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Novel methanol-blocking proton exchange membrane achieved via self-anchoring phosphotungstic acid into chitosan membrane with submicro-pores



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ABSTRACT

A novel chitosan/phosphotungstic acid composite proton exchange membrane was prepared by self-anchoring phosphotungstic acid into chitosan membrane with submicro-pores (*smp*CTS/HPW). The *smp*CTS/HPW membrane exhibits enhanced proton conductivity and excellent methanol-blocking performance. The proton conductivity of the composite membrane is significantly affected by the content of HPW which could be modulated by introducing soft template P123 into the membrane to obtain varied porosity. The highest proton conductivity (σ) of the composite membrane, $2.9 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C, was achieved with soft template P123 content of 40%. Moreover, the *smp*CTS/HPW membrane showed very stable proton conductivity under deionized water condition due to HPW molecules self-anchored in the CTS matrix. The methanol permeability (P) of 40%-*smp*CTS/HPW membrane was $4.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was 60% lower than that of Nafion 212 membrane. The highest selectivity factor (σ/P), $2.27 \times 10^4 \text{ S cm}^{-3} \text{ s}$, was obtained on 40%-*smp*CTS/HPW membrane. A direct methanol fuel cell (DMFC) based on the 40%-*smp*CTS/HPW membrane achieved a peak power density of 16 mW/cm^2 at 80 °C. This study indicates the promising potential of *smp*CTS/HPW membrane as alternative proton exchange membrane for DMFCs application.

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1. Introduction

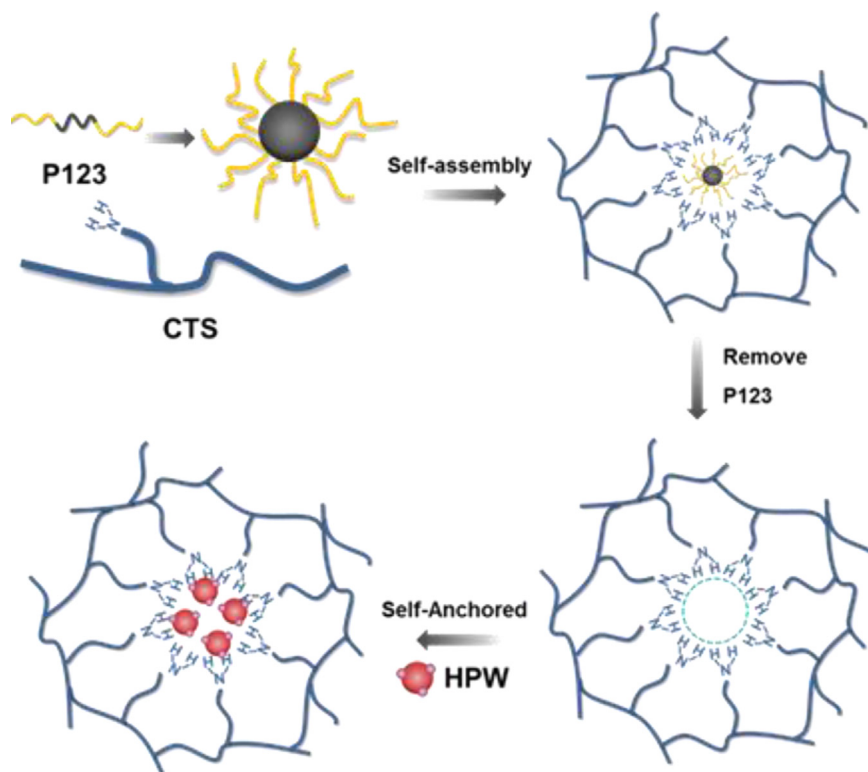
Direct methanol fuel cells (DMFCs) have caught much attention for the quick start-up at low temperature, high energy density, rich sources, and convenient transportation and storage of fuel methanol [1,2]. In DMFCs, the Nafion membrane produced by DuPont is used most widely due to its high proton conductivity as well as excellent chemical, mechanical and thermal stability [3], however, the methanol permeability and high cost limit its scalable application [4–7]. In the past two decades, a continuing effort has been made to develop polymer electrolyte membrane integrated with high conductivity, low methanol permeability and low cost [8–13]. Chitosan (CTS), a kind of abundant and low cost natural polymer material with low methanol permeability [14], has shown promising properties as proton exchange membrane (PEM) for DMFCs [15–18]. However, the very low inherent proton conductivity of pristine CTS membrane limits its application in DMFCs. Inorganic proton acids (such as H_2SO_4 [19] and H_3PO_4 [20]) are often introduced into

the CTS membrane to improve the proton conductivity, but they are easy to leach, which leads to the unstable proton conductivity of membrane and inferior mechanical performance. Thus, it is a great challenge to obtain high and stable proton conductivity of CTS-based PEMs with satisfied mechanical performance.

Heteropoly acids (HPAs), such as phosphotungstic acid (HPW), are well known superionic proton conductors in the fully hydrated states [21], and are widely used to enhance proton conductivity [22] or as the only proton conductor of solid electrolyte for fuel cell applications [23]. However, it is difficult to introduce HPW into CTS to prepare PEMs because white flocculent precipitate will produce when they are mixed directly (Fig. S1 in ESI†), which makes HPW retains at the surface of membrane and could not enter into the bulk phase to form continuous proton transport pathway (Fig. S2), as well as the failure of membrane preparation through solution casting. To overcome this issue, M. Santamaria and C.M. Pecoraro et al. used the porous anodic alumina to prepare flat homogenous CTS/HPW membranes with good performance in terms of power density [24,25]. Recently, novel PEMs were developed in our work by self-assembling HPW into mesoporous inorganic materials [26] or self-anchoring HPW into polymer

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Scheme 1. Schematic illustration of the preparing process for the *smpCTS/HPW* membrane.

matrices (PES/PVP) through the interaction between HPW and N-heterocycles of PVP [27], which exhibited excellent comprehensive performance (such as competitive conductivity and high stability) and hold satisfied applications in fuel cells.

Herein, we present a strategy to fabricate a novel CTS-based PEM for DMFCs by self-anchoring HPW into prepared CTS membrane with submicro-pores (*smpCTS/HPW*). The *smpCTS/HPW* membrane exhibits enhanced proton conductivity and maintains good methanol-blocking performance. Furthermore, the *smpCTS/HPW* membrane shows very stable proton conductivity under a deionized water condition during a test period of 108 h. As a result, the DMFC based on the composite membrane exhibited a peak power density of 16 mW/cm² at 80 °C. This strategy offers a new way for the preparation of PEM with both high proton conductivity and low methanol permeability.

2. Experimental

2.1. Materials

Chitosan powder (the deacetylation degree $\geq 95\%$) had the molecular weight of 60,000 g mol⁻¹ supplied by JINAN HAIDEBEI MARINE BIOENGINEERING CO. LTD. Glacial acetic acid and sodium hydroxide were produced by Beijing Chemical Works. Phosphotungstic acid (H₃PW₁₂O₄₀ · nH₂O) was supplied by Sinopharm Chemical Reagent Beijing Co. Ltd. The average molecular weight of Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (PEG-PPG-PEG* Pluronic[®] P123) was about 5800.

2.2. Membrane preparation

CTS powder was dissolved in 2% (V/V) acetic acid aqueous solution under stirring for 2 h at room temperature to get a 2.5 wt% homogeneous CTS solution. Simultaneously, 0.75 wt% P123

aqueous solution was obtained by dispersing 0.75 g P123 into 100 mL deionized water with stirring for 12 h. Afterwards, P123 aqueous solution with different volume (10 wt%, 20 wt%, 30 wt% and 40 wt% corresponding to CTS) were mixed with CTS solution under constant stirring for another 4 h. The mixed solution was then cast onto a clear glass plate and dried at 40 °C for 24 h, 70 °C for 2 h and 100 °C for 1 h in turn. The obtained membrane was immersed in 1 M NaOH solution for 12 h to remove residual acetic acid solvent, followed by washing with deionized water at 60 °C for 12 h to ensure most of P123 is removed. Finally, the CTS membranes with submicro-porous structure were immersed in 1 wt% HPW aqueous solution for 24 h. The prepared membranes were all marked as *n-smpCTS/HPW* (*n* denoted the weight percentage of P123 corresponding to CTS).

2.3. Membrane characterization

The morphologies and the elemental composition of the *smpCTS/HPW* membrane were observed by using field emission scanning electron microscope (FESEM, JMS-7500F) equipped with a probe for energy-dispersive X-ray scanning at 20 kV accelerating voltage. For SEM characterization, the cross-section of samples was obtained by rupturing in liquid nitrogen. And then the cross-section and surface of the samples were sputtered of gold for 60 s. The chemical structures of the membranes were characterized by Fourier transform infrared spectrometer (FTIR, Nicolet AVATAR 470) in the wavelength range from 4000 to 600 cm⁻¹.

2.4. The HPW content

To analyze the HPW content of the *smpCTS/HPW* membrane, the *smpCTS/HPW* membrane and the corresponding *smpCTS* membrane were dried at 80 °C for 24 h to achieve a constant weight state, then the weight of membrane samples were measured quickly, marked as *M*₁ and *M*₂, respectively. The final values

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