Highly selective transport of lithium across a supported liquid membrane

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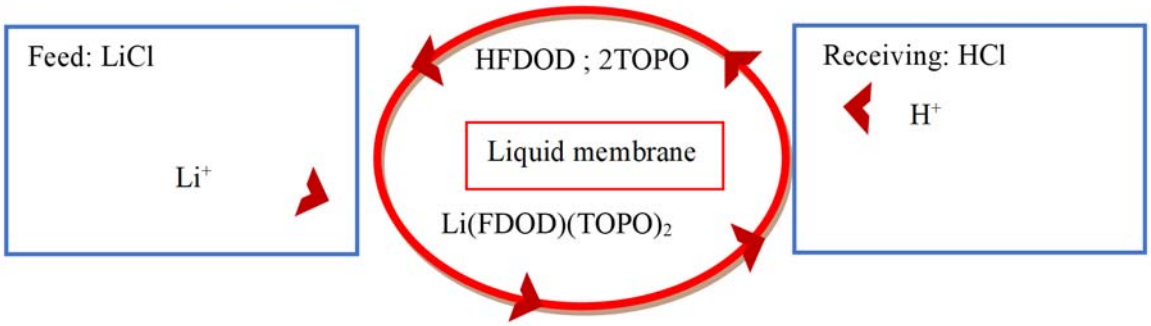
Graphical Abstract



Abstract

Lithium extraction is a major concern in view of the increase in battery manufacturing. Separation of lithium from sodium is still challenging due to the similar chemical behavior of the two alkali metals. Sources such as brines or seawater usually contain large amounts of sodium which requires a high selectivity for the lithium extraction process. In this study, we demonstrate the application of a supported liquid membrane (SLM) with very high selectivity for the separation of lithium from sodium. A synergistic system made of heptafluoro-dimethyloctanedione (HFDOD) and tri-octyl phosphine oxide (TOPO) was selected based on its extraction efficiency (>99% of lithium extracted) and selectivity for lithium over sodium (separation factor≈400). Several parameters were studied using a SLM made of HFDOD and TOPO (lithium concentration, sodium to lithium ratio, HFDOD: TOPO ratio). It was found that high lithium permeation rates can be obtained even for low lithium concentrations and high

sodium concentration. Membrane stability was evaluated and was found to be poor (loss of performances after one cycle of use), due to the leakage of the organic phase and change in HFDOD: TOPO ratio. This SLM system is suitable for the extraction of lithium from brines and seawater.

Keywords: Lithium, liquid membrane, membrane stability, fluorinated compounds, brines

Introduction

The unique physicochemical properties of lithium (Li) are used for diverse applications. Actually, the addition of lithium to aluminum and copper alloys results in the family of alloys with improved properties such as lower density and higher specific stiffness for aerospace applications [1], [2]. Lithium salts due to their high hygroscopicity of lithium salts are used in air conditioning systems. Lithium also plays a key role in the glass and ceramics industry (35% of worldwide lithium consumption) [3], [4]. In the long-term, lithium is an option considered for the production of isotopes used for thermonuclear reactions [5]. However, lithium consumption is expected to increase especially in the short- and medium-term perspectives. Thanks to their high charge to weight ratio, lithium batteries are the current solution to empower electric cars and to store energy, impacting the consumption of lithium [6].

The recovery of lithium from various sources such as minerals [7], seawater [8], or spent lithium-ion batteries [9] has been extensively studied in recent years. Nowadays, lithium-rich brine water remains the most important source of lithium [10]. The extraction of lithium from this kind of water source remains challenging due to the high salinity of the sources treated, and particularly in the presence of sodium and potassium, elements having similar physico-chemical properties to those of lithium [11].

Recently, different techniques have been shown to recover lithium selectively from brine water such as ion-exchange resins [12] or electrochemical-based processes systems [13]. In particular, lithium-ion sieves has shown great potential due to their high selectivity [14], but the synthesis of these new materials requires metal consumption (manganese, titanium…), and harsh chemical conditions.

Among the already available separation methods, membrane techniques allow to obtain a continuous and selective extraction of lithium with a low environmental impact [15]. The

separation of lithium from magnesium and sodium was demonstrated using nanofiltration and reverse osmosis [16].

Supported liquid membranes (SLM) is a kind of membrane process for which the transport is chemically driven [17]. The pores of solid membrane support are filled with a solvent phase, containing a specific organic ligand (carrier or extractant) dissolved in a diluent. Then, this SLM is placed between two aqueous phases [18]. The organic ligand binds selectively to the target metal in the first solution (feed solution), the metal-ligand complex is then diffusively transported through the membrane support and finally, it is released in the second solution (receiving or acceptor phase).

Using the SLM technique, the extraction and back extraction of the metal is done in one step with a low volume of organic reagents (as compared with liquid-liquid extraction), and the extraction is potentially highly selective. However, mainly due to the leaking of the organic phase to the aqueous phases during the process, the stability of the process is relatively low. SLM demonstrated good selectivity for lithium among other alkali metals ([17], [19]). but in these cases, they could be not used continuously for more than two days due to the instabilities.

To separate lithium from sodium, solvent extraction is the most selective technique. Synergistic systems based on an association of acidic and neutral extractants have shown their interest for this purpose [20], [21], [22]. In this last one, , the acidic extractant exchanges its labile proton with the lithium ion under ammoniacal conditions in the aqueous phase. The synergism induced by the solvating extractant enhances lithium extraction efficiency. Since the lithium ion has the highest charge density of the alkali elements, the synergism is much higher for lithium rather than the other alkali elements.

The solvating extracting molecule can be chosen among a large range of neutral organophosphorous extractants. In this study, we used tri-octyl phosphine oxide (TOPO) as a synergistic agent because it has been demonstrated the highest synergistic effect for lithium [23]. Several acidic extracting molecules can be used, such as di-(2-ethylhexyl)phosphoric acid ([17], [24], [25]) or α-acetyl-m-dodecyl acetophenone ([26], [27]) and other β-diketones ([28], [21], [29]). In the present study, we compared several commercial acidic extractants (Figure 1), namely di-(2-ethylhexyl)phosphoric acid (DEHPA), benzoyltrifluoroacetone (HBTA), thenoylfluoroacetone (HTTA), bis(trimethylpentyl)phosphonic acid (HBTMPP) and

heptafluoro-dimethyl octanedione (HFDOD), and applied the most efficient in a supported liquid membrane. The relevant parameters were outlined and used to separate lithium from sodium using a SLM. The long-term stability of the SLM was evaluated, as well as several experimental parameters (initial lithium concentration, the ratio of extracting molecules in the liquid membrane phase,…) to maximize both lithium extraction efficiency and lithium/sodium separation ability.

2. Materials and methods

2.1. Reagents

Tri-*n*-octyl phosphine oxide (TOPO, 98% purity), di-(2-ethylhexyl)phosphoric acid (DEHPA, 95%), benzoyltrifluoroacetone (HBTA, 99%), and thenoyltrifluoroacetone (HTTA, 99%) were purchased from Alfa Aesar. Bis-(trimethylpentyl)phosphinic acid (HBTMPP, >90%) was obtained from Carbosynth. Heptafluoro-dimethyl octanedione (HFDOD, 98%), *n*-dodecane (>99%) and analytical grade hydrochloric acid (HCl) were purchased from Sigma Aldrich. Sodium and lithium chloride (NaCl and LiCl, >99%) were purchased from Prolabo. Analytical grade ammonia (NH_4OH) was obtained from Fischer Scientific. All chemicals used in this work were used as received. The structure of the acidic extractants can be seen in Fig.1. Hydrophobic polyvinylidene fluoride (PVDF, Merck) is used as polymeric support due to its good chemical resistance and compatibility with organic solvents. The characteristics of this porous support are shown in Table 1. De-ionized water (18 mΩ.cm) was obtained with a Purelab Option Q apparatus.

Composition	Nominal pore size,µm	Porosity, %	Thickness, µm
Hydrophobic PVDF	0.45	75	125

Table 1. Properties of the PVDF support used according to the supplier

2.2. Solvent extraction

The organic and aqueous phase were prepared by diluting the extracting molecules in dodecane and the metal salts in de-ionized water, respectively. Exact mass (±0.1 mg) of the components was added to both phases using a Sartorius BP 221S balance. The organic phase was slightly heated and shaken to improve the dissolution of TOPO. The alkalinity of the aqueous phase was adjusted by adding an ammonia solution. The solvent phase (extracting

molecules dissolved in dodecane) was mixed with the aqueous phase at 1400 rpm and 25°C with a Biosan TS-100 Thermoshaker for 30 minutes. Phases were then separated after centrifugation at 9500 rpm for 2 minutes with a VWR Microstar apparatus. Small aliquots of the aqueous phases before and after extraction were diluted in HCl (1%) and analyzed with a Varian 720 ES ICP-OES. The wavelengths selected were 610.365 nm and 588.995 nm for lithium and sodium, respectively. The aqueous concentration of metals was used to calculate the distribution ratio of the metals (D_M), which is defined by the concentration of metal in the organic phase divided by the concentration of metal in the aqueous phase after extraction, and is calculated according to the following equation:

$$D_M = \frac{[M]_{before} - [M]_{after}}{[M]_{after}} \times \frac{V_{aq}}{V_{org}} \quad (1)$$

$[\mathrm{M}]_{\mathrm{before}}$ and $[\mathrm{M}]_{\mathrm{after}}$ being the metal concentration in the aqueous phase before and after extraction, respectively. $\frac{\mathrm{V_{aq}}}{\mathrm{V_{org}}}$ is the aqueous to organic phase volume ratio, which is fixed to one in our case (0.6 mL of each phase).

The separation factor for lithium over sodium was calculated according to the following equation:

$$SF_{Li/Na} = \frac{D_{Li}}{D_{Na}} \quad (2)$$

2.3. Preparation of supported liquid membrane

The supported liquid membrane was prepared according to the method reported by Ansari et *al.* by impregnation of porous polytetrafluoroethylene support [30],[31]. In brief, the virgin PVDF support was soaked into the organic phase of the desired composition. The membrane was removed after 10 minutes. The organic phase entered in the pores of the support, as evidenced by the change of color of the support (from white to translucid). The excess organic phase on the surface was carefully removed with a tissue paper. The supported liquid membrane was then weighed to estimate the mass of the organic phase within the pores. It is also weighed after the transport experiments to estimate the losses of liquid membrane. The membrane is left to dry for a few hours at ambient temperature before weighing.

2.4. Membrane transport

The membrane transport experiments were carried out at ambient temperature, using the experimental device described in a previous study [32]. In brief, the membrane (effective area *A* is 17.8 cm^2) was inserted between the two compartments of a glass membrane contactor (Verlabo), each compartment having a volume (*V*) of 250 mL. The aqueous phases were agitated at 50 rpm. Aliquots of each phase are withdrawn regularly at various time intervals and aqueous metal concentration was determined by ICP-OES. The permeability (*P*, $cm.s^{-1}$) is defined by the following equation [33].

$$\ln \frac{C_t}{C_0} = -\frac{A}{V} \times P \times t \quad (3)$$

C_0 and C_t being the aqueous metal concentration in the feed phase initially and at time "t" (s). The permeability P is calculated from the slope of the linear representation ln C*t*/ C_0 versus time after three hours of transport.

3. Results and discussion

3.1. Solvent extraction

Using a process combining solvent extraction and membrane, Theisen et *al.* investigated the reactive and diffusive transport of rare earth element through a porous media [34]. Their work shows that the diffusive resistance created by the porous membrane is prevalent only at low distribution coefficients. Hence, in order to operate an efficient process, distribution coefficients should be at least D_M > 10 or higher (typically, D_M>50), signifying a low impact from membrane diffusive resistance.

Thus, we investigated several organic molecules combined in a synergistic system with TOPO. Since TOPO has low solubility in the organic phase, we used a constant TOPO concentration of 0.1 $mol.L^{-1}$. The aqueous solutions containing 15 mM of NaCl and LiCl at pH = 11.4 were mixed with TOPO and HFDOD, HBTA, HTTA, DEHPA or HBTMPP in dodecane. The effect of the nature of acidic extractant on the distribution ratio and separation factor value for lithium over sodium are shown in Fig. 1.

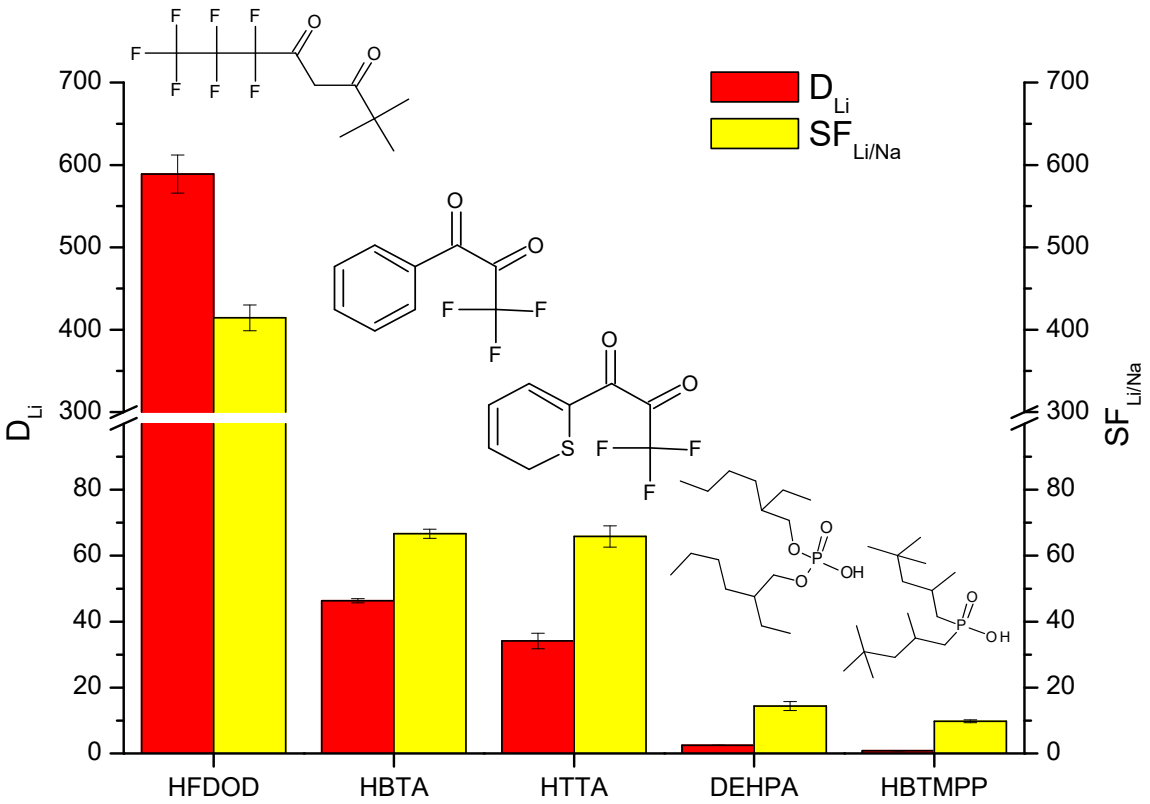


Figure 1. D_{Li} and $SF_{Li/Na}$ depending on the acidic extractant (0.1 mol.L^{-1}) used in combination with TOPO (0.1 mol.L^{-1}) dissolved in dodecane. Aqueous phase: LiCl and NaCl (15 mmol.L^{-1}), pH=11.4

From this data, it can be seen that D_{Li} follows the following order: HBTMPP<DEHPA<<HTTA<HBTA<<HFDOD. The high distribution ratio values were obtained for lithium for all of the β-diketones investigated. Their affinity and complexation ability for the lithium ions is much higher, which explains the higher distribution ratio values obtained than with the acidic DEHPA and HBTMPP extractants. Among the β-diketones, HFDOD is by far the most efficient and the selectivity for lithium over sodium follows the order HBTMPP≈DEHPA <HTTA≈HBTA<HFDOD.

The fluorinated alkyl chain of HFDOD has a high impact on its complexation ability as it was previously evidenced by Seeley and Baldwin [35],[36]. It is well known that the keto-enol tautomerism of β-diketones is an important feature for the extraction of metals. The enol form is able to exchange its proton with the metal ion. The organic diluent used has also a high impact on metal extraction since the enol form is obtained with apolar solvents. Among the diluents, dodecane was selected since it allows to obtain a high extraction and has moderate volatility and toxicity [22].

The presence of electronegative fluorine atoms in the extractant composition helps to enhance the acidic character of the molecule ([35], [36]) as evidenced in Figure 2. The distribution ratio values for lithium with HFDOD or HBTA in combination with TOPO obtained at pH=8.5 (Fig. 2) are much lower than those obtained at pH=11.4 (Fig. 1). However, while the distribution ratio for lithium obtained with HBTA extractant is almost negligible (D_{Li} is close to 0.25), the distribution ratio obtained with HFDOD remains significant. Thus, HFDOD is selected as an acidic extractant due to its better performance in terms of efficiency and selectivity and allows to work on a broader range of pH (as long as it is sufficiently high).

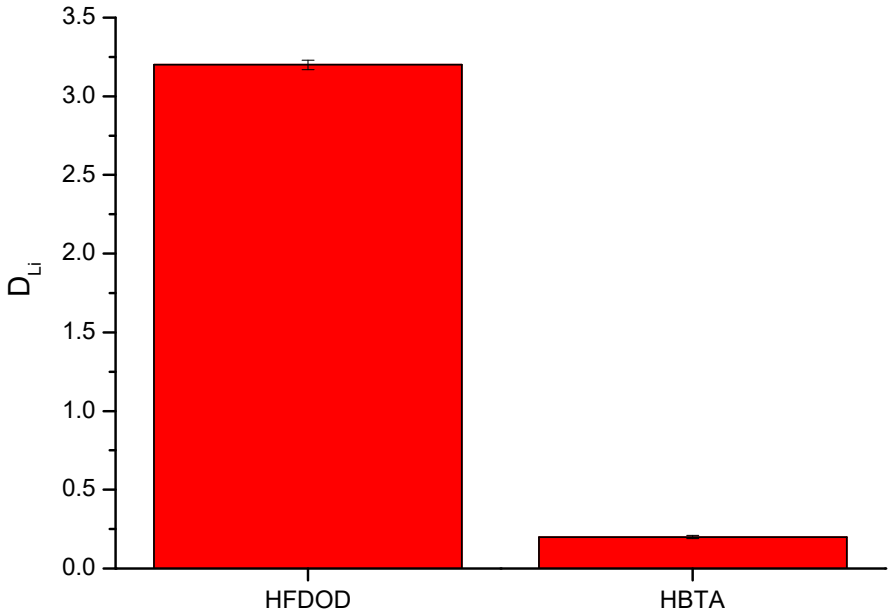


Figure 2. D_{Li} with HFDOD or HBTA (0.1 mol.L^{-1}) used in combination with TOPO (0.1 mol.L^{-1}). Aqueous phase: LiCl (15 mmol.L^{-1}), pH=8.5

It is well known that the effect of both molecules ratio in the organic phase is a relevant parameter in synergistic systems. Hence, different HFDOD:TOPO ratio were studied for the solvent extraction of the lithium ion (Fig. 3).

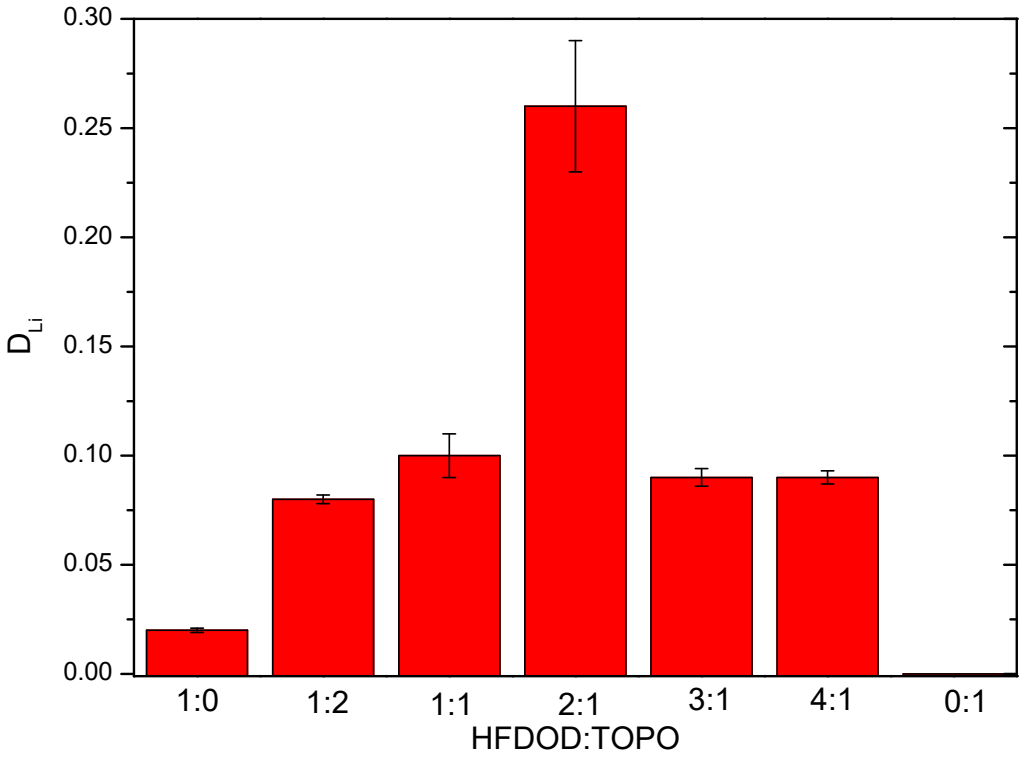


Figure 3. D_{Li} with various HFDOD:TOPO ratios. TOPO concentration is fixed at 0.1 mol.L^{-1}. Aqueous phase: LiCl (15 mmol.L^{-1}), pH=7.5

A low distribution ratio is obtained when using HFDOD (0.1 mol.L^{-1}) alone (D_{Li}<0.25). No extraction of lithium is obtained when using TOPO alone, evidencing the synergistic effect obtained when using both molecules combined in the organic phase. D_{Li} reaches a maximum for HFDOD:TOPO=2:1 which was also found to be the optimal ratio for other synergistic systems based on β-diketones [37], [22]. For others ratios, D_{Li} is found to be lower, even if the extraction is significant as compared to the distribution ratio obatained with both molecules used independently. It can also be seen from Fig. 3 that D_{Li} at pH=7.5 is lower than D_{Li} obtained at pH=8.5 and 11.4 (Fig. 2 and Fig. 1). Therefore, this solvent extraction system can only be applied to basic solutions.

According to Seeley et al. ([35]) the extraction of lithium occurs *via* cation exchange with the proton of the β-diketone according to the following equation:

$$(Li^+)_{aq} + x(HFDOD)_{org} + y(TOPO)_{org} \leftrightarrow (Li(FDOD)_x(TOPO)_y)_{org} + (H^+)_{aq} \quad (4)$$

where the subscript “aq” and “org” refers to the aqueous and organic phase, respectively. Seeley *et al.* proposed a (1:1:1) or (1:1:2) complex between lithium, HFDOD and TOPO, *i.e.* x=1 and y=1 or 2 depending on the TOPO concentration in the solvent phase.

3.2. Supported liquid membrane studies

3.2.1. Lithium transport though SLM

The SLM transport scheme proposed is displayed in Figure 4. Stripping of lithium from a loaded organic phase is done with hydrochloric acid solution (0.5 mol.L^{-1}) [35].

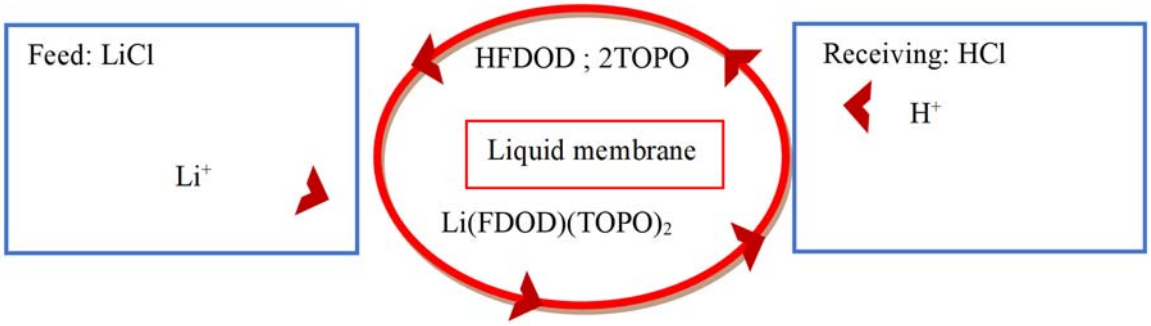


Figure 4. Scheme of the proposed mechanism of transport using SLM

Lithium is extracted from ammoniacal solutions at the feed/liquid membrane interface according to Eq. 4. Aqueous pH of 12 was selected to favor lithium extraction while avoiding the degradation of the PVDF membrane, which could undergo dehydro-fluorination under highly alkaline conditions [38]. Lithium is then diffusively transported as lipophilic $Li(HFDOD)(TOPO)_2$ complex inside the membrane porous. At the liquid membrane/receiving phase, lithium is released in the receiving phase by exchange with the protons of the acid.

Using this configuration, the evolution of lithium concentration in both aqueous phases is shown in Figure 5. The HFDOD:TOPO ratio and the aqueous phase pH is selected based on the solvent extraction results, in order to maximize lithium extraction efficiency.

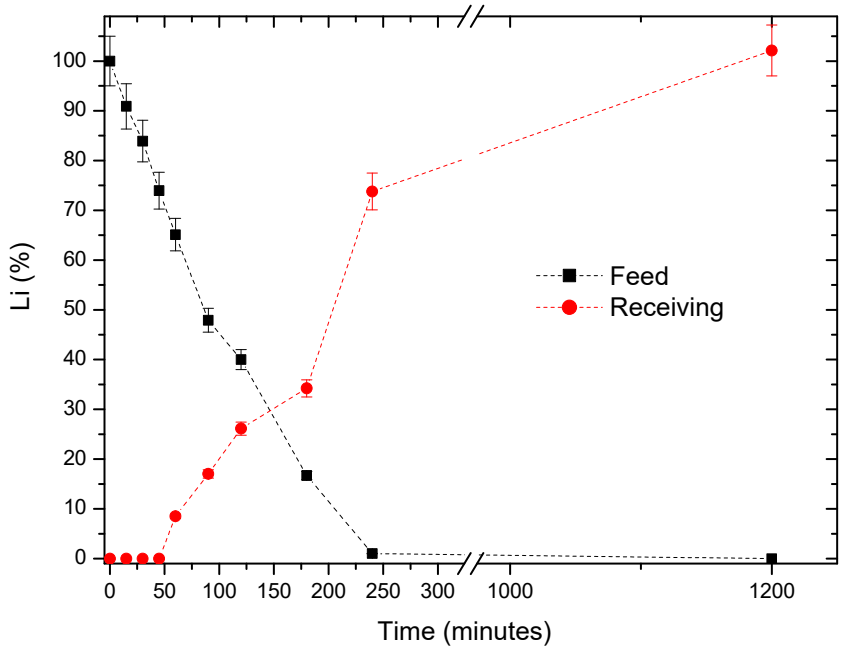


Figure 5. Evolution of lithium concentrations in the aqueous phases. Feed phase: LiCl (0.1 mmol.L^{-1}), pH=12. Supported liquid membrane: HFDOD (0.2 mol.L^{-1}) and TOPO (0.1 mol.L^{-1}) in dodecane. Receiving phase: HCl (0.5 mol.L^{-1}).

Lithium concentration in the feed phase is decreasing fast, 50% of the initial lithium being removed from the aqueous feed phase in less than 2 hours. However, it can be seen that lithium is below the detection limits in the receiving phase during the first 50 minutes of the experiment, which clearly indicates that lithium is accumulated in the liquid membrane. Lithium appears in the receiving phase after 60 minutes of transport though the membrane, its concentration being gradually increased.

After 1200 minutes about 100% of lithium has been removed from the aqueous phase and transferred in the receiving phase. This experiment confirms the extraction of lithium by the liquid membrane phase and the efficiency of lithium stripping.

The effect of the molar ratio between HFDOD and TOPO extractants was investigated with the supported liquid membrane (Fig. 6).

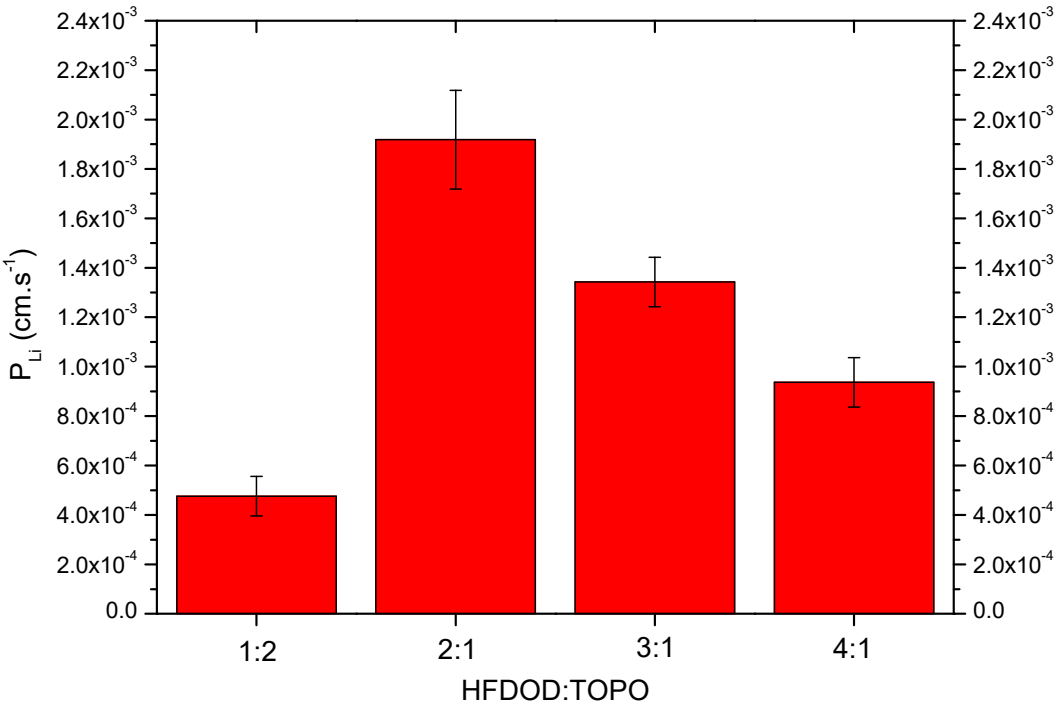


Figure 6. P_{Li} depending of the molar ratio HFDOD: TOPO. Liquid membrane: HFDOD (variable) and TOPO (0.1 mol.L^{-1}) in dodecane. See Fig. 5 for the composition of the aqueous phases.

Large variations in lithium permeation can be evidenced from Figure 6, depending on the HFDOD: TOPO molar ratio in the liquid membrane. The slower transport is obtained with a HFDOD: TOPO ratio of 1:2, for which the lowest P_{Li} is obtained. In this case, the amount of HFDOD available at the interface is too low to obtain an efficient transport of lithium. The fastest lithium transport is obtained with a (2:1) molar ratio, which gave the highest distribution ratio when using solvent extraction (Fig. 3). Despite the higher amount of HFDOD available at the interface, the molar ratio of (3:1) and (4:1) gave a slower transport speed after 90 minutes of transport. The highest efficiency is obtained with a (2:1) molar ratio, which follows the same trend as the one proposed by Cai et al. using HTTA and TOPO in a polymer inclusion membrane [39]. The higher permeation was obtained for the molar ratio value of 2:1. Therefore, the molar ratio was maintained at 2:1 for further experiments.

The effect of lithium initial concentration in the feed solution on lithium permeation is shown in Figure 7.

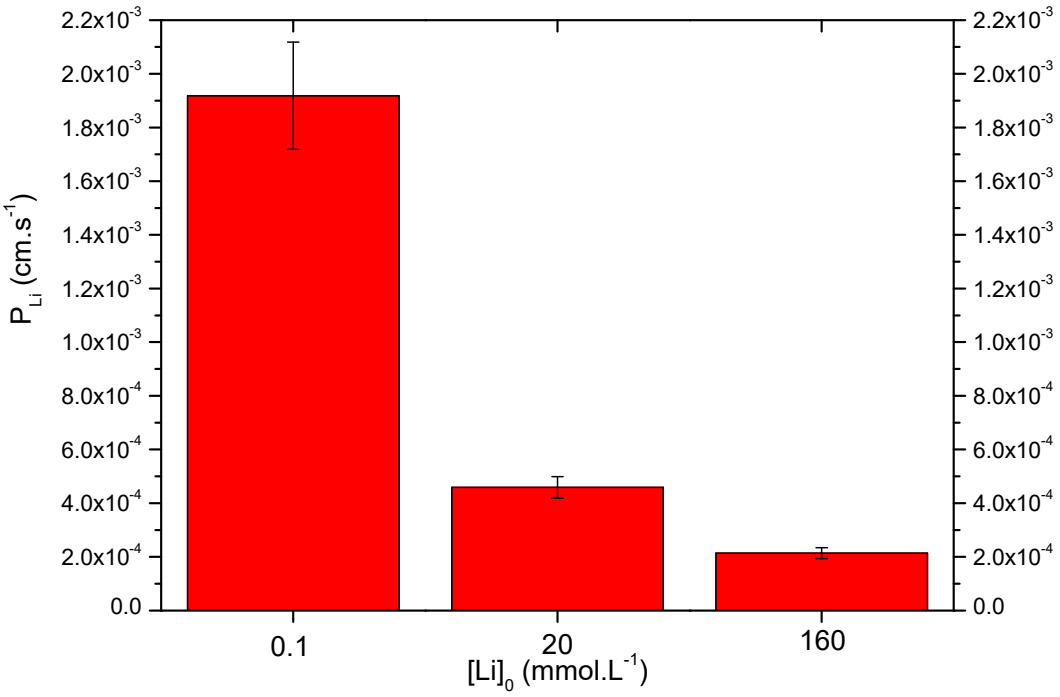


Figure 7. P_{Li} depending on the lithium initial concentration. Feed phase: LiCl (variable), pH=12. Liquid membrane: HFDOD (0.2 mol.L^{-1}) and TOPO (0.1 mol.L^{-1}) in dodecane. Receiving phase: HCl (0.5 mol.L^{-1})

P_{Li} shows a large dependency on lithium initial concentration. The lithium permeation coefficient diminishes when the lithium initial concentration is increased. This trend is often encountered using SLMs [40], [41]. This trend was attributed to a saturation of the membrane pores with metal-extractant species, which could form an extractant layer at the interface, therefore reducing lithium permeation. Due to the low amount of extractant retained into the pores of the support, the SLM technique is more suitable for the treatment of lowly concentrated solutions. To treat higher-grade solutions, increasing membrane area and/or change of membrane configuration appears to be mandatory.

3.2.2. Lithium separation from sodium

Lithium extraction from various sources requires its separation from sodium. Thus, the selectivity of the liquid membrane process was evaluated using various initial lithium/sodium ratio in the aqueous feed phase. P for lithium and sodium is shown in Fig. 8.

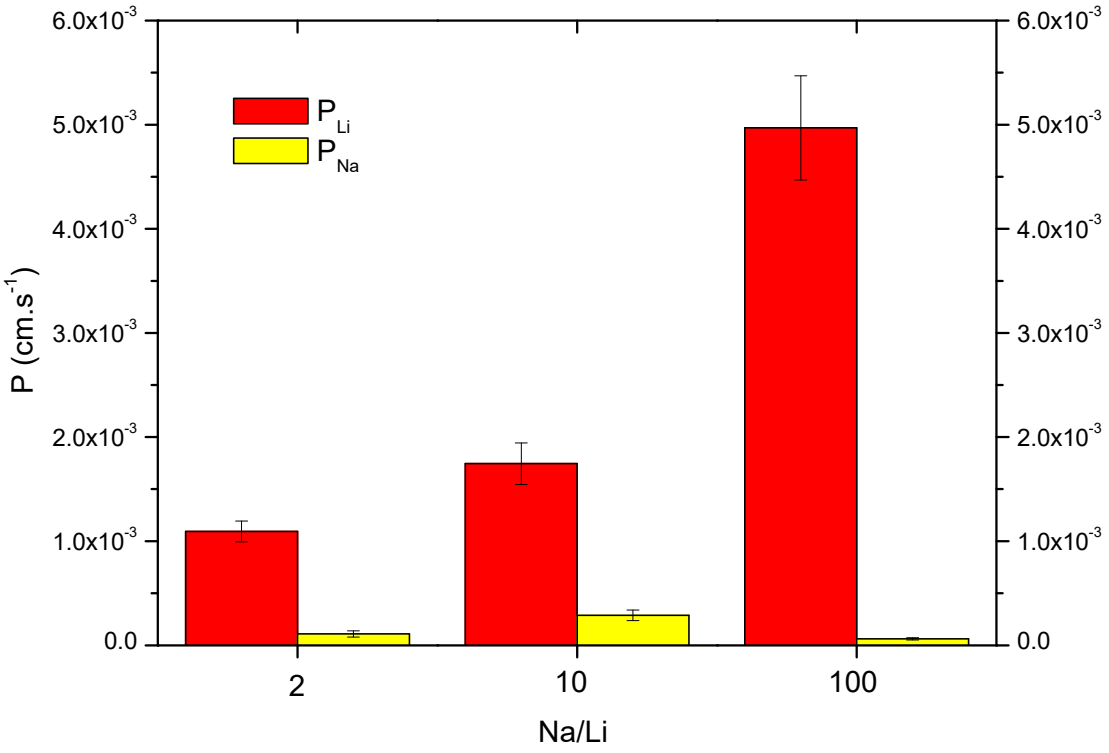


Figure 8. P_{Li} for lithium (red) and sodium (yellow) depending on the sodium/lithium initial molar ratio in the aqueous feed phase. Feed phase: LiCl (1 mmol.L^{-1}) and NaCl (variable), pH=12. See Fig. 5 for the composition of the liquid membrane and the receiving phase

Sodium permeation is impacted by the initial sodium/lithium ratio. Sodium flux is very low because the synergistic system used in the liquid membrane has a high selectivity for lithium (Fig. 1). Moreover, sodium permeation is diminished when increasing its initial concentration and becomes almost negligible for a sodium/lithium ratio of 100.

Lithium permeation is also affected by the sodium concentration in the aqueous feed phase. P_{Li} is increasing when the concentration of sodium is high. When introducing a high concentration of sodium salt in the aqueous phase, the salt lowers the activity coefficient of water molecules, which increases the activity coefficient of the metals and improve their transport though the membrane [42]. The saturation effect observed for lithium in Fig. 7. does not appear for sodium since this metal is poorly extracted by the extractants used. Thus,

lithium separation from sources containing large amounts of sodium such as brines or seawater is promising with this SLM system. The permeation coefficients obtained for lithium in this work (P_{Li} up to $5x10^{-3}$ $cm.s^{-1}$) are higher than the permeation oefficients reported in the literature so far for the extraction of lithium [17], [19], [32]. The selectivity for lithium is also very promising, since the permeation ratio of sodium is not higher than $3X10^{-4}$ $cm.s^{-1}$.

3.2.3. Supported liquid membrane stability

Membrane stability is an important feature using SLM. P_{Li} is shown in Fig. 9 with the same liquid membrane used over several cycles for lithium extraction.

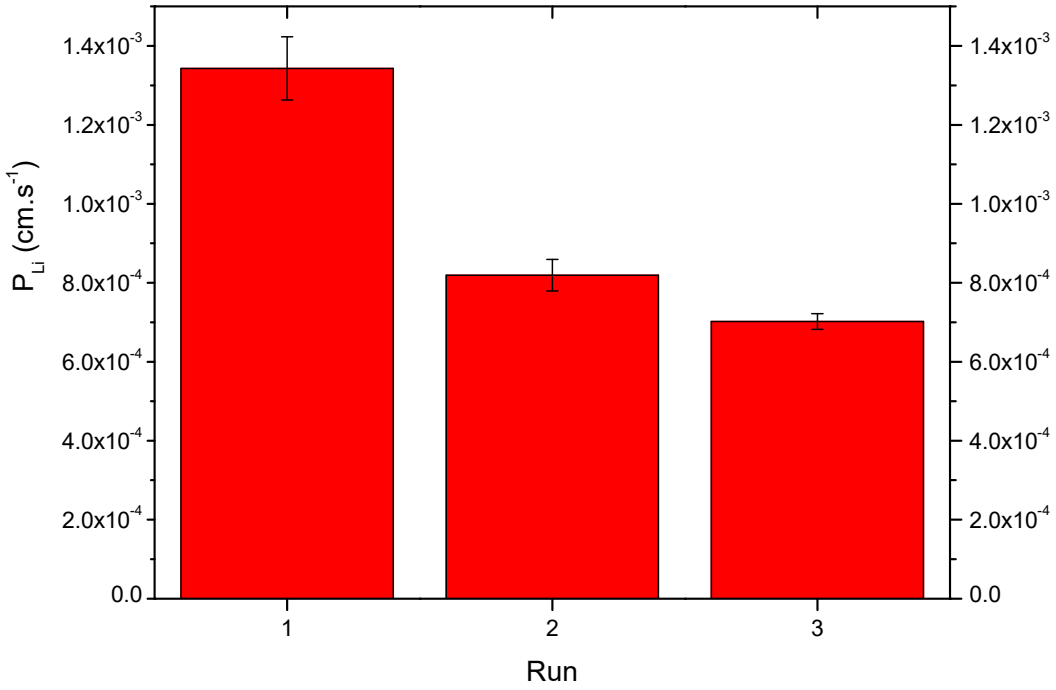


Figure 9. P_{Li} over several cycles of use. Liquid membrane: HFDOD (0.3 $mol.L^{-1}$) and TOPO (0.1 $mol.L^{-1}$) in dodecane. See Fig. 5 for the composition of the aqueous phases

P_{Li} is decreasing after the first run, and gets lower after each cycle of use, which means that the performances of the SLM are degraded. Numerous causes of degradation lead to leakage of the organic phase from membrane pores [43], [44]. As evidenced in Fig. 10, the mass of the liquid membrane after three consecutive cycles of use is far lower than the original mass of the liquid membrane, after impregnation. Thus, it can be concluded that part of the organic phase was removed from membrane pores and this is responsible for the diminution of lithium permeation. However, the permeation ratio remains significant after several cycles of use,

which means that there are still some extractant molecules remaining into the membrane pores.

Fig. 11 shows a picture of the membrane after extraction. Part of the membrane turns white (original color of PVDF support), confirming the removal of the organic phase. Interestingly, yellowish traces appear on the membrane support. These traces are attributed to HFDOD and indicate that this fluorinated extractant is retained into the membranes. The affinity of fluorinated compounds for the fluorinated polymer is a way to avoid the leaching of the organic phase and to promote membrane stability [45]. In our case, lithium extraction and transport performances are highly related to the concentration and ratio of extractants molecules in the organic phase (Fig. 3 and Fig. 6). Thus, even if HFDOD is not removed from the membrane, the solubilization of dodecane and/or TOPO will change the HFDOD: TOPO molar ratio and consequently affect lithium transport efficiency.

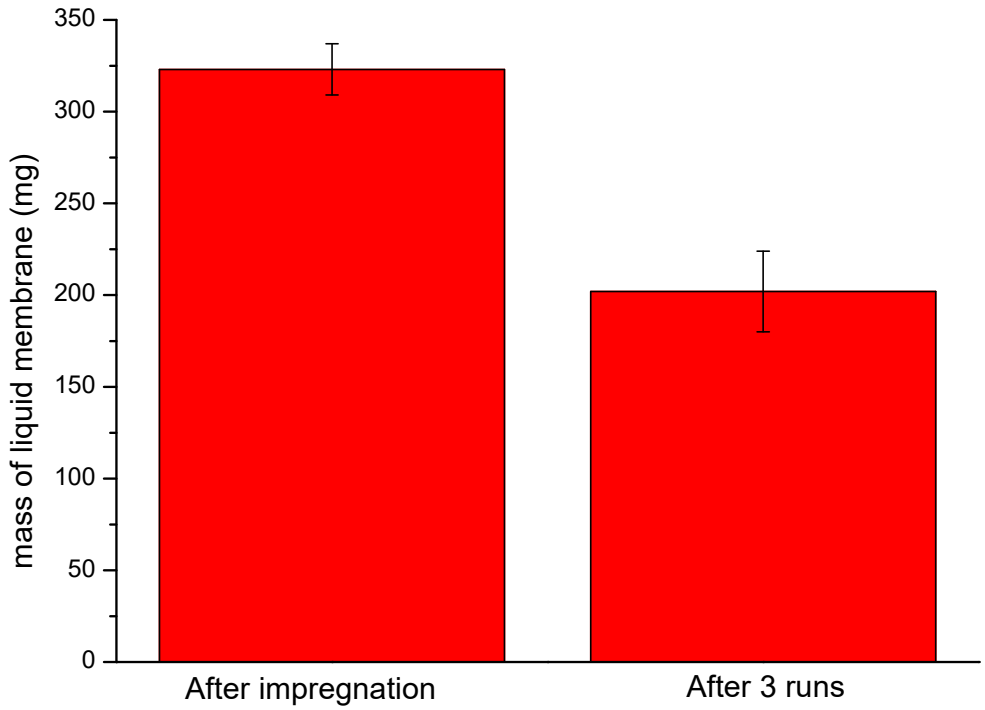


Figure 10. Membrane mass before impregnation, after impregnation and after 3 cycles of use. See Fig. 5 for the composition of the liquid membrane and the aqueous phases

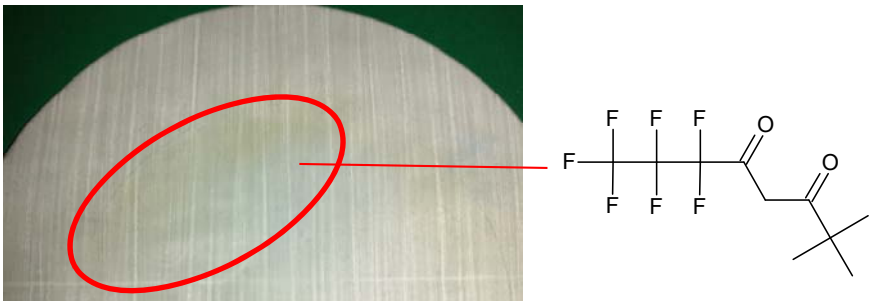


Figure 11. Picture of the liquid membrane after 3 cycles of use

4. Conclusions

A supported liquid membrane process was developed and showed high efficiency and ultra-high selectivity for lithium over sodium. Among the various acidic extractants studied, HFDOD was the most efficient and was used in combination with TOPO as a synergistic agent. Different parameters such as initial lithium concentration, sodium: lithium ratio in the aqueous phase and HDOD: TOPO ratio in the liquid membrane have a large effect on lithium transport efficiency. It was found that a low lithium concentration and a higher sodium concentration promoted lithium transport with very high selectivity. Membrane stability was poor since lithium permeation is diminished after two cycles of use of the liquid membrane. This poor stability was attributed to the leaking of the organic phase, which changes the ratio of extractant in the liquid membrane. Fluorinated compounds have a higher affinity for the polymer and their use could be a way to improve membrane stability. However, the high peristance in the environment of the fluorinated molecule together with its high toxicity make it unpractical for large scale use.

Acknowledgments

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References

[1] E.J. Lavernia, N.J. Grant, Aluminium-lithium alloys, J Mater Sci. 22 (1987) 1521–1529. https://doi.org/10.1007/BF01132370.

[2] R.J.H. Wanhill, Aerospace Applications of Aluminum–Lithium Alloys, in: Aluminum-Lithium Alloys, Elsevier, 2014: pp. 503–535. https://doi.org/10.1016/B978-0-12-401698-9.00015-X.

[3] B. Swain, Recovery and recycling of lithium: A review, Separation and Purification Technology. 172 (2017) 388–403. https://doi.org/10.1016/j.seppur.2016.08.031.

[4] B. Swain, Recovery and recycling of lithium: A review, Separation and Purification Technology. 172 (2017) 388–403. https://doi.org/10.1016/j.seppur.2016.08.031.

[5] W. Lu, W. Pu, D. Chu, J. Yang, S. He, K. Li, W. Wang, Fabrication and characteristics of lithium metatitanate tritium breeder via polymer-assisted sedimentation method under different sintering conditions, Journal of Nuclear Materials. 524 (2019) 218–225. https://doi.org/10.1016/j.jnucmat.2019.07.007.

[6] H. Vikström, S. Davidsson, M. Höök, Lithium availability and future production outlooks, Applied Energy. 110 (2013) 252–266. https://doi.org/10.1016/j.apenergy.2013.04.005.

[7] B. Tadesse, F. Makuei, B. Albijanic, L. Dyer, The beneficiation of lithium minerals from hard rock ores: A review, Minerals Engineering. 131 (2019) 170–184. https://doi.org/10.1016/j.mineng.2018.11.023.

[8] T. Ryu, J. Shin, S.M. Ghoreishian, K.-S. Chung, Y.S. Huh, Recovery of lithium in seawater using a titanium intercalated lithium manganese oxide composite, Hydrometallurgy. 184 (2019) 22–28. https://doi.org/10.1016/j.hydromet.2018.12.012.

[9] R. Sattar, S. Ilyas, H.N. Bhatti, A. Ghaffar, Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries, Separation and Purification Technology. 209 (2019) 725–733. https://doi.org/10.1016/j.seppur.2018.09.019.

[10] G. Liu, Z. Zhao, A. Ghahreman, Novel approaches for lithium extraction from salt-lake brines: A review, Hydrometallurgy. 187 (2019) 81–100. https://doi.org/10.1016/j.hydromet.2019.05.005.

[11] T. Nguyen, M. Lee, A Review on the Separation of Lithium Ion from Leach Liquors of Primary and Secondary Resources by Solvent Extraction with Commercial Extractants, Processes. 6 (2018) 55. https://doi.org/10.3390/pr6050055.

[12] F. Arroyo, J. Morillo, J. Usero, D. Rosado, H. El Bakouri, Lithium recovery from desalination brines using specific ion-exchange resins, Desalination. 468 (2019) 114073. https://doi.org/10.1016/j.desal.2019.114073.

[13] S. Kim, H. Joo, T. Moon, S.-H. Kim, J. Yoon, Rapid and selective lithium recovery from desalination brine using an electrochemical system, Environ. Sci.: Processes Impacts. 21 (2019) 667–676. https://doi.org/10.1039/C8EM00498F.

[14] S. Wei, Y. Wei, T. Chen, C. Liu, Y. Tang, Porous lithium ion sieves nanofibers: General synthesis strategy and highly selective recovery of lithium from brine water, Chemical Engineering Journal. 379 (2020) 122407. https://doi.org/10.1016/j.cej.2019.122407.

[15] X. Li, Y. Mo, W. Qing, S. Shao, C.Y. Tang, J. Li, Membrane-based technologies for lithium recovery from water lithium resources: A review, Journal of Membrane Science. 591 (2019) 117317. https://doi.org/10.1016/j.memsci.2019.117317.

[16] A. Somrani, A.H. Hamzaoui, M. Pontie, Study on lithium separation from salt lake brines by nanofiltration (NF) and low pressure reverse osmosis (LPRO), Desalination. 317 (2013) 184–192. https://doi.org/10.1016/j.desal.2013.03.009.

[17] A.D. Sharma, N.D. Patil, A.W. Patwardhan, R.K. Moorthy, P.K. Ghosh, Synergistic interplay between D2EHPA and TBP towards the extraction of lithium using hollow fiber supported liquid membrane, Separation Science and Technology. 51 (2016) 2242–2254. https://doi.org/10.1080/01496395.2016.1202280.

[18] V.S. Kislik, ed., Liquid membranes: principles and applications in chemical separations and wastewater treatment, 1. ed, Elsevier, Amsterdam, 2010.

[19] P. Ma, X.D. Chen, M.M. Hossain, Lithium Extraction from a Multicomponent Mixture Using Supported Liquid Membranes, Separation Science and Technology. 35 (2000) 2513–2533. https://doi.org/10.1081/SS-100102353.

[20] R.E.C. Torrejos, G.M. Nisola, M.J. Park, A.B. Beltran, J.G. Seo, S.-P. Lee, W.-J. Chung, Liquid–liquid extraction of Li^+ using mixed ion carrier system at room temperature ionic liquid, Desalination and Water Treatment. 53 (2015) 2774–2781. https://doi.org/10.1080/19443994.2014.931534.

[21] L. Zhang, L. Li, D. Shi, X. Peng, F. Song, F. Nie, W. Han, Recovery of lithium from alkaline brine by solvent extraction with β-diketone, Hydrometallurgy. 175 (2018) 35–42. https://doi.org/10.1016/j.hydromet.2017.10.029.

[22] L. Zhang, D. Shi, L. Li, X. Peng, F. Song, H. Rui, Solvent extraction of lithium from ammoniacal solution using thenoyltrifluoroacetone and neutral ligands, Journal of Molecular Liquids. 274 (2019) 746–751. https://doi.org/10.1016/j.molliq.2018.11.041.

[23] T.V. Healy, Synergism in the solvent extraction of alkali metal ions by thenoyl trifluoracetone, Journal of Inorganic and Nuclear Chemistry. 30 (1968) 1025–1036. https://doi.org/10.1016/0022-1902(68)80322-7.

[24] R.E.C. Torrejos, G.M. Nisola, M.J. Park, A.B. Beltran, J.G. Seo, S.-P. Lee, W.-J. Chung, Liquid–liquid extraction of Li^+ using mixed ion carrier system at room temperature ionic liquid, Desalination and Water Treatment. 53 (2015) 2774–2781. https://doi.org/10.1080/19443994.2014.931534.

[25] T. Hano, M. Matsumoto, T. Ohtake, N. Egashir, F. Hori, RECOVERY OF LITHIUM FROM GEOTHERMAL WATER BY SOLVENT EXTRACTION TECHNIQUE, Solvent Extraction and Ion Exchange. 10 (1992) 195–206. https://doi.org/10.1080/07366299208918100.

[26] Y. Pranolo, Z. Zhu, C.Y. Cheng, Separation of lithium from sodium in chloride solutions using SSX systems with LIX 54 and Cyanex 923, Hydrometallurgy. 154 (2015) 33–39. https://doi.org/10.1016/j.hydromet.2015.01.009.

[27] E.E. Çelebi, M.S. Öncel, M. Kobya, M. Bayramoğlu, Extraction of lithium from wastewaters using a synergistic solvent extraction system consisting of Mextral EOL and Cyanex 923, Hydrometallurgy. 185 (2019) 46–54. https://doi.org/10.1016/j.hydromet.2019.01.016.

[28] Kim, Young-Sang, In, Gyo, Choi, Jong-Moon, Chemical Equilibrium and Synergism for Solvent Extraction of Trace Lithium with Thenoyltrifluoroacetone in the Presence of Trioctylphosphine Oxide, Bulletin of the Korean Chemical Society. 24 (2003) 1495–1500. https://doi.org/10.5012/BKCS.2003.24.10.1495.

[29] L. Zhang, D. Shi, L. Li, X. Peng, F. Song, H. Rui, Solvent extraction of lithium from ammoniacal solution using thenoyltrifluoroacetone and neutral ligands, Journal of Molecular Liquids. 274 (2019) 746–751. https://doi.org/10.1016/j.molliq.2018.11.041.

[30] S. Ansari, P. Mohapatra, D. Prabhu, V. Manchanda, Transport of Americium(III) through a supported liquid membrane containing N,N,N′,N′-tetraoctyl-3-oxapentane diamide (TODGA) in n-dodecane as the carrier, Journal of Membrane Science. 282 (2006) 133–141. https://doi.org/10.1016/j.memsci.2006.05.013.

[31] S.A. Ansari, P.K. Mohapatra, D.R. Prabhu, V.K. Manchanda, Evaluation of N,N,N',N'-tetraoctyl-3-oxapentane-diamide (TODGA) as a mobile carrier in remediation of nuclear waste using supported liquid membrane, Journal of Membrane Science. 298 (2007) 169–174. https://doi.org/10.1016/j.memsci.2007.04.015.

[32] G. Zante, M. Boltoeva, A. Masmoudi, R. Barillon, D. Trébouet, Lithium extraction from complex aqueous solutions using supported ionic liquid membranes, Journal of Membrane Science. 580 (2019) 62–76. https://doi.org/10.1016/j.memsci.2019.03.013.

[33] P.R. Danesi, Separation of Metal Species by Supported Liquid Membranes, Separation Science and Technology. 19 (1984) 857–894. https://doi.org/10.1080/01496398408068598.

[34] J. Theisen, C. Penisson, J. Rey, T. Zemb, J. Duhamet, J.-C.P. Gabriel, Effects of porous media on extraction kinetics: Is the membrane really a limiting factor?, Journal of Membrane Science. 586 (2019) 318–325. https://doi.org/10.1016/j.memsci.2019.05.056.

[35] F.G. Seeley, W.H. Baldwin, Extraction of lithium from neutral salt solutions with fluorinated β-diketones, Journal of Inorganic and Nuclear Chemistry. 38 (1976) 1049–1052. https://doi.org/10.1016/0022-1902(76)80027-9.

[36] F.G. Seeley, W.J. McDowell, L.K. Felker, Extraction of several metals from chloride salt solutions with heptafluorodimethyloctanedione, J. Chem. Eng. Data. 31 (1986) 136–143. https://doi.org/10.1021/je00044a002.

[37] L. Zhang, L. Li, D. Shi, X. Peng, F. Song, F. Nie, W. Han, Recovery of lithium from alkaline brine by solvent extraction with β-diketone, Hydrometallurgy. 175 (2018) 35–42. https://doi.org/10.1016/j.hydromet.2017.10.029.

[38] M.F. Rabuni, N.M. Nik Sulaiman, M.K. Aroua, N.A. Hashim, Effects of Alkaline Environments at Mild Conditions on the Stability of PVDF Membrane: An Experimental Study, Ind. Eng. Chem. Res. 52 (2013) 15874–15882. https://doi.org/10.1021/ie402684b.

[39] C. Cai, F. Yang, Z. Zhao, Q. Liao, R. Bai, W. Guo, P. Chen, Y. Zhang, H. Zhang, Promising transport and high-selective separation of Li(I) from Na(I) and K(I) by a functional polymer inclusion membrane (PIM) system, Journal of Membrane Science. 579 (2019) 1–10. https://doi.org/10.1016/j.memsci.2019.02.046.

[40] X. Yang, Q. Zhang, Z. Wang, S. Li, Q. Xie, Z. Huang, S. Wang, Synergistic extraction of gold(I) from aurocyanide solution with the mixture of primary amine N1923 and bis(2-ethylhexyl) sulfoxide in supported liquid membrane, Journal of Membrane Science. 540 (2017) 174–182. https://doi.org/10.1016/j.memsci.2017.06.043.

[41] F.J. Alguacil, A.G. Coedo, M.T. Dorado, Transport of chromium (VI) through a Cyanex 923–xylene flat-sheet supported liquid membrane, Hydrometallurgy. 57 (2000) 51–56. https://doi.org/10.1016/S0304-386X(00)00103-1.

[42] C. Sorel, MODELISATION DE L'EXTRACTION DU NITRATE DE CESIUM PAR UN CALIXARENE Application à la modélisation du transport à travers des membranes liquides supportées, 1996.

[43] P.R. Danesi, L. Reichley-Yinger, P.G. Rickert, Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long-term stability of the membranes, Journal of Membrane Science. 31 (1987) 117–145. https://doi.org/10.1016/S0376-7388(00)82223-1.

[44] A.M. Neplenbroek, D. Bargeman, C.A. Smolders, Mechanism of supported liquid membrane degradation: emulsion formation, Journal of Membrane Science. 67 (1992) 133–148. https://doi.org/10.1016/0376-7388(92)80021-B.

[45] E. Jean, D. Villemin, L. Lebrun, New ionic liquids with fluorous anions for supported liquid membranes and characterization, Journal of Fluorine Chemistry. 227 (2019) 109365. https://doi.org/10.1016/j.jfluchem.2019.109365.