Structural effects of anion exchange composite membranes in non-aqueous redox flow batteries

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ABSTRACT

In this study, two different structured poly(diallyldimethylammonium chloride) (PDDA)/urushi composite membranes on porous supports were prepared, and their effects on the efficiency of non-aqueous Fe-Ni redox flow batteries (RFBs) were investigated. Chemically/mechanically stable urushi, which was thermally polymerized from urushiol, was chosen as the matrix, and PDDA was used as the anion-exchange material. A thin-layered composite membrane was fabricated by coating a PDDA/urushiol solution on top of the porous support. Moreover, a charged-porous structure was prepared by the penetration of a DDA/urushiol solution into the pores of the porous support, followed by thermal polymerization. The composite membranes exhibited reduced permeabilities; however, their ion conductivities were of the same order as that of the commercial FAP450 membrane.

The coulombic efficiency (CE) and energy efficiency (EE) of the RFBs with charged-porous composite membranes were 90.7% and 76.2%, respectively; the CE and EE values were 79.0% and 68.7% for the non-aqueous Fe-Ni RFBs with thin-layered composite membranes, at a current density of $0.5\,\mathrm{mA\,cm^{-2}}$, which are higher than those obtained with a commercial FAP450 membrane. These results indicate that controlled porosity in an anion-exchange material on a chemically and dimensionally stable porous membrane contribute to the successful application of RFBs in energy storage systems.

1. Introduction

Redox flow batteries (RFBs) are attracting a significant amount of attention, with respect to the development of large-scale energy storage systems, especially for integration with renewable energy sources [1]. The power in an RFB is generated by the potential difference between the active species in the anolyte and catholyte solutions, which are separated by a membrane [2,3]. The role of the membrane is to prevent the crossover of active species, while transporting charge carrier ions to complete the current circuit of the RFBs. Several aqueous RFBs, including all-vanadium RFBs, have been studied and commercialized [4–7]. However, the cell voltage is limited, due to the narrow electrochemical window of the water used as the solvent for the active species. One method to improve the efficiency of RFBs is to utilize organic solvents with wider electrochemical potential windows than water, to form non-aqueous RFBs [8–10]. A chemically stable Nafion perfluorinated membrane is essential to the success of aqueous RFBs. However, non-aqueous RFBs are still in the early stages of development, due to the lack of appropriate active species and membranes for device operation.

Recently, anion exchange membranes (AEMs) were suggested for use in non-aqueous RFBs. In these membranes, the anions of the supporting electrolyte are transported through the membrane to achieve electroneutrality, while active cations are prevented from entering the membrane, which reduces the crossover contamination to draw the decrease of the efficiency of the cell. Although there are several commercial AEMs specially developed for the chlorination process such as Neosepta AHA (Astom, Japan) and FAP (fumatech BWT GmbH, Germany) [11–13], none of them are applicable in non-aqueous RFBs, due to their low chemical stability, low ionic conductivity, and high swellability in the electrolyte. A high degree of swelling in organic solvents leads to dimensional distortions, and results in a high crossover of active redox species, which decreases the cell performance. In addition to their chemical instability, their insufficient ionic conductivity also limits their applicability, given that the current density for RFB operation is affected by ion conductivity. However, a low ion conductivity is inevitable, given that the size of an anion is larger than that of a proton, and the anion moves more slowly than a proton. These demerits lead to a decrease in both the efficiency and cyclability of non-aqueous RFBs. Therefore, the development of membranes for non-

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aqueous RFBs with improved ion conductivity and selectivity is necessary to prevent crossover contamination using chemically stable materials for the successful operation of non-aqueous RFBs under harsh operating conditions.

Dense AEMs generally consist of anion exchange sites for the transfer of ions into the neutral matrix which maintains the mechanical strength of the membrane. It is necessary to optimize the number of ion exchange sites, as there is a trade-off between the ion conductivity and mechanical/dimensional stability. An increase in the number of anion exchange sites results in an increase in the conductivity; however, the mechanical strength of the membrane decreases significantly, due to the increased swelling of the matrix.

In addition, it is known that ion transport through dense membranes follows a hopping mechanism; ion transport depends on the size of the ions and flexibility of the matrix, which limits anion transport. It can be improved using a porous membrane, through which ions can be easily transported [14–16]. There are several reports on porous membranes for non-aqueous RFBs [14–16], however, porous membranes such as the commercial Celgard membrane, exhibit no selectivity even though their ion conductivity is relatively high. The non-selectivity between the active species and support electrolytes in the porous membrane is due to the large pore size than the size of the redox active species, and leads to crossover contamination, when compared with that of dense structured anion exchange membranes [17].

A solution to this problem is the fabrication of thin selective layers with anion exchange materials on porous supports, to make composite membranes [14–16]. There are several reports on the coating of anionic exchange materials on the surfaces of porous supports, to achieve selectivity and reduce crossover through the membrane. However, there is an intrinsic limitation to the improvement of the ion conductivity of such membranes, as their thicknesses are high; thus, they act as a barrier for ion transport, although the thickness of the coating layer on the porous membrane is lower than that of a dense membrane. Therefore, other approaches are necessary to improve the ion conductivity while retaining the selectivity, and this can be accomplished by controlling the pore size. In this context, charged-porous composite membranes can be fabricated to reduce crossover contamination without a significant decrease in ion transport [18].

The aim of this study is to investigate the structural effects of charged-porous and thin-layered composite membranes on the efficiency of non-aqueous Fe-Ni RFBs, as shown in Scheme 1. A Celgard 2400 membrane with high chemical/dimensional stability was chosen as the porous support, and poly(diallyldimethylammonium chloride) (PDDA) was chosen as the anion exchange material [19,20]. Commercial PDDA was used to prepare the thin-layered membrane, whereas a DDA monomer (the precursor of PDDA) was used to fabricate the

charged-porous composite membrane.

A natural urushi polymer (oriental lacquer) was selected as the chemically stable matrix of the membrane, to maintain dimensional stability under the RFB operating conditions. Network-structured urushi was formed by the thermal crosslinking of urushiol, which was obtained from the sap of *Rhus vernicifera* trees [21]. The chemical structures of urushiol and the possible structure of thermally crosslinked urushi are presented in Scheme 2. Given that urushiol is a catechol derivative that contains alkyl chains with 0–3 olefins, it could be converted into a polymeric network by oxidative polymerization [21,22]. Traditionally, urushi is formed by the energy-saving and environmentally friendly laccase-catalysed polymerization method at a relative humidity of 80–90%, and temperature in the range of 20–30 °C [21]. However, this traditional process involves a long drying time. To lead the fast reaction and/or free of the restrictions to control the activity of the laccase, a thermo-curing technique was employed in this study, to prepare the PDDA/urushi anion exchange materials.

2. Experimental

2.1. Chemicals

Diallyl dimethyl ammonium chloride (DDA, 97 wt%); 20 wt% PDDA (Mw = 400–500 kDa) aqueous solution; 2,2′-azobis(2-methylpropionamidine) dihydrochloride (97%); 2,2′-bipyridyl (99%); iron(II) tetrafluoroborate hexahydrate (97%); tetraethylammoniumtetrafluoroborate (TEABF$_4$, 99%); methanol; diethyl ether; and propylene carbonate (PC) were sourced from Sigma–Aldrich, Korea. Nickel(II) tetrafluoroborate hexahydrate and urushiol were sourced from Alfa Aesar and Fujii Urushi Kogei Co. Ltd., Japan, respectively. All chemicals were used as received. The commercial membranes of Nafion 212 (Dupont, USA) and FAP450 (FuMa-Tech GmbH, Germany) were purchased, and the Celgard 2400 support membranes were supplied by Celgard (Korea).

2.2. Preparation of the membranes

A 25 µm-thick commercial Celgard 2400 membrane (polypropylene) was chosen as the porous support substrate. The charged-porous composite membrane with polyDDA/urushi was prepared by casting an appropriate amount of a viscous DDA/urushiol solution onto the Celgard support, and waiting until the membrane was completely wetted. The DDA/urushiol solution was prepared by completely mixing 1.52 g of 66 wt% of DDA aqueous solution and 1.5 g of urushiol. Thereafter, radical polymerization was conducted in an oven at 100 °C for 24 h. Most of the DDA/urushiol solution penetrated the pores of the
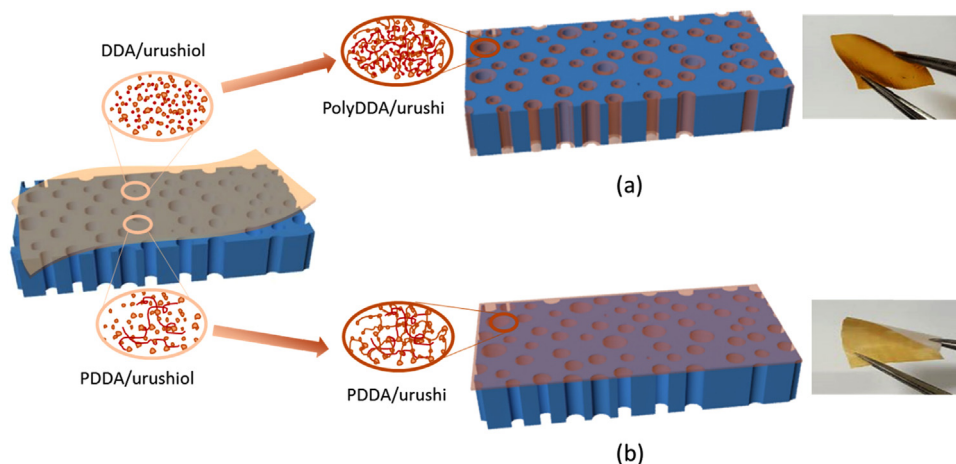
Scheme 1. Concept of composite membranes: (a) charged-porous and (b) thin-layered AEM on porous supports.