Three-Dimensional Stable Cation-Exchange Membrane with Enhanced Mechanical, Electrochemical, and Antibacterial Performance by in Situ Synthesis of Silver Nanoparticles

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ABSTRACT: In this study, a simple and facile approach was proposed to synthesize silver nanoparticles (AgNPs) loaded cation-exchange membranes (CEMs). A wide analytical study involving scanning electronic microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy was accomplished to corroborate that the in situ generated AgNPs were uniformly dispersed in the polymer matrix. In addition, as a result of the proposed synthesis strategy, the cross-linking structure inside the membrane was formed. The proper particle size and dispersibility of the AgNPs improved the mechanical properties of the membranes. Besides, the optimal AgNP-loaded CEM exhibited excellent bacterial killing activities against Gram-negative bacteria and showed a controlled improvement in the electrochemical performance of the prepared membranes. These effects were caused by the obtained distribution of AgNPs near ion-exchange groups that increased the aggregation of water molecules around them, improving the efficiency of ion transport due to the formation of array broad ion-transport channels. The optimized CEM (sulfonated polysulfone (60SPSF)-C3#-Ag-2) exhibited an enhanced NaCl removal ratio of 67.5% with a high current efficiency (96.9%) and a low energy consumption (5.84 kWh kg⁻¹). The distance of the inhibition zone from the boundary of the membrane of SPSF-C3#-Ag-2 reached 4.8 mm. These results led us to suggest that the proposed synthesis strategy may have potential applications in the field of antibacterial and desalting ion-exchange membranes.

1. INTRODUCTION

One of the most pervasive challenges affecting researchers around the world is the deficient access to prevent biofouling when using membrane technology.1–4 Taking into account their intrinsic physicochemical surface characteristics,5,5 traditional cation-exchange membranes (CEMs) are highly prone to biofouling even in humid air conditions. By secreting extracellular polymers, the bacteria will adhere to the surface of the membrane, resulting in an increase in membrane resistance, reduction in ion-transport efficiency, increase in energy consumption (EC), and restriction of useful membrane life, which dramatically affect the membrane performance in industrial application. Although adding buffer to the stack for the cleaning or replacement of the membranes is a valid method to solve the above problems, it will eventually increases the operating costs.46–10

Addressing the problem attracts a number of research to explore methods of purifying water using membrane technology at lower cost and with less energy while minimizing the use of chemicals and impact on the environment.

Besides, to mitigate the membrane bacterial fouling from the water source, modification of membrane material itself is still one of the most effective methods. The presence of agents such as chitosan, capsaicin, nanosilver, nanocopper, nanozinc dioxide, graphene, carbon nanotubes, etc. embedded in the polymer matrix improves the antibacterial and conductivity properties of doped membranes.11–13 Among them, silver nanoparticles (AgNPs) are widely used as a metal-type antibacterial agent in electronic products, biosensors, food industry, cosmetics, medical equipment, and other industries.14 Zhang et al.15 successfully immobilized nanosilver particles (AgNPs) on the surface of poly(vinylidene difluoride) (PVDF) membrane using poly(acrylic acid). The static contact angle test showed that dispersed AgNPs provide a significant improvement to the hydrophilic character of membranes.

Besides, antibacterial experiments confirmed that the modified PVDF membranes exhibit good biofouling resistance. Eribo et al.16 integrated polystyrene sulfonate (PSS), polydiallyldimethylammonium chloride, and AgNPs as stable thin (15 nm) layer into polyethers. The results showed that the combination of AgNPs and PSS increased the hydrophilicity and enhanced the biocidal property of the modified membranes.

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However, the traditional method for preparing AgNPs is complicated, and the chemical reagents used are mostly toxic and not eco-friendly.

Thus, in situ synthesis methods have emerged in recent years. Shen et al.\textsuperscript{17} coated a polydopamine (PDA) layer on the surface of pristine anion-exchange membranes, and then Ag was reduced by PDA with 2,5-diaminobenzene sulfonic acid grafted onto PDA layer. The modified AEMs exhibited a significant inhibition effect on \textit{Escherichia coli}. Besides, Shen et al.\textsuperscript{18} fabricated a "sandwich"-like structure [composed of PDA and poly(sodium 4-styrene sulfonate) (PSS)/hydroxypropyltrimethyl ammonium chloride chitosan–nanosilver particles (HACC-AgNP) on a commercial AEM]. The results are indicative of the available antibacterial activities of \textit{E. coli}. However, in general, the in situ synthesis methods for fabricating AgNPs are limited by the attachment of Ag\textsuperscript{+} and reductants\textsuperscript{19,20} which results in AgNPs being only modified on the membrane surface, such as surface grafting, layer-by-layer assembly, in situ covalent surface functionalization, and so on.\textsuperscript{15,16,19,21–38}

In addition to surface modification, known for the combination of the advantages of polymer and inorganic materials, incorporation of nanomaterials into matrix of ion-exchange membranes (IEMs) have drawn a lot of interest for offering IEMs with new remarkable properties.\textsuperscript{11,12}
However, as for traditional mixed matrix membranes, AgNPs should be prepared first\(^{19,39-41}\) and then blend with the casting solution during the process of fabrication, which is complex and not effective in dispersing nanoparticles uniformly in the membrane (Scheme 1a). Therefore, it is worth exploring to find a simple process for preparing AgNPs to modify the membrane.

The photon quantum reduction method is to reduce silver ions by the electrons generated in the solution after ultraviolet light irradiation.\(^{41}\) During the reaction, less Ag nucleus are initially produced, and the reduced Ag is continuously deposited to form a cluster of atoms with uniform particles. Furthermore, it will be more efficient to reduce AgNPs by combining the chemical method with the UV induction.\(^{39,42}\) In this study, a simple method based on UV radiation technology is accomplished to directly synthesize AgNPs while cross-linking structure is formed in the polymer matrix. Through the ion-exchange process, \(\text{Ag}^+\) is absorbed near the \(-\text{SO}_3^-=\). After UV treatment, the in situ generated AgNPs are uniformly dispersed in the polymer matrix, avoiding the problem of agglomeration caused by the postmixing procedure (Scheme 1b). The prepared CEMs were investigated by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX). Besides, their physicochemical, electrochemical, and antibacterial properties were also investigated. The chosen optimal silver nanoparticle-loaded cross-linked membranes have a lower electrical resistance, higher current efficiency (CE), and lower energy consumption, with potential applications in the field of antimicrobial membranes.

2. RESULTS AND DISCUSSION

2.1. Characterization of in Situ Synthesis of AgNPs in the Prepared CEMs. It is observed from Figure 1a,b that AgNPs were successfully synthesized in the sulfonated polysulfone (60SPSF)-C3#-Ag3 CEMs, and their uniform dispersion and nanometric size (about 20 nm) were competent to access a good coordination with membrane matrix. As can be seen from Figure S1, when the addition amount of AgNO\(_3\) was low (60SPSF-C3#-Ag-1), fewer AgNPs were generated. As the addition of AgNO\(_3\) increased, consequently the amount of generated AgNPs was higher. The 60SPSF-C3#-Ag-2 and 60SPSF-C3#-Ag-3 samples exhibited uniform NP distribution characterized by a good dispersion without aggregation and with a narrow size distribution.\(^{20,29-31,43}\) The presence AgNPs dispersed not only on the surface but also inside of the membrane, determining the surface hydrophilicity and induced microphase structure of hydrophilic/hydrophobic separation in CEMs, which was crucial for the ion-transport behavior in the performance of IEMs.\(^{43,44}\) The optimized sample with excellent dispersion and decoration was 60SPSF-C3#-Ag-2. Figure 1c exhibits the diffractograms of the prepared CEMs with different amounts of AgNPs [60SPSF, 60SPSF-C3# and 60SPSF-C3#-Ag-X (X = 1–3)]. The plane located observed at 20° was ascribed to the polymer structure. The diffractograms associated to AgNPs exhibited peaks at 38, 45, 65, and 78°, which were associated with the crystalline planes 111, 200, and 311, respectively.\(^{31}\) Besides, strong silver signals of the nanoparticles were detected from XPS (Figure 1d). As expected, the binding energy peaks at 368 eV (Ag 3ds\(_{1/2}\) orbital) and 374 eV (Ag 3ds\(_{3/2}\) orbital) were obviously observed in the high-resolution XPS spectrum of Ag peaks, further affirming the successful formation of AgNPs.\(^{20}\)

Table 1. Tensile Strength and Elongation at Break of Prepared CEMs [60SPSF, 60SPSF-C3#, and 60SPSF-C3#-Ag-X (X = 1–3)]

| membrane | tensile strength (MPa) | elongation at break (%) |
|----------|-----------------------|-------------------------|
| 60SPSF   | 8.29                  | 19.85                   |
| 60SPSF-C3# | 18.46               | 23.25                   |
| 60SPSF-C3#-Ag-1 | 21.85               | 22.35                   |
| 60SPSF-C3#-Ag-2 | 24.38               | 24.86                   |
| 60SPSF-C3#-Ag-3 | 23.87               | 25.97                   |

Figure 2. Mechanism of the formation of AgNPs in CEMs.

The presence AgNPs were detected from XPS (Figure 1d). As expected, the binding energy peaks at 368 eV (Ag 3ds\(_{1/2}\) orbital) and 374 eV (Ag 3ds\(_{3/2}\) orbital) were obviously observed in the high-resolution XPS spectrum of Ag peaks, further affirming the successful formation of AgNPs.\(^{20}\) Figure 2 illustrates the mechanism of the preparation of AgNP-loaded CEMs and their digital pictures.

2.2. Mechanical Properties of Membranes. The mechanical properties of polymer nanocomposites depended on the dispersion of nanoparticles within the polymer matrix and the interfacial bonding established between the nanofiller and the polymer matrix,\(^{29,42}\) which was suitable for AgNP-loaded CEMs. To investigate the effects of loaded AgNPs in the polymer matrix on membrane’s mechanical properties, the analysis of the tensile strength and elongation at break properties was carried out. Table 1 summarized the tensile strength and elongation at break of the prepared CEMs. As expected, the tensile strength was enhanced after cross-linking (60SPSF-C3# compared with 60SPSF). Furthermore, it was observed that the incorporation of AgNPs to the polymer structure improved the membrane’s mechanical behavior to some degree. As the addition of AgNO\(_3\) increased, and consequently the amount of loaded AgNPs was higher, the mechanical properties of the cross-linked membranes were accordingly improved. The tensile strength and elongation at the break of 60SPSF-C3#-Ag-1 reached 21.85 MPa and 22.35%, respectively, better than that of 60SPSF-C3# (18.46 MPa, 23.25%), whose plant mechanical structure was formed because of the cross-linking. Besides, the mechanical properties of 60SPSF-C3#-Ag-2 were better than those of 60SPSF-C3#-Ag-1 as a consequence of a more uniform distribution of AgNPs with moderate size. However, the performances of 60SPSF-C3#-Ag-2 and -3 were almost the same because of the limitation of the amount of light energy and the cross-linking agent, which acted as a reducing agent, causing the saturation of the amount of AgNPs generated. This effect also revealed the successful synthesis of AgNPs inside the membrane structure. This method, which did not require postphysical mixing, has simple operability and uniformity.

2.3. Determination of Ion-Exchange Capacity (IEC), Water Uptake (WU), and Linear Expansion Ratio (LER). IEC, WU, and LER of the prepared membranes were strongly affected by AgNPs at room temperature. It was observed that...
the IEC of AgNP-loaded CEMs strongly decreased compared to that of the primary sample (Figure 3), which was likely due to the formation of AgNPs and the addition of cross-linking agents. Moreover, both WU and LER significantly decreased after cross-linking as shown in Figure 4. Besides, the WU and LER of AgNP-loaded CEMs increased compared to that of 60SPSF-C3# due to the presence of AgNPs, which promoted changes in the internal humidification. However, the cross-linking structure significantly decreased the free volume, thus water molecules were hindered by the membrane inside, suppressing the effects of hydrophilicity of AgNPs to a certain extent, which was particularly effective at higher temperatures. Besides, all of the samples have higher WU and LER, exhibiting a positive correlation with the increasing temperature (Figure 4). The most significant changes in the WU and LER values for the selected temperature interval (from 20 to 70 °C) were observed for 60SPSF-C3# in comparison with the pristine membrane. The successive incorporation of NPs into the membrane structure slightly alters both WU and LER for modified membranes, but both are evidently, showing an apparent increasing trend as the added amount of NPs is increased. AgNP-loaded cross-linked membranes may offer an effective application in electrodialysis (ED) considering its appropriate WU (25−50%) from 20 to 60 °C.

2.4. Determination of Membrane’s Electrochemical Properties. Area resistance and transport number of the prepared CEMs were compared with those of commercial membranes (Figure 5). It was observed that the conductive performance of CEMs decreased after cross-linking. The explanation can be associated to the effects promoted by the cross-linking structure formed, which efficiently diminished the free volume and resulted in a higher hydrophobicity, restricting the ion transport and hence causing the area resistance to increase. The values observed for modified CEMs decreased in the following order 60SPSF-C3#-Ag-1 > 60SPSF-C3#-Ag-2 ≈ 60SPSF-C3#-Ag-3 (from 1.58 to 1.42 and 1.39 Ω cm$^{-2}$, respectively). As the AgNPs are loaded, the membrane surface resistance was reduced and the transport number increased. The AgNPs near the sulfonate ion increase the hydrophilicity, promoting the adsorption of water, improving the internal humidification, broadening the ion-transport channels, and forming an adequate connection of internal channels. The cation transport mechanisms in CEMs before and after AgNP loading can be demonstrated in Figure 6. Donnan exclusion was enhanced and the permselectivity significantly improved due to the effects mentioned above, which promoted the transport of counter ions through the internal phase.

In ED application, when the applied current reaches a certain value, concentration polarization is generated, where transfer of ions is depleted at the interface between the membrane and the solution. As a result, the voltage across the boundary layer will be extremely increased, resulting in water splitting and causing a higher energy consumption as well as a lower current efficiency. To operate electrodialysis under suitable condition, the limiting current density of ED-fabricated CEMs needs to be tested. As Figure 7 shows, the curves directed by the test all show three regions: one Ohmic
region and two non-Ohmic regions; the second indicated that the water began to dissociate. After cross-linking, the limiting current density of the CEMs decreased; however, as the AgNPs were loaded, the value was increased. It can be explained that the lower membrane resistance and suitable ion channels reduced the difference of ion-transport velocity between the membrane inside and the solution, thereby increasing the limiting current density. The AgNP-loaded CEMs showed a higher limiting current density than the commercial membrane. The result suggested that 15 mA cm$^{-2}$ was suitable for application in desalinating experiment.

2.5. Antibacterial Properties of Prepared CEMs. The AgNP-loaded membranes have antibacterial properties, so bacteria cannot grow in their vicinity. As can be seen from Figure 8, the bacteria adhered to the membrane surfaces of 60SPSF (Figure 8a) and 60SPSF-C3# (Figure 8b), around which was full of bacteria. On the other hand, the inhibition zone appeared around 60SPSF-C3#-Ag-$X$ ($X = 1$–$3$), and its size increased with the increase of Ag loading. The distance of the inhibition zone from the boundary of the membrane of SPSF-C3#-Ag-$X$ ($X = 1$–$3$) reached 2.5 mm (Figure 8c), 4.8 mm (Figure 8d), and 4.9 mm (Figure 8e). The reason why the distances of 60SPSF-C3#-Ag-2 and -3 were similar was because the amount of reduction of AgNPs in this experiment reached extreme value. This suggested that silver ions were possibly released from the membranes when ionized in aqueous medium. Increasing the concentration of AgNPs significantly enhanced the antibacterial property. While the similar loaded amount of AgNPs in SPSF-C3#-Ag-2 and -3 resulted in their bacteriostatic effect per unit time to be similar, leading to similar diameters of the inhibition zone. It was worth noting that the largest total antimicrobial diameter of the sample in this study was 2.4 times the width of the sample itself, with the performance better than that of the surface-modified AgNP membranes in our previous work (about 2 times). The above results indicated that the AgNP-loaded membranes exhibited excellent antibacterial properties.

2.6. Electrodialysis. According to the observed results (Figure 9a,b), there was a possible trend that the AgNP-loaded CEMs have excellent ion transport properties. During the experiment, the conductivity in the dilute chamber became less and less, which means that the ions gradually migrate into the concentration chamber. Besides, the ion migration in the dilute chamber lacking the load current caused the voltage to gradually rise. After a certain time, the AgNP-loaded CEMs began to show their intrinsic properties: the conductivity of the dilute chamber decreased more quickly compared with the ED fabricated with other kind of CEMs. Among them, as indicated by the previous results, 60SPSF-C3#-Ag-1 and -2 exhibited the best performance. This was because the proper connection structure brought by AgNPs increased the speed of ion transport. After 2 h of experimentation, the salt removal ratios of 60SPSF-C3#-Ag-1, -2, and -3 were 65.1, 67.5, and...
68.1%, respectively, all of which were higher than that of 60SPSF without any modification (Figure 9c). In the case of 60SPSF-C3#, despite the ameliorative three-dimensional structure, the increase of the charge density improved the desalination performance to some degree. The presence of AgNPs further enhanced the ion removal ratio, which was in agreement with the filler content. The 60SPSF-C3#-3 exhibited the highest current efficiency but the lowest energy consumption (Figure 9d), which was associated with its moderate water absorption, swelling ratio, electrical resistance, and higher transport number. In addition, the performance of all AgNP-loaded CEMs surpassed that of the commercial CEM (NEOSEPTA CMX), indicating a good option for commercial application.

3. CONCLUSIONS

In this study, a simple and facile approach has been explored to fabricate AgNP-loaded CEMs. Through the ion-exchange process and UV induction, the in situ generated AgNPs were uniformly dispersed in the polymer matrix, avoiding the problem of agglomeration caused by the postmixing common procedure. The incorporation of AgNPs into the polymeric CEMs combined the advantages of the both materials. The proper particle size and dispersibility of the AgNPs improved the mechanical properties of the membranes. The AgNPs synthesized near the ion-exchange groups increased the aggregation of water molecules and broaden the ion-transport channels, contributing to an adequate connection of ion channels. The chosen optimal AgNP-loaded CEM exhibited excellent bacterial killing activities against Gram-positive bacteria and a controlled improvement in electrochemical performance. The optimized CEM (60SPSF-C3#-Ag-2) exhibited enhanced NaCl removal ratio of 67.5% with a high current efficiency (96.9%) and a low energy consumption (5.84 kWh kg\(^{-1}\)). The distance of the inhibition zone from the boundary of the membrane of SPSF-C3#-Ag-2 reached 4.8 mm. This study provided a practicable strategy for the in situ AgNP generation and potential applications of membranes in the field of antibacterial materials.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. Sulfonated polysulfone (60SPSF, designated in our previous work, \(M_w = 86,000\), polydispersity index = 2.24) was provided by Yanjin Technology Co. Ltd. (China). The purification process was as follows: the raw material was first dissolved in \(N,N\)-dimethylacetamide (DMAc), filtered through a sand core funnel (G4), precipitated, and vacuum dried at 120 °C for 24 h. Besides, pentaerythritol tetraacrylate (97%) was purchased from Macklin, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (TPO, 97%) was purchased from Sigma-Aldrich, and silver nitrate (99.8%) and sodium nitrate (99.0%) were provided by Aladdin. Organic solvents \(N,N\)-dimethylacetamide (DMAc) and ethyl alcohol (99.7%) were provided from Lingfeng Reagent Co. Ltd. and Anhui Ante Food Co. Ltd., respectively. Reagents used in the test including sodium chloride (99%), potassium chloride (99%), and sodium sulfate were from Aladdin (China). Commercial IEMs including AEMs (type I, Fuji film, Japan) for electrodialysis test and CEMs (NEOSEPTA CMX, Asahi Kasei Corporation, Beijing) for performance comparison were used in this study.

4.2. Preparation of the Cross-Linked CEMs with in Situ AgNPs. The cross-linked CEMs with in situ AgNPs were synthesized by solvent evaporation inversion initiated by UV radiation method. The AgNPs were simultaneously generated when three-dimensional network structure of polymer was formed. For the in situ anchoring of AgNPs in the blend of CEMs, 1 g of 60SPSF (sufficiently decontaminated) was stirred in 10 mL of DMAc at 60 °C until completely dissolved. And then, the additives containing 0.05 g of silver acetate, 0.25 g of ethylene glycol diacetate, and 0.05 g of TPO were added to the solution at room temperature with continuous stirring.
for another 3 h to allow the exchange of Ag⁺ with dissociated K⁺ from −SO₃⁻ groups (SPSF membrane matrix). Ultimately, the casting solution was poured onto a self-made mold and exchanged Ag⁺ was further reduced into the metallic state (Ag) due to the presence of electron and reducing radical group induced by UV treat (Scientz03-II). The ultraviolet wavelength used was 365 nm, and the power of the UV lamp was 40 W. All samples were treated for 20 min and then immediately placed in a vacuum drying oven to evaporate solvent. After the dry samples were washed with ethyl alcohol for three times, the samples were soaked into 0.5 M sodium nitrate solution for 24 h to exchange unreacted Ag⁺. The CEMs using AgNO₃ with 0.125, 0.250, and 0.500 g were designated as 60SPSF-C3 AgX (X = 1−3), respectively.

### 4.3. Membrane Characterization

#### 4.3.1. X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM)

The results of XRD were characterized using an XPERT PRO (PANalytical, Netherlands) instrument with Cu Kα radiation with a 0.02° step at room temperature. The prepared CEMs were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan). Also, the anode was mono [Al (Mono)] (45 W). The morphologies of the prepared CEMs were characterized using scanning electronic microscopy (SEM) (Hitachi S-4800) at an accelerating voltage of 15 kV.

#### 4.3.2. Mechanical Properties Measurement

Tensile strength and elongation at break of membrane samples (2 × 6 cm²) were determined by automatic mechanical analyzer (CTM2050).

#### 4.3.3. Ion-Exchange Capacity (IEC)

Ion-exchange capacity refers to the amount of ions that can be exchanged per unit volume or mass of ion-exchange material, which determines the ion-transport rate during electrodialysis to some extent. Before testing, 1 M HCl aqueous solutions were prepared with samples soaked for at least 24 h to ensure that the counter ions were totally converted to H⁺, followed by three rinses with deionized water to remove excess H⁺. Subsequently, 1 M NaCl aqueous solution was prepared where the samples were soaked for 24 h. Ultimately, potentiometric titration (T50) purchased from Mettler Toledo was utilized to titrate the concentration of H⁺ in the solution. Also, the IEC was measured from eq 1:

\[
\text{IEC} = \frac{V \times c_{H^+}}{W_{\text{dry}}} 
\]

where \( V \), \( c_{H^+} \), and \( W_{\text{dry}} \) represent the volume of NaCl solution, the concentration of H⁺, and the dry weight of samples, respectively.

#### 4.3.4. Determination of Water Uptake (WU) and Linear Expansion Ratio (LER)

WU reflected the intrinsic water content combined with the reactive group in the membrane, and linear expansion ratio referred to the change of the area before and after the membrane sample was soaked into the solution under certain conditions. In the process of testing, deionized water was first prepared with the samples soaked in until an equilibrium was obtained at distinct temperature. Also, then a filter paper was used to remove moisture outside the samples. After accurate values of weights and sizes were recorded immediately, the samples were dried in a vacuum drying oven to evaporate water. Ultimately, the parameters of the samples (both weight and sizes in wet and dry conditions) were recorded. WU and LER were measured from eqs 2 and 3:

\[
\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% 
\]

\[
\text{LER} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% 
\]

where \( W_{\text{wet}} \) and \( W_{\text{dry}} \) are the weight of the samples in wet and dry conditions, respectively. \( L_{\text{wet}} \) and \( L_{\text{dry}} \) are average length where \( L_{\text{wet}} = \sqrt{L_{\text{wet1}}^2 + L_{\text{wet2}}^2} \) and \( L_{\text{dry}} = \sqrt{L_{\text{dry1}}^2 + L_{\text{dry2}}^2} \) are the lengths and widths of the samples in wet and dry conditions, respectively.

#### 4.3.5. Membrane Surface Area Resistance

Membrane surface area resistance depended on the electromigration velocity of the counter ions in the membrane and provides some information for the microstructure. Two compartments were designed in the testing device, between which is fixed a membrane container filled with 0.5 M NaCl solution. Also, 0.3 M Na₂SO₄ solution was circulated in electrode cells. The applied current was 0.05 A. Before testing, 0.5 M NaCl aqueous solutions were prepared with samples soaked for at least 12 h. The voltage between two silver chloride electrodes (V) was determined by a digital multimeter. Ultimately, membrane surface area resistance was measured by the following equation (eq 4):

\[
R_m = \frac{E_m - E_0}{I \times S} 
\]

where \( E_m \) (with sample assemble) and \( E_0 \) (without sample assemble) are the testing voltage (V) between two silver chloride electrodes; \( I \) is the operating current (A); and \( S \) is the testing CEM’s valid area (cm²).

#### 4.3.6. Determination of Transport Number and the Limiting Current Density

The transport number characterizes the selective permeation performance of the membrane for counter ions. Before testing, 0.15 M KCl solutions were prepared with samples soaked for at least 12 h. During the test, two middle compartments were filled with two kinds of KCl solutions (0.1 and 0.2 M, respectively). The voltage between two silver chloride electrodes (V) was determined by a digital multimeter. The transport number \( \bar{t} \) was measured from eq 5:

\[
\bar{t} = \frac{E_m + E_0}{2E_0} 
\]

where \( E_m \) is the the testing voltage (V) across the membrane and \( E_0 \) is the voltage between two kinds of KCl solutions (0.1 and 0.2 M, respectively).

The polarization current–voltage curves of ED stack fabricated with the prepared CEMs were measured by an electrochemical workstation (Metrohm Autolab PGSTAT302N). In this test, 0.2 M NaCl aqueous solution was used as a feed solution and 0.3 M Na₂SO₄ was used as an electrode solution, which was circulated using a pump.

#### 4.3.7. Antibacterial Properties

Gram-negative E. coli was selected as the model bacteria in this test. The inhibition zone method was used to measure the antibacterial activity of the prepared membranes. Before testing, Luria–Bertani (LB) agar plates (containing 10 g L⁻¹ of peptone, 5 g L⁻¹ of yeast extract, 10 g L⁻¹ of sodium chloride, and 16 g L⁻¹ of agar at pH of 7.0) were prepared, on which sterilized samples were placed. Also, then the LB was cultivated with E. coli (concentration of 10⁶
c.f.u mL$^{-1}$) and incubated at 37 °C overnight. The distance of the inhibition zone from the boundary of the membranes in the sample disks were measured finally.

4.3.8. Electrodialysis. A four-cell device was used to evaluate the desalting performance. The four cells include a concentrate cell, a dilute cell, and two electrode cells. The volume of the two middle cells was 80 mL and NaCl solution (0.5 M) was filled in at the beginning of the test. At the start of the test, 0.3 M Na$_2$SO$_4$ solution was circulated in electrode cells, and the conductivity of the solution in two middle cells and the stack voltage were recorded every 10 min. The testing CEM’s valid area was 19.625 cm$^2$, and the applied current was 0.3 A (15 mA cm$^{-2}$). The NaCl removal ratio (%), current efficiency (CE, %), and energy consumption (EC, kWh kg$^{-1}$) of ED with CEMs were measured from eqs 6 to 8$^{17}$

$$R_W = \frac{\delta_t - \delta_i}{\delta_0}$$

$$\eta = \frac{zF(C_t - C_i)V_t}{NIAt} \times 100\%$$

$$E = \int_{0}^{t} \frac{UI}{c_iV_M} - dt$$

where $\delta_i$ and $C_i$ are the content and concentration in dilute cell (0.5 M NaCl in this experiment), respectively; $\delta_t$ and $C_t$ are the content and concentration in concentrate cell, and $V_t$ is the content, concentration, and volume in dilute cell at time $t$, respectively; $I$ is the operating current value and $U$ represents the voltage of the ED stack; $Z$, $F$, and $N$ represent the absolute valence of Na$^+$, Faraday constant, and number of repeating units ($N = 1$), respectively. Besides, $M_b$ is the molecular weight of NaCl.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02537.

SEM images of 60SPSF-C3#-Ag-3 CEMs (PDF)

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Notes

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NOMENCLATURE

IEM, ion-exchange membrane
CEM, cation-exchange membrane
SPSF, sulfonated polysulfone
ED, electrodialysis
TPO, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide
IEC, ion-exchange capacity
WU, water uptake
LER, linear expansion ratio
$I_{lim}$, limiting current density
$I-V$, current–voltage
$R_m$, membrane surface area resistance
EC, energy consumption
CE, current efficiency

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