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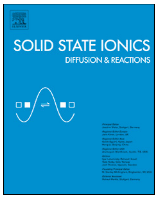

High ionic selectivity of low permeable organic composite membrane with amphiphilic polymer for vanadium redox flow batteries

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ABSTRACT

Blend membranes comprising sulfonated poly(ether ether ketone) (sPEEK), poly(vinylidene fluoride) (PVdF), and urethane acrylate non-ionomer (UAN) were prepared for application in vanadium redox flow batteries (VRFBs). The key idea of this work is to combine the high proton-conducting property of sPEEK and low vanadium permeability of PVdF by introducing the amphiphilic UAN to the immiscible blend of sPEEK and PVdF, UAN makes the two polymers miscible. The blend membranes are characterized by water uptake, dimensional change, proton conductivity, vanadium ion permeability, and cross-sectional morphology. By introducing small amounts of UAN (1–2 wt%) to the sPEEK/PVdF blend, proton conductivity increases, while vanadium permeability shows a very small change, resulting in higher proton selectivity against vanadium ion transport. Therefore, VRFBs employing the sPEEK/PVdF/UAN blend membrane exhibit significant improvements in discharge capacity and energy efficiency (EE) in comparison with those based on the sPEEK/PVdF blend and even with a Nafion 212 membrane. These results show that UAN-assisted compatible sPEEK/PVdF/UAN blend membranes can be useful for enhancing the VRFB performance.

1. Introduction

Redox flow batteries (RFBs) are electrochemical systems that exploit fluid-type electrochemical redox reactions for reversible conversion between electric energy and chemical energy. Among various types of RFBs, all vanadium redox flow batteries (VRFB) developed by Kazacos have received special attention in energy storage systems because of commercialization level [1, 2]. It possesses higher equilibrium cell voltage, high energy efficiency, flexible design, long cycle life and capacity to use the same oxidized/reduced chemicals at both the positive and negative poles [3, 4]. Using a common element, vanadium, as the active material for both poles, crossover contamination of the positive and negative cell electrolyte can be eliminated, although the crossover of vanadium ions across the membrane inevitably reduces cell efficiency [5]. The electrochemical reactions of the positive and negative electrodes are represented by Eqs. (1), (2) and (3) respectively [6, 7].

Positive electrode:

$$VO^{2+} + H_2O \rightleftharpoons VO_2^{+} + 2H^{+} + e^{-}\,(V^{4+} \rightleftharpoons V^{5+} + e^{-})\,(E^{\circ} = 1.0\ V) \quad (1)$$

Negative electrode:

$$V^{3+} + e^{-} \rightleftharpoons V^{2+}\,(E^{\circ} = -0.26\ V) \quad (2)$$

Over all reaction:

$$VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^{+} + 2H^{+} + V^{2+}\,(E^{\circ} = 1.26\ V) \quad (3)$$

As described in the reaction equations (Eqs. (1) and (2)), protons formed from H_2O at the positive electrode during charging migrate to the negative electrode across a polymer electrolyte membrane such as Nafion, and then drift back to the positive electrode during discharging as shown in Fig. 1.

The polymer electrolyte membrane used as a separator is an essential component that determines the battery performance. It prevents electrical shorting between the cathode and anode, and provides proton transfer. Nafion, a perfluorinated sulfonic acid, has been widely used in VRFBs because of its high chemical stability and high proton

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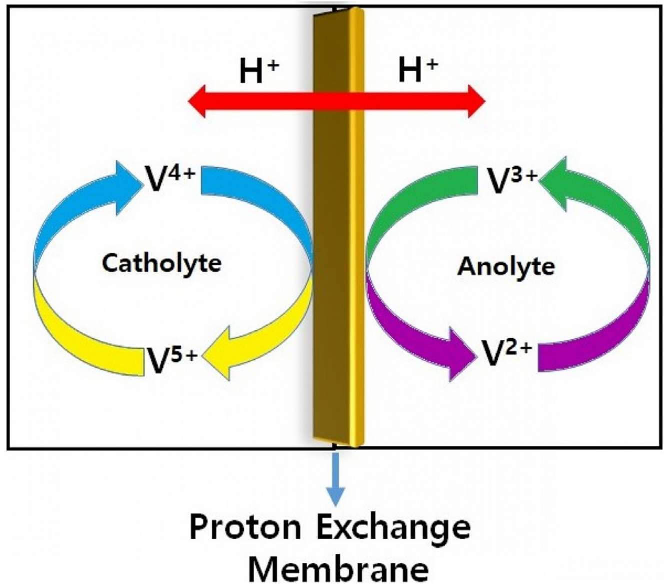

Fig. 1. Proton transport phenomenon through membranes.

conductivity [8]. However, it does not completely prohibit vanadium transfer, resulting in voltage and capacity loss [9]. Its high cost is another factor delaying wider commercialization of the VRFB [10]. In this regard, many researchers have attempted to replace Nafion through hybrid composite and hydrocarbon-based membranes [10, 11]. Some examples include sulfonated poly(ether ether ketone) (sPEEK), which has a higher voltage efficiency and higher discharging power than Nafion, and sulfonated poly(sulfone), sulfonated poly(fluorenyl ether ketone), and sulfonated poly(arylene ether sulfone) which commonly improve CE and energy efficiency (EE) owing to their low vanadium permeability [12–15]. Previous work also suggests an important design guide for hydrocarbon-based membranes. Among the different types of hydrocarbon membranes, sPEEK has considered as an efficient polymer membrane materials for VRFB applications because of easier synthetic process, high stability and low cost [16]. Furthermore, the degree sulfonation can be successfully modified to the sPEEK polymer, which is mainly related to the proton conductive properties of the membranes [17]. There are numerous kinds of analysis were reported for enhancing the sPEEK membranes properties by blend with organic polymers and incorporation of inorganic additives in sPEEK polymer matrix [17–22]. As water uptake by the hydrocarbon membrane decreases, vanadium crossover decreases, and chemical and mechanical stability increase at the expense of proton conductivity [23]. Therefore, the degree of sulfonation, which increases water uptake, should be carefully adjusted to balance performance and durability of hydrocarbon membrane. In order to solve the excessive water uptake problem, a blend membrane of hydrophobic poly(vinylidene fluoride)(PVdF) and hydrophilic sPEEK has been suggested for use in polymer electrolyte fuel cells. Due to the large difference in water uptake for sPEEK (97.5%) and PVdF (2.5%), the mechanical and chemical stability of the cell significantly improved. Phase separation between sPEEK and PVdF was identified from the cross-sectional images [24, 25]. We speculated that such advantages provided by the blend approach can be further enhanced by adjusting the dimensions of phase separation. Here, we suggest a new method to modulate the phase structure of the blend membrane for VRFB applications. The key idea of this work is the introduction of a urethane acrylate non-ionomer (UAN), an amphiphilic polymer, to the blend of PVdF and sPEEK to control its phase structure. The amphiphilic nature of UAN stabilizes the sPEEK/PVdF interface, resulting in a higher degree of compatibility. In the technology field of VRFBs, such a phase modulation strategy has not been attempted yet. Water uptake, proton conductivity, vanadium permeability, proton selectivity, and cross-sectional morphology of the blend membranes were investigated by varying the UAN content. Hence, the electrochemical performance of the corresponding VRFB, including the blend membrane, was evaluated.

2. Experimental

2.1. Materials

Vanadyl sulfate ($VOSO_4$, 98%, NeWell, Korea), magnesium sulfate ($MgSO_4$, 99%, Duksan, Korea), Poly(ether ether ketone) (PEEK, KT-820 NT, Solvay), poly(vinylidenefluoride) (PVDF, KYNAR 2801, Solvay), Sulfuric acid (H_2SO_4, 95%, Duksan, Korea), α,α′-azobis(isobutyronitrile) ($[(CH_3)_2C(CN)]_2N_2$, AIBN, 98%, Junsei, Japan), Dimethyl sulfoxide-d$_6$ ($(CD_3)_2SO$, 99.9%, Sigma-Aldrich), Poly (propylene oxide) triol (PPO triol, Mw = 1000), 2,4-toluene diisocyanate (TDI), 2-hydroxyethyl methacrylate (2-HEMA), and polyethylene glycol (PEG, Mw = 1500, Sigma Aldrich), *N*,*N*-dimethyl acetamide (DMAc, $(CH_3CON(CH_3)_2$, 99.5%, Daejung, Korea), and Nafion®212 membrane (DuPont, USA) were used in the present investigations.

2.2. Sulfonation of PEEK

PEEK (12 g) and sulfuric acid (300 mL) were placed in a 500-mL three-necked flask with a mechanical stirrer for 36 h at room temperature (RT). After sulfonation, the resulting solution was poured into excess de-ionized (DI) water to precipitate sPEEK. The fibril precipitates of sPEEK were washed with DI water several times until the remaining water became neutral. Then, sPEEK was dried at 50 °C under vacuum for 24 h. The degree of sulfonation was determined by 300 MHz ^{1}H

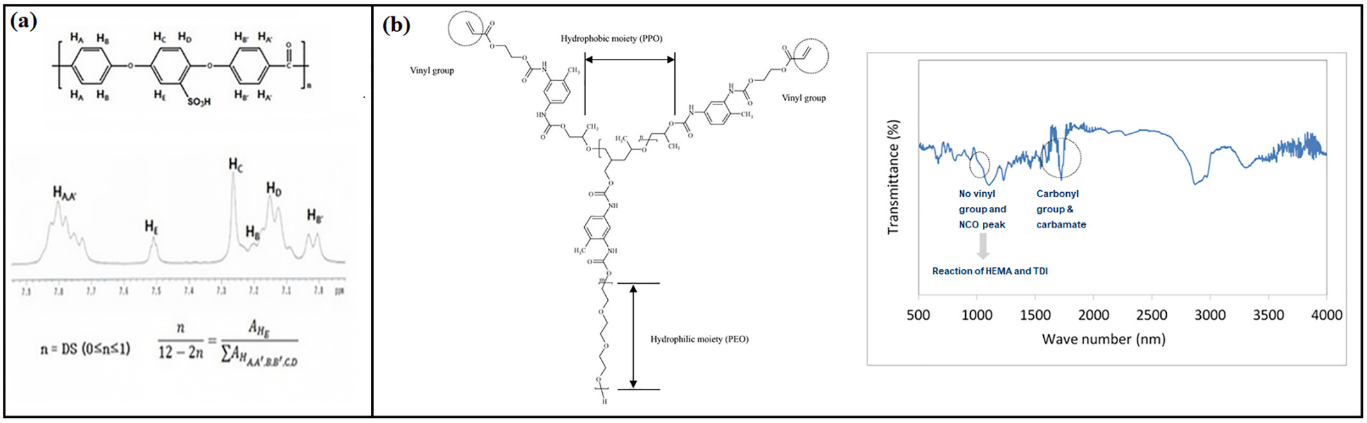

Fig. 2. (a) Structure and ^{1}H NMR spectra of sPEEK, and (b) structure and FT-IR spectra of UAN.