



Enhancing water retention and low-humidity proton conductivity of sulfonated poly(ether ether ketone) composite membrane enabled by the polymer-microcapsules with controllable hydrophilicity–hydrophobicity

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HIGHLIGHTS

- Polymeric microcapsules with tunable hydrophilicity–hydrophobicity were prepared.
- The four kinds of microcapsules possessed different water retention.
- SPEEK/microcapsules composite membranes were prepared.
- The composite membranes exhibited enhanced low-humidity proton conductivity.

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ABSTRACT

Four kinds of polymer microcapsules (PMCs) with different hydrophilicity–hydrophobicity are synthesized via distillation–precipitation polymerization (polymer microcapsules form by self-crosslinking of monomers/crosslinkers in this process) and incorporated into sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare composite membranes. To improve the water retention of the PMCs, the hydrophilicity–hydrophobicity of the PMCs is manipulated by regulating the proportion of hydrophilic ethylene glycol dimethacrylate (EGDMA) and hydrophobic divinylbenzene (DVB) crosslinkers in the synthesis formula. The hydrophilicity of the PMCs decreases with increasing the content of polyDVB in the PMCs. The four kinds of PMCs exhibit different water retention properties. The PMCs with appropriate hydrophilic/hydrophobic balance (EGDMA: DVB = 1:1) possess the best water retention properties. Incorporation of PMCs into SPEEK matrix enhances the water-retention properties, and consequently increases proton conductivity to 0.0132 S cm^{-1} under 20% relative humidity, about thirteen times higher than that of the SPEEK control membrane. Moreover, the incorporation of PMCs reduces the activation energy for proton conduction and the methanol permeability of the membranes. This study may be helpful to rational design of excellent water-retention materials.

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1. Introduction

Nanoengineered multifunctional polymer microcapsules (PMCs) with tailored structures and properties have stimulated great interest due to their wide applications, spanning medicine, biotechnology, catalysis and synthetic chemistry [1–3]. Recently, PMCs have been demonstrated as effective water-retention and proton-conduction fillers for proton exchange membranes (PEMs)

under operation conditions (high temperature and/or low humidity) [4–6], which is greatly desired for high fuel cell performances [7–10]. The PMCs, mimicking the water-storage mechanisms in plant cells, possess high water uptake and slow water release [5]. The dehydration of the resulting membrane was remarkably retarded by the incorporation of these versatile fillers with tailored structures and tunable chemical compositions, resulting in notably enhanced proton conductivity under operation conditions. Moreover, the high density of proton conductive groups in the shell of the PMCs can further promote proton conduction [5,6,11].

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A series of PMCs, bearing different functional groups such as carboxylic acid [5], sulfonic acid [4,5], phosphoric acid [12,13] and imidazole [6] were designed and incorporated into PEMs to enhance their water retention and proton conductivity. For instance, the chitosan composite membranes based on carboxylic acid functionalized PMCs exhibited a proton conductivity one to two orders of magnitude higher than that of chitosan control membrane under 20% relative humidity (RH) [5]. Incorporation of sulfonated polystyrene microcapsules into Nafion sustained proton conductivity up to 0.01 S cm^{-1} at $120 \text{ }^\circ\text{C}$, while the proton conductivity of the control Nafion membrane was below 0.0013 S cm^{-1} [4]. The Single H_2 -PEMFC test at $70 \text{ }^\circ\text{C}$ using dry H_2/O_2 verified the impactful role of PMCs functionalized with sulfonic acid or carboxylic acid in sustaining higher proton flux as compared to Nafion control membrane [14]. All these results indicate the potential of PMCs for fuel cell applications. Moreover, the variability of physical structures and chemical compositions endow the PMC with a large scope of improvement in terms of water retention and proton conduction. Although various studies have well-established the influence of functional groups, lumen sizes, and shell thicknesses of the PMCs on their water retention and proton conduction properties, one issue unexplored in PMCs is the role of hydrophilicity–hydrophobicity of PMCs in water retention and proton conduction properties of the PMCs.

It is widely accepted that hydrophilic substance in polymer matrix binds water through hydrogen bond or electrostatic interaction and facilitates water sorption and diffusion, while hydrophobic substance in polymer matrix has a weak interaction with water and suppresses water sorption and diffusion [15]. Thus, manipulating the hydrophilicity–hydrophobicity of PMCs can control water sorption and water release rate. In nature, a common strategy for desert plant to restrain water from releasing is evolving a layer of cuticle (hydrophobic fatty acid) with the ability of decreasing moisture evaporation rate [16–18]. Moreover, the currently employed approaches to improve water retention of PEMs focused on improving hydrophilicity of membrane [5,19], while enhancing water retention by adjusting hydrophilicity–hydrophobicity of membrane has been rarely involved. Therefore, it is essential that improved water retention of PEMs (enhanced water uptake and decreased water release) can be obtained by rationally tuning the hydrophilicity–hydrophobicity of PMCs.

In this study, both the water retention and low-humidity proton conductivity of SPEEK composite membrane were enhanced by the incorporation of polymer microcapsules with tunable hydrophilicity–hydrophobicity, which was controlled by regulating the proportion of hydrophilic ethylene glycol dimethacrylate (EGDMA) and hydrophobic divinylbenzene (DVB) crosslinkers in the distillation–precipitation polymerizations (polymer microcapsules formed by self-crosslinking of monomers/crosslinkers in this process) [20]. SPEEK is chosen as the matrix polymer on account of its outstanding thermomechanical stability, low cost and low fuel crossover features [8,21,22]. Moreover, the physiochemical and methanol barrier properties of the membranes were investigated.

2. Experimental

2.1. Materials and chemicals

Ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB, 80% divinylbenzene isomers) and tetraethyl orthosilicate (TEOS) were supplied by Alfa Aesar and used without further purification. 3-(Methacryloxy) propyltrimethoxysilane (MPS) were supplied by Aldrich and distilled under vacuum. Methacrylic acid (MAA) was purchased from Tianjin Guangfu Fine Chemical Engineering Institute and purified by vacuum distillation. 2,2'-Azobisisobutyronitrile

(AIBN) was provided by Tianjin Guangfu Fine Chemical Engineering Institute and recrystallized from methanol. Acetonitrile was supplied by Tianjin Kewei Ltd. and was dried over calcium hydride and purified by distillation. Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was supplied by Nanjing Yuanbang Engineering Plastics Co., Ltd. Dimethylformamide (DMF), sulfuric acid and methanol were supplied from Tianjin Kewei Ltd. De-ionized water was used throughout the experiment.

2.2. Synthesis of the PMCs and SPEEK

The synthesis of polymer microcapsules was illustrated in Fig. 1. Silica microspheres with diameter around 200 nm were synthesized according to Stöber method [23]: TEOS was added into the mixture of ethanol, water and aqueous solution of ammonium hydroxide under vigorous stirring at $30 \text{ }^\circ\text{C}$ for 24 h. Excess MPS was then added into the silica mixture with a reaction time of 24 h to modify the silica with carbon–carbon double bonds. The coating of polymer on MPS-modified silica spheres was carried out by distillation–precipitation polymerization in acetonitrile [5,20]. In a dried 100 ml flask attached to a fractionating column, Liebig condenser, and receiver, 0.20 g of silica particles was dispersed into 80 ml acetonitrile assisted by sonication. The monomer MAA (0.35 ml, 0.371 g), crosslinker EGDMA (0.65 ml, 0.624 g), and initiator AIBN (0.02 g, 2 wt% relative to the comonomers) were then dissolved into the MPS-modified silica solution. The mixture was heated from ambient temperature till boiling state and then the solvent was distilled from the reaction system. After 40 ml of acetonitrile was distilled out, the reaction was terminated and the resultant hybrid microspheres were purified by three cycles of ultracentrifugation, decanting, and resuspension in acetonitrile. Two-stage polymerization was utilized to get the polymer shell with controlled thickness and uniform shape. Three parallel syntheses were carried out using MAA as monomer and different crosslinkers, including EGDMA–DVB mixed crosslinker with a volume ratio of 3:1 and 1:1, and neat DVB crosslinker. The volume ratio of the crosslinker fraction in the comonomer feed was maintained as 0.65. The synthesized hybrid microspheres were etched by HF solution (10 wt%) for 2 h followed by several centrifugation/washing cycles in water till neutral pH was reached. The four types of PMCs with a constant MAA ratio as 35 vol% were prepared via altering the crosslinker: neat EGDMA, EGDMA–DVB with a volume ratio of 3:1 and 1:1, and neat DVB, which were designated as PMC-I, PMC-II, PMC-III and PMC-IV, respectively.

SPEEK was synthesized by sulfonation of PEEK: PEEK was dried for 24 h in a vacuum oven at $60 \text{ }^\circ\text{C}$. The dried PEEK (28.0 g) was then dissolved into concentrated sulfuric acid (95–98 wt%, 200 ml) at room temperature. The reaction mixture was stirred vigorously at $50 \text{ }^\circ\text{C}$ for 9.5 h, cooled to room temperature, and then added into excessive cold water under continuous agitation. The precipitated SPEEK was washed with water till pH of 7.0 and then dried, first at room temperature for 48 h and then at $60 \text{ }^\circ\text{C}$ for 24 h under vacuum. The degree of sulfonation of SPEEK was 68.2% determined by titration method.

2.3. Preparation of the membranes

A certain amount of the PMCs were dispersed into DMF (3.0 ml) solution under ultrasonic treatment for 12 h. Simultaneously, SPEEK (0.65 g) was dissolved into DMF (4.0 ml) solution and stirred vigorously for 24 h at room temperature. The two solutions were then mixed under vigorous stirring for 2 h followed by 1 h ultrasonic treatment. The mixture was cast onto a glass plate and dried at $60 \text{ }^\circ\text{C}$ in an oven for 12 h followed by drying at $80 \text{ }^\circ\text{C}$ for another 12 h. The membrane was removed from the glass plate by

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