

## Supporting information

### Engineering novel polyelectrolyte complex membranes with improved mechanical properties and separation performance

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## 1.1 Chemical structures and abbreviations of PEC components.

Fig. S1 gives the chemical structures and abbreviations of PEC components. In this manuscript, PSS, PVS and DSS are used as strong polyacid, which are complexed with positive CS via ionic-interaction. It can be seen from Fig. S1 that the DSS chains contain hydrophilic hydroxyl groups, while PSS chains bear hydrophobic benzene rings. As shown in Fig. S1, the monomer units of CMC and DSS have similar cyclic ester and hydroxyl groups, but different ion-groups. CMC chains have carboxylate groups, and DSS chains have sulfonate groups.

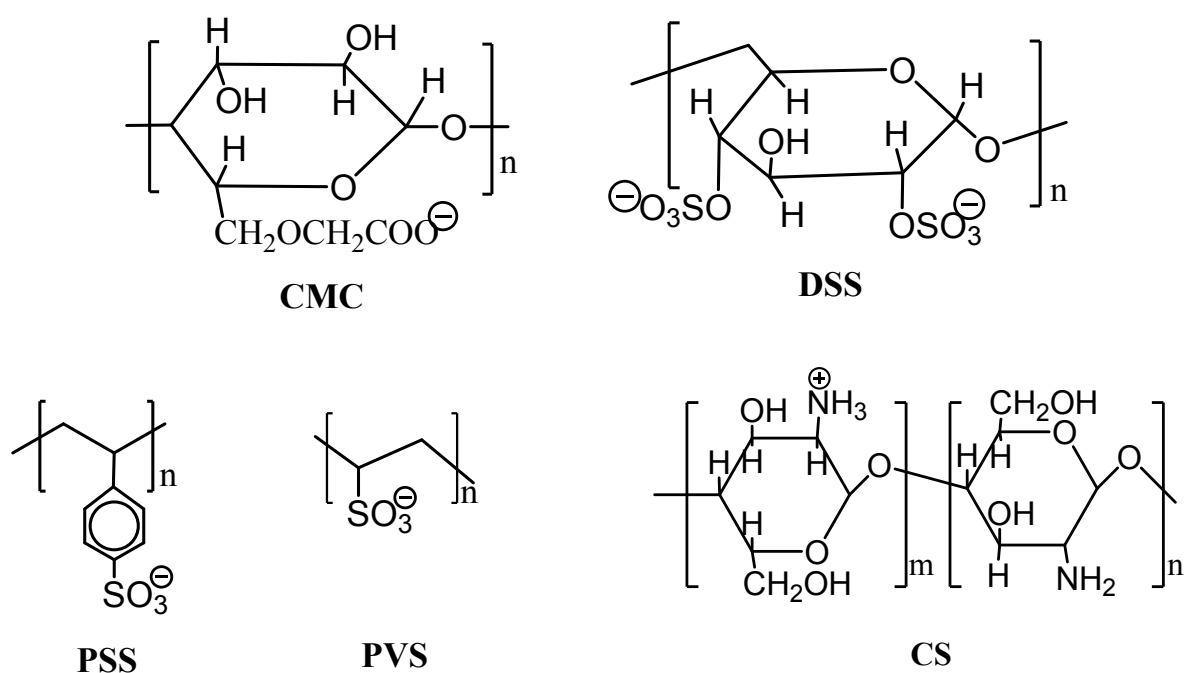


Fig. S1 Chemical structures and abbreviations of PEC components.

## 1.2 Optical photographs of the preparing DSS/CS and S-DSS/CS-1 complexes.

Fig. S2 shows the optical photographs of the preparing DSS/CS and S-DSS/CS-1 complexes. It can be clearly seen from Fig. S2 (b) that a turbidity is instantly observed in CS solutions upon the addition of DSS solutions, indicative the formation of ionic-complexation between CS and DSS.<sup>1</sup> As the added DSS further increased, the CS solutions become more turbid as shown in Fig. S2 (c). As shown in Fig. S2 (d), DSS/CS complexes are precipitated out after standing for 2 h, which indicates the end of ionic complexation between DSS and CS. It can be observed from Fig. S2 (e) that the stirring DSS/CS is turbid, and a macroscopic phase separation is easily appeared when the stirring is stopped. Moreover, the solubility of DSS/CS complex is examined in various solvents under different conditions (Fig. S3). DSS/CS complex appears fairly insoluble. From Fig. S2 (f), it

is seen that the S-DSS/CS-1 solution after the sulfation of DSS/CS complexes is homogenous, and stable even standing for 100 d. Combining Fig. S2 (e) and (f), it can be concluded that the sulfation of DSS/CS is successfully proceeded.

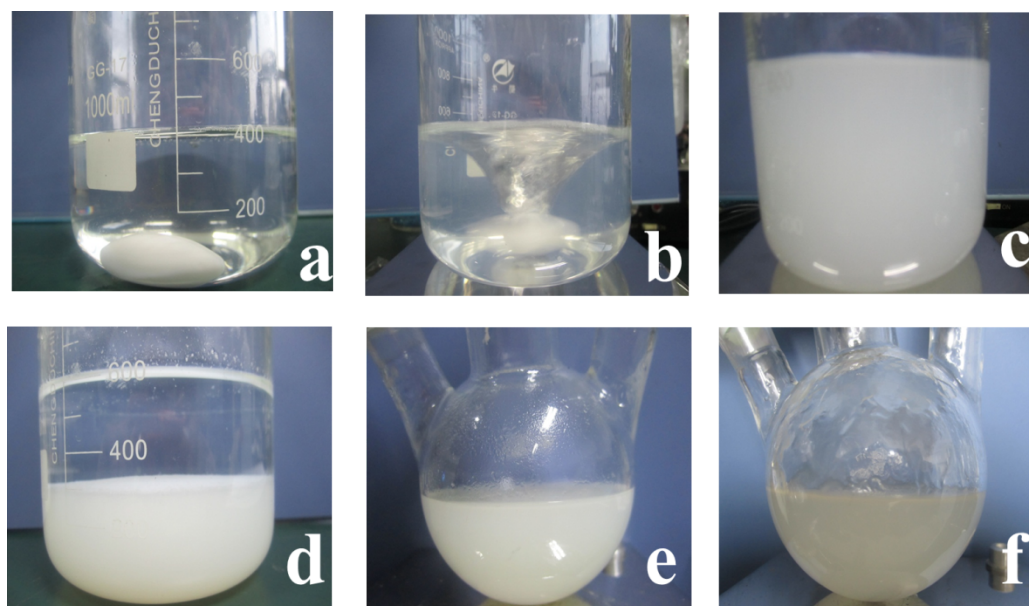


Fig. S2 Optical photographs of 400 mL CS solution (0.01M, pH 6.05) (a), CS solution (400 mL) added with 5 mL (b), 200 mL (c) DSS (0.01M, pH 6.05), 2 h after the stirring (c) was stopped (d), the obtained DSS/CS complexes stirring in water (e), the standing S-DSS/CS-1 PEC aqueous solution for 100 d (f).

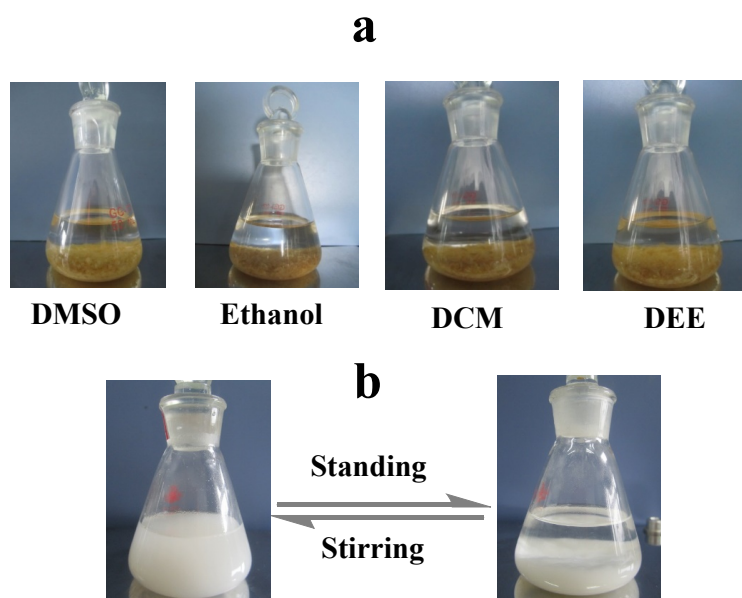


Fig. S3 (a) Optical micrographs of 1.0wt% DSS/CS solids in different types of solvents after stirring at 30 °C for 24 h, (b) 1.0 wt% DSS/CS solids in 4.5 M aqueous NaCl solution after stirring at 30 °C for 24 h, and standing for 0.5 h.

### 1.3 Schematic diagram of synthesis of SCMC and SCMC/CS complex as well as their chemical compositions determined by XPS.

Fig. S4 shows the schematic diagram of synthesis of SCMC and SCMC/CS complex. As shown in Fig. S4a, CMC was sulfated in DMA solvent by using  $\text{SO}_3/\text{pyridine}$  complex as sulfate agent.<sup>2</sup> The feed monomer ratio of sulfate agent to CMC was 1 and the composition of SCMC was determined by XPS, as shown Table S1. The ratio of  $\text{SO}_3\text{Na}$  to  $\text{COONa}$  groups in SCMC-0.12 was 0.12.

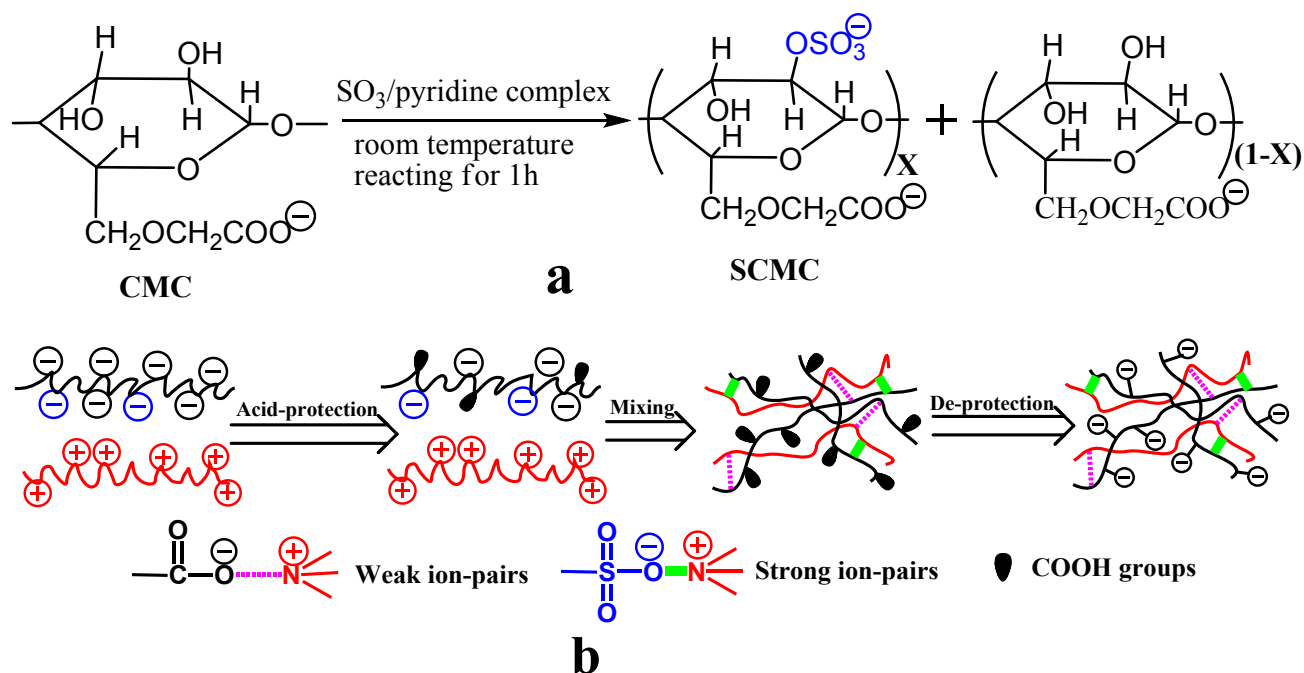


Fig .S4 (a) Schematic diagram of synthesis of SCMC, (b) fabrication of SCMC/CS PECs.

As shown in Fig. S4b, the schematic diagram for fabricating SCMC/CS with the acid-protected strategy as previously reported.<sup>3</sup> Firstly, the negatively charged SCMC solutions (2.5 g/L) and positively charged CS solutions (1.6 g/L) were prepared, whose pH values were tuned at 2.5. Subsequently, the CS solutions were dropped into the SCMC solutions under vigorous stirring (600 rpm). A macroscopic phase-separation was observed at the end of the ionic complexation between SCMC and CS. Finally, the obtained SPEC precipitates were thoroughly rinsed with de-ionized water, and dried at 60 °C for 24 h. The obtained SCMC/CS SPECs were dispersed in NaOH aqueous solutions (0.10 mol/L) to form a homogeneous solution (2 wt. %), which was due to the existence of the unionized carboxyl groups (COOH) in SPECs. CMC/CS was also prepared with this acid-protection method, and the prepared pH was controlled at 3.0 to reach the similar ionic-crosslinking degree with SCMC/CS. The as-prepared SCMC/CS possess both strong and weak ion-pairs, while that for CMC/CS has only weak ion-pairs. The compositions of CMC/CS and

SCMC/CS PECs were determined by XPS, as shown in Table S2. It can be seen that the degree of ionic-complexation of CMC/CS is 0.43, which is similar with that of SCMC/CS at 0.42. The degree of ionic-complexation of S-DSS/CS-1 is also 0.42 as shown in Table S1.

Table S1 Composition of CMC/CS and SCMC/CS PECs determined by XPS

Sample	O (At. %)	N (At. %)	S (At. %)	O:N	S:N	Molar ratio (SCMC:CS)	X	DC <sup>a</sup>
CMC/CS	31.84	1.57	—	20.28	—	0.43	—	0.43
SCMC	56.14	—	0.96	—	—	—	0.12	—
SCMC/CS	38.26	1.76	0.74	—	0.42	0.42	—	0.42

DC <sup>a</sup>: Degree of complexation.

#### 1.4 Hydration ability of PEC membranes measured by ATR-FTIR and DSC as well as TGA.

To investigate the hydration ability of PEC membranes, ATR-FTIR and DSC as well as TGA were carried out, and the results are given in Fig. S5 and Fig. S6. The DSC was obtained with a Perkin-Elementer Pyris 1 DSC (Waltham, MA) under a nitrogen atmosphere. The DSC curves were accomplished by fast sample cooling from 25 to -100 °C, following by a reheating to room temperature at the scanning rate of 10 °C/min. The TGA of a membrane was obtained with a Perkin-Elementer Pyris 1 TGA at a heating rate of 20 °C/min. PEC membranes were dried under vacuum at 35 °C for 24 h and then equilibrated with the ambient conditions such as the humidity of the atmosphere maintained at 30% for ca. 6 h, which was the same as the membranes used for tensile testing. Fig. S5a gives the changes in the wavenumber of the hydroxyl stretching vibration in the PEC membranes determined by ATR-FTIR. From Fig. S4a, the absorption peaks of 2920 cm<sup>-1</sup> and 3405 cm<sup>-1</sup> are observed, which correspond to the OH stretching vibration, and are ascribed to the water molecules in the first (Type I) and secondary (Type II) hydration layers in these membranes, respectively, (i.e. bound water).<sup>4</sup> Moreover, the absorption intensities of Type I and Type II water molecules in S-PEC membranes in the order of CMC/CS < SCMC/CS < S-DSS/CS-1 < S-DSS/CS-2 < S-DSS/CS-3. CMC/CS < SCMC/CS < S-PEC membranes are arisen from the high hydration ability of strong poly-acid.<sup>5</sup> It can be inferred from Fig. S5a that the amount and the increase margin of Type II in PEC membranes play a substantial role. Meanwhile, there are no absorption peaks in the range of 3650 cm<sup>-1</sup> to 3900 cm<sup>-1</sup>, which are associated with the OH stretching vibration of free water.<sup>6</sup> The result demonstrates the water existed in these membranes is

the mainly form of bound water. As shown in Fig. S5b, a peak of ice-melting at ca. 0 °C is absent on DSC curves of the water absorbed in PEC membranes, which further confirms no free water molecules are existed in these membranes.<sup>7</sup>

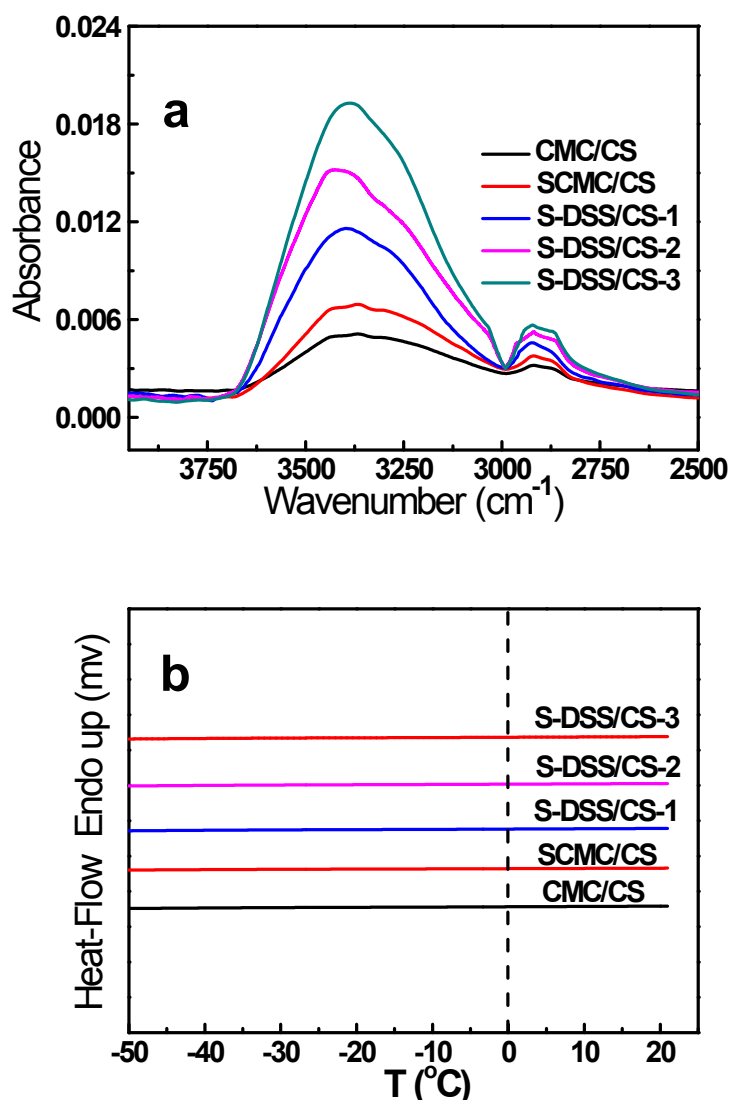


Fig. S5 (a) Changes in the wavenumber of the hydroxyl stretching vibration determined by ATR-FTIR, (b) DSC curves of the water absorbed of PEC membranes. PEC membranes were dried under vacuum at 35°C for 24 h and then equilibrated with the ambient conditions such as the humidity of the atmosphere maintained at 30% for ca.6 h.

To further determine the water content of PEC membranes, TGA for PEC membranes was implemented (Fig. S6). The weight loss ranging from 30 to 250 °C before decomposition was observed, which is attributed to the evaporation of absorbed water in these membranes. All membranes start to decompose at ca. 250 °C, as evidenced by the rapid weight decrease. A similar TGA result is observed for the graphene oxide reinforced poly(vinyl alcohol) membranes.<sup>8</sup> The

water content of PEC membranes in the sequence of CMC/CS < SCMC/CS < S-PEC membranes further confirms the high hydration ability of strong polyacid. Another important feature in Table S2 is that the water content for S-DSS/CS membranes exhibits an increase with the degree of sulfation. For instance, the water content of S-DSS/CS-3 membrane is 14.54 %, which is much higher than the S-DSS/CS-1 membrane (10.99 %). The increasing water content with the degree of sulfation is stemmed from the hydration ability of free sulfate groups in S-DSS/CS membranes. The water content for all PEC membranes in the tensile state is less than 20 %, which induces no free water molecules and corresponds well with the documented literature.<sup>9</sup> Herein, it is concluded that S-PEC membranes endowed with high hydration ability, and this ability can be further enhanced by increasing the content of free sulfate groups.

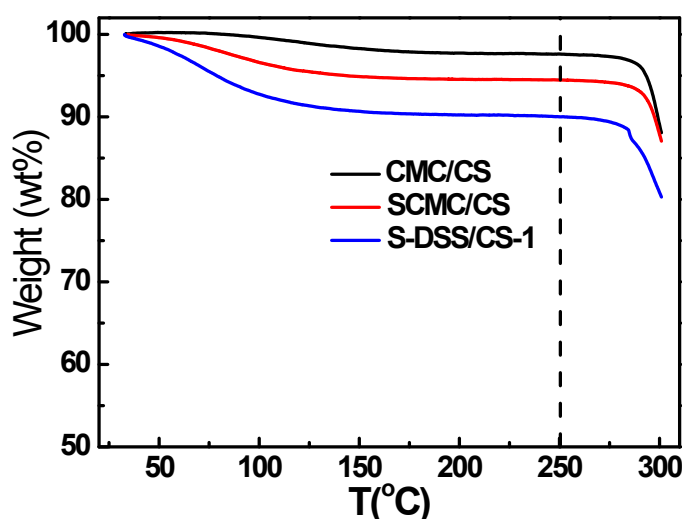


Fig. S6 TGA curves for CMC/CS, SCMC/CS and S-DSS/CS-1 membranes dried under vacuum at 35°C for 24 h and then equilibrated with the ambient conditions such as the humidity of the atmosphere maintained at 30% for ca.6 h.

Table S2 Total water content of PEC membranes determined by TGA.

Samples	CMC/CS	SCMC/CS	S-DSS/CS-1	S-DSS/CS-2	S-DSS/CS-3
Total water content (%)	2.39	5.27	10.99	11.97	14.54

1.5 Comparison of pervaporation performance of S-PEC membranes with the previously reported membranes for ethanol dehydration and the pervaporation performance of S-DSS/CS-3 membranes in the dehydration of water-isopropanol and water-n-butanol mixtures.

Table S3 Comparison of pervaporation performance of S-PEC membranes with the previously reported membranes for ethanol dehydration.

Membrane	Feed ethanol (wt. %)	Feed temperature (°C)	$J$ (g/m <sup>2</sup> h)	Water in permeate (wt.%)	Reference
PVA <sup>a</sup>	90	60	≈120	92.74	11
HPA/CS	90	50	250	99.65	12
GACS/PCP <sup>b</sup>	90	80	1390	99.30	13
PAA/CS	95	30	1008	93.65	14
CS/CMC	90	70	1140	99.10	3
PDDA/SCMC	90	70	1760	98.71	15
S-DSS/CS-3	90	70	2100	99.58	This work

<sup>a</sup> Dimethylolurea crosslinked; <sup>b</sup>the active layer constructed by sequential spin-coating and self-assembly of GACS and PCP, which was ca. 300 nm.

Abbreviations: PVA: poly (vinyl alcohol); HPA: heteropolyacid,  $H_{14}[NaP_5W_{30}O_{110}]$  (HPA); CS: chitosan; GACS: glutaraldehyde crosslinked chitosan; CP: carbopol; PAA: poly (acrylic acid); CMC: carboxymethyl cellulose; SCMC: sulfated carboxymethyl cellulose; PDDA: poly (diallyldimethylammonium chloride); DSS: dextran sulfate sodium.

Table S3 presents the comparison of S-DSS/CS membranes with recently reported membranes in the dehydration of water-ethanol mixtures via pervaporation. It can be clearly seen that S-DSS/CS-3 membranes exhibit higher pervaporation performance compared with the poly(vinyl alcohol) and polyelectrolyte membranes.<sup>11-14</sup> Moreover, S-DSS/CS-3 membranes also show higher flux and selectivity in comparison with the homogenous PEC membranes containing weak acid groups we previous prepared,<sup>3,15</sup> which is attributed to the higher hydrophilic property for strong acid groups than that for weak-acid groups.<sup>16</sup> Furthermore, in the dehydration of 10 wt% water-ethanol mixture at 70 °C, both the selectivity and flux of S-DSS/CS-3 maintain at 2100 g/m<sup>2</sup>h and 99.5 wt% in the continuous operation of 60 h (Fig. S7), indicating the S-DSS/CS membrane is stability in the alcohol solution with a little water. Fig. S8 shows the pervaporation performance of S-DSS/CS membranes in dehydrating 10 wt% water-isopropanol and 10 wt% water-n-butanol mixtures. For both feed mixtures, it can be seen that the S-DSS/CS membranes based on strong poly-acid exhibit high pervaporation performance. For instance, S-DSS/CS-3 membranes show enhanced flux of 3880g/m<sup>2</sup> h and 5275g/m<sup>2</sup> h in the dehydration of 10 wt% water-isopropanol and



10 wt% water-n-butanol mixtures at 70 °C, respectively. Meanwhile, the water content in permeate for S-DSS/CS-3 membranes in dehydrating both feeds is above 99.5 wt%. This superior separation performance of S-DSS/CS PEC membranes is probably because they combine the enhanced hydrophilicity associated with free strong-acid groups and the strong ionic-crosslinking interaction contributed by complexed strong acid groups.<sup>5,17</sup>

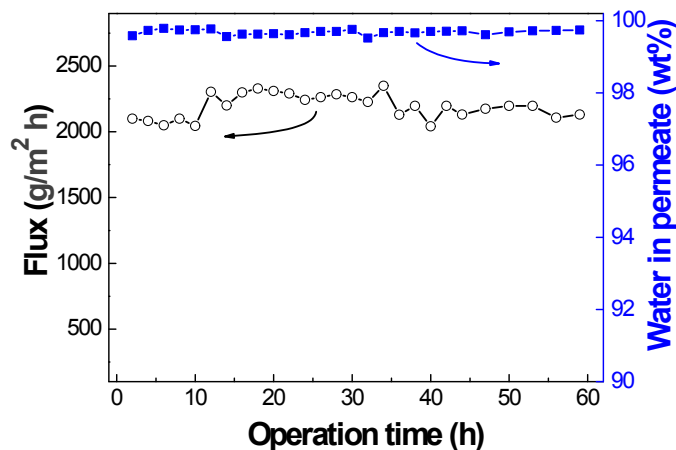


Fig. S7 Performance stability of S-DSS/CS-3 membrane in dehydrating 10wt% water-ethanol mixtures at 70 °C.

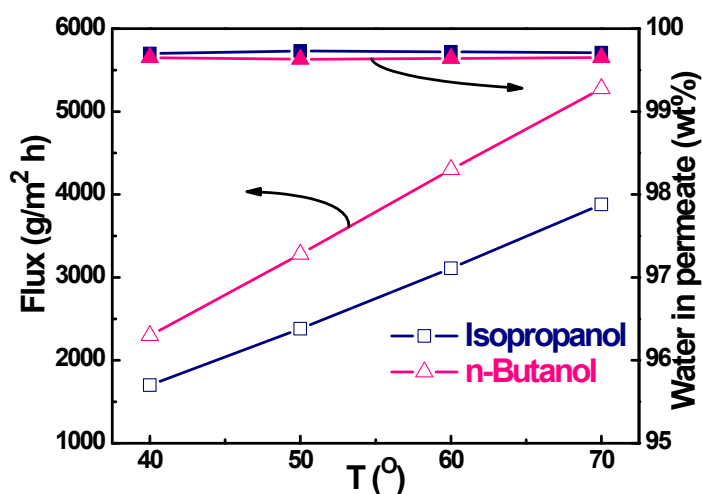


Fig. S8 Effect of feed temperature on pervaporation dehydration for S-DSS/CS-3 membranes of 10wt% water-isopropanol mixtures and 10 wt% water-n-butanol mixtures.

1.6 Compositions of S-PSS/CS-1 and S-PVS/CS-1 determined by XPS and their mechanical properties and pervaporation performance.

In addition to fabricate solution-processable S-DSS/CS PECs, we also prepare solution-processable S-PSS/CS and S-PVS/CS with this complexation-sulfation method, both of whose are based on strong polyacid. This indicates this strategy exhibit a good applicability to solve the solution-processability of PECs based on strong polyacid. The chemical compositions of these S-

PECs were determined by XPS, as shown in Table S4. As shown in Table S4, the ratios of S to N atoms in the pristine PVS/CS, DSS/CS and PSS/CS complexes is 0.40, 0.42, 0.42. In other words, the ratio of the monomer unit of DSS to CS in DSS/CS complexes is 0.42, which indicates that there is *ca.* 58 % (molar percent) of residual NH<sub>2</sub> groups on CS chains in DSS/CS complexes, which are not complexed with sulfonate groups on DSS chains. Therefore, the degree of sulfation in all prepared S-DSS/CS is less than 58 % (Table 1). S-PSS/CS-1, S-PVS/CS-1 and S-DSS/CS-1 possess the similar degree of sulfation, which indicates the analogical free sulfate groups. It can be seen from Fig. S9a, both the strength and flexibility of S-PEC membranes are in this sequence: S-PSS/CS-1 < S-PVS/CS-1 < S-DSS/CS-1. It is expected that the content of bound water in S-PEC membranes is increased from the hydrophobic PSS to hydrophilic DSS component, which induces the increase in the elongation at break from S-PSS/CS-1 to S-DSS/CS-1 membranes. S-DSS/CS-1 membranes containing hydroxyl groups are entitled with the formation of hydrogen bond, which leads to a higher tensile strength for S-DSS/CS-1 membranes. S-PSS/CS-1 membranes containing hydrophobic benzene rings are more brittle and easily fractured, and endowed with lower tensile strength.<sup>18</sup> Both the flux and selectivity for S-PEC membranes are in the order of S-PSS/CS-1 < S-PVS/CS-1 < S-DSS/CS-1 (Fig. S9b). The hydrophilic hydroxyl groups in DSS chains could resist the swelling of organics into membrane matrix.<sup>15</sup> S-PSS/CS-1 membranes containing hydrophobic benzene rings exhibit the lowest hydration ability, and the organics are more inclined to permeate into these membranes. Hence, the S-DSS/CS membranes show the highest pervaporation dehydration performance of aqueous ethanol.

Table S4 Composition of PECs and their S-PECs determined by XPS.

Sample	Molar ratio (sulfated agent :CS)	S (At. %)	N (At. %)	S:N	DC <sup>a</sup>	DS <sup>b</sup>
PVS/CS	—	1.43	3.52	0.40	0.40	—
PSS/CS	—	1.35	3.21	0.42	0.42	—
DSS/CS	—	0.97	2.31	0.42	0.42	—
S-PSS/CS-1	1	1.39	2.35	0.59	—	0.17
S-PVS/CS-1	1	1.46	2.56	0.57	—	0.17
S-DSS/CS-1	1	1.21	2.08	0.58	—	0.16

DC <sup>a</sup>: Degree of complexation, DS <sup>b</sup>: Degree of sulfation.

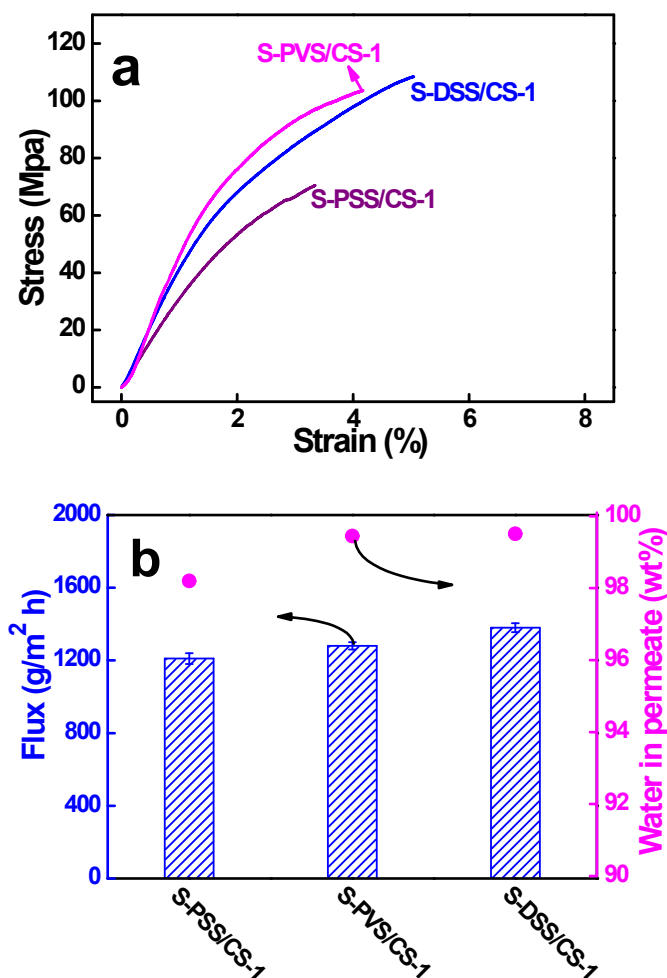


Fig. S9 (a) Stress–strain curves and (b) pervaporation performance of S-PEC membranes with different PECM components.

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