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Imidazolium functionalized poly(vinyl chloride-co-vinyl acetate)-based anion exchange membrane

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ABSTRACT

Poly(vinyl chloride-co-vinyl acetate) functionalized with the imidazolium cation was synthesized for anion exchange membranes. The chemical structure of the membrane was confirmed by ¹H NMR and FTIR analyses. Scanning electron microscopy and thermogravimetric analyses were performed to ascertain the surface and thermal properties of the membrane. The anion exchange membranes were characterized by water uptake, hydroxide ion conductivity, and alkaline stability analyses. The maximum of 11.4% degree modification with the imidazolium cation was achieved with a 1,2-dimethylimidazole/poly(vinyl chloride-co-vinyl acetate) weight ratio of 8:1. The water uptake, ionic conductivity, thermal stability, and alkaline stability were correlated to the degree of imidazolium. The resulting anion exchange membrane exhibited a water uptake capacity of 28% with a hydroxide ion conductivity of 10 mScm⁻¹ at 80 °C. The membranes were thermally stable up to 160 °C. Both the cationic group and the polymer backbone were found to be stable in 1 M KOH solution at 60 °C over 72 h.

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Introduction

Pollution and global warming are serious concerns of the 21st century that have fuelled the drive toward alternative energy resources that are clean, convenient, and efficient to meet the ever-growing energy demand. At present, the fuel cell is considered one of the most promising technologies for future energy generation, spanning applications from a wrist watch to a large city [1–3]. To remove the dependency of fuel cells on proton exchange membranes (PEMs), research activities have recently been extended to anion exchange membranes for the development of an efficient and low-cost alkaline fuel cell

[4,5]. AEMs are not only an alternative for PEMs but are used specially in potential fuel cell technology like urea, ammonia, biogas based fuel cell where PEMs are not compatible [6]. However, anion exchange membranes (AEMs) are not competitive with PEMs in terms of alkaline stability and ionic conductivity. There is thus a need for improvement of the AEM [7,8] to enhance the ionic conductivity and stability of the cationic head group.

In order to address the stability issue, imidazolium-based AEMs [9–13] have recently taken the center stage in laboratory-scale research because of their good alkaline stability compared to other cationic head groups like quaternary ammonium [14,15], phosphonium [8,16], and guanidinium

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[17,18] groups. It is reported that among the various C2-substituted imidazolium cationic head groups, 1,2-dimethyl imidazolium-based cationic head group is more stable due to the steric hindrance of the C2-substituent, which protects the imidazolium cations against hydroxide attack [19]. Moreover, in comparative theoretical evaluation of various C2-substituted imidazolium cations, 1,2-dimethyl imidazolium was found to have the highest LUMO energy, which makes it the most stable cation in alkaline solution.

Research activities have shown that the alkaline stability of the anion exchange membrane is not only related to the cationic head group but also depends on the membrane's backbone structure [20]. Different polymer backbones with the same imidazolium cation exhibit differences in chemical stability in alkaline solution [21,22]. The polysulfone-imidazolium-based [21] AEM membrane deteriorates in 3 M NaOH solution at 60 °C after 24 h, whereas the poly(styrene-co-butyl methacrylate)-imidazolium-based AEM [22] can remain stable in 6 M NaOH at 80 °C even after 120 h. Thus, the stability of the anion exchange membrane is influenced by the chain structure of the polymer. Most commonly, polystyrene (PS) [23], polyphenyloxide (PPO) [20], polysulfone [24], polyethylene [25], and polyetheretherketone [26] have been used as the backbone building blocks in AEMs. The main problem in this category is the introduction of the chlorine functional group in the polymer backbone for converting into the anion exchange membrane. This strategy is generally based on the use of chlorinating agents, which are known carcinogens. An attractive way to avoid this chlorination process is to use a polymer that already contains a chloride group. In this respect, PVC can be a choice for this purpose. However, it is a rigid and horny material. Therefore, to make it flexible, popular poly(vinyl chloride-co-vinyl acetate) copolymer has been chosen. It is a potential candidate to satisfy this criterion [27]; its excellent film-forming, mechanical, and chemical resistance properties as well as relatively low cost have encouraged its use for fuel cell applications [28]. The hydrophobic nature of this copolymer may be an added advantage for controlling the water uptake properties of the membrane.

A twofold approach is employed in this study; the first is to avoid the chlorination process and to insert quaternized moieties into the poly(vinyl chloride-co-vinyl acetate) structure in a simple, one-step process and the other is to control the water uptake properties of the membrane while maintaining the good ionic conductivity.

In the present work, we report a simple, one-step, straightforward, low-cost, adequately chemically stable imidazolium functionalized poly(vinyl chloride-co-vinyl acetate)-based

anion exchange membrane. The chlorine atom of poly(vinyl chloride-co-vinyl acetate) is replaced by a nitrogen atom at the 3 position of 1,2-dimethylimidazole via nucleophilic substitution reaction.

Experimental

Materials

Poly(vinyl chloride-co-vinyl acetate) (PVCVA), 1,2-dimethylimidazole (Dmim), KOH, toluene, and tetrahydrofuran (THF) were purchased from Aldrich Chemical Company (Korea).

Modification of poly(vinyl chloride-co-vinyl acetate) using 1,2-dimethylimidazole

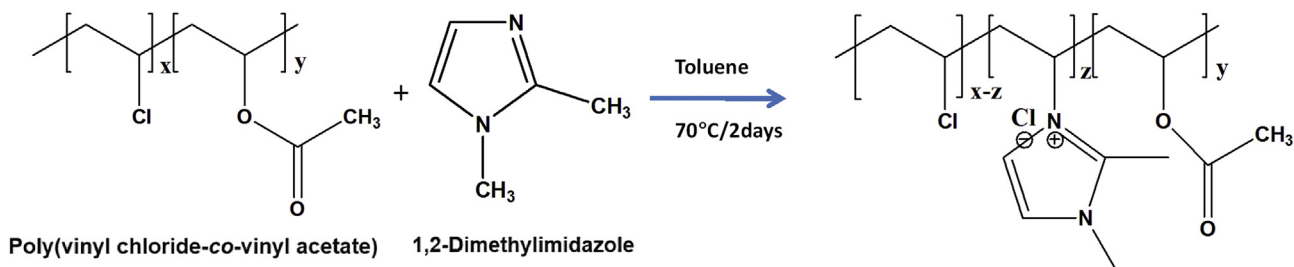
Two grams of poly(vinyl chloride-co-vinyl acetate) (PVCVA) powder with different amounts of 1,2-dimethylimidazole were dissolved in toluene. The reaction was stirred for 48 h at 70 °C to ensure sufficient reaction between poly(vinyl chloride-co-vinyl acetate) and 1,2-dimethylimidazole (Scheme 1). The product was precipitated by adding 100 ml of methanol/water (50%, v/v) under sonication. The precipitated product was washed with ethanol to remove the unreacted 1,2-dimethylimidazole and the toluene solvent. The product was dried at room temperature for overnight under vacuum. The product was further dissolved in THF and re-precipitated in ethanol to eliminate any residues of 1,2-dimethylimidazole.

Preparation of membrane

Modified poly(vinyl chloride-co-vinyl acetate) containing the 1,2-dimethylimidazole salt was dissolved in THF solvent. The membrane was cast in a Petri dish. The thickness of the cast membranes was maintained between 100 μm and 150 μm . Subsequently, the Cl^- form of the membranes was converted into the OH^- form by treating the membranes in 1 M KOH solution at 60 °C for 1 d. The membranes were washed several times with deionized water (DI) to remove the KOH and stored in deionized water (DI) for 24 h before use.

Fourier transform infrared (FT-IR) spectroscopy

A Bruker Vertex 70 FT-IR instrument was used for the Fourier transform infrared (FT-IR) spectroscopic measurements.



Scheme 1 The reaction between poly(vinyl chloride-co-vinyl acetate) and 1,2-dimethylimidazole.

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