



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Electrically aligned ion channels in cation exchange membranes and their polarized conductivity

Ju-Young Lee, Ju-Hyuk Lee, Seungbo Ryu, Sung-Hyun Yun, Seung-Hyeon Moon\*

School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-Gwagiro (Oryong-dong), Buk-gu, Gwangju 500-712, Korea

## ARTICLE INFO

## Article history:

Received 16 October 2014

Received in revised form

22 December 2014

Accepted 28 December 2014

Available online 5 January 2015

## Keywords:

Ion exchange membrane

Ion channel

Microstructure

Proton conductivity

## ABSTRACT

The formation of ion channels is crucial in preparation of high-performance ion exchange membranes. We studied the alignment of ion channels in a desired direction to improve the ion conductivity of a membrane. In this study, sulfonic groups, attached to poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO), were aligned according to the direction of the applied electric field. For the proof-of-concept experiment, the ion channels were aligned on a glass plate under an electric field while drying the polymer solution. The formation of in-plane ion channels was confirmed by polarized ion conductivity, atomic force microscopy (AFM), and field emission transmission electron microscopy (FE-TEM). The electrical alignment method was further tested to fabricate an ion exchange membrane with aligned ion channels in the through-plane (thickness) direction, which was then characterized in terms of ion conductivity, transport number, and water uptake. The results show that ion conductivity of the membrane was enhanced up to 12 times without loss of ion selectivity. This study successfully demonstrated an electrical alignment of nanoscale ion channels to increase the ion conductivity of an ion exchange membrane at a given ion exchange capacity.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Electrochemical energy systems based on galvanic and electrolytic cells require ion exchange membranes, which block the electron flow and transport the desired ions or charge carriers [1]. Ion exchange membranes have numerous nano-sized pathways internally and contain functional groups, such as sulfonic or amine groups [2]. The functional groups trigger ion migration through the pathways, which is known as ion channel. To date, ion channel studies have focused primarily on Nafion membranes, a perfluorosulfonate aliphatic ion exchange membrane. Ion channels in a Nafion membrane have been investigated using small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), electron spin resonance (ESR), and  $^2\text{H}$  NMR spectroscopy [3–6]. As a result, a spherical cluster of 4 nm in diameter has been formed by aggregating sulfonic groups; simultaneously, ion channels of 1 nm in diameter are connected [7,8]. This configuration has been explained by the fringed-rod-based microgel model based on their stretched cylindrical appearance into random directions [9]. The reason for the random direction is that the membranes are prepared by a casting process using a polymer solution, while

the polymer solution is dried, hydrophilic and hydrophobic moieties in the polymer solution are randomly self-assembled [10], after which the hydrophilic moieties create non-polarized ion channels [11,12]. This morphology retards the ion transportation rate due to the tortuous route of an ion channel. To reduce the migration path, ion channels should be aligned in a unified direction [13].

This work suggests the electrical alignment methods for the polarization of ion channels in a desired direction using aromatic structural polymers in which functional groups on the polymer pendant have electrical charge property. A sulfonic group has a negative charge, and its corresponding counter-ion, a proton, is bound in the molecular structure [7]. The configuration of the two charged parts may form a dipole, which can be rotated by means of an external homogeneous electric field [14]. The resulting energy is exerted to enforce alignment of the molecular structure, as follows:

$$U = nEqd(1 - \cos \theta) \quad (1)$$

where  $U$  is the rotational energy,  $n$  is the number of molecules,  $E$  is the external homogeneous electric field,  $q$  is the charge,  $d$  is the distance between two charged particles, and  $\theta$  is the angular condition between an electric field and the dipole orientation or dipole angle. In this study, a constant electric field was applied to

\* Corresponding author. Tel.: +82 62 715 2435; fax: +82 62 715 2434.

E-mail address: [shmoon@gist.ac.kr](mailto:shmoon@gist.ac.kr) (S.-H. Moon).

a polymer solution to align the dipoles; thereby the alignment behavior of ion channels and the reorientation of the morphological structure were discussed.

## 2. Experimental

### 2.1. Synthesis of domain polymer material

The domain polymer employed to align the ion channels in this study was SPPO, as illustrated in Fig. 1.

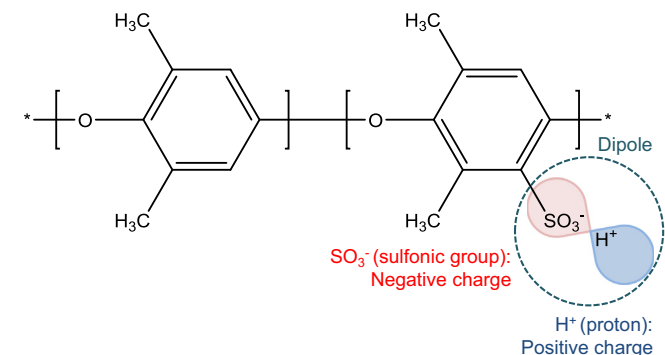
SPPO was synthesized by sulfonating 20 g of PPO (poly(2,6-dimethyl-1,4-phenylene oxide); Aldrich) by mixing with 3.5 ml of

chlorosulfonic acid (CSA; Aldrich) in 200 ml of chloroform solvent (Fisher Scientific) at ambient temperature. From the solution, SPPO of  $1.64 \text{ meq g}^{-1}$  IEC was obtained. The polymer solution for membrane synthesis was prepared by dissolving 4 g of the SPPO in 16 ml of dimethylacetamide (DMAc; Aldrich).

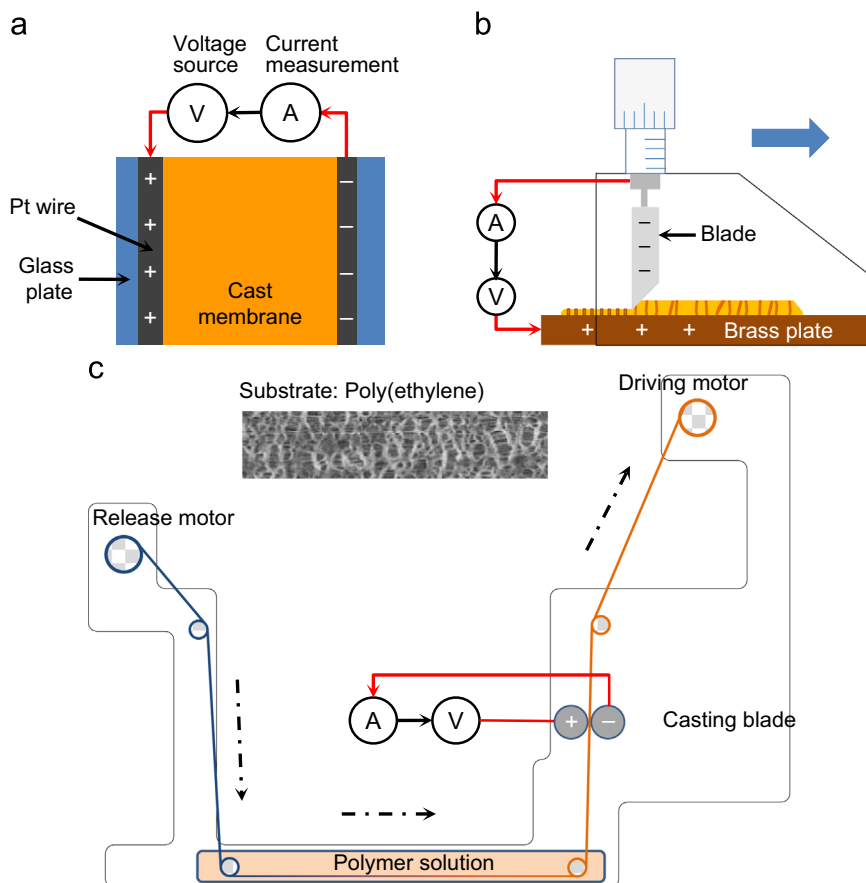
### 2.2. Preparation of ion exchange membranes under an electric field

Ion channels of SPPO were aligned using 3 contact modes of the electric field. For the proof-of-concept experiment, ion channels were first aligned in the in-plane direction to investigate their morphological structure perspicuously.

As shown in Fig. 2(a), Pt wires (Aldrich) were placed on a glass plate with a distance of 2 cm. A power supply (6613C, Agilent) and a pico-ammeter (6487, Keithley) were connected to the Pt wires in series. Then, the polymer solution was cast onto the glass plate, covering the Pt wires [15,16]. The current was monitored in the course of the electrical alignment at 50 V. Subsequently, a modified casting method was designed, as depicted in Fig. 2(b), to prepare the membrane with through-plane alignment. The polymer solution was poured on a positively charged brass plate, and then the negatively charged blade moved at a constant speed. This method enables contact between the electric-conducting materials and the polymer solution, while a membrane was formed from the polymer solution. Finally, the continuous casting was conducted using a laboratory-scale roll-to-roll device of 16.5 cm in width. A porous poly(ethylene) (PE, Celgard<sup>®</sup>) substrate was first wound on the left reel, while the substrate was shifted to the right reel at a rate of  $0.6 \text{ cm min}^{-1}$ , the substrate was immersed in the SPPO solution to fill the pores with the polymer solution, which



**Fig. 1.** Structure of SPPO (sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)). The polymer used in this study contains sulfonic group, which has a negative charge. To make neutral net charge, proton is attached to the sulfonic group, forming a dipole.



**Fig. 2.** Schematics of devices for electrical alignment of ion channels: (a) a view in the top of the device used to prove the research concept, in which the ion channels were aligned in the in-plane direction, (b) an electrical casting device used to align ion channels in the through-plane direction, and (c) a laboratory-scale continuous caster to align ion channels in large-scale membrane preparation.

Download English Version:

<https://daneshyari.com/en/article/633198>

Download Persian Version:

<https://daneshyari.com/article/633198>

[Daneshyari.com](https://daneshyari.com)