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Quaternary phosphonium-functionalized poly(ether ether ketone) as highly conductive and alkali-stable hydroxide exchange membrane for fuel cells

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ABSTRACT

A series of quaternary phosphonium-functionalized poly(ether ether ketone)s (PEEK-QPOHs) have been synthesized by phosphorization reaction, and their membranes have been prepared by a solution casting method. Ion exchange capacity (IEC) of PEEK-QPOH membranes ranges from 0.89 to 1.19 mmol g⁻¹ with the degree of chloromethylation from 70% to 126%. Not only are PEEK-QPOH polymers soluble in typical high-boiling-point membrane-forming solvents, but also they are soluble in some low-boiling-point water-miscible solvents (low alcohols), implying their ability to serve as both membranes and ionomers. PEEK-QPOH membranes showed high hydroxide conductivity, e.g., a PEEK-QPOH 126% membrane (with IEC of 1.19 mmol g⁻¹) exhibited 61 and 89 mS cm⁻¹ at 20 °C and 60 °C, respectively. Based on the same polymer backbone of PEEK, quaternary phosphonium-functionalized PEEK membranes are more hydroxide-conductive and more alkali-stable than quaternary ammonium- and imidazolium-functionalized counterparts. All these properties indicate PEEK-QPOH is one of the most promising HEM materials for potential applications in alkaline membrane fuel cells.

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1. Introduction

Proton (H⁺) exchange membrane fuel cells (PEMFCs) are promising clean power sources for portable applications, because of their high power density, high energy efficiency, and low environmental impacts [1]. High cost and unsatisfied durability of their catalysts (typically, platinum) have, however, hampered PEMFCs' large-scale commercialization [2]. By switching the working ion from proton to hydroxide (OH⁻), hydroxide exchange membrane fuel cells (HEMFCs) have been shown to have the potential to fundamentally solve the cost and durability problems of PEMFCs [3,4]. In alkaline environments, non-precious metals can be used as active catalysts (e.g. silver and nickel), and they are also more durable than in acidic media [5–7].

Key to HEMFCs, hydroxide exchange membranes (HEMs) serve as both hydroxide conductors and fuel/oxidant separators

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simultaneously, drastically controlling HEMFCs' performance [8,9]. The hydroxide conductivity is particularly important for HEMs, as the ionic conductivity is intrinsically lower for HEMs than for PEMs. The specific solubility, i.e., in low-boiling-point water-miscible solvents, is also required for HEM polymers to serve as ionomers to build the efficient triple-phase-boundary in catalyst layers for high electrode-performance. Typically, HEM polymers are constructed by polymer matrix and a hydroxide-conducting functional group, both of which have been recognized to have fundamental impacts on the HEM properties [3,10–13].

Poly(ether ether ketone) (PEEK), as an important high-performance aromatic engineering polymer, has been successfully introduced as polymer matrix for HEM application [14–19]. Structurally, two strongly electron-donating ether bonds are expected to endow the benzene rings of PEEK with fairly high electron-density, leading to high basicity of the linked hydroxide-conducting functional group. This is evidenced by the previous observation that PEEK-based quaternary ammonium-functionalized (PEEK-QAOH) HEM showed higher hydroxide conductivity than less-electron-density polymers-based ones reported (with very close ion exchange capacity and the same preparation method)[19]. Similarly, the PEEK-based imidazolium-functionalized HEM has also been

found to exhibit higher hydroxide conductivity than less-electron-density polymer-based imidazolium-functionalized HEMs in our recent work [14,20], e.g., with the same IEC ($\sim 2.0 \text{ mmol g}^{-1}$), PEEK-ImOH has a 10 mS cm^{-1} higher hydroxide conductivity than polysulfone (PSf)-based imidazolium-functionalized HEM ($52 \text{ vs. } 42 \text{ mS cm}^{-1}$). Besides, PEEK-based HEMs have also shown high mechanical strength and excellent flexibility, e.g., a PEEK-ImOH HEM showed as high as 78 MPa of tensile strength and corresponding 168% of tensile strain. High hydroxide conductivity, high mechanical strength, and many other attractive properties make PEEK one of the most promising HEM matrices.

On the other hand, a unique tris(2,4,6-trimethoxyphenyl)-constructed quaternary phosphonium functional group (QPOH) has been successfully designed for both ionomer and membrane applications. QPOH-functionalized polymers have shown high hydroxide conductivity, excellent chemical stability, and desired specific solubility in low-boiling-point water-miscible solvents (lower alcohols). Such a desired solubility in lower alcohols enables QPOH-functionalized polymers to serve as ionomers in electrodes for high-performance HEMFCs, e.g., a QPOH-functionalized PSf ionomer drastically increased the peak power density (3.5 times) and at the same time reduced the internal resistance (50%) in an HEMFC [3]. Equally importantly, the QPOH functional group also exhibited the highest IEC-specific hydroxide conductivity in HEM among all available HEM functional groups, e.g., with the same PSf as polymer matrix and the same homogeneous membrane structure, the IEC-specific hydroxide conductivity of QPOH-functionalized HEM (PSf-QPOH152, $39 \text{ mS g cm}^{-1} \text{ mmol}^{-1}$) is about twice those of QAOH-functionalized HEM (PSf-QAOH, $19 \text{ mS g cm}^{-1} \text{ mmol}^{-1}$ [5]) and ImOH-functionalized HEM (PEEK-ImOH, $20 \text{ mS g cm}^{-1} \text{ mmol}^{-1}$ [20]), implying much higher basicity. The QPOH-functionalized polymer ionomer and HEM incorporated HEMFCs delivered very high cell performances, e.g., a peak power density of 258 mW cm^2 and an internal resistance of $0.21 \Omega \text{ cm}^2$ at 70°C cell temperature with a $50 \mu\text{m}$ PSf-QPOH152 membrane [21]. In addition, QPOH functional groups have also shown capable of performing both physical crosslinking [22] and chemical crosslinking [23] to improve dimensional stability and/or solvent-resistance for their HEMs.

In this work, we combine the PEEK polymer matrix and the unique QPOH functional group to prepare a highly-conductive and alkali-stable PEEK-based QPOH-functionalized HEM (PEEK-QPOHs). Their properties of water uptake, swelling ratio, hydroxide conductivity, thermal stability, and alkali stability are comprehensively investigated, and the impacts of functional groups on the HEM properties are also discussed.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (VESTAKEEP[®] 4000G) powder was generously provided by the Evonik Degussa (China) Co. Ltd. Chloromethyl octylether (CMOE) was synthesized by ourselves according to the Ref. [24]. Sulfuric acid (92.8%), potassium hydroxide, methanol, ethanol, *n*-propanol, *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP) and tris(2,4,6-trimethoxyphenyl) phosphine (TTMPP) were obtained commercially and used as received without further purification. All the chemicals used are analytical grade. In order to reduce the possible effect of CO_2 dissolved in deionized water on the membrane characterization, the deionized water was boiled to completely degassed prior to use.

2.2. Synthesis of chloromethylated PEEK (CMPEEK)

CMPEEKs with high degrees of chloromethylation (DCs) were synthesized by chloromethylation of PEEK using CMOE as chloromethylating agent and concentrated sulfuric acid as solvent/catalyst as our previous work [19]. Specifically, 2 g PEEK was dissolved into 120 mL 92.8% concentrated sulfuric acid at 0°C with stirring, and then the temperature was lowered to -10°C , followed by addition of 40 mL freshly synthesized CMOE. Subsequently, the reaction was kept for 60, 80, 100, 120, and 150 min, respectively. The polymer product, CMPEEK, was separated from the reaction mixture by precipitation in ice water, followed by thorough washing with deionized water, and then air-drying at room temperature. In order to completely remove the impurities, the separated CMPEEK was further purified by dissolution in NMP, precipitation in ethanol, then washing with ethanol completely, and finally air-drying at room temperature.

2.3. Synthesis and preparation of quaternary phosphonium-functionalized PEEK (PEEK-QPOH) membranes

Initially, quaternary phosphonium chloride-functionalized PEEK (PEEK-QPCL) was synthesized by the Menshutkin reaction between CMPEEK and TTMPP. Specifically, 0.15 g CMPEEK was completely dissolved in 3 mL NMP at room temperature, and then a strictly stoichiometric amount of TTMPP was added into the solution. Note that the high purity of TTMPP is critical to the final membrane properties and its purity must be checked carefully before the use of the TTMPP chemical received. The temperature was raised to 80°C and kept for 12 h. Subsequently, the reaction-completed solution was poured onto a glass plate to cast the membrane. After curing and drying at 80°C for 48 h, a membrane was formed and peeled off from the glass plate. Finally, the quaternary phosphonium hydroxide-functionalized PEEK (PEEK-QPOH) membrane was obtained by ion-exchanging the PEEK-QPCL membrane 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 additional 48 h to completely remove the residual KOH. The chemical structures and synthetic process are shown in Fig. 1.

2.4. ^1H NMR

^1H NMR spectroscopy was used to confirm the synthesis of both CMPEEK and PEEK-QPOH. ^1H NMR spectra of TTMPP, CMPEEK, and PEEK-QPOH were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz. $\sim 1 \text{ wt } \%$ TTMPP, CMPEEK, and PEEK-QPOH solutions were prepared by dissolving them into $\text{DMSO-}d_6$ solvent, respectively. Tetramethylsilane (TMS) was used as the internal standard in all cases.

2.5. Ion exchange capacity (IEC)

The IEC of the PEEK-QPOH membrane was measured by the back titration method. Initially, 0.2 g PEEK-QPOH membrane sample was equilibrated with 50 mL 0.01 M HCl standard solution for 24 h, followed by back titration of 0.01 M NaOH standard solution with phenolphthalein as the indicator. The 50 mL 0.01 M HCl standard solution was used as the blank sample for the control experiment. The measured IEC (IEC_m) of the PEEK-QPOH membrane was calculated by the following equation:

$$\text{IEC}_m = \frac{(V_b - V_s) \times C_{\text{HCl}}}{W_{\text{dry}}} \times 1000$$

where V_b and V_s are the consumed volumes (L) of the NaOH solution for the blank sample and the PEEK-QPOH membrane

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