



Polybenzimidazole-crosslinked poly(vinylbenzyl chloride) with quaternary 1,4-diazabicyclo (2.2.2) octane groups as high-performance anion exchange membrane for fuel cells

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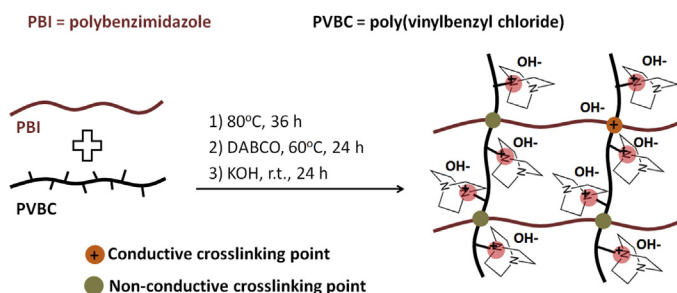
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HIGHLIGHTS

- A uniform, compact and tough AEM is prepared by crosslinking between PBI and PVBC.
- Two kinds of crosslinking points are identified in the crosslinked AEM.
- DABCO is used as the quaternization reagent and only one nitrogen atom is converted.
- The AEM presents high ionic conductivity, low swelling and superior stability.
- The fuel cell using AEM herein shows high power output and durability.

GRAPHICAL ABSTRACT



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ABSTRACT

Development of anion exchange membrane (AEM) with high conductivity, good dimensional stability, desirable toughness and long life-time simultaneously is still a challenge for the practical application of AEM fuel cells. Herein, a novel AEM (denoted as PBI-c-PVBC/OH) is fabricated by applying polybenzimidazole (PBI) and 1,4-diazabicyclo (2.2.2) octane (DABCO) as the macromolecular crosslinker and quaternizing reagent for poly(vinylbenzyl chloride) (PVBC), respectively. With the aid of crosslinking by PBI, PBI-c-PVBC/OH exhibits good flexibility and strength both in dry and water-saturated state. Moreover, high hydroxide conductivity ($>25 \text{ mS cm}^{-1}$ at room temperature) and low swelling ratio ($\sim 13\%$) is obtained, especially the swelling ratio nearly does not increase with temperature. The membrane is also advanced for the superior chemical stability in alkaline environment due to the stable polymer backbone and ionic conductive group (only one nitrogen atom in a DABCO molecule is quaternized). Furthermore, a peak power density of 230 mW cm^{-2} at 50°C is obtained on the H_2/O_2 fuel cell using PBI-c-PVBC/OH, and the membrane presents high durability both in the constant current and continuous open circuit voltage testing. Therefore, it is considered that the PBI crosslinking together with DABCO quaternization can be regarded as a promising strategy in the development of AEM for fuel cells.

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1. Introduction

Anion exchange membrane fuel cell (AEMFC) working under alkaline conditions has many advantages compared with its counterpart, proton exchange membrane fuel cell, such as faster electrode kinetics, lower alcohol crossover and non-noble metal electrocatalysts [1–3]. In an AEMFC, anion exchange membrane (AEM) is a crucial component, which plays the role as transporting OH^- and preventing the mix between oxygen/air and fuel. AEMs are generally made up of polymer matrix and anion exchange groups. The polymer matrix is usually hydrophobic and it is used to support the whole membrane, while anion exchange groups are hydrophilic and they can be dissociated into fixed cationic head groups and free hydroxide after absorbing water, giving the ion transporting ability to AEM. As a polymer electrolyte membrane, high ionic conductivity is always admired, which usually requires large quantity of ion exchange groups in the membrane, especially for the AEM, because the mobility of OH^- is only ~57% that of H^+ in aqueous phase [3]. Nevertheless, more anion exchange groups means more water will be absorbed by the AEM, resulting in severe swelling and poor strength [1–5]. Several strategies have been put forward to attempt to resolve this problem, such as crosslinking [6–9] and self-aggregation strategy [10–13]. However, it is still a challenge to obtain AEM with desirable conductivity, dimensional stability and toughness simultaneously. There are reasons to believe that fabricating an AEM consisting of two components with mechanical-supporting and hydroxide-conducting function, respectively, perhaps better overcomes the difficulty. Thus, composite AEM [14,15] and semi-interpenetrated polymer network (semi-IPN) [16,17] were developed, which are usually formed by combining a hydroxide-conducting polymer with a supporting polymer having high thermal, mechanical and chemical stabilities. Nevertheless, the separation of two components would occur in the semi-IPN or composite membrane due to the obvious differences in properties and the weak interaction between them, which often results in poor performances [18,19].

In addition to the aforementioned dilemma, another challenge faced by AEM is the degradation of polymer backbone (e.g., aromatic-ether structure) and anion exchange group (e.g., quaternary ammonium) following Hofmann Elimination or nucleophilic substitution by OH^- [1,4]. Constructing more stable polymer structure and adopting alkaline-resistant cationic head group are believed to be effective solutions to this troublesome problem [20–24]. For example, benzyltrimethylammonium quaternary ammonium (QA) is the most commonly used ionic conductive group in AEMs, but its chemical stability under alkaline environment needs to be enhanced [3]. Subsequently, it was found that the QA group converted from 1,4-diazabicyclo (2.2.2) octane (DABCO) with only one nitrogen group reacted was highly alkaline resistant due to its rigid cage structure despite that β -hydrogen atoms existed in this group [2,3]. However, it was difficult to produce AEM with such structure, because both of the two nitrogen atoms in DABCO tended to react, forming crosslink [25–28]. Unfortunately, the DABCO-formed crosslinks will give rise to materials with low alkaline stability [2,3].

In the present work, a novel AEM was prepared based on polybenzimidazole (PBI) and poly(vinylbenzyl chloride) (PVBC), in which the tough and alkaline-resistant PBI was adopted as the mechanical-supporting component, while 1, 4-diazabicyclo (2.2.2) octane (DABCO) partially quaternized PVBC took charge of conducting hydroxide. In this AEM, crosslinking was formed between two polymers via the reaction of chloromethyl groups of PVBC with benzimidazole groups of PBI, thus the interaction between the two different components was strong and the component separation was avoided, producing a uniform distribution of ionic conductive

groups in the AEM [29]. Moreover, thanks to the crosslinking with PBI, excess swelling of AEM by water was suppressed, and the mechanical properties of PVBC were improved. The ionic conductive group was introduced by quaternizing the remaining chloromethyl groups of PVBC with DABCO, and the novelty was that only one nitrogen atom of the DABCO molecule was reacted, i.e., the “selective conversion of DABCO” (i.e., only one nitrogen in a DABCO molecule was quaternized) was realized. The high stability of cationic head groups obtained was eventually confirmed by experiments. In addition, the AEM here was fabricated without chloromethylation reaction, which was restricted because of the application of highly carcinogenic reagent (e.g., chloromethyl methyl ether) and the difficulty of precise controlling the location and degree of chloromethylation [30].

2. Experimental section

2.1. Materials

Polybenzimidazole (PBI, $M_w = 9.6 \times 10^4 \text{ g mol}^{-1}$ measured by viscometric method using Ubbelohde viscometer) was synthesized in our lab and its nuclear magnetic resonance (NMR) spectrum (Fig. S1) and Fourier transform infrared (FT-IR) absorption spectrum (Fig. S2) was in good agreement with those shown in literature [31]. 1, 4-diazabicyclo (2.2.2) octane (DABCO) and poly(vinylbenzyl chloride) (PVBC, 60/40 mixture of 3- and 4-isomers average $M_n \sim 55,000$, average $M_w \sim 100,000$ by GPC/MALLS, powder) were procured from Sigma–Aldrich. Benzimidazole (Blm) and benzyl chloride (BC) came from Aladdin (China) and J&K Chemical, respectively. The electrocatalyst used in the fuel cell testing was 70 wt.% Pt/C (Johnson Matthey) and the ionomer was AS-4 ionomer (Tokuyama Co., Japan). The polymer concentration of AS-4 is 5 wt.% with 1-propanol as the solvent; the polymer has linear hydrocarbon backbone with quaternary ammonium group; the ion exchange capacity of the polymer is 1.3 mmol g^{-1} and the HCO_3^- conductivity is 13 mS cm^{-1} at 40°C (http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/amfc_050811_fukuta.pdf). All other chemicals used were commercially available with analytical grade. Moreover, all chemicals were used without further treatment.

2.2. Preparation of PBI-c-PVBC/OH membrane

Typically, a PBI and PVBC mixed solution was prepared by dissolving 0.15 g PBI in N-methyl-2-pyrrolidone (NMP) followed by adding 0.15 g PVBC. After complete dissolution, the mixed polymer solution was casted on a glass plate, and dried in an oven at 80°C . A petri dish was covered on the top of the casting solution to slow down the evaporation rate of solvent. After 24 h, the petri dish was taken away and the membrane was heated for another 12 h to remove the solvent completely, obtaining a membrane denoted as PBI-c-PVBC. Subsequently, the PBI-c-PVBC membrane was quaternized by soaking in 0.5 mol L^{-1} DABCO ethanol solution for 24 h at 60°C , giving rise to a Cl^- form AEM, named as PBI-c-PVBC/Cl. Next, PBI-c-PVBC/Cl was converted to the OH^- form membrane (PBI-c-PVBC/OH) by immersing PBI-c-PVBC/Cl in a 1 mol L^{-1} KOH aqueous solution for 24 h. In order to remove residual KOH from PBI-c-PVBC/OH, the membrane was washed by ultrapure water repeatedly and sealed in ultrapure water for 36 h.

2.3. Model reaction

In order to investigate the structure of reaction product between PBI and PVBC, a model reaction was performed using Blm and BC under similar reacting conditions with that of PBI-c-PVBC

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