Journal of Membrane Science 553 (2018) 82–89

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation of high-conductivity QPPO (quaternary-aminated poly (2,6-dimethyl-1,4-phenyleneoxide)) membranes by electrical treatment

Jae-Hun Kim, Seungbo Ryu, Ju-Young Lee, Seung-Hyeon Moon*

School of Earth Science and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-Gwagiro (Oryong-dong), Buk-gu, Gwangju 61005, South Korea

ARTICLE INFO

Keywords:
Ion exchange membrane
Anion exchange membrane
Ion conductivity
Electrical alignment
Ion channel

ABSTRACT

Anion exchange membranes (AEMs) have been studied to improve conductivity for their high performance in energy conversion systems such as reverse electrodialysis, alkaline polymer fuel cells, and redox flow batteries. The functional groups with positive charge on backbones in AEMs form ion channels, which is the most significant factor in determining the conductivity of anions through the membrane. A typical method frequently used to enhance ionic conductivity is increasing the ion exchange capacity (IEC). However, AEMs with excessive amounts of positively charged functional groups may reduce ion selectivity or increase ion crossover by weakening mechanical properties due to high water uptake and the swelling ratio. To overcome this problem, we studied in this paper the alignment of ion channels for quaternary-aminated poly (2,6-dimethyl-1,4-phenyleneoxide) (QPPO) by applying an electric field to improve conductivity while retaining ion permselectivity with reasonable mechanical properties. We observed that the conductivity of the aligned QPPO membranes was enhanced up to three times using the same ion exchange material. Further, characteristic changes in the AEMs were investigated for the aligned ion channels using X-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), and atomic force microscopy (AFM).

1. Introduction

Ion exchange membranes (IEMs) have been developed to enhance performance for electrical energy systems such as reverse electrodialysis (RED), fuel cells (FCs), redox flow batteries (RFBs), etc [1–5]. Fundamentally, these electrical energy systems require advanced AEMs of high conductivity or low electrical resistance [6–8]. Accordingly, to fabricate AEMs with high conductivity, the amounts of the functional group (or the IECs) have been increased [9,10].

However, high IEC occasionally causes weak mechanical properties and immoderate swelling in aqueous solutions [11]. In extreme cases, AEMs with the excessive IEC are difficult to apply in energy systems due to the phenomenon of dissolution in the hydrophilic electrolyte. In addition, when comparing anion exchange membranes (AEMs) with cation exchange membranes (CEMs), the anionic conductivity of the AEMs for an alkaline fuel cell (AFC) or a RED system is lower than the conductivity of the CEMs for a proton electrolyte fuel cell, because the hydroxide (20.64×10^{-8} m^2 s^{-1} V^{-1}) or chlorine ion mobility (7.91×10^{-8} m^2 s^{-1} V^{-1}) is lower than the proton mobility (or conductivity) value (36.23×10^{-8} m^2 s^{-1} V^{-1}) [12]. Furthermore, quaternary ammoniums in AEMs have been estimated to have weak basicity ($pK_b \cong$ the order of 4) compared with the strong sulfonic acid in CEMs (such as aryl sulfonic acid, $pK_a \leq$ the order of one) [12,13]. This weak basicity in AEMs may pose a significant obstacle to the conductivity of anions containing hydroxyl ions. Thus, for AEMs to be as promising as possible, they must have high conductivity without weak mechanical properties or excessive swelling.

In order to address this issue, our group has previously reported on electrical alignment methods based on a sulfonated poly (2,6-dimethyl-1,4-phenlyene oxide) (SPPO) polymer at room temperature [14,15]. This concept was based on Amundson's [16] and Morkved's papers [17], which have commonly been cited to describe the effects of an electric field in block-copolymers. The Yu group reported fabricating an aligned Nafion membrane under high voltage (15 kV) in a non – contact mode with flowing high-temperature nitrogen (120 °C) [18]. On the other hand, this study was performed under the relatively low voltage in a contact mode to fabricate the membrane. Generally, CEMs having functional groups (e.g., SO^{3-}, COO^-, PO_3^{2-}) have ion channels, which are a type of pathway to move cations [4,5]. Likewise, in AEMs, ion channels that consist of positively charged groups ($-NH_3^+$, NR_2H^+, NRH_2^+, NR_3^+) could be expected to improve conductivity by applying an electric field.

* Corresponding author.
E-mail address: shmoon@gist.ac.kr (S.-H. Moon).

https://doi.org/10.1016/j.memsci.2017.12.009
Received 19 September 2017; Received in revised form 3 December 2017; Accepted 4 December 2017
Available online 06 December 2017