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A facile method to construct highly efficient methanol resistive polyamide-based proton exchange membrane

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ABSTRACT

A highly efficient methanol resistive organic–organic hybrid polyamide proton exchange membrane was prepared via a facile method and the proton conductive channels (PCCs) in the membrane were optimized to adjust the proton conductivity, mechanical stability and methanol permeability. The hybrid membrane with the optimized PCCs exhibits remarkable proton conductivity of 0.232 S/cm at 80 °C, much higher than the value of a Nafion 117 membrane (0.192 S/cm). At the same time, the methanol permeability of the optimized membrane becomes as low as 6.21×10^{-7} cm²/s, one order of magnitude smaller than that of the Nafion 117 membrane. The tensile strength of the membrane is 13 MPa, comparable to that of the Nafion 117 membrane. This hybrid membrane is therefore promising for applications in direct methanol fuel cell (DMFC).

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Introduction

Direct methanol fuel cells (DMFCs) have shown great potential for application in portable electronic devices as the power sources due to the high energy density of methanol [1]. As one of the key components in a DMFC, proton exchange membrane (PEM) profoundly influences the electrochemical performance and life time of a DMFC since the PEM serves as both a proton conductor and a separator in the fuel cell [2,3]. Today, Nafion membranes dominate the PEM market for DMFC applications due to their relatively high proton conductivity and strong mechanical and thermal stabilities. However, the high

cost and severe methanol permeation of Nafion membranes have hindered large-scale commercialization of DMFCs [4]. Numerous studies have been carried out to develop alternative polymeric proton conductive materials for DMFC applications to replace Nafion, including partially fluorinated [5–11] and non-fluorosulfonated polymers [12–22]. Kim et al. [9] synthesized partially fluorosulfonic poly (arylene ether) and poly (arylene ether nitrile) with proton conductivity of 135.4 mS/cm at 80 °C. Much lower methanol permeability (2.68×10^{-7} cm²/s) than that of Nafion membrane was also obtained. Nevertheless, the partially fluorosulfonic PEMs are still expensive to meet the demand of large scale applications.

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Zhang et al. [13] prepared a covalently cross-linked PEEK membrane, which is a typical non-fluorosulfonated PEM, with good overall performance at the temperature up to 130 °C.

Construction of appropriate proton conductive channels (PCCs) has been deemed to be one of the key factors simultaneously affecting proton conductive, fuel permeation and mechanical properties in a PEM [23]. Efficiently constructed PCCs would offer a high degree of phase-separation between hydrophobic segments and hydrophilic segments in a membrane and lead to well-connected PCCs [23,24]. However, the balance between proton conductivity and fuel permeability in the PCC design and construction must be carefully considered because both proton transport and methanol diffusion in the PEM are strongly dependent on water molecules, which intimately affect the PCC structures [25]. Significant efforts have been made to balance these two properties via PCC construction with different strategies. Wu et al. [26,27] embedded two acid-base connected “barriers” into PCCs for methanol blocking and the hydrogen bonded acid-base interaction facilitates protons transport at the same time. As a result, the membrane exhibits much lower methanol permeability (30% of values of a Nafion membrane) and slightly higher proton conductivity (90 mS/cm at room temperature) than that of Nafion membrane. Another method to balance proton conductivity and methanol permeation resistivity of a PEM is to incorporate perfluoroalkyl sulfonic acid groups into polymeric proton conductors [28–30]. Nakagawa et al. [31] introduced perfluoroalkyl sulfonic acids into the side chains to improve the proton conductivity by taking advantage of the well-controlled PCCs arising from the different polarities between the hydrophilic side chains and the hydrophobic main chains. Xu et al. [32] placed flexible hydrophilic side chains in the rigid backbones with a high fluorine content and the resultant PEM displays comparable conductivity to that of Nafion membrane. At the same time, the gas permeability through the membrane was found to be smaller than that of the Nafion membrane. In addition, well connected PCCs can also be constructed via self-assembling by using chemical incompatibility between covalent unions [33–40].

In a previous study, we proposed a concept to construct hierarchical proton conductive channels (HPCCs) in hyperbranched polyamide proton conductive macromolecules [41,42]. In the HPCCs, dense $-\text{SO}_3\text{H}$ groups built within the $-\text{COOH}$ end-capped macromolecules was used to form the first-order PCCs (FOPCCs) and the intermolecular hydrogen bonds among the $-\text{COOH}$ groups form the second-order PCCs (SOPCCs). In this paper, we aim to modify the SOPCCs in the HPCCs by mildly adjusting the hydrogen bond strength and the water retention capacity of the SOPCCs to optimize the overall performance of the PEM. Hyperbranched polyamide macromolecules with different end-capping groups ($-\text{COOH}$ for E-HBM1 and $-\text{NH}_2$ for E-HBM2 as shown in Fig. 1) were designed and prepared for fabrication of a hybrid membrane. The SOPCCs in the hybrid membrane was adjusted by tuning the weight ratio of E-HBM1 to E-HBM2. By making use of the difference of hydrogen bonding strengths of $-\text{COOH}\sim-\text{COOH}$, $-\text{COOH}\sim-\text{NH}_2$, $-\text{NH}_2\sim-\text{NH}_2$ [43,44] and the different hydrophilicity between the $-\text{COOH}$ group and the $-\text{NH}_2$ group [45], we successfully fabricated a hybrid PEM with the optimal overall performance.

Experimental

Materials

Trimesic acid (TA, Shanghai Dibo Chemical Reagent Co., Ltd.), lithium chloride anhydrous (LiCl, Shanghai Qiangshun Chemical Reagent Co., Ltd.) and 2,4-diaminobenzenesulfonic acid (DSA, Adamas Reagent, Ltd.) were dried at 80 °C for 24 h before using. N-Methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd.), triphenylphosphite (TPP, Sinopharm Chemical Reagent Co., Ltd.) and Pyridine (Py, Shanghai Lingfeng Chemical Reagent Co., Ltd.) were purified by distillation from KOH.

Polymerization

E-HBM1: TA (2 mmol), *p*-DSA (2 mmol), LiCl (0.32 g), TPP (1 mL), NMP (8 mL) and Py (3 mL) were added into a 50 mL two-necked round-bottom flask, and the reaction was maintained at 100 °C for 2 h with stirring under argon atmosphere. After the reaction was completed, the product was washed with methanol and ultrapure water several times. The product was finally dried at 80 °C in a vacuum oven for 24 h.

E-HBM2: TA (1 mmol), *p*-DSA (2.1 mmol), LiCl (0.15 g), TPP (1 mL), NMP (4 mL) and Py (3 mL) were added into a 50 mL two-necked round-bottom flask, and the reaction was maintained at 100 °C for 2 h with stirring under an argon atmosphere. Same as the polymer E-HBM1, the product was washed with methanol and ultrapure water several times after the reaction was completed. The dried product was finally dried at 80 °C in a vacuum oven for 24 h.

PEM preparation

Membranes were prepared via a solution-cast technique using dimethyl sulfoxide (DMSO) as solvent. The mixed solution of

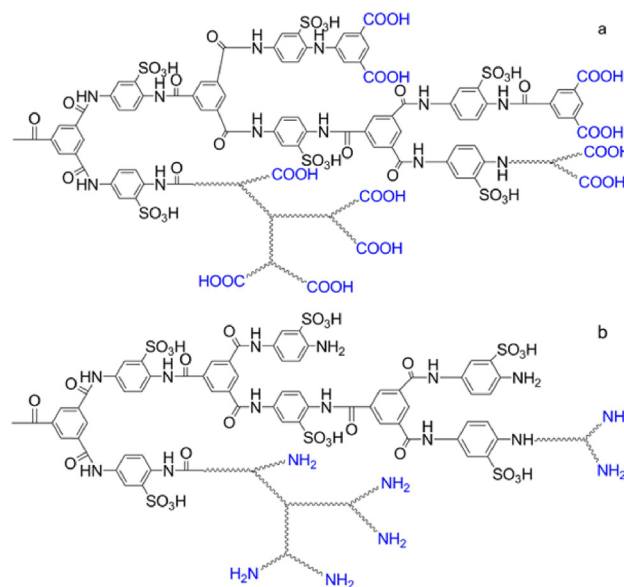


Fig. 1 – The molecular structures of (a) E-HBM1 and (b) E-HBM2.

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