



Imidazole microcapsules toward enhanced phosphoric acid loading of polymer electrolyte membrane for anhydrous proton conduction



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ABSTRACT

Polymer electrolyte membrane (PEM) with high loading, stable ion solvents remains challenging at present and significantly impedes its practical application in energy-relevant devices including hydrogen fuel cell. Here, a series of imidazole microcapsules (ImMCs) are synthesized and utilized as distinct reservoirs to access high phosphoric acid retention for PEM. We demonstrate that the ImMCs can significantly enhance the acid loading capability using the large lumens, bringing abundant proton-hopping sites and hence significantly enhanced proton conduction of membrane. In particular, 10 wt% ImMCs can afford a 78 wt% phosphoric acid loading and a consequent 75 times' increase of proton conductivity relative to the control membrane. Additionally, the cross-linked imidazole shells render membrane high acid retention ability. The acid release is almost stopped after immersing in water for 40 min, helping the membrane to retain as high as 62% of the initially loaded phosphoric acid. These features readily impart notably boosted hydrogen fuel cell performances to composite membrane under the desired conditions of elevated temperature and reduced humidity. As a further description, the acid retention and proton conduction properties of membrane can be efficiently tailored by adjusting microcapsule architectures (lumen size and shell thickness).

1. Introduction

Highly conductive materials play pivotal role in diverse chemical/biological processes and technological devices [1,2]. Of special interest is the hydrogen fuel cell, using proton conducting membrane as electrolyte, realizing efficient energy conversion through almost zero-emission electrochemical reactions [2,3]. In this regard, significant contributions have been devoted to developing high-performance polymer electrolyte membrane (PEM) including the optimization of membrane microstructure or chemical component. Until now, perfluorosulfonated ionomers and sulfonated aromatic polymers have been successfully prepared to PEMs, which readily achieve adequate proton conductivity ($\sim 0.1 \text{ S cm}^{-1}$) in hydration condition [4]. Nevertheless, PEMs with high conductivity in a water-free environment are still sorely needed, because they can permit the fuel cell working at intermediate-temperature (120–200 °C). The high temperature can help the fuel cell enhance cell efficiency and catalyst tolerance for CO, simplify water/heat management, and reduce cost [5,6]. However, most of the PEMs suffer sharp conductivity decay by few or several orders of magnitude under these conditions due to the water loss that reduces proton

vehicles and interrupts proton pathways in membrane. This is because for the conduction mechanism of short-range proton hopping, even very thin transfer barriers can drastically reduce ion conductivity [7].

One strategy to address this problem is to use amphoteric proton vehicles that allow anhydrous proton conduction, for example phosphoric acid (H_3PO_4 , PA). PA with the intrinsic advantages including high proton-solvating ability, high self-ionization property, and strong intermolecular H-bond networks, is regarded as superior proton carrier relative to other acidic groups [8,9]. These features hint proton transfer through a structural-diffusion mechanism among PA molecules – resulting in a high conductivity of 0.6 S cm^{-1} at 150 °C [9,10]. To be applicable in fuel cell, PAs have to be incorporated into the membrane *via* covalent bonds or weak interactions. Considering the limitations of available monomer, multi-step process and inhibited group mobility in covalent-bonding method, incorporating PAs directly may be more generic, facile, and effective. Successive attempts have been made to enhance the proton conductivity of PEM in anhydrous condition by adding PAs, and moreover, the conductivity of membrane increases over hundred times with PA loading increasing from 0 wt% to 100 wt% [11–13]. Mecerreyes *et al.* have prepared porous polybenzimidazole

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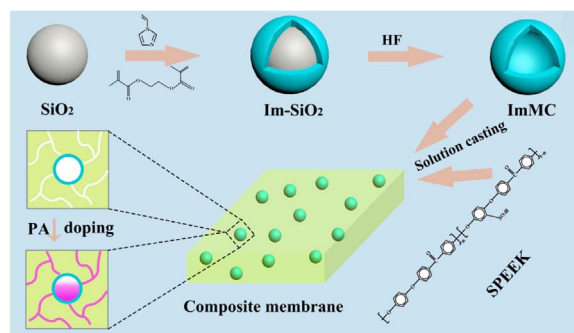
(PBI) membrane, and found that the PA loading increased from 132 wt % for pure PBI membrane up to 439 wt% for the porous membrane. Concomitantly, the proton conductivity boosted from 1.5 to 50 mS cm⁻¹ [14]. Suzuki and co-workers found that the proton conductivity of a phosphoric acid doped sulfonated polyimide-polybenzimidazole blend membrane could reach 0.5 S cm⁻¹ at 120 °C and 45% RH [15]. Since PA is in free form and liquid state, one unavoidable shortcoming is the PA loss from membrane, which causes the decline of conductivity and fuel cell performance. To sum up, two approaches have been employed to address this issue: physically confining PAs in nanopores (e.g., silica, zeolite, etc.) or chemically bonding PAs with basic groups (e.g., imidazole, pyridine, etc.) [12,13,16,17]. Ghosh et al. have incorporated phosphate anion containing imidazolium ionic liquid modified silica nanoparticles into PBI membrane to enhance PA absorbing and retention capability. And the resultant composite membrane showed a 58% reduction of PA loss (from 120% to 50%) and almost two fold increment in proton conductivity compared to the pure PBI membrane [18]. For these methods, larger storage spacing or more bonding groups can support high PA loading capability; however, this usually conflicts with the requirements of high PA retention ability and high PA mobility. Moreover, the retention for PAs of the ever reported methods is mostly temporary when compared with the long-term operation.

Recently, polymeric microcapsules have attracted research interest as mass retention reservoirs. Their larger lumens can provide physical spacings for high mass loading, whilst the polymer shells can manipulate mass release by strong chemical interactions [19–21]. Such independent regulation may offer great opportunities to realize both high acid loading and low acid loss. However, there is so far no report on the utilization of polymer microcapsules for storing acidic proton solvents including sulphuric acid, phosphoric acid, and carboxylic acid. Here, imidazole microcapsules (ImMCs) with tunable lumen size and shell thickness are synthesized via a distillation-precipitation polymerization and then incorporated in polymer membrane to efficiently load phosphoric acid. Apart from the inherent amphoteric feature for water-free conduction, imidazole groups are chosen as polymer shell because of their strong interaction and excellent adsorption ability with PAs. Sulfonated poly(ether ether ketone) (SPEEK) is selected as membrane matrix owing to its low cost and good film-forming ability. After incorporating ImMCs, the membrane is impregnated by PAs to prepare composite membrane. Similarly, imidazole microspheres (ImMSs) are synthesized to prepare composite membrane as a reference. The PA retention ability (including PA loading and dynamic loss), anhydrous proton conduction, and hydrogen fuel cell performance of composite membranes are measured systematically. Moreover, the microstructures and physicochemical properties of the membranes are also investigated in detail.

2. Experimental

2.1. Materials and chemicals

Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was supplied by Nanjing Yuanbang Engineering Plastics Co., Ltd, and it was post-sulfonated by concentrated H₂SO₄ with the sulfonation degree of about 64%. Tetraethyl orthosilicate (TEOS), 3-(methacryloxy) propyltrimethoxysilane (MPS), and ethylene glycol dimethacrylate (EGDMA) were purchased from Alfa Aesar. Vinylimidazole(VI) was supplied by Aldrich. MPS, EGDMA and VI were purified by vacuum distillation before utilization. 2,2-Azoisobutyronitrile (AIBN) was provided by Tianjin Guangfu Fine Chemical Engineering Institute and recrystallized from methanol. Dimethylformamide (DMF), acetonitrile, phosphoric acid and hydrofluoric acid (HF, 40%) were supplied by Kewei Chemistry Co., Ltd as analytical grade. De-ionized water was used in all experiments.



Scheme 1. Schematic of synthesis processes of ImMC and composite membrane.

2.2. Synthesis of the ImMCs and ImMPs

The ImMCs and ImMPs were synthesized through distillation-precipitation polymerization with and without silica templates, respectively. The regular silica particles with tailored diameter were prepared by Stöber method, the surface of which was then modified by MPS to introduce reactive vinyl groups [22,23]. A typical procedure for synthesizing silica/P(EGDMA-co-VI) microspheres (Scheme 1) was [24]: MPS-modified silica (0.30 g), EGDMA (0.60 mL), VI (0.60 mL), and AIBN (0.024 g) were dissolved in acetonitrile (80 mL) in a two-necked flask through full ultrasonic treatment. The mixture was heated to boiling point and then half of acetonitrile was distilled out. The hybrid microspheres were purified. Core-shell hybrid microspheres were synthesized similar to the above procedure using the semi-batch mode as cores. Adjusting the silica size allowed a controlled lumen size, and adjusting the cycle of polymerization process allowed a tailored thickness. The hybrid microspheres were etched in HF solution and followed by water washing. Then, the final ImMCs were obtained after drying and named as 1# to 5# as listed in Table 1. Similarly, P(EGDMA-co-VI) microspheres (ImMSs, 0#) were prepared by the similar process but without silica templating.

2.3. Preparation of the membranes

The SPEEK control and composite membranes without doping PA were prepared through solution casting method (Scheme 1). Certain amount (0.075 g) of ImMCs or ImMSs was dispersed into DMF (10.0 g) solution under ultrasonic treatment for 2 h at room temperature. Afterwards, SPEEK (0.75 g) was added to the above solution and stirred vigorously for another 24 h at room temperature. The above solution was cast onto a glass plate and dried at 60 °C in an oven for 12 h followed by drying at 100 °C for another 12 h. The resultant membranes were designated as SPEEK/X, where X represented the fillers, and the weight ration of the filler to SPEEK was set to 10 wt%. SPEEK control membrane was obtained via a similar procedure as mentioned above without adding fillers, and was designated as SPEEK.

The as-prepared membrane (4.0 × 4.0 cm) was used to prepare PA-doped composite membrane. The membrane sample was immersed in phosphoric acid solution (85 wt%) under ultrasonic treatment at 60 °C. After being immersed in the solution for a certain time to reach

Table 1
The lumen size and shell thickness of the imidazole microspheres and microcapsules.

Sample	Lumen size/nm	Shell thickness/nm	Membranes
0#	0	611 ± 15	SPEEK/0#-PA
1#	223 ± 4	99 ± 2	SPEEK/1#-PA
2#	405 ± 8	101 ± 4	SPEEK/2#-PA
3#	603 ± 3	102 ± 3	SPEEK/3#-PA
4#	405 ± 8	165 ± 2	SPEEK/4#-PA
5#	405 ± 8	248 ± 7	SPEEK/5#-PA

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