Electrospun nanofibrous membrane for electrodialysis

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Abstract. The direct fabrication of homogenous membrane for electrodialysis has become the research hotspots in the field of water purification. A novel multi-jet electrospinning method with sheath gas was presented to study the fabrication of homogenous electrodialysis membrane. By soaking into sulfuric acid, the reactive exchange groups can be introduced into the electrospun nanofibrous membrane that has been hot pressed. Thanks to the pores among nanofibers, electrospun electrodialysis membrane had advantages of higher porosity, higher water uptake and lower membrane resistance, which promoted the ion transmission through the membrane. The porosity, water uptake and ion exchange capacity (IEC) reduced with the increase of membrane thickness. An electrodialysis separation system was set up to test its separation performance. The results showed that the desalinization ratio of NaCl solution could be reached to 58.15% within 30 minutes. The electrospun nanofibrous membrane for electrodialysis provides a simple and effective way to expand its industrial application.

1. Introduction
Electrodialysis [1-2] is a novel membrane separation method, which has shown great application potentials in the fields of water treatment, sea water desalination and medical industries [3-5]. However, the widely used preparation processes for separation membranes such as lamination are with complex procedures and high cost, which limits the further development of electrodialysis [6-7]. A simple process to prepare the homogenous membrane has been required urgently for the research of electrodialysis.

With the advantages of small diameter, high porosity and large specific surface area, electrospun nanofibers have been widely used in various fields, including air filtration [8], battery separator [9] and water treatment [10-11], which indicates a great application prospect for the rapid preparation of ion exchange membrane [12-13]. Pan [14] et al prepared cation exchange membranes by electrospinning and hot-pressing treatment, which showed approximately 4 times higher in the alkali dialysis coefficient compared with previous solution casting membrane. In addition, Pan’s group [15] also fabricated anion exchange membrane by electrospinning for acid recovery, which exhibited both higher acid permeability and selectivity, underling the advantages of electrospun nanofibrous membrane in diffusion dialysis.
application. Electrodialysis is a technology based on the ion exchange membrane, then the fabrication of electrodialysis membrane by the method of electrospinning has been a potential way to improve its selective permeability further.

However, the low productivity of traditional electrospinning method with single-needle spinneret largely limits its industrial application. Multi-nozzle electrospinning is a straightforward method to improve the productivity of electrospun nanofibers, nevertheless there are mutual electrical interferences among the nozzles, which halts the increasing of charged jet density and the stable continuous ejection of charged jets [16-17]. Various auxiliary methods have been proposed to achieve multi-jet electrospinning with weakened interferences, such as the shield ring [18], the cylindrical electrode [19], the plate electrode [20], etc. How to fabricate uniform and compact nanofibrous membrane at a high efficiency has been the hotspot to expand its applications.

In this paper, a novel multi-nozzle spinneret with sheath gas was introduced into the fabrication of homogenous membrane for electrodialysis. The exchange performances of electrospun nanofibrous membrane were investigated and an electrodialysis separation system was set up to test its separation performance.

2. Materials and Methods

2.1. Preparation of electrospun membrane for electrodialysis

The schematic diagram of multi-jet electrospinning with the constraint of sheath gas to prepare electrospun nanofibrous membrane is shown in Figure 1, including a novel multi-jet spinneret, a precision syringe pump, a high voltage power source, an air compressor and a collector. The multiple nozzle tips of the spinneret were arranged in a triple layer equilateral hexagon configuration to achieve the high efficiency of electrospun nanofibers. Then, the assisted sheath gas was introduced into the spinneret as well. In our previous work, it has been reported that the sheath gas in laminar flow provided an additional constraining and stretching force to overcome the mutual interferences among the nozzles, decrease the critical voltage for multi-jet ejection, reduce the nanofiber diameter and promote the uniformity of electrospun nanofibrous membrane [21-23]. The design of the novel multi-jet electrospinning spinneret provides an available way to promote the simultaneous ejection of multiple jets and improve the nanofiber productivity.

To fabricate the electrospun nanofibrous membrane, the polyvinylidene fluoride (PVDF, Mw=1,000,000 g/mol) powder was dissolved in the mixture solvent of N, N-Dimethylformamide and acetone with volume ratio of 5:5 (v:v). The mass concentration of the prepared solution was 10 wt%. A precision syringe pump (Pump 11 Pico Plus Elite, Harvard Apparatus America, USA) was used to supply polymer solution through the liquid inlet to the spinneret at the flow rate of 6,000 μl/h. Then, the solution could be supplied into each nozzle equally through the liquid cavity of the spinneret. A DC high voltage power source (DW-SA403-1ACE5, Dongwen high voltage power source Ltd. of Tianjin, China) was used to generate the high electrical field between the spinneret and the collector. The anode of the DC high voltage power source was connected to the nozzles of the spinneret, and the cathode was connected to the grounded collector of thin copper plate. The applied voltage was set to be 16 kV. An air compressor was used to pump the assisted gas into the spinneret through the gas inlet with the gas pressure of 25 kPa. The distance between the lowest nozzle tip and the collector was 8 cm. The collector was fixed on the XY motion platform (GXY1515GT4, Googoltech, China) to guide the electrospun nanofibers deposited into a uniform membrane.

After the electrospinning process, the membrane was hot-pressed at the temperature of 80°C to promote its mechanical strength. Then, to prepare the electrodialysis membrane with selective permeability, the electrospun membrane was soaked into 98% concentrated sulfuric acid for 12 hours at the temperature of 60°C to introduce the reactive exchange groups into membrane. Next, the membrane was cleaned with 60% sulfuric acid, 30% sulfuric acid and deionized water, successively to remove the sulfuric acid at the membrane surface. Finally, the prepared electrodialysis membrane was kept at the deionized water for further testing. In the experiments, the micro/nano morphologies of the membrane
were observed and recorded by a field emission scanning electron microscope (SEM, Hitachi SU-70, Japan).

![Figure 1. Schematic diagram of multi-jet electrospinning with the constraint of sheath gas.](image)

2.2. Characterization of electrospun membrane for electrodialysis

2.2.1. Porosity. The porosity of membrane was measured according to the n-butanol uptake method. The electrodialysis membrane was cut into the square shape with each side length of 2 cm. Then, it was thrown into n-butanol to fill with the holes inside the membrane. 2 hours later, it was taken out from the n-butanol and the residual solution was removed slightly. The porosity of the membrane could be calculated as [24]:

$$\varepsilon = \frac{m_2 - m_1}{\rho Ah}$$  (1)

Where, $m_1$ and $m_2$ represented the mass of membrane before and after soaked into n-butanol, $\rho$ was the density of n-butanol, $A$ was the area of membrane, $h$ was the thickness of membrane.

2.2.2. Water uptake. The water uptake of membrane was an index that performed the water content inside the membrane. The membrane of square shape with each side length of 2 cm was thrown into the deionized water for 24 hours. Then, it was dried in a vacuum oven at the temperature of 80 °C to remove the water completely. Then, the water uptake of membrane could be calculated as [24]:

$$C_w = \frac{w_1 - w_2}{w_1} \times 100\%$$  (2)

Where, $w_1$ and $w_2$ were the mass of wet membrane and dry membrane, respectively.

2.2.3. Ion exchange capacity (IEC). The ion exchange capacity (IEC) was measured according to the conventional Mohr method. The membrane was dried in a vacuum oven for 2 hours. Then, it was thrown into the NaCl solution was concentration of 0.5 mol/L for 24 hours, so that the H\(^+\) inside the membrane and the Na\(^+\) in the solution could be transferred fully. Finally, the released amount of H\(^+\) was determined through titration with 0.01 mol/L NaOH solution. The value of IEC could be calculated as [25]:

$$IEC = \frac{w_0 - w_1}{w_0} \times 100\%$$  (3)
Where, \( V \) was the volume of NaOH solution used for titration, \( c \) was the concentration of NaOH solution, \( m \) was the mass of dry membrane.

3. Results and Discussion

The morphology of electrospun nanofibrous membrane for electrodialysis was investigated first. The SEM images of electrodialysis membrane fabricated by lamination and electrospinning are shown in Figure 2a and Figure 2b, respectively. Compared with most commercial membrane fabricated by complex processes such as lamination, the electrospun membrane was composed of a large number of nanofibers and there existed several pores among nanofibers, which increased the contact area between membrane and solution, contributing to the promotion of ion transmission. After soaked into 98% concentrated sulfuric acid, the surface morphology of nanofibers became rougher and waver with the average diameter increasing from 0.68 μm to 0.83 μm. Due to the water swelling of active groups, there would be some small granular structures on the surface of nanofibers and some nanofibers would gather together, as shown in Figure 2c.

Figure 2. SEM images of electrodialysis membrane fabricated by lamination and electrospinning.

The performances of electrodialysis membrane fabricated by lamination and electrospinning were tested, as given in Table 1. It could be concluded that the electrospun membrane has a larger porosity and water uptake due to the large specific area inside the membrane. However, limited by the present reaction condition, ionic exchange capacity (IEC) for the electrospun membrane was a bit smaller, which could be enhanced by optimizing the post-processing of membrane and introducing more reactive exchange groups. As the nanofiber deposited layer by layer and the thickness of nanofibrous membrane increased, the porosity, water uptake and IEC of membrane decreased. When the average thickness of electrospun membrane increased from 43 μm to 164 μm, the porosity, water uptake and IEC reduced from 79.8% to 64.6%, 65.3% to 62.2% and 0.507 mmol/g to 0.370 mmol/g, respectively. Attributing to the larger porosity and water uptake, there were more ion transmission passageways inside the electrospun membrane, resulting in a much smaller membrane resistance than that of the membrane fabricated by lamination, which was beneficial for the ion exchanging and the energy consumption reducing. In Table 1, sample 1 is an electrodialysis membrane fabricated by lamination, while other samples are all electrodialysis membranes fabricated by electrospinning.

Table 1. Exchange performances of electrodialysis membrane.

| Sample | Thickness (μm) | Porosity (%) | Water uptake (%) | IEC (mmol/g) |
|--------|---------------|--------------|------------------|--------------|
| 1      | 44            | 39.1         | 40.1             | 0.707        |
| 2      | 43            | 79.8         | 65.3             | 0.507        |
| 3      | 49            | 79.5         | 64.8             | 0.504        |
| 4      | 94            | 71.2         | 64.9             | 0.431        |
| 5      | 103           | 72.2         | 64.2             | 0.430        |
| 6      | 152           | 68.1         | 63.4             | 0.385        |
| 7      | 164           | 64.6         | 62.2             | 0.370        |
Then, a simple experimental setup was established to test the electrodialysis performance of electrospun nanofibrous membrane, as illustrated in Figure 3, including an anode chamber, a dilute chamber and a cathode chamber. An electrospun nanofibrous membrane of which the cation exchange groups had already been introduced was fixed between the cathode chamber and the dilute chamber, while an anion-exchange membrane was fixed at another side to transmit the ions in the solution selectively. A 30 V direct-current voltage was supplied between the anode and the cathode to provide a driving force for ion transmission. Here, 0.025 mol/L NaCl solution was utilized to investigate the ion separation behavior for electrospun nanofibrous membrane. The varieties of solution conductivity in each chamber were recorded as time going by as depicted in Figure 4. The solution conductivity in the dilute chamber decreased from 3.8 mS/cm to 1.59 mS/cm in 30 minutes while those in the anode and cathode chambers increased, which indicated that the ions had been separated selectively, verifying the feasibility of the electrospun nanofibrous membrane in the application of electrodialysis.

![Figure 3](image3.png)

*Figure 3. Experimental setup for electrodialysis performance.*

![Figure 4](image4.png)

*Figure 4. Relationship between NaCl solution conductivity and testing time with different chambers.*

4. Conclusions
The technology of multi-jet electrospinning is introduced into the fabrication of electrodialysis membrane. To promote the simultaneous ejection of multiple jets, a novel multi-jet spinneret with the constraint of sheath gas was proposed, thus uniform nanofibrous membrane could be obtained at a high productivity. Then, through the processes of hot-pressing, introducing the reactive exchange groups and removing the surface sulfuric acid, electrospun membrane for electrodialysis was achieved successfully. Compared with electrodialysis membrane fabricated by lamination, the electrospun membrane for electrodialysis presented a higher porosity, a higher water uptake and a lower membrane resistance. From the membrane electrodialysis experiments, it could be seen that the desalinization ratio of NaCl
solution could be reached to 58.15% within 30 minutes, exhibiting an excellent performance in electrodialysis for electrospun nanofibrous membrane.

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