



Improvement of alkaline stability for hydroxide exchange membranes by the interactions between strongly polar nitrile groups and functional cations



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ABSTRACT

Hydroxide exchange membrane fuel cells (HEMFCs) are attracting growing interest owing to their advantages such as low cost and high power density. However, their applications are hindered due to the poor stability of the membrane. Here, we proposed a novel strategy to improve the alkaline stability of hydroxide exchange membranes (HEMs) using the interactions between strongly polar nitrile groups and side-chain functional cations. A poly(ether nitrile) (PEN) was synthesized by the polycondensation of bisphenol A and 2,6-difluorobenzonitrile, and then imidazolium and morpholinium functional groups were integrated by the typical chloromethylation-functionalization method. The existence of the interactions between nitrile groups and cation groups i.e. imidazolium and morpholinium, was proved by the density functional theory calculations. The interactions have two positive effects that contribute to the improvement of the alkaline stability of the PEN based membranes. On the one hand, they increase the LUMO energies of the functional groups; and on the other hand they reduce the free volume around hydrated cationic groups. As a result, PEN based membranes showed much better alkaline stabilities compared to the membrane based on commercial polysulfone that has a similar chemical structure. In addition, given similar swelling ratios, PEN based membranes exhibited higher hydroxide conductivities than simple polysulfone based ones.

1. Introduction

Hydroxide exchange membrane fuel cells (HEMFCs) are new, clean and efficient energy technologies that are attracting international attention [1–3]. Working in a basic environment, HEMFCs have several advantages over proton exchange membrane fuel cells (PEMFCs), namely, enhanced kinetics of both fuel oxidation and oxygen reduction, usability of non-precious metal catalysts (e.g. silver and nickel), and good stability of catalysts [4–8]. Therefore, HEMFCs have the potential to achieve a low cost and a long durability which are necessary for a large-scale commercialization.

The hydroxide exchange membranes (HEM) is the core of HEMFCs. It serves as a hydroxide conductor as well as a fuel/oxidant separator [9–12]. A high hydroxide conductivity, a low swelling ratio and a good alkaline stability are the major requirements for HEMs to

achieve durability and a high energy density of the fuel cell [13]. Many efforts have been focused on developing high performing HEMs. The most frequent route that has been used is grafting functional side chains onto the polymers by the easy reaction between benzyl halide groups of the polymer backbone and the monomers containing functional groups. Benzyl halide groups can be simply introduced by radiation-grafting vinyl benzyl chloride onto fluorinated polymers [14,15], the halomethylation of benzene rings in aromatic polymers [16] or the halogenating reaction of methyl groups in benzene rings of polymers [17]. HEMs are afterwards functionalized with ammonium [18,19], imidazolium [16,17,20], phosphonium [21,22], morpholinium [23] or guanidinium [24,25]. The ionic conductivity of hydroxide ion in HEMs is usually lower than the one of the proton in PEMs, due to the size and the inherently difficult mobility of hydroxide ion. Ion exchange capacity (IEC) has a great effect on hydroxide conductivity and swelling

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ratio in this type of HEMs. A high IEC could favor the formation of continuous hydroxide conducting channels, thus achieving a high hydroxide conductivity [26], however, it also causes excessive swelling of the membranes, resulting in a loss of dimension stability [27–29]. The swelling ratio of HEMs could be reduced by increasing the interactions between polymer chains. Increasing the charge density of the polymer main chain could enhance the interactions between polymer chains by Van der Waals forces [20]. Crosslinking could offer a strong covalent bonding between polymer chains which can resist the relaxation of polymer chains [30–35]. Semi-interpenetrating polymer networks (sIPNs) could create an architecture of permanent entanglement and interlocking of polymer chains [36,37]. Multiple functionalizations per repeating unit or per side chain could endow HEM materials with more hydrophobic units compared to a single functionalization. This could facilitate the dense packing of hydrophobic parts, thus increasing the interaction between polymer chains [38–42]. All these strategies can offer an opportunity to obtain highly-conductive and swelling-resisted HEMs [43–45]. However, the alkaline stability of HEMs remains the major concern. The poor stability may stem from the OH⁻ attack on the methylene group situated between the benzene of the polymer backbone and the functional groups [46].

In this study, we proposed a novel strategy to improve the alkaline stability of HEMs using the interactions between strongly polar nitrile groups and side-chain functional cations. A poly(ether nitrile) (PEN) was synthesized by the polycondensation of bisphenol A and 2,6-difluorobenzonitrile, followed by the synthesis of imidazolium- and morpholinium- functionalized PENs using the consecutive chloromethylation and quaternization reactions. The density functional theory calculations were used to witness the existence of the interactions between nitrile groups and the functional groups. These interactions have two effects that enhance the alkaline stability of the membranes. The first one is increasing the LUMO energies of functional groups, and the second is inhibiting the formation of the transition state, caused by the S_N2 degradation pathway, by reducing the free volume around hydrated functional groups. Consequently, the PEN based membranes showed improved alkaline stabilities compared to the membranes that employ the commercial polysulfone as a polymer backbone.

2. Experimental

2.1. Materials

2,6-difluorobenzonitrile (DFBN) (99%, Energy Chemical, China), bisphenol A (BPA) (98%, Aladdin, China), tin chloride anhydrous, 1,2-dimethylimidazole, 4-methylmorpholine, sodium hydroxide, hydrochloric acid (37–38%), ethanol, dichloromethane, and N,N'-dimethylacetamide (DMAc) were used as received without any further purification. All the used chemicals were analytical grade in the experiments. Chloromethyl octyl ether (CMOE) was self-synthesized [16]. The deionized water was boiled to be completely degassed in order to reduce the possible effect of dissolved CO₂ on the membrane characterization.

2.2. Synthesis of poly(ether nitrile)

The poly(ether nitrile) was synthesized by the polycondensation of 2,6-difluorobenzonitrile and bisphenol A, as shown in Fig. 1. DFBN (10.0 g, 71.2 mmol), BPA (16.4 g, 71.2 mmol), K₂CO₃ (11.9 g, 85.4 mmol), DMAc (53 mL), and toluene (25 mL) were added into a 100 mL three-necked round bottom flask equipped with a Dean-Stark trap and a nitrogen inlet/outlet. The mixture was kept under a constant nitrogen flow at 140 °C for 6 h to remove the water and toluene. Then the reaction was carried out at 170 °C for another 40 h. Afterwards, the solution was cooled to 80 °C and poured into ice water to obtain the precipitate as a white fibrous solid product. Finally the product, poly(ether nitrile) (PEN), was obtained by washing with water several

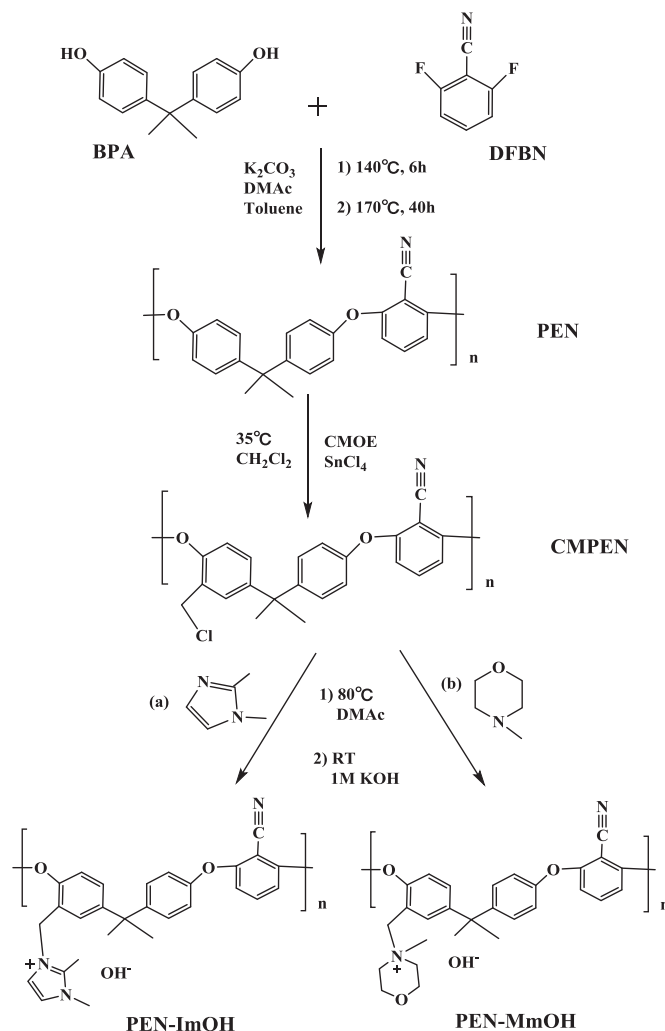


Fig. 1. Synthesis of the PEN, CMPEN, PEN-ImOH and PEN-MmOH.

times, immersing in boiling water for 2 h, and drying under vacuum at 80 °C for 24 h (yield: 97%).

2.3. Synthesis of chloromethylated poly(ether nitrile)

1.5 g PEN was added into 60 mL dichloromethane with stirring. After a complete dissolution, 15 mL CMOE and 0.3 mL anhydrous tin chloride were added successively. The mixture was stirred at 35 °C for a certain time. Then the white solid was collected by precipitation in ethanol and repeatedly washed several times. Finally, the product, chloromethylated PEN (CMPEN), was obtained by vacuum-drying at room temperature. The chemical structures and synthetic processes are shown in Fig. 1.

2.4. Preparation of imidazolium- and morpholinium-functionalized PEN membranes

0.2 g CMPEN was completely dissolved in 5 mL DMAc at room temperature, and then 1.5 mol equiv chloromethyl of 1,2-dimethylimidazole or 4-methylmorpholine was added into the solution. The reaction was kept at 80 °C for 10 h. Subsequently, the solution was poured onto a glass plate. After curing and drying at 60 °C for 24 h, the membrane was formed and peeled off from the glass plate. Finally, the imidazolium- or morpholinium- functionalized PEN (PEN-ImOH or PEN-MmOH) membrane was obtained by ion-exchanging by 1 M KOH solution at room temperature for 48 h, followed by washing and immersion with deionized water in a tightly sealed container for

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