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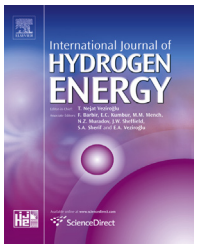

Enhancement of proton conductivity of polymer electrolyte membrane enabled by sulfonated nanotubes

Haoqin Zhang, Chuanming Ma, Jingtao Wang, Xuyang Wang, Huijuan Bai, Jindun Liu*

School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China

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ABSTRACT

Proton exchange membrane (PEM) with high proton conductivity is crucial to the commercial application of PEM fuel cell. Herein, sulfonated halloysite nanotubes (SHNTs) with tunable sulfonic acid group loading were synthesized and incorporated into sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare nanocomposite membranes. Physicochemical characterization suggests that the well-dispersed SHNTs enhance the thermal and mechanical stabilities of nanocomposite membranes. The results of water uptake, ionic exchange capacity, and proton conductivity corroborate that the embedded SHNTs interconnect the ionic channels in SPEEK matrix and donate more continuous ionic networks. These networks then serve as proton pathways and allow efficient proton transfer with low resistance, affording enhanced proton conductivity. Particularly, incorporating 10% SHNTs affords the membrane a 61% increase in conductivity from 0.0152 to 0.0245 S cm^{-1}. This study may provide new insights into the structure-properties relationships of nanotube-embedded conducting membranes for PEM fuel cell.

1. Introduction

Nanotubes, typical one-dimensional nanostructures, have become a subject of intense research owing to their unique mechanical, electrical, and geometrical properties, and have diverse applications spanning energy storage and energy conversion devices, sensors, drug delivery, semiconductor devices, and proton-conducting electrolytes [1,2]. Moreover, the properties and performances of nanotubes can be significantly intensified through coordination effects by modification with inorganic or organic components [3,4].

Proton-conducting materials with high conductivity are essential both in biological contests and in materials for alternative energy, such as proton exchange membrane fuel cell (PEMFC) [5–7]. For PEMFC, after oxidation of hydrogen at the anode, the resulting protons must be transported across a polyelectrolyte to reach the cathode and complete the conversion of chemical energy to electrical energy. The polyelectrolyte (that is proton exchange membrane, PEM) is considered to be the central and performance-limiting part. Concurrently, the state-of-the-art PEM material is perfluorinated polymer such as Nafion due to its physical and chemical stabilities coupled with high proton conductivity [8].

* *Corresponding author*. Tel./fax: +86 371 63887135.
E-mail address: jingtaowang@zzu.edu.cn (J. Wang).

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Nafion is a free radical initiated copolymer of a crystalline tetrafluoroethylene monomer backbone sequence, with pendant side chains of perfluorinated vinyl ether perfluorosulfonic acid terminated groups. The amphiphilic feature between hydrophobic backbone and hydrophilic pendant side chain drives the sulfonic acid groups to assemble into 4.0 nm clusters as inverted micelles arranged on a lattice, which are interconnected by pores or channels (about 1.0 nm) [9,10]. These clusters and channels working as fast proton transfer pathways are well-established to be the first step necessary to high proton conductivity. The connected clusters therefore afford Nafion high proton conductivity (0.1 S cm^{-1}) and low activation energy (0.092 eV) [11]. Nevertheless, these channels are much larger than the diameter of fuel molecules (e.g., 0.38 nm for CH_3OH, 0.29 nm for H_2), and consequently leads to serious fuel crossover (e.g., 3.0×10^{-6} cm^2 s^{-1} for CH_3OH, 1.0 mA cm^{-2} for H_2) [12,13]. The crossed fuels will drastically reduce the PEMFC performances due to the mixed potential effect and catalyst poisoning. Besides the high fuel crossover, the high cost and complex synthesis process of perfluorinated polymer restrict the large-scale applications of Nafion. Fortunately, sulfonated poly(ether ether ketone) (SPEEK), which is synthesized through a facile sulfonation reaction to graft sulfonic acid groups into poly(ether ether ketone) (PEEK) chains, has been considered to be one of the promising candidates for Nafion [14–17]. Similar to Nafion, SPEEK membrane also displays nanophase separation between the hydrophobic backbone and hydrophilic side chain. However, owing to its weak amphiphilic feature, SPEEK membrane exhibits narrower ion-channel size (0.5–1.0 nm), more "dead ends" and phase discontinuity in comparison to Nafion [15]. Such morphologies are beneficial to enhancing the fuel barrier properties and thus conferring SPEEK membrane much lower fuel crossover (e.g., 10^{-7} cm^2 s^{-1} for CH_3OH, 10^{-6} mA cm^{-2} for H_2) [16]. Yet the energy barrier for proton transfer would be also increased as testified by the high activation energy of 0.13 eV, in turn resulting in lower proton conductivity (around 0.01 S cm^{-1}) [18].

One facile and efficient approach to address this issue is to incorporate proton-conducting inorganic fillers for interconnecting the ionic channels (especially the dead ends) within SPEEK bulk [19–22]. Meanwhile, these inorganic fillers are usually fuel impermeable which can often reduce the fuel crossover by blocking fuel transport paths. To sum up, embedding nano-, submicron-, or micron-sized fillers within SPEEK bulk can both interconnect the channels and consequently increase proton conductivity. In particular, embedding nano-sized fillers can reduce the probability of filler agglomeration or sedimentation and then provide more conducting pathways [19]. Compared with spherical fillers (e.g., silica) and sheet fillers (e.g., montmorillonite), tubular fillers (e.g., carbon nanotube) display most significant effects in interconnecting the ionic channels and hence forming long-range uninterrupted trajectory for proton transport [20]. Among acid-group-bearing (e.g., $-SO_3H$), base-group-bearing (e.g., $-NH_2$), and neutral-group-bearing (e.g., $-OH$) fillers, acid group-bearing fillers exhibit excellent proton conductivity as a result of their high proton dissociation capability which then provide additional free protons and proton-hopping sites (i.e., $-SO_3^-$) [22]. It is thus presumed that sulfonic acid-bearing nanotubes are promising fillers to enhance the conductivity of SPEEK membrane; yet to the best of our knowledge, related investigation concerning sulfonic acid-bearing nanotubes has not been reported. While for other PEMs with similar morphologies, such as Nafion, sulfonated poly(ether sulfone ether ketone ketone) (SPESEKK), sulfonic acid-bearing nanotubes have been found to obviously facilitate proton transfer [23,24]. For instance, Pillai et al. [23] synthesized sulfonated single walled carbon nanotube (S-SWCNT) through microwave treatment followed by PTFE membrane filtration, and found that incorporation of 0.05% S-SWCNTs could give ten-times higher proton conductivity to Nafion and reduce the activation energy from 0.12 to 0.072 eV. Zhou et al. [24] synthesized sulfonated carbon nanotube (SCNT) through high-temperature sulfonation under nitrogen protection, and found that 1.5% SCNTs enhanced the conductivity of SPESEKK from 2.94 to 4.39 mS cm^{-1}.

In this study, we describe first example of using sulfonated nanotubes as inorganic fillers to enhance the conductivity of SPEEK membrane for PEMFC application. Halloysite nanotubes (HNTs), naturally two-layered aluminosilicate clay mineral ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) and available in abundance in the world, are chosen and sulfonated via a facile distillation–precipitation polymerization. Sulfonated halloysite nanotubes (SHNTs) are then impregnated into SPEEK matrix to fabricate nanocomposite membranes. The microstructure and physicochemical properties of the membranes are investigated in detail. Besides, the proton conductivity and transfer barrier of the membranes at different temperatures are systematically evaluated.

2. Experimental

2.1. Materials and chemicals

3-(Methacryloxy) propyltrimethoxysilan (MPS) was purchased by Aldrich and distilled under vacuum. Divinylbenzene (DVB, 80% divinylbenzene isomers) was supplied as technical grade by Shengli Chemical Technical Faculty, Shandong, China, and was washed with 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulfate. Styrene (St) was obtained from Aldrich and distilled under vacuum. Halloysite nanotubes were refined from clay minerals in Henan province, China. Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was obtained from Nanjing Yuanbang Engineering Plastics Co., Ltd. 2, 2′- Azobisisobutyronitrile (AIBN), dimethylformamide (DMF), acetonitrile, and sulfuric acid were purchased from Kewei Chemistry Co., Ltd. De-ionized water was used throughout the experiment.

2.2. Synthesis of the SHTNs and SPEEK

SHTNs were synthesized through distillation–precipitation polymerization method [25]: HNTs (10.0 g) were immersed into the mixture of ethanol (180 mL), water (20 mL) and aqueous solution of ammonium (15 mL) with vigorous stirring at 25 °C for 24 h. Then, excess MPS (2.0 mL) was added into the resultant mixture. After being stirred for 24 h, the MPS-modified HNTs were purified by three cycles of