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Enhanced water retention and low-humidity proton conductivity of sulfonated poly(ether ether ketone) hybrid membrane by incorporating ellipsoidal microcapsules

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ABSTRACT

Two kinds of polymeric ellipsoidal microcapsules (EMCs) with different functional groups (phosphoric acid groups and imidazole groups) were synthesized *via* precipitation polymerization and incorporated into sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare hybrid membranes. The structure, thermal stability and composition of EMCs were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The quasi-one dimensional structure endowed EMCs with high water uptake and water retention. Especially, for the hybrid membranes filled with 5 wt.% phosphoric acid-functionalized polymeric EMCs, water uptake was increased from 19.0% for pristine SPEEK membranes to 58.2%, and the water retention was 15.1% after 180 min testing at 40 °C and 20% RH, which is threefold and ninefold higher than those of pristine SPEEK membranes, respectively. Particularly, the proton conductivity at low RH was still up to 3.51×10^{-3} S/cm after 60 min testing. The results manifested that the ellipsoidal microcapsules, as a new kind of filler, had great potential in enhancing the water retention and low-humidity proton conductivity of proton exchange membranes.

Introduction

Polymer electrolyte membrane (PEM) plays a critical role in proton exchange membrane fuel cells (PEMFCs), and thus has been attracting broad R&D attentions [1–4]. Theoretically, vehicle mechanism and Grotthuss mechanism are the two most accepted mechanisms of proton transfer through PEM [5–8]. The former indicates that protons diffuse with water *via* forming hydrated proton (*i.e.* H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$).

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The latter indicates that protons hop *via* proton carrier sites through hydrogen bonds and neighboring acid or basic functional groups. Accordingly, enhancing the water retention of membranes can be a feasible strategy to improve proton conduction at low humidity. To date, the commercialized perfluoro-sulfonated PEMs (e.g. Nafion) and the alternative sulfonated aromatic PEMs (such as poly(arylether ketone)s, poly(arylethersulfone)s, polyimides, etc.) often suffer from substantial water loss at low humidity, which results in sharp decline of proton conductivity [4,9–11]. Inspired by the water-retention phenomena and principles in plant cells, microcapsules have been designed and filled into membrane bulk as water-retention media, furnishing water to the hydropenic membrane matrix continuously [12]. Compared with solid spheres, microcapsules possess special hollow structure, which affords the following three merits as fillers for PEMs: (I) ensuring the homogeneous dispersion in the polymeric matrix; (II) holding more free water to confer membranes a higher water content; (III) possessing low proton transfer resistance to make proton transport more effective [8,13–15]. Meanwhile, the permeable shell of the microcapsules can manipulate absorption and release of water so that the water environment in the membrane can be flexibly tuned [16]. In addition, the incorporation of microcapsules can render membranes numerous proton-transfer sites and optimize the hydrophilic domain structures within the membrane matrix.

Generally, microcapsules can be categorized into inorganic and polymeric microcapsules. Inorganic microcapsules (mainly hollow silica spheres), which have special hollow core structure, mesoporous shell, and large amounts of surface hydroxyl groups [17], possess good water retention capacity. Yuan et al. [14] designed hollow silica spheres (HSSs) and incorporated HSS into Nafion matrix. At 5wt.% filler content, the water uptake of Nafion/HSS hybrid membrane increased to 64% from 45% of pure membrane at elevated temperature (100 °C), and proton conductivity increased by about 37.5% under the same condition. However, the poor compatibility of HSSs with the polymer matrix and the low conductivity of inorganic components limited the further improvement of hybrid membrane properties. Lou et al. [17] synthesized poly(vinylbenzyl phosphonic acid) (PVBPA) grafted HSSs (HPSSs) *via* emulsion polymerization, which were utilized for preparing Nafion/HPSS hybrid membrane. Under the conditions of 80 °C and 100% RH, the water uptake of hybrid membrane with filler content of 30 wt.% increased to 70% from 37% of unfilled membrane and proton conductivity increased by about 141%. Though the poor compatibility and low conductivity problems can be alleviated by proper modification, some other drawbacks of inorganic microcapsules still exist, such as too fast water release, low water uptake, less proton-conducting ability [12]. To solve these problems, polymeric hollow spheres, or polymeric capsules may be more promising candidates. Wang et al. [12] designed a series of polymeric microcapsules (PMCs) and reported a 21.4-fold increase of proton conductivity under 20% RH and 40 °C by embedding 15 wt.% of carboxylic acid-functionalized microcapsules into chitosan membrane.

Based on the water retention mechanisms of plants [18], water tends to be retained in the tapered ends of embolized cells or intercellular spaces by capillary forces. Therefore, it can be envisioned that incorporating microcapsules with tapered ends structure (for instance, ellipsoidal microcapsules (EMCs)) will endow membranes with higher water retention than spherical microcapsules (SMCs). In addition, EMCs can be considered as quasi-one dimensional structure fillers because of the high aspect ratio, which renders the possibility of constructing continuous proton-conduction pathways within hybrid membranes and optimizing the proton conduction properties [19–21]. Tailoring the aspect ratio of microcapsules may further enhance the target functions of microcapsules in hybrid membranes [22].

In this study, phosphoric acid group-functionalized polymeric ellipsoidal microcapsules (EMC-P) and imidazole group-functionalized polymeric ellipsoidal microcapsules (EMC-N) are synthesized *via* distillation–precipitation polymerization, and incorporated into sulfonated poly(ether ether ketone) (SPEEK) matrix to fabricate the corresponding SPEEK/EMC hybrid membranes for low humidity PEMFCs. SPEEK is chosen as the bulk polymer because of its low cost, excellent thermal stability and low fuel crossover features. The successful synthesis of EMCs are confirmed by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The thermal stability, water uptake and water release and proton conductivity of the hybrid membranes will also be discussed.

Experimental

Materials and chemicals

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) were purchased from Tianjin Kewei Ltd. Ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB, 80% divinylbenzene isomers) and dimethyl vinylphosphonate (DMVP) were supplied by Alfa Aesar. Tetraethyl orthosilicate (TEOS) and vinylimidazole (VI) were purchased from Sigma. 3-(Methacryloxy) propyltrimethoxysilane (MPS) and 2,2′-Azoisobutyronitrile (AIBN) were supplied by Aldrich. Poly(ether ether ketone) (PEEK) was purchased from Victrex England. Other reagents used in the experiment were purchased locally. All the reagents were of analytical grade and used as received. De-ionized water was utilized throughout the experiment.

Synthesis of polymeric ellipsoidal microcapsules

Synthesis of Fe_2O_3 ellipsoidal nanoparticles

A typical synthesis procedure of Fe_2O_3 ellipsoidal nanoparticles was as follows [23,24]: 1.0812 g $FeCl_3 \cdot 6H_2O$ and 0.0468 g $NaH_2PO_4 \cdot 2H_2O$ were dissolved in 200 mL H_2O and then hydrolyzed at 100 °C for 3 days. The product was separated by three cycles of centrifugation and washing with deionized water. After drying in a vacuum oven for 24 h, monodisperse Fe_2O_3 ellipsoidal nanoparticles were obtained.

Synthesis of Fe_2O_3/SiO_2/MPS ellipsoidal nanoparticles

Fe_2O_3/SiO_2/MPS ellipsoidal nanoparticles were synthesized by Stöber method as reported previously [12,25]. 0.1 g Fe_2O_3 ellipsoidal nanoparticles were dispersed in a mixture of