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Influence of membrane structure on the operating current densities of non-aqueous redox flow batteries: Organic–inorganic composite membranes based on a semi-interpenetrating polymer network

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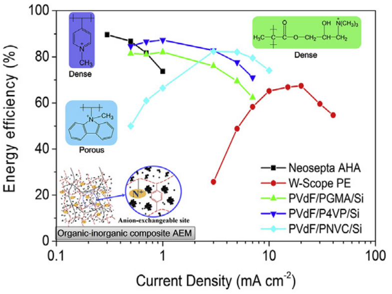
HIGHLIGHTS

- Organic–inorganic composite AEMs based on semi-interpenetrating polymer network.
- Adjustment of physical and chemical membrane structure by monomer type.
- Determination of operating current densities by physical membrane structure.
- Effect of chemical membrane structure on ion transport phenomena.
- High performance of porous charged membrane at high current density.

GRAPHICAL ABSTRACT



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ABSTRACT

We develop three types of organic–inorganic composite membranes based on a semi-interpenetrating polymer network (SIPN) to explore the effects of membrane structure on the possible operating current densities of a non-aqueous redox flow battery (RFB) system. Poly(vinylidene fluoride) (PVdF) is selected as a supporting polymer matrix for improving the chemical and thermal stability of the organic–inorganic composite membranes. We also introduce silica nanoparticles (5 wt% of PVdF) into the membranes to ensure the low crossover of active species. The fabrication of SIPN through the addition of glycidyl methacrylate, 4-vinylpyridine, or N-vinylcarbazole enables control of the membrane structure. Depending on monomer type, the membrane structure is determined to be either aliphatic or aromatic in terms of chemical properties and either dense or porous in terms of physical properties. These chemical and physical structures affect the electrochemical properties that correspond to charge/discharge performance and to the range of possible operating current densities. An important requirement is to examine charge/discharge performance at the possible range of operating current densities by using various membrane structures. This requirement is discussed in relation to a proposed design strategy for non-aqueous RFB membranes.

1. Introduction

Non-aqueous redox flow batteries (RFBs) are being developed as a promising grid-level energy storage system with high power density because such batteries provide a stable supply of electricity

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harvested from renewable energy sources, such as wind, sunlight, and tidal power [1]. Given that the energy density of aqueous RFBs is limited by the electrical breakdown of water, researchers have considered using organic solvents (non-aqueous solutions) to solve this problem. Specifically, considerable attention has been paid to redox couples that can expand the electrical window (typically >2 V) [2]. Some of the redox couples adopted are (1) a single-metal complex (e.g., vanadium [3–5], chromium [6], manganese [7], ruthenium [2,8–10], cobalt [11], and uranium [12]); (2) a dual-metal complex (e.g., nickel/iron (Ni/Fe) [13], cobalt/Fe [14]); (3) an all-organic redox couple consisting of 2,2,6,6,-teramethyl-1-piperidinylxy and *N*-methylphthalimide [15]; and (4) a metal-organic redox couple based on a modified anthraquinone and lithium metal [16]. Among these, vanadium acetylacetonate ($V(acac)_3$) has been the most frequently used redox couple for anolyte and catholyte because it features a thermodynamic potential of 2.2 V, a single electron disproportion, and a relatively insignificant electrolyte rebalancing [3,17,18]. The applied current density for the charge/discharge operation of non-aqueous vanadium RFBs (VRFBs) ranges from 0.008 to 2.2 mA cm^{-2}; such range depends on electrode material, membrane type, and electrolyte concentration [14,19,20].

Despite the progress made in research, few studies have been devoted to the development of a suitable membrane for non-aqueous RFBs. To address this deficiency, we first conducted a preliminary study to briefly introduce the charge/discharge efficiencies of non-aqueous VRFBs with various membranes in a review article: the commercial separators, commercial anion exchange membranes (AEMs) and lab-made membranes were evaluated. We confirmed that the charge/discharge conditions and efficiencies are affected by membrane structure [1]. On the basis of the insights derived from the review, we proposed a property-tunable AEM based on poly(vinyl chloride) (PVC) for non-aqueous RFBs with a single vanadium complex electrolyte [18]. Kim et al. [21] synthesized AEMs by pore filling with a thin porous substrate and produced membranes with high ion conductivity and selectivity. The authors indicated that such AEMs enhance the charge/discharge performance of non-aqueous RFBs with a Ni/Fe complex electrolyte [21]. The pore-filled AEMs and PVC-based AEM enable the charge/discharge operation of non-aqueous RFBs in the level of a current density of 0.1 mA cm^{-2}. Aqueous RFBs have been used for most membrane types at a current density of 10–100 mA cm^{-2}. However, the current density range of non-aqueous RFBs is one or two orders of magnitude lower than that required for aqueous RFBs because of the slow mobility of ions inside the membrane [1]. A challenge that confronts researchers, therefore, is the need to improve the operating current density of non-aqueous RFBs, even though it presents a high output voltage because of the replacement of aqueous solutions with non-aqueous organic solvents.

An ion exchange membrane is one of the core constituents of a non-aqueous RFB system. It generally plays an important role in preventing the crossover of active electrolytes and transporting charge carrier ions to complete the current circuit of RFBs. The ideal membrane is designed to operate at the desired current density to ensure high power density in non-aqueous RFBs. Unlike the current density of aqueous RFBs, however, the low current densities of non-aqueous RFBs constrain the achievement of high power density. This restriction is attributed to the possibility that the transport rate of ions in a membrane is a determining factor of current density for charge/discharge operation. Enhancing the operating current density of non-aqueous VRFBs necessitates the design of an appropriate membrane structure. To this end, a desirable approach is to recognize the effects of chemical, physical, and electrical membrane structures on the determination of operating current density.

This work aims to investigate the correlation between membrane structure and the possible range of operating current densities of a non-aqueous VRFB system. To control the chemical and physical structures of the membrane, we fabricated a membrane structure characterized by a semi-interpenetrating polymer network (SIPN) by incorporating different monomers into the membrane. We selected poly(vinylidene fluoride) (PVdF) as a supporting matrix; PVdF has been evaluated as a chemically and thermally stable material for inert membrane matrices [22]. The three types of monomers used—glycidyl methacrylate (GMA), 4-vinylpyridine (4VP), and N-vinylcarbazole (NVC)—convert membrane structures into chemically (e.g., aliphatic or aromatic) and physically (e.g., dense or porous) different forms. GMA and 4VP, which have typical aliphatic and aromatic structures, respectively, were used to prepare a dense membrane; the aromatic NVC was used to fabricate a porous membrane. The strategic step in reducing the crossover of active electrolytes was the addition of silica nanoparticles (SiO_2NPs) into the membrane matrix [23,24]. We physically and electrochemically characterized the membranes to analyze the factors that may affect current density. Subsequently, we carried out charge/discharge operation to observe the possible range of operating current densities. This study contributes to the improvement of the operating current density of non-aqueous VRFBs in that it features a characteristic analysis of membranes in accordance with their chemical (aliphatic or aromatic), physical (dense or porous), and electrical (charged or non-charged) structures.

2. Experimental

2.1. Materials and chemicals

Silica powder (SiO_2NPs, S5130, fumed, 0.007 μm), PVdF (347078, average Mw = 530,000), benzoyl peroxide (BPO, 517909), divinylbenzene (DVB, 414565, technical grade, 80%), *N,N*-dimethylacetamide (DMAc, 271012, anhydrous, 99.8%), 1,2-dichloroethane (DCE, 284505, anhydrous, 99.8%), iodomethane (I8507, 99%), petroleum ether (32247), and trimethylamine (TMA, 243205, anhydrous, 99%) were purchased from Sigma–Aldrich Co. LLC, USA. GMA (151238), 4VP (V3204), and NVC (277592) were obtained from the same company and used without further purification. Acetonitrile (ACN, 271004, anhydrous, 99.8%) and $V(acac)_3$ (22710, 97%) were purchased from Sigma–Aldrich. 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in ACN (SL14-1486, Panax E-tec Co., Ltd., South Korea) was used to prepare an active electrolyte for the non-aqueous VRFB.

2.2. Preparation of organic–inorganic composite AEMs based on SIPN

In a typical example, the 5 wt% SiO_2NPs added to PVdF were dispersed in 25 mL DMAc solvent by ultrasonication (Branson 2510, Bransoon Ultrasonics Co., USA). Then, PVdF solution was prepared by dissolving 2.5 g of PVdF in the previously formulated mixture at a temperature higher than 60 °C with stirring for about 3 h. DVB as the crosslinking agent and BPO as the initiator were added into the homogeneous PVdF solution. The monomer-to-DVB mole ratio was 5:1 for GMA and 4VP, and that for NVC was 1:1; a lower mole ratio was adopted for NVC because of its high rigidity. The final polymer solution was first polymerized at 80 °C with stirring for 40 min. A polymer film with controlled thickness was lifted from the glass plate by using a doctor blade. The polymer film was then thermally polymerized at 90 °C for 12 h in a drying oven to fabricate a new polymer network (Fig. 1). The polymerized GMA (PGMA) was functionalized in TMA solution. For the polymerized 4VP (P4VP) and NVC (PNVC), quaternization was carried out by soaking the