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Interpenetrating anion exchange membranes using poly(1-vinylimidazole) as bifunctional crosslinker for fuel cells

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ABSTRACT

There is a balance between ionic conductivity and dimensional stability in anion exchange membranes (AEMs). High conductivity resulting from densely charged groups is normally accompanied with high water uptake and excessive swelling. Herein, a series of novel AEMs with interpenetrating network was prepared by the incorporation of poly(vinylbenzyl chloride) (PVBC) and poly(1-vinylimidazole)(PVIm) into the PVA matrix. PVBC and PVIm act as bifunctional macromolecular crosslinking agents to provide both imidazolium cations and to form crosslinked network in the membranes. The resulting AEMs were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The effect of crosslinking density on conductivity, water uptake, swelling ratio and stability was investigated. The results reveal that the addition of PVBC-c-PVIm could be simultaneously conducive to higher conductivity and lower swelling ratio. Notably, the membrane containing 50 wt% PVBC-c-PVIm had IEC of 1.86 meq g⁻¹, water uptake of 39.4%, and hydroxide conductivity of 21.9 mS cm⁻¹ at 30 °C. A maximum power density of 37.1 mW cm⁻² is achieved at a current density of 64 mA cm⁻². The crosslinked AEMs also exhibit excellent alkaline stability in a 4 M KOH solution at 60 °C for 1320 h.

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1. Introduction

The emergence of fuel cells has significantly broadened the application of membrane technology due to its high energy efficiency and environmental friendliness [1,2]. Proton exchange membranes (PEMs), a key component for proton exchange membrane fuel cells (PEMFCs), have been attracting increasing attention in the last few decades because they possess high proton conductivity and excellent stability. Nevertheless, the commercialization is still impeded by some intrinsic weakness in PEMFCs, including limited oxygen reduction kinetics, poor selectivity and dependence on expensive catalysts (such as platinum) [3–5]. Hence, as an alternative, anion exchange membrane fuel cells (AEMFCs) are attracting increasing interest due to their incomparable advantages, such as the potential use of non-noble metal catalysts (silver and nickel) and their higher oxygen reduction kinetics than the PEMFCs [6,7].

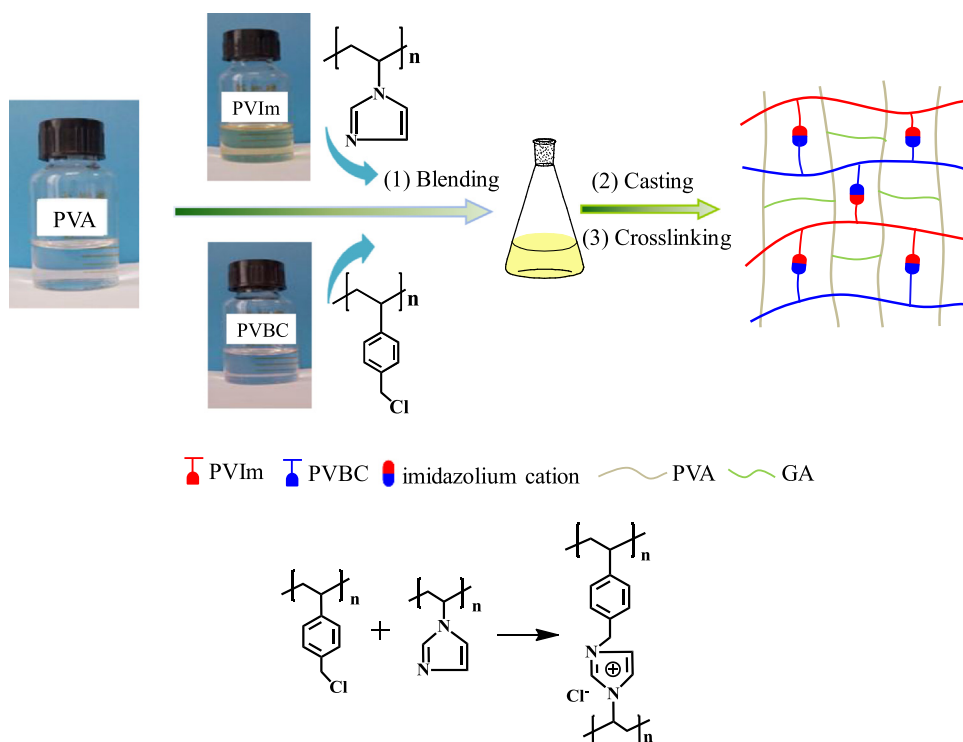
AEMs with functional groups capable of transporting the hydroxyl anions are a key component in AEMFCs [2]. Recently, much effort has been devoted to the fabrication of three main types of

AEMs including homogeneous, hybrid and interpenetrating network (IPN) membranes. Homogeneous AEMs, which are made from polymer material with cationic groups covalently bound to the polymer backbones, have been widely explored [8]. A variety of polymers with main chain structures such as poly(arylene ether)s [9], poly(olefin)s [10], polystyrene [11], poly(phenylene oxide) [12] and poly(phenylene) [13] have been reported. Hybrid membranes combine the features of both organic and inorganic materials, for instance PVA-SiO₂ hybrid composites [14] and poly(arylene ether sulfone)-ZrO₂ composites [15]. The third kind of AEMs belonging to (semi)IPN membranes generally have hydrophobic crosslinked network and hydrophilic linear main chain bearing functional cationic groups [16,17]. This characteristic often brings in good dimensional and chemical stability hence attracting growing research. A series of PVA-based (semi)IPN membranes has been reported recently such as PVA/QHECE [18], PVA/PDDA [19], and PVA/FP [20]. Although these AEMs display good stability and fabrication simplicity, their conductivity needs further improvement at relatively low water uptake.

Actually, there still exists universal antinomy in designing AEMs with excellent performance. In order to boost the ionic conductivity of the AEMs for practical application, enhancing the density of conductive groups such as quaternary ammonium [21], imidazolium [22], guanidinium [23], and phosphonium [24] is a

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Scheme 1. Illustration of the preparation of the interpenetrated membranes.

straightforward method. Unfortunately, high ionic exchange capacity (IEC) usually results in excess water uptake, poor dimensional and mechanical stability as well. To conquer this trade-off, a versatile crosslinking approach can be employed. However, most of the crosslinking was realized at the expense of functional groups in AEMs, which inevitably causes a reduction in conductivity. Therefore, further exploration for an appropriate crosslinking agent is highly desirable.

Herein, we report the preparation a new kind of interpenetrating network AEMs, combining the attractive virtues of blend membranes and crosslinking technique. Initially, poly(vinylbenzyl chloride) (PVBC) was used as the hydroxide conducting polymer after being crosslinked with poly(1-vinylimidazole) (PVIm). Considering that the pristine crosslinked PVBC-c-PVIm is too brittle to be applicable in fuel cells, the cost-effective poly(vinyl alcohol) (PVA) was adopted as the matrix for its flexibility and good film forming property with excellent miscibility between other components [18,19,25]. PVA was treated with an amount of glutaraldehyde to promote its stability in an aqueous solution [19,26]. The novelty of this scheme stems from the fact that the macromolecular PVBC and PVIm acting as bifunctional crosslinkers in blend AEMs, can effectively suppress swelling by the formation of crosslinked network, and can simultaneously provide hydroxide conducting imidazolium groups, thereby facilitating desirable ionic conductivity. Moreover, the applied composite technique would have inspiring phenomena resulting from each blend component. Imidazolium is generally regarded to possess promising alkali resistance, the AEMs based on a polymerizable imidazolium salt reported by Li et al. [27] exhibit fairly good alkaline stability under high pH conditions although the conductivity is moderate. The new composite AEMs with various PVBC-c-PVIm contents were fabricated. The effect of crosslinking on IEC, conductivity, water uptake, swelling ratio, mechanical property and thermal stability was thoroughly discussed. We anticipate that this newly developed crosslinking strategy based on PVA matrix would tremendously contribute to the current trade-off dilemma.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) with a polymerization degree of 1750 ± 50 and hydrolysis degree of 98–99% was purchased from Sinopharm Chemical Reagent Co. Ltd. Poly(vinyl benzyl chloride) (60/40 mixture of 3- and 4- isomers with average molecular weight of Mn 55,000) was purchased from Sigma Aldrich. 1-Vinylimidazole (99%), 2,2-azobisisobutyronitrile (AIBN, 98%) and glutaraldehyde (GA, 50 wt% aqueous solution) were commercially obtained from Aladdin Industrial Inc. The radical initiator AIBN was purified by recrystallizing from a methanol solution prior to use. CaH₂ was stirred in N,N-dimethylformamide (DMF) (AR, Sinopharm, China) for 24 h, distilled under reduced pressure and filtered over 4 Å molecular sieves. All other chemicals were supplied from Shanghai Sinopharm Chemical Reagent Co., Ltd (China) and used as received.

2.2. Preparation of anion exchange membranes

2.2.1. Synthesis of poly(1-vinylimidazole)

Poly(1-vinylimidazole) (PVIm) was synthesized by the method described in the literature [28]. A typical process is summarized below. 4.0 g of 1-vinylimidazole (42.5 mmol) and 15 mL of DMF were added into a 50 mL three-necked round-bottomed flask equipped with a condenser and a magnetic stirrer. 0.04 g of AIBN (0.244 mmol) was added into the flask and the mixture was slowly heated to 70 °C under a nitrogen atmosphere. After radical polymerization for 24 h, the resulting yellow viscous solution was cooled to room temperature and precipitated into 300 mL of acetone followed by filtration to yield a crude solid. The resultant solid was Soxhlet extracted with acetone for 12 h and vacuum dried at 60 °C for another 24 h to obtain a faint yellow product. The chemical structure of the as-synthesized homopolymer was characterized using ¹H NMR.

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