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Stability of composite anion exchange membranes with various functional groups and their performance for energy conversion

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A B S T R A C T

In this study, we report the relative stabilities of anion exchange membranes (AEMs) comprised of different functional groups. The base membrane was synthesized from vinylbenzyl chloride (VBC) that was cross-linked by divinylbenzene (DVB) using a porous polyethylene (PE) substrate, and subsequently quaternized by functional groups including ammonium, diammonium, and phosphonium types. Every synthetic process was confirmed by FTIR spectra, and hydroxide ion conductivity, ion-exchange capacity, and water uptake. For the various functional groups, the membrane stabilities were examined under alkaline and accelerated oxidative conditions. The membranes were found to be reasonably stable under alkaline conditions, whereas the oxidative stability was significantly dependent on the structures of the functional groups. Moreover, an alkaline fuel cell test was performed at 60 °C for selected membranes. Membranes quaternized with trimethylamine (PE-TMA) and triethylamine (PE-TEA) showed the highest power density, while PE-TEA exhibited a higher oxidative stability. Also, the PE-TEA composite membrane was successfully tested for a non-aqueous vanadium redox flow battery.

1. Introduction

Anion exchange membranes (AEMs) have been widely employed in a diverse range of physicochemical and electrochemical ion transport processes, including energy conversion-storage devices [1], recovery of organic–inorganic materials [2], analytical separation in chromatographs [3], water treatments [4,5], and purification systems [6]. During the last decade, electrochemical alkaline-membrane systems, including fuel cells (FCs) [1], microbial fuel cells (MFCs) [7], and redox flow batteries (RFBs) [8], have further evolved due to their sustainable potential as future alternative energy resources. Recently, membrane based separation technologies, particularly pressure-retarded osmosis (PRO) [9,10], and reverse electrodialysis (RED) [9,11] in combination with microbial processes, have shown their potential as an alternative renewable energy resource. Along with the increased attention on alkaline processes, the requirements and potential limitations of AEMs based on a systemic environment are now being discussed. Selective ion transport is a basic role of the AEMs, and additional requirements have been promoted for successful system operation, such as anion (hydroxide ion) conductivity, ion-exchange capacity (*IEC*), water content, and improvements in mechanical, thermal, and chemical stability. Among these criteria, high hydroxide ion conductivity and chemical durability have been considered as the most important properties for use in practical systems [1,12,13].

AEMs often contain quaternary alkylammonium (QA) functional groups and the degradations of these functional groups at a high pH and its mechanisms have been comprehensively studied. Even though the QA functional groups tend to degrade at a higher pH, they showed better alkaline stability and fuel cell performance than the diammonium and phosphonium functional groups [14]. Alkaline environment not only initiates the degradation of functional groups but also causes severe degradation in polymer backbone and reinforced substrate. Reinforced substrates such as poly(vinylidene fluoride) and poly(vinyl chloride) are simply degraded in alkaline medium by dehydrohalogination reaction [15–17]. To overcome this issue, several candidates such as cross-linked polystyrene, poly(vinyl benzyl)s, poly(phenylene oxide), poly(sulfone ether)s, and their derivatives have been frequently examined. Among them, bi-guanidinium bridged poly (silsesquioxane) [18], poly(vinylbenzyl chloride-g-melamine) [19], quaternary ammonium poly(etherketone) hydroxide [20], chloromethylated poly(phthalazinone ether ketone) [21], quaternized poly(hexafluoropropylene-co-tetrafluoroethylene)-g-vinylbenzyl chloride [22], and poly(ether imide) and its derivatives [23], have been studied for alkaline stability. The studies suggest that additional efforts are required to improve the alkaline stability of AEMs at elevated temperature. For this purpose, large bulky substituents to the polymer backbone [20] or chemically inert polymers such as

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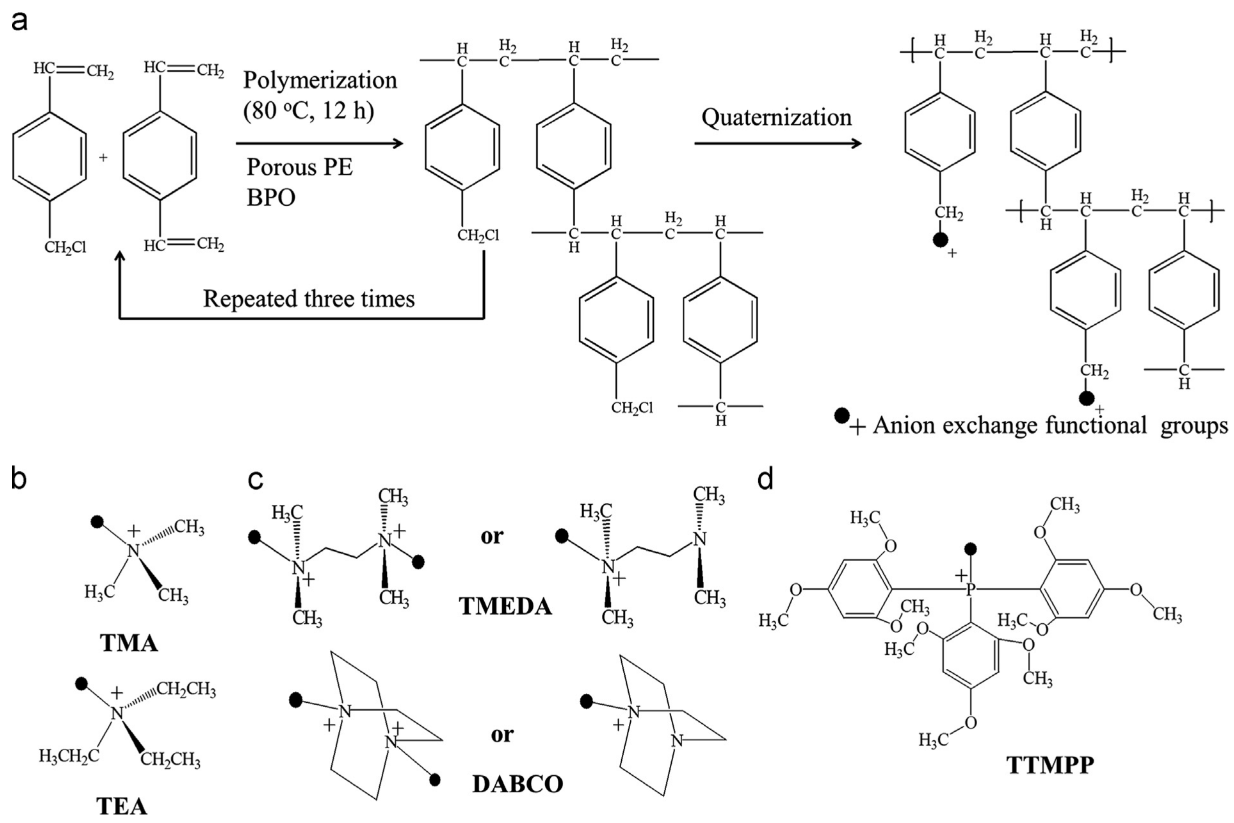

Scheme 1. Chemical structure of pore-filled anion exchange composite membranes based on (a) vinylbenzyl chloride cross-linked by divinylbenzene having various functional groups; (b) ammonium, (c) diammonium, and (d) phosphonium types.

poly(ethylene) (PE) [16,24] and poly(tetraflouro ethylene) (PTFE) [18] were introduced to AEMs.

However, alkaline stability is not enough to ensure membrane durability. Besides alkaline stability, a major limiting factor in the expected lifetime (chemical durability) of AEMs is the oxidative stability. Indeed, the oxidative stability should be considered, since AEMs are exposed to oxidative conditions in energy conversion systems. During the fuel cell operation, hydroxyl (OH•) and peroxyl (OOH•) radicals are formed due to the electrode reactions, and transport of formed radicals along with the hydroxide ion may cause severe degradation of the membranes [25]. Also, aqueous and non-aqueous RFBs are generally operated under harsh conditions, because the metal complexes used as redox couple are dissolved into strong acid (i.e., hydrochloric acid, sulfuric acid) [26,27] or organic solvents (i.e., acetonitrile, propylene carbonate) [28,29] for their high solubility. Metal complex ions existing in redox flow systems undergo oxidation or reduction for over hundreds of cyclic operation as rechargeable batteries. Repeated redox reactions and sustained exposure to the electrolytes in a RFB may cause the oxidative degradation in membranes. Often Fenton's reagent is used to evaluate the oxidative stability of AEMs in simulated oxidative medium [30–32].

In the present work, we synthesized membranes from 4-vinylbenzyl chloride cross-linked by divinylbenzene via a pore-filling method [1], followed by quaternization and the stability of different anion exchangeable functional groups (ammonium, diammonium and phosphonium) in alkaline and oxidative medium were evaluated. The properties of the synthesized AEMs were then analyzed electrochemically. In particular, their alkaline stability and oxidative stability were examined using a 1 N NaOH solution and Fenton's reagent (4 ppm Fe^{2+} and 3% H_2O_2) at 60 °C. Subsequently, we have discussed their structural relationships according to the type of functional groups. Finally an alkaline fuel cell test and a non-aqueous RFB cell test were performed to demonstrate the feasibility of the composite AEMs with stable functional groups for energy conversion systems.

2. Experimental

2.1. Materials

Porous polyethylene (PE) (Celgard® Monolayer PE battery separator) substrate with a thickness of 20 μm and 40–50% porosity was used as the base substrate. Synthetic monomers including 4-vinylbenzyl chloride (VBC), divinylbenzene (DVB), and a thermal initiator (benzoyl peroxide (BPO)) were purchased from Sigma-Aldrich Co., USA. Trimethylamine (TMA), triethylamine (TEA), 1,4-diazabicyclo[2.2.2]octane (DABCO), N,N,N,N-tetramethylethylenediamine (TMEDA), tris(2,4,6-trimethoxyphenyl)-phosphine (TTMPP), vanadium(III) acetylacetonate ($V(acac)_3$), tetraethylammonium tetrafluoroborate ($TEABF_4$) and anhydrous acetonitrile (CH_3CN) from Sigma-Aldrich were used without further purification.

2.2. Membrane synthesis

A monomer solution was prepared using 95 wt% VBC, 5 wt% DVB, and 2.5 wt% BPO. Then, a porous PE substrate was immersed in the monomer solution for 1 h at room temperature to allow complete impregnation of monomers into the porous substrate. After the monomer sorption process, the PE films were sandwiched between Si-coated PVC films (100 μm thick, Hwashin Engineering Co., Seoul, South Korea) and polymerized at 80 °C for 12 h after removing the excessive monomer solution. The polymerization step was then repeated three times in order to maintain the membrane thickness. The polymerized film was