



Anisotropic radio-chemically pore-filled anion exchange membranes for solid alkaline fuel cell (SAFC)



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ABSTRACT

Anion exchange pore-filled membranes based on meso-porous polyethylene support are fabricated through a radio-chemical grafting process. Vinylbenzylchloride (VBC) monomers are grafted onto porous polyethylene substrate by a simultaneous irradiation grafting method. The porous polyethylene substrate provides high chemical and mechanical stability. The pore-filled membranes are subsequently functionalized by trimethylamine (TMA) and ion exchange with sodium hydroxide, yielding alkaline anion exchange membranes that are capable of conducting hydroxide ions. The meso-porous support structure contributes to a reduction in dimensional swelling while maintaining high water uptake, high ion exchange capacity, and enhanced mechanical strength of over 50 MPa. In particular, these radio-chemically pore-filled membranes exhibits anisotropic through-plane oriented ion conductive behavior due to the low resistance of the hydrated cross-sectional structure derived from the nonwoven porous substrate. As a result of reinforced mechanical strength and anisotropic electrochemical property, the membrane exhibits good membrane-electrode assembly (MEA) performance (at 0.6 V, max. current density = 174 mA cm⁻² and max. power density = 127 mW cm⁻²) in solid alkaline fuel cell.

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1. Introduction

Solid alkaline fuel cell (SAFC) has gained much attention as an alternative to proton exchange membrane fuel cells (PEMFC) [1–5]. SAFC has the potential to utilize non-noble metal catalysts due to the high kinetic activation energy in alkaline medium [6–8]. The anion exchange membrane (AEM) is a key component determining the electrochemical performance of alkaline fuel cells. However, the often poor chemical stability and low hydroxide ion conductivity of AEMs have been critical issues in attaining high performance alkaline fuel cells [9–11]. The strong basic conditions during SAFC operation can cause the chemical degradation of anion conductive polymer membrane, including polymer main

chain [12–14] and the alkyl ammonium quaternary groups [15–17] by SN₂ reaction or Hoffman elimination due to the attack of hydroxide ions. Moreover hydroxide ion conductivity tends to be lower than proton conductivity through ion exchange membranes because hydrated hydroxide ion mobility is two times lower than hydrated proton mobility [18,19].

To overcome such limitations, the development of Anion Exchange Membranes (AEM) with superior alkali stabilities and ionic conductivities is an obvious target. To achieve this goal, considerable efforts have been focused on the preparation of AEMs through chloromethylation of commodity polymers [20,21]. However, chloromethyl ether is required for the chloromethylation reaction which is a potent carcinogen [22]. The synthesis of AEMs through radiation grafting of vinylbenzyl chloride (VBC) onto aliphatic polymer matrices has been shown to be an effective way of avoiding the use of chloromethyl ether [23–27]. Most available commodity fluorinated polymers including polytetrafluoroethylene (PTFE) [28,29], fluorinated ethylene propylene (FEP) [30,31], tetrafluoroethylene perfluoro(propyl vinyl ether) copolymer [32,33], poly(vinylidene fluoride) (PVDF) [34,35],

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ethylene-tetrafluoroethylene copolymer (ETFE) [36,37] have been investigated as polymer substrate films for the radical grafting reaction because of their chemical and/or mechanical stability. Despite some of the advantages of these polymers, there are instances of radiation-induced chain scission in fluorinated polymer membranes due to the relatively weaker C–C bond compared with the C–F bond, causing a reduction in molecular weight [38]. On the other hand, polyethylene substrate films have a greater tendency to undergo cross-linking rather than main-chain scission, upon irradiation by high energy gamma rays, and their high depth penetration also facilitate a more uniform grafting of functional groups [39]. As a result, the prepared membranes exhibit high mechanical stability, chemical stability towards strongly basic conditions; and enhanced conductivity due to uniform grafting.

There are two representative methods to graft vinylbenzyl chloride (VBC) onto aliphatic polymer films by using gamma irradiation, which are pre-irradiation and simultaneous irradiation. In previous work, Sherazi et al. [40] fabricated AEMs by grafting VBC onto ultrahigh molecular weight PE powder via the pre-irradiation method. In this process entails generating radicals in inert atmosphere using gamma rays by cleavage of C–H bonds in PE, followed by grafting VBC monomer onto the reactive radical sites by thermal reaction. This pre-irradiation method is convenient to control the degree of grafting (DG) by the reaction temperature and reaction time [39,40]. On the other hand, in the simultaneous irradiation process, a mixture of base polymer or membrane and monomer solution are exposed simultaneously to gamma radiation, which results in radical generation on the base polymer and *in situ* monomer grafting. This is regarded as a convenient grafting method for better reproducibility because it can lessen any side reactions caused from residual oxygen [41]. Simultaneous gamma irradiation grafting has been successfully applied to synthesize vinylbenzylchloride-grafted PTFE membranes, which exhibited high ion exchange capacity (IEC) over 1.8 meq g⁻¹ and hydroxide ion conductivity [42]. However, due to the trade-off relationship between dimensional stability and IEC, the high IEC of these membranes resulted in excessive swelling and poor mechanical properties, leading to low MEA electrochemical performances in alkaline fuel cell operation systems. Several efforts have been made to control such trade-off behavior by developing composite membranes based on porous polymer substrates [43–46]. Various types of anion exchange composite membranes have been fabricated by different pore-filling protocols such as impregnation [43], ultra-violet (UV) radiation cross-linking [44], and thermal polymerizations [45,46]. Jung et al. [43] incorporated tetramethylammonium group functionalized biphenylsulfone (BPS) polymer into polyimide porous substrate to reduce methanol crossover for direct methanol fuel cell successfully. Lee et al. [44] cross-linked quaternized poly(vinylbenzyl) ammonium with N,N'-bis(acryloyl)piperazine in porous polyolefin substrate by using UV radiation radical polymerization. The pore-filled membranes exhibited greatly enhanced chemical durability against strong basic conditions. Zhang et al. [45] and Zhao et al. [46] also developed composite membranes filled with quaternized polyvinyl benzyl chloride into a porous poly olefin substrate or PTFE substrate by thermal polymerization to obtain enhanced mechanical properties and high thermal stability. However, these approaches to fabricating pore-filled membranes by conventional methods may still sacrifice high ion conductivity and high ion exchange capacity, although they generally provide the excellent mechanical properties and chemical stability, compared to homogeneous membranes.

This study presents a new concept of aminated pore-filled membranes (APF) fabricated by grafting PVBC onto meso-porous polyethylene (PE) substrate directly. The mechanically tough meso-porous PE substrate reinforces the AEMs and is more

chemically resistant to strongly basic conditions compared with many other fluorinated polymers. It also provides a high internal surface area for functionalization with PVBC, leading to high ion exchange capacity. Simultaneous irradiation with high energy gamma rays provides an effective strategy for pore-filling hydrophobic meso-porous substrate. The radio-chemically pore-filled membranes possess unique meso-porous functionalized structures, which exhibit both suppressed swelling behavior by excellent PE substrate reinforcement and high through-plane anisotropic conductivity from its high IEC, thereby enhancing the MEA single cell performances for AEMs.

2. Experimental

2.1. Materials and chemicals

Porous polyethylene membrane (Celgard 2730, USA) having pores with the diameter from 50~150 nm was used after washing with methanol (Ducksan Industry) and complete drying. Vinylbenzylchloride (Sigma Aldrich, 97%, mixture of 3- and 4- isomer) monomer and 1,2-dichloroethane (Sigma Aldrich) solvent were used as received. Trimethylamine aqueous solution (45%, Sigma Aldrich) was used to functionalize the pore-filled membranes.

2.2. Fabrication of pore-filled anion exchange membrane

2.2.1. PVBC branch grafting by using simultaneous γ irradiation

Vinylbenzylchloride (VBC) monomer was mixed with 1,2-dichloroethane with volume ratio of 40%, which was optimized for controlling the kinetic of grafting reaction. The porous polyethylene substrate and polyethylene film samples of the size 4 × 4 cm² were immersed in VBC solution (40 mL). The VBC solution was purged of dissolved air by bubbling nitrogen gas for 10 min to prevent the oxidation reaction during simultaneous irradiation. The substrates in VBC monomer solution were exposed to gamma irradiation using Co-60 gamma source (Korean Atomic Energy Research Institute, KAERI). The samples were irradiated for a range of total absorbed doses i.e., 20–80 kGy with a dose rate of 2 kGy h⁻¹. After irradiation, polyvinylbenzylchloride (PVBC) grafted pore-filled polyethylene membrane was washed by 1,2-dichloroethane for 1 day, changing the solvent two or three times in order to remove the residual VBC monomer inside the membranes. The washed membranes were then dried at 60 °C *in vacuo* until constant weight. After washing and complete drying, the DG was measured on a weight gain basis (Eq. (1)), which represents the amount of VBC monomer grafted onto the polyethylene chains. DG data are reported as the average of four samples with uncertainty taken as one standard deviation from the mean.

$$DG (\%) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o is the weight of dried substrate and W_g is the weight of VBC grafted membrane after washing and complete drying.

2.2.2. Amination of PVBC grafted pore-filled membrane

Pre-washed and dried PVBC grafted pore-filled membranes were then processed for the amination reaction. The membranes were treated with 45% trimethylamine aqueous solution at room temperature for 24 h. Tetramethylammonium (TMA) functionalized pore-filled membranes were washed with deionized water (DI water) for 24 h, changing the water every 6 h. The functionalized membranes were immersed in NaOH (1 M) aqueous solution for at least 12 h for the conversion of chloride ion (Cl⁻) form to

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