Anion exchange membrane crosslinked in the easiest way stands out for fuel cells

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HIGHLIGHTS

- Self-crosslinked AEM prepared by immersion technique using aq. dimethylamine.
- Highly crosslinking network (~94%) is formed by this simple crosslinking process.
- Fabricated membrane shows exceptional water swelling properties at high temperature.
- Membrane exhibits no decline in hydroxide conductivity in 1 M KOH at 60 °C for 360h.

GRAPHICAL ABSTRACT
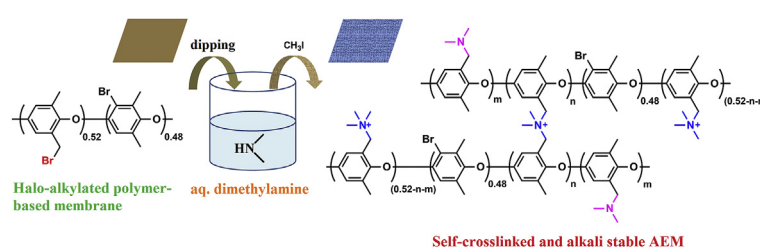
ABSTRACT

Covalent crosslinking is an effective method to stabilize anion exchange membranes (AEMs) against water swelling and high alkaline environment, yet complicated process is required. We report herein a straightforward approach to prepare highly crosslinked, transparent and flexible AEM by simply immersing a halo-alkylated polymer (e.g., brominated poly-(2,6-dimethyl-phenylene oxide)) based membrane in aqueous dimethylamine solution at room temperature and the following methylation. During this crosslinking process, a robust self-crosslinking network is formed which shows a gel fraction in N-methyl-2-pyrrolidone of (up to) 94%. Self-crosslinked membranes show low water uptakes (20–42%) and dimensional swelling (9–16%) compared to non-crosslinked membrane but good hydroxide conductivities (up to 26 mS cm^{-1}) at room temperature. Besides, the resulting membranes show some interesting features: the membranes do not immensely change its room temperature water swelling properties at high temperature but exhibits good hydroxide conductivities (up to 60 mS cm^{-1} at 80 °C). Noting that, the self-crosslinked AEM reported here has no β-hydrogens, exhibiting extremely high alkaline stability (no decline in hydroxide conductivity in 1 M KOH at 60 °C for 360h). Membrane electrode assembly consists of fabricated membrane shows moderate fuel cell performance reaching peak power density 31 mW cm^{-2} at 60 °C in a H$_2$/O$_2$ alkaline fuel cell.

1. Introduction

There have been tremendous demands for renewable energy or clean energy sources for the past few decades. As fuel cell devices proficiently transform the chemical energy stored in a fuel (e.g., H$_2$ or CH$_3$OH) directly into electrical energy, they are currently being studied for a variety of applications [1]. Among fuel cells, proton exchange membrane fuel cell (PEMFC, working in acidic condition) has been widely studied. Unfortunately, the oxygen reduction reaction in PEMFC is not kinetically favored and noble metal catalysts such as Pt are

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needed. Switching the working environment from acidic (as in PEMFC) to basic, significantly enhanced oxygen reduction kinetics as well as better fuel oxidation kinetics are observed in alkaline anion exchange membrane fuel cells (AEMFC) [2,3]. These enhancements can lead to higher efficiencies and allow the use of non-noble metal catalysts such as nickel, greatly reducing the cost of the device.

As the core component in AEMFC, anion exchange membrane (separating oxidant from fuels) must demonstrate good ionic conductivity at desired operation conditions, adequate water uptake (with minimal dimensional change) to facilitate ion conduction and good chemical stability under high alkaline environment [4]. Compared with proton conduction in PEMFC or PEM, hydroxide conduction in AEMFC or AEM is intrinsically slower because of the lower mobility of hydroxide ions. A way to enhance ion conductivity of AEMs is to increase the ion exchange capacity (IEC). However, because of severe membrane swelling which is caused by excessive water absorption, mechanical integrity of the AEMs is generally compromised at high IEC. Besides, maintaining high ion conductivity of AEM in basic environment by preventing/mitigating the degradation of functional groups is also a critical challenge.

Covalently crosslinking AEMs, especially those with high IEC values, can minimize membrane swelling and in the meantime, reduce the chance for OH$^-$ to attack either the polymer backbone or the functional groups, thus leading to enhance alkaline stability. Different strategies were utilized to crosslink AEMs, for example, photo-induced radical mediated thiol−ene "click" chemistry [5–7], Menshutkin reaction between halo-methylated polymer and commercially available diamines [8–10], ring-opening metathesis polymerization (ROMP) [11,12], olefin metathesis [13,14] and thermal crosslinking [15–18].

A common limitation for maximum of the aforementioned methods is the control over membrane fabrication as polymerization and/or crosslinking happens concurrently during membrane casting. Apart from this, there are still other issues to be solved. For example, major challenges in diamine based crosslinking methods are gelation and the alkaline stability because the functional groups based on diamine is degraded by hydroxide through Hoffmann elimination as it contains β-hydrogen [4]. And thermal crosslinking generally requires high temperature and elongated reaction times which increase the process complexity. Also, side reactions (such as degradation of the cationic groups) become more inclined at high temperatures.

More recently, Pan et al. reported a non-solvent processable one-pot synthesis of secondary amine based crosslinked AEM by reacting chloromethylated poly(sulfone) with stoichiometric quantities of diethylamine and trimethylamine, resulting in a polymer with both tertiary amino group and quaternary ammonium group [19]. During the membrane casting process, remaining chloromethyl groups reacted with the tertiary amino group on the polymer backbone to form crosslinked network. Nevertheless, this technique on a practical basis has been to a certain extent limited since direct N-alkylation of secondary amines frequently results in the generation of the quaternary ammonium salt and a mixture of the starting secondary amine and the anticipated tertiary amine [20–22].

Herein, we present a simple and unparalleled method to prepare highly crosslinked transparent membrane by just immersing halo-methylated polymer-based (brominated poly-(2,6-dimethyl-phenylene oxide) (BPPO)) membrane into aqueous dimethylamine (DMA) solution at room temperature, followed by methylation. The key tertiary amine functionality of the intermediate membrane provides the necessary amine-functionality for quaternization chemistry. The employment of this highly efficient immersing crosslinking technique allowed the fabrication of an AEM material under mild conditions, thus diminishing side reactions along the polymer chains (e.g., degradation) as well as eliminating gelation. In addition, the self-crosslinked ionomers based on an amine having no β-hydrogen exhibited extremely good chemical stability. The AEM produced was thoroughly characterized by FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), IEC titration, dynamic mechanical analysis, thermo gravimetric analysis, water

uptake, dimensional swelling, hydroxide conductivity, alkaline stability and finally assembled and assessed in a lab-scale fuel cell stack.

2. Experimental

2.1. Materials

Brominated poly-(2,6-dimethyl-phenylene oxide) (BPPO) (52 mol% bromomethylated) was kindly provided by Tianwei Membrane Company (Shandong, China) and was purified by dissolving in N-methyl-2-pyrrolidone (NMP), precipitation in water and then collected by filtration, followed by drying in an oven at 40 °C. DMA (33% in water) was purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) and used as received. Methyl iodide (98%) was obtained from Energy Chemical Reagent Co. Ltd., (Shanghai, China) and used as received. All solvents (methanol, 1-methyl-2-pyrrolidone, etc.) were purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received. Other chemicals used were of reagent grade.

2.2. Crosslinked anion exchange membrane, CQPPO-x

CQPPO-x anion exchange membrane was prepared by the following three steps, i.e. fabricating base membrane, treating BPPO membrane with DMA and quaternizing intermediate membrane (Fig. 1).

2.2.1. BPPO base membrane

BPPO (4 g) was dissolved in NMP (50 mL). The resulting homogeneous solution was then cast onto a flat, preheated (60 °C) clean glass plate and heated at 60 °C for ~12h. A transparent film was removed peeled off by dipping the glass plate in deionized (DI) water.

2.2.2. Treating BPPO membrane with DMA

BPPO base membrane obtained in section 2.2.1 was immersed in DMA aqueous solutions (with concentration at 2–10% (w/v)) at room temperature for 48h. Then, the membrane was repeatedly washed with DI water. Finally, a transparent, crosslinked membrane of ~50 μm thick was obtained, denoted as C-TA-PPO-x, where x corresponds to the concentration of DMA aqueous solution employed here. To remove trace amount of ammonium bromide salt from the membrane matrix, C-TA-PPO-x was immersed in aqueous potassium hydroxide solution (0.1 M) at room temperature for 12h. The membrane was then repeatedly washed with DI water to remove residual alkali.

2.2.3. Quaternizing C-TA-PPO-x

C-TA-PPO-x was treated with methyl iodide aqueous solution (1 wt %) at 40 °C for 72 h to fabricate fully quaternized C-TA-PPO-x membrane (designated as CQPPO-x). The membrane was then washed several times in DI water to remove residual methyl iodide. The halide ion in CQPPO-x was thoroughly exchanged in sodium chloride or potassium hydroxide aqueous solution (1 M) for 72h. Finally, ion exchanged CQPPO-x membranes were soaked in DI water for 48h, during which period DI water was refreshed at least 10 times to remove any remaining salt or base.

2.3. Benchmark quaternized BPPO (QPPO) membrane

BPPO base membrane was immersed in trimethylamine (TMA) aqueous solution (10% (w/v)) at 25 °C for 72h, followed by thorough wash with DI water. The resultant QPPO membrane in the Br$^-$ ion form was exchanged to the chloride/hydroxide form as described above for CQPPO-x membrane.

2.4. FTIR, XPS, dynamic mechanical analysis and TGA

The membranes were characterized by a Fourier-transform infrared (FT-IR) spectrometer (Nicolet iS10, Thermo-Fisher, USA) with universal