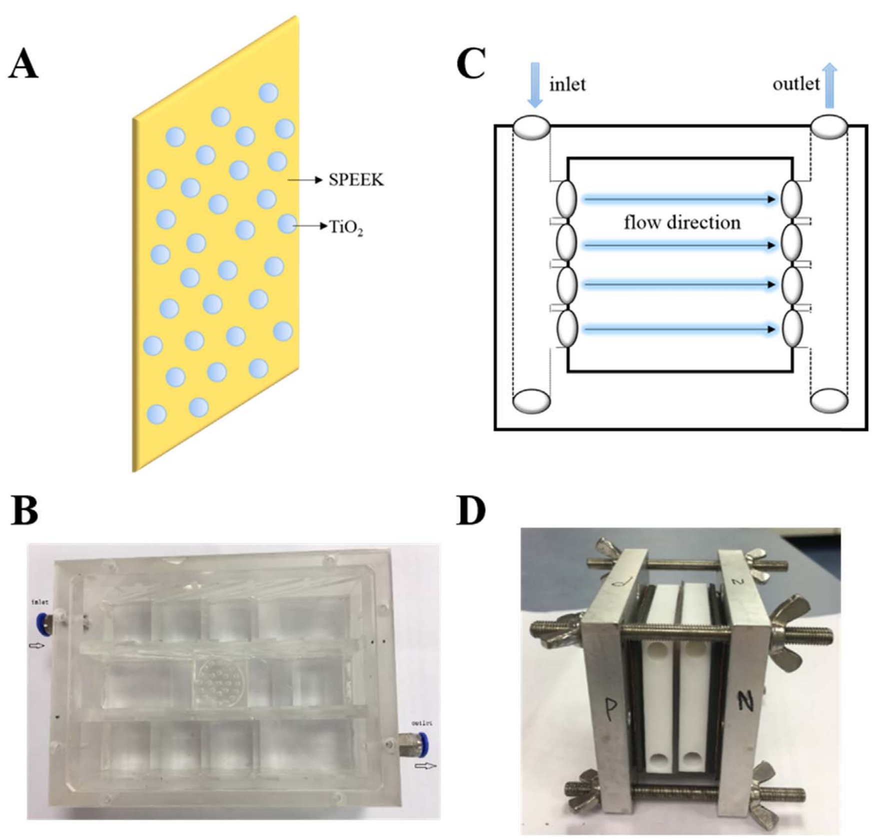

Fig. 1. (A) Scheme of SPEEK/TiO_2 membrane. (B) Digital photo of set-up for membrane flux test. (C) Scheme of teflon flow frame. (D) Digital photo of VRFB single cell configuration.