Pore-filled anion-exchange membranes for electrochemical energy conversion applications

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ABSTRACT

Novel pore-filled anion-exchange membranes (PFAEMs) have been developed by a simple method for electrochemical energy conversion applications. The PFAEMs with the different degrees of crosslinking are successfully fabricated by filling cationic polyelectrolytes into a highly porous PTFE substrate (thickness = ca. 80 μm) with chemically stable anion-exchangeable sites. The PFAEMs are shown to possess excellent electrochemical properties and stability. Especially the alkaline stability of the PFAEMs is superior to that of the commercial membrane (i.e., AMX, Astom Corp.) owing to the structural stability of ion-exchange sites and the nature of a highly hydrophobic PTFE substrate. The PFAEMs are also tested for the applications to all-vanadium redox flow battery (VRFB) and alkaline direct liquid fuel cells (ADLFCs). The VRFB employing the PFAEM with high crosslinking degree exhibits excellent energy efficiency (>85%) which is much superior to those of the Nafion and commercial anion-exchange membranes (78.7% and 80.1%, respectively). A promising performance in ADLFC is also achieved by employing the PFAEM with high crosslinking degree owing to the low fuel crossover but the further improvement in the ion conductivity is required.

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1. Introduction

Polyelectrolyte membranes (ionomer or ion-exchange membranes) which consist of polymer backbones attached with fixed charge groups have been widely used in various water treatment processes such as electrodialysis for a desalination of brackish water [1–4]. Recently, they have also gained industrial importance in electrochemical energy conversion and storage processes such as reverse electrodialysis [5,6], fuel cells [7–11], redox flow batteries [12–14], etc. Their intrinsic properties such as electrical resistance and permselectivity are the key parameters dominating the electrochemical energy conversion efficiencies.

Especially, in recent years, alkaline direct liquid fuel cells (ADLFCs) employing anion-exchange membranes (AEMs) as a fuel barrier have attracted significant attention as promising alternative energy sources. ADLFCs are allowed to use more abundant anode catalysts which are cheaper than the catalyst used in that using hydrogen fuel. They could also mitigate the crossover of liquid fuels (anode to cathode) observed that using hydrogen fuel

since the moving direction of ions (i.e., hydroxyl ions) is opposite to that of protons (cathode to anode). Those facts may consider less technical difficulty in fabricating anodic electrode and anion-exchange membranes [15–20]. However, the ion conductivity of AEMs is still not as high as those of proton-exchange membranes (PEMs) such as Nafion and the stability in a strong alkaline condition should be improved further for practical applications.

Meanwhile, redox flow batteries (RFBs) known as one of the promising large-scale energy storage systems also require high performance polyelectrolyte membranes for the efficient separation of the electrolytes containing different redox materials [21–23]. All-vanadium redox flow battery (VRFB) which employs vanadium ions in different oxidation states as the active electrode materials is the most widely used rechargeable flow battery [21–25]. Traditionally, PEMs such as Nafion with high proton permeability have been utilized as a separator in a VRFB system [26]. However, the PEMs intrinsically cannot prevent the crossover of cationic redox ions through the membrane. The use of highly expensive membranes such as Nafion can also increase the system

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cost [24,27]. In addition, the irreversible fouling degrading the ion-exchange capacity significantly could be originated from the coordinative interactions between cationic redox materials and anionic fixed charge groups in PEMs [28]. In this respect, the use of anion-exchange membranes (AEMs) in VRFB seems to be more desirable and advantageous for long-term operation [24,29–34]. However, as ADLFCs do, the properties of AEMs should be further improved and optimized for the VRFB application.

Among various types of ion-exchange membranes, pore-filled membranes (PFMs) composed of a chemically inert and mechanically strong porous substrate and a polymer with ion-exchange groups (i.e. polyelectrolyte or ionomer) that is filled in the pores can provide both high ion conductivity and excellent mechanical properties [35–41]. Undesirable excessive swelling of ion-exchange membranes can also be effectively prevented by the tough porous substrate. In addition, they could be produced in a cheaper way, e.g., a roll-to-roll continuous process.

In this work, we have developed novel pore-filled anion-exchange membranes (PFAEMs) with chemically stable cationic ion-exchangeable groups for the applications to VRFB and ADLFCs. The PFAEMs with a thickness of approximately 80 μm and the different degrees of crosslinking have been successfully prepared and systematically characterized via various electrochemical analyses.

2. Experimental

2.1. Materials and membrane preparation

A highly porous polytetrafluoroethylene (PTFE) film (Hydrophobic grade, t_m = 80 μm, pore size = 0.20 μm, porosity = 74%, Advantec MFS, Inc., Japan) was employed as the substrate for preparing pore-filled ion-exchange membranes. N,N'-Dimethylaminoethyl methacrylate (DMAEMA, Sigma-Aldrich Co., USA) was purified with an inhibitor-removal column before use. Divinylbenzene (DVB, Sigma-Aldrich Co., USA) was also purified by treating with 10 wt% sodium hydroxide aqueous solution and then washing with distilled water several times. p-Xylylene dichloride (XDC, Sigma-Aldrich Co., USA) for the quaternization of the polymer and benzophenone (BP, Sigma-Aldrich Co., USA) for the initiation of the photopolymerization were used as received. Neosepta® AMX membrane (Astom Co., Japan) and Nafion117 (DuPont, USA) were chosen as the references to compare with the membranes prepared in this study.

The reaction schemes of DMAEMA-DVB copolymer and polyelectrolyte quaternized by XDC are illustrated in Fig. 1. First monomer mixture solutions consisting of 89–98 wt% DMAEMA, 1–10 wt% DVB, and 1 wt% BP were prepared. A piece of porous PTFE substrate was then immersed in the monomer mixture for an hour, followed by a radical polymerization process conducted in a UV chamber (lab-made, UV lamp power = 1 kW) for 10 min. For quaternization, the porous film filled with poly(DMAEMA-DVB) copolymer was treated in a 0.05 M XDC-EtOH solution at 50 °C for 12 hr, followed by sequential treatments with 0.5 M NH$_4$Cl, 0.5 M HCl, and distilled water. Finally, the prepared membranes were stored in 0.5 M NaCl or 1.0 M KOH solution before use. As shown in Fig. 1, the quaternary ammonium groups are formed by the crosslinking reaction between XDC and amines. As a result, two ion-exchange groups are combined with each other by the crosslinker. We called the structure as 'fused ion-exchange sites' in this paper.

2.2. Membrane characterizations

The chemical structure of the prepared membranes was checked through a FT-IR/ATR (460 plus, Jasco, Japan) measurement. The morphological features of the as-prepared membranes were investigated by using a field emission scanning electron microscopy (FE-SEM, TESCAN, Czech). The water uptake (WU, %) of the membranes was measured by comparing the wet and dry weights [1]:

$$WU = \left(\frac{W_{wet} - W_{dry}}{W_{dry}} \right) \times 100 \tag{1}$$

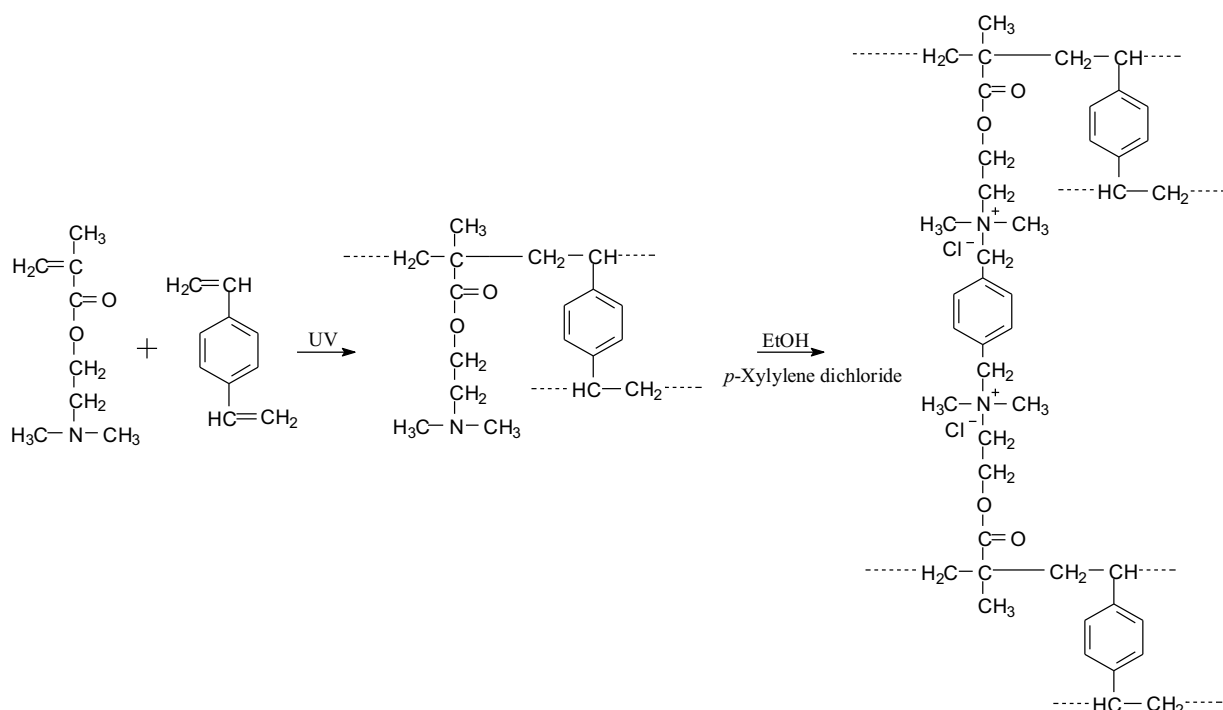Fig. 1. Reaction schemes of DMAEMA-DVB copolymer and polyelectrolyte quaterinized with p-xylene dichloride.