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Protic ionic liquid/functionalized graphene oxide hybrid membranes for high temperature proton exchange membrane fuel cell applications



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ABSTRACT

The 1-(3-aminopropyl)-3-methylimidazolium bromide ([APMIm][Br]) functionalized graphene oxide ([APMIm][Br]-GO) and 1-methylimidazolium trifluoromethanesulfonate ([MIm][TfO]) are prepared and used as fillers and proton carrier in the preparation of high temperature hybrid proton exchange membranes (PEMs), respectively. The PEMs are obtained via photo-initiated polymerization of a mixture containing polymerizable oil (styrene/acrylonitrile and divinylbenzene), protic ionic liquid (PIL, [MIm][TfO]), and different content of [APMIm][Br]-GO. The resultant membranes show good thermal stability and excellent mechanical properties. Incorporation of proper amount of [APMIm][Br]-GO significantly increases the proton conductivity of the hybrid membranes, and the membranes with 1.0 wt% [APMIm][Br]-GO shows the highest conductivity (up to $1.48 \times 10^{-2} \text{ S cm}^{-1}$ at 160 °C). Compared with the plain membrane without [APMIm][Br]-GO, the hybrid membranes with [APMIm][Br]-GO show much better PIL retention ability. These properties make this type of PIL-based hybrid membranes suitable for the application of high-temperature proton exchange membrane fuel cells (PEMFCs).

1. Introduction

Proton exchange membranes (PEMs) operating at high temperatures above 100 °C have been received much attention because of their practical application of proton exchange membrane fuel cells (PEMFCs) in vehicular transportation and other portable devices [1,2]. As one of the core components of PEMFCs, the PEMs play a key role in transporting protons and separating the oxidant and fuel chambers [3]. The PEMFCs which operating at elevated temperatures above 100 °C under anhydrous conditions owns several merits include simplifying heat and water management, increasing the fuel cell efficiency and improving the catalyst tolerance to CO. However, the most commonly used humidified perfluorosulfonic acid membranes (Nafion) are not appropriate for high temperature operation above 100 °C because of the rapid evaporation of water from the membrane, which results in a rapid loss of membrane proton conductivity [4,5]. Therefore, development of PEMs with high proton conductivity at elevated temperature above 100 °C is in great demand in the development and application of PEMFCs.

In the last several decades, much work has been done to develop alternative membranes in order to overcome the drawbacks of the current widely used Nafion membranes [6,7]. Fabrication of organic-inorganic hybrid membrane by incorporating inorganic nanoparticles such as SiO₂ and TiO₂ into Nafion membranes is a common approach to improve water retention at high temperatures [8,9]. Compare with plain Nafion membranes, the hybrid membranes showed much better water retention ability at elevated temperature [10–12]. However, high pressure is required to keep high humidity for the hybrid membranes maintain proton conductivity at elevated temperature [13].

Recent years, the synthesis of sulfonated polymers with the sulfonic acid groups has become an important approach to replace Nafion membranes in the application of high temperature PEMFCs [13–16]. The proton conductivity of PEMs based on sulfonated polymers depends very heavily on the sulfonation degree of polymers, this behavior is due to the higher degree of sulfonation result in the bigger number of ionic species which favor the transfer of proton in PEMs [17,18]. However, the high sulfonation degree leads to the sulfonated polymers highly hydrophilic, which causing big swelling, poor mechanical properties

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and high fuel permeability [17]. What is more, PEMs based on sulfonated polymers can hardly maintain high conductivity above 100 °C [19].

Using nonaqueous proton carriers instead of water is another simple and effective method to obtain PEMs with high proton conductivity at high temperature [20–29]. In recent years, protic ionic liquids (PILs), which consisting of combinations of Brønsted acids and bases, have been attracted much attention as proton carriers in the application of high temperature PEMs [30]. Compared with the humidified membranes based on sulfonated polymers and perfluorosulfonic acid polymer, PIL-based PEMs could be operated above 100 °C under anhydrous conditions without having conductivity decreasing due to its negligible volatility and excellent thermal stability [31]. However, the PIL that dispersed in a polymer matrix is usually water-soluble, and it could be taken away from membrane by the water generated at the cathode of fuel cells [32].

The polymerization of ionic liquids is an effective way in holding the ionic liquid in the membranes. However, the conductivity of polymeric ionic liquids is much lower than that of ionic liquid due to the reduced number of mobile ions. The conductivity of polymeric ionic liquids depend strongly on the chemical nature of monomeric ionic liquids. Recently, high conductivity values above 1.1 S cm^{-1} at 200 °C have been reported for pure poly[1-(3H-imidazolium)ethylene] bis(trifluoromethanesulfonyl)-imide by Pina et al., and the results suggested a feasible approach for the synthesis and practical applications of polymeric ionic liquids-based PEMs for high temperature PEMFCs [33]. More recently, a series of polymeric ionic liquids based PEMs were prepared by Pina's group [34–36], the porous polybenzimidazole (PBI) skeleton provides the mechanical reinforcement, and the polyionic liquid in porous PBI exhibits proton conductivity. These work presented a feasible strategy to obtain PEMs with high conductivity, enhanced physicochemical and mechanical properties by constructing hierarchical polymeric ionic liquids channels into a PBI matrix.

Incorporation of inorganic or organic nanoparticles into PIL-based membranes is another simple and effective way to hold the ionic liquid in the membranes [32,37–40]. However, the additional quantity of inorganic nanoparticles was limited since their strong tendency to aggregate in the polymeric matrix. Therefore, effective incorporation and homogeneous dispersion of inorganic nanoparticles within the polymer matrix are the key challenges to be addressed [38,39]. In the recent years, graphene oxide (GO) has received much attention due to its high specific surface area and can be easily chemical modification [40]. Recently, polymer/GO composites have been used in supercapacitors [41], electrode [42] and electrolyte of dye-sensitized solar cells [43]. In our previous work, zwitterion-coated graphene oxide (ZC-GO) containing ammonium and sulfonic acid groups was synthesized and incorporated into PBI-based PEMs, and the homogeneous dispersion of the ZC-GO could increase the proton conductivity of PBI-based PEMs under RH 100% and low temperature (below 80 °C) [44]. Though GO have been used as inorganic filler for the preparation of PEMs which operated under high humidity and low temperature, the potential advantages for improving the performance of high temperature PEM (above 100 °C) by using GO has not been fully realized.

In the present work, we report the synthesis and characterization of poly(styrene-co-acrylonitrile)/PIL/functionalized GO hybrid PEMs for anhydrous proton exchange membrane application. Protic ionic liquid, 1-methylimidazolium trifluoromethanesulfonate ([MIm][TfO]), was synthesized and used as the proton carrier. 1-(3-Aminopropyl)-3-methylimidazolium bromide ([APMIm][Br]) functionalized GO ([APMIm][Br]-GO) were synthesized and used as organic additives for the preparation of PIL-based hybrid PEMs. The effects of [APMIm][Br]-GO content on the properties of hybrid membrane, such as thermal stability, mechanical properties, PIL retention stability and proton conductivity were systematically studied.

2. Experimental

2.1. Materials

Trifluoromethanesulfonic acid, 1-methylimidazole, styrene, divinylbenzene (DVB), acrylonitrile, ethyl acetate, benzoin ethyl ether, ether, ethanol, 3-bromopropylamine hydrobromid were used as purchased.

2.2. Synthesis of 1-(3-aminopropyl)-3-methylimidazoliumbromide ([APMIm][Br])

In a typical synthetic procedure, a mixture of 1-methylimidazole (4.11 g, 50 mmol) and 3-bromopropylamine hydrobromide (10.95 g, 50 mmol) in 50 mL ethanol were heated at 60 °C for 24 h under nitrogen atmosphere to synthesize [APMIm][Br] [43]. After cooling down, the ethanol was evaporated and the viscous liquid was washed with ether for three times and dried under vacuum at 80 °C for 24 h. $^1\text{H NMR}$ (400 MHz, DMSO): 9.23 (s, 1H), 7.97 (s, 2H), 7.83–7.84 (dd, 1H), 7.76–7.77 (dd, 1H), 4.30–4.35 (t, 2H), 3.88 (s, 3H), 2.80–2.85 (m, 2H), and 2.08–2.18 (m, 2H).

2.3. Synthesis of 1-methylimidazolium trifluoromethanesulfonate ([MIm][TfO])

Protic ionic liquid, [MIm][TfO], was synthesized as follows: 1-methylimidazole (4.10 g, 50 mmol) was dissolved in ethyl acetate in an ice bath, and then trifluoromethanesulfonic acid (7.50 g, 50 mmol) was added drop wisely with vigorous stirring. The reaction mixture was warmed to room temperature slowly and stirred continuously for another two days, and white solid was observed. The ethyl acetate was evaporated and the white solid was washed with ethyl acetate and ether twice, respectively, and then dried in dynamic vacuum at 80 °C for 24 h before use. $^1\text{H NMR}$ (400 MHz, DMSO): 9.03 (s, 1H), 7.68 (dd, 1H), 7.66 (dd, 1H), 3.86 (s, 3H).

2.4. Preparation of [APMIm][Br]functionalized graphene oxide([APMIm][Br]-GO)

Graphene oxide (GO) was prepared following the Hummers method as our previous work [43]. [APMIm][Br]-GO prepared as follows [45]: [APMIm][Br] (100 mg) was added into 100 mL of GO/water (0.5 mg/mL) solution, and 100 mg KOH was added into the mixture, then the mixture was ultrasonicated for 30 min to get a homogeneous solution. [APMIm][Br]-GO was synthesized by an epoxide ring-opening reaction between GO and [APMIm][Br]. Here, the KOH was used as catalyst for the ring-opening reaction of epoxides. The resultant homogeneous solution was stirred at 80 °C for 24 h. The obtained solid product [APMIm][Br]-GO was centrifuged and washed with water to remove the unreacted [APMIm][Br].

2.5. Preparation of PIL-based hybrid PEMs

A typical procedure of the PIL-based hybrid membranes was as follows: a mixture of styrene/acrylonitrile (1:3 wt ratio, 60 wt%), [MIm][TfO] (40 wt%), divinylbenzene (2 wt% to the formulation based on the weight of vinyl monomer), 0.5 wt% of benzoin isobutyl ether (photo-initiator), and with or without [APMIm][Br]-GO was stirred to obtain a homogeneous solution. Then the mixture solution was cast onto a glass mold and photo-cross-linked by irradiation with UV light of in a glass mold for 30 min.

2.6. Characterization

$^1\text{H NMR}$ spectra were performed using a Varian 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra of the [APMIm][Br]-

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