Enhanced proton conductivity under low humidity of sulfonated poly(ether ether ketone) composite membrane enabled by multifunctional phosphonic acid polymeric submicrocapsules

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HIGHLIGHTS

- The phosphonic acid polymeric submicrocapsules are designed and synthetized.
- The submicrocapsules have multifunctions in water retention and proton transfer.
- The composite membranes exhibit high water uptake and water retention.
- The composite membranes exhibit high proton conductivity under low humidity.

ARTICLE INFO

ABSTRACT

Phosphonic acid polymeric submicrocapsules (PASCs) are synthesized and incorporated into a sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare composite membranes. The microstructure and physicochemical properties of the PASCs and the membranes are characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDX), field emission scanning electron microscope (FESEM), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Compared with the SPEEK control membrane, the PASC-filled composite membranes exhibit elevated water uptake and proton conductivity at 25 °C and 100% relative humidity (RH). The proton conductivity depends strongly on water content within the membranes. Under 40 °C and 20% RH, the composite membrane filled with 15 wt.% PASCs (128 nm lumen) shows the highest proton conductivity of 0.0142 S cm^{-1} after 90 min testing, about twelve times higher than that of the SPEEK control membrane (0.0011 S cm^{-1}), which is positively correlated with the water retention of the membrane. These results suggest that the PASC-filled composite membranes may find encouraging application as efficient water-retention and proton-conduction materials in proton exchange membrane fuel cells (PEMFCs).

1. Introduction

For a proton exchange membrane fuel cell (PEMFC), the membrane is a core and performance-determinant component, through which proton transfers from anode to cathode to fulfill the conversion of chemical energy into electrical energy [1]. Generally, proton transfers through a PEM via two principal mechanisms [2,3]: one is vehicle mechanism wherein proton diffuses as water-solvated species, such as H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$; the other is Grotthuss mechanism wherein proton hops from one water molecule or functional group to the next by forming and breaking of hydrogen bonds. Accordingly, water in PEMs is vital to proton transfer and thus it is crucial to acquire membranes with high water retention, especially under low humidity [4,5].

To this end, various efforts have been devoted to enhancing water retention of PEMs, for example: (i) introducing abundant hydrogen-bonding sites for water molecules by incorporating hygroscopic fillers, such as solid, porous and hollow organic or inorganic fillers into membranes [6–15]; (ii) enhancing the hydrophilicity of membranes by grafting or blending with hydrophilic materials [16–18]; (iii) acquiring the optimum free volume characteristics or hydrophilic domains by manipulating membrane microstructure [19–22]. Among them, incorporating hygroscopic fillers into membranes has been demonstrated as a convenient and efficient approach. Recently, polymeric microcapsules were discovered to exhibit unique features in water retention. For

instance, Wang et al. prepared imidazole polymeric microcapsules (IMCs) and embedded them into PEMs (e.g. sulfonated poly(ether ether ketone) (SPEEK)) to improve membrane water retention [13]. Compared with the control membrane, the composite membrane filled with 15 wt.% IMCs exhibited about seven times higher water retention and over ten times higher proton conductivity under relative humidity (RH) as low as 20%. For polymeric microcapsules, the functional groups on the shell played crucial roles in tuning water retention properties of the microcapsules and the membranes. In another study, Wang et al. synthesized three kinds of polymeric microcapsules with carboxylic acid, sulfonic acid, and pyridyl groups on the shell (designated as PMC-C, PMC-S, and PMC-N, respectively) [14]. Carboxylic acid group on the microcapsule shell possessed the highest hydration energy, which conferred the PMC-Cs and the PMC-C-filled membranes the highest bound-water content. As a result, the PMC-C-filled membranes displayed the lowest water release and the highest water retention, and hence the highest proton conductivity. In contrast, pyridyl group of PMC-Ns possessed the lowest hydration energy. Consequently, the PMC-N-filled membranes showed the lowest water retention and subsequently the lowest proton conductivity under identical conditions. It can be thus envisaged that developing polymeric microcapsules with both high water-retention and high proton conduction is essential to high performance PEM.

Although carboxylic acid group shows high water retention property, its intrinsic proton conductivity is low, due to its weak acidity and low dissociation (e.g. pKa = 4.19 for benzoic acid) [23]. In comparison, phosphonic acid group can also render superior water retention property [10], arising from its high binding energy [24]. Meanwhile, phosphonic acid group exhibits high self-dissociation and dissociation constant is 1.42 (phenylphosphonic acid), in turn conferring phosphonic acid-bearing materials higher Grotthuss-type proton conductivity than carboxylic acid-bearing materials [25,26]. In addition, phosphonic acid group possesses pronounced amphoteric properties, i.e. good proton donor and acceptor properties, accompanying with fast dynamic hydrogen-bond networks [25]. The above features may endow phosphonic acid group with high proton conductivity under the practical operating conditions of fuel cells. To the best of our knowledge, phosphonic acid polymeric microcapsules have rarely been exploited as the versatile fillers in PEMs.

In this study, phosphonic acid polymeric submicrocapsules (PASCs) were designed and synthesized via a facile distillation–precipitation polymerization [10,27,28]. The PASCs were then embedded into a SPEEK matrix for preparing a series of composite membranes. The compositions, structure and physicochemical properties of the PASCs and the membranes were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), field emission scanning electron microscope (FESEM), and thermogravimetric analysis (TGA). Water retention properties and proton conductivity of the PASCs and the membranes at 40 °C and 20% RH were evaluated. Furthermore, methanol barrier property of the membranes was investigated.

2. Experimental

2.1. Materials and chemicals

3-(Methacryloxy)propyltrimethoxysilane (MPS, 98%) and tetraethyl orthosilicate (Si(OEt)$_4$, TEOS, 98%) were provided by Aldrich Chemical Co., Inc. Ethyleneglycol dimethacrylate (EGDMA, 98%) and dimethyl vinylphosphonate (DMVP, 98%) were supplied by Alfa Aesar and purified by vacuum distillation. 2,2′-Azoisobutyronitrile (AIBN) as analytical grade was purchased from Tianjin and

recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagent II Co.) was dried with calcium hydride and purified by distillation prior to utilization. Hydrofluoric acid (HF, containing 40% of HF) was available from Tianjin Chemical Reagent Institute. Dimethylformamide (DMF), sulfuric acid and methanol were of analytical grade and used without any further purification. De-ionized water was used throughout the study.

2.2. Synthesis of the PASCs

Silica particles with different diameters were synthesized according to classical Stöber method [29] and the MPS-modified silica submicrospheres were obtained by coupling silica alcosol particles according to the literature [30]. A typical procedure for synthesizing core–shell phosphonate polymeric submicrospheres (PSs) with silica core and phosphonate shell was [27,28]: MPS-modified silica (0.30 g), EGDMA (0.60 mL), DMVP (1.00 mL), and AIBN (0.032 g) were dissolved in acetonitrile (80 mL) in a dried flask, attached with a fractionating column, Liebig condenser and a receiver. The reaction mixture was heated from room temperature till the boiling state within 10 min and the reaction mixture was kept under reflux state for further 10 min. After 40 mL acetonitrile was distilled off from the reaction system, the reaction was stopped and the resultant core–shell PSs were purified by repeated centrifugation, decantation, and resuspension in acetonitrile with ultrasonic-bathing for three times. The hybrid particles were immersed in 40% HF solution for 2 h. Then the excess HF and newly formed SiF$_4$ were expelled out by several centrifugation/washing cycles in water till the pH of 7. Subsequently, the synthesized phosphonate polymeric submicrocapsules were dispersed into excess HCl aqueous solution (10 mol L^{-1}) at 100 °C for 24 h. Three kinds of PASCs with lumen sizes of 128, 204 and 335 nm were obtained and designated as PASCs-1#, PASCs-2# and PASCs-3#, respectively. The resultant PASCs were finally dried in a vacuum oven at 50 °C until constant weight.

2.3. Preparation of SPEEK

PEEK (28 g) was dried at 60 °C till constant weight followed by dissolving in concentrated sulfuric acid (200 mL, H$_2$SO$_4$, 95–98 wt.%) with vigorous stirring at room temperature for 3 h and then at 45 °C for another 8 h. The sulfonation reaction was terminated by precipitating the polymer solution into water under continuous agitation. The precipitate was washed repeatedly with de-ionized water until the pH of 7, and then dried at room temperature for 2 days followed by drying at 60 °C for 24 h under vacuum. The degree of sulfonation (DS) of SPEEK was determined by acid–base titration.

2.4. Preparation of the membranes

An aliquot of PASCs were dispersed into DMF (3.0 mL) solution with ultrasonic treatment and stirred for 12 h. Simultaneously, SPEEK (0.7 g) was dissolved into DMF (4.0 mL) solution and stirred vigorously at room temperature for 24 h. Then, these two solutions were mixed under vigorous stirring for another 2 h. After degasification, the mixture was cast onto a clear glass plate and dried at 60 °C in a vacuum oven for 12 h, and then at 80 °C for another 12 h. After cooling down to room temperature, the membrane was peeled off from the glass plate. Then the membrane was immersed into 2.0 M H$_2$SO$_4$ solution for 2 days and rinsed with de-ionized water until the pH of 7, and then dried under vacuum at 60 °C. The composite membranes were designated as SPEEK/PASCs–N–X, where N (=1, 2, or 3 #) represented the type of the synthesized PASCs, and X (=2.5, 5, 10 or 15) was the weight percentage of the fillers to SPEEK. The SPEEK control membrane was also fabricated