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Novel composite membrane coated with a poly(diallyldimethylammonium chloride)/urushi semi-interpenetrating polymer network for non-aqueous redox flow battery application

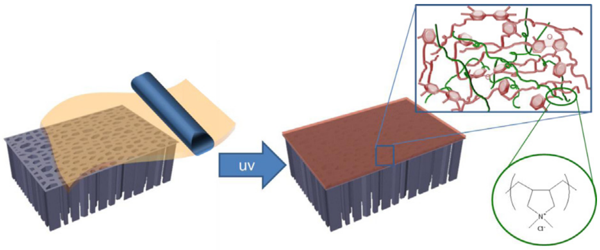
Eunhae Cho, Jongok Won*

Department of Chemistry, Sejong University, 209, Neungdong-ro, Gwangjin-gu, Seoul, 05006, Republic of Korea

HIGHLIGHTS

- A new anion exchange membrane for a non-aqueous redox flow battery is prepared.
- PDDA/urushi semi-IPN layers were coated on the porous support.
- Energy efficiency increased with increasing PDDA in PDDA/U layer.
- High energy efficiency values compared with that of commercial membranes were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel composite membranes of a semi-interpenetrating network (semi-IPN) coated on the surfaces of a porous Celgard 2400 support are prepared and investigate for application in a non-aqueous redox flow battery (RFB). A natural polymer, urushi, is used for the matrix because of its high mechanical robustness, and poly(diallyldimethylammonium chloride) (PDDA) provides anionic exchange sites. The PDDA/urushi (P/U) semi-IPN film is prepared by the photo polymerization of urushiol in the presence of PDDA. The thin layer composed of the P/U semi-IPN on the porous support provides selectivity while maintaining the ion conductivity.

The coulombic and energy efficiencies increase with increasing amounts of PDDA in the P/U semi-IPN layer, and the values reach 69.5% and 42.5%, respectively, for the one containing 40 wt% of PDDA. These values are substantially higher than those of the Neosepta AHA membrane and the Celgard membrane, indicating that the selective layer reduces the crossover of the redox active species through the membrane. This result implies that the formation of composite membranes using semi-IPN selective layers on the dimensionally stable porous membrane enable the successful use of a non-aqueous RFB for future energy storage systems.

1. Introduction

Renewable energy resources, such as solar, wind, wave and geothermal power, are considered to be green energies for solving

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* Corresponding author.
E-mail address: jwon@sejong.ac.kr (J. Won).

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global warming and climate change, but their generated electric signals fluctuate over time and throughout the environment. Therefore, energy storage systems, such as redox flow batteries (RFBs), are necessary for a stable electricity supply from renewable energy sources to be associated with the electrical grid system. In an RFB, redox-active species stored in external tanks are pumped into the positive and negative half-cells of the RFB, which are separated from each other by a membrane, when power is needed [1–4].

Among the various types of RFBs, non-aqueous RFBs using organic electrolytes are emerging since they have wider electrochemical potential window and/or the possibility of the high solubility for the redox active species in organic solvent, offering the possibility for high energy densities in RFB [5–7]. Most of the efforts in non-aqueous RFBs have been focused on identifying new redox active species, and vanadium acetylacetonate ($V(acac)_3$) has been predominantly studied [5,8,9]. The electrolyte containing $V(acac)_3$ initially exists in both compartments of an RFB. The redox reactions at the negative and positive electrodes are as follows:

$$\text{Positive electrode: } [V(acac)_3] \leftrightarrow [V(acac)_3]^+ + e^- \quad (1)$$

$$\text{Negative electrode: } [V(acac)_3]^- \leftrightarrow [V(acac)_3] + e^- \quad (2)$$

Currently, anion exchange membranes (AEMs) are preferred in non-aqueous RFBs because they prevent cations from entering the membrane because of the Donnan exclusion effect, while they transport the anions of the supporting electrolyte (e.g., BF_4^-) to achieve electroneutrality. Although Neosepta AHA (astom, Japan) commercial AEM including FAP4 (FuMa-Tech Co.) and AMI-7001 (Membrane International Inc., USA) have been investigated for non-aqueous RFBs [8,10,11], their limited chemical stability and insufficient ionic conductivity are inevitable because the large size of anions yield intrinsically lower mobilities than that of protons. All of these drawbacks lead to the decrease of both cyclability and efficiency, thus, preventing commercialization [12]. Therefore, the key challenges are maintaining or improving the ionic conductivity, achieving high selectivity to prevent the crossover of active species through the membrane and imparting chemical stability at a low cost for the application of RFBs.

Because a dense AEM has its intrinsic disadvantage with the transport of the anion through the membrane, an improvement of the ion conductivity can be achieved using a porous support, having a high ion conductivity [13–15]. However, their selectivity of the porous support is significantly less than that of a dense AEM because the relatively large pore size than those of the ionic species has no selectivity for the redox-active species. This results in a higher permeability for all of the reactive species, and leads lower columbic efficiencies because of the crossover of the active species [16]. Since the difficulty in making the pore-size smaller than the size of reactive species and larger than that of the balancing ions is a challenge to achieving a suitable selectivity, a new composite membrane having a thin selective anion exchange layer on the porous support for non-aqueous RFBs is considered, as illustrated in Scheme 1.

We designed a composite membrane coated on both sides with anion exchangeable polymer electrolyte layers based on a semi-interpenetrating polymer network (semi-IPN), which is based on chemically crosslinked urushi polymer networks by incorporating electrolyte polymers such as poly(diallyldimethylammonium chloride) (PDDA). PDDA, which possesses a permanently charged quaternary ammonium group in its cyclic unit, was chosen to be an anion exchange material. The reason for choosing PDDA is that it was previously shown that a poly(vinyl alcohol)–PDDA composite membrane showed good ionic conductivity in fuel cell operations [17,18]. The role of the matrix in a composite membrane is important because the operational environment of a non-aqueous RFB is rather harsh for the membrane, therefore, urushi was chosen. The urushi, or oriental lacquer, is a natural polymeric material with a high durability and toughness that has been used for centuries in Asia [19]. A highly crosslinked urushi structure is formed by the crosslinking of urushiol, which is a mixture of catechol derivatives with n = 15 carbon chains with 0–3 olefins, by oxidative polymerization [20]. Urushiol is a promising natural material that is consistent with the responsible resource management using bio-based materials, and a chemical structure of a typical urushiol is shown in Scheme 1. Laccase-catalysed polymerization followed an aerobic oxidative polymerization under 80%–90% relative humidity and at 20–30 °C is the mechanism of the traditional polymerization of urushiol [20]. Although the enzyme-catalysed polymerization has advantages such as an energy-saving and environmentally friendly process, it needs a long drying time. To fabricate a fast drying and/or free of the restrictions of relative humidity and temperature approach, a UV-curing technique was employed in this research.

2. Experimental

2.1. Chemicals

Poly(diallyldimethylammonium chloride) (PDDA, 20% aqueous dispersion, average molecular weight of 400,000–500,000), vanadium acetylacetonate ($V(acac)_3$, 97%), tetraethylammoniumtetrafluoroborate ($TEABF_4$, 99%), and anhydrous acetonitrile (99.5%) were purchased from Sigma-Aldrich Chemical Co. Urushiol (water content of 3%) was purchased from Fujii Urushi Kogei Co. Ltd. (Japan). All of the chemicals were used without further purification. Nafion 212 and Neosepta AHA membranes were purchased from Dupont, USA and Astom Corporation, Japan, respectively. Celgard 2400 composed of polypropylene having an average pore size of 41 nm × 120 nm and a porosity of 41% was kindly provided by Celgard Korea.

2.2. Preparation of the membranes

The PDDA/urushi (P/U) semi-IPN free-standing film was prepared by a solution-casting method: an appropriate amount of PDDA was mixed with the urushiol paste under mechanical agitation, using controlled amounts of PDDA of 30, 35, and 40 wt%. The mixture was cast on a Teflon-coated glass substrate, doctor bladed (300 μm) and exposed to a UV lamp (365 nm main wavelength, 411 W power capacity, Raynics) at room temperature for 10 min. The gap between the lamp and the sample is 10 cm (in the UV-intensive range of 180 $MWcm^{-2}$). The dried P/U semi-IPN free-standing film peeled off from the substrate. Because the urushi film was not obtained under these photopolymerisation conditions, a thermally crosslinked free-standing urushi film was prepared at 100 °C for 10 h for comparison.

A composite membrane with a selective layer of the P/U semi-IPN on both sides of a porous Celgard support was prepared by casting the PDDA/urushiol solution onto the surface of the Celgard support, followed by using a doctor blade (50 μm) and crosslinking by the UV-irradiation. The process is same as that of the free-standing film preparation. To form the selective layer on both sides of the porous support, the membrane was turned over, and the back side of the Celgard membrane was coated by the same process as the top layer.