Electronic Supplementary Information

High performance cation exchange membranes synthesized via in-situ emulsion polymerization without organic solvents and corrosive acids

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1. Solubility study of LiSS in green solvents

Lithium styrenesulfonate (LiSS) is used to replace styrene. However, one challenge is that unlike styrene, LiSS cannot be dissolved in divinylbenzene directly. Therefore, a solvent is needed.

Green solvents, including dimethyl sulfoxide (DMSO) and water, are considered as the solvent candidates instead of conventional toxic solvents, such as dimethylacetamide (DMAc), dimethylformamide (DMF), n-methylpyrrolidone (NMP), and tetrahydrofuran (THF). Another reason for considering DMSO as the solvent for LiSS is that, based on the information provided by the manufacturer of LiSS, DMSO is among the best organic solvents for LiSS.

It is important to get a good understanding of LiSS solubility in DMSO and water. Ideally, the higher the solubility, the better. There are several reasons. Firstly, the solvent is an "unrelated" chemical and the only role of the solvent is to provide a media for the reactants. Secondly and more importantly, for the synthesis method used in this study, the solvent will compete with the reactants for pores in the membrane support. If the solubility is low, more pores in the support will be occupied by the solvent. As a result, less amount of functional polymers can grow into and onto the support. Moreover, high amount of solvent could also have an adverse effect on the bonding strength between functional polymers and membrane support. Although the reaction is carried out in 80 °C for a couple of hours, it does not necessarily mean that all the solvent will be evaporated during the reaction. This is because the reaction is carried out in a "semi-sealed" reactor (i.e., the stainless steel plate), due to the use of large-size spacers in combination with the pressure applied on the reactor. Moreover, DMSO has a high boiling point compared to the reaction temperature. As a result, a considerable proportion of solvent, especially DMSO, will remain in the membrane after polymerization. Therefore, the key point here is to increase the ratio of LiSS to solvent as high as possible. That means it is important to carry out a solubility study of LiSS in DMSO and water.
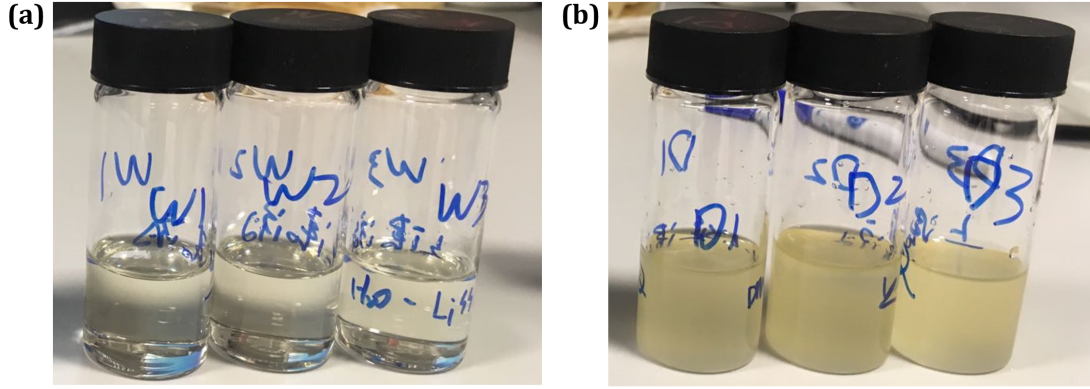
1.1. Solvent Evaporation Method

Figure S1. Real pictures of supernatant (i.e., saturated LiSS solution). (a) LiSS-water solution. (b) LiSS-DMSO solution.

In practice, it was found that the experiment to determine solubility of LiSS in water was much easier compared to that of DMSO. The procedures were briefly discussed as follows. LiSS was added into the solvent, and the mixture was stirred. When the mixture became clear, added some more LiSS. This process was repeated until undissolved LiSS remained in the mixture. Next, some supernatant (i.e., saturated solution) was taken out and put into another glass vial (shown in Figure S1). Then, the remaining mixture was dried in an oven until the weight did not change any more.

The following relationships were established.

$$MF_{s-LiSS} = \frac{W_{s-LiSS}}{W_{supernatant}} \qquad (S1)$$

Where:

- MF_{s-LiSS} was mass fraction (i.e., solubility) of LiSS in the supernatant (i.e., saturated solution).
- W_{s-LiSS} was the weight of LiSS in the supernatant.
- $W_{supernatant}$ was the weight of the supernatant.

$$W_{supernatant} = W_{s-LiSS} + W_{s-solvent} \qquad (S2)$$

Where:

- $W_{\text{s-solvent}}$ was the weight of solvent in the supernatant.

$$W_{s-LiSS} = W_{LiSS} - W_{r-LiSS} \tag{S3}$$

Where:

- W_{LiSS} was the weight of LiSS powder added into the glass vial.
- $W_{\text{r-LiSS}}$ was the weight of LiSS remained in the glass vial after supernatant was taken out from the vial.

$$W_{s-solvent} = W_{solvent} - W_{r-solvent} \tag{S4}$$

Where:

- W_{solvent} was the weight of the solvent added into the glass vial.
- $W_{\text{r-solvent}}$ was the weight of solvent remained in the glass vial after supernatant was taken out from the vial.

$$W_{total} = W_{vial} + W_{solvent} + W_{LiSS} \tag{S5}$$

Where:

- W_{total} was the total weight of the mixture and the container.
- W_{vial} was the weight of the glass vial, including the glass body, the lid, and the magnetic stir bar.

$$W_{supernatant} = W_{total} - W_{r-total} \tag{S6}$$

Where:

- $W_{\text{r-total}}$ was the total weight of the remaining mixture and the container after supernatant was taken out from the vial.

$$W_{r-LiSS} = W_{r-total} - W_{vial} \tag{S7}$$

Where:

- $W_{\text{r-total-dry}}$ was the total weight of the remaining mixture and the container after supernatant was taken out from the vial, and then after the container was dried in an oven to remove

solvent.

$$W_{r-solvent} = W_{r-total} - W_{r-total-dry} \qquad (S8)$$

Based on the above relationships, the solubility (in terms of mass fraction) of LiSS in DMSO or water can be calculated in a couple of ways (each way will return very similar result), such as using the following equation:

$$mf_{LiSS} = \frac{W_{LiSS} - W_{r-total-dry} + W_{vial}}{W_{solvent} - W_{r-total} + W_{LiSS} + W_{vial}} \qquad (S9)$$

All the weight values on the right-hand side of equation S9 were experimentally obtained using the balance. Using equation S9, the solubility of LiSS in water was calculated to be 43.15%±0.22%, and the solubility of LiSS in DMSO was calculated to be 35.97%±0.86%. The above calculation was based on the assumption that the weight of LiSS did not change during the heating process. However, this assumption was not accurate. LiSS heating experiments revealed that the mass loss of LiSS during heating was about 7.63%±0.10%, possibly due to the loss of absorbed water in the LiSS sample. Therefore, the amended solubility of LiSS in water was 41.13%±0.20% while the amended solubility of LiSS in DMSO was 34.26%±0.97%. The solubility result for LiSS in water was accurate because it agreed well with experimental observations and analysis. However, the solubility result for LiSS in DMSO was not accurate. The calculated value was based on the assumption that all DMSO was removed during the drying process. Unfortunately, this was not true for DMSO. It was found that it was very difficult to remove DMSO completely even though the glass vial containing the LiSS-DMSO mixture was dried for 3 days at 60 °C in a general oven, 60 °C in a vacuum oven, and 80 °C in a vacuum oven, successively. As a result, the remaining chemicals in the glass vial contained both LiSS and DMSO, rather than LiSS only. In other words, the experimental W_{r-LiSS} value was higher than its real value while the experimental $W_{r-solvent}$ was lower than it real value (the weight of the remaining mixture was accurate). Therefore, the experimental W_{s-LiSS} value was lower than its real value while the experimental $W_{s-solvent}$ was higher than it real value (the

weight of the supernatant was accurate). As a result, the $MF_{s\text{-LiSS}}$ (i.e., solubility) value was lower than its real value.

Table S1. Mass fraction of LiSS in DMSO

DMSO (g)	LiSS (g)	AD?	More LiSS (g)	Total LiSS (g)	AD?	Mass Fraction 1	Mass Fraction 2
9.8597	6.8761	Yes	0.3013	7.1774	No	41.09%	42.13%
10.6092	6.5813	Yes	1.1436	7.7249	No	38.28%	42.13%
9.2831	6.6204	Yes	0.2124	6.8328	No	41.63%	42.40%

Note: AD was short for all dissolved; Mass Fraction 1 = LiSS (g)/[DMSO (g)+LiSS (g)]; Mass Fraction 2 = Total LiSS (g)/[DMSO (g)+Total LiSS (g)].

A revised procedure was designed aiming to solve this issue. Briefly speaking, an appropriate amount of LiSS-DMSO supernatant was dropwise added into a glass dish so the supernatant had a larger "surface evaporation area". The dish was dried to remove DMSO. Using equation S1, the mass fraction of LiSS in the solution was calculated to be 48.50%±3.82%. The amended solubility of LiSS in DMSO was 52.41%±10.60%. However, this time, the calculated value was higher than its real value. The reason was the same, namely incomplete removal of DMSO. As a result, the experimental weight of LiSS in the solution was higher than its real value while the weight of DMSO in the solution was lower than its real value (the weight of the solution was accurate). In short, the real solubility of LiSS in DMSO should be a value between 34.26%±0.97% and 52.41%±10.60% (amended ranges based on mass loss of LiSS during the drying process). This range was obviously too large. The good news was, during the experiments, LiSS was not added at one time, but was added into the solution after all the LiSS added previously was fully dissolved. As revealed by Table S1, the real solubility of LiSS in DMSO should be in the range of 41-42% (in terms of mass fraction).

1.2. Ultraviolet–Visible Spectroscopy Method

In order to get a better understanding of the solubility of LiSS in DMSO, a further technique was adopted and the procedures were designed. The methodology was that the relationship between absorbance and concentration of LiSS solution could be quantified using ultraviolet–visible spectroscopy (UV-Vis) technique. When there were excess LiSS in the LiSS-DMSO mixture, the absorbance of the supernatant solution was expected to be the same. Therefore, a curve to describe unsaturated solution and a horizontal line to describe the saturated solution could be obtained. The solubility of LiSS in DMSO could be obtained by calculating the value at the intersection point of the curve and the line.
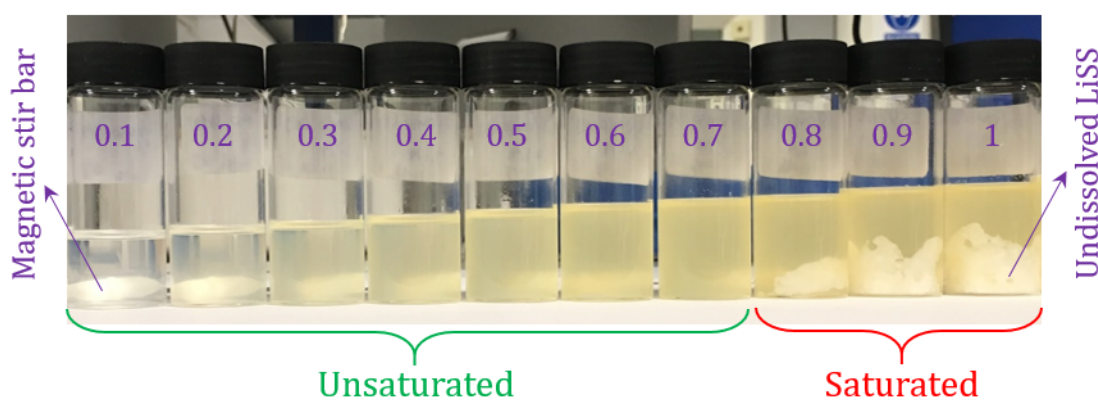

Figure S2. Real pictures of the LiSS/DMSO system under different LiSS/DMSO mass ratios.

As shown in Figure S2, as the m_{LiSS}/m_{DMSO} ratio (i.e., LiSS/DMSO mass ratio) increased, the color of the solution deepened, changing from colorless to light yellow, and finally yellow. When the ratio was below 0.7 (including 0.7), there were no precipitates at the bottom. In other words, the solution was unsaturated and some more LiSS could still be dissolved into the solution. When the ratio was higher than 0.8 (including 0.8), there were precipitates (i.e., undissolved LiSS) at the bottom. In other words, the solution was saturated. Therefore, the solubility of LiSS in DMSO was expected to be a number between 0.7 and 0.8 (in terms of m_{Liss}/m_{DMSO} ratio). Though it was feasible to set more m_{Liss}/m_{DMSO} ratios between 0.7 and 0.8 using bisection method, a well-known method in mathematics, to find the boundary value between unsaturated and saturated solution, the work to find this value could be laborious. More importantly, theoretically it was not possible to find the exact value using bisection method.

Therefore, instead of using the bisection method, UV-Vis spectrophotometer was used as a tool to measure solubility.
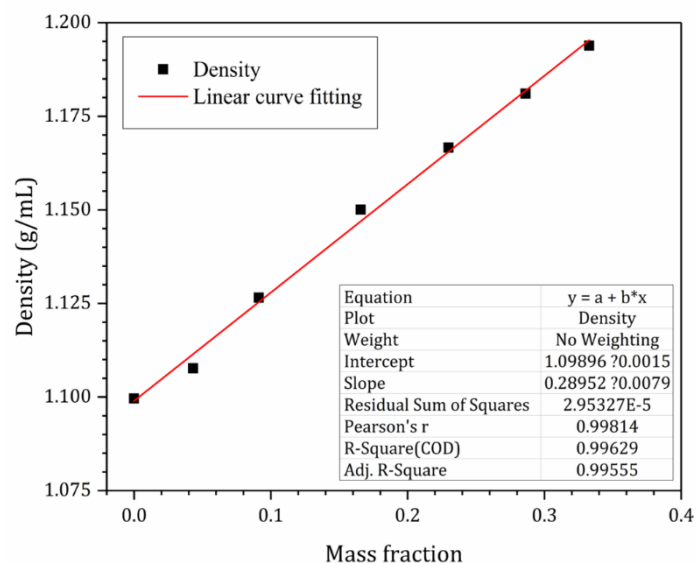

Figure S3. Relationship between density of LiSS solution (solvent: DMSO) and mass fraction of LiSS in the solution.

First of all, the relationship between density of LiSS solution (solvent: DMSO) and mass fraction of LiSS in the solution was established via experiments. As shown in Figure S3, density had a linear relationship with mass fraction. Their relationship was expressed in equation S10.

$$D = a \times MF + b \qquad\qquad (S10)$$

Where:

- MF was mass fraction of LiSS in the solution (unit: g/g or dimensionless).
- D was short for density of LiSS solution (unit: g/mL).
- a and b were constants, and based on Figure S3, a = 0.290, b = 1.099.

Besides, the relationship between concentration, density, and mass fraction could be expressed using the following equation:

$$C = \frac{1000 \times D \times MF}{MW_{LiSS}} \tag{S11}$$

Where:

- C was short for concentration of LiSS in the solution (unit: mol/L).

- MW_{LiSS} referred to molecular weight of LiSS (190.15 g/mol).

Combining equation S10 and S11, the following equation could be established:

$$C = \frac{1000a \times MF^2 + 1000b \times MF}{MW_{LiSS}} \tag{S12}$$

Based on Beer–Lambert law [1,2], absorbance has a linear relationship with concentration, which is expressed in equation S13:

$$A = \varepsilon \times l \times C \tag{S13}$$

Where:

- A was short for absorbance.

- ε referred to molar absorption coefficient.

- l was the length of the absorbing medium.

Combining equation S12 and S13, the following equation could be established:

$$A = \frac{1000a\varepsilon l \times MF^2 + 1000b\varepsilon l \times MF}{MW_{LiSS}} \tag{S14}$$

As revealed by equation S14, absorbance had a quadratic relationship with mass fraction, instead of a linear relationship. That was why quadratic curve fitting was applied in the following discussion.

Figure S4 showed the UV-Vis spectra LiSS/DMSO system at different LiSS/DMSO mass ratios. Quadratic curve fittings were conducted under different wavelengths and coefficient of

determination was used to evaluate the fittings (Figure S5). The coefficient of determination, which is commonly denoted as R^2, is a very useful tool to evaluate how well the regression model agrees with the experimental data [3,4]. Generally, the R^2 value ranges from 0 to 1. The closer the R^2 value to 0, the worse the fitting. The closer the R^2 value to 1, the better the fitting. If the R^2 value equals to 1, it means the models agrees perfectly with the data.
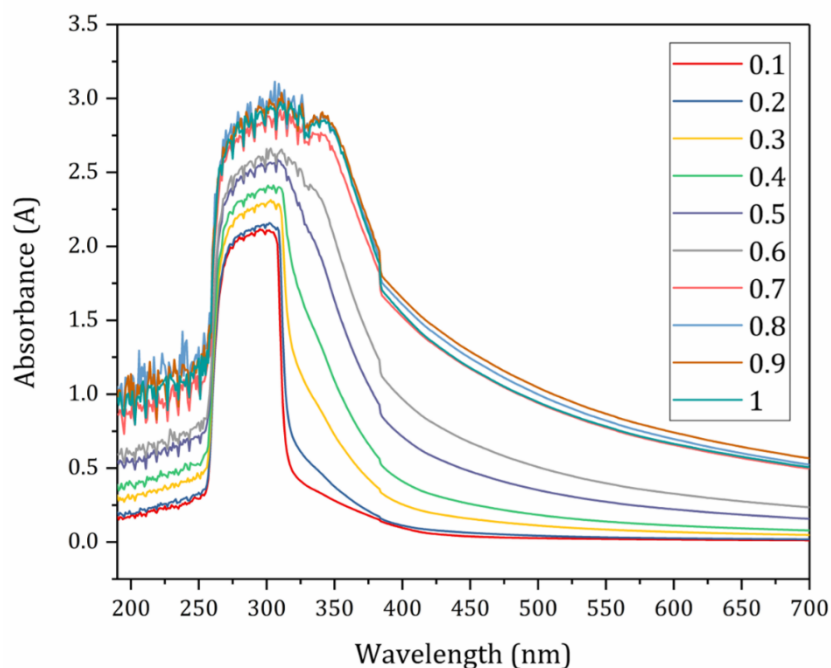

Figure S4. UV/Vis spectra of LiSS/DMSO system under different LiSS/DMSO mass ratios. The measurements were repeated at least three times and the average value was used.

Interestingly, as shown in Figure S5, the distribution of R^2 seemed to be "organized". In the wavelength range of 348-351 nm, R^2 values were the highest and three nines (i.e., 0.999) were achieved (Figure S6). Therefore, the relationships between absorbance and mass fraction in the wavelength range of 348-351 nm were used to calculate solubility. As shown in Table S2, the solubility of LiSS in DMSO was around 42%, which agreed well with the result calculated by the solvent evaporation method.
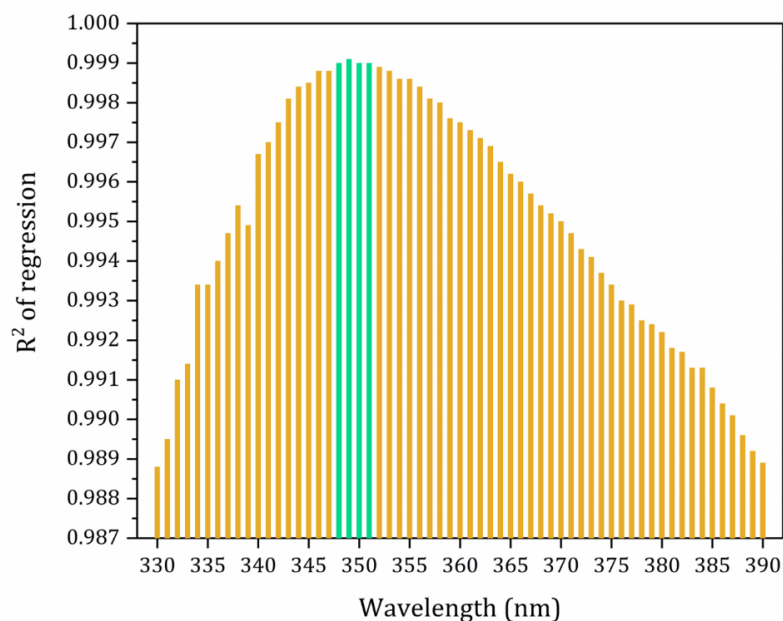
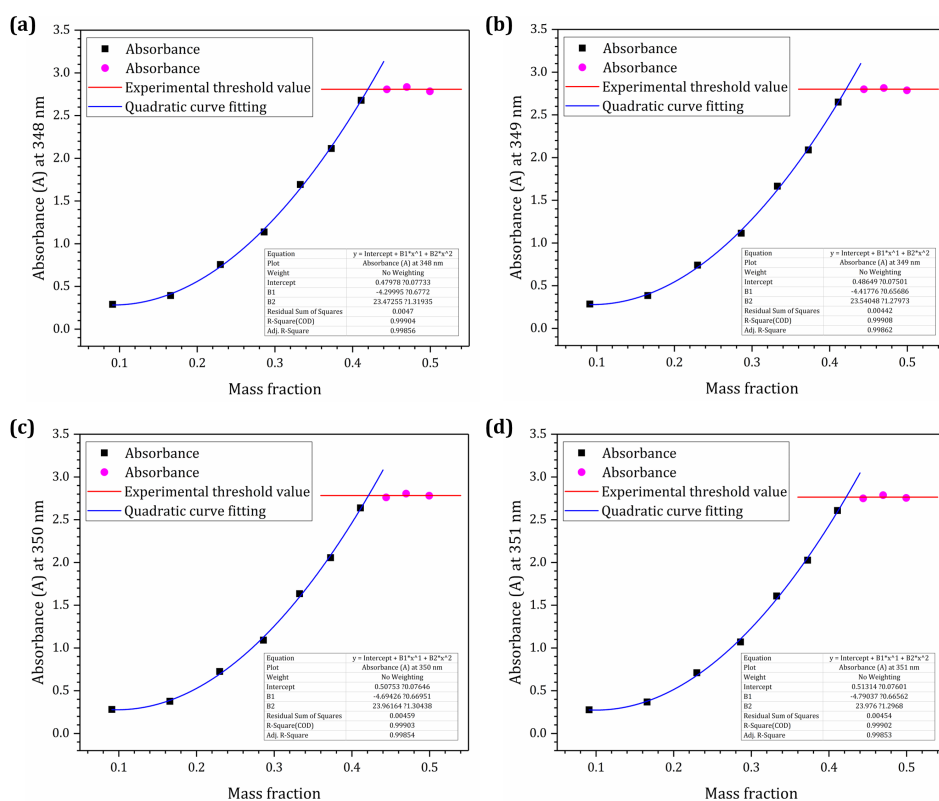Figure S5. R^2 of quadratic curve fittings at different wavelengths.

Figure S6. Relationship between absorbance and mass fraction at different wavelengths. (a) 348 nm. (b) 349 nm. (c) 350 nm. (d) 351 nm.

Table S2. Solubility of LiSS in DMSO calculated via the UV-Vis method

W (nm)	Relationship Between A and MF	Threshold A Value	Solubility
348	$A = 23.473MF^2 - 4.300MF + 0.480$	2.808	41.96%
349	$A = 23.540MF^2 - 4.418MF + 0.486$	2.800	42.11%
350	$A = 23.962MF^2 - 4.694MF + 0.508$	2.782	42.12%
351	$A = 23.976MF^2 - 4.790MF + 0.513$	2.764	42.22%

Note: W was short for wavelength; A was short for absorbance; MF was short for mass fraction.

However, it should be pointed out that Beer–Lambert law, which was used in the theoretical calculations above, had its limitations. Normally, Beer-Lambert law is accurate only when the solution is very dilute and the absorbance is less than 2 [1,2]. When the concentration is high, the interactions among the molecules cannot be ignored any more. However, the concentration of LiSS solution in this study was very high and the absorbance also exceeded 2 (Figure S6). Interestingly, despite this violation, the experimental results corresponded well with theoretical calculations. The underlying reason was not clear, but here was one possible explanation. Although the concentration was high in this study, the linear relationship between absorbance and concentration was still valid in certain concentration ranges (instead of the whole ranges). For example, the revised relationship could be: $A = a' \times C + b'$ where C was greater than 0 and a' and b' could be different values in different C ranges. Therefore, although equation S13 and S14 were no longer accurate, the relationship between absorbance and mass fraction was still quadratic. This explanation was partly supported by a minor difference between the above theoretical calculations and experimental results. To be specific, as revealed by equation S14, when MF was 0, A also equaled to 0. However, from Table S2, when MF was 0, A was not equal to 0 (around 0.5). In other words, the equations in Table S2 were not applicable in low mass fractions.

Based on the above discussions, it was concluded that water and DMSO demonstrated comparable performance in dissolving LiSS. In terms of solubility, both water and DMSO could be regarded as good solvent candidates for membrane synthesis. In the next section, the practicability of using DMSO as the solvent to prepare CEMs was further discussed.

1.3. Membrane Preparation Using DMSO/water as the Solvent

At first, DMSO was used as the solvent to prepare CEMs. However, the prepared CEMs had two critical issues. The first issue was, the amount of functional polymers formed in/onto the porous support was low. To be specific, the mass ratio of functional materials to porous support was only about 20%. The main reason was that the LiSS-DMSO solution was very viscous and thus its fluidity was very poor. As a result, it was difficult for the liquid mixture to permeate into the pores of the support. In other words, a majority of functional materials were formed on the surface instead of the pores inside. The second issue was, after reaction, the surface of the membrane was viscous. In other words, DMSO did not evaporate completely during the heating process. As discussed before, the main reason was that DMSO had a very high boiling temperature. As a result, the synthesized membranes were not stable because the formed materials were not firmly connected with the porous support.

Although DMSO and water showed similar capacity for dissolving LiSS (based on solubility), some differences were observed. The first one was, the saturated LiSS-DMSO solution was more viscous than the saturated LiSS-water solution (Figure S1). The second one was, when there was an excessive amount of LiSS in the LiSS-DMSO mixture, the undissolved LiSS agglomerated together and precipitated at the bottom (Figure S2). The agglomerated and precipitated LiSS was very hard and thus it was not feasible to get it uniformly dispersed in the mixture even under stirring. However, the undissolved LiSS in the LiSS-water mixture did not agglomerate and thus it was very easy to get it uniformly dispersed under stirring. Therefore, it was practical to prepare a uniform mixture of LiSS-water under stirring where the amount of LiSS in the mixture exceeded the maximum amount of LiSS that could be dissolved. But this was not applicable for DMSO.

To conclude, compared to DMSO, water demonstrated more favorable properties as the solvent for LiSS. Therefore, water was finally chosen as the solvent for membrane synthesis.

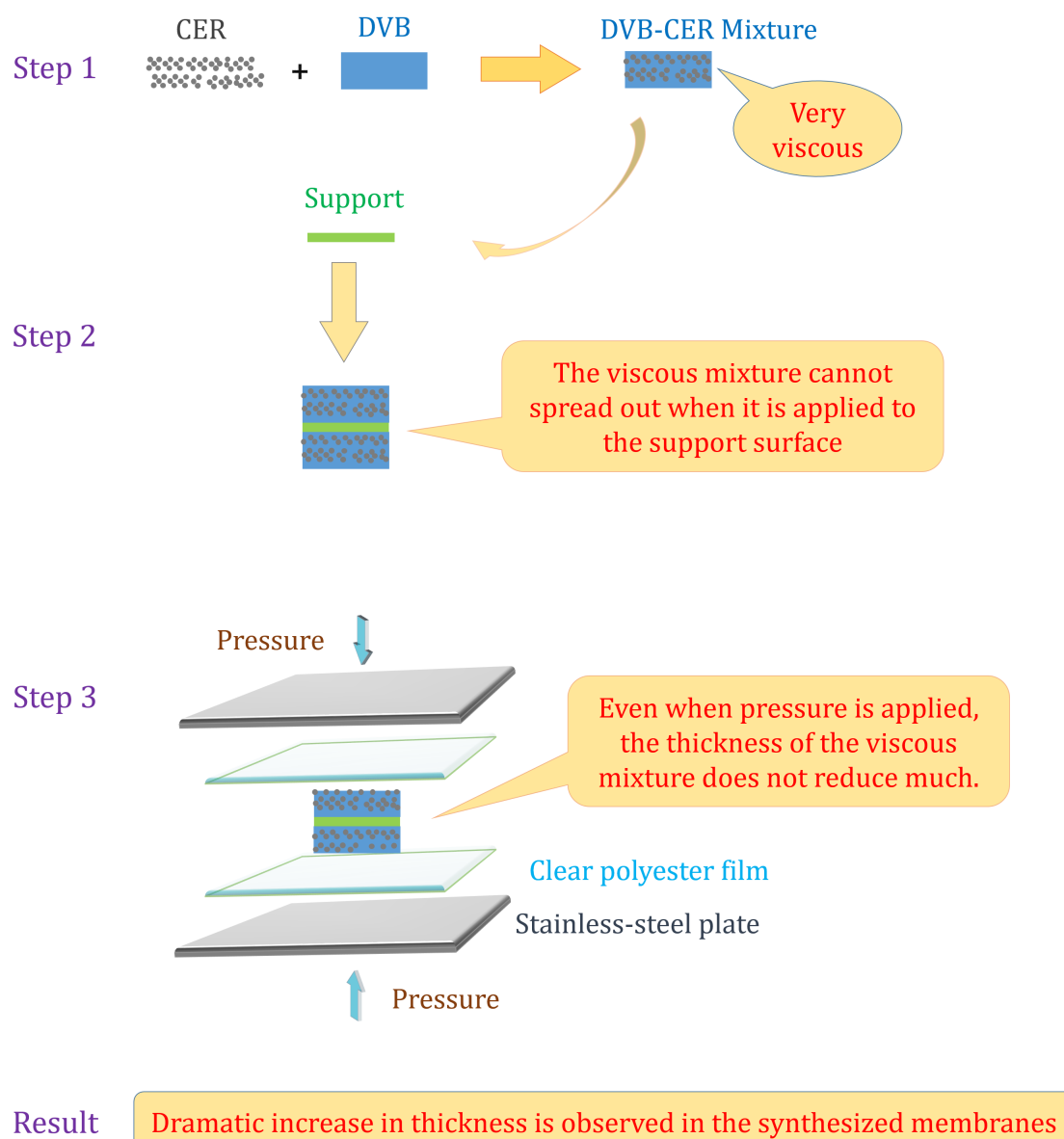## 2. Membrane thickness increase in the M_{CDX} series

Step 1   CER   +   DVB   →   DVB-CER Mixture

Very viscous

Support

Step 2

The viscous mixture cannot spread out when it is applied to the support surface

Pressure

Step 3

Even when pressure is applied, the thickness of the viscous mixture does not reduce much.

Clear polyester film

Stainless-steel plate

Pressure

Result   Dramatic increase in thickness is observed in the synthesized membranes

Figure S7. Schematic illustration of the dramatic increase in thickness observed in the M_{CDX} series. CER referred to cation exchagne resin; DVB referred to divinylbenzene.

3. Theoretical derivations of ion exchange capacity

Because:

$N = IEC_{load} \times (W_m - W_p)$ and also $N = IEC_m \times W_m$

Where:

N was the amount of exchangeable functional sulfonate groups in membrane samples (unit: millimole, mmol);

IEC_{load} was the IEC of loaded functional materials;

IEC_m was the IEC of synthesized membrane samples;

W_m was the weight of membrane samples (sodium form);

W_p was the weight of membrane support.

Therefore:

$IEC_{load} \times (W_m - W_p) = IEC_m \times W_m$

Therefore:

$$IEC_m = IEC_{load} \times \frac{W_m - W_p}{W_m}$$

$$= IEC_{load} \times \frac{W_m - W_p}{W_m - W_p + W_p}$$

$$= IEC_{load} \times \frac{\dfrac{W_m - W_p}{W_p}}{\dfrac{W_m - W_p + W_p}{W_p}}$$

$$= IEC_{load} \times \frac{\dfrac{W_m - W_p}{W_p}}{1 + \dfrac{W_m - W_p}{W_p}}$$

$$= IEC_{load} \times \frac{LR}{1 + LR}$$

$$= IEC_{load} \times \frac{1 + LR - 1}{1 + LR}$$

$$= IEC_{load} \times (1 - \frac{1}{1 + LR})$$

Where:

LR was short for loading ratio and $LR = \dfrac{W_m - W_p}{W_p}$

Further:

$$IEC_{load} = IEC_{max} \times \frac{R_L \times \frac{MW_S}{MW_L}}{1 + R_L \times (\frac{MW_S}{MW_L} - 1)}$$

$$= \frac{1000}{MW_S} \times \frac{R_L \times \frac{MW_S}{MW_L}}{1 + R_L \times (\frac{MW_S}{MW_L} - 1)}$$

$$= \frac{1000}{MW_L \times \left(\frac{1}{R_L} - 1\right) + MW_S}$$

$$= \frac{1000}{190.15 \times \left(\frac{1}{R_L} - 1\right) + 206.19}$$

Where:

MW_S was molecular weight (or molar mass) of sodium p-styrene sulfonate (206.19 g/mol);

MW_L was molecular weight of lithium p-styrene sulfonate (190.15 g/mol);

IEC_{max} was theoretical maximum IEC of sodium p-styrene sulfonate and IEC_{max} = 1000/206.19 ≈ 4.85 mmol/g;

R_L was the ratio of sulfonate groups (in terms of LiSS) in the loaded functional materials.

One purpose of the above derivation was to convert IEC (lithium form) to IEC (sodium form) as the experimental IEC was measured in sodium form. If assuming all water was removed during membrane preparation and all water soluble substances were removed during conversion, then:

$$R_L \approx \frac{W_L}{W_L + W_D + W_S}$$

Where:

W_L was the weight of real LiSS in the liquid mixture used for synthesis;

W_D was the weight of DVB in the mixture;

W_S was weight of styrene in the mixture.

Therefore:

$$\text{IEC}_{load} \approx \frac{1000}{190.15 \times \dfrac{W_D + W_S}{W_L} + 206.19}$$

Therefore:

$$\text{IEC}_m \approx \frac{1000}{190.15 \times \dfrac{W_D + W_S}{W_L} + 206.19} \times \left(1 - \frac{1}{1 + LR}\right)$$

$$= \frac{1000 \times LR}{(190.15 \times DR + 206.19) \times (1 + LR)}$$

Where DR was the mass ratio of DVB and styrene to LiSS and $DR = \dfrac{W_D + W_S}{W_L}$

4. ED test

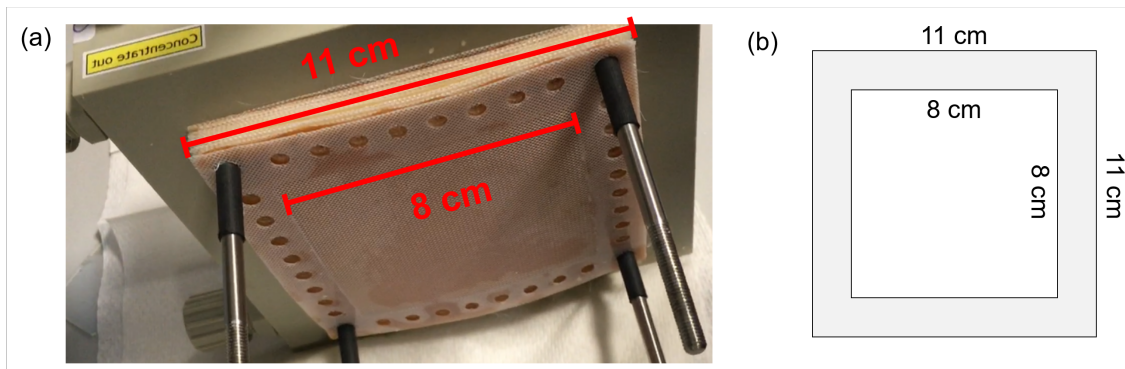## 4.1. Membrane size and active membrane area

Figure S8. Membrane size and active membrane area for ED test. (a) Real picture of the ED cell and membrane stack. (b) Schematic illustration of membrane size and active membrane area.

As shown in Figure S8, each membrane has a square shape, and the length/width is 11 cm. The active membrane surface area is 64 cm^2, where the membrane comes in contact with the electrolyte.

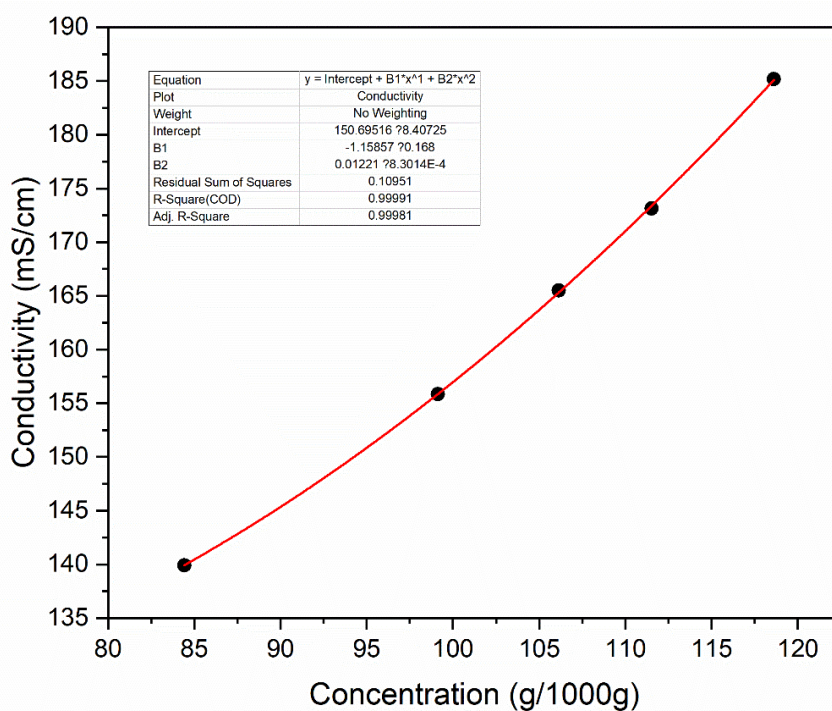## 4.2. Relationship between conductivity and concentration

Figure S9. Relationship between conductivity and concentration.

As revealed by Figure S9, the relationship between conductivity (mS/cm) and concentration (g/1000g solution) was quadratic. Theoretical derivations also proved this quadratic relationship.

The relationship between concentration (mol/L) and mass fraction or concentration (g/1000g solution) could be quantitatively expressed using the follow equation.

$$C_m = \frac{D \times C_g}{MW_{NaCl}}$$

Where:

C_m was short for concentration (mol/L);

D was short for density (g/mL);

C_g was short for concentration (g/1000g solution);

MW_{NaCl} was the molecular weight of NaCl, 58.44 g/mol.

Also, D had a liner relationship with Cg. Therefore, D could be expressed using the following equation.

$$D = a \times C_g + b$$

Where a and b were constants.

Therefore:

$$C_m = \frac{(a \times C_g + b) \times C_g}{MW_{NaCl}}$$

$$= \frac{a \times C_g{}^2 + b \times C_g}{MW_{NaCl}}$$

Also, conductivity had a direct linear relationship with concentration (mol/L):

$$C = a' \times C_m + b'$$

Where:

C was short for conductivity (mS/cm);

a' and b' were constants.

Therefore:

$$C = a' \times \frac{a \times C_g{}^2 + b \times C_g}{MW_{NaCl}} + b'$$

$$= \frac{a' \times a \times C_g{}^2 + a' \times b \times C_g}{MW_{NaCl}} + b'$$

$$= a'' \times C_g{}^2 + b'' \times C_g + b'$$

Where a" and b" were constants and their relationship with a, a', b and MW$_{NaCl}$ were expressed as follow.

$$a'' = \frac{a' \times a}{MW_{NaCl}}$$

$$b'' = \frac{a' \times b}{MW_{NaCl}}$$

According to Figure S9,

$$a'' = 0.01221$$

$$b'' = -1.15857$$

$$b' = 150.69516$$

$$C = 0.01221 \times C_g{}^2 - 1.15857 \times C_g + 150.69516$$

5. Large-scale production and yield of membranes

Using the proposed methodology in this study, it is possible for large-scale production of membranes.[5] As illustrated in Figure S10, clear polyester film serves as the spacer for membrane fabrication. If assuming N pieces of membranes are fabricated at one time, and assuming every piece of membrane has the same circle shape and the radius is r, then the yield of each reaction can be calculated using the following equation:

$$Y = \pi \times r^2 \times N$$

Where:

Y is the yield of each reaction (unit: m^2);

r is the radius of each piece of membrane (unit: m);

N is the number of membranes fabricated at one time.

For example, if ten pieces of membranes are fabricated at one time, and the radius of each membrane is 1 m, then the yield of each production is about 31.4 m^2.
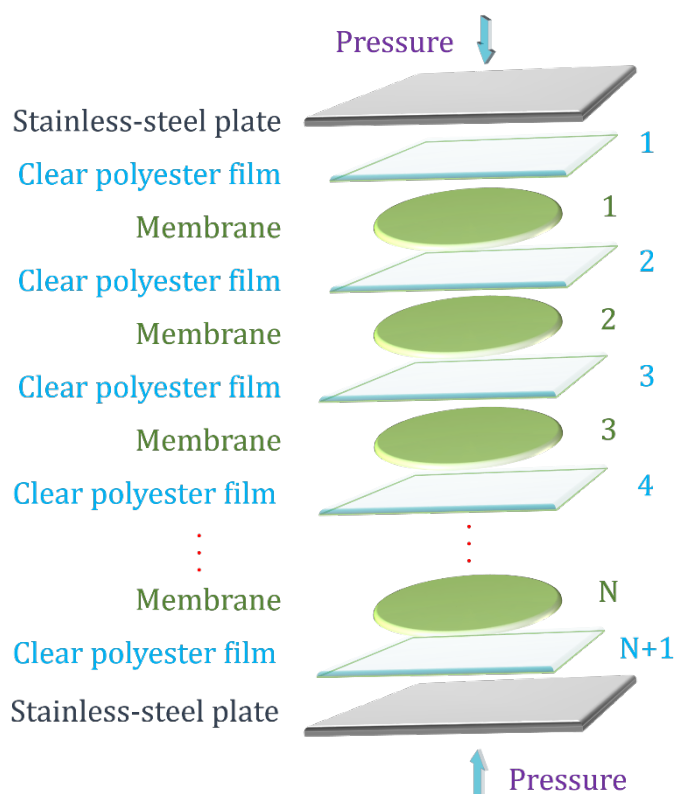

Figure S10. Schematic illustration of large-scale production of membranes using the methodology proposed in the study.

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