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Preparation and performance of different amino acids functionalized titania-embedded sulfonated poly (ether ether ketone) hybrid membranes for direct methanol fuel cells

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ABSTRACT

A series of amino acid functionalized titania submicrospheres were synthesized and incorporated into sulfonated poly (ether ether ketone) (SPEEK) to fabricate organic–inorganic hybrid proton exchange membranes. Pristine TiO₂ with a uniform particle size of ~200 nm were synthesized and functionalized with four kinds of amino acids including oxidized L-cysteine, O-phospho-L-serine, aspartic acid and histidine, designated as TiO₂-Scys, TiO₂-Pser, TiO₂-Asp and TiO₂-His, respectively. The effects of amino acid attribute on the membrane properties were investigated. At the filler content of 15 wt%, the TiO₂-Scys embedded membrane exhibited the highest proton conductivity of about $5.98 \times 10^{-3} \text{ S cm}^{-1}$ (20 °C, 100% RH), while the TiO₂-His embedded membrane exhibited the lowest conductivity due to the strong acid-base interaction between the basic imidazole groups of histidine and the sulfuric acid groups of SPEEK. The TiO₂-Pser embedded membrane exhibited the highest selectivity of $17.10 \times 10^3 \text{ S s cm}^{-1}$. In addition, the methanol crossover of the hybrid membranes was reduced by two folds, and the anti-swelling property and thermal stability of the hybrid membranes were also enhanced.

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1. Introduction

Direct methanol fuel cells (DMFCs) as promising portable and transport power sources have drawn wide attention due to their high power density, low pollution, long life time and compact cell design [1,2]. Proton exchange membrane (PEM) is one of the key components of DMFCs. The current state-of-art PEMs represented by Nafion (Dupont) suffer from high cost, serious methanol crossover and proton conductivity loss at high temperature, thus hindering their practical application in DMFCs [2,3]. Membranes with enhanced proton conductivity, reduced methanol permeability and acceptable cost are required for DMFCs [4–6]. To meet these requirements, various approaches have been explored in recent years [7]. Among them, the employment of organic–inorganic hybrid PEMs seems attractive because of their ability to rationally combine the characters

Abbreviations: oxidized L-cysteine, Scys; O-phospho-L-serine, Pser; aspartic acid, Asp; histidine, His; sulfonation degree, DS; ion-exchange capacity, IEC; sulfonated poly(ether ether ketone), SPEEK

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of organic moiety and inorganic moiety [8,9]. Incorporation of inorganic additives into polymers could endow the hybrid membranes with enhanced mechanical stability and better water-retaining property [6,10,11]. However, proton conductivity usually decreases with increasing filler content due to the rather low proton conductivity of inorganic additives and their considerable dilution effect on the proton conductive groups [12]. Anchoring extra proton-conducting groups, such as sulfonic acid group [13–15] and phosphonic acid group [16–19] etc., onto the surface of inorganic particles could provide more facile hopping sites for protons, which in turn would help to increase the proton mobility, thus resulting in the enhancement of proton conductivity [10].

In living organisms, proton transfer plays a key role in the cellular energy interconversion which occurs along proton channels such as the M2 proton channel of influenza A virus [20], cytochrome-oxidase complex in mitochondria [21] and bacteriorhodopsin in Halobacterium [22]. Proton transfer operates very efficiently through these amino acid-lined channels, for example, 10^5 protons are conducted per second through one channel at a 100 mV potential drop in adenosine triphosphate (ATP) synthase systems [23]. Inspired by the proton conducting mechanism in organisms where each amino acid acts as acceptor and donor simultaneously in proton transfer, amino acids were introduced

into PEMs by many researchers. Hong Wu et al. [24] synthesized a series of titania submicrospheres grafted with various functional groups including amino acid group, amino group, carboxyl group and phenyl group, and incorporated them into sulfonated poly(ether ether ketone) (SPEEK) to fabricate hybrid membranes. Among all the membranes, the membranes embedded with amino acid functionalized TiO_2 displayed a superior proton-conducting ability. Leem et al. [23] attached different kinds of amino acids (L-lysine, aspartic acid, glutamic acid and methionin) to silica nanoparticles and incorporated them into porous membranes (polyethylene terephthalate, polycarbonate). No power output was observed in the absence of amino acids while a variable power output depending on the nature of the amino acids and the chemical addition was observed. These distinct differences were ascribed to the structure of the amino acids and the amino acid-water surface layer formed on nanoparticles.

Although it has been demonstrated that amino acids could mediate the transport of protons in PEMs, few efforts have been dedicated to investigate the influence of various kinds of amino acids on the membrane performance. In this study, four kinds of amino acids were selected for comparison, including oxidized L-cysteine, O-phospho-L-serine, aspartic acid and histidine. These four kinds of amino acids have similar structures with different end groups including sulfonic acid groups (strong acidic), phosphonic acid groups (mediate strong acidic), carboxyl groups (weak acidic) and imidazole groups (alkaline), exhibiting different capacity to donate or accept protons. A series of amino acid functionalized titania submicrospheres were synthesized and doped into SPEEK to fabricate hybrid proton conducting membranes for potential application in DMFCs. The as-prepared membranes were extensively evaluated in terms of swelling degree, water uptake, methanol permeability and proton conductivity.

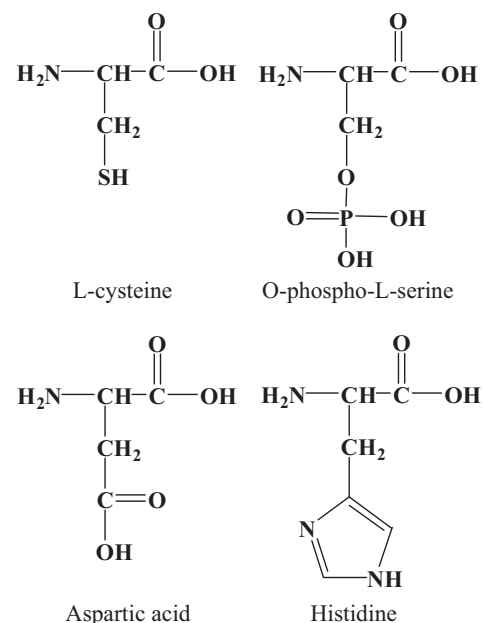
2. Experimental

2.1. Materials and chemicals

Poly(ether ether ketone) (PEEK) was purchased from Victrex High-performance Materials Co., Ltd. (Shanghai, China). 3-(3,4-dihydroxyphenyl) propionic acid was purchased from Alfa Aesar. Tetrabutyl titanate (TBT, > 98%), histidine, aspartic acid, L-cysteine, hydrochloric acid (HCl, 36%–38%) and N,N-Dimethylformamide (DMF, > 99.5%) from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), and O-phospho-L-serine from Sigma-Aldrich were used as received without further purification.

2.2. Preparation of functionalized TiO_2 submicrospheres

Preparation of TiO_2 submicrospheres was carried out via a modified sol-gel method as described before [25]. For the carboxylation of TiO_2 , a facile chelation procedure was conducted [26]. A certain amount of TiO_2 powders were suspended in hydrochloric acid aqueous solution (pH=2) under ultrasonic treatment for 2 h to break aggregates. The obtained solution was poured into a large excessive of 4 mg L^{-1} 3-(3,4-dihydroxyphenyl) propionic acid solution, followed by vigorous stirring for 0.5 h. The carboxyl functionalized TiO_2 submicrospheres were collected by centrifugation, washed with deionized water till neutral pH and dried overnight. The obtained TiO_2 submicrospheres were designated as $\text{TiO}_2\text{-Car}$. For modifying TiO_2 with amino acid, L-cysteine, O-phospho-L-serine, aspartic acid and histidine (molecular structures shown in Scheme 1) were used as modification reagents. 1.0 g of $\text{TiO}_2\text{-Car}$ were added into 200 mL of 4-Morpholineethanesulfonic acid (MES, 50 mM, pH=6.5) under ultrasonic treatment for 15 min, and then 6 mmol of 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 30 mmol of



Scheme 1. Molecular structures of the modification reagents.

N-Hydroxysuccinimide (NHS) were added into the above solution under vigorous stirring at room temperature for 1 h to activate the carboxyl groups on $\text{TiO}_2\text{-Car}$ [27]. After activation, the $\text{TiO}_2\text{-Car}$ were washed with deionized water to remove the unreacted EDC and NHS, and collected by centrifugation. Then, the as-collected $\text{TiO}_2\text{-Car}$ were suspended respectively in the MES solution of the four kinds of amino acid, and reacted under room temperature for 4 h, followed by centrifugal separation and washed to neutral pH. Herein, the obtained L-cysteine functionalized TiO_2 submicrospheres were treated with 1 wt% oxidize hydrogen for 24 h to get oxidized. The final obtained functionalized TiO_2 grafted respectively with oxidized L-cysteine, O-phospho-L-serine, aspartic acid, and histidine were designated as $\text{TiO}_2\text{-Scys}$, $\text{TiO}_2\text{-Pser}$, $\text{TiO}_2\text{-Asp}$, and $\text{TiO}_2\text{-His}$.

2.3. Sulfonation of PEEK

PEEK was firstly dried in oven at 80°C for 24 h before sulfonation. Then, 28 g of dried PEEK was dissolved into 200 mL concentrated sulfuric acid (H_2SO_4 , 95–98%) under vigorous stirring at room temperature for 4 h and then at 45°C for 8 h. The obtained solution was added into a large excess of ice-cold water under continuous stirring. The white precipitate was removed and washed with deionized water until neutral pH to remove residual acid. The sulfonated polymer was dried at room temperature for 24 h followed by drying at 60°C under vacuum [28]. The degree of sulfonation (DS) was determined to be 61% through titration method [29].

2.4. Preparation of hybrid membranes

1.2 g of SPEEK was dissolved in 8 g of DMF under stirring at room temperature. A specific amount of functionalized TiO_2 submicrospheres were dispersed into 4 g of DMF under ultrasonic treatment for 24 h. Then, the above two solutions were mixed and stirred for another 24 h. The resulting mixture was cast onto a clean glass plate, dried first at 60°C for 12 h and then 80°C for

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