

Zwitterionic Microcapsules as Water Reservoirs and Proton Carriers within a Nafion Membrane To Confer High Proton Conductivity under Low Humidity

Guangwei He,^{†,‡} Zongyu Li,^{†,‡} Yifan Li,^{†,‡} Zhen Li,^{†,‡} Hong Wu,^{†,‡} Xinlin Yang,^{‡,§} and Zhongyi Jiang^{*,†,‡}

[†]Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

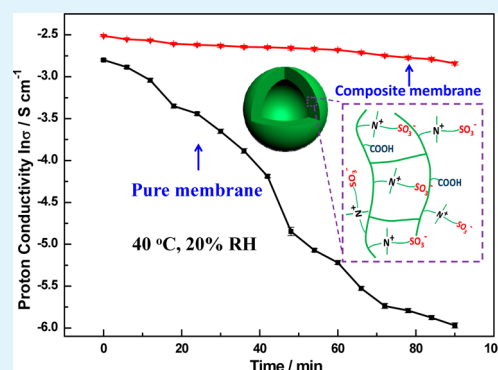
[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

[§]Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

S Supporting Information

ABSTRACT: Zwitterionic microcapsules (ZMCs) based on sulfobetaine with tunable hierarchical structures, superior water retention properties, and high proton conduction capacities are synthesized via precipitation polymerization. The incorporation of ZMCs into a Nafion matrix renders the composite membranes with significantly enhanced proton conductivity especially under low humidity. The composite membrane with 15 wt % ZMC-I displayed the highest proton conductivity of $5.8 \times 10^{-2} \text{ S cm}^{-1}$ at 40 °C and 20% relative humidity after 90 min of testing, about 21 times higher than that of the Nafion control membrane. The increased proton conductivity is primarily attributed to the versatile roles of ZMCs as water reservoirs and proton conductors for rendering a stable water environment and an additional proton conduction pathway within the membranes. This study may contribute to the rational design of water-retaining and proton-conducting materials.

KEYWORDS: zwitterionic microcapsules, Nafion, composite membranes, water retention, proton conductivity, low humidity



1. INTRODUCTION

Proton transport plays a vital role both in biological contexts and in clean-energy applications such as a proton-exchange membrane fuel cell (PEMFC).^{1,2} A proton-exchange membrane (PEM) is a key component of a PEMFC.^{2,3} However, the most commonly employed PEMs, such as Nafion and sulfonated hydrocarbon membranes, suffer from dehydration under low humidity, resulting in a significant decline of the proton conductivity.^{2,3} Therefore, it is essential to improve the proton conductivity of PEMs under low relative humidity (RH; i.e., <50%) in a facile and efficient way.^{2–5}

Among various strategies to develop membranes with high proton conductivity under low RH, the incorporation of hydrophilic polymer microcapsules (PMCs) into a membrane matrix has been demonstrated as a successful example.^{6–8} Enhancement of the proton conductivity is due to the capacity of PMCs to afford the membrane with better water retention properties and additional proton conduction carriers.^{6–8} For instance, the chitosan (CS)/carboxylic acid microcapsules composite membrane showed a proton conductivity 14-fold higher than that of CS control membrane under 20% RH.⁶ The desired PMCs utilized for PEMs should satisfy two basic criteria, i.e., possessing superior water retention properties to facilitate the vehicle-type proton conduction and bearing

abundant highly effective proton conduction carriers to facilitate Grotthuss-type proton conduction.⁹ However, state-of-art PMCs had difficulty achieving this win–win goal.

Incorporating zwitterions into PMC structures may be a novel solution. Zwitterionic materials such as poly-(sulfobetaine) are well-known superhydrophilic and ultralow biofouling materials.¹⁰ The zwitterionic groups can bind water molecules more strongly via electrostatically induced hydration, in comparison with the water retention materials based on hydrogen-bonding-induced hydration.^{10,11} Another distinct feature of sulfobetaine (SB) is its possession of one sulfonic acid/quaternary ammonium pair segregated by three carbon atoms per molecule. Besides the sulfonic acid group with highly effective proton conduction capacity,² dissociation of the sulfonic acid could be facilitated by the electrostatic attraction of the quaternary ammonium in such a molecular structure, enabling rapid proton transport via the Grotthuss mechanism.^{12–14} Thus, zwitterionic microcapsules (ZMCs) with SB functional groups would possess both high water retention and proton conduction properties.¹⁵ Moreover, the quaternary

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Scheme 1. Synthesis of the ZMCs

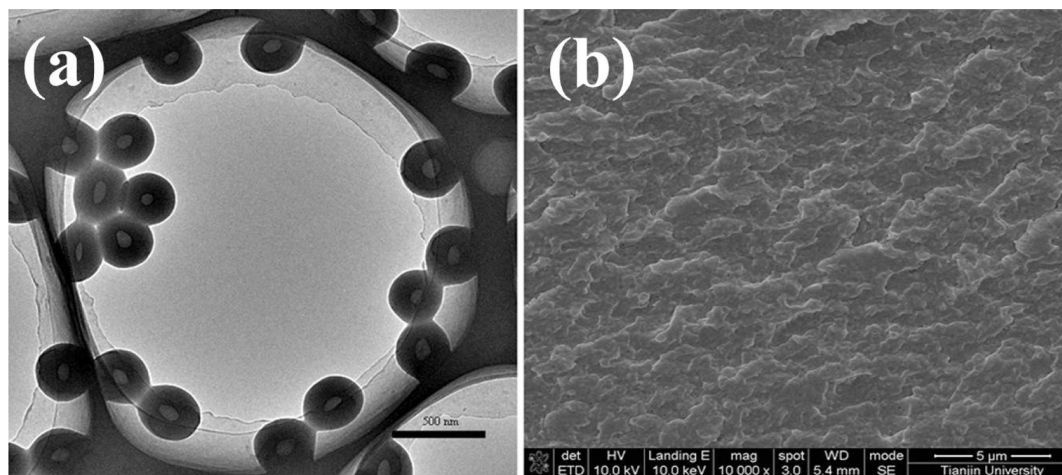
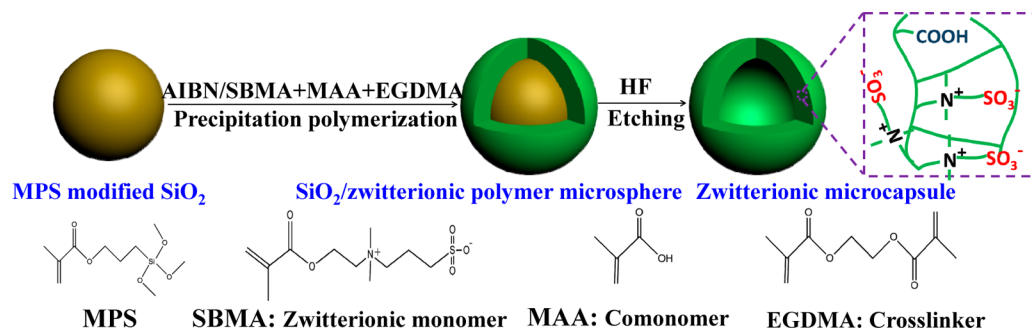


Figure 1. (a) TEM image of ZMC-I. (b) FESEM image of a cross section of the Nafion/ZMC-I-30 (referring to 30 wt % of ZMC-I in the membrane) composite membrane.

Table 1. Synthetic Formula, Lumen Size, Shell Thickness, Sulfur Content, Water Uptake, and Water State of the ZMCs

sample	template mass (g)	mol wt of SBMA/MAA/EGDMA (mmol)	lumen size (nm)	shell thickness (nm)	sulfur content (wt %)	water uptake (%)	free water (%)	bound water (%)
ZMC-I	0.12 ^a	1.43/1.17/2.12	100 ± 3	110 ± 4	3.29	314	228	86
ZMC-II	0.16 ^b	1.43/1.17/2.12	222 ± 5	139 ± 4	3.52	269	166	103

^aCorresponding to a template of 200 nm. ^bCorresponding to a template of 360 nm.

ammonium groups on the surface of ZMCs can bind with acidic polymer through electrostatic interaction, forming compact acidic polymer/ZMC interfaces and facilitating the preparation of the composite membrane. To the best of our knowledge, ZMCs have rarely been reported in membrane-relevant processes.

Herein, we report the design and preparation of a novel ZMC based on SB via precipitation polymerization (Scheme 1) and the corresponding Nafion/ZMC composite membrane. ZMCs showed superior water retention properties and notably enhanced proton conductivity of the Nafion-based membrane by 21-fold compared with the Nafion control membrane under 20% RH.

2. RESULTS AND DISCUSSION

Scheme 1 illustrates a synthetic route of the ZMC via selective removal of the SiO₂ core from a SiO₂/zwitterionic polymer core-shell microsphere,¹⁶ which was synthesized by precipitation polymerization employing a [3-(methacryloxy)propyl]-trimethoxysilane-modified SiO₂ microsphere as the template, azobis(isobutyronitrile) as the initiator, sulfobetaine methacrylate (SBMA) as the zwitterionic monomer, methacrylic acid

(MAA) as the comonomer, and ethylene glycol dimethacrylate (EGDMA) as the cross-linker via a vinyl capture process.^{6,16} Precipitation polymerization was chosen as the fabrication technique because it is a simple, straightforward, and highly efficient protocol for fabricating uniform polymer particles precluding the need of any stabilizer in the polymerization process.¹⁷ As we know, it is difficult to synthesize hydrophilic polymer microspheres by precipitation polymerization because the predominantly used solvent acetonitrile is unable to dissolve some hydrophilic monomers (like SBMA).^{6,17} Herein, acetonitrile–water (60/20, v/v) cosolvent was employed to dissolve the monomers/cross-linkers and initiator, while the formed oligomers precipitated from the homogeneous solution and were captured by the templates because of their low solubility in the cosolvent. The addition of MAA was essential to the formation of core-shell-structured microspheres because hydrogen bonding among MAA units and electrostatic bonding between MAA and SBMA units acted as driving forces to promote polymerization.

The transmission electron microscopy (TEM) image of ZMCs in Figure 1 show that the polymeric shells were dense and the microcapsules maintained their integrity and were

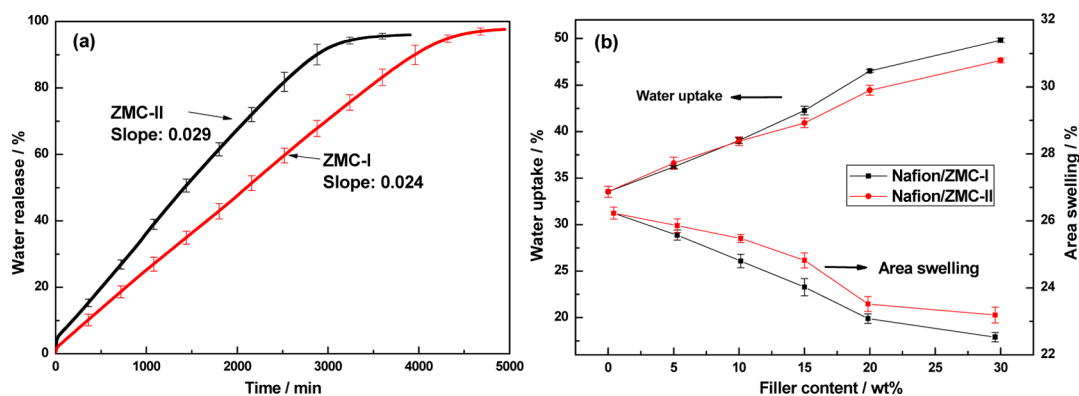


Figure 2. (a) Water release of ZMCs as a function of time at 40 °C and 20% RH. (b) Water uptake and area swelling of the membranes at 25 °C and 100% RH.

nearly monodisperse. The lumen size and shell thickness of the ZMCs were tuned by varying the silica template size and monomer/silica feed ratio by weight, resulting in two types of ZMCs, e.g., ZMC-I (diameter: 320 nm) and ZMC-II (diameter: 500 nm) (Table 1). The Fourier transform infrared (FTIR) spectra of ZMCs (see Figure S2 in the Supporting Information, SI) revealed the characteristic peaks at 1048 and 1187 cm^{-1} corresponding to the stretching vibration of $\text{O}=\text{S}=\text{O}$ in the $-\text{SO}_3^-$ group. The peak at 1734 cm^{-1} was attributed to the $\text{C}=\text{O}$ stretching vibration in the $-\text{COOH}$ group. The thermogravimetric analysis (TGA) data of fully hydrated ZMCs is shown in Figure S2 in the SI. The inductively coupled polymerization (ICP) result showed that ZMC-I contained 3.29 wt % sulfur, corresponding to 29 wt % poly(SBMA) zwitterionic polymeric chains. The fabrication method reported here demonstrates that surface-grafted precipitation polymerization can be extended to hydrophilic monomers such as SBMA, which cannot be dissolved in acetonitrile. This finding may be useful to the design of a variety of functional polymer nanoparticles.

Field-emission scanning electron microscopy (FESEM) images in Figures 1 and S3 (see the SI) depict that the composite membrane was dense and void-free and ZMCs maintained their structure and were homogeneously distributed within the Nafion matrix even at 30 wt % filler content. This excellent dispersion reflected the good compatibility between the polyelectrolyte and low-density polymer filler, which originates from both electrostatic attraction between Nafion and ZMCs and the low polymer–polymer mixing enthalpy.¹⁸

Table 1 showed that water uptake of ZMC-I and ZMC-II was 314% and 269%, respectively. The ZMC-I displayed higher water uptake compared with other reported PMCs with similar structures (e.g. water uptake of carboxylic acid, sulfonic acid, phosphoric acid, and imidazole functionalized PMCs being 176.8, 154.7, 212.9 and 132.2%, respectively).^{6,7,19} The superior water uptake can be attributed to the superhydrophilicity of the zwitterion which led to notable swelling of ZMCs, providing more room for water. About eight water molecules were tightly bound with one SB unit, and additional water molecules over 8:1 ratio mainly swelled the poly(SB) matrix.¹¹ The number of water molecules bound with one SB unit is much greater than that of other hydrophilic groups such as ethylene glycol (one water molecule per unit) and carboxylic acid (three water molecules per unit).^{11,20}

Figure 2 revealed that the incorporation of ZMCs significantly increased the water uptake and slightly decreased

the area swelling of the composite membrane at 25 °C and 100% RH. The enhanced water uptake was due to the presence of ZMCs as water reservoirs within the membrane. The decreased swelling can be attributed to the electrostatic attraction between Nafion and ZMCs and the swelling resistance of the highly cross-linked ZMCs. Thus, this water retention approach renders the possibility of crossing the trade-off hurdle between the water uptake and swelling resistance of PEMs.³ Considering the unique role of ZMCs in increasing the water uptake and decreasing the swelling of the membrane simultaneously, these ZMCs were highly favored for PEM applications.

Besides water uptake, another essential parameter to evaluate the water retention properties of ZMCs is the dynamic water release (Figure 2). Linear water release behavior was observed for ZMC-I and ZMC-II, and the slope (S) indicated the water loss rate of ZMCs. The water release rate of ZMC-I ($S = 0.024$) was lower than that of ZMC-II ($S = 0.029$). Because the two types of ZMCs had similar chemical compositions and nearly identical bound water ratios, the slower water release of ZMC-I can be ascribed to stored water within the confined cavity. In such a case, the vapor pressure obeys Kelvin and Young–Laplace equations. Accordingly, a larger lumen size would elevate the vapor pressure and hence the chemical potential of water within ZMCs. ZMC-I displayed a lower water release rate compared with that of other reported PMCs (e.g., water release slopes of carboxylic acid, sulfonic acid, phosphoric acid, and imidazole PMCs being 0.04, 0.055, 0.032, and 0.053, respectively).^{6,7,19} This ultralow water release rate could be due to the capacity of the zwitterionic groups binding with water molecules more tightly by strong electrostatic interaction. As a comparison, other PMCs held water molecules mainly via hydrogen-bond interaction, which was weaker than electrostatic interaction.¹¹ Another important factor retarding the water release was that the zwitterionic groups can bind with more water molecules,¹¹ which was confirmed by the highest bound water content of ZMC-I (ratio of bound water weight to the dry weight of ZMC-I, 86%) compared with that of the reported PMCs (the bound water contents of carboxylic acid, sulfonic acid, and imidazole-functionalized PMCs were 67, 49, and 34%, respectively).^{6,7}

Water retention is evaluated by both water uptake and water release. ZMC-I displayed better water retention (see Figure S4 in the SI) because of higher water uptake and slower water release compared with those of ZMC-II. ZMC-I displayed the best water retention compared with other reported PMCs.^{6,7,19}

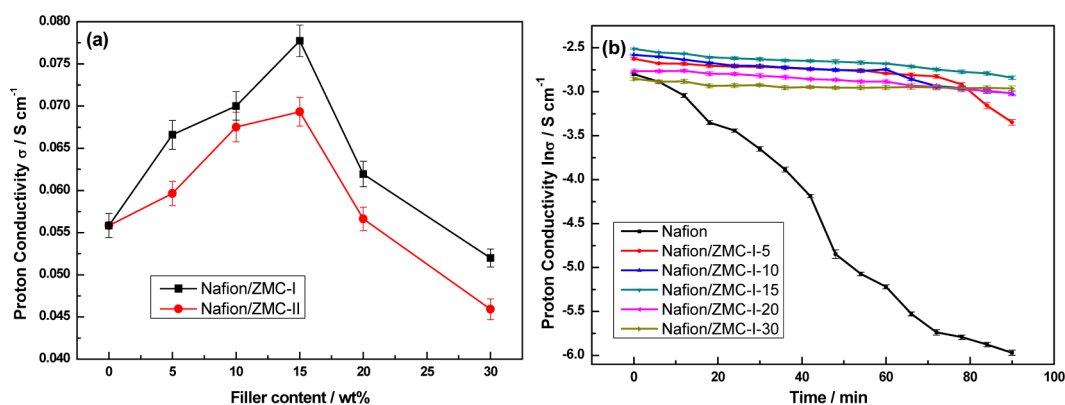


Figure 3. (a) Proton conductivity of the membranes at 25 °C and 100% RH. (b) Time-dependent proton conductivity of the ZMC-I-based membranes at 40 °C and 20% RH.

It can be conjectured that ZMC-I was capable of acting as a superior water reservoir within membranes to enhance the water retention properties of the membranes.

The proton conductivity was enhanced by the incorporation of ZMCs with contents below 20 wt %, as shown in Figure 3. For example, the proton conductivity increased from 0.056 $S\ cm^{-1}$ of the Nafion control membrane to 0.078 $S\ cm^{-1}$ of Nafion/ZMC-I-15 (39% increase). The increment of the proton conductivity can be attributed to the following three factors: (i) ZMCs contained numerous highly conductive sulfonic acid groups and abundant bound water molecular, which can facilitate proton conduction via the Grotthuss mechanism; the dissociation of sulfonic acid could be promoted by the zwitterion effect¹² via their ionic interactions, which further facilitated the Grotthuss-type proton conduction.^{9,13–15}

(ii) The zwitterionic groups can induce the formation of a hydration layer, which can facilitate proton conduction via a vehicle mechanism.^{9,10} (iii) The quaternary ammonium groups on the surface of ZMCs can self-assemble with Nafion by electrostatic attraction, which may generate a continuous hydrophilic channel for rapid proton transport.²¹ It should be emphasized that these proton-conductive ZMCs with chemical composition similar to that of polymerized ionic liquids can find promising applications in electrochemical realms.²²

The time-dependent conductivity of the membranes under low RH of 20% relied heavily on water retention of the membranes, as reflected by Figure 3. The proton conductivity decreased over time for all of the membranes, originating from dehydration of the membranes. The proton conductivity of the Nafion control membrane showed a reduction of 95.8% from 6.1×10^{-2} to 2.6×10^{-3} $S\ cm^{-1}$ within 90 min of testing. The reduction could be attributed to substantial dehydration, leading to shrunken and disconnected proton conduction nanochannels. Encouragingly, the ZMC incorporation considerably retarded the proton conductivity decline of the composite membranes because the released water from ZMCs could compensate for the evaporated water and maintain a percolated water network within the membranes. For instance, the conductivity reductions were 51.5% (from 7.2×10^{-2} to 3.5×10^{-3} $S\ cm^{-1}$), 35.1% (from 7.6×10^{-2} to 4.9×10^{-3} $S\ cm^{-1}$), 28.0% (from 8.1×10^{-2} to 5.8×10^{-2} $S\ cm^{-1}$), 22.2% (from 6.3×10^{-2} to 4.9×10^{-2} $S\ cm^{-1}$), and 10.4% (from 5.8×10^{-2} to 5.2×10^{-3} $S\ cm^{-1}$) during the measurement when 5, 10, 15, 20, and 30 wt % ZMC-I, respectively, were incorporated. ZMC-I retarded the decline of the proton conductivity more significantly than the previous

studies.^{6–8,21} The primary reason was that ZMC-I possessed better water retention properties, expediting vehicle-type proton conduction. Meanwhile, the sulfonic acid groups in ZMCs could facilitate Grotthuss-type proton transfer more effectively. The stability of the proton conductivity revealed that ZMCs as water reservoirs and proton carriers could retain the high proton conductivity of the membrane under low RH. Incorporating hydrophilic fillers into the membranes has been widely utilized to enhance the proton conductivity under low RH of the membranes.^{5,23–25} In particular, composite membranes composed of sulfonated polyimide (SPI) nanofibers exhibited proton conductivity 10 times higher than that of the pure SPI membrane under 30% RH.²⁵ The present study demonstrates the promising application potential of ZMCs in fuel-cell fields.

3. CONCLUSIONS

In the present study, ZMCs based on SB were facilely synthesized through surface-grafted precipitation polymerization and homogeneously incorporated into a Nafion matrix to prepare composite membranes. Because of the superior water retention and desirable proton conduction properties of ZMCs, the composite membrane with 15 wt % ZMC-I displayed the highest proton conductivity of 5.8×10^{-2} $S\ cm^{-1}$ at 40 °C and 20% RH after 90 min of testing, about 21 times higher than that of the Nafion control membrane.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional experimental data including TEM of the core–shell microspheres and ZMC-II, SEM images of the membranes, FTIR spectra of ZMCs, TGA of fully hydrated ZMCs, water retention of ZMCs, time-dependent proton conductivity of ZMC-II-based membranes, temperature-dependent proton conductivity of the Nafion/ZMC-I and Nafion/ZMC-II composite membranes at 100% RH, and relevant discussions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhyjiang@tju.edu.cn. Tel: 86-22-27406646. Fax: 86-22-23500086.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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