Endeavor to increase lithium extraction performance by adding sulfonated poly (ether ether ketone) into block-copolymer ethylene vinyl alcohol membrane

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Abstract

BACKGROUND: Highly efficient membrane extraction (ME) for extraction of lithium from brine has been constrained by the membrane mass transfer resistance. We reported here a new solvent resistance membrane from ethylene vinyl alcohol (EVAL) and sulfonated polyether ether ketone (SPEEK).

RESULTS: Effect of the SPEEK on effect of thermodynamics and kinetics of demixing to the membrane morphology was systematically investigated. About 0.5 wt.% of SPEEK was sufficient to reduce the mass transfer resistance of Li^+ . The membrane thickness showed linear correlation with the lithium flux, but was limited by the weak mechanical strength. Finally, a composite EVAL/SPEEK membrane supported by a thin loose non-woven fabric showed a stress of 12.5 MPa, nearly 10 fold as that of the non-supported membrane, and the highest lithium extraction flux of $4.80 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$.

CONCLUSION: The work provides a rationale for developing mechanically stable, high extraction flux membranes for ME.

Keywords: Membrane extraction; lithium extraction; solvent resistant; ion exchange; mechanical strength

1.Introduction

Membrane extraction is a highly efficient separation technique combining membrane materials and liquid-liquid extraction [1]. The broader range of membrane extraction covers supported liquid membrane [2-5] and membrane contactors [6-8] in which the organic extractant is impregnated inside a porous substrate. Long time stability was the main issue caused by loss of organic extractant [2] as well as the low solvent stability of the membrane materials [9, 10]. By applying a hydrophilic coating layer to a porous substrate, attempt to stabilize the liquid membranes failed mainly by the weak solvent stability of porous organic materials [10-15]. Inorganic membranes have been reported as the substrate due to the excellent solvent resistance, but acid/base resistance and high mass transfer resistance hindered the further commercial interest [16].

We have identified a new configuration, thus named as membrane extraction, in which water and organic phases flow on both sides of a membrane which allow ions to freely diffuse,

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but block the direct contact of both organic and aqueous phases. Different from conventional liquid membrane, the membrane is intrinsically hydrophilic, thus water swollen and ion permeable. It acts as a barrier for organic extractant, meaning that the contact of the membrane materials to the organics is only at the interface, therefore, prolonged stability is expected. Besides the benefit of avoiding back-mixing/flooding occurring in conventional liquid-liquid extraction equipment, no loss of organic to aqueous phase attributes membrane extraction as an green environmentally friendly separation technology [17-19]. Because polymeric membrane barrier is utilized in this system, solvent resistant membranes are the first requirement; improvement of the extraction efficiency via reduction of the mass transfer resistance by the barrier membrane is critical as well [1].

Endeavor to explore the potential applications using a solvent resistant membrane has been carried out in our group in the past decade, for extraction lithium from salt-lake brine. Lithium is recognized as crucial energy metal for automobile, electronics and chemical industries [1, 20, 21]. In recent years, with the development of lithium battery technology, the consumption and demand of lithium increase rapidly [20-23]. Because of low concentration of lithium in seawater [24] and diminishing supply in ore [25, 26], the brine with lithium has become the main source of lithium, particularly in the northwest part of china where lithium chloride and lithium carbonate are the main resources [27]. In these regions, environmental issues on loss organic extractant requires a green sustainable extraction technology. In previous reports, the

pros-and-cons of various lithium extraction technologies, i.e. chemical precipitation [28, 29], ion exchange [30-33], nanofiltration [34-36], electrodialysis [37-39], adsorption [40-42], have been discussed and we have identified membrane extraction as one of the potential candidates [1, 27].

Commercial ion exchange membranes have been utilized for promotion of ion diffusion in membrane contactors [6, 43, 44]. **There was no long-term stability evidence using ion exchange membranes for extraction purpose, although the solvent resistance has been significantly improved [45, 46].** Song et al. reported using the SPEESK/PES blend membranes for lithium extraction [18] and separation of copper and nickel [47], but with limited stability. Because EVAL has both hydrophobic solvent resistant segment and hydrophilic ion permeable units, resulting EVAL membrane is solvent resistance [17, 19]. Due to the semicrystalline characteristic of EVAL, competition of liquid-liquid demixing and solid-liquid demixing during membrane preparation process tend to form nanosize interconnected pores structure; however, the mass transfer resistance is still high [17]. Low ethylene content corresponds to high lithium extraction flux due to preferential absorption of water, which contributes to low mechanical strength [19]. Further improvement in the lithium transport by maintaining sufficient mechanical strength is required for improvement in the membrane materials.

Enlightened by the findings from Geise et al. [48, 49] that sulfonated polymers show improved cations diffusion and reduce diffusion resistance to cations, we selected sulfonated

polyether ether ketone (SPEEK) as a new approach to improve the lithium extraction performance of EVAL membrane. The main objective of this study is to investigate the potential of SPEEK on the EVAL membranes in extraction for lithium ions from brine. The thermodynamics and kinetics of membrane formation were systematically investigated and correlated to the membrane structure and performance. The ratio of SPEEK and EVAL, the membrane thickness was analyzed from both morphology and diffusion test. We finally used a non-woven as supported thin EVAL/SPEEK membrane as a demonstration for an ultimate strategy for optimization of high extraction flux membranes for lithium extraction.

2. Experimental

2.1. Chemicals and materials

A copolymer poly (ethylene-co-vinyl alcohol, average ethylene content 44%), was purchased from Kuraray Co., Ltd., and was dried for 24 h at 65 °C before use. Sulfonated polyether ether ketone (SPEEK) was prepared in the lab and characterized following the same procedure as described in previous report [50] and the degree of sulfonation (DS) is 0.62. Polyethylene terephthalate (PET) non-woven fabric was kindly supplied by Henan Radiation Chemical High Technology co., LTD. Dimethylacetamide (DMAc), and tributyl phosphate (TBP) were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Sulfonated kerosene (Petrochemical Corporation, China) was used as diluent for organic extractant.

Lithium chloride (anhydrous, Analytic grade), magnesium chloride and hydrochloric acid (HCl) were kindly supplied by Sinopharm Chemical Reagent Co. Ltd (China) and used as received. All chemicals of chemical grade and used without further purification. Deionized water was used the experiments.

2.2. Preparation of EVAL/SPEEK membranes

Self-supported: Both EVAL and SPEEK both were dissolved in DMAc to form homogeneous EVAL/SPEEK casting solutions at 90 °C, at a total polymer concentration of 21 wt.% (referring to Table 1 for compositions). Homogenous solutions were filtered with 40 µm stainless steel filters and degassed statically before use. The flat sheet membranes were casted onto a pre-heated (45 °C) clean glass plates at a relative humidity of $50 \pm 5\%$. The nascent membranes are immersed in a deionized water bath at 3.0 ± 0.2 °C for precipitation. Finally, the membranes were rinsed in deionized water for 24 h to remove trace solvent and then stored in DI water.

Non-woven supported: Clean PET non-woven fabric was first taped onto a glass plates. The fabric was pre-wetted by DMAc to avoid defects in the membrane. The EVAL/SPEEK-1.0 (Table 1) was casted onto the non-woven fabric using a stainless rod. The other preparation conditions were the same as above.

Table 1 Characteristics of EVAL/SPEEK solutions.

Membrane code	EVAL(wt.%)	SPEEK (wt.%)	DMAc(wt.%)	Ea (kJ/mol)	Tc (°C)
EVAL/SPEEK-0	21/0	0	79	26.8	-4.64
EVAL/SPEEK-0.5	20.5/0.5	0.5	79	28.5	-5.21
EVAL/SPEEK-1	20/1.0	1.0	79	29.0	-7.38
EVAL/SPEEK-2.6	18.4/2.6	2.6	79	37.5	-8.23

2.3. Solution characterization

Viscosity: The viscosity of casting solutions at a temperature range of 50-90 (± 0.2 °C) was measured using a viscometry (Brookfield engineering labs. Inc. Model LVDV-II+P, spindle of S31, 12 rpm).

Differential scanning calorimetry: The crystallization temperature of casting solution was measured using a differential scanning calorimeter (DSC 200F3, NETZSCH). Set the temperature program to heated from ambient temperature to 80 °C, and maintained at 80 °C for 5 min, then cooled to -30 °C at a rate of 10 K/min. The result recorded the dynamic crystallization temperature (Tc) as the onset of formation of EVAL crystallines in the solution [17, 19].

Frontier of demixing: A digital optical microscope (Olympus BX53) equipped with a CCD camera was used to record the frontier of demixing for analysis of the kinetics of the phase

separation for EVAL/SPEEK/DMAc solution in water. The gelation front displacement (d) at different time (t) was measured, and the gelation diffusion coefficient D_e was calculated according to Eq. 1 [51, 52].

$$d^2 = 4D_e \times t \quad (1)$$

where D_e is the mean diffusion coefficient of non-solvent through the precipitated polymer layer.

2.4. Instrument characterization

Scanning electron microscopy: A scanning electron microscopy (SEM, HITACH, TM1000) examined the membrane morphology at low magnification. A field emission scanning electron microscopy (FESEM, JEOL, JSM-7800F PRIME) used for high magnification. The membrane samples were fractured in liquid nitrogen and freeze-dried overnight. And the membrane samples were sputtered with a thin layer of gold using a sputter coater.

Mechanical properties: A tensile machine (LLOYD, LFPlus) measured the membrane mechanical properties at room temperature. The EVAL/SPEEK blend membranes are kept wet when measured. The tensile stress (MPa) and strain at breakage (%) were reported.

2.5. Diffusion

A double-channel cross-flow diffusion setup was used to measure the diffusion of lithium (30 ± 0.2 °C), and the details were reported in our previous paper [18]. Briefly, the membrane

samples were clamped in the test module. The feed chamber was filled with a 0.1 mol/L LiCl solution, and the receiving chamber was filled with deionized water. The conductivity of the lithium ion in DI water was tracked every five minutes. The Li^+ concentration was calculated based on a calibration curve, and the lithium ion flux (J) was determined as:

$$J = -\left(\frac{V}{A}\right) \frac{d[\text{Li}^+]}{dt} \quad (2)$$

where V is the volume of deionized water (L) and A is the effective area of membrane (cm^2).

2.6. Membrane extraction

A synthetic brine was prepared by dissolving certain amounts of LiCl (0.9 mol/L) and MgCl_2 (3.8 mol/L) in deionized water, and adjusted pH of the feed phase to 2.5 by HCl. The component and acidity are same as the real salt-lake brine. The extractant solution was NaFeCl_4 • $\text{TBP}_{(\text{O})}$ in kerosene at 75 vol.% [53]. Main parameters in membrane extraction are listed in Table 2 [53]. An experimental membrane extraction process is shown in Fig. S1 (referring to Supplementary Information). The extractant was sampled at certain time intervals and the concentration of Li^+ were determined by an Inductive Coupled Plasma Emission Spectrometer (ICP, SHIMADZU ICPE9000, 178 JAPAN). The Li^+ extraction flux ($\text{mol cm}^{-2} \text{ s}^{-1}$) was calculated according to Eq. 2.

Table 2 Experimental parameters for membrane extraction of lithium from synthetic brine.

Parameters	Value
Feed composition, mol/L	[MgCl ₂]=3.8; [Li ⁺]=0.9
Feed pH	2.5
Organic extractant	NaFeCl ₄ • TBP _(O) in kerosene, 75 vol.%
Flow rate of feed, L/min	0.1
Flow rate of extractant, L/min	0.1
Effective membrane area, cm ²	30
Temperature, °C	30

3. Results and discussion

3.1. Effect of SPEEK on the EVAL/SPEEK casting solution thermodynamics

Figure. 1a shows the relationship of the logarithm of solution viscosity verse the reciprocal

of absolute temperature, $\ln V - 1/T$. A linear correlation fits well to the Arrhenius formula as [54].

$$\ln k = \frac{-E_a}{R} * \frac{1}{T} + C \quad (3)$$

The slope was calculated to extrapolate the apparent activation energy of casting solution, representing the sensitivity of viscosity to temperature [54]. The apparent activation energy of EVAL/SPEEK solutions increases following an increase of SPEEK content for from 26.8 kJ mol⁻¹ (EVAL/SPEEK-0) to 37.5 kJ mol⁻¹ (EVAL/SPEEK-2.6). At a higher apparent activation energy, the polymer chains in the solution tend to move with more resistance, which is an important kinetic parameter of demixing in immersion precipitation [55].

Fig. 1b is the DSC scans of EVAL/SPEEK polymer solutions. The T_c of EVAL/SPEEK follows a decrease from -4.64 °C (EVAL/SPEEK-0) to -8.23 °C (EVAL/SPEEK-2.6). EVAL is a semicrystalline polymer and the exothermal peak was a result from the crystallization of EVAL polymers in the solution. Addition of SPEEK tend to constrain the EVAL chains to form crystalline nuclei, thus disrupt the structural regularity of the EVAL molecular chain. However, the crystallization temperatures of all casting solutions are below the temperature of coagulation bath (3 °C). Thus, EVAL polymers would not form nuclei upon contact with the coagulation bath; a liquid-liquid phase separation is preferable in the coagulation process [17, 19].

Fig. 1. (a) an inverse plot of the natural logarithm of the viscosity of EVAL/SPEEK casting solution as a function of absolute temperature. (b) DSC curve of EVAL/SPEEK casting solution, T_c : Crystallization temperature of polymer solution.

3.2. Effect of SPEEK on membrane formation kinetics

Fig. 2 shows series of photographs taken during the precipitation process. After introduce of water, demixing of EVAL/SPEEK polymers started and a frontier of the demixing could be seen in the photos as some finger-like structure grew into the homogeneous region. The formation of the finger membranes can be clearly seen with the optical microscope. This resembled closely the SEM micrographs, which indicated that optical microscope photos were good representative for the real membrane morphology. Occurrence of finger-like macrovoids were explained by two steps [56-58]: (1) Immediately after the casting solution is in contact with water, a homogeneous polymer layer is formed at the interface due to loss of solvent; the

polymer layer contracts due to the exchange between solvent and non-solvent. Shrinkage stress in the solidified polymer cannot be relieved by creep relaxation of the polymer, and the homogeneous layer ruptures. Fingers grow at the rupture in the polymer layer; (2) due to osmotic pressure across the polymer layer, the fingers expand further into the homogeneous solution layer without external constraints, but strongly dependent on the solution viscosity[51].

The gelation diffusion coefficient D_e was utilized as a quantitative measure for the speed of demixing. D_e decreases from $738 \mu\text{m}^2/\text{s}$ (EVAL/SPEEK-0) to $365 \mu\text{m}^2/\text{s}$ (EVAL/SPEEK-2.6) as the SPEEK content increases. We noticed that the D_e values for EVAL/SPEEK system were much lower than that of other hydrophobic polymer solution system (i.e. $D_e=3336.4 \mu\text{m}^2/\text{s}$ of poly (phthalazine ether ketone)/NMP/water system [59]). Because both EVAL/SPEEK are hydrophilic, the precipitation speed in water is low. At higher SPEEK content, both increased hydrophilicity and viscosity would slow down the demixing process.

The consequence of the slow-down of demixing process has a side-effect on the membrane morphology. Growth of finger structure consumes solvent in the stable region of the polymer solution. If formation of finger structure is delayed, the exchange of solvent and water at the interface becomes more important than the case where liquid-liquid demixing occurring quickly. Therefore, the total polymer concentration EVAL/SPEEK at the region (close to the interface) increases before liquid-liquid demixing starts. This may lead to more compact skin layer, thus higher diffusion resistance.

Fig. 2. The optical microscope photos of EVAL/SPEEK casting solution at different SPEEK addition (gelation bath: deionized water; Temp: 3.0 ± 0.2 °C).

3.3. Effect of SPEEK on structure and Li^+ diffusion flux

Fig. 3 shows SEM photos of EVAL/SPEEK membrane with various SPEEK content. From cross-section view, it appears that by adding 0.5 wt.% and 1.0 wt.% SPEEK into the solutions lead to slight increase in the finger-like macrovoids, (Fig. 3 EVAL/SPEEK-0.5, 1.0); however, as the SPEEK content increase to 2.6 wt.%, the number of finger-like macrovoids decreased, but enlarged. Because the macrovoids are freely accessible for ions [60, 61], the highest resistance comes from the top skin layer. Fig. 3 shows that following the increase of SPEEK,

the top skin layer become compact. For EVAL/SPEEK-2.6, no visual nanosize pores are observed. The EVAL/SPEEK-2.6 is clearly the thinnest among all membranes as shown in Fig.

3. Large amount of outflow of solvent from the membrane solution before demixing was the main cause. This result is also the other indirect support for above observation.

Fig. 3. SEM images of the Cross-section (1.0 k) and top skin layer (20.0 K) of EVAL/SPEEK membranes containing different SPEEK (wt.%). Gap of the casting knife: 100 μm . The coagulation bath temperature: 3 ± 0.2 $^{\circ}\text{C}$.

As shown in Fig. 4, the lithium diffusion fluxes of EVAL/SPEEK membranes follow an increase from $2.51 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ (EVAL/SPEEK-0) to $2.96 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ (EVAL/SPEEK-2.6). Addition of SPEEK indeed promotes the lithium diffusion of EVAL/SPEEK membranes for about 20% at a rather low SPEEK content of 0.5 wt.%. Further increase of SPEEK concentration did not show appreciate impact to the lithium diffusion flux. This results suggest that at even a very low concentration, the addition of SPEEK facilitates

the diffusion of lithium ions is very effective due to the effect of aforementioned absorption of sulfonation groups to cation Li^+ [48, 49, 62].

At higher SPEEK content, the nearly stable the lithium diffusion flux might be understood by the following factors: (1) when the anion groups in the amount reaches a certain threshold, all ions in the neighborhood of anions groups are deficient of lithium ions, thus effect is limited; (2) due to increase in the compactness of the membrane skin layer (Fig. 3), increase in mass transfer resistance contradicts to the effect of SPEEK; as a result, the lithium flux is unchanged at even much higher SPEEK content; (3) Because the porous channels are free for the lithium ion diffusion, thus the anionic chemistry in the membrane materials (wall of pores) is not as significant as that in dense membrane. Literature described that the hydrated ions in dense membrane are highly affected by the charges in the polymer materials [48, 49]. But our membrane is actually not dense, but porous (Fig. 3). This might explain why addition of SPEEK into the membrane did not show much improvement in the lithium ion diffusion. Nonetheless, an increase in diffusion flux about 20% was obtained at a rather low SPEEK content. It seems that mass transfer resistance for ion diffusion could not be significantly improved by only modifying the chemistry of the membrane material.

Fig. 4. Effect of SPEEK content on the diffusion flux of EVAL/SPEEK membranes. Gap of the casting knife: 100 μm . The coagulation bath temperature: 3 ± 0.2 $^{\circ}\text{C}$.

3.4. Effect of thickness

Fig. 5 shows the membrane morphology transition from sponge-like to finger-like structure as the membrane thickness increases. Here, we selected EVAL/SPEEK-1.0 solution due to the relatively low mass transfer resistance. The number of finger-like macrovoids increases following the increase in the thickness. The morphology transition of different thickness membranes is influenced by the kinetic transport process of the casting solution in the coagulant bath. When the membrane is very thin, the boundary condition for the membranes strongly influences the exchange process between the solvent and water, resulting in a fully sponge-like structure [24-28]. When the thickness increased to certain threshold value, this situation is not valid anymore, formation of finger-like macrovoids are favored due to “viscous

fingering effect” [56-58]. The enlarged SEM photos of the top skin layer for all membranes showed similar nanoporous structure as that of EVAL membrane [17, 19], but no obvious difference was observed (thus not shown here).

Fig. 5. The cross section (1.0 K) and the top layer (20.0 K) SEM picture of different thickness EVAL/SPEEK -1.0 membrane. The coagulation bath temperature: 3 ± 0.2 °C. Polymer solution: EVAL/SPEEK-1.0 (Table 1). Note: the scale bar of the last membrane is 30 μ m.

Fig. 6 a shows the effect membrane thickness on the lithium diffusion flux of EVAL/SPEEK membrane. Very interestingly, Li^+ diffusion flux follows a linear decrease as the thickness increase, independent from the variations in membrane morphology. The diffusion flux of lithium ion increases due to decrease in the membrane diffusion resistance. This indicates that the influence of membrane thickness on membrane resistance is greater than the change of

membrane structure.

Fig. 6 b indicates that the Li^+ extraction flux of different thickness follows an increase from $3.27 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ (100 μm) to $4.88 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ (50 μm). Obviously, thin membranes correspond to low mass transfer resistance, but the thin water swollen membranes are mechanically weak for physical handling, as evidenced by missing extraction results of membrane of 30 μm due to leakage during experiment. As shown in Fig. 6 c, the stress at breakage increases as the membrane thickness increases; the elongation at breakage increases first from 30 μm to 50 μm , then slightly decreases at 70 μm , followed by a sharp drop at 100 μm . The elongation at breakage of EVAL/SPEEK membrane at 50 μm reached the highest value of 143%. Reduction in the stress is unexpected as thicker membranes are obviously stronger, as indicated by increase in the force at breakage. However, when considering the volume of macrovoids of thicker membranes, the force per average cross-section area of the membrane decreases because of weak mechanical strength of void-filled structure. On the other hand, the nanosized sponge-like morphology tends to show much larger elongation. Therefore, as the membrane thickness increases, both reduction of sponge-like structure and increase in the numbers of macrovoids contribute to the decline in the elongation value.

As a summary, the strategy of reducing the membrane thickness is definitely the best choice to improve the membrane performance. But the mechanical strength of the membrane is predominant parameter in application. Therefore, EVAL/SPEEK membrane material alone

cannot achieve very high lithium extraction flux due to limitation of the mechanical strength.

Fig. 6. (a) The Li^+ diffusion flux of different thickness EVAL/SPEEK membrane. (b) Extraction flux of different thickness EVAL/SPEEK membrane. (c) Effect of membrane thickness on EVAL/SPEEK membrane mechanical.

3.5. To strengthen the EVAL/SPEEK membrane by non-woven support

Fig. 6 shows that below 50 μm , the EVAL/SPEEK membrane was not robust enough to withstand the extraction test, although the lithium extraction flux is expected to be higher at

lower thickness. Therefore, we attempted to use a thin loose fabric support for enhancement of the membrane mechanical strength as well as maintain the lithium extraction flux. Fig. 7 shows the cross-section of non-woven fabrics, EVAL/SPEEK-1.0 membrane (30 μm) and non-woven supported NW-EVAL/SPEEK composites membrane. The composites membrane structure is basically divided in three layers: the skin layer, the finger-like structure and the non-woven fabrics binding polymer layer. The polymer membrane bottom layer clings to the nonwoven fabric in the 35 μm composites membrane, forming a non-woven fabric and polymer binding layer. Fig. 7 d shows that the bottom surface of NW-EVAL/SPEEK membrane, which is completely different from that of the non-woven support. Clearly, EVAL/SPEEK polymers was imbedded into the fabric fibers.

Comparing Fig. 7b with Fig. 5 (30 mm), current membrane shows large and fully grown macrovoids. This was related to the different casting approaches for both membranes. To cast the nonwoven supported membrane, DMAc wetted the substrate for a better adhesion, but the membrane in Fig. 5 was cast onto a dry clean glass. Because of this difference, the immersion phase separation behavior varies: during immersion phase separation, a liquid-liquid demixing occurs, leading to polymer-rich phases (as continuous phase in this case) and polymer-lean phases [61, 63]; if polymer-lean phases are enlarged by inflow of solvent in vicinity, the polymer-lean phases would grow into large voids; Otherwise, the polymer-lean phases would result in small pores or cells (as shown in Fig. 5 for most of the polymer-lean phases). When

casting onto a solvent wetted substrate, there is a reservoir of DMAc at the frontier of the phase separation; some of the polymer-lean phases could grow by inflow of solvent/nonsolvent into the phases and result to macrovoids. This morphology is similar to previous reported co-casting process where the polymer solution was cast on to another polymer solution, leading to formation of more large macrovoids [61, 63].

Fig. 7. Cross-section (a) and bottom surface (c) SEM picture of non-woven fabrics. Cross-section (b) and bottom surface (d) SEM picture of composite membrane. The coagulation bath temperature: 3 ± 0.2 °C. Polymer solution: EVAL/SPEEK-1.0.

Fig. 8 shows the stress-strain curves of the support, the EVAL/SPEEK-1.0 and NW-EVAL/SPEEK membranes. The non-woven fabric shows a very low stress at break and low

strain at break. This is main due to the loose aggregation of the fibers which results in very low resistance to the deformation (Supplementary Information Fig. S3). EVAL/SPEEK membrane shows even lower stress at break at a relatively high strain at breakage of 58%. Surprisingly, although the strain of NW-EVAL/SPEEK membrane was not significantly higher than that of the support, the stress at break increased from 1.6 MPa (non-woven fabrics) and 1.0 MPa (EVAL/SPEEK membrane) up to 12.5 MPa. This unexpected results were reproduced in the lab and confirmed. A combination of a weak non-woven support and a weak membrane actually strengthen the mechanical properties for both materials. We attribute the improvement in mechanical strength to the probable adhesion of elastic EVAL polymers to loose fibers in the support.

The non-woven support consists of rather loose fabric fiber (Fig. 7). Upon mechanical stress, the fibers tend to disentangle from each other because of no intimate interaction (Supplementary Information Fig. S3). Thus the strength of the fibers was not demonstrated. After impregnating the EVAL/SPEEK polymers into the gap of fibers, the polymers act as the adhesive of the originally loose fibers; the intimate Van der Waals and/or hydrogen bonds between the molecules of polymers and PET might contribute to the increased stress. The other factor is the adhesive effect of the EVAL/SPEEK polymers would bring fibers in a closer range which might results in entanglement of fibers in some part of the support. This would also increase the strength of the membranes. Further scientific unravel of the phenomenon requires

detailed scientific research.

Fig. 9 shows a comparison of the lithium extraction flux of the non-woven support EVAL/SPEEK membrane (35 μm) to the literature reported results using pure EVAL (100 μm) and EVAL/SPEEK (100 μm) membrane. The stress of NW-EVAL/SPEEK membrane is 12.5 MPa, higher than EVAL/SPEEK (0.66 MPa) and EVAL membrane (2.8 MPa) [17]. Besides the mechanical strength, obviously, the strengthened membrane shows a significantly higher extraction flux than the other two. The results demonstrate that the current strategy to improve the lithium extraction flux by preparing a non-woven supported composite membrane is promising. We are currently working on further investigation to improve the lithium extraction flux by adjusting the EVAL/SPEEK coating layer thickness using this support. A scale-up of such composite membrane is required in the next research to prepare large extraction modules for pilot experiment.

Fig. 8. Mechanical properties of non-woven fabrics, EVAL/SPEEK membrane and NW-EVAL/SPEEK membrane.

Fig. 9. The Extraction flux of EVAL membrane, EVAL/SPEEK blend membrane and NW-EVAL/SPEEK membrane.

4. Conclusions

Hydrophilic ion-exchange EVAL/SPEEK blend membranes were prepared via immersion precipitation and utilized as the barrier in membrane extraction of lithium ions from synthetic salt-lake brine. The crystallization temperature measurement for EVAL/SPEEK solutions indicated that EVAL/SPEEK/DMAc/ H_2O system follows a liquid-liquid demixing rather than solid-liquid demixing. Addition of SPEEK into EVAL solution increases the viscosity and suppressed growth of the finger-like structure. Increase SPEEK content showed a small content is enough to increase lithium diffusion flux, but further increase of SPEEK lead to highly

compact skin layer counteracting the benefit of anion group. Decrease in the membrane thickness corresponds linearly increase in the lithium diffusion flux, but limited by the weak mechanical strength. Consequently, using a thin loose PET fabric, a non-woven supported EVAL/SPEEK membrane (about 35 microns) demonstrated significantly improved stress than individual non-woven support and the EVAL/SPEEK membrane. The lithium extraction flux of this membrane was the highest in literature using the same characterization method.

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