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Constructing facile proton-conduction pathway within sulfonated poly(ether ether ketone) membrane by incorporating poly(phosphonic acid)/silica nanotubes

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HIGHLIGHTS

- Poly(phosphonic acid)/silica nanotubes with diverse aspect ratios were prepared.
- The nanotubes were incorporated into SPEEK to prepare composite membrane.
- Effect of aspect ratios of the nanotubes on proton conductivity was studied.
- The composite membranes showed enhanced proton conductivity and stability.

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ABSTRACT

The objective of this study is to exploit the one-dimension structure and good proton conduction of phosphorylated silica nanotubes for high proton conductivity of proton exchange membrane (PEM). Three types of poly(vinylphosphonic acid-*co*-divinylbenzene)/silica nanotubes with different aspect ratios are synthesized and incorporated into the sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare composite membranes. The poly(vinylphosphonic acid) segments in the nanotubes could construct facile proton-conduction pathway along this one-dimensional nanostructure. The nanotubes with high aspect ratio exhibit more pronounced effect in elevating the proton conductivity of membranes, revealing the importance of continuity of conduction pathway on proton transport. The membrane incorporated with the nanotubes of the largest aspect ratio of 45.9 exhibits the highest proton conductivity of 0.1032 S cm^{-1} at 30 °C, 100% RH, which was 84% higher than that of SPEEK control membrane. Moreover, the nanotubes can reduce the methanol permeability, and improve mechanical stability of the membranes.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been extensively developed as a potential power source candidate for stationary and portable applications due to their high energy-conversion efficiency and low emission of pollutants [1,2]. Proton exchange membrane (PEM) is an essential component of a PEMFC [1–3]. Currently, the most commonly used PEM are perfluorosulfonate ionomers such as Nafion, which have excellent hydrolytic and oxidative stability and high proton conductivity [1]. However, Nafion exhibits three major drawbacks: high cost; loss of conductivity at high temperature (above 100 °C) or low humidity (below 50% RH); and high fuel permeabilities [4,5]. Tremendous efforts have been dedicated to the development of alternative membranes such as sulfonated poly(ether ketones), poly(ether sulfone)s, and polyimides due to their excellent thermomechanical stability, low cost and low fuel permeabilities [4,6]. However, one key problem is that that these polymers exhibited low proton

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conductivity owing to the fact that they are phase-separated into smaller sulfonic acid-aggregated ion nanochannels which are less interconnected, when compared with Nafion membrane [7].

Creating hybrid nanostructures to construct facile pathways for proton transport is a straightforward and effective strategy to solve the above problem [1,8]. Among them, incorporation of acid-functionalized nanofiller (mainly sulfonic acid and phosphonic acid) into PEM has attracted much attention on account of the following two merits: (i) the acid groups on the filler are capable of enhancing proton conductivity of the composite membrane [9–12]; (ii) the filler is capable of blocking fuel permeation as well as imparting good mechanical and thermal stability to the composite membrane [5,13]. To date, acid-functionalized nanofillers with tubular structure showed significant efficacy in elevating proton conductivity due to the constructed facile proton pathways in membrane [14–17]. Liu et al. reported the incorporation of Nafion-functionalized multiwalled carbon nanotubes (Nafion-CNTs, 12 wt% Nafion fraction) into Nafion matrix [18]. The high sulfonic acid contents on the CNTs rendered the Nafion-CNTs capable of acting as a continuous pathway for facile proton transport, resulting in 400% increase of proton conductivity compared to the Nafion control membrane. Moreover, the Nafion-CNTs showed excellent compatibility with the Nafion matrix, resulting in 50% increase of mechanical strength. This study implies that acidic polymer functionalized nanotube is a novel filler to modify sulfonated hydrocarbon membrane due to the introduction of high acid contents along the tubular structure for facile proton transport, as well as the compatibility between the acidic polymer functional groups and the membrane matrix. Proton conductors based on phosphonic acid are considered quite promising due to their high proton conductivity with low dependence on moisture, excellent thermal stability, and good oxidation resistivity of the protogenic group [19–21]. However, almost all the existing nanotube fillers were sulfonic acid modified nanotubes, and there is no report on poly(-phosphonic acid) functionalized nanotube for PEM use. Furthermore, the aspect ratios of nanotube significantly influence the ultimate properties of the composites such as mechanical, electrical, rheological, thermal, and flammability properties [22–24]. Huang et al. reported that the dielectric constant of poly(vinylidene fluoride)/CNT composite with higher aspect ratio of CNT was greater than that with lower aspect ratio of CNT [24]. Park reported that multiwalled CNTs of smaller aspect ratio dispersed more evenly within acrylonitrile butadiene styrene matrix resulting in lower electrical resistivity of the composite [23]. Thus, it is conjectured that aspect ratio of nanotubes, which may determine the dispersion and continuity of the nanotubes and thus the formation of continuous proton-conduction pathways within composite membranes [14], could affect proton conductivity of the nanotube-based PEM. Obviously, continuity of proton-conduction pathway is a critical factor influencing proton conductivity of the membrane [3]. However, the influence of aspect ratio of the nanotube fillers on the proton conductivity has not been reported till now.

In this study, a novel crosslinked poly(vinylphosphonic acid) functionalized silica nanotube (PANTs) was designed and synthesized, and subsequently incorporated into sulfonated poly(ether ether ketone) (SPEEK) to prepare composite membrane. Poly(-vinylphosphonic acid) (PVPA) was chosen due to its high concentration of phosphonic acid groups directly connected to a flexible polymer main chain. The successful synthesis of PANTs was confirmed by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), Zeta PALS, transmission electron microscopy (TEM), and field emission scanning electron microscopy (FESEM). Proton conductivity, methanol permeability, water uptake, dimensional stability, thermal properties, and mechanical stability of the membranes were evaluated. The influence of aspect ratio of the nanotube on the proton conductivity was explored.

2. Experimental section

2.1. Materials

Dimethyl vinylphosphonate (DMVP), divinylbenzene (DVB, 80% divinylbenzene isomers) and tetraethyl orthosilicate (TEOS) were purchased from Alfa Aesar and used as received. 3-(Methacryloxy)propyltrimethoxysilane (MPS) was supplied by Aldrich and distilled under vacuum. Methacrylic acid (MAA) was purchased from Tianjin Guangfu Fine Chemical Engineering Institute and distilled under vacuum before use. 2,2′-Azoisobutyronitrile (AIBN) was provided by Tianjin Guangfu Fine Chemical Engineering Institute and recrystallized from methanol. Acetonitrile and aluminum chloride hexahydrate were supplied by Tianjin Kewei Ltd. and acetonitrile was dried over calcium hydride and purified by distillation. Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was provided by Nanjing Yuanbang Engineering Plastics Co., Ltd. Dimethylformamide (DMF), sulfuric acid, hydrochloric acid, ammonia and methanol were purchased from Tianjin Kewei Ltd. De-ionized water was used throughout the experiment.

2.2. Synthesis of the monodisperse P(PVPA-co-DVB)/silica nanotubes and SPEEK

Nanorods with carbon–carbon double bonds were synthesized. Firstly, the boehmite nanorod templates with different aspect ratios were synthesized [25]. Secondly, the as-synthesized nanorod templates were further surface-modified with TEOS and MPS to introduce silica layer and carbon–carbon double bonds, which served as grafting sites for the following polymer coating. Briefly, 0.15 g boehmite nanorods were dispersed in 200 ml of ethanol, 12 ml of water, 1.2 ml of ammonia and 0.3 ml of TEOS under stirring at 30 °C for 24 h. Then, 0.2 ml of MPS was added into the above solution with a reaction time of 24 h to modify the nanorods with carbon–carbon double bonds.

The coating of polymer on the MPS-modified nanorods was carried out by distillation–precipitation polymerization [26,27]. In a typical synthesis, the MPS-modified nanorod templates (0.05 g) were dispersed in acetonitrile under sonication for 60 min. The monomer DMVP (0.6 ml), crosslinker DVB (0.4 ml), and initiator AIBN (0.02 g, 2 wt% relative to the total amount of monomer and crosslinker) were then added into the above template solution. The mixture was heated from ambient temperature till boiling state and then the solvent was distilled off from the reaction system. After 40 ml of acetonitrile was distilled out, the reaction was terminated and the resultant core–shell nanorod was purified. The polymer grafting thickness was controlled by varying the (monomer + crosslinker)/templates feed ratio by weight. Subsequently, the nanorod was dispersed into excess HCl aqueous solution (10 mol L^{-1}) at 100 °C for 24 h to transform poly(dimethyl vinylphosphonate) segments into poly(vinylphosphonic acid) segments, and etch the boehmite nanorod templates. The synthesized P(PVPA-*co*-DVB)/silica nanotubes were designated as PANTs-1#, PANTs-2# and PANTs-3#, corresponding to their aspect ratios of 2.6, 18.7, and 45.9, respectively.

SPEEK was synthesized by sulfonation of PEEK: PEEK was dried at 60 °C for 24 h and then dissolved in concentrated sulfuric acid at room temperature under agitation for 3 h. The reaction mixture was then heated to 45 °C and kept stirring for 8 h. The reaction was terminated by decanting the solution into excessive cold water under agitation. The crude product was washed with water till