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Polymer-inorganic hybrid proton conductive membranes: Effect of the interfacial transfer pathways

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ABSTRACT

For hybrid membrane, the polymer-inorganic interface along filler surface can be facilely created to be distinctive and controllable pathway for mass transfer. Herein, three kinds of fillers are used as inorganic additives including zero-dimensional silica (0-D, SiO_2), one-dimensional halloysite nanotube (1-D, HNT), and two-dimensional graphene oxide (2-D, GO), which are functionalized by sulfonated polymer layer to ensure close surface component. Then the fillers are incorporated into two types of polymer matrixes (phase-separated sulfonated poly(ether ether ketone) and non-phase-separated chitosan) to prepare three series of hybrid membranes with single-kind filler, double-kinds fillers, or triple-kinds fillers, respectively. The microstructures, physicochemical properties, and proton conduction properties (under hydrated and anhydrous conditions) of the membranes are extensively investigated. It is found that (i) for the single-kind filler-filled membranes, 2-D filler has the strongest promotion ability for proton conductivity of membrane due to the constructed wide and long-range pathways for proton transfer; (ii) while for the hybrid membranes with double-kinds fillers, instead of synergistic promotion effect, the fillers cause more tortuous transfer pathways within membranes and then decrease proton conductivity; (iii) the hybrid membranes with triple-kinds fillers exhibit similar behavior but a little higher conductivity than the membranes with double-kinds fillers.

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1. Introduction

Nowadays, organic-inorganic hybrids as advanced functional materials are growing rapidly and have a land of promising applications in many energy- and environment-relevant fields, including optics, electronics, ionics, medicine, functional smart coatings, fuel and solar cells, catalysis, sensors, *etc* [1–4]. Promoted by the synergistic effect, hybrids could possess the properties and performance well beyond those of organic and inorganic materials, especially resulting from interfacial domains [5–7]. The interfacial morphology could on one hand affect the thermal/mechanical and free volume properties of hybrids *via* manifold interactions, and on the other hand could regulate the separation performance by constructing controllable transfer pathways using the functional groups from inorganic filler and/or polymer [1,8–13].

As the core component of hydrogen fuel cell, proton exchange membrane (PEM) requires high proton conductivity and excellent thermal/mechanical stability to achieve high and long-term fuel cell performances [14–17]. Although various polymers including phase-separated ones (perfluorinated sulfonic acid polymer, sulfonated aromatic polymer, *etc.*) and non-phase-separated ones (chitosan, polyvinyl alcohol, *etc.*) have been developed, the poor proton conduction ability and/or weak structural and thermal stabilities under elevated temperature and low humidity (the desirable operation conditions) impede their practical application [18–22]. Hybridizing inorganic fillers with conducting groups on surface have been demonstrated to be one promising approach to overcome these issues. Helped by the synergistic effect of organic and inorganic components, the relevant performances of hybrid membrane could be efficiently improved by regulating polymer chain packing and creating conduction pathway along filler surface [23–27]. For instance, acid functionalized fillers have been examined to obviously reinforce the conductivity and properties (mechanical/thermal stability and swelling-resistance ability) of Nafion-based membrane (the state-of-the-art PEM). Joseph et al. prepared Nafion/phosphonic acid-grafted mesostructured silica (0-D) hybrid membrane and reported a 1.9 times increase of proton conductivity with 10 wt.% fillers [28]. Similarly, 1-D functionalized carbon nanotubes (PCNTs) bearing $-PO_3H_2$ groups were utilized by He et al. to attain a 3.3 times increase of conductivity with 5 wt.%

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PCNTs [19]. 2-D laponite clay containing sulfonic acid groups (Lp-g) was also utilized successfully by Bébin et al. to enhance the proton conductivity of Nafion by 5.4 times with 10 wt.% Lp-g, which also improved the water-retention ability of hybrid membrane by 3.3 times [29].

It is believed that the overall performances (especially for proton conduction ability) of hybrid membrane are strongly related to the interfacial morphology, which is determined by the structure and surface component of inorganic filler. Accompanied by the variation of filler structure, the generated interfacial pathways can be crooked and short-range for 0-D or 3-D filler, long-range for 1-D filler due to high aspect ratio, or wide and long-range for 2-D filler due to high aspect ratio and specific surface area [6,30]. Recently, one study has been conducted to investigate the influence of interfacial morphology on proton conduction of PEM. For comparison purpose, three kinds of IL-functionalized carbon materials including 0-D carbon black, 1-D carbon nanotubes and 2-D reduced graphene oxide were utilized [31]. Interestingly, the authors noted that the ionic transfer ability of hybrids varied with the structures of fillers (in the order of reduced graphene oxide > carbon nanotube > carbon black). Meanwhile, another study by Wu et al. prepared SiO_2-GO composites, and then incorporated them into polysulfone membrane to enhance the ultrafiltration performance [32]. It was found that the SiO_2-GO-filled hybrid achieved superior performance over SiO_2-filled hybrid and GO-filled hybrid in terms of water permeation rate and protein rejection. The elevated separation performance should be resulted from the synergistic promotion effect of hydrophilic nature of SiO_2 and high specific surface area of GO. Based on these points, the exploration for synergistic effect of multi-kinds inorganic fillers on interfacial morphology and subsequent membrane performance is of great significance not only for the design of high-performance PEM but also for the further advancement in related fields. To the best of our knowledge, however, systematic investigation of synergistic effect of multi-kinds inorganic fillers is rare not only in PEM but also in separation membrane.

Herein, we prepared a series of comparable hybrid membranes by incorporating single-kind filler, double-kinds fillers, or triple-kinds fillers (0-D SiO_2, 1-D HNT, and 2-D GO) into polymer membrane. Prior to incorporation, these fillers were modified with sulfonated polymer layer, ensuring close surface component for better comparison. To test and verify the universality, two kinds of polymers, sulfonated poly(ether ether ketone) (SPEEK, phase-separated structure, acidic polymer) and chitosan (CS, non-phase-separated structure, basic polymer) were chosen as membrane matrixes. The microstructures and physicochemical characteristics of hybrid membranes were investigated in detail. The proton conductivities (under hydrated and anhydrous conditions and various temperatures) and transfer mechanism were systematically evaluated to explore the functions of the interfacial morphology on membrane performance.

2. Experimental section

2.1. Materials and chemicals

Natural graphite powder (45 μm, Sigma-Aldrich), poly (ether ether ketone) (Victrex®PEEK, grade 381G), and CS (deacetylation degree of 91%, Golden-Shell Biochemical Co.) were used as received. Halloysite nanotube (HNT) was refined from clay mineral (>80%, 40–100 nm in diameter, 0.4–1.0 μm in length, Henan, China). SiO_2 and GO were synthesized according to literatures through stöber sol-gel method and improved Hummer method, respectively [33,34]. 3-(Methacryloxy) propyltrimethoxysilan (MPS) (>97%) and styrene (St) were provided by Aldrich and distilled prior to use. Divinylbenzene (DVB) (80% divinylbenzene isomers, Shengli Chemical Technical Faculty, Shandong, China), 2,2-azobisisobutyronitrile (AIBN) (Kewei Chemistry Co.), acetonitrile (AR, Kewei Chemistry Co.), N,N-dimethylformamide (DMF) (>99.5%, Kewei Chemistry Co.), sulfuric acid (98%, Luoyang haohua Co.) and acetic acid (Kewei Chemistry Co.) were used as supplied. De-ionized water was used throughout the experiment. SPEEK was obtained through post-sulfonation of PEEK and the sulfonation degree was determined by titration method to be 64.9%.

2.2. Synthesis of sulfonic acid functionalized fillers ($SSiO_2$, SHNT, and SGO)

The sulfonation of fillers was conducted through distillation-precipitation polymerization method. Taking the sulfonation of GO as the example: GO (1.0 g) was dispersed into the mixture of ethanol (160 mL), water (10 mL), and ammonium hydroxide aqueous solution (15 mL) with vigorous stirring at 25 °C for 24 h. Then, MPS (1.0 mL) was added into the resultant mixture. After being stirred for another 24 h, the MPS-modified GO was purified by centrifugation and followed by drying in a vacuum oven. MPS-GO (0.30 g), St (0.50 mL), crosslinker DVB (0.50 mL), and AIBN (0.02 g) were dissolved by ultrasonic treatment in acetonitrile (80 mL) in a dried flask. The mixture was heated and kept boiling state until half acetonitrile was distilled out. Then the modified GO was purified and dried, followed by being sulfonated in sulfuric acid (98%) at 40 °C for 4 h to obtain SGO. $SSiO_2$ and SHNT were prepared through the same process using SiO_2 and HNT as cores, respectively. For simplification, $SSiO_2$, SHNT, and SGO were designated as A, B and C, respectively.

2.3. Preparation of membranes

2.3.1. SPEEK control and hybrid membranes

SPEEK control membrane was prepared through solution casting method: SPEEK (0.7 g) was dissolved into DMF (8.0 g) at 25 °C. After being stirred vigorously for 12 h, the mixture was cast onto a glass plate and dried first at 60 °C for 12 h, then at 80 °C for 12 h. The resultant membrane was designated as SP.

SPEEK hybrid membranes: certain amount of fillers were dispersed into DMF (8.0 g) solution under ultrasonic treatment for 8 h at 25 °C. Afterwards, SPEEK (0.7 g) was dissolved in the above solution and stirred vigorously for another 12 h at 25 °C. The resultant mixture was cast onto a glass plate and dried at 60 °C for 12 h followed by drying at 80 °C for another 12 h. The prepared membranes were designated as SP/A, SP/B, SP/C, SP/AB, SP/AC, SP/BC, and SP/ABC, respectively. The loading amount of each kind of filler in hybrid membrane was 5 wt.% of that of SPEEK, and the detailed filler contents and corresponding membrane thicknesses were shown in Table 1. In addition, another series of multi-kinds filler-filled membranes were also prepared in order to investigate

Table 1
The filler contents and membrane thicknesses of SPEEK control membrane and hybrid membranes.

SPEEK-based membrane	Filling level	Thickness/μm
SP	–	62 ± 2
SP/A	A (5%)	61 ± 2
SP/B	B (5%)	65 ± 2
SP/C	C (5%)	67 ± 2
SP/AB	A (5%) + B (5%)	70 ± 2
SP/AC	A (5%) + C (5%)	69 ± 2
SP/BC	B (5%) + C (5%)	71 ± 2
SP/ABC	A (5%) + B (5%) + C (5%)	73 ± 2
SP/AB′	A (2.5%) + B (2.5%)	62 ± 2
SP/AC′	A (2.5%) + C (2.5%)	66 ± 2
SP/BC′	B (2.5%) + C (2.5%)	67 ± 2
SP/ABC′	A (1.67%) + B (1.67%) + C (1.67%)	65 ± 2

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