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Fabrication of sulfonated poly(ether ether ketone)-based hybrid proton-conducting membranes containing carboxyl or amino acid-functionalized titania by *in situ* sol–gel process

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HIGHLIGHTS

- Carboxylic acid or amino acid functionalized titania sol are prepared.
- Functionalized titania is incorporated into SPEEK through *in situ* sol–gel method.
- The proton conductivity of hybrid membrane is 3.5 times higher than pure SPEEK.
- The methanol permeability of hybrid membranes is effectively suppressed.

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ABSTRACT

Functionalized titania are used as fillers to modify the sulfonated poly(ether ether ketone) (SPEEK) membrane for improved proton conductivity and methanol barrier property. The functionalized titania sol which contains proton conductive carboxylic acid groups or amino acid groups are derived from a facile chelation method using different functional additives. Then the novel SPEEK/carboxylic acid-functionalized titania (SPEEK/TC) and SPEEK/amino acid-functionalized titania (SPEEK/TNC) hybrid membranes are fabricated via *in situ* sol–gel method. The anti-swelling property and thermal stability of hybrid membranes are enhanced owing to the formation of electrostatic force between SPEEK and titania nanoparticles. The hybrid membranes exhibit higher proton conductivity than plain SPEEK membrane because more proton transfer sites are provided by the functionalized titania nanoparticles. Particularly, the proton conductivity of SPEEK/TNC membrane with 15% filler content reaches up to 6.24×10^{-2} S cm^{-1}, which is 3.5 times higher than that of the pure SPEEK membrane. For methanol permeability, the SPEEK/TNC membranes possess the lowest values because the acid-base interaction between sulfonic acid groups in SPEEK and amino groups in functionalized titania leads to a more compact membrane structure.

1. Introduction

The serious depletion of fossil fuels in our modern society has been necessitating the exploitation of other energy convertible and environmentally benign devices. Proton exchange membrane fuel cell (PEMFC) can convert chemical energy into electrical energy directly with high power density, fast response to load changes and low pollutant emission, so it is currently considered as a promising technology for power generation systems [1,2]. Direct methanol fuel cells (DMFCs) have attracted much attention due to their high efficiency and simple design [3]. Notably, methanol is regarded as one of the most promising fuels except hydrogen for its high energy density, high solubility in aqueous electrolytes, low cost, ease of storage, etc [4]. One of the main factors currently affecting the performance of DMFCs is the property of proton exchange membranes (PEMs). The drawbacks of commercial Nafion-based PEMs such as serious proton conductivity reduction at high temperature, high methanol permeability and high cost, impede the commercialization of DMFCs [5,6]. In this sense, novel PEMs with sufficient

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proton conductivity and low methanol permeability remain to be further developed and researched.

Generally, the protons are transferred inside the membrane through two mechanisms [7,8]: (i) Vehicle mechanism, in which the protons diffuse together with H_2O molecules by forming different hydronium ions; (ii) Grotthuss mechanism, in which the protons jump via adjacent proton transfer sites. Organic-inorganic hybrid approach is extensively studied because the hygroscopic groups in inorganic particles can retain water to some extent, thus enhancing the vehicle-type proton transfer in hybrid membrane [9,10]. Usually, the hybrid membranes are prepared by physical mixing method [11,12] or *in situ* sol–gel method [13,14]. The *in situ* sol–gel method is a promising technology due to its controllable process and mild reaction conditions, most importantly, the sol–gel chemistry endows the inorganic nanoparticles with confined growth inside the organic matrix, which avoids the agglomeration of nanoparticles and leads to highly homogenous morphology [15–17]. Inorganic particles or network such as SiO_2, TiO_2, ZrO_2, etc. have been incorporated into polymer matrix through *in situ* sol–gel method to improve the water sorption ability of the membranes [16,18,19]. Moreover, the introduction of inorganic parts using *in situ* sol–gel method is also helpful to methanol resistance because of lengthened paths along which methanol molecules are transported [20,21].

To improve the Grotthuss-type proton transfer, the proton carriers, which are usually Brønsted acids or bases, should be introduced to build nanochannels inside the membrane. For acidic functional groups, $-SO_3H$, $-PO_3H_2$, $-COOH$ are usually used to constitute conductive pathways for protons [22–24]. The weak acidic carboxyl groups have strong hydrogen-bonding interactions with H_2O molecules, which contribute to water retention as well as proton hopping [25]. Alabi and Davis [26] grafted carboxylic acid groups onto the inner pore walls of MCM-41 to improve the proton conductivity, the conductivity of prepared solid acid is an order of magnitude higher than pristine MCM-41, showing promising potential of carboxylic acid groups as proton transfer sites. It has been found in literature that the amino acids play a crucial role in proton conducting mechanism in organisms [27]. The carboxyl groups in amino acids act as proton donors and the amino groups represent proton acceptors [28]. So the acidic and basic groups can form acid-base pairs, which offer low-energy barrier for proton conduction through Grotthuss mechanism [29]. We previously incorporated amino-acid functionalized titania particles into SPEEK, the hybrid membrane displayed a high conductivity of 0.066 S cm^{-1} at 20 °C, showing promising potential as PEMs [30].

The aim of this study is to pursue high proton conductivity and low methanol permeability by preparing a novel kind of SPEEK/functionalized titania hybrid membrane. The functionalized titania sol with proton conductive carboxylic groups or amino groups is derived from a facile chelation method. *In situ* sol–gel method is chosen as fabrication method for the controllable process as well as uniform dispersion of inorganic nanoparticles. The membranes are evaluated in terms of thermal stability, ionic exchange capacity, swelling behavior, proton conductivity, methanol permeability, etc. The effect of proton transfer sites on the performance of membranes is investigated and discussed.

2. Experimental

2.1. Materials and chemicals

Poly(ether ether ketone) (PEEK) was obtained from Victrex High-performance Materials (Shanghai, China) Co., Ltd. 3-(3,4-dihydroxyphenyl) propionic acid was obtained from Alfa Aesar, 3-(3,4-dihydroxyphenyl)-L-alanine (L-Dopa) was purchased from Yuancheng Technology Development Co., Ltd. (Wuhan, China). Tetrabutyltitanate (TBT, purity >98%), acetylacetone (AcAc, purity >98%), N, N-Dimethyl formamide (DMF), sulfuric acid (H_2SO_4,95–98wt.%) and other reagents were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China).

Sulfonated poly(ether ether ketone) (SPEEK) was prepared by direct sulfonation of PEEK as shown in literature [31]. Typically, PEEK (14 g) was dried in oven at 80 °C overnight, the dried PEEK was dissolved into 120 mL $H_2SO_4$for about 4 h at 25 °C, followed by vigorous stirring at 45 °C for about 8 h. Finally, the solution was precipitated in deionized water gradually under mechanical agitation. The obtained polymer SPEEK was filtered, washed several times with water until the pH was neutral, then dried at 25 °C for 24 h and at 60 °C for another 24 h. The degree of sulfonation (DS) of as-prepared SPEEK was 67% through measuring by acid-base titration method [32].

2.2. Preparation of hybrid membranes

The carboxylic acid and amino acid functionalized titania sols were prepared by sol–gel based reaction as follows: a predetermined stoichiometric amount of TBT and AcAc was dissolved in DMF and stirred at room temperature for 4 h. The obtained solution was hydrolyzed by water for 10 h, then a certain amount of 3-(3,4-Dihydroxyphenyl) propionic acid or L-Dopa was added into the solution to get the titania sol functionalized. The synthesis process of two different functionalized sols is show in Fig. 1a. To prepare hybrid membranes, 1.2 g SPEEK was dissolved in 8 g DMF, afterwards, a measured amount of functionalized titania sol and SPEEK solution were mixed and the resultant mixture was stirred for 1 h to ensure complete mixing. The mixture was cast onto a clean glass plate, heated at 40 °C for 12 h, followed by drying at 80 °C for 10 h and annealing at 120 °C for 2 h. The fabricated hybrid membranes are designated as SPEEK/TC-X and SPEEK/TNC-X, where TC and TNC represents the carboxyl functionalized titania and amino-acid functionalized titania, respectively, X (= 10, 15, 20 or 25) is the weight ratio of inorganic titania to SPEEK. The overall preparation process of SPEEK-based hybrid membranes is given in Fig. 1b. As a comparison, the pure SPEEK membrane and SPEEK incorporated with non-functionalized titania sol (SPEEK/T) were also prepared using the same procedure. All the membranes had an average thickness in the range of 60–70 μm.

2.3. Characterizations

The chemical structures of the functionalized sol and membranes were characterized by Fourier transform infrared spectrometer (FTIR, Nicolet MAGNA-IR 560).

The cross-sectional morphologies and the elemental composition of the membranes were observed by using field emission scanning electron microscope (FESEM, Nanosem 430) equipped with a probe for energy-dispersive X-ray scanning. The cross-sections were prepared by freeze-fracturing membrane samples in liquid N_2 and then coated with a thin layer of sputtered gold.

The thermal stability of membranes were measured by Thermogravimetric analyzer (TGA, Perkin–Elmer Pyris) over a temperature range of 30–800 °C at a heating rate of 10 °C min^{-1} under N_2 flow. Before measurement, all the membrane samples were vacuum-dried for 24 h to remove the absorbed water.

2.4. Water uptake and dimensional swelling

Each membrane sample (4.0 cm × 4.0 cm) was dried at 60 °C for 24 h, then it was weighed (W_{dry}, g) and measured (A_{dry}, cm^2). After that, the sample was soaked in water at room temperature for 24 h, after full hydration, the membrane was immediately re-weighed