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Enhanced proton conductivity of hybrid membranes by incorporating phosphorylated hollow mesoporous silica submicrospheres

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ABSTRACT

Hollow mesoporous silica submicrospheres (HMSS) are prepared with one-dimensional hexahedral mesopores regularly aligned along the radial directions of the silica shells. Both the outer and the inner surfaces of the mesoporous shells, as well as the mesopore walls are phosphorylated (PHMSS). Moreover, the lumen of PHMSS serves as accommodation for amino tris(methylene phosphonic acid) (ATMP) with large amount of phosphoric acid groups. Phosphorylated submicrospheres (PHMSS-ATMP) with multi-functionalities are thus prepared. After incorporating PHMSS-ATMP into chitosan (CS) matrix, the hybrid membranes were fabricated. The water uptake, anti-swelling properties and the proton conductivities are all enhanced. Particularly, the proton conductivities are considerably elevated and the highest proton conductivity is $9.4 \times 10^{-2} \text{ S cm}^{-1}$ at 110 °C 100% RH for the membrane with 7.5 wt% of PHMSS-ATMP; the proton conductivities of CS/PHMSS-ATMP hybrid membranes at 80 °C and low humidity are increased by two orders of magnitude compared to the pristine CS membrane. The enhanced performance could be attributed to the proton conducting groups introduced by PHMSS-ATMP: $-\text{PO}_3\text{H}_2$ groups are anchored on the surface of PHMSS-ATMP, and proton conducting channels could be formed by the mesopores of the silica shell, and the lumen could serve as acidic reservoirs.

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1. Introduction

Direct methanol fuel cell (DMFC) is recognized as a competitive technology option for energy conversion because of the growing environment and energy problems [1]. As the key component of fuel cells, the proton exchange membranes (PEMs) are developed to achieve higher proton conductivity at elevated temperature and low humidity [2]. The most widely studied PEMs are employing sulfonated acid groups ($-\text{SO}_3\text{H}$) as proton conducting groups represented by Nafion[®] membranes. However, it has been increasingly accepted that PEMs adopting proton conducting groups with suitable proton-donating capacity and proton-accepting capacity are potential alternative candidates especially at elevated temperature and low humidity conditions [3]. Phosphoric acid group ($-\text{PO}_3\text{H}_2$) is such a group that could provide excess protons as proton donor and also stabilize excess protons as proton acceptor [2]. Extensive hydrogen network could be formed in phosphoric acid, and $-\text{PO}_3\text{H}_2$ groups exhibit moderate water retention property and

lower proton barrier when compared to $-\text{SO}_3\text{H}$ groups (the water bending energy for $-\text{PO}_3\text{H}_2$ and $-\text{SO}_3\text{H}$ groups is 44.4 kJ mol^{-1} and 47.3 kJ mol^{-1} , respectively, and the average zero point energy for $-\text{PO}_3\text{H}_2$ and $-\text{SO}_3\text{H}$ groups is 37.2 kJ mol^{-1} and 69.6 kJ mol^{-1} , respectively) [4–6].

Phosphorylated proton exchange membrane matrix has been synthesized by post-phosphorylation of polymers or direct polymerization of monomers with $-\text{PO}_3\text{H}_2$ groups [7]. For the complexity of the preparation methods, many more efforts have been put into doping phosphoric acid directly into the membrane matrix, especially into membranes with basic groups like polybenzimidazole (PBI) membranes [8]. To prevent the possible leaching of phosphoric acid, $-\text{PO}_3\text{H}_2$ groups could be immobilized onto inorganic skeletons to form organic–inorganic hybrid membranes. PEMs with enhanced performance were fabricated by direct blending of organic matrix with phosphorylated inorganic materials, including phosphorylated silica, phosphorylated titania, zirconium phosphates, phosphonated carbon nanotubes, etc. [9–15]. Alternatively, inorganic precursors could be phosphorylated first and then introduced into membrane matrix by *in situ* sol–gel process [16,17]. The phosphorylated silica additives were synthesized by hydrolysis and polycondensation of phosphoryl-silane with orthosilicate and incorporated into Nafion membrane to enhance

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the membrane proton conductivity at low humidity [18]. With the content of 10 wt% of phosphorylated silica, the proton conductivity of the hybrid membrane was $2.6 \times 10^{-2} \text{ S cm}^{-1}$ at 85 °C and 50% RH, which was 24% higher than that of the pristine Nafion membrane. Phosphoryl-silane could also crosslink with orthosilicate first and then be added to PBI to allow further intercrosslinking with imidazole –NH groups [19]. It was confirmed that the $-\text{PO}_3\text{H}_2$ groups anchored on the inorganic phase were helpful for the proton conduction in the membrane. Phosphorylated hybrid membranes are a kind of promising proton exchange membranes for fuel cell applications.

The meso-structure of ordered mesoporous silica is beneficial for the functionalization of proton conducting groups on the pore walls, and could also promote water retention property by the moisture adsorption inside the mesopores [20,21]. Moreover, proton conducting groups, such as heteropolyacids and protic ionic liquids (PILs) could be confined in the mesopores to form proton conducting channels. Phosphotungstic acid (HPW) was assembled on mesoporous silica matrix, and the membrane was proved to operate efficiently at temperatures below 200 °C [22]. Meso-structure was suggested to raise the PIL retention ability of the membranes by the capillary forces introduced by the mesopores [23]. Similar to the accommodation property of the mesoporous structure, organic or inorganic capsules with hollow structures can also provide retention properties for proton conducting groups or water molecules [24]. Hollow silica spheres with amorphous pores in the shell were modified by phosphorylated polymers, and when added into membrane matrix the cavities acted as reservoirs for water retention [13]. When considering the polymer as PEM matrix, Nafion[®], sulfonated poly(ether ether ketone), sulfonated poly(aryl ether sulfones), sulfonated polyimides have been studied widely [25–30]. Proton conducting channels could be formed by the phase separation of the hydrophilic region (containing $-\text{SO}_3\text{H}$ groups) and the hydrophobic region (mainly providing the robust stability of the membrane matrix), leading to fast proton conduction [1]. However, the price of Nafion[®] membrane is high and the fuel permeation is often severe, meanwhile, there is a trade-off between the proton conducting property and the methanol permeability of the other kinds of PEMs. Polymers like chitosan (CS) have also been studied as PEMs [31]. CS polymers could be prepared by the deacetylation of chitin, which is quite abundant in nature. Besides the low price, the fuel permeability could be significantly decreased for the semi-crystal nature of CS polymers. While it is obvious that there is no microphase separation structure in CS matrix, no obvious proton conducting channels could be formed in the microscopic scale, leading to relative lower proton conducting properties of chitosan membranes compared to those of many other proton exchange membranes such as Nafion[®]. But, it could be speculated that chitosan would be suitable as the polymer matrix of the organic–inorganic hybrid membranes to reveal the effects of the inorganic fillers in rendering both the proton conducting sites and the proton conducting channels [32].

In this study, hollow mesoporous silica submicrospheres (HMSS) were prepared, and one-dimensional hexahedral mesopores regularly aligned along the radial directions in the silica shells. The silica submicrospheres were phosphorylated by different methods: both the outer and inner surfaces of the hollow structures, together with the meso-pore walls of the silica shells were phosphorylated (PHMSS); furthermore, amino tris(methylene phosphonic acid) (ATMP) with large amount of phosphoric acid groups was encapsulated in the lumen of PHMSS (PHMSS-ATMP). Afterwards, the phosphorylated submicrospheres (PHMSS-ATMP) were incorporated into chitosan (CS) membrane matrix to fabricate phosphorylated hybrid membranes (CS/PHMSS-ATMP). The performance of the hybrid membranes, including water

uptake property, methanol permeability and proton conductivity at high temperature and low humidity were explored. Proton conducting groups were supposed to be anchored on the surface of PHMSS-ATMP, and proton conducting channels could be formed in the mesoporous shells; moreover, large amounts of proton conducting groups could be kept in the acidic reservoirs of the hollow structures.

2. Experiment

2.1. Materials and chemicals

Cetyltrimethylammonium bromide (CTAB, 99%), amino tris (methylene phosphonic acid) (ATMP, 50 wt% aqueous solution), chitosan (CS, high viscosity > 400 mPa s, 179.17 (MW)) were purchased from Aladdin-reagent. Tetraethyl orthosilicate (TEOS, reagent grade), 3-glycidyloxypropyltrimethoxysilane (GPTMS, AR) and phosphorus oxychloride (POCl_3 , > 98 wt%) were purchased from Sigma-Aldrich Co. LLC., J&K Scientific Ltd. (Beijing) and Shanghai Guangzan Chemical Scientific Ltd., respectively, and used without further purification. Toluene (AR) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. and was distilled prior to use.

All the other materials and chemicals were commercially available with analytical pure degree, and used without purification. De-ionized water was used throughout the work.

2.2. Preparation and phosphorylation of the hollow mesoporous silica submicrospheres

2.2.1. Preparation of solid silica submicrospheres as the core (sSiO₂)

Hollow mesoporous silica submicrospheres (HMSS) were prepared by the method reported in the literature [33]. First, solid silica submicrospheres (sSiO₂) were prepared by the typical Stöber method [34]: TEOS (9.5 mL) was added dropwise to the well-mixed solution of ethanol (200 mL), water (20 mL), and ammonia solution (7 mL) under vigorous stirring and the solution was kept stirring at room temperature overnight. The sSiO₂ were purified by three cycles of centrifugation and re-suspended in ethanol with ultrasonic bathing (ethanol washing), and dried in a vacuum oven at room temperature till constant weight. The product sSiO₂ was used as the core in the following process.

2.2.2. Preparation of the mesoporous silica shell on the solid silica submicrosphere core (CTAB@SiO₂/sSiO₂)

250 mg of the as-prepared sSiO₂ were homogeneously dispersed in 50 mL of de-ionized water by vigorous stirring for 30 min. The suspension was then added into the well-mixed solution of CTAB (375 mg), water (75 mL), ethanol (75 mL), and ammonia solution (1.375 mL) and the mixture was stirred at room temperature for 0.5 h. Then 0.625 mL of TEOS was added quickly and the reaction was kept stirring for 6 h. The products CTAB@SiO₂/sSiO₂ were purified by three cycles of centrifugation (water washing) and re-suspended in 50 mL of de-ionized water.

2.2.3. Etching the silica submicrosphere core to prepare hollow structure (hollow CTAB@SiO₂)

The product CTAB@SiO₂/sSiO₂ was homogeneously dispersed in 0.2 mol L⁻¹ of Na₂CO₃ aqueous solution. After the solution was stirred at 50 °C for 19 h, the products hollow CTAB@SiO₂ were purified by three cycles of centrifugation (water washing), and dried in a vacuum oven at room temperature till constant weight.

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