Supporting Information

Symmetrically recombined nanofibers in a high-selectivity membrane for cation separation in high temperature and organic solvent

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1. Theories

1.1. The theory of dissolved and recombined of poly(p-phenylene terephthalamide) nanofibers.

The negatively charged DSA with a couple of symmetrical amidogen groups (Fig. S1a). The aramid nanofibers are the highly ordered and asymmetric alternate structure of long PPTA molecular chains, and the intermolecular hydrogen bonds between the molecular. These interactions should be dissolved into dimethyl sulfoxide (DMSO) (the potassium hydroxide as the catalyst) in the 70 $^{\circ}$ C oil-bath and keep stirring for 3 days then formed the PPTA solution (Fig. S1b).

Fig. S1 The chemical structure of DSA (a) and the synthesis of membrane casting solution process (b).

1.2. The theory of ions with/without hydrated diameters.

The around of hydrated ion water molecules could be seen as the Coordination Solvent mixing Zone and Random change Zone. Especially in the Coordination-Solvent mixing Zone, part of the water molecules forms a strong coordination bond with the ion, which named as coordination water molecule. There are some water molecules will not forms a strong coordination bond with ions, which named as non-coordination water molecule as shown in Fig. S2.

Fig. S2 The structure of hydrated ions.

1.3. The theory of selective separation of monovalent cations by electro-driven membranes.

Two important theories for CEMs with selective separation of monovalent cations:

1) The fixed ion exchange sites and the solution counter ions electrostatic repulsion forces effect, see in Fig. S3a;

2) The hydrated ionic diameter of different anions and AEMs structure sieving effect, see in Fig. S3b;

F=F'-F''If F > 0, cations through the membrane; If F < 0, cations will not through the membrane.

If $\Phi > D$, cations through the membrane; If $\Phi < D$, cations will not through the membrane. (The channel should fixed with ion exchange groups!)

2. Materials

2.1 Chemicals

Kevlar aramid nanofibers were obtained from, (United States). Potassium hydroxide (KOH, 85%) in the form of pellets was obtained from Acros Organics NV. Dimethyl sulfoxide (DMSO, 99.5%) was obtained from VWR International BVBA. 1-ethyl-3-(3-dimethylami-nopropyl) carbodiimide hydrochloride (EDC-HCl), N-hydroxy succinimide (NHS) was purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). 2,5-diaminobenzenesulfonic acid (DSA), Sodium hydrogen oxide (NaOH), hydrochloride acid (HCl), sodium chloride (NaCl), sodium sulfate (Na₂SO₄) ammonium sulfate ((NH₄)₂SO₄), lithium sulfate (Li₂SO₄), Magnesium sulfate (MgSO₄), acetone and all other chemicals were obtained from Sigma-Aldrich (Germany) and without any further purification.

2.2 Commercial ion exchange membranes

Product	Туре	Thickness/	Surface electric	Brust	Manufacture
Name		μm	resistance/ $\Omega \cdot m^2$	strength/kPa	
СМХ	Cation exchange	110-160	1.8-3.8	> 400**	ASTOM
	membrane		in 0.5 M NaCl		
FJCI	Cation exchange	135	1.3	2.4 (wet)	FUJIFILM
	membrane		in 2.0 M NaCl		
FJAI	Anion exchange	125	0.8	2.7 (wet)	FUJIFILM
	membrane		in 2.0 M NaCl		

Table S1. The data of commercial membranes.*

*Data from manufactures.

**Measured by a Mullen Vrust Strength Device.

3. Experimental section

3.1. Preparation of PDP membranes.

4% PPTA, 6% KOH and 90% DMSO were mixed in the round-bottom flask with magnetic stirring, and then added the DSA. Under the oil-bath (70 $^{\circ}$ C), 3 days later, membrane casting solution then obtained, then standing for one week in the confined round-bottom flask.

One week later, the casting solutions were poured onto a clean glass plate, by using a casting knife and cast the gel membrane with the thickness of 250 μ m at 25 °C. Then, the glass plate was immediately immersed into the catalysts solution (1 g L⁻¹ EDC HCl and 0.6 g L⁻¹ NHS solution). 15 min later, the membranes were carefully peeled off from the glass plate and transferred to the new catalysts solution (1 g L⁻¹ EDC HCl and 0.6 g L⁻¹ NHS solution). 5 days later (time of amide condensation reaction), the gel membranes were carefully cleaned by pure water for five times and put on the surface of non-woven polypropylene fabric.

Then, the as-prepared gel membranes were dried in an oven at 65 $^{\circ}$ C by air dry oven for 8 hours. Finally, the PDP membranes were obtained.

3.2. Ion exchange capacity measurement.

In this work, the ion exchange capacity (IEC) is measured by acid-base titration method. the dry PDP membranes were weighed (m_{dry}) and measured into 1 M HCl for 48 h. Then, the PDP membranes were cleaned 3 times by pure water and make sure there was no absorbed HCl on the surface of PDP membranes. Then the PDP membranes was immersed in 0.5 M NaCl for 48 h. 0.01 M NaOH were chose as the titrated solution and phenolphthalein is used as the indicator. The IEC was calculated by

$$IEC = \frac{(V_s - V_b) \cdot c_{NaOH}}{M_{dry}}$$

where V_s is the volume of consumed NaOH by membranes; V_b is the volume of consumed NaOH without membranes and c_{NaOH} is the concentration of NaOH, which

is 0.01 M; M_{Dry} is the weight of the dry membranes.

3.3. Water content measurement.

The water content was calculated through measuring the membrane weight changes before and after hydrating. Before to the measurement, the membrane was samples were dry in a vacuum oven at 60 $^{\circ}$ C for 12 h. After that, the membrane samples were immersed in water for 48 h. Then, the membranes' water content were calculated as

$$W(\%) = \frac{M_{Wet} - M_{Dry}}{M_{Dry}} \times 100\%$$

where M_{Wet} is the weight of wet membrane samples, M_{Dry} is the weight dry membrane samples.

3.4. Swelling rate measurement.

The swelling rate was measured by measuring the change of length before and after the membrane become a hydrated state. Prior to the measurement, the a membrane samples were obtained by drying in a vacuum oven at 60 $^{\circ}$ C for 12 h. After that, the membrane samples were immersed in water for 48 h. Then the swelling rate were calculated as

$$S(\%) = \frac{L_{Wet} - L_{Dry}}{L_{Dry}} \times 100\%$$

where L_{Wet} is the length of wet membrane samples, L_{Dry} is the length of dry membranes.

3.5. Membrane surface electric resistance measurement.

In this work, the membrane surface electrical resistance (the effective area of the membrane was 7.065 cm²) was tested in a 0.50 M NaCl solution, and 0.2 M Na₂SO₄ was chosen as the electrode solution, under the 0.04 A of current. The surface electrical resistance R_{SER} ($\Omega \cdot cm^2$) was calculated as

$$R_{SER} = \frac{U - U_0}{I} \times S$$

where U is the voltage of the membranes and U_0 is the voltage of the blank expressed in V, I is the constant current through the membranes, expressed in A. S is the effective area of the membrane, expressed in cm².

3.6. Membrane zeta potential measurement.

The zeta potential of the PDP membranes were measured by using a SurPASS[™] 3 electro-kinetic analyzer (Anton Paar, Graz, Austria). Membrane samples were washed and rinsed in pure water for 24 hours before measuring. The zeta potential was determined in a background electrolyte of 1 mM KCl solution over a pH range from 3.5 to 10.0 in 25 °C.

3.7. Current-voltage curves measurement.

In this work, the membrane current-voltage curves were measured in 0.1 M NaCl solution in ED. Besides, the $0.2 \text{ M Na}_2\text{SO}_4$ was chosen as the electrode solution.

3.8. Scanning electronic microscopy (SEM), energy dispersive x-ray spectroscopy (EDS).

The morphologies and structures of surface and cross-sectional of membrane were characterized by using scanning electronic microscopy (SEM, Hitachi S-4800) at an accelerating voltage of 10.0 kV. The EDS maps C, O, N and S element over the membrane surface were provided at the same time.

3.9. Transmission electron microscopy (TEM).

Projected area of samples was obtained using a probe-lens corrected JEOL ARM200F operating at 200 kV, equipped with cold-field emission source.

3.10. Atomic force microscope (AFM).

Atomic force microscopy (AFM, Bruker, United States) equipped with a noncontact type scanner was used to acquire three dimensional topography of membrane surface. These images were captured under tapping mode at room temperature (~ $25 \,$ C).

3.11. X-ray photo-electron spectroscopy (XPS).

In this work, the elemental compositions of the membranes were analyzed by X-ray photo-electron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan). The anode was mono (Al (Mono)) (45 W). The charge neutralizer was on current 1.8 A, balance 3.3 V and bias 1.0 V.

3.12. Attenuated total reflection Fourier transforms infrared (ATR-FTIR).

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, United States) was used to monitor the change of the functional groups of membrane surface. Membranes were dried thoroughly in vacuum oven at $60 \,^{\circ}$ C before measurements.

3.13. Thermogravimetric analysis (TGA).

The thermogravimetric analysis Mrtter is used to evaluated the thermal property of membranes. In this work, membrane samples were tested under the N2 atmosphere from 30 to $1000 \,^{\circ}$ with the 10 $^{\circ}$ min⁻¹ of heating rate.

3.14. PDP membranes application in ED.

In electrodialysis, as shown in Fig. 3a, the resulting membrane samples are put in the middle of the device, and two anion exchange membrane are set on the both side of the device. In desalination, 100 mL 11.0 g L⁻¹ Na₂SO₄ were chosen as the initial electrolyte solutions in dilute cell and 100 mL 2.0 g L⁻¹ Na₂SO₄ were chosen as the initial electrolyte solutions in concentrated cell. The electric solution was the 300 mL 10.0 g L⁻¹ Na₂SO₄. Every 10 min, the concentration of Na⁺ was measured in both

dilute and concentrated cells (under the constant voltage and the voltage was 15.0 V).

The desalination efficiency calculated (D %) as

$$D\% = \frac{c_0 - c_t}{c_0} \times 100\%$$

where c_0 is the initial concentration of dilute cell and c_t is the concentration of dilute cell at time t, expressed in g L⁻¹.

3.15. Membranes desalination performance $(NH_4)_2SO_4$, Li_2SO_4 , Na_2SO_4 and $MgSO_4$.

All the steps are the same as shown in 3.14 expect changing the electric solution and the initial electrolyte solutions in diluteand concentrated cells.

3.16. Thermostability measurement.

The PDP-1.0 and CMX membranes were selected and measuring into 500 mL pure water and in the round-bottom flask with magnetic stirring 750 rpm. Under the oil-bath ($60/100^{\circ}$ C) for 24 h, the final membranes were test in electrodialysis as the steps shown in 3.14.

3.17. Resistance of organic solvent measurement.

The PDP-1.0 and CMX membranes were selected and measuring into 200 mL aqueous acetone solutions (40% and 80%) in the round-bottom flask with magnetic stirring 750 rpm. 24 h later, the final membranes were test in electrodialysis as the steps shown in 3.14.

4. Results and analysis

4.1. Resulting membranes.

With the increasing of DSA monomers, the resulting membranes show a brown color and present an increasing trend of both color depth and membrane thickness (Fig. S4a to S4f).

Fig. S4 The prepared membranes and inset are the membrane thickness of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

4.2. SEM membrane cross-section images.

SEM cross-section images are used to observe and characterize the PDP membranes. The nanofibers of the membranes can be clearly distinguished from the zoom-in images of PDP-0, PDP-0.1, PDP-0.2, PDP-0.5, PDP-1.0 and PDP-2.0 membranes.

Fig. S5 The SEM cross-section images and inset are the zoom-in images of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

4.3. AFM membrane surface images.

The AFM surface images are used to observe and characterize the three dimensional topography of the PDP membranes. The nanofibers of the membranes can be clearly observed from the images of PDP-0, PDP-0.1, PDP-0.2, PDP-0.5, PDP-1.0 and PDP-2.0 membranes.

Fig. S6 The 2D and 3D SEM images of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

4.4. TEM image.

The PPTA casting solution was observed by the TEM and the nanofibers caould be clearly distinguishd.

Fig. S7 The TEM image of PDP-1.0 membrane.

4.5. SEM membrane surface images.

As shown in the SEM membrane surface images, with increasing of the DSA monomers, the membranes are denser.

Fig. S8 The SEM surface images and inset are the zoom-in images of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

4.6. SEM membrane surface element mapping image of PDP-0 membrane.

There is no sulfur element can be found in PDP-0 membrane surface.

Fig. S9 The SEM element mapping image of PDP-0 membrane surface.

4.7. XPS results.

Compared to the PDP-0 membrane (Fig. S10a), which fit the peaks at 284.2 eV (C-C vibration), 284.7 eV (C-C & C=C vibration), 287.7 eV (C=O vibration) and 285.3 eV (C-N vibration), a new peak appeared at 286.4 eV (C-S vibration) (Fig. S10b to S10f).

Fig. S10 The XPS high resolution C 1s of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

The O 1s could be fit into two peaks in PDP-0 membrane, which are assigned to the vibration of O-C (530.9 eV), O=C (531.5 eV). However, the O 1s could be fit into four peaks in PDP-1.0 membrane, which are assigned to the vibration of O-C (530.9 eV), O=C (531.5 eV), O=S (532.25 eV) and O-S (533eV).

Fig. S11 The XPS high resolution O 1s of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

There are no peaks in the PDP-0, while the S 2p could be fit into the peaks of S-O vibration (167.4 eV), S=O vibration (168.0 eV), and S-C vibration (168.8 eV).

Fig. S12 The XPS high resolution S 2p of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

The high resolution N 1s in all the membranes only have one peak (N-C vibration), which is indicative of the amide condensation reaction between the DSA and PPTA nanofibers without any other bond formation.

Fig. S13 The XPS high resolution N 1s of PDP-0 (a), PDP-0.1 (b), PDP-0.2 (c), PDP-0.5 (d), PDP-1.0 (e) and PDP-2.0 (f) membranes.

4.8. ATR-FTIR results.

Fig. S14 The ATR-FTIR spectra of resulting membranes

4.9. Zeta potential results.

Fgirue S15. The zeta potential of PDP membranes.

4.10. The current-voltage curves.

Fig. S16 The current-voltage curves of PDP membranes.

Fig. S17 Membranes separation performance in dilute and concentrated cells of PDP-0.1 (a), PDP-0.2 (b), PDP-0.5 (c), PDP-1.0 (d), PDP-2.0 (e) CMX (f) and FJCI (g) membranes.

Fig. S18 Membranes desalination efficiency (Na₂SO₄) of PDP-0.1 (a), PDP-0.2 (b), PDP-0.5 (c), PDP-1.0 (d), PDP-2.0 (e) CMX (f) and FJCI (g) membranes.

4.12. Membranes separation performances of (NH₄)₂SO₄.

Fig. S19 Membranes desalting efficiency $((NH_4)_2SO_4)$ of PDP-1.0 (a), CMX (b) and FJCI (c) membranes.

4.13. Membranes separation performances of Li₂SO₄.

Fig. S20 Membranes desalting efficiency (Li_2SO_4) of PDP-1.0 (a), CMX (b) and FJCI (c) membranes.

4.14. Membranes separation performances of MgSO₄.

Fig. S21 Membranes desalting efficiency $(MgSO_4)$ of PDP-1.0 (a), CMX (b) and FJCI (c) membranes.

4.15. The thermogravimetric analusis.

Fig. S22 The thermogravimetric curves of the resulting membranes.

4.16. Membranes separation performances of Na_2SO_4 immersed into water in 60 °C and 100 °C for 24 h.

Fig. S23 Membranes desalting efficiency (Na₂SO₄) of PDP-1.0 membrane after immersed into water in 60 $^{\circ}$ C (a) and 100 $^{\circ}$ C (b) for 24 h.

Fig. S24 Membranes desalting efficiency (Na₂SO₄) of CMX membrane after immersed into water in 60 $^{\circ}$ C (a) and 100 $^{\circ}$ C (b) for 24 h.

4.17. Membranes separation performances of Na_2SO_4 immersed into water in 40% and 80% acetone solution for 24 h.

Fig. S25 Membranes desalting efficiency (Na_2SO_4) of PDP-1.0 membrane after immersed into water in 40% (a) and 80% (b) acetone solution for 24 h.

Fig. S26 Membranes desalting efficiency (Na_2SO_4) of CMX membrane after immersed into water in 40% (a) and 80% (b) acetone solution for 24 h.

5. Videos supporting Information

5.1. Movie SV1

Preparation and the phenomenon of PDP-0 gel membranes.

5.2. Movie SV2

Preparation and the phenomenon of PDP-1.0 gel membranes.

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