



# Novel composite polymer electrolyte membrane using solid superacidic sulfated zirconia - Functionalized carbon nanotube modified chitosan

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## ARTICLE INFO

### Article history:

Received 4 November 2017

Received in revised form

15 January 2018

Accepted 22 January 2018

### Keywords:

Chitosan

Carbon nanotubes

Sulfated zirconia

Proton exchange membranes

## ABSTRACT

Utilization of proton conductor functionalized carbon nanotube (CNT) as an additive is an effective way to simultaneously improve the mechanic strength and proton conductivity of polymer electrolyte membranes (PEMs). Herein, superacidic sulfated zirconia coated carbon nanotube (SZr@CNT), a combination of excellent proton conductor and effective reinforcements, was fabricated via a facile surface-deposition method. And then, SZr@CNT was used as a functional additive in chitosan (CS) to prepare PEMs. Owing to the SZr coating, the SZr@CNT possesses desirable dispersibility and compatibility with the polymer matrix. Therefore, the obtained CS/SZr@CNT composite membranes exhibit better mechanical properties than that of pure CS membrane. Meanwhile, the proton conductor on the surface of CNT could afford the opportunity to build new long-range proton conducting pathways along the interfaces between CS and SZr@CNT, thus enhancing the proton conductivity of the composites. Satisfactorily, incorporation of 0.5% SZr@CNT shows a 1.3-fold increase of proton conductivity when compared with pure CS membrane. As a consequence, such superior proton transport ability guarantees outstanding fuel cell performances of the composite membranes. The maximum power density of the CS/SZr@CNT-0.5 composite membrane is  $64.6 \text{ mWcm}^{-2}$  at  $70^\circ\text{C}$ , which is nearly the double of that of pure CS membrane (only  $36.3 \text{ mWcm}^{-2}$ ). Furthermore, the durability test confirms that the CS/SZr@CNT-0.5 composite membrane still possesses satisfactory stability even after continuous operation at  $70^\circ\text{C}$  for 100 h.

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## 1. Introduction

Polymer electrolyte membrane fuel cells, including proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), are recognized as one of the promising options for green energy conversion devices because of growing

environmental and energy problems [1]. As a key component of PEMFCs and DMFCs, polymer electrolyte membranes (PEMs) must simultaneously fulfill a number of operation requirements including high proton transport ability, low fuels permeability, low cost and adequate chemical stability, etc. [2]. Currently, the best known commercialized membrane materials for PEMs are perfluorosulfonic acid polymers (represented by DuPont's Nafion series) that exhibit good thermal and chemical stabilities, and excellent proton conductivity under wet conditions. Nevertheless, Nafion series membranes suffer from some drawbacks, such as severe fuel permeability and dramatically decreased proton conductivity at low hydration levels, which significantly affect the efficiency and performance of fuel cells. Moreover, the complex preparation process and high cost of Nafion also bring adverse

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effects on the large-scale commercial application of PEMFCs and DMFCs. Accordingly, numerous studies have been performed for the development of alternative PEMs with adequate properties and low cost [3–5].

Abundant and inexpensive natural polymers such as chitosan [6,7], alginate [8] and cellulose [9] have been widely applied in the field of membrane technologies in order to meet high requirements for sustainability and environmental friendliness. In particular, chitosan (CS) has attracted numerous researchers' interest due to its low toxicity and cost, easy chemical functionalization and low methanol permeability. However, the relatively poor mechanical properties and low intrinsic proton conductivity of pristine CS limit its application as PEMs [10]. Creation of organic-inorganic composite nanostructures to improve the mechanical strength and construct facile channels for H<sup>+</sup> migration is a straightforward and effective strategy to solve the above problems [11].

Among many inorganic materials, carbon nanotube (CNT) has drawn considerable attention to develop high-performance polymer based nanocomposites in the field of energy materials due to their remarkable mechanical stability, high aspect ratio and unique thermal properties [12–14]. Unfortunately, the aggregation behavior and poor compatibility of CNT in polymer matrices result in many defect sites and thus seriously impair the performance of nanocomposites. Besides, although the short-circuiting risk of using CNT to modify PEMs can be avoided by controlling the CNT content below the percolation threshold [15], the inert proton conduction activity of CNT remains to be resolved. Hence, how to simultaneously enhance the dispersibility, compatibility and proton conduction activity of CNT has become the focus of application of CNT in the field of PEMs [16–18]. One proposed approach is utilization of proton conductor to modify CNT, which can not only increase the interfacial interaction between CNT and membrane matrices, but also endow CNT with proton transport ability. Liu's group used different polymer proton conductors (Nafion [19], poly(styrene sulfonic acid) [20] and polybenzimidazole [17]) to coat CNT via an ozone-mediated four-step chemical reaction process. Jiang et al. [21] obtained acrylate-modified CNT with various functional groups (–COOH, –PO<sub>3</sub>H<sub>2</sub>, and –SO<sub>3</sub>H) using a surface-initiated distillation precipitation polymerization method. These proton conductors on the surface of CNT ensured the uniform dispersion of CNT and increased the compatibility between polymer matrices and CNT. As expected, due to the newly formed H<sup>+</sup> conducting channels along the surface of functionalized CNT, these composite membranes exhibited significant improvement in mechanical properties and proton conductivity. However, it must also be mentioned that the preparation processes for these reported proton conductor functionalized CNT were complicated and time-consuming, leading to a high processing cost.

Herein, cost-effective and easily prepared inorganic proton conductor functionalized CNT are the focus of our research. We recently have demonstrated the utility of inorganic proton conductor-boron phosphate (BPO<sub>4</sub>) coated CNT (BPO<sub>4</sub>@CNT) by a facile polydopamine-assisted sol-gel method, and then prepared sulfonated polyether ether ketone (SPEEK)/BPO<sub>4</sub>@CNT composite membranes [22]. Obvious increases in the thermal stability, tensile properties and fuel cell performance were found in the case of these SPEEK/BPO<sub>4</sub>@CNT composite membranes. Hence, this work reports our continuing efforts on the use of inorganic proton conductor-functionalized CNT for modification of polymer electrolyte membranes. In this work, solid superacidic sulfated zirconia (SZr) with excellent hydrophilicity, proton conductivity and stability [23–25] was selected to coat CNT via a facile surface-deposition method. Then, the obtained SZr-coated CNT (SZr@CNT) was utilized to prepare CS based PEMs. The effects of SZr@CNT on the structure and properties of the CS/SZr@CNT

composite membranes were then investigated in details.

## 2. Experimental

### 2.1. Materials

Chitosan ( $M_w = 1000$  kDa, degree of deacetylation = 92.5% according to manufacturer instructions) was purchased from Golden-shell Biochemical Co., Ltd. (China). Multi-walled carbon nanotubes (average diameter: 50 nm, average length: 5  $\mu$ m) were supplied by Shenzhen Nanotech Port Co., Ltd. (China). Zirconium (IV) oxychloride octahydrate (A.R.), ethanol absolute (A.R.) acetic acid (A.R.) and ammonia (A.R.) were supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Sulfuric acid (98%) was supplied by Kaifeng Shenma Group Co., Ltd. (China).

### 2.2. Synthesis of SZr@CNT

SZr@CNT was prepared using a facile chemical precipitation method [26]. Firstly, the pristine CNT was treated in concentrated HNO<sub>3</sub> with stirring at 120 °C for 4 h. And then, the suspension was filtered and washed with deionized water until the filtrate became neutral to obtain acidified CNT (CNT-COOH). Secondly, an appropriate amount of CNT-COOH was dispersed in the ZrOCl<sub>2</sub>·8H<sub>2</sub>O solution (0.20 M). After being stirred for 1 h, a diluted ammonia solution was added drop wise to adjust the pH to 10, followed by continuous stirring for 24 h. The obtained mixture of ZrO<sub>2</sub>·nH<sub>2</sub>O sol and CNT-COOH was washed with deionized water until the Cl<sup>–</sup> could no longer be detected by silver nitrate (AgNO<sub>3</sub>) and followed by drying in an oven. Subsequently, the mixture was added to a sulfuric acid aqueous solution (0.5 M) under vigorous stirring for 1 h, and the solution was then filtered and dried. Finally, the powder was calcined at 620 °C under N<sub>2</sub> flow for 1 h to yield sulfated zirconia-coated CNT (SZr@CNT).

### 2.3. Preparation of CS/SZr@CNT composition membranes

The CS/SZr@CNT composite membranes were fabricated using a solution casting technique as follows: first, an amount of CS powder was dissolved in acetic acid solution (2 vol %) at room temperature. Meanwhile, a desired amount of SZr@CNT powder was sonicated in ethanol for 1 h. The SZr@CNT suspension was then mixed with the CS solution to get a homogeneous mixture. Subsequently, the homogeneous solution was poured on a flat glass and dried at 40 °C overnight. Finally, the membranes were ionic crosslinked by immersion in a H<sub>2</sub>SO<sub>4</sub> solution (2 M). The obtained composite membranes were named as CS/SZr@CNT-*x*, where *x* was the mass percent of the SZr@CNT in the CS matrix.

### 2.4. Characterization of the SZr@CNT and membranes

Nicolet 380 Fourier transform infrared spectrometer (Thermo Electron Co., USA), D8 X-ray diffractometer (Bruker Co., Germany) and an Escalab 250Xi X-ray photoelectron spectrometer (Thermo Electron Co., USA) were used to determine the composition and chemical structure of SZr@CNT. The morphology of SZr@CNT was observed by JEM-2100F transmission electron microscope (Hitachi Co., Japan), with an accelerating voltage of 200 kV. In order to verify the dispersion of SZr@CNT in the composite membranes, Tescan mira3 scanning electron microscope (Zeiss Co., Germany) equipped with an X-50 max energy-dispersive X-ray spectrometer (Oxford Co., England) was used to observe the cross-sections of the membranes. The thermo-gravimetric analysis (TGA) was probed by STA 499F instrument (NETZSCH Co., Germany) from 50 to 800 °C (10 °C min<sup>–1</sup>) under N<sub>2</sub>. Before measurement, all the samples were heated

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