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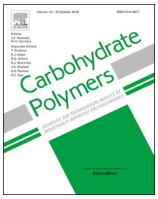

Anatase titania coated CNTs and sodium lignin sulfonate doped chitosan proton exchange membrane for DMFC application

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ABSTRACT

Anatase titania coated CNTs (TCNTs) and sodium lignin sulfonate (SLS) were introduced to chitosan membrane to improve the conductivity based on extra proton transfer channels built by TCNTs and sulfonate groups supplied by SLS. Water uptake, mechanical properties, oxidation stability and methanol-rejecting property of composite membranes were characterized. The results show that TCNTs and SLS doped membranes have enhanced conductivity and the sample with 5% TCNTs and 2% SLS doped (CS/TCNT-5/SLS-2) achieved a conductivity of 0.0367 S cm^{-1} at room temperature and 0.0647 S cm^{-1} at 60 °C, which is much higher than pure chitosan membrane. Moreover, with TCNTs incorporation, the mechanical properties, oxidation stability and methanol-rejecting property also improved. Overall, selectivity of CS/TCNT-5/SLS-2 sample achieved 28.2×10^4 S s cm^{-3} which is much higher than 3.8×10^4 S s cm^{-3} of pure chitosan membrane. Thus, with enhanced properties, chitosan composite membrane could be promising as proton exchange membrane (PEM) in the use of direct methanol fuel cell (DMFC).

1. Introduction

Transferring chemical energy into electricity efficiently, DMFC as one kind of proton exchange membrane fuel cell (PEMFC) is a promising energy conversion device (Nataraj et al., 2015). Compared with traditional battery, fuel cell is an energy generator other than an electricity storage device. As a core component in DMFC (Yamada & Honma, 2004), PEM transfers protons and block fuel to the counter compartment (Mukoma, Jooste, & Vosloo, 2004), ensuring the fuel cell normal work (Muthumeenal, Neelakandan, Kanagaraj, & Nagendran, 2016). The development of PEM is a significant branch of fuel cell technology advance. Conductivity is a key property of PEM, high conductivity of PEM represents efficient fuel cell work. Besides conductivity, other aspects such as methanol block property, water uptake, mechanical property and oxidation stability are also considered to design PEM materials.

Chitosan is one kind of natural polymer with excellent biocompatibility, high hydrophilicity and low methanol permeability (Alshahrani, Al-Zoubi, Nghiem, & in het Panhuis, 2017; Cao et al., 2016; Yamada & Honma, 2005). However, chitosan membrane has a low proton conductivity because of the poor water absorption though protonated amino groups and sulfate ions in chitosan cross-linked structure facilitate the proton transfer. And low conductivity limits chitosan using as proton exchange membrane material (Liu, Gong et al., 2016). According to Grotthuss mechanism and vehicular mechanism, proton transport in proton exchange membrane depends on free volume pores and channels (Bai et al., 2014). In the case of Grotthuss mechanism, H^+ is delivered by water molecules, on the basis of which, proton transfer sites are essential (Yin, Xu, Shen, Wu, & Jiang, 2014). Besides free volume pores and channels for water molecules delivery, ionic groups also strengthen the proton transfer. Anionic groups can supply extra sites in proton transfer process, so introducing sulfonic acid groups is a widely used approach to enhance PEM proton conductivity (Pecoraro, Santamaria, Bocchetta, & Di Quarto, 2015; Santamaria, Becton, Cooper, Weber, & Park, 2015; Vijayalekshmi & Khastgir, 2017). Inorganic dopants may provide extra pathways for proton transport in polymer network. Closely related to the interfacial morphology, proton conductivity of the membrane is influenced by the properties of inorganic fillers (Chen, Hao, Wu, Li, & Wang, 2016; Shirdast, Sharif, & Abdollahi, 2016). Besides, inorganic dopants also increase the thermal stability and aggrandize the mechanical properties which can be ascribed to the structure and properties of inorganic materials. Dopants such as MOF (metal-organic framework) materials (Yan, Jiang, Zhao, Zeng, & Zhao, 2016; Zhang et al., 2017) and graphene oxide are widely used in PEM (Pandey, Shukla, Manohar, & Shahi, 2017; Zhang et al., 2016; Zhao, Fu, Hu, & Lü, 2016).

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As 1-D material, carbon nanotubes (CNTs) have extraordinary electrical, thermal, and mechanical properties. Thus, CNTs are promising in modern composite materials (Bounos, Andrikopoulos, Karachalios, & Voyiatzis, 2014). It is believed that CNTs form extra pathways and free volume pores for proton transport in proton exchange membranes. However, doping CNTs into PEMs is restrained mainly by two reasons. One is CNTs formed electronic channels may cause short-circuiting in fuel cells because CNT is conductive in the condition of structure relatively integrated (Liu, Wang et al., 2016). Besides, carbon nanotubes (CNTs) are easily agglomerated because of the intrinsic Van der Waals force among tubes, thus poor dispersity restrains the utility of CNT in many respects. In order to solve this problem, functionalization of CNT is widely applied (Araújo et al., 2016; Munirasu, Albuerne, Boschetti-de-Fierro, & Abetz, 2010).

In the present work, hybrids including inorganic phrase doped in PEM are widely researched, but dopants with a certain crystalline phrase are rare. Besides, reports about sodium lignin sulfonate used as surfactant to prepare titania coated CNT and as organic dopant in PEM are seldom. TCNTs with a certain crystalline phrase represents comparatively stable morphology and structure, and may build proton transfer pathways when doped in polymers. Moreover, SLS may enhance the proton conduction property of chitosan PEM.

The main novelty of our work is providing a feasible method to prepare titania coated CNT with the use of SLS and proving that SLS as dopant can enhance proton transfer in chitosan proton transfer membrane. In this work, a surfactant-warping method was used to obtain anatase titania coated CNTs and the product was then doped into chitosan membranes that aimed to build extra proton transfer pathways. To prove that, varied amounts of TCNTs were doped in the samples and the proton conductivity was tested. SLS was introduced in chitosan membranes to provide sulfonate ions which played a role as proton carriers in chitosan composite membranes. And properties of samples in another group with SLS doped were studied. The synthesis of TCNTs was confirmed by Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and X-ray diffraction (XRD). The synthesized membranes were characterized with Fourier transform infrared spectroscopy (FTIR), scanning electron telescope (SEM), thermogravimetric analysis (TG), and mechanical properties, water uptake, oxidation stability, ion exchange capability (IEC), conductivity and methanol permeability analyses to interrogate application promise in DMFC.

2. Materials and methods

2.1. Materials

Chitosan (≥90% degree of deacetylation) was provided by Shanghai Lanji technology development Co., Ltd. Sulfuric acid (98%), acetic acid (Analytical Reagent, AR)and tetrabutyl titanate(Analytical Reagent, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. sodium lignin sulfonate (80%) was supplied by Tianjin Beilian Fine Chemicals Co., Ltd. Carboxyl multi-walled CNTs (o-CNTs, 10–20 nm, –COOH content 2 wt%) was provided by Chengdu Organic Chemicals Co., Ltd.

2.2. The preparation of TCNTs

A surfactant-warping method was used in TCNTs preparation. And SLS was used as surfactant to functionalize o-CNTs. A desired amount of sodium lignin sulfonate, o-CNTs and distilled water were mixed and ground for 1 h. After ultrasonic treatment and stirring, sodium lignin sulfonate coated MWCNTs-COOH (SCNTs) was prepared. Then the sediment was vacuum filtered and dried in 60 °C.

As for SCNTs treatment, 50 mg SCNTs were added to 100 mL ethanol and ultrasonically dispersed under 100 Hz for 15 min. Then 1 mL distilled water added and stirred for 15 min. After the SCNTs were well-dispersed, 2 mL TBT was added and stirred for 4 h. The mixture then was centrifuged at a moderate speed at 8000 rpm to remove the free TiO_2 ions. The sediment was washed by distilled water till the supernatant was transparent. After the preceding process, the suspension was vacuum filtered and dried in 60 °C for 3 h. TCNTs were then calcined in 500 °C for one hour to get anatase TCNTs.

2.3. The preparation of TCNT chitosan membrane and sodium lignin sulfonate (SLS) doped TCNT chitosan membrane

A solution casting method was used in preparation of TCNT chitosan membrane (TCNTs doped in membranes were calcined TCNTs). A desired amount of TCNTs was added to 2% acetic solution and ultrasonically dispersed. Then chitosan was added and stirred under room temperature for 4 h. Then the mixture was poured in a square mold and dried in drying oven in 60 °C for 4 h. The dried membrane was then soaked in 0.5 mol L^{-1}sulfuric acid solution for 24 h for fully crosslinked. Then the membranes were washed by distilled water to remove superfluous sulfuric acid on the membrane surface. A series of composite membranes with different TCNTs content were prepared (0%, 1%, 3%, 5%, 7%, 9%) and named as CS, CS/TCNT1, CS/TCNT3, CS/TCNT5, CS/TCNT7, CS/TCNT9 respectively. And sodium lignin sulfonate doped TCNT chitosan membranes were prepared using the same method, 5 wt.% TCNTs (based on the result shown in Fig. 5(a)) and different amount of SLS (1%, 1.5%, 2%, 2.5%) were added to 2% acetic solution and then ultrasonically dispersed. A desired amount of chitosan then added in the solution and stirred for 4 h at room temperature. Then the mixture was injected in the mold mentioned before. Drying and crosslinking treatment are the same as mentioned before. And the samples were named as CS/TCNT-5/SLS-1, CS/TCNT-5/SLS-1.5, CS/TCNT-5/SLS-2 and CS/TCNT-5/SLS-2.5 respectively.

2.4. Characterization

2.4.1. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) studies were performed to find any group in cross-linked chitosan membrane and TCNTs samples using a Nicolet iS50 spectrometer. And information of the wavenumber region from 4000 to 450 cm^{-1} was collected.

2.4.2. XRD analysis

The degree of crystallinity of the TCNTs were characterized by powder X-ray diffraction (XRD, D8 DISCOVER, Bruker). The XRD patterns with diffraction intensity were recorded from 5° to 80°at a speed of 8° min^{-1}.

2.4.3. SEM studies

The morphology of chitosan membranes were collected by scanning electron telescope (SEM, Hitachi S4800) at required magnification. The membrane samples were dried in vacuum oven for 12 h at 60 °C and coated with gold before test.

2.4.4. TEM studies

The morphology of TCNTs was observed by transmission electron microscope (TEM, Hitachi H7650) at an accelerating rate of 120KV. The TCNTs sample was dispersed in ethanol, and several drops of dispersion were placed on a copper grid then dried before test.

2.4.5. Thermogravimetric (TG) analysis

Thermogravimetric analysis (TG, STA449F3) was applied to study chitosan membrane samples thermal stability. The samples was heated in 50–800 °C at the rate of 10 °C per minute at nitrogen atmosphere.

2.4.6. Tensile strength and elongation

Tensile strength and elongation of chitosan membrane samples were tested by a SANS-20 kn tensile strength tester. Before the test, the