



Enhanced proton conductivity of the proton exchange membranes by the phosphorylated silica submicrospheres

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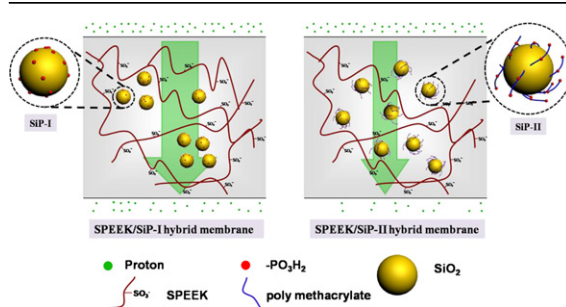
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HIGHLIGHTS

- ▶ Phosphorylated silica with different chain lengths and $-\text{PO}_3\text{H}_2$ amounts were prepared.
- ▶ SPEEK membranes doped with phosphorylated silica were fabricated.
- ▶ Proton conductivity was dependent on the $-\text{PO}_3\text{H}_2$ amounts and grafted chain lengths.
- ▶ The highest conductivity was 0.335 S cm^{-1} at 60°C (100 RH).
- ▶ The proton conduction was tentatively explained by effective acidic group amounts.

GRAPHICAL ABSTRACT



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ABSTRACT

Two kinds of phosphorylated silica submicrospheres were synthesized and incorporated into the sulfonated poly(ether ether ketone) (SPEEK) matrices to fabricate the hybrid membranes. Phosphorylation was carried out by the reaction of phosphorus oxychloride and the epoxy groups on the silica surface introduced by glycidyl-silane (SiP-I) or poly(glycidyl methacrylate) (SiP-II). The length of the chains and the amount of phosphoric acid groups ($-\text{PO}_3\text{H}_2$) grafted on the silica surface were tuned by the above two different phosphorylation methods. The dispersion of SiP-II, anti-swelling and methanol resistant property of the SPEEK/SiP-II hybrid membranes were all enhanced. And the proton conductivity was increased by doping with both kinds of phosphorylated silica particles. While the SPEEK/SiP-I hybrid membranes with less amounts of $-\text{PO}_3\text{H}_2$ groups showed unexpectedly much higher proton conductivities than the SPEEK/SiP-II hybrid ones at the same loadings ranging from 5 wt% to 20 wt%, and the highest reached 0.335 S cm^{-1} at 60°C and 100% RH. The result was tentatively discussed in terms of effective proton-conducting groups/sites instead of the absolute amount of acidic groups.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are potential candidates for applications in energy conversion and storage, and can be used in diverse fields, including portable, stationary and transportation uses [1]. Direct methanol fuel cells (DMFCs) are attractive for the use of liquid feed fuel which simplifies the fuel delivery and storage to some extent [2]. Extensive studies have been reported to

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develop organic–inorganic hybrid membranes for the enhancement of the fuel cell performance, attributed from the combination of the advantages of the inorganic fillers (e.g., mechanical, thermal and chemical stability) and the organic polymer matrix (e.g., flexibility, ductility and the ease of processability) [3].

Nowadays, sulfonic acid groups ($-\text{SO}_3\text{H}$) are most widely used as proton conducting sites which are sensitive to the humidity [4]. To render the PEMs with enhanced water retention property, a variety of hygroscopic solid or porous inorganic fillers have been incorporated into polymer matrix, which exhibited high concentration of hydroxyl or/and acidic groups and rich hydrogen-bonding sites [1,5]. Among them, silica is most widely used due to its hygroscopic nature, versatile functionality and rich amount in nature. To endow silica the proton conductive property, sulfonation was explored extensively because of the relatively high proton conductivity of the $-\text{SO}_3\text{H}$ groups at highly hydrated conditions and the liability of functionalization. Sulfonation could be achieved by the reaction with reagent like chlorosulfuric acid and the proton conductivity of the hybrid membranes could be compensated or improved after the introduction of the proton-conducting acidic sites [6].

Recently, much more attention has been directed toward PEMs based on phosphoric acid groups ($-\text{PO}_3\text{H}_2$) as alternatives for DMFC applications. Compared with $-\text{SO}_3\text{H}$ groups, the amphoteric and high dielectric constant property of the $-\text{PO}_3\text{H}_2$ groups can facilitate the self-dissociation and charge separation of the acid and thus leading to a high concentration of proton, which is especially beneficial for the membrane performance in the high temperature and low humidity environments [7,8]. The higher water binding energy (47.3 kJ mol^{-1} and 44.4 kJ mol^{-1} for $-\text{PO}_3\text{H}_2$ and $-\text{SO}_3\text{H}$, respectively) and the lower average zero point energy of $-\text{PO}_3\text{H}_2$ (37.2 kJ mol^{-1} and 69.9 kJ mol^{-1} for $-\text{PO}_3\text{H}_2$ and $-\text{SO}_3\text{H}$, respectively) imply the higher water retention property and lower proton conduction barrier [9]. $-\text{PO}_3\text{H}_2$ groups also display better thermo-oxidative stability [7]. Hence, PEMs such as phosphorylated polymeric or organic–inorganic hybrid membranes have triggered intensive research interest. Different from the vast kinds of sulfonated polymer materials, the direct polymerization of the phosphorylated monomers or the post-phosphorylation of the polymer main chains were studied sparsely due to the more complicated chemistry and synthetic procedures [10]. Facile phosphorylation methods were developed by doping phosphoric acid (H_3PO_4) into the polymer matrix, mainly polybenzimidazole (PBI) [11]. While H_3PO_4 was soluble in water and could leach out under the humid fuel cell application environments, thereby phosphorylated hybrid membranes made by fixing $-\text{PO}_3\text{H}_2$ groups on inorganic supports, like silica materials, were competitive candidates. The phosphorylated silica materials could be synthesized via co-condensation of hydrolyzed phosphoric-silane and tetraethyl orthosilicate (TEOS) [12,13]. When utilized in the intermediate-temperature and low-humidity PEMFCs, the inherent water retention capacity, high thermal stability and the contribution to the proton conductivity of the phosphorylated silica materials, were advantageous for the improvement of the membrane performance. The proton conductivity at $85 \text{ }^\circ\text{C}$ and 50% RH of the hybrid membrane doped with phosphorylated silica was reported to be 0.026 S cm^{-1} , which was 24% higher than that of the pristine Nafion[®] membrane. It was accepted that small condensed units, such as oligomers, were preferentially yielded with the sol–gel reactions of the trifunctional organoalkoxysilanes (phosphoric-silanes) [14], thus silica materials could be synthesized first and phosphorylated consequently. Because the Si-OH groups were relatively inert to the phosphorylation reactions, the surface of silica were usually modified first, e.g., by titanium isopropoxide, and then phosphorylated [15]. The phosphorylation degree was restricted by the direct modification methods mentioned above, since only a monolayer of

the functional groups could be formed on the particle surface. Such a limitation could be alleviated by introducing phosphorylated polymer chains with more $-\text{PO}_3\text{H}_2$ groups. Diisopropyl *p*-vinylbenzyl phosphonate (DIPVBP) was emulsion-polymerized on the surface of silica spheres, and it was beneficial for the enhancement of the proton conductivity of the hybrid membranes (0.16 S cm^{-1} at $125 \text{ }^\circ\text{C}$ and 100% RH, while the proton conductivity of the recast Nafion[®] membrane decreased severely with the temperature exceeding $100 \text{ }^\circ\text{C}$) [16,17]. The hygroscopic silica materials functionalized with phosphoric acid groups are promising for PEMs.

In this study, phosphorylated silica submicrospheres were incorporated into the sulfonated poly(ether ether ketone) membrane matrix to construct proton exchange membrane containing $-\text{PO}_3\text{H}_2$ groups. The silica submicrospheres were synthesized first to provide robust regular structure and then the phosphorylation was carried out on the silica surface to inhibit acid leaching and ensure stable acid immobilization. To realize facile phosphorylation, the silica surface was activated first by epoxy groups. The amounts of $-\text{PO}_3\text{H}_2$ groups were controlled by changing the modification methods. Meanwhile the existence form of the acid groups was altered by varying the chain lengths immobilized on the silica surface. The influences of the amounts of acidic groups and the chain lengths on the performance of the hybrid membranes, including proton conductivity, methanol permeability and the dispersions of fillers were explored.

2. Experiment

2.1. Materials and chemicals

TEOS (reagent grade), 3-glycidyloxypropyltrimethoxysilane (GPTMS, analytical reagent (AR)), 3-aminopropyltriethoxysilane (APTES, AR), glycidyl methacrylate (GMA, AR), phosphorus oxychloride (POCl_3 , >98 wt%) and polyether ether ketone (PEEK 381G) were purchased from Sigma–Aldrich Co. LLC., Aladdin-reagent, J&K Scientific Ltd. (Beijing), Aladdin-reagent, Shanghai Guangzan Chemical Scientific Ltd. and Victrex England, respectively, and used without further purification. Toluene (AR) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. and was distilled prior to use. Triethylamine, 2-bromoisobutyl bromide, CuBr and N,N,N',N',N'-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma–Aldrich Co. LLC. and used without further purification (reagent grade).

All the other materials and chemicals were commercially available with analytical pure degree, and used as received. Deionized water was used throughout the work.

2.2. Preparation of the phosphorylated glycidyl-silane modified silica submicrospheres (SiP-I)

2.2.1. Preparation of silica submicrospheres (SiO_2)

Silica submicrospheres (SiO_2) were prepared by the Stöber method [18]: TEOS (10 mL) was added dropwise to the well-mixed solution of ethanol (200 mL), water (20 mL), and ammonia solution (6 mL) under vigorous stirring and the solution was kept stirring at room temperature overnight. The SiO_2 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.

2.2.2. Preparation of submicrospheres modified by glycidyl-silane (SiO_2 -epoxy)

2 mL GPTMS was used to react with 2 g dry SiO_2 . To avoid the silane coupling agents from hydrolyzing before reacting, SiO_2 was dispersed in 120 mL anhydrous toluene and then the mixture was

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