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A new strategy for designing high-performance sulfonated poly(ether ether ketone) polymer electrolyte membranes using inorganic proton conductor-functionalized carbon nanotubes

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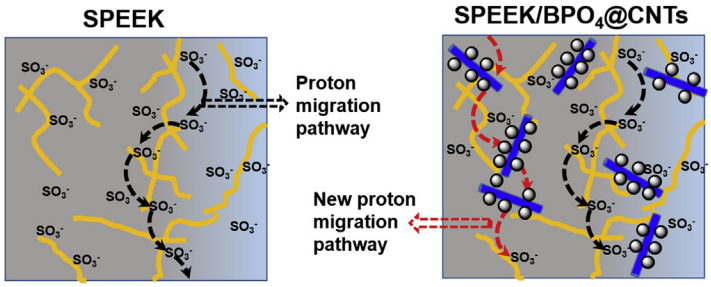
HIGHLIGHTS

- A proton conductor BPO_4 coated CNTs was prepared by a PDA-assisted sol-gel method.
- BPO_4 layer reduces the short circuit of CNTs while acts as new H^+ transfer sites.
- The composite membranes composed of SPEEK and BPO_4@CNTs were fabricated.
- Simultaneously improved mechanical property and proton conductivity are obtained.
- Providing a new strategy to modify PEMs using proton conductors-modified CNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

Remarkable progress has been made on the use of polymer electrolyte membranes (PEMs) for renewable-energy-related research. In particular, carbon nanotubes (CNTs) have emerged as versatile nanomaterials to modify PEMs. However, the inert ionic conduction ability and possible short-circuiting risk are the two major obstacles to their further development. In this work, CNTs are firstly functionalized with an inorganic proton conductor, boron phosphate (BPO_4), using a facile polydopamine-assisted sol-gel method to yield BPO_4@CNTs. This new additive is then used to modify sulfonated poly(ether ether ketone) (SPEEK). Polydopamine coating layer can act as an extraordinary glue to homogeneously adhere BPO_4 nanoparticles on CNTs, thereby not only reducing the risk of short-circuiting, but also fabricating new proton-conducting pathways in the composite membranes. A comprehensive characterization reveals that the thermal stability, tensile properties, and dimensional stability of PEMs are significantly improved. Compared with pure SPEEK, the proton conductivity of SPEEK/BPO_4@CNTs-2 is improved by 45% and 150% at 20 °C and at 80 °C, respectively. Furthermore, the H_2/O_2 cell performance of SPEEK/BPO_4@CNTs-2 membrane exhibits a peak power density of 340.7 mW cm^{-2} at 70 °C, which is

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significantly better than that of pure SPEEK (254.2 mW cm^{-2}), demonstrating the great potential of proton conductors-functionalized CNTs in PEMs.

1. Introduction

Polymer electrolyte membranes (PEMs) are a critical component in energy conversion devices, including proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [1,2]. Their main functions are to transport protons and block the direct contact of fuels and oxidants. The most widely used PEMs are Dupont's Nafion-based perfluorinated sulfonic acid membranes, which possess inert chemical properties and high proton conductivity in the fully hydrated state. However, the high cost and unstable proton conductivity at high temperatures are the major obstacles for its large-scale commercial application.

Seeking alternatives to Nafion has been the major research focus in recent decades. Sulfonated aromatic polymers, such as sulfonated polyether sulfone [3,4], sulfonated polyimide [5,6], and sulfonated poly(phenylene oxide) [7,8], have been considered to be promising candidates. Among these sulfonated aromatic polymers, sulfonated poly(ether ether ketone) (SPEEK) has drawn considerable attention due to its relative high proton conductivity, excellent thermo-chemical properties, simple preparation procedures and low cost [9]. However, similar to the other sulfonated aromatic polymers, one of the shortcomings of SPEEK is the fewer number of connected sulfonic acid-aggregated hydrophilic ion channels when compared with perfluorinated sulfonic acid polymers. Although increasing the sulfonation degree of SPEEK is a simple solution to increase its proton conductivity, excessive water swelling followed by deteriorated mechanical properties unfortunately emerge at the same time [1,9]. Among the several strategies explored, fabricating composite membranes of SPEEK and inorganic additives was an effective way to retain the proton conductivity without compromising the mechanical properties [10].

Currently, carbon nanotubes (CNTs) have emerged as a novel type of advanced inorganic fillers due to their unique properties including an extremely high tensile modulus and strength, a large surface-to-volume ratio, high flexibility, excellent electrochemical activity and potential utilization in the field of energy materials [11] as high-performance nanocomposites [12]. Since the first report by Liu et al. [13] in 2006 explained that the risk of short-circuiting in PEMs caused by the excellent electrical conductivity of CNTs could be eliminated by controlling the CNT concentration below the percolation threshold, many studies have focused on the use of CNTs to enhance the performance of PEMs.

Except for the inert proton conduction nature of pristine CNTs, their poor dispersion in PEMs has limited their functions and wide application. Several modification methods have been proposed to improve their dispersion and maximize their functions in PEMs. Pillai's group demonstrated the use of sulfonic acid-functionalized single-walled CNTs [14] and multiwalled CNTs [15] for enhancing the proton conductivity and mechanical strength of Nafion. Subsequently, they further verified that phosphonated CNTs can effectively prevent the leaching of phosphoric acid in phosphoric acid-doped polybenzimidazole (PBI) membranes during sustained operation [16,17]. Apart from modifying CNTs through these simple acid groups, ion-conductive polymers were also used to modify CNTs to enhance their proton conductivity as well as compatibility in PEMs. Liu et al. [18] prepared Nafion-functionalized CNTs using an ozone-mediated process and used them as additives in the fabrication of Nafion-based composite membranes. The composite membrane with a Nafion-functionalized CNT content of 0.05 wt% exhibited a five-fold increase in proton conductivity and a 1.5-fold increase in tensile strength compared to a pristine Nafion membrane. They proposed that Nafion chain-coated layers could make the functionalized CNTs act as a direct proton-conducting pathway for rapid proton transport through the composite membranes. In their following work, they used Nafion-, PBI- and poly(styrene sulfonic acid)-functionalized CNTs to modify PBI [19] and chitosan [20] membranes and confirmed the availability of these functionalized CNTs. However, these authors also highlighted that the concentration of functionalized CNTs should be controlled at a low value, such as 1.0 wt%, to prevent CNT aggregation and a sharp increase in electrical conductivity in the PEMs. To disperse high concentrations of CNTs uniformly inside the PEM matrix without causing short-circuiting, polysiloxane-functionalized CNTs were synthesized by covalently grafting hydrophilic layers composed of poly(oxyalkylene) diamines and tetraethyl orthosilicate-reinforced polysiloxane in a layer-by-layer manner onto the surface of CNTs and were then used as an additive to modify Nafion [21]. The results showed that the polysiloxane coating layer can effectively prohibit electron conduction through the composite membranes even with high CNT contents (5–20 wt%). However, the preparation process for these polysiloxane-functionalized CNTs was complex and time consuming, representing the main obstacle for their practical applications in PEMs. Therefore, effective coating materials and facile coating method are crucial for fully playing the functional modification role of CNTs in the PEMs field.

Recently, we prepared insulated and hydrophilic silica-coated CNTs (SiO_2@CNTs) using a facile sol-gel process and used these CNTs as a new additive to modify SPEEK [22] and natural polymer chitosan [23] to fabricate PEMs. Silica-coated CNTs not only eliminated the risk of short-circuiting but also enhanced the interfacial interaction between the CNTs and matrix and thus promoted the homogeneous dispersion of the CNTs in the polymer matrix. Although they had improved mechanical properties and high thermal and oxidative stability, the composite membranes exhibited decreased proton conductivities in both cases because of the inert proton conduction activity of silica. To address this issue, in this research, boron phosphate (BPO_4), which is a super inorganic proton conductor that has been widely proved in other studies [24–26] and our previous work [3], was first utilized to modify CNTs using a facile polydopamine-assisted sol-gel method to simultaneously enhance the proton conductivity and mechanical properties of SPEEK. The SPEEK/BPO_4-coated CNT (BPO_4@CNTs) composite membrane was extensively characterized to understand how the BPO_4@CNTs effect the structure, morphology, thermal and mechanical properties and proton conduction behavior of the composite membranes.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) victrex® 450 PF was purchased from Victrex Inc. (England) and was dried under high vacuum at 100 °C for 10 h before use. Multi-walled CNTs (MWCNTs)