Chitosan-graft-benzo-15-crown-5-ether/PVA Blend Membrane with Sponge-Like Pores for Lithium Isotope Adsorptive Separation

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ABSTRACT: Crown ether exhibits a high separation coefficient for lithium isotope separation owing to its precise size selectivity to cations. A crown ether-based solid–liquid extraction method for the lithium isotope separation with a high extraction efficiency is regarded as a valid alternative to the classic liquid–liquid method. A chitosan-graft-benzo-15-crown-5-ether (CTS-g-B15C5)/polyvinyl alcohol (PVA) porous blend membrane for lithium isotope adsorptive separation was fabricated by immersion–precipitation–phase inversion. Results indicated that the finger-like structure of the blend membrane was replaced gradually by a sponge-like structure with the increase of the CTS-g-B15C5 concentration from 20 to 50 wt %. Meanwhile, the porosity and mechanical strength of the blend membrane slightly decreased from 76.9% and 2.68 MPa to 72.5% and 2.02 MPa, respectively, whereas the average pore size increased from 0.33 to 0.73 μm. The obtained CTS-g-B15C5/PVA (50/50 wt/wt) blend membrane exhibited a sponge-like asymmetrical gradient structure and good mechanical strength and used for the solid–liquid extraction experiment. It is found that the distribution coefficient increased from 13.50 to 49.33, and the single-stage separation factor increased from 1.008 to 1.046 with the immobilization amount of crown ether from 1.07 to 2.60 mmol-g⁻¹. It also meets the acceptable separation factor of 1.03 in a large scale of lithium isotope separation. In addition, ⁶Li and ⁷Li were enriched in the solid or membrane phase and the aqueous phase, respectively. In summary, the blend membrane has great potential applications in the development of green and highly efficient membrane chromatography for lithium isotope separation.

1. INTRODUCTION

Lithium is the lightest metal, and naturally occurring lithium consists of two stable isotopes, ⁶Li (7.5%) and ⁷Li (92.5%). Both lithium isotopes have been more and more attended in the nuclear power industry owing to their different nuclear properties of thermal neutron adsorption. As an important material for nuclear fusion reactors, ⁶Li can be cracked into tritium (T) and helium (He) by neutron bombarding. ⁷Li is usually utilized as a pH controller and a coolant for the nuclear fusion reactors. Until now, the mercury amalgam method has been the only method that has been applied for lithium isotope separation on a large scale. However, a large amount of toxic by-products have been produced, which have given rise to environmental and safety concerns. Therefore, the development of a novel and high-efficiency method for lithium isotope separation is of great challenge.

In the recent decades, many other techniques have been developed to separate the lithium isotope, such as electromigration, laser, electrochemical, solvent extraction, chromatography, and membrane separation. Among them, solvent extraction and chromatography using crown ether as an extracting agent have been proven to be effective techniques for lithium isotope separation.

Specifically, the derivatives of 15-crown-5 ether for the lithium isotope adsorptive separation through liquid–liquid extraction have been paid great attention. This is because the cavity size of 15-crown-5 ether (1.70 Å) is close to the diameter of Li⁺ (1.20 Å). For instance, the separation factor obtained by liquid–liquid extraction using benzo-15-crown-5 (B15C5) was approximately 1.042. However, the liquid–liquid extraction system with a low extraction efficiency and a high loss rate of crown ether limits its practical applications.

A crown ether-based solid–liquid extraction method for lithium isotope separation with a high extraction efficiency is regarded as a valid alternative to the classic liquid–liquid method. For example, Otake et al. proposed a phenol-type B15C5 resin by chemical bonding for lithium isotope separation. The maximum separation factor obtained was up...
to 1.033. The more important is that the resin is producible. Further, Zhou et al. synthesized mesoporous silica materials doped with ionic liquids and B15C5 for lithium isotope separation, and the separation factor obtained was up to 1.046.

Recently, our group reported that a polyvinyl alcohol-graft-benzo-15-crown-5 ether (PVA-g-FB15C5) film was prepared from PVA and 4-formoxybenzo-15-crown-5 ether (FB15C5), and the maximum separation factor obtained by the solid-liquid extraction system of the isopropanol–Li/PVA-g-FB15C5 film at 20 °C was up to 1.060. Similarly, a polymer of the chitosan-graft-benzo-15-crown-5 ether (CTS-g-FB15C5) polymer was synthesized via a Schiff base reaction between FB15C5 and CTS. Results showed that the lithium isotope separation factor of CTS-g-FB15C5 polymer obtained was 1.037, which was higher than the acceptable separation factor of 1.03 in a large scale of lithium isotope separation.

However, high internal diffusion resistance and low separation efficiency during the solid–liquid extraction by the resins limit its practical application because of the low porosity and small pore size of the resins. An alternative technique is to prepare a porous functional polymeric membrane with a low internal diffusion resistance so as to improve the separation efficiency.

As is well known, CTS is a naturally nontoxic and biorenewable polymer that is being extensively used in a number of applications. For instance, Liu et al. successfully developed a CTS macroporous membrane by a selected dissolution technology using silica particles as the porogen agent. Li et al. also fabricated a CTS nanoporous membrane by selective dissolution with polyethylene glycol as the porogen. However, the CTS membrane shows a poor mechanical property because CTS has a high molecular weight and hard backbones. Consequently, CTS blending with other polymers as the most common approach could be used to solve the abovementioned issue.

The aim of the present study is to prepare a CTS-g-FB15C5/PVA porous blend membrane and improve the lithium isotope separation efficiency by solid–liquid extraction. Meanwhile, the compatibility of the blend systems and the morphologies of the blend membrane were characterized by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) analyses. The effects of the immobilization amount of crown ether grafting onto CTS and polymer morphology on the lithium isotope separation performance were explored.

2. RESULTS AND DISCUSSION

2.1. DSC Analysis of the Blend Polymer Systems. DSC was utilized to observe the compatibility of CTS-g-FB15C5 and PVA at different mass ratios, as shown in Figure 1. It can be seen in Figure 1a that there was an endothermic peak at 125 °C, which was attributed to the dissociation process of hydrogen of CTS-g-FB15C5. In addition, no significant glass-transition temperature ($T_g$) was found in the experimental range. The main reason is that CTS has a high $T_g$ and will probably start to decompose before melting. The result was in agreement with the previous works by Lewandowska and Wan et al. Further, it can also be found from Figure 1g that the melting endothermic peak of pure PVA with a relatively sharp and large curve can be observed at 232.0 °C. Moreover, the peak of the endothermic curve gradually shifted from 220.9 to 230.0 °C with the increase of PVA content from 40 to 80 wt%. The reason is that there was a strong hydrogen bonding interaction between CTS-g-FB15C5 and PVA. Particularly, the endothermic curve of the blend system became sharper with the increase of PVA content in the blend system. This indicated that the degree of PVA crystallization decreased after blending with CTS-g-FB15C5. In consequence, it implied that there is a good miscibility between CTS-g-FB15C5 and PVA polymers.

2.2. Characterization of the Blend Membrane.

2.2.1. Blend Membrane Morphologies. The composition and viscosity of the casting solutions with different mass ratios of CTS-g-FB15C5/PVA (7 wt % of polymer concentration) are listed in 1. The blend membranes were prepared via the immersion–precipitation–inversion process. The SEM images of M0 (CTS-g-FB15C5 membrane), M1, M2, M3, M4, and M5 membranes are shown in Figure 2. It can be seen that M0 (Figure 2a) and M1 (Figure 2b) exhibited a typical asymmetric structure throughout with a finger-like support layer and a dense skin layer. In addition, macrovoids appeared in the M1 membrane. Surprisingly, the finger-like structure of the blend membrane was replaced gradually by a sponge-like structure with the increase of the CTS-g-FB15C5 concentration from 30 wt % (M2) to 40 wt % (M3) (Figure 2b,c). On further increase to 50 wt % of CTS-g-FB15C5, a blend membrane with a completely sponge-like structure (M4) was obtained, as shown in Figure 2d. The reason is that the viscosity of the casting solution increased from 1057.5 to 1992.5 mPa·s with the increase of the CTS-g-FB15C5 concentration from 20 to 50 wt %, leading to a slow mutual diffusion between the solvent and the nonsolvent during phase inversion. Finally, the finger-like structure and the macrovoids in the polymeric membranes were totally suppressed.

Furthermore, M5 with sponge-like pores were also obtained when the coagulation bath temperature decreased from 35 to 25 °C, as illustrated in Figure 2e. Differently, the pore size of M5 became smaller than that of M4. To further observe the asymmetrical gradient structure of the blend membranes, Figure 3 showed different parts of SEM photographs derived from the M4 membrane at a large magnification.

Further, it can be found from Table 1 that the porosity of the resultant blend membrane slightly decreased from 76.9 to 72.5% with an increase in the concentration of CTS-g-FB15C5 from 20 to 50 wt %, whereas its average pore size increased from 0.33 to 0.73 μm. This is because a higher CTS-g-FB15C5 concentration would result in a delayed phase separation which caused the obtained membrane with a sponge-like asymmetrical gradient structure and a loose top layer structure. Specifically,
the M5 membrane exhibited a porous structure similar to that of the M4 membrane. However, both the average pore size and the porosity of M5 were larger than those of the M4 membrane. This can be interpreted that the affinity between the solvent and the nonsolvent becomes weaker at a low coagulation bath temperature so as to retard the fast nonsolvent intrusion. Under this condition, a larger average pore size and a higher porosity were obtained (M4 and M5).

| no. | mass ratio of CTS-g-FB15C5/PVA | coagulation bath temp (°C) | viscosity (mPa·s) | porosity (%) | average pore size (μm) |
|-----|--------------------------------|-----------------------------|------------------|--------------|-----------------------|
| M1  | 20:80                          | 35                          | 1057.5           | 76.9 ± 1.8   | 0.33                  |
| M2  | 30:70                          | 35                          | 1650.0           | 75.5 ± 1.1   | 0.51                  |
| M3  | 40:60                          | 35                          | 1820.0           | 74.3 ± 2.0   | 0.60                  |
| M4  | 50:50                          | 35                          | 1992.5           | 72.5 ± 1.0   | 0.73                  |
| M5  | 50:50                          | 25                          | 1977.5           | 75.9 ± 1.2   | 0.98                  |

Figure 2. SEM images of the blend membranes: (a) M0; (b) M1; (c) M2; (d) M3; (e) M4; and (f) M5.
In addition, X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical components of the top surface and the bottom surface of M4. The C/N/O atom ratios of M4 in the top and bottom surfaces were 1:0.059:0.0466 and 1:0.06:0.455, respectively. This implied that the top and bottom surfaces of the blend membranes have the same chemical composition, and the two polymers (CTS-g-FB15C5 and PVA) are mixable at the ratio of 50/50 wt/wt.

2.2.2. Mechanical Property of Blend Membranes. The mechanical property of blend membranes is illustrated in Figure 4. As shown in Figure 4, the breaking strength and the elongation of the blend membranes gradually decreased from 2.68 MPa and 15.8% (M1) to 1.81 MPa and 8.7% (M3) with the increase of the CTS-g-FB15C5 concentration from 20 to 40 wt %, respectively and then slightly increased to 2.02 MPa and 11.80% (M4) when the CTS-g-FB15C5 concentration further increased to 50 wt %. It is well-known that the mechanical property of the CTS polymer membrane can be improved if it blends with PVA. However, the mechanical property of the M4 membrane was higher than that of the M3 membrane, which is related to the sponge-like asymmetrical gradient structure without finger-like pores or macrovoids (M4). Generally, the mechanical property of the membrane with the sponge-like structure was better than that of the membrane with the finger-like structure.

Furthermore, both the breaking strength and the elongation of the M5 membrane with a structure similar to the M4 membrane were lower than those of the M4 membrane. This was closely related to the porosity. The membrane with a low porosity or high compaction would exhibit a good mechanic performance.

2.3. Lithium Isotope Adsorption Separation. 2.3.1. CTS-g-FB15C5/PVA Blend Membrane for Lithium Ion Adsorption. The cross-linked CTS-g-FB15C5/PVA blend membranes obtained by the cross-linking reaction for 60 min were introduced into the solid–liquid extraction system to explore their lithium ion adsorption property, as demonstrated in Figure 5. It can be clearly seen from Figure 5 that the values of the distribution coefficient \( K_d \) first increased from 16.96 (M1) to 50.20 (M4) and then decreased to 42.23 (M5). This phenomenon is exactly consistent with the average pore size of the blend membranes. On the one hand, a large average pore size would bring about a low operating pressure so as to reduce the mass-transfer resistance between crown ether and lithium ion. Therefore, the mass-transfer efficiency was enhanced, and the obtained \( K_d \) increased gradually with the increasing of the average pore size. On the other hand, further increase in the average pore size would decrease the retention time of the lithium ion on the blend membrane. Simultaneously, a portion of lithium ion solution flowed directly through the membrane from the pore of the membrane without sufficient contact with the crown ethers on the blend membranes during adsorption. In summary, \( K_d \) is closely related to the porous structure of the blend membrane.

2.3.2. Effect of the Immobilization Amount of Crown Ether on Lithium Isotope Adsorptive Separation. As discussed above, the M4 membrane with a sponge-like asymmetrical gradient structure presented excellent lithium ion adsorption performance. The following work is to investigate the effect of the immobilization amount of crown ether on lithium isotope separation. The CTS-g-FB15C5/PVA blend membranes with different immobilization amounts \((I_A)\) of crown ether were prepared under the same preparation condition as with the M4 blend membrane. The effects of the immobilization amount of crown ether on CTS, distribution coefficient \( K_d \), and single-stage separation factor \((\alpha)\) are shown in Figure 6.
It can be seen from Figure 6 that $K_d$ increased from 13.50 to 49.33 and $\alpha$ also increased from 1.008 to 1.046 with an increase of $I_a$ from 1.07 to 2.60 mmol·g$^{-1}$. The main reason is that the crown ether molecules dispersedly grafted on the CTS chains would increase the chance for each crown ether molecule to complex with lithium ions and enhance the efficiency of isotope adsorptive separation. The results were in good agreement with the solid–liquid extraction results obtained by the LiI–H$_2$O/PVA-g-FB15C5 film system$^{19}$ and the LiCl–methanol/PSF-g-AB15C5 polymer system.$^{11}$ This also implies that the separation performance obtained from the CTS-g-FB15C5/PVA blend membrane has also been improved. It is noted that an acceptable separation factor for lithium isotope separation in a large scale is 1.03.$^{21}$ That is to say, the CTS-g-FB15C5/PVA blend membrane has great potential applications in the development of green and highly efficient technologies for lithium isotope adsorptive separation.

In addition, it was found that the light isotope ($^6$Li) and the heavy isotope ($^7$Li) were enriched in the solid (membrane) phase and the solution phase, respectively. This can be explained by Bigeleisen’s theory.$^{37}$ In general, $^4$Li is usually concentrated in the organic phase, whereas $^7$Li is enriched in the aqueous phase in traditional liquid (aqueous solution)–liquid (crown ether/CHCl$_3$) extraction systems. The lithium ions adsorbed in the solid phase had a lower hydratability than those in the solution phase, and the bonding environment of B15C5 for the lithium isotope was not changed after crown ethers were grafted onto CTS. That is to say, the bonding environment of the CTS-g-FB15C5/PVA blend membrane was weaker than that of the solution phase. According to Bigeleisen’s theory, heavy isotopes are easily concentrated in “stronger bonding environments”. Consequently, $^7$Li was concentrated in the solid phase (membrane) and $^6$Li was enriched in the aqueous phase.

2.3.3. Effect of CTS-g-B15C5 Polymer Morphology on Lithium Isotope Adsorptive Separation. The CTS-g-FB15C5/PVA blend membrane and the CTS-g-FB15C5 film as extracting agents were used to investigate the influence of the polymer morphology on $K_d$ and $\alpha$ under the same conditions and the immobilization amount of crown ether (2.60 mmol·g$^{-1}$). The results are shown in Table 2. It can be seen from Table 2 that the $K_d$ obtained from the CTS-g-FB15C5/PVA blend membrane using LiI aqueous solution as an extracting solution was up to 49.33, which was much higher than that obtained from the LiI–H$_2$O/CTS-g-FB15C5 film (1.20). This suggested that the adsorption property of lithium ions by the Table 2. FB15C5 and CTS-g-FB15C5 Polymer for Lithium Isotope Separation$^a$

| extraction agent       | $K_d$     | $\alpha$     |
|------------------------|-----------|--------------|
| FB15C5                 | 1.022 ± 0.002 |              |
| CTS-g-FB15C5 film      | 1.20 ± 0.3  | 1.035 ± 0.001 |
| CTS-g-FB15C5/PVA membrane | 49.33 ± 1.9 | 1.046 ± 0.002 |

$^a$LiI aqueous solution with a concentration of 3 mg/L was used. All extraction experiments were performed for 30 min at 20 °C.

CTS-g-FB15C5/PVA blend membrane as an extracting agent was improved dramatically.

Further, the $\alpha$ value obtained by the CTS-g-FB15C5/PVA blend membrane was 1.046, which was also higher than that obtained from the CTS-g-FB15C5 film (1.035). The main reason is that the crown ether molecules grafted on the CTS film had a low probability to contact with the lithium ion, and the Li$^+$-crown ether complex mostly formed on the surface of the CTS-g-FB15C5 film. However, the CTS-g-FB15C5/PVA blend membrane is a porous material with a porosity of 72.5%, and the crown ether molecules of the blend membrane were easily and fully utilized to complex lithium ions. The formed Li$^+$-crown ether complex not only existed on the porous surface of the blend membrane but also in internal pores. For this reason, a larger $K_d$ and $\alpha$ were obtained from the extraction system of the LiI–H$_2$O/CTS-g-FB15C5/PVA blend membrane. Similarly, the heavy isotope ($^7$Li) was concentrated in the aqueous phase, and the light one ($^6$Li) was concentrated in the CTS-g-FB15C5 film and the CTS-g-FB15C5/PVA blend membrane, respectively.

In comparison, the lithium isotope separation performance of FB15C5 was conducted by typical liquid–liquid extraction.$^{38}$ The results are also illustrated in Table 2. It can be found from Table 2 that $\alpha$ obtained from the H$_2$O–LiI/CHCl$_3$–FB15C5 liquid–liquid extraction system was 1.022, which was obviously lower than that obtained from the CTS-g-FB15C5 film (1.035) and the CTS-g-FB15C5/PVA blend membrane (1.046). This showed that the lithium isotope separation effect was improved by grafting crown ether onto a CTS polymer.

3. EXPERIMENTAL SECTIONS

3.1. Materials. CTS powder with a degree of decacylation of 87.3% and a molecular weight cutoff of 540 kDa was purchased from National Pharmaceutical Group of China Ltd., Beijing, China. FB15C5 was prepared by the method that Ungaro et al.$^{39}$ reported. PVA with a degree of polymerization of 1750±50 was purchased from Tianjin Guangfu Technology Development Co. Ltd., China. All other reagents were analytical reagent and obtained from Tianjin Guangfu Technology Development Co. Ltd. without further purification.

3.2. Preparation of the CTS-g-FB15C5/PVA Blend Membrane. The CTS-g-FB15C5 polymer was prepared as described by Changhong et al.$^{40}$ The dissociative crown ethers were further washed with ethanol in a Soxhlet extractor for 48 h. The CTS-g-FB15C5/PVA blend membrane was prepared by an immersion–precipitation–phase inversion process.$^{41}$ First, the CTS-g-FB15C5 polymer was dissolved in 2% (v/v) acetic acid at 30 °C for 6 h. At the same time, PVA was dissolved in distilled water at 90 °C for 6 h and cooled to room temperature. Then, CTS-g-FB15C5 solution and PVA solution were mixed in a certain weight proportion. The obtained mixture solution was stirred at room temperature for 6 h to form a homogeneous solution and degassed to remove
microbubbles was casted using an automated membrane applicator (Elcometer 4340, England) with a gap of 800 μm on a clean glass plate at a certain temperature and then immersed into a coagulation bath with saturated Na2SO4 solution for the immersion–precipitation process at 35 °C for 30 min to prepare the blend membrane. After that, the obtained blend membrane was immersed into a bath with a chemical cross-linking agent of 0.03 mol/L glutaraldehyde, 0.96 mol/L saturation sodium, and 0.15 mol/L concentrated sulfuric acid at 20 °C for 60 min for the cross-linking reaction to improve the chemical stability of the blend membrane in aqueous solution or acidic medium. The Schiff Base was also stable in the process of membrane fabrication because of the existence of benzene rings. Finally, the cross-linked CTS-g-FB15C5/PVA blend membrane was obtained after freeze-drying for 12 h.

3.3. Characterization of the Polymer Blend System and Membrane. DSC (DSC2014F1, Germany) analysis of blend systems was carried out to observe the endothermic peak in the temperature range of 25–250 °C at a heating rate of 10 °C/min. The content of CTS-g-FB15CS in the blend systems varied from 100 to 0%.

XPS (Thermo Fisher K-Alpha) with a monochromated Al Kα X-ray source (hv = 1486.6 eV) was used to further study the top and bottom surface chemical change of the blend membranes. The range of 0–1350 eV of the survey spectrum including the high-resolution C 1s spectra was collected, and the surface elemental composition was calculated from the peak area with a correction for atomic sensitivity.

The morphologies of the cross-linked CTS-g-FB15C5/PVA blend membranes were characterized by SEM (Zeiss Gemini SEM 500). The average pore size of the blend membranes was examined by a pore size analyzer (Bei-Shi-De 3H-2000PB, China). Membrane porosity was determined by a dry weight method. At first, a certain area of the membrane sample was maintained in distilled water and weighed after removing the superficial water using a filter paper. Then, the wet membrane was dried under a vacuum condition at 40 °C for 12 h up to a constant weight, and the dry membrane weight was measured. The porosity of the blend membrane was calculated by eq 1:

\[ \varepsilon = \frac{w_1 - w_2}{Ad \rho_m} \]

where \( \varepsilon \) is the porosity of membrane (%); \( w_1 \) and \( w_2 \) are the weights of the wet and dry membranes (g), respectively; \( \rho_m \) is the density of distilled water (g/cm³). \( A \) is the area of the membrane, and \( d \) is the thickness of the membrane (cm²).

The immobilization amount (\( I_A \) mmol/g) of crown ethers on PSF chains was determined by an elemental analyzer (Vario EL/micro cube), as defined by eq 2:

\[ I_A = \frac{w_N \%}{14} \times 1000 \]

where \( w_N \% \) is the nitrogen content of the graft polymers determined by the elemental analyzer, and 14 is the atomic weight of nitrogen.

3.4. Lithium Isotope Adsorptive Separation. To determine the single-stage separation factor of lithium isotope separation by the blend membrane, a dynamic cyclic adsorption mode, that is, solid–liquid extraction was employed. Firstly, the CTS-g-FB15CS/PVA blend membrane was fixed in a flat-sheet membrane module with a diameter of 1.4 mm. Li aqueous solution (3 mg/L, 100 mL) as an extracting solution flowed through the membrane at a speed of 15 mL/min at 20 °C and then recycled back to the feed tank. After extracting for 30 min, the concentration of lithium ions in the aqueous solution was determined by inductively coupled plasma optical emission spectrometry (Varian 715). The distribution coefficient, \( K_d \), can be calculated from the initial and final lithium ion concentrations by eq 3:

\[ K_d = \frac{(C_0 - C_f)}{C_f} \times \frac{V_f}{V_m} \]

where \( K_d \) is the distribution coefficient; \( C_0 \) is the initial concentration of the lithium ion (mg/L); \( C_f \) is the final lithium ion concentration after extraction (mg/L); \( V_f \) is the volume of lithium salt solution (mL); and \( V_m \) is the volume of the CTS-g-B15CS/PVA blend membrane (mL).

After complexing with lithium ions, the blend membrane was flushed with ultrapure water at a flow rate of 15 mL/min to remove the Li+ ions. Subsequently, the ratio of isotopic \(^6\text{Li}/^7\text{Li}\) in the obtained aqueous solution could be measured by high-resolution inductively coupled plasma-mass spectrometry (Finnigan MAT, Germany). The single-stage separation factor, \( \alpha \), can be calculated by eq 4:

\[ \alpha = \frac{(\text{^6Li}/\text{^7Li})_m}{(\text{^6Li}/\text{^7Li})_i} \]

where \((\text{^6Li}/\text{^7Li})_m\) and \((\text{^6Li}/\text{^7Li})_i\) represent the isotopic ratio. The subscripts of m and i refer to the stationary phase (membrane) and the initial solution phase, respectively.

4. CONCLUSIONS

A CTS-g-FB15CS/PVA blend membrane was successfully prepared for the selective separation of lithium isotopes by the immersion–precipitation–phase inversion process. The morphologies and performance of the blend membrane were affected by the addition of PVA. It was found that the CTS-g-FB15CS/PVA blend system exhibited a good blend compatibility owing to the strong hydrogen-bonding interaction between CTS-g-FB15CS and PVA polymers, resulting in a delayed demixing and the obtained membrane with a sponge-like asymmetrical gradient structure with the increase of the CTS-g-B15CS concentration from 20 to 50 wt %. Simultaneously, the porosity and mechanical strength of the blend membrane slightly decreased from 76.9% and 2.68 MPa to 72.5% and 2.02 MPa, respectively, whereas the average pore size increased from 0.33 to 0.73 μm. The obtained CTS-g-B15CS/PVA (50/50 wt/wt) blend membrane exhibited a sponge-like asymmetrical gradient structure and good mechanical strength. The distribution coefficient of the CTS-g-FB15CS/PVA blend membrane increased from 13.50 to 49.33, and the separation factor also increased from 1.008 to 2.60 mmol/g·L⁻¹. Further, the remarkable separation factor obtained by the LiCl–H₂O/CTS-g-FB15CS/PVA blend membrane extraction system was up to 1.046, which was higher than those obtained by the CTS-g-FB15CS film (1.035) and FB15CS (1.022). This indicated that the lithium isotope separation effect was improved by grafting crown ether onto CTS polymers. Furthermore, the heavy isotope, \(^7\text{Li}\), was enriched in the aqueous phase, whereas the lighter one, \(^6\text{Li}\), was concentrated in the film or membrane phase. In a word, the blend membrane has great potential applications in the development of green.
and highly efficient technologies including membrane chromatography for lithium isotope separation.

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**Notes**

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