



Enhanced hydroxide ion conductivity of imidazolium functionalized poly(ether ether ketone) membrane by incorporating *N,N,N',N'*-tetramethyl-1,4-phenylenediamine



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ABSTRACT

Anion-exchange membranes (AEM) are prepared from chloromethylated poly(ether ether ketone) (CMPEEK), which is quaternized by *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) and 1-methylimidazole using a two-step method. TMPD can not only improve the mechanical properties but also provide more ion exchange groups and improve the availability of quaternary ammonium (QA) groups. By varying the amount of TMPD in the membrane casting solution, the comprehensive properties of the membranes are optimized and intensified. The anion conductivity is increased from 0.028 S cm^{-1} of the imidazolium functionalized poly(ether ether ketone) (ImPEEK) control membrane to 0.042 S cm^{-1} of the TMPD/ImPEEK membrane with a TMPD content of 5 wt%. Meanwhile, a 31.5% increase in ultimate tensile strength and a 27.8% increase in Young's modulus of the TMPD/ImPEEK membrane are achieved. This study exploited a facile approach to solving the trade-off relation between anion conductivity and mechanical properties.

1. Introduction

With the increasing demand for clean and efficient energy worldwide, fuel cells are attracting more and more attention as an environmentally friendly power source substituting conventional fossil fuels. Until now, the majority of efforts have been devoted to developing proton exchange membrane fuel cells (PEMFCs) based on proton exchange membranes (PEMs). However, only some noble metal can be used as catalysts in these acidic operating conditions, which is a huge obstacle in the broad commercialization of PEMFCs [1–5]. The alkaline exchange membrane fuel cell (AEMFC) is considered as a very promising energy conversion device PEMFC. The alkaline condition of AEMFCs renders high stability of metals as well as fast electrode kinetics, which guarantee the application of non-noble metal as catalyst, such as Fe, Ni, etc. Meanwhile, AEMFCs possess many other advantages including lower alcohol permeability and easier water management [6–11].

Alkaline exchange membrane (AEM) is the core component of AEMFC, which should possess the features of high ionic conductivity, excellent mechanical properties and high dimensional stability

[12–16]. Whereas, the conductivity of AEM is often low due to the inferior ionic mobility of hydroxide ions, which constitutes constraints for the development of AEMFC. As we know, ion exchange capacity (IEC) indicates the amount of charge carriers per unit weight of the polymer. Increasing IEC can provide more hydroxide ion carriers to raise the hydroxide conductivity significantly [17]. However, the high IEC usually causes the excessive water uptake and the destructive dimensional swelling, leading to the decreased mechanical properties of membranes [17,18]. Crosslinking can reinforce the mechanical properties of the membranes [19–21], but traditional crosslinking methods often based on hydrophobic groups or ion-resistant groups, which lead to discontinuous hydrophilic regions. Therefore, a great challenge remained to be achieved the balance between high hydroxide conductivity and good mechanical property.

Employing diamine as both crosslinking and quaternizing reagent may be a promising strategy to address the above challenge. Diamines can react with two halogenmethyl groups of different polymer chains to form quaternary ammonium groups, which play two roles. 1) Crosslinking the polymer chains to improve mechanical properties: by introducing two quaternary ammonium groups, diamines can

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efficiently crosslink within the polymer matrix and enhance mechanical properties [22,23]. 2) Increasing the IEC by the generation of the dual QA groups: two molar equivalent hydroxide conducting groups are created through one molar equivalent crosslinking of diamine. Thus, the IEC of AEM is increased, which is the distinct advantage of the diamine crosslinker over the other kinds of crosslinkers. In addition, the employment of diamines as crosslinking and quaternizing reagent can hold the QA groups around the polymer chains, improving the approachability of QA groups and finely tuning the microstructure of the membrane, rendering a better connectivity of the ionic clusters, thus donating more continuous pathways for anion transport [24–27]. By this strategy, the trade-off effect between hydroxide conductivity and mechanical properties could be surmounted. After quaternized by diamine, the continuous ionic domains establish the unobstructed ion conduction without the need for microphase separation.

Based on the above analysis, a new kind of diamine-crosslinked AEM was prepared. The structures and properties of membranes were investigated in detail. The as-prepared membranes exhibited high hydroxide conductivity and excellent mechanical properties simultaneously, which may be suitable for potential AEMFC applications.

2. Experiment

2.1. Materials

1-Methylimidazole (analytical reagent, 99.9 wt%) was supplied by TCI, Shanghai, China. Dimethylformamide and isopropanol were purchased from Shanghai Aladdin Industrial Corporation. Poly(ether ether ketone) (VictrexPEEK, grade 381G) was purchased from Nanjing Yuanbang Engineering Plastics Co. Ltd. 2,3,5,6-tetramethyl-1,4-phenylenediamine were purchased from Heowns (Tianjin, China). Concentrated sulfuric acid (analytical reagent, 98.2 wt%) was purchased from Tianjin Jiangtian Chemical Scientific Ltd. Sodium chloride, calcium chloride, sodium hydroxide and hydrochloric acid were purchased from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). All the reagents not mentioned were commercially available with an analytical pure degree and used as received. Deionized water was used throughout the experiments.

2.2. Chloromethylation of PEEK

PEEK was chloromethylated using sulfuric acid as solvent and chloromethyl octyl ether (CMOE) as chloromethylation reagent based on Blanc chloromethylation reaction. The CMOE was prepared by bubbling hydrogen chloride into the mixture of paraformaldehyde, *n*-octanol, and chloroform, as reported in literature [28]. 8 g PEEK was sufficiently dissolved in 480 mL concentrated sulfuric acid at 0 °C with stirring, and then the temperature was lowered to –10 °C. Then, 40 mL fresh CMOE was added, and the temperature was raised to 0 °C. Subsequently, the reaction was kept for about 20–60 min. By pouring the reacted mixture into ice water, chloromethylated PEEK (CMPEEK) was precipitated. Then, the mixture was washed with ethanol (EtOH) until no sulfonated acid and octanol left. For further purification, the raw CMPEEK was re-dissolved in methyl-2-pyrrolidinone (NMP) to obtain a 10 wt% solution and re-precipitated in cold EtOH. The purified CMPEEK was dried at 40 °C under vacuum for about 48 h and stored at –10 °C.

2.3. Preparation of the membranes

The membrane was fabricated by the solution-casting method. Initially, CMPEEK (0.4 g) was dissolved in DMF (3 mL). 0.05 mL 1-methylimidazole was added afterward. The solution was treated by stirring and ultrasonic processing alternately. After stirring for 3 h, a certain amount *N,N,N',N'*-tetramethyl-1,4-phenylenediamine was added to the solution and stirred under high speed until it became

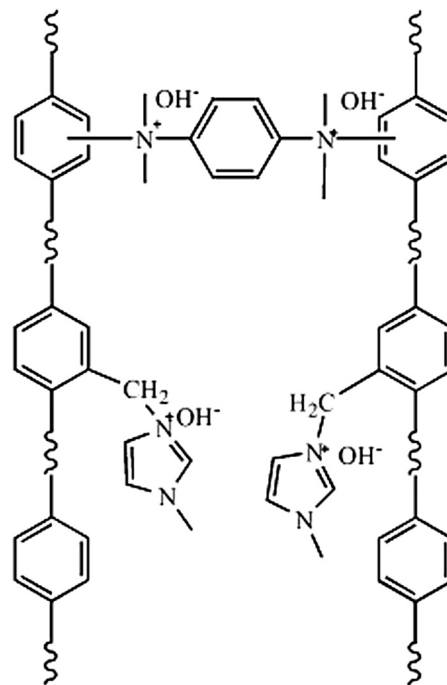


Fig. 1. Quaternization of CMPEEK.

bluish violet. Finally, 0.01 mL 1-methylimidazole was added into the solutions in order to ensure sufficient reaction of chloromethyl group. The as-prepared mixed solution was then cast onto clear a glass plate and dried in a vacuum oven at 60 °C for 12 h, and then kept at 80 °C for another 12 h. After cooled and peeled off from the glass, the membrane was immersed in 1.0 M NaOH solution for 48 h and then washed with water until the rinse water was at neutral pH and dried at 60 °C. The membranes were designated as ImPEEK/TMPD-X, where X represented the weight percentage of the TMPD relative to ImPEEK (Fig. 1).

2.4. Characterizations

The crystalline structure of ImPEEK membrane and ImPEEK/TMPD membranes was confirmed by X-ray diffraction (XRD, Rigaku D/max 2500 v/pc). Field emission scanning electron microscope (FESEM, Nanosem 430) analysis was conducted to investigate the cross-section morphology of the membrane. TGA (NETZSCH-TG209 F3) of membranes were performed at a heating rate of 10 °C min⁻¹ within a temperature range of 40–800 °C in a nitrogen atmosphere. Differential scanning calorimetry (DSC, 204 F1 NETZSCH) was conducted under a nitrogen atmosphere to detect the glass transition temperature (*T*_g) of the membranes (heating rate: 10 °C min⁻¹, cooling rate: 15 °C min⁻¹). The sample was preheated from 20 °C to 150 °C, then cooled to 90 °C and reheated to 260 °C. Stress-strain curves of the membranes were obtained using an electronic stretching machine (Yangzhou Zhongke WDW-02) at room temperature with a strain rate of 10 mm min⁻¹. The dimension of the samples was approximately 10–30 mm. The thicknesses of the samples are listed in Table S1 (see the Supporting information).

2.5. Water uptake and area swelling

The samples were dried in a vacuum oven at 80 °C until both the measured weight (*W*_{dry}, g) and the surface area (*A*_{dry}, cm²) were constant. The dried membrane was then immersed in deionized water and kept in a tightly sealed container for more than 10 h to ensure the full hydration. After the water was immediately wiped off with filter paper, the membranes were measured again for weight (*W*_{wet}, g) and surface

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