



Imidazolium-functionalized poly(ether ether ketone) as membrane and electrode ionomer for low-temperature alkaline membrane direct methanol fuel cell

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HIGHLIGHTS

- Imidazolium-functionalized poly(ether ether ketone) was successfully synthesized.
- PEEK-ImOH HEMs exhibit improved dimensional stability.
- PEEK-ImOH HEMs exhibit high hydroxide conductivity (e.g., 52 mS cm⁻¹ at 20 °C).
- PEEK-ImOH HEMs exhibit good mechanical property (e.g., 78 MPa of tensile strength).
- The methanol/O₂ fuel cell employing PEEK-ImOH shows high performance.

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ABSTRACT

A series of imidazolium-functionalized poly(ether ether ketone)s (PEEK-ImOHs) were successfully synthesized by a two-step chloromethylation–Menshutkin reaction followed by hydroxide exchange. PEEK-ImOH membranes with ion exchange capacity (IEC) ranging from 1.56 to 2.24 mmol g⁻¹ were prepared by solution casting. PEEK-ImOHs show selective solubility in aqueous solutions of acetone and tetrahydrofuran, but are insoluble in lower alcohols. PEEK-ImOH membranes with IEC of 2.03 mmol g⁻¹ have high hydroxide conductivity (52 mS cm⁻¹ at 20 °C), acceptable water swelling ratio (51% at 60 °C), and great tensile strength (78 MPa), and surprising flexibility (elongation-to-break of 168%), and high thermal stability (Decomposition temperature: 193 °C). In addition, PEEK-ImOH membranes show low methanol permeability (1.3–6.9 × 10⁻⁷ cm² s⁻¹). PEEK-ImOH membrane was tested in methanol/O₂ fuel cell as both the HEM and the ionomer impregnated into the catalyst layer; the open circuit voltage is 0.84 V and the peak power density is 31 mW cm⁻².

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1. Introduction

Low-temperature direct methanol fuel cells (DMFCs) are proposed as alternative power sources for portable applications [1]. Methanol is easily handled, has high energy density, and is widely

availability. Most DMFCs have been based on proton exchange membranes (PEMs) [2–4]. However, PEM based DMFCs show sluggish electrode kinetics, substantial alcohol crossover and require high weight loading of precious metal catalysts which have hampered commercialization [5–7]. By switching the electrolyte from the acid to base, the electrode kinetics of low-temperature DMFC can be significantly enhanced [8–10]. Further, low-cost non-precious metals can be used as active catalysts (e.g. silver, nickel, and tin) [11–14]; these catalysts are also more durable [15–17]. The methanol crossover can be substantially reduced because hydroxide (OH⁻) conduction opposes the methanol diffusion [8].

Hydroxide exchange membranes (HEMs) are the key components of low-temperature alkaline membrane DMFC (AMDMFC). HEMs

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serve as fuel/oxidant separators and hydroxide conductors [18,19]. High hydroxide conductivity, alcohol tolerance, and dimensional stability are critically required for high-performance HEMs in low-temperature AMDAMCs. Selective solubility is also required for HEM materials; they should be insoluble in alcohols but they should be soluble in low-boiling-point solvents that allow them to be cast as membranes and incorporated into catalyst layers, building efficient triple-phase-boundary necessary for high electrode performance.

Hydroxide conducting functional groups are responsible for the fundamental properties of HEMs, including solubility, conductivity, and stability [15,20]. Novel functional groups, e.g., quaternary phosphonium [15,21–23], guanidinium [24–27], and imidazolium [28–43], have been introduced to HEM materials to improve the solubility, conductivity, and/or stability. All three novel functional groups form polymer that are soluble in low-boiling-point solvents, facilitating processing to make membranes or incorporation into the catalyst layer. The imidazolium based HEM materials are unique in that they are insoluble in alcohols and their aqueous solutions. This desirable selective solubility makes the imidazolium functional group a great choice of developing high-performance HEMs for low-temperature AMDMFC.

The polymer matrix provide many other important HEM properties, including but not limited to dimensional stability, thermal stability, and mechanical property. Initially, aliphatic main-chain polymers (e.g., polyvinyl alcohol [29], poly(styrene–acrylonitrile–ethylene) [30], poly(ethylene methyl methacrylate) [31,34], and polystyrene [32,37]) were used to prepare imidazolium-functionalized HEMs. Subsequently aromatic main-chain polymers (e.g., polysulfone [28,33], bromomethylated poly(2,6-dimethyl-1,4-phenyleneoxide) [35], polyfluorene [39], and fluorinated poly(aryl ether oxadiazole)s [36]) were used. Among all the imidazolium-functionalized HEMs, imidazolium-functionalized polysulfone membranes show the highest hydroxide conductivity (53 mS cm^{-1} at 20°C) [28], arising from its high ion exchange capacity (2.19 mmol g^{-1}). However, its dimensional stability and mechanical strength need improvement especially at elevated temperatures.

Enhancing the van der Waals interactions among polymer chains could improve dimensional stability [23]. Poly(ether ether ketone) (PEEK) has higher van der Waals interactions among polymer chains than PSF does. PEEK should be a good matrix to prepare an imidazolium-functionalized membrane with high conductivity, excellent alcohol tolerance, and good swelling resistance simultaneously. In this work, a series of imidazolium-functionalized PEEKs (PEEK-ImOHs) were synthesized through the simple and efficient Menshutkin reaction. Their properties of water uptake, dimensional stability, hydroxide conductivity, thermal stability, mechanical property, and methanol permeability were comprehensively investigated. Methanol/ O_2 fuel cells employing imidazolium-functionalized polymer as both the HEM and the electrode ionomer were tested.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (VESTAKEEP® 4000G) powder was provided by Evonik Degussa (China) Co. Ltd. Chloromethyl octylether (CMOE) was synthesized according to the method published in the Ref. [44]. Potassium hydroxide, H_2SO_4 (92.8%), methanol, ethanol, acetone, tetrahydrofuran (THF), and 1-methylimidazole (1-MIM) were obtained commercially and used as received without further purification. All the chemicals used were analytical purity grade. In order to reduce the effect of CO_2 on the membrane characterization, the deionized water was boiled to completely remove CO_2 prior to use.

2.2. Preparation of imidazolium hydroxide functionalized-PEEK (PEEK-ImOH) membranes

Imidazolium chloride-functionalized PEEK (PEEK-ImCl) was synthesized by the Menshutkin reaction between chloromethylated PEEK (CMPEEK) and 1-methylimidazole. CMPEEK was synthesized by the chloromethylation of PEEK using CMOE as chloromethylating agent and concentrated sulfuric acid as solvent, as described in our previous work [45]. Then 0.25 g CMPEEK was completely dissolved in 3 ml 1-methylimidazole at room temperature, followed by casting the solution onto a glass plate. During curing and drying of the cast film at 80°C for 48 h, the CMPEEK reacted with 1-methylimidazole to form the imidazolium chloride-functionalized PEEK (PEEK-ImCl). The membrane was peeled off the glass plate when all the unreacted 1-methylimidazole solvent was evaporated. The PEEK-ImCl membrane was ion exchanged with 1 M KOH solution at room temperature for 48 h producing an imidazolium hydroxide-functionalized PEEK (PEEK-ImOH) membrane. The hydroxide exchanged membrane was immersed in deionized water in a sealed container for additional 48 h to completely remove the residual KOH. The synthetic and ion-exchanging processes are summarized in Fig. 1.

2.3. ^1H NMR

^1H NMR spectroscopy confirmed the synthesis of both CMPEEK and PEEK-ImCl; it was also used to determine the degree of chloromethylation (DC) of CMPEEK precursor. ^1H NMR spectra of 1-MIM, CMPEEK, and PEEK-ImCl were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz. Circa 1 wt. % solutions of 1-MIM, CMPEEK, or PEEK-ImCl were prepared by dissolving them into $\text{DMSO-}d_6$. Tetramethylsilane (TMS) was used as an internal standard in all cases. The degree of chloromethylation (DC) of CMPEEKs was calculated from the NMR peak areas: $\text{DC} = 2A(H_d)/A(H_c)$, where $A(H_d)$ and $A(H_c)$ are the integral area of the H_d peak and H_c peak in Fig. 2, respectively, as defined in our previous work [45].

2.4. Ion exchange capacity (IEC)

The IEC of the PEEK-ImOH membrane was measured by back titration. 0.2 g PEEK-ImOH 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 measured IEC (IEC_m) of the PEEK-ImOH membrane was calculated by the following equation:

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

where V_b and V_s are the consumed volumes (L) of the NaOH solution for the blank sample and the PEEK-ImOH membrane sample, respectively, C_{HCl} is the concentration (M) of HCl solution, and W_{dry} is the mass (g) of dry membrane sample.

2.5. Water uptake and swelling ratio

After ion exchange the PEEK-ImOH membrane was immersed into deionized water for more than 10 h. The weight and dimension (length and width) of the wet membrane were measured. Then the membrane was vacuum-dried at 50°C for 12 h, and the weight and dimension of dry membrane were measured. The water uptake and swelling ratio were calculated by the two following equations, respectively:

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