Composite proton conductive membranes composed of sulfonated poly(ether ether ketone) and phosphotungstic acid-loaded imidazole microcapsules as acid reservoirs

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ABSTRACT

Imidazole microcapsules loaded with phosphotungstic acid (IMCs–HPW) were prepared and incorporated into the sulfonated polyether ether ketone (SPEEK) matrix to fabricate composite proton conductive membranes for potential use in direct methanol fuel cells. The hollow imidazole microcapsules (IMCs) were prepared via distillation–precipitation polymerization, immersed into HPW solution to obtain the acid loaded microcapsules (IMCs–HPW) which were subsequently embedded into membrane as acid-reservoirs. The Fourier transform infrared spectroscopy and the concentration-absorption UV–vis spectrum of the IMCs–HPW revealed the tight immobilization of HPW in the IMCs. The introduction of HPW greatly enhanced the thermal stability of the IMCs. The as-prepared SPEEK/IMCs–HPW membranes exhibited reduced swelling degree, reduced methanol crossover and in particular dramatically enhanced proton conductivity. The maximum conductivity at room temperature was 0.0316 S cm^{-1} for the SPEEK/IMCs–HPW composite membrane with a doping content of 15 wt%, which was nearly three times higher than that of the pristine SPEEK membrane. Incorporation of the IMCs–HPW acid reservoirs not only rendered the composite membranes with improved water-retention property but also provided additional proton-transfer pathways, leading to a superior proton conduction even under 20% relative humidity which was two orders of magnitude over the pure SPEEK membranes.

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1. Introduction

Direct methanol fuel cells (DMFCs) with high energy density, low pollution and fast start-up have attracted increasing attention as promising alternative power sources [1–3]. Intermediate temperatures and low humidity operations of DMFCs are desired to achieve efficient water and thermal management, enhanced CO tolerance and accelerated oxidation reaction kinetics. However, the perfluorosulfonic acid membranes typically presented by the Nafion® series membranes as the primary type of commercially available membranes for DMFCs show a severe fuel crossover and a dramatic loss of proton conductivity under dehydration conditions due to the destruction of the water-dependant proton-conducting nanochannels within the membrane [4,5]. Over the last several decades, development of proton conducting membranes with sustained adequate proton conductivity under low

humidity has become an increasingly popular research field. Inorganic fillers such as TiO$_2$ [6], SiO$_2$ [7] and ZrO$_2$ [8] particles have been incorporated into polymer membrane matrix as hygroscopic agents. These hydrophilic fillers can provide numerous hydrogen bond sites for high water uptake of membranes. However, the resultant composite membranes often display reduced proton conductivity because of the low intrinsic proton conductivity and poor water retention ability of these inorganic fillers [9,10]. Moreover, the weak interactions between the organic polymer matrix and the rigid inorganic additives in the hybrid membrane always result in poor interfacial morphology [11,12]. Surface modification of the inorganic fillers with functional groups (such as amine groups, sulfonic acid groups and so on) or organic chains by post-grafting approach is suggested in order to overcome these problems [13–16]. Unfortunately, the low reactive activity of the inorganic particles always results in a limited grafting degree and thus a limited improvement in proton conductivity. Furthermore, since the modification usually occurred only on the particle surface, the bulk of the solid particles is not proton-conductive and thus contributes little to proton transfer [17]. A family of inorganic hollow spheres has been developed and

exhibited advantages over their solid particle counterparts for their special hollow core structure, higher specific surface and lower density. The hollow structure enabled them to bear more active sites, hold more water molecules and reduced the dosage of the inorganic compounds. Sulfonic acid- and phosphonic acid-functionalized hollow silica spheres were synthesized through the soft template method to fabricate proton exchange membranes with superior water uptake and proton conductivity [18–20].

Polymeric microcapsules with a hollow structure have recently aroused our interest for their more tunable nature than the hollow inorganic spheres. A variety of polymers can be used to construct the capsule shell whose thickness can be tuned by controlling the polymerization process. The polymer shell can also be crosslinked and/or modified with various functional groups to manipulate its hydrophilic-hydrophobic character and density [21,22]. In addition, the flexibility of the polymer microcapsules improves the interfacial compatibility with the polymer membrane matrix. A series of polymeric microcapsules with diverse surface groups were prepared as water reservoirs and incorporated into membranes to manipulate the water uptake and water release performance of membranes [23]. The resultant composite membranes displayed not only outstanding water absorption ability but also water retention property. It is commonly accepted that the proton transport in membranes occurs by vehicle mechanism and Grotthuss mechanism, according to which the protons diffuse together with water molecules or jump from one water molecule/proton-conducting site to another through hydrogen bonds, respectively. Therefore, increasing water content and introducing proton-conducting sites are recognized as two primary approaches to facilitate proton transfer. High water content provides abundant charge carrier species to promote proton transport by forming hydrated ions. A large number of functional sites permit proton fast hopping along continuous network with low energy barrier. Inorganic acids such as phosphoric acid and sulfuric acid are expected as proton conductors to endow proton exchange membranes with high proton conductivity [24,25]. Solid heteropolyacids (HPAs) are regarded as efficient proton conductors owing to their unique structure and strong acidity. Its primary structure is characterized by Keggin-units where a central P atom in tetrahedral coordination is surrounded by 12 edge-sharing metal–oxygen octahedral (WO_6). The acidic protons reside directly on the polyanions as isolated acid protons or are solvated by water to form protonated water molecules (H_3O^+ and $H_5O_2^+$). The isolated acid protons, which are the origin of the strong acidity in the pseudoliquid phase, migrate between the neighboring polyanions rapidly, resulting in a high inherent proton conductivity of 0.02–0.1 S cm^{-1} at room temperature [26–28]. The distinct hydrophilicity of HPA is beneficial in holding much water even under high temperature and low humidity. Various HPA additives have been embedded into Nafion [29] and aromatic polymers [30] to fabricate composite membranes. Numerous additional protons present in HPA are responsible for increased proton conductivity of these membranes, which exceeds 10^{-2} S cm^{-1} at room temperature. Masayuki Nogami et al. prepared phosphotungstic acid–modified 3-glycidoxypropyl-trimethoxysilanes (HPW–GPTMS) composite membranes as the electrolyte for fuel cell [31]. The conductivity of the original GPTMS was low, 10^{-5} S cm^{-1} at 80 °C and 100% RH. When HPW was incorporated in GPTMS, the membrane conductivity was significantly increased to 10^{-2} S cm^{-1} at 5% of HPW content. HPW was anchored and assembled into ordered mesoporous silica by San Ping Jiang et al. [32]. Continuous proton transport pathways were constructed through the Keggin-type HPW clusters and silica hydroxyl, leading to a reduced activation energy for proton transfer and thus an increased proton conductivity. The proton conductivity of the HPW/mesoporous silica inorganic proton exchange membranes was found to be increased

from 0.018 S cm^{-1} to 0.045 S cm^{-1} when the temperature increased from 25 °C to 150 °C.

In this study, an attempt to enhance the membrane proton conducting property was made by introducing "acid reservoirs" into membranes. Phosphotungstic acid-loaded imidazole microcapsules were synthesized and incorporated into sulfonated poly (ether ether ketone) (SPEEK) membrane matrix. The composite membranes were evaluated extensively in the terms of water uptake property, swelling behavior, methanol crossover and proton conductivity.

2. Experimental

2.1. Materials and chemicals

Poly (ether ether ketone) (PEEK) from Nanjing Yuanbang Engineering Plastics Co., Ltd was used as the polymer matrix for composite membranes. Ethyleneglycol dimethacrylate (EGDMA) was provided by Alfa Aesar as a crosslinking agent. Tetraethoxysilane (TEOS), 3-(methacryloxy)propyltrimethoxysilane (MPS) and vinylimidazole (VI) were purchased from Aldrich and used without any further purification. 2,2′-Azobisisobutyronitrile (AIBN), dimethylformadide (DMF), acetonitrile and concentrated sulfuric acid were purchased locally. Other reagents of alytical grade were obtained from commercial source and all chemicals were utilized as received.

2.2. Synthesis of phosphotungstic acid-loaded imidazole microcapsules (IMCs–HPW)

Imidazole microcapsules (IMCs) were prepared. Firstly, monodispersed silica microspheres were synthesized via the Stöber method reported in the literature [33]. Secondly, excess MPS was added to the resultant silica mixture with vigorous stirring at room temperature and reactive vinyl groups were introduced onto silica by reacting with MPS. Then, the silica/p(EGDMA-co-VI) core–shell nanoparticles were prepared by distillation–precipitation polymerization. Typically, the silica particles obtained in the second step (0.30 g) were suspended in acetonitrile (80 mL) in a dried two-necked flask. VI comonomers (0.45 mL), AIBN (0.018 g, 2 wt% relative to the comonomers) and EGDMA (0.45 mL) were introduced into the above suspension. The flask equipped with a fractionating column, a Liebig condenser and a receiver was submerged in a heating mantle. The reaction mixture was heated from room temperature to boiling state within 10 min and then kept under refluxing state for additional 10 min. The solvent begun to distill off the reaction system and the polymerization was stopped after 40 mL of acetonitrile was distilled out. The silica/p(EGDMA-co-VI) core–shell nanoparticles were achieved and collected by centrifugation and washing successively with acetonitrile. The same polymerization reaction was conducted again to obtain a desired film thickness. Finally, the resultant core–shell composite particles were immersed in 10% HF solution for 2 h and purified by repeated centrifugation/washing steps in water until neutral. The hollow imidazole microcapsules were dried in a vacuum oven at 40 °C.

The as-prepared imidazole microcapsules were dispersed in deionized water under ultrasonic treatment. Then, phosphotungstic acid (Keggin-type) was added to achieve an acid solution of 0.1 M. The mixture was stirred continuously for 72 h. Afterwards centrifugation and washing were conducted several times to remove residual phosphotungstic acid. The final products, phosphotungstic acid-loaded imidazole microcapsules, were obtained by drying in a vacuum oven at 40 °C and denoted as IMCs–HPW.