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Preparation and characterization of directional conducting and lower methanol permeable ultrathin membrane based on poly (vinyl alcohol) and imidazolium compounds

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ABSTRACT

To produce directional conducting and lower methanol permeable ultrathin membrane for fuel cell, the imidazolium salt as both cross-linking agent and proton donor has been designed to build a directional proton conducting channel in a poly (vinyl alcohol)-based membrane. The methanol permeability of directional conducting membrane is very low, which is about twice smaller than that of Nafion₁₁₇. In addition, the membranes show a relatively high oxidative durability in H₂O₂ solutions, with only about 10% weight loss after the membrane being immersed in 3% H₂O₂ solution for 120 h. All the properties of prepared directional conducting membrane indicate their promising prospects in proton conducting membrane applications.

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Introduction

Fuel cells are electrochemical energy conversion devices, which directly transform chemical energy into electricity [1,2]. In fuel cells, proton exchange membrane (PEM) serves as the electrode separator in addition to its primary role as a continuous medium for conducting protons from anode to cathode [3–6]. As commercially available PEM, Nafion has been widely studied due to high proton conductivity, excellent chemical and mechanical properties [7,8]. However, PEM based direct methanol fuel cell shows sluggish electrode kinetics, high cost and substantial alcohol crossover which has hampered further larger scale commercialization [9–13].

Methanol crossover can lower specific cell power output and also reduce the overall efficiency. Therefore, it is very necessary to prepare novel conducting membranes with ultrathin thickness, low cost and low methanol permeability [14]. Recently, many studies have been carried out to develop new kinds of ionic/proton conducting membranes. Polymers such as poly(benzimidazole) [15], poly(ethylenimine) [16], poly(ethyleneoxide) [17], polydimethylsiloxane [18], poly(ether sulfone) [19,20], poly(vinyl phosphonic acid) [21] and poly(4(5)-vinyl-imidazole) [22] have been used as host polymers for preparing ionic/proton conducting membranes.

Admittedly, poly (vinyl alcohol) (PVA) has been studied extensively because of its good film-forming, low cost, low

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methanol permeability and good chemical resistant properties [23]. Specially, PVA membranes have been used in ethanol dehydration to circumvent the ethanol-water azeotrope, because they can selectively pass water molecules over ethanol or methanol [24,25]. However, the unstable morphology of PVA membrane must be controlled. In general, cross-linking is regarded as an efficient and simple method for reducing membrane swelling and improving mechanical stability, which allows the conducting polymer membranes to be cost-effective. In recent years, many researches about cross-linking of PVA have been carried out. Qiao et al. reported the preparation of anion-exchange membranes using PVA as a base material and glutaraldehyde (GA) as a cross-linking agent [26]. Meanwhile, poly(acrylamide-co-diallyldimethyl ammonium chloride) was doped in the membrane without any chemical bonding effect for offering anions as charge carriers conducting hydroxide. The membranes exhibited excellent anion conductivity, better thermal stability and lower methanol permeability. Liu et al. [14] prepared the poly(vinyl alcohol)/hexafluoroglutaric acid membrane with benzenesulfonic acid sodium salt and GA as binary reaction agents. The cross-linked membranes acquired effective proton transport, high ion exchange capacity (IEC) and good water management. However, in these membranes, cross-linking is only a general strategy to suppress the membrane swelling [13,26–30], ionic conducting direction is uncontrollable and the thickness of membranes is larger than 100 μm due to a mass of doping. These problems lead to more electric energy wasting because of poor flexibility and high resistance of membrane. Therefore, new strategy for fabricating ultra-thin polyelectrolyte films with proton directional conducting is necessary [31]. Meanwhile, it should be paid more attention on the correlations between the properties and the structures of the prepared membranes.

Herein, our strategy is the utilization of the binary reaction agents as both cross-linking agent and proton donor to build a directional proton conducting channel in the membrane. The advantage of such a composition strategy lies on offering higher conductivity by decreasing membrane thickness and making proton directional conducting. So, sulfuric acid-functionalized 1,3-bis(carboxymethyl)imidazole ([Mim(CM)₂]HSO₄) is used as binary reaction agents to prepare the PVA membranes. In the meantime, we compared directional conducting (chemically cross-linked) with undirectional conducting (physically doped) membranes, which focused on

investigating the effect of molecular structures on the properties of proton conducting membranes.

Experimental section

Materials

PVA (98–99%, hydrolyzed, average molecular weight $M_w = 88,000\text{--}97,000$) was purchased from the Alfa Aesar. All the other chemicals, including glycine ($\geq 99\%$), glyoxal, para-formaldehyde and methanol, were obtained from Sino-pharm Chemical Reagent Co., Ltd (SCRC). The deionized water was used.

Preparation of sulfuric acid-functionalized 1,3-bis(carboxymethyl)imidazole

In a typical preparation, 50.0 mmol glycine, 2.66 mL (40%) glyoxal and 25.0 mmol para-formaldehyde were mixed and heated in water at 95 °C for 2 h. The water was then removed by rotary evaporator. The residue was washed with a small amount of water, and large amounts of methanol were added. The obtained precipitate was separated from the solution and dried. Equimolar amounts of precipitate and sulfuric acid were dissolved in water and stirred for 12 h at 80 °C. The product was washed with ether three times, and then evaporated with rotary evaporator. The obtained product was dried in vacuo (Fig. 1) [32–34]. The ¹H NMR (D₂O, δ ppm): 1H 8.75 (s, 1H), 7.42 (d, 2H), 4.89 (s, 4H).

Membrane preparation

The polymer membranes were prepared through solution casting method. A 10 wt% PVA aqueous solution was prepared by dissolving PVA in deionized water at 90 °C with vigorous stir until a transparent solution was obtained. Then, PVA solution and [Mim(CM)₂]HSO₄ were mixed in a molar ratio of PVA/[Mim(CM)₂]HSO₄ being 1:0.03. To investigate the effect of directional conducting of protons on membrane performances, preparation process was proceeded by the two following ways: (i) chemically cross-linked for directional conducting of protons: the complex solution of PVA/[Mim(CM)₂]HSO₄ was heated to 80 °C for 4h. After that, the solution was cooled, poured and casted onto a flat Plexiglas

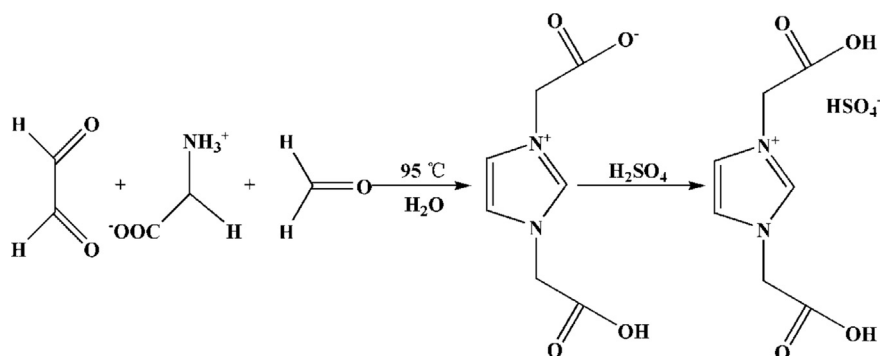


Fig. 1 – Synthesis of sulfuric acid-functionalized 1,3-bis(carboxymethyl)imidazole.

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