



A poly(vinyl alcohol)-based composite membrane with immobilized phosphotungstic acid molecules for direct methanol fuel cells



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ABSTRACT

Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW) molecules were anchored onto carbon nanotubes (CNTs) by electrostatic self-assembly using poly(diallyldimethylammonium chloride) (PDDA); subsequent incorporation of these particles into poly(vinyl alcohol) (PVA) afforded a methanol-blocking membrane for direct methanol fuel cell (DMFC) application. The prepared membrane exhibited a significantly higher proton conductivity of 9.4 mS cm^{-1} at 60°C and satisfactory proton conductivity stability over a 120-h test than a PVA membrane. Moreover, the composite membrane showed a decrease in the methanol permeability by $\sim 40\%$ compared to a PVA membrane ($6.10 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) and much better proton-to-methanol selectivity because of a higher dimensional stability after the incorporation of CNTs. A single DMFC based on the prepared membrane exhibited a maximum power density of 16 mW cm^{-2} at 60°C . Thus, CNT-PDDA-HPW/PVA membranes have a great potential as an alternative proton exchange membrane for DMFC application.

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1. Introduction

Direct methanol fuel cells (DMFCs) are an alternative power source for portable devices because of their high energy density, low environmental emissions, and long life-time [1–3]. Perfluorosulfonic polymers such as Nafion are commonly used in DMFCs as the electrolytes because of their high proton conductivity, chemical durability, and mechanical strength [4,5]. However, methanol permeation from anode to cathode through a Nafion membrane decreases the open circuit voltage (OCV) and poison the electrocatalyst in the cathode [6,7]. The methanol crossover and high cost of Nafion membranes hinder the commercialization of DMFCs [8,9].

Much effort has been made to develop alternative proton exchange membranes (PEMs) for DMFCs with improved functionality and low cost [10]. An effective way to decrease the extent of methanol crossover is to replace Nafion membrane with methanol-blocking polymeric materials such as chitosan [11], poly(vinyl alcohol) (PVA) [12], poly(ether ether ketone) [13–15], and polybenzimidazole [16]. PVA is one of the best methanol-blocking polymers because it can selectively transport water over methanol [17]. However, PVA membranes suffer from poor proton

conductivity because PVA does not contain any ionic functional group [18]. Therefore, a proper functionalization of PVA membrane is required to improve the proton conductivity. In general, PVA membranes can be functionalized using two methods. One is the sulfonation of PVA membranes [19] or reaction with sulfonated polymers [20] to incorporate ionic functional groups. The other is the incorporation of organic materials such as 2-methyl-1-propanesulfonic acid [21] and sulfonated poly(ether ether ketone) [22], or inorganic materials such as phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW) [23] and graphene oxide [24] with proton conductivity property as the filler.

Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW), a solid heteropoly acid, is an outstanding proton conducting material because of its unique structure and strong acidity [25]. The incorporation of HPW into polymeric materials is a useful approach to increase the proton conductivity of membranes [26–28]. However, HPW can be easily removed in water owing to its high water solubility [29], making it challenging to retain HPW in membranes to maintain a high proton conductivity. Diverse methods have been developed in our previous work to immobilize HPW in a PEM, thus reducing its leaching and improving the membrane stability. For instance, HPW molecules were assembled into the ordered nano-channel of the mesoporous silica (MCM-41) via vacuum impregnation method. The composite membrane showed competitive conductivity and high stability [30]. Furthermore, HPW was anchored onto a polyvinylpyrrolidone [31,32] or chitosan [11] matrix with NH_2 or

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NR₂ functional groups owing to the strong interaction between HPW and these functional groups. However, the immobilization of HPW in a polymer matrix without functional groups such as PVA is still a challenge.

In this study, electrostatic self-assembly method was used to anchor HPW on carbon nanotubes (CNTs) using poly(diallyldimethylammonium chloride) (PDDA). Then, the CNT-PDDA-HPW particles were added to PVA to prepare a PEM for DMFC application as shown in [Schematic 1](#). CNTs were functionalized with PDDA to form positively charged PDDA-CNTs [33]. HPW was then self-assembled onto CNTs via the electrostatic force between the negatively charged HPW and positively charged PDDA-functionalized CNTs. Finally, the CNT-PDDA-HPW particles were incorporated into PVA membranes to form composite membranes. The mechanical properties, proton conductivity, methanol permeability, selectivity factor, and single cell performance of the composite membranes were studied in detail for potential application in DMFCs.

2. Experimental

2.1. Materials

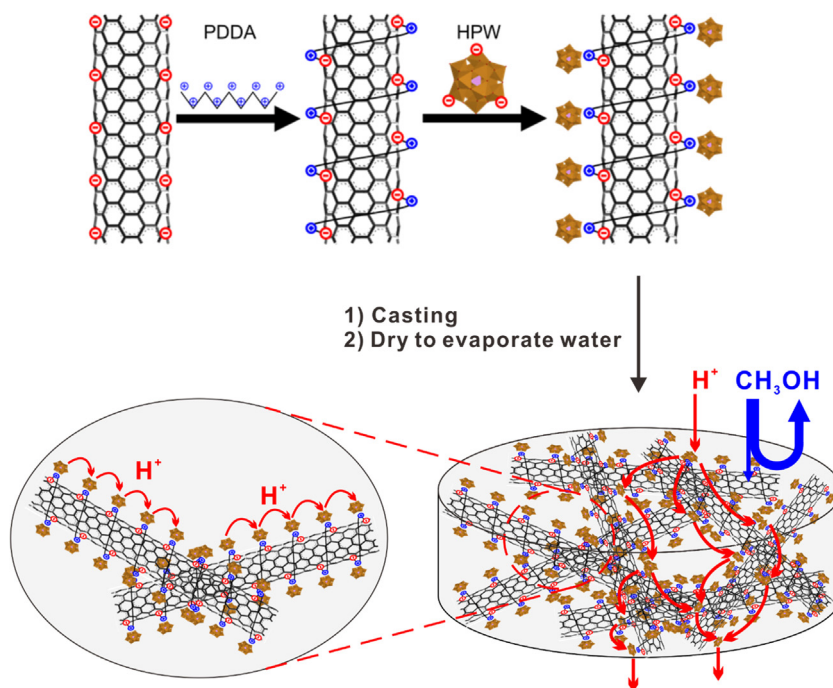
PVA (97%, Mw ≈ 77000), methanol (AR grade), and ethanol (AR grade) were purchased from Beijing Chemical Reagent Company. CNTs (95%) were purchased from Nanjing Xianfeng Nano-materials Technology Co., Ltd (China). Aqueous PDDA solution (35%) was purchased from Aladdin Company. HPW (AR grade) was purchased from Tianjin Jinke Fine Chemical Research Institute (China). Commercial Nafion212 (EW 2100, thickness ~50 μm) membrane was purchased from Du Pont Co. Pt/C (40 wt%) and PtRu black for preparing the catalyst ink were purchased from E-TEK. All the reagents were used as received without further purification.

2.2. Preparation of CNT-PDDA-HPW particles

The preparation of CNT-PDDA-HPW composite is shown in [Schematic 1](#). PDDA solution (6 g, 35 wt%) was added to ultra-pure water (100 mL) to form a 2 wt% PDDA solution. Then, CNTs (2 g) were added to 2 wt% PDDA solution (100 mL), and the solution was ultrasonically dispersed three times at 30 min intervals, 10 min each time. The CNT-PDDA particles were filtered, washed with ultra-pure water several times, and added to 0.5 wt% HPW solution (100 mL). The solution was ultrasonically dispersed and filtered as described above. The CNT-PDDA-HPW particles were washed with ethanol and dried at 50 °C in vacuum for 4 h.

2.3. Preparation of CNT-PDDA-HPW/PVA membranes

The CNT-PDDA-HPW/PVA membranes were denoted as x %-CNTs-PDDA-HPW/PVA, where x refers to the ratio of the weight of CNT-PDDA-HPW particles to the total weight of composite membranes. For example, the 1%-CNT-PDDA-HPW/PVA membrane was fabricated as described below. PVA (5 g) was added to ultra-pure water (95 mL) and dissolved by heating to form a 5 wt% PVA solution. The PVA solution was filtered to remove the insoluble impurities. CNT-PDDA-HPW particles (2.5 mg) were added to ultra-pure water (2 mL) and ultrasonically dispersed as described above. Then, 5 wt% PVA solution (5 mL) was blended with the above solution. The blended solution was dispersed 20 times at 7 s intervals, 5 s each time using an ultrasonic cell disruptor. The polymer solution was degassed, cast onto a glass plate, and dried at 70 °C for 24 h and 100 °C for 1 h to obtain the 1%-CNT-PDDA-HPW/PVA membrane. For comparison, 3%-HPW/PVA composite membrane and pure PVA membrane were also prepared.



Schematic 1. Preparation of CNTs-PDDA-HPW/PVA membranes. HPW molecules were self-assembled on PDDA-functionalized CNTs via electrostatic interaction. Then, the CNTs-PDDA-HPW particles were incorporated into PVA membranes to form a composite membrane. The red and blue arrows represent the possible proton and methanol transport pathways, respectively.

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