

Membrane-based technologies for lithium recovery from water lithium resources: A review

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Abstract

Lithium production has become increasingly critical for sustainable development. The extraction of lithium from aqueous sources, particularly salt-lake brine, has become a trend in the lithium recovery industry because of its low cost and abundant reserves. Among various technologies applied for lithium recovery, membrane processes driven by pressure, electrical field, and thermal gradient have received considerable attention in the past few decades because of their high energy efficiency and low environmental impact. This paper presents a comprehensive review of the advantages and challenges of the current membrane-based technologies applied to the recovery of a water lithium resource. Here, we highlight that the combination of membrane processes (e.g. nanofiltration, selective electrodialysis, and membrane distillation crystallization) with a conventional lithium precipitation process will lead to higher performance efficiency and lower cost. Although the membrane-based separation technology is technically feasible, it is restricted by its high capital and operating costs. Therefore, the future development of membrane-based technologies should include efforts for the improvement of the separation efficiency, material stability, and some engineering aspects such as membrane fouling control, module design, and process optimisation.

Keywords: Lithium recovery; Water lithium resources; Membrane-based technology; Hybrid membrane process; Techno-economic evaluation

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List of abbreviations

CDI	Capacitive deionization
ED	Electrodialysis
IIM	Ion imprinted membrane
IIP	Ion imprinted polymer
LISM	Lithium ion-sieve membrane
MCDI	Membrane capacitive deionization
MD	Membrane distillation
MDC	Membrane distillation crystallization
NF	Nanofiltration
PSMCDI	Permselective exchange membrane capacitive deionization
RO	Reverse osmosis
S-ED	Selective electrodialysis
SLM	Supported liquid membrane

1. Introduction

Lithium is the lightest alkali metal with a density of 0.534 g/cm^3 [1–2]. Notably, lithium is electrochemically active with a high electrode potential of -3.05 V and has the highest specific heat capacity of any solid element [1–2]. These properties make lithium compounds highly attractive in many commercial applications. Fig. 1a presents the global distribution of lithium end-uses in various applications in 2016. The application areas of lithium compounds include well-known battery technologies, ceramics and glass, lubricating greases, and polymer production. During the period of 2010 to 2017, global lithium consumption increased by approximately 6% annually and is projected to reach approximately 95,000 tons in 2025.

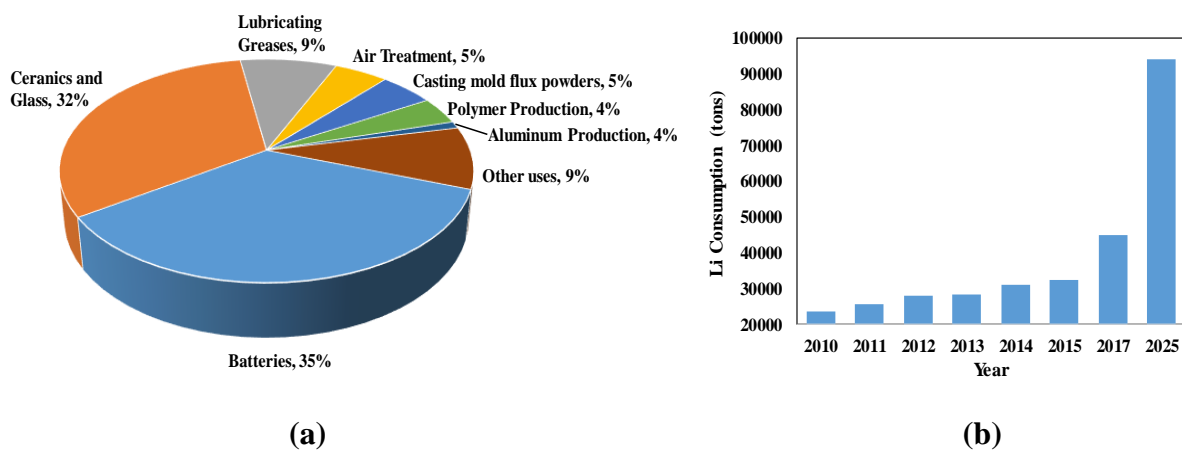


Fig. 1. (a) Distribution of global lithium end-uses in various applications in the year of 2016, and (b) global lithium production in the years from 2010 to 2025. Part (a) and Part (b) of the figure were obtained from references [3–4], respectively, with copyright permissions from Elsevier.

Lithium resources are divided into two main categories: solids (e.g. minerals ores, recycled waste lithium-ion batteries, and electronic waste), and liquids (e.g. salt-lake brine, geothermal brine, and seawater) [5]. For the current commercial lithium production, the continental brine

is the biggest resource (59%), followed by hard rock (25%), hectorite (7%), and geothermal brines (3%) [3]. Therefore, obtaining lithium from aqueous resources has been a trend in industrial lithium extraction because of its lower cost and more available reserves (more than 85% of recoverable lithium). Seawater is the richest resources of lithium (2.3×10^{11} t), but it is still not of technological interest because of its low lithium concentration of 0.1–0.2 ppm [6]. The concentration of lithium ions in geothermal brine is considerably higher (10 and 20 ppm) [7]. However, geothermal brine contains high concentrations of other metals, such as arsenic, mercury, and boron, because of the underground contact between the hot water and the rocks [8]. Alternatively, salt-lake brine resources contain a high concentration of lithium ions, ranging from hundreds of parts per million to thousands of parts per million. The key difficulty of lithium extraction from salt-lake brine is the excessively high concentration of the interfering ions, particularly magnesium. In general, the ratio of Mg^{2+}/Li^+ is larger than 40, and larger than 200 in some extreme cases [9]. On the basis of the above mentioned chemical compositions of the major the major water lithium resources, the recovery of lithium from an aqueous environment is still a considerable challenge. The low Li^+ concentration in solution but the high concentration of the interfering ions (e.g. Mg^{2+} , Ca^{2+} , Na^+ , and K^+) is a significant obstacle for a high-efficiency and environment-friendly extraction of lithium [10].

Traditional methods to extract lithium from water resources include solar evaporation, chemical precipitation, and solvent extraction [11–13]. As a commonly used technology, the solar evaporation process consists of several stages to precipitate and crystallise Li_2CO_3 [11]. Unfortunately, this process is extremely time-consuming. In addition, the Li_2CO_3 product is mixed with other undesirable salts, e.g. $NaCl$, $Mg(OH)_2$, and $MgCO_3$, and needs further purification. The chemical precipitation process induces the precipitation of lithium as lithium aluminate or carbonate through the addition of aluminium chloride or soda ash, respectively [12]. This method, however, is not suitable for brines with a large ratio of

interfering salts such as high Mg^{2+}/Li^+ salt-lake brines. Furthermore, this method uses a large number of chemicals and generates large quantities of sludge. The solvent extraction method can selectively extract lithium in the presence of other metal ions by using a specific chelating agent such as trioctylphosphine oxide and tributyl phosphate [13]. However, this method is only applicable to low Mg^{2+}/Li^+ brines. More seriously, the high-volume usage of organic solvents as the extractants not only corrodes the process equipment but also pollutes the environment. Therefore, the development of sustainable technologies for lithium extraction from water resources is crucial.

Membrane-based separation technology is considered a promising and environmentally friendly alternative for the recovery of lithium, owing to its advantages of high energy efficiency and easy operation in a continuous process [14–16]. A nanofiltration membrane can extract monovalent ions without any chemicals with the mechanisms of Donnan exclusion, dielectric exclusion, and steric hindrance. Membrane distillation crystallization can simultaneously produce fresh water and recover minerals from high-concentration brine by using low-grade heat. The supported liquid membrane, ion-imprinted membrane, and ion-sieve membrane immobilise highly selective adsorbents towards Li^+ such as ionic liquids, ion-imprinted polymers, and ion sieves onto the membrane carriers, respectively. Compared with the conventional solvent extraction methods, these adsorption membrane-based processes can increase adsorption capacity, decrease energy consumption, and facilitate continuous operation (easy regeneration). Further, electricity-driven membrane-based technologies involving selective electrodialysis and the capacitive deionization of permselective exchange membranes use monovalent selective ion-exchange membranes as the separation media to efficiently separate the monovalent cations/anions under the electric field.

Thus far, almost no comprehensive reviews concerning membrane-based separation

technologies for lithium recovery, particularly the challenges and potential opportunities posed by membrane-based separation processes. Therefore, in this paper, we critically review the current and the emerging membrane-based technologies for the implementation of lithium recovery with a focus on the features of the membrane material and on the engineering process. Simultaneously, the techno-economics of membrane-based technologies in comparison with other conventional technologies are analysed. The challenges of the membrane separation technologies and the potential improvement opportunities are also discussed.

2. Membrane-based separation technologies for lithium recovery

The most important characteristics of the membrane separation technologies to recover a lithium resource from an aqueous environment are summarised in Table 1. The different separation mechanisms of these membrane technologies lead to different application areas and technical features. The application and the contribution of these membrane separation technologies will be described in further detail below.

Table 1. State-of-the-art membrane-based technologies for lithium recovery from aqueous environment

Method	Mechanism	Water resource	Technological maturity	Efficiency of lithium extraction	Advantage	Limitation	Refs.
Nanofiltration membrane	Steric hindrance and Donnan exclusion	Seawater/salt-lake brine geothermal brine	Full scale	Separation factor of Li^+ over Mg^{2+} is 2.6–10.4, and is 1815 with MOF-based membrane	Low footprint	Membrane fouling High investment and operating costs	[17–29]
Supported liquid membrane	Selective transport of ions by solvent impregnated into membrane	Seawater/geothermal brine	Laboratory stage	Recovery > 95%	Large adsorption capacity, high selectivity, and low footprint	Leakage of organic solvent and necessity to use chemical reagent for desorption	[32–36, 39]; [41–42]
Ion-imprinted membrane	Selective adsorption of ions by chelating	Seawater/geothermal brine	Laboratory stage	Separation factor of Li^+ over Na^+ , K^+ , Ca^{2+} , and Mg^{2+} is 4–51 Adsorption amount is 4–50 mg g^{-1}	High selectivity	Low adsorption capacity and necessity to use chemical reagent for desorption	[49–53]
Ion-sieve membrane	Selective adsorption of ions by intercalation	Seawater/geothermal brine	Laboratory stage	Separation factor of Li^+ over Na^+ , K^+ , Ca^{2+} , and Mg^{2+} is 99–5312 Adsorption amount is 10.3–27.8 mg g^{-1}	Large adsorption capacity, high selectivity, and chemical stability	Leakage of inorganic particles and necessity to use chemical reagent for desorption	[57–65]
Membrane	Vapour pressure	Seawater/salt-lake	Pilot scale	Recovery > 73%	Simultaneously	Membrane wetting	[67–73]

distillation crystallization	gradient generated across hydrophobic membrane	brine/geothermal brine			produce fresh water and salts Utilisation of different energy sources	resulting from fouling and salt separation are critical issues	
Selective Electrodialysis	Electrical potential difference as a driving force for moving ions	Seawater/salt-lake brine/geothermal brine	Pilot scale	Recovery > 95%	High selectivity of monovalent ions, and eco-friendly	Membrane fouling Energy cost increases with increasing salinity	[76–85]; [87–91]
Permselective exchange membrane capacitive deionization	Electrostatic adsorption	Seawater/salt-lake brine/geothermal brine	Laboratory stage	Recovery > 83%	High efficiency and eco-friendly	Low desorption efficiency	[96–97]; [100–109]

2.1. Nanofiltration membrane

Nanofiltration (NF) has been applied for lithium extraction from brine on the basis of both Donnan exclusion and steric hindrance, which make it capable of rejecting multivalent ions but allowing monovalent ions to pass [17]. In general, the typical mass ratio of Mg^{2+} and Li^+ is larger than 20 in the lithium-rich brine [11]. The selective separation of Li^+ becomes more challenging with an increasing in the Mg^{2+}/Li^+ ratio. Wen *et al.* [18] first investigated the applicability of NF for the recovery of LiCl from diluted brine by using a Desal-5 DL membrane. The separation factor of Li^+ over Mg^{2+} ($S_{Li,Mg}$) could reach 3.5. Another commercial membrane Desal DK with a negatively charged surface was chosen to separate lithium from synthetic brine with a mass ratio of Mg^{2+} and Li^+ of 24 [19]. $S_{Li,Mg}$ was 2.6 at the operating pressure of 1.0 MPa. A similar $S_{Li,Mg}$ of 3.3 was obtained in the study of Sun *et al.* by using the Desal DL-2540 membrane module for treating a synthetic brine with the mass ratio of Mg^{2+} and Li^+ of 64 [20]. Other commercial DK-1812 and NF90 membranes also exhibited almost 85% separation between Mg^{2+}/Li^+ for the diluted salt-lake brine [21–22].

To further enhance the filtration stability, Li *et al.* [23] evaluated the effects of salinity and pH on the separation of Mg^{2+}/Li^+ . The flux decreased significantly with an increase in the feed salinity because of the high viscosity and the severe concentration polarisation. Although pH had little effect on the flux, it was better to separate Li^+ and Mg^{2+} under low pH conditions because of the enhanced dielectric exclusion to multivalent ions. The solution pH was crucial in a two-stage NF process [24]. At a lower pH value of 3.5, the Mg^{2+}/Li^+ ratio decreased from the initial value of 13.25 to 0.17 after separation by the two-stage NF process.

In contrast to negatively charged membranes, positively charged NF membranes present a more efficient separation of multi-valent cations such as Ca^{2+} and Mg^{2+} because of the Donnan exclusion [25]. This property is particularly crucial for the separation between

$\text{Mg}^{2+}/\text{Li}^+$. Unfortunately, most commercially available NF membranes with polyamide skin layers are negatively charged. Therefore, the fabrication and the application of positively charged NF membranes are highly attractive for lithium recovery. For example, Zhang *et al.* [26] fabricated a positively charged three-channel capillary NF membrane via interfacial polymerisation (IP) with polyethyleneimine (PEI) and trimesoyl chloride (TMC). A better separation factor $S_{\text{Li,Mg}}$ of 10.4 was presented for treating diluted brine with the mass ratio of Mg^{2+} and Li^+ of 14, as compared to $S_{\text{Li,Mg}}$ of around 3 for a negatively charged membrane prepared under similar conditions. Similarly, a positively charged hollow fiber NF membrane was fabricated by Li *et al.* via interfacial polymerisation (IP) with 1,4-Bis(3-aminopropyl) piperazine and trimesoyl chloride (TMC) [25]. Another positively charged NF membrane was modified by EDTA, which has the capability to form a complex with divalent cations such as Mg^{2+} . Therefore, the EDTA-functionalized NF membrane exhibited a separation factor $S_{\text{Li,Mg}}$ of 9.2 [27]. Another approach to fabricate a high-selectivity NF membrane was developed by Cuo *et al.* [28]. A novel polymer-functionalised metal organic frameworks (MOF)-based membrane was constructed to achieve extremely fast and selective Li^+ separation. The resultant membrane possessed an outstanding separation selectivity $S_{\text{Li,Mg}}$ of 1815, which was the highest separation factor reported; the flux of lithium ions could simultaneously be maintained at a relatively high value of $6.7 \text{ mol m}^{-2} \text{ h}^{-1}$. Wang *et al.* [29] developed another series of MOF membranes including ZIF-8 and UiO-66 to selectively separate lithium from a monovalent ion-rich solution such as sodium and potassium. Molecular dynamics simulations revealed that the Li^+ mobility was enhanced, whereas the K^+ and Na^+ mobility was reduced in ZIF-8. Consequently, a higher selectivity of Li^+ with K^+ and Na^+ was obtained.

Although NF is the only membrane technology for large-scale applications, membrane fouling is still a significant issue encountered in lithium recovery, leading to the decline in membrane permeability and selectivity. For instance, the NF permeability declined by 50%

and selectivity decreased after 6 h of filtration due to membrane fouling [22]. Meanwhile, a further understanding of the trade-off between membrane permeability and selectivity to lithium is crucial for membrane selection.

2.2. Supported liquid membrane

Conventional liquid–liquid extraction has been extensively used as an easy and effective strategy for the industrial production of chemicals and metals. However, it requires a very large volume of organic solvent, which becomes unacceptable from the environmental and safety perspectives [30], and the subsequent reuse of the waste solvent is also costly and energy-consuming.

Unlike classical solvent extraction, a supported liquid membrane (SLM) uses a membrane support that soaks in an organic phase to separate two aqueous phases, whereby a substance is transferred from one feed phase to a stripping aqueous phase (Fig. 2) [31]. For the separation of highly hydrophilic metal ions, the organic phase should contain an organic extracting molecule that selectively binds to a target metal ion and forms lipophilic metal-organic ligand species. Thus, the SLM technology can be used as an alternative approach for lithium recovery because of the attractive features of low energy consumption and solvent usage, high selectivity, and the integration of extraction and stripping into one stage. A good stable extraction solvent is indispensable to obtain an efficient and complete transport of the target metal. A combined solvent of LIX54 (*α*-acetyl-*m*-dodecylacetophenone) and TOPO (tri-octyl phosphine oxide) was used for the synergic complexation of Li⁺ ions in an SLM process [32]. The optimum extraction efficiency could reach $\geq 95\%$ with a model solution containing Na⁺, K⁺, and Li⁺. Importantly, a stable permeability of the system was displayed in the initial stage. Another extractant of di-2-ethyl hexyl phosphoric acid (D2EHPA) and tri-*n*-butyl phosphate (TBP) was used for the selective extraction of Li⁺ from

simulated seawater by using a hollow-fiber SLM module [33]. The separation factor of Li^+ was demonstrated to have decreased with an increase in the concentrations of the Na^+ and K^+ ions and the decrease in the pH values in the feed phase. Compared with the flat sheet membrane module, the hollow-fiber membrane module provided a higher surface area [34–35]. The hollow-fiber SLM, as a green technology, has the potential for designing a large module with a high packing density so as to achieve the demand for quantitative extraction.

However, the lack of stability of the SLMs limits their application at an industrial scale. This instability is results from the solubility of the organic phase in the adjacent aqueous phases or the pressure difference across the membrane. The use of ionic liquids (ILs) could overcome this limitation because of their unique properties, such as high viscosity or negligible vapour pressure [36]. SLMs based on ILs have demonstrated promising results for the selective solvent extraction of lithium in recent studies [37–39]. Shi *et al.* [37] suggested that TBP acting as the extractant in the imidazolium-based ionic liquids [C4mim][NTf2] could significantly enhance the extraction efficiency of lithium (92%) compared with that (7%) in the conventional organic solvent. The effects of a series of 1-alkyl-3-methylimidazolium-based ILs on the extraction efficiency of lithium from salt-lake brine with a high $\text{Mg}^{2+}/\text{Li}^+$ ratio were investigated by Gao *et al.* [38]. The 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquid showed the highest extraction efficiency of 86.3%. Zante *et al.* [39] further confirmed that the combination of TBP and an imidazolium ionic liquid not only improved the membrane stability but also achieved the lithium extraction efficiency of up to 80% from complex acidic solutions. The design of suitable ionic liquids will open up new potential industrial applications of the supported liquid membranes in the field of lithium recovery.

Unfortunately, the efficiency of lithium extraction significantly decreased after a period of operation because of the solvent leakage and the membrane swelling [33, 40]. To improve the

filtration stability and reduce the solvent-induced swelling, Song *et al.* [41] prepared a blend membrane consisting of a sulfonated polyether ether ketone (SPEEK) blend with hydrophobic polyethersulfone (PES) by using a kerosene/TBP extractant. Although the membrane's mechanical strength and permeate flux remained nearly unchanged after a long-term test in the solvent of kerosene, the SPEEK/PES blend membrane was unstable in some other organic solvents, such as benzene and toluene. Another solvent-resistant commercially available block copolymer poly(ethylene-co-vinylalcohol) (EVAL) was used for the fabrication of a nanoporous membrane [42]. This block-copolymer consisted of hydrophobic solvent-resistant blocks, ethylene, hydrophilic ion-permeable blocks, and vinyl alcohol. The resultant membrane was resistant to a wider range of solvents including benzene, toluene, acetone, sulfonated kerosene, 1-propanol, TBP, DMF, and THF. A stable performance of the EVAL barrier membrane was achieved for > 1000 h [43].

Although extensive research has been carried out to strengthen the long-term stability, the solvent resistance and solvent leakage remain considerable challenges. In addition, the acid/base resistance, process design and cost should be considered to assess the potential of the SLM technology for large-scale applications in practice.

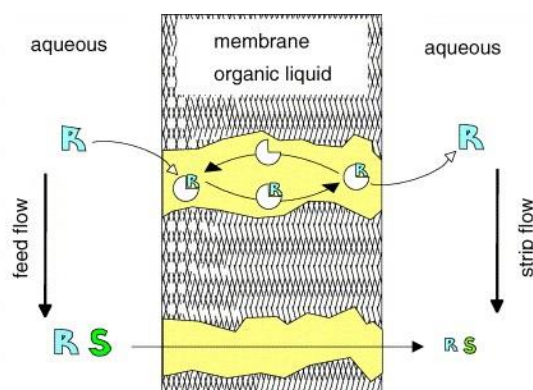


Fig. 2. Schematic diagram of separation principle of a supported liquid membrane. Figure obtained from reference [31] with copyright permission from Elsevier.

2.3. Ion-imprinted membrane

An ion-imprinted membrane (IIM) is commonly fabricated by grafting an ion-imprinted polymer (IIP) at the membrane surface. To synthesise the IIP, a cross-linking reaction can be performed between the template molecules and the functional monomers. The subsequent removal of the template molecules forms the binding sites with molecular recognition properties [44–45]. IIP thus has a high affinity for template molecules as compared to other structurally related molecules. IIM combines the advantages of a porous membrane material and IIP, which providing the membranes with the benefits of specific selectivity toward the host ions, easy regeneration, and low energy consumption [46]. IIM has provided extensive applications in the recovery of resources such as alkali metals, heavy metals, and rare earth metals [47–48]. For instance, Xu *et al.* [47] successfully synthesised Cd(II) IIPs for the selective extraction and quantitative determination of Cd(II) ions in the environmental samples. Similarly, the As(III) ion-imprinted polymer prepared by Liu *et al.* [48] was used as a sorbent in a solid-phase extraction column for the high efficiency of As(III) removal in the treatment of waste effluents.

In recent studies, the Li⁺-templated IIM technology has attracted considerable attention for capturing lithium. The functional monomers generally include crown ether and calixarenes [49–50]. These functional monomers can form stable metal chelate complexes with lithium ions because of an electron-rich cavity. In addition, the crown ring of crown ether and the cup-like structure of calixarene have a similar size with lithium ions. Calix[4]arenes-functionalised imprinted mesoporous membranes were fabricated by Wang *et al.* [49]. The high selectivity of Li⁺ towards Na⁺, Mg²⁺, K⁺, Ca²⁺, and Cs⁺ was 72, 193, 93, 146, and 117, respectively, exhibiting high efficiency in Li⁺ extraction. In addition, 12-crown-4 and its analogues (for instance, benzo-12-crown-4 and 2-methylol-12-crown-4) were attached to the polymer matrix for the recovery of lithium (Fig. 3). For instance, a crown ether (CE)-based Li⁺ adsorbent microfibrillar membrane was fabricated by using the

cross-linking reaction of crown ether with polyvinyl alcohol matrix via acetalisation with glutaraldehyde [50]. The as-prepared CE-based macroporous fibrous membrane demonstrated an adsorption capacity of 22.2 mg g⁻¹. Meanwhile, the selectivity separation factors of Li⁺ towards Na⁺, Mg²⁺, Ca²⁺, and K⁺ were 1134, 815, 1078, and 156, respectively. Another novel macroporous Li⁺-imprinted membrane was fabricated by Sun *et al.* [51] by using PVDF as the polymer matrix and 2-(allyloxy) methyl-12-crown-4 as the adsorbing units. The maximum adsorption amount and the maximum selective factor of Li⁺ over Mg²⁺ of the as-prepared IIM were 19.2 mg g⁻¹ and 4.4, respectively. The maximum adsorption amount only decreased by approximately 9% after six cycles of adsorption/desorption, presenting high regeneration stability. Another highly-selective multi-layered Li⁺-imprinted membrane was fabricated with polydopamine modification to achieve the high adsorption capacity of 50 mg g⁻¹ and excellent regeneration ability after repeatedly adsorbing/desorbing for five cycles [52]. Despite their impressive separation performances, IIMs face the challenge of high membrane costs. Another critical challenge of the IIM technology is membrane fouling, particularly biofouling, which not only limits the permeate flux but also destroys the regeneration of the IIM [53–55].

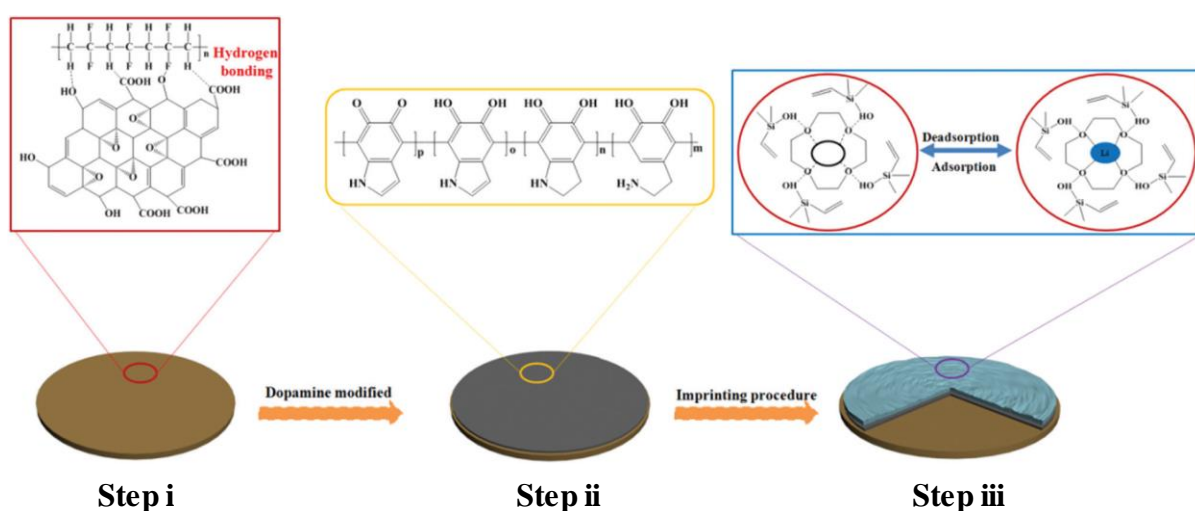


Fig. 3. Schematic diagram of the procedure for the preparation of IIMs for selective adsorption of Li⁺: (i) fabrication of the PVDF/GO hybrid membranes; (ii) PDA coating on

PVDF/GO substrate as the anchor for loading imprinted sites; (iii) immobilization of 12-Crown-4-ether on the membrane surface. Figure obtained from reference [53] with copyright permission from the Royal Society of Chemistry.

2.4. Ion-sieve membrane

The adsorption method is a promising technology for lithium recovery from seawater and salt-lake brine because of its easy operation and cost-effectiveness. In particular, inorganic lithium ion-sieves with high selectivity, high capacity, and high stability have attracted considerable attention. Among the inorganic adsorbents, $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ ($x = 0.3, 0.4, \text{etc.}$) with a spinel structure has been widely used for the adsorption of lithium. The formation of the Li^+ and OH^- bond was conducive to the lithium re-injection after extraction [56]. However, the use of powdery lithium ion-sieves in the column operation resulted in a severe pressure drop and a loss of adsorbents, which therefore limits their industrial application.

Recently, many efforts have been focused on the development of lithium ion-sieve membranes (LISMs). LISMs combine the advantages of both ion-sieves (i.e., high specific surface area and high selectivity) and ~~the~~ membranes (i.e., immobilised sorbents and low energy consumption), which enables continuous industrial operation. A series of membrane-type adsorbents were prepared by adding LISMs precursors into a mixture of a polymer (e.g., PVC or PVDF) and a solvent (e.g. N,N-dimethyl formamide (DMF)) [57–59]. The maximum adsorption capacity and separation factor $S_{\text{Li},\text{Mg}}$ of LISM were 27.8 mg g^{-1} and 4.7, respectively [59]. Another PSf/non-woven fabric composite membrane with $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ was developed by Chung *et al.* to recover Li^+ from seawater [60]. In a study by Zhu *et al.* [61], a series of LISMs incorporating the adsorbent of PVC– $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ were prepared using the solvent exchange method. The optimum separation factors of Li^+ over the co-existing ions (Na^+ and Mg^{2+}) ranged from 454 to 4555. Such high-selectivity factors were

largely ascribed to the larger free energy of hydration of these co-existing ions, which hinders the access of these ions to the adsorption sites.

Another effective way to fabricate mixed matrix membranes incorporating ion sieves is the use of nanofibers via electrospinning. Nanofibers have unique structural properties such as high specific surface area, high porosity, and favourable morphology. A poly-(acrylonitrile) (PAN) nanofiber blended with an $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ lithium ion-sieve was fabricated by electrospinning [62]. The as-prepared nanofibers exhibited a lithium adsorption capacity of 10.3 mg g^{-1} , high lithium separation factors of 99–5312, and minimal adsorption loss ($< 4\%$) after ten cycles. Similar electrospun mixed matrix nanofibers dispersed with particulate lithium ion-sieves of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ were prepared to achieve superior adsorption capacity and selectivity towards Li^+ (Fig. 4) [63–64].

In addition to the pressurised flow system and flow-through systems, a lithium ion-sieve composite electro dialysis membrane prepared by magnesium-doped lithium manganese oxide is another interesting lithium recovery technique [65]. The as-prepared membrane not only avoided acid generation in the electro dialysis separation process but also showed high Li^+ removal efficiency with a removal rate of 1.44 mmol/h .

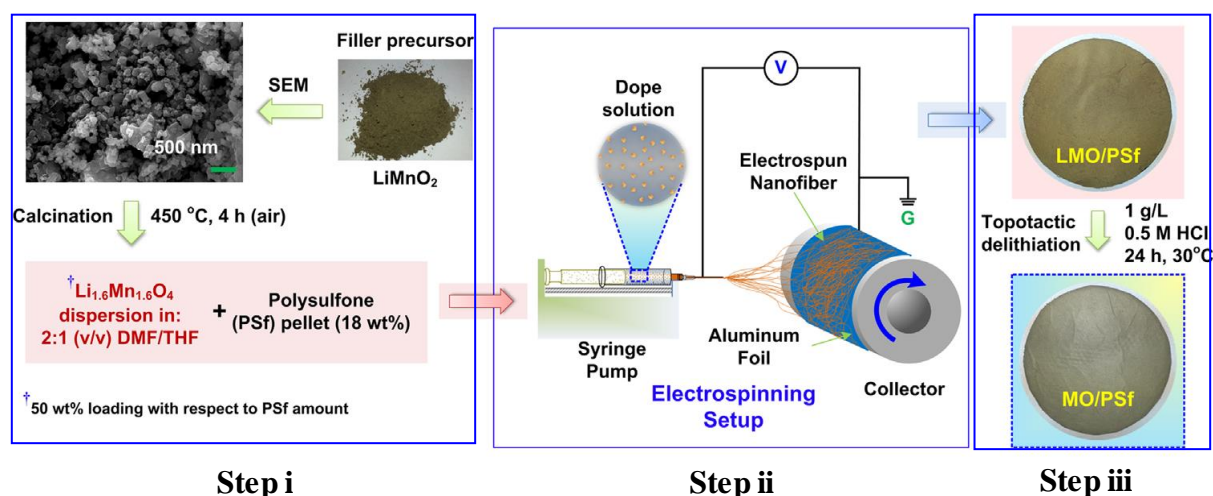


Fig. 4. Schematic illustration of the PSf based mixed matrix nanofibers membrane with

lithium ion sieves: (i) preparation of lithium ion sieves particles; (ii) preparation of mixed LMO/PSf electrospun nanofibers; (iii) activation of mixed LMO/PSf membrane. Figure obtained from reference [63] with copyright permission from Elsevier.

Although LISM provides large adsorption capacity, high selectivity, and chemical stability, a similar problem with LISM regarding the leakage of the extractant should be solved. Meanwhile, future research on the design of the LISM filtration system from engineering aspects is highly encouraged for large-scale industrial application.

2.5. Membrane distillation crystallization

Membrane distillation crystallization (MDC), which couples membrane distillation (MD) to a crystallization process (Fig. 5), has been used to recover minerals from high-concentration brine. Compared with the traditional crystallization process, MDC displays rapid rates of crystallization and well-controlled nucleation kinetics [66]. MDC can be potentially applied for lithium extraction from brine. In the MDC system, the volatile components (e.g. water) can transport through the hydrophobic membrane under a thermal gradient across the membrane, and condense on the permeate site. In this way, the lithium concentrated in the brine can be subsequently recovered in the crystalliser through induced crystallization.

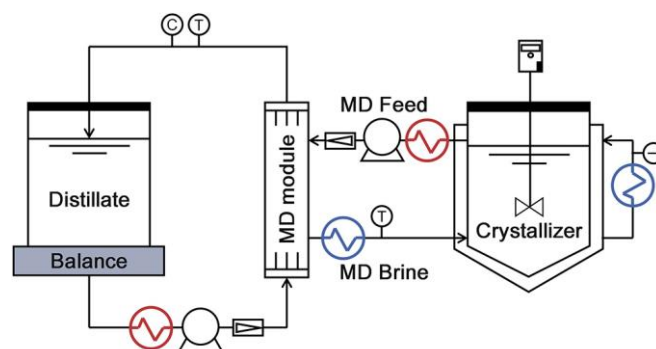


Fig. 5. Schematic diagram of the MDC system. Figure obtained from reference [67] with copyright permission from Elsevier.

MDC has been used to treat the RO concentrate with an overall recovery of $\geq 90\%$ [68]. Indeed, this innovative membrane desalination process displays the potential to achieve zero liquid discharge while recovering salts such as magnesium and lithium in high quantities and qualities. Quist-Jensen *et al.* [69] investigated the effect of the configurations of membrane distillation on the recovery of salt crystals from a single-salt LiCl solution. It was found that direct-contact membrane distillation and osmotic membrane distillation cannot effectively extract lithium because of the high osmotic pressure caused by the high solubility of LiCl (14 M). However, vacuum membrane distillation, in which vacuum is applied at the permeate side, can eliminate the osmotic phenomenon and achieve lithium recovery. A study revealed that the recovery was up to 73.8% from the RO brine when using MDC [70]. Another advantage of MDC is the low operating cost because of the use of low-grade heat such as waste heat [71–73]. According to Macedonio's study, the water cost of MD decreased from USD 1.17 to USD 0.64 per cubic metre with low-grade heat, which was comparable to that of RO (USD 0.5 per cubic metre) [73].

The application of MDC for lithium recovery is still immature for large-scale application. One of the key limitations is the requirement of an additional Li purification method because the concentrate consists of different minerals. Another major challenge is the high energy cost of MDC. To decrease the energy consumption and increase the separation efficiency, future research and development should be focused on the fabrication of super-hydrophobic membranes, optimisation of MD modules, and improvement of the mass and heat transfer.

2.6. Selective Electrodialysis

Electrodialysis (ED), an electro-membrane separation process, is widely used in the desalting of salty water, treatment of industrial effluents, and the production of organic acids [74]. In an ED process, the cation and anion exchange membranes are placed alternatively (Fig. 6a). An electrical field is applied, and thus, cations and anions migrate through the respective ion exchange membrane towards the corresponding electrode. However, conventional ion exchange membranes cannot separate ions with the same charge (such as $\text{Li}^+/\text{Mg}^{2+}$). The development of a monovalent ion exchange membrane, which separates monovalent ions from divalent ions, is extremely important for the application of ED to extract lithium from salt-lake brine or seawater. Selective electrodialysis (S-ED) was proposed as a new type of ED, in which standard ion-exchange membranes are replaced with monovalent selective ion-exchange membrane as the separation media [75]. The principle of the S-ED stack is that the monovalent cations (Li^+ , Na^+ , and K^+) migrate through the monovalent selective cation-exchange membranes, which causes an increase in the monovalent ion concentration in the concentrating compartment. At the same time, the divalent cations (Ca^{2+} and Mg^{2+}) are blocked by the monovalent selective cation-exchange membranes and retained in the desalting compartment. Subsequently, the concentrated mixed monovalent ion solution is subjected to the precipitation of lithium carbonate at $80\text{ }^\circ\text{C}$ – $90\text{ }^\circ\text{C}$ by using sodium carbonate. As a result, a high-purity and good-crystalline lithium carbonate can be produced [12].

Nie *et al.* [76] quantitatively investigated the feasibility of S-ED for extracting Li^+ from synthetically prepared brine with a $\text{Mg}^{2+}/\text{Li}^+$ mass ratio of 150. Surprisingly, a high Li^+ recovery of 95.3% was achieved, and the corresponding $\text{Mg}^{2+}/\text{Li}^+$ mass ratio was decreased to 8 after treatment with the S-ED process. S-ED exhibited technical superiority for the fractionation of $\text{Mg}^{2+}/\text{Li}^+$ with a high mass ratio in comparison to NF. To further verify and optimise the adaptability of S-ED, the effects of the operating conditions and the feed

characteristics on the separation performance were investigated [77]. The results showed that the constant-current mode exhibited superior selectivity, but its specific energy consumption was an order of magnitude higher than that for the constant-voltage mode. Therefore, the constant-voltage mode is more feasible for lithium recovery in S-ED. In addition, Li^+ recovery can be achieved effectively with different $\text{Mg}^{2+}/\text{Li}^+$ ratios, indicating wide adaptability of S-ED for lithium extraction from real salt-lake brine. The influences of the co-existing monovalent cations (K^+ and Na^+) and anions (SO_4^{2-} and HCO_3^-) on the lithium migration were investigated in a recent study by Yuan *et al.* [78–79]. They found that compared with Na^+ , K^+ presented a significant influence on the lithium migration because of the relatively low hydrated ionic radius. The co-existing anions mainly affect the migration of Mg^{2+} rather than Li^+ . This phenomenon is attributed to the fact that Mg^{2+} not only has a strong attraction with SO_4^{2-} but also forms MgHCO_3^+ with HCO_3^- . Recently, Ge *et al.* [80] used an NF membrane instead of a monovalent cation exchange membrane for the selective separation of Na^+ and Mg^{2+} . The selectivity of Na^+ to Mg^{2+} obtained from the NF membrane was almost two times higher than that obtained from the monovalent ion exchange membrane.

Unlike the traditional ED process discussed above, bipolar membrane electro dialysis (BMED), in which ED is combined with a bipolar membrane, is another typical approach for the extraction of lithium hydroxide (LiOH) from aqueous saline solutions [81–84]. During the BMED process, the bipolar membrane induced the dissociation of water into H^+ and OH^- ions under an electrical field, and then lithium was recovered as LiOH (Fig. 6b). The BMED process has been proven to be a practicable technology to produce LiOH with a high purity of 95% from the Li_2CO_3 solution [81–82]. Notably, the process conditions have a significant effect on lithium recovery [83]. The higher sample volume leads to the longer time required to achieve a steady state. The recovery efficiency of lithium could reach the maximum limit

at an optimum applied electrical potential, instead of continuously increasing at a higher applied electrical potential. This phenomenon is attributed to the fact that the density of lithium ion desorption did not enhance in direct proportion to the increasing current [84].

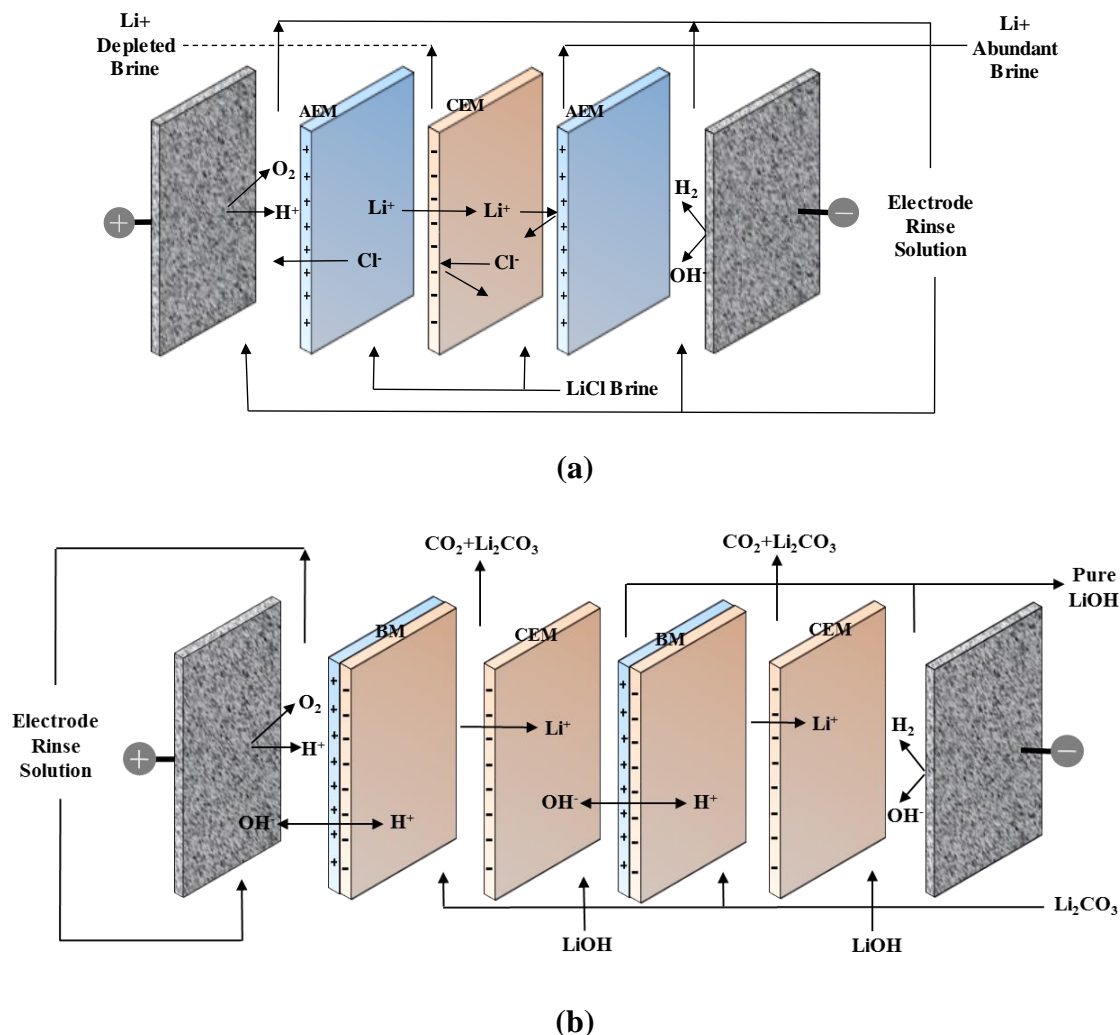


Fig. 6. Schematic illustration of (a) conventional ED stack and (b) BMED stack for recovering lithium. Figure obtained from reference [81] with copyright permission from ACS Publications.

Although the S-ED with monovalent selective ion-exchange membranes can effectively remove divalent ions, it still faces challenges for high-efficiency lithium recovery from mixtures containing different monovalent ions (Na^+ , K^+ , and Li^+) [85–86]. Ionic liquids (ILs) as a promising solution have attracted considerable interest in the field of solvent extraction

processes because of their high selectivity, high stability, and negligible volatility. In particular, some functionalised ILs with a metal-coordinating group have been successfully applied for the extraction of metal ions from an aqueous solution [87–89]. For this purpose, Hoshino [89] proposed a novel ED combined with an ionic liquid TMPA-TFSI, which prevented the passing of Li^+ from the anode to the cathode because of the low conductivity of Li^+ . Therefore, the concentrated Li^+ on the anode side was easily recovered. The separation factor of Li^+ over Na^+ and K^+ could be 2 and 3.5 after the application of a voltage of 2–3 V, respectively. Another ionic liquid PP13-TFSI with a high selectivity of Li^+ was used to prepare an ionic-liquid-impregnated organic electro dialysis membrane [90]. Then, a high Li^+ recovery ratio of 22.2% was achieved after 2 h of dialysis. To overcome the poor durability of the ionic membrane and increase the Li^+ selectivity, the Li ionic superconductor was used as a Li^+ separation membrane, which was only permeable only to Li^+ [91]. The Li^+ concentration difference across the lithium ion separation membrane led to a spontaneous transport of Li^+ ions (approximately 7% of the total lithium content) from the Li^+ -rich side to the Li^+ -receiver side without any electrical supply. Indeed, an electrical power of 0.04 V and 0.1 mA was simultaneously generated [91].

The S-ED based methods are valuable technologies, which are relatively economical and environment-friendly. Future research should focus on the design of an S-ED system and the development of ion exchange membranes with high selectivity and low resistance so as to realise a more effective lithium extraction from salt-lake brine.

2.7. Permselective exchange membrane capacitive deionization

In addition to the ED process, another emerging eco-friendly and efficient electrochemical method is capacitive deionization (CDI). In the CDI process, the anions and cations are selectively adsorbed on the electrodes from an aqueous electrolyte solution with the help of

an electric field [92–94]. The ions are desorbed by discharging or charging the electrical potential in a reverse manner to regenerate the electrodes (Fig. 7). To enhance the deionization efficiency of conventional CDI, membrane capacitive deionization (MCDI) was explored, in which the cation and anion exchange membranes were added between two porous oppositely charged electrodes [95–96]. The cations or anions could directionally migrate onto oppositely charged electrodes because of the ion selectivity of the ion-exchange membrane, which consequently prohibited the migration of interfering ions and thus increased the deionization efficiency [97]. To selectively separate specific ions from mixed ions, the permselective exchange membranes were used in the MCDI, and this process was named as permselective exchange membrane capacitive deionization (PSMCDI) [98]. The developed PSMCDI with a monovalent ion exchange membrane was confirmed to not only effectively remove monovalent ions but also have low energy consumption [99].

Herein, the PSMCDI process with a monovalent selective cation exchange membrane was used by Shi *et al.* for the recovery of lithium from magnesium-rich brine [100]. A typical PSMCDI setup is shown in Fig. 7. Li^+ ions migrated through the monovalent selective cation exchange membrane and were then temporarily adsorbed in the cathode in the developed PSMCDI process. However, Mg^{2+} ions were blocked by the monovalent selective cation exchange membrane and thus retained in the feed solutions. The lithium selectivity coefficient could reach above 2 for treating the synthetic brine with a $\text{Mg}^{2+}/\text{Li}^+$ ratio of 20. A similar PSMCDI system combined with a monovalent selective anion exchange membrane was extensively applied for the defluorination of high-fluoride water. The fluoride selectivity coefficient was 1.4 with a model-mixed NaF and Na_2SO_4 aqueous system [97]. In particular, Kim *et al.* [101] investigated two carbon electrodes that were directly coated with the cation-exchange polymers of cross-linked poly(vinyl alcohol) (PVA) with sulfur succinic acid (SSA) and poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA) and the anion-exchange

polymers of aminated polysulfone (APSf), respectively. The researchers found that the introduction of the ion-exchange polymer enhanced the removal efficiency of the monovalent salt of NaCl for treating a mixed feed solution of NaCl, MgCl₂, and CaSO₄. Recently, the implementation of NF membranes such as NF270 within the PSMCDI system for the selective separation of divalent and monovalent ions was studied by Nativ *et al.* [102]. It presented a very good separation of the monovalent and divalent anions of Cl⁻ and SO₄²⁻ because of the stronger repulsion between the divalent anions and the NF270 membrane with a negative surface charge. In addition to the above mentioned polymeric monovalent anion exchange membrane, a lithium superionic conductor (NASICON)-type solid-state electrolyte was used as the lithium-ion selective membrane placed next to the anode [103].

The replacement of a conventional porous carbon electrode with some lithium-capturing electrodes [104–109] may be beneficial for further increasing the efficiency of lithium recovery. For instance, the Na⁺/Li⁺ ratio decreased from the initial 100 in the sodium-rich brine to 5 in the obtained analyte using LiFePO₄ as a lithium-capturing cationic electrode [104]. This result was attributed to the fact that the FePO₄ lattice can preferentially accept lithium as compared to other cations [105]. The amount of lithium captured in LiFePO₄ can be as high as 46 mg Li⁺ per gram of solid, whereas the uptake of other ions such as Na⁺, K⁺, and Mg²⁺ is <3 mg per gram of solid [106]. LiMn₂O₄ is another effective electrode material for lithium recovery because of its high selectivity for lithium ions and fast lithium-ion deintercalation/intercalation [107–109].

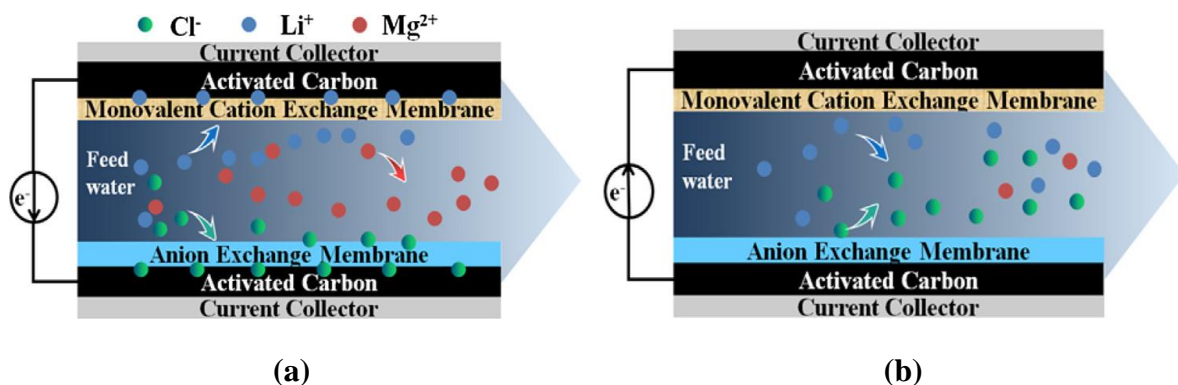


Fig. 7. Schematic illustration of PSMCDI lithium recovery system of (a) adsorption and (b) desorption processes. Figure obtained from reference [100] with copyright permission from Elsevier Publications.

In brief, this PSMCDI process presents an alternative practical and eco-friendly lithium recovery technology without the use of any toxic agents. Further studies should be focused on the optimisation of the electrical potential systematic process and the increase in the desorption efficiency by using real salt-lake or Li-spiked waters.

3. Economic evaluation

Lithium recovery from salt-lake brine is more attractive than that from sea water because the latter suffers from a low extraction amount and a high production cost. The production cost from seawater is estimated to be USD 80 kg⁻¹, which is considerably higher than that from salt-lake brine (USD 2–3 kg⁻¹) [10]. The cost of lithium extraction includes capital cost, operation cost, and maintenance cost. The capital cost mainly includes the costs related to equipment, construction of plants and land. Operational costs include the energy cost (e.g. electric power) and the costs of equipment replacement and maintenance, consumables, and labour. The costs and energy consumption of the various lithium recovery processes are summarised in Table 2.

Table 2. Cost and energy consumption of lithium recovery processes

Resources	Process	Energy consumption	Cost requirements	Refs.
Salt-Lake brine	NF, precipitation, evaporation	35–48 kWh kg ⁻¹ product	USD 5–7 kg ⁻¹ product	[110–111]
Synthetic brine	MDC	9 kWh kg ⁻¹ product	USD 2.18 kg ⁻¹ product	[69]
Synthetic brine	Precipitation, clarification, filtration, evaporation,	6–21 kWh kg ⁻¹ product	USD 3.86 kg ⁻¹ product	[81]

	electrolysis, S-ED			
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The enrichment of lithium from water resources by NF is generally followed by a sequential precipitation process for the purification and recovery of lithium carbonate. Although the NF technology is unable to recover the lithium resource directly and completely, lithium enrichment by an NF process could be an efficient and cost-effective alternative to evaporation from an industrial perspective [112]. NF as the only commercial available process is preferred because of not only its mature technology but also its high cost efficiency as compared to the other membrane-based processes with the limitations of higher cost and operation complexity. According to Yaksic *et al.* [110], the energy consumption and the cost of lithium carbonate production by NF from salt-lake brines and geothermal brines is approximately 35–48 kWh kg⁻¹ and USD 5–7 kg⁻¹, respectively. It is, therefore, an attractive technology because of the high market price of lithium carbonate products of approximately USD 24 kg⁻¹ [111]. Certainly, the control of membrane fouling is still a critical issue for the long-term stable operation of NF processes.

MDC is another attractive process that can concurrently produce desalted water and recover lithium resources. The water recovery could be increased to 90% by using MDC to treat the RO retentate; as a comparison, the single RO unit only produced a recovery of 50%. According to the economic evaluation conducted by Drioli *et al.* [113] in a laboratory study, the capital cost from the membrane was almost the same as that with the integrated NF/RO/MDC system or the conventional NF/RO system. An increase in the water recovery and production of salt could produce a higher profitability and reduce the environmental disruption caused by the brine disposal. While it is technically possible to extract lithium from seawater by using an NF/RO/MDC system, it is not economically viable (USD 5,000 kg⁻¹) resulting from the low lithium concentration in seawater (<1 ppm). An economic

evaluation of the LiCl production by MDC using a single LiCl aqueous solution was carried out by Quist-Jensen *et al.* [69]. This economical calculation was performed on the basis of the assumptions that the capacity of the system was $1 \text{ m}^3 \text{ h}^{-1}$ and a pre-filtration treatment system was used. The results showed that the unit LiCl cost was calculated to be USD 2.18 kg^{-1} ; meanwhile, the capital cost and the annual operating cost were USD 12,886 year^{-1} and USD 10,509 year^{-1} , respectively.

Compared with the pressure- and the thermal-driven membrane-based separation technologies, S-ED exhibited a higher lithium recovery rate (95%), a higher selectivity ($S_{\text{Li/Mg}}$ reached 20–30), and a lower energy consumption [18,76]. For instance, a preliminary economic evaluation of the S-ED with bipolar membranes for the production of LiOH was conducted by Xu *et al.* [80]. The energy consumption was estimated to be in the range of 6–21 kWh kg^{-1} . The energy consumption would decrease at an increased feed concentration and/or a reduced current density. At the optimum production of LiOH with a purity of 95%, the capital cost was USD 2.56 kg^{-1} and the energy cost was USD 1.3 kg^{-1} . Compared with the market price of LiOH (USD 14.6 kg^{-1}) in China, it has a huge commercial potential. Although the electrical energy is the main operational cost, the cost of the pre-treatments also need to be added to the operational cost. This is because the suspended solids need to be removed from the feed by using pre-treatments such as sand filtration or ultrafiltration. Another pre-treatment (e.g. acidification and anti-scalant addition) to avoid the scale formation on the membrane surfaces is also required. In addition, because of the high cost of the ion-exchange membranes, the S-ED equipment accounts for a majority of the total cost. A major problem encountered in the operation was the short lifetime of the membrane pairs [114]. The main cause of the short lifetime of the membranes was the high-voltage trials. High voltages result in a decline in the process efficiency because of electrolysis and chlorine production, which further damages the membranes. Therefore, the low-priced

chlorine-resistant ion-exchange membrane is favourable for the large-scale applications.

Another electrically driven technology PSMCDI still cannot be widely used in large-scale systems, mainly because of the economic challenges. On the one hand, the desorption efficiency is considerably lower (only 45%) than that of the conventional desorption process. On the other hand, the investment cost is higher than that of the conventional adsorption process because of the relatively expensive PSMCDI equipment. However, this method is still a promising and environmentally friendly technology without the use of an acidic solution for releasing lithium ions.

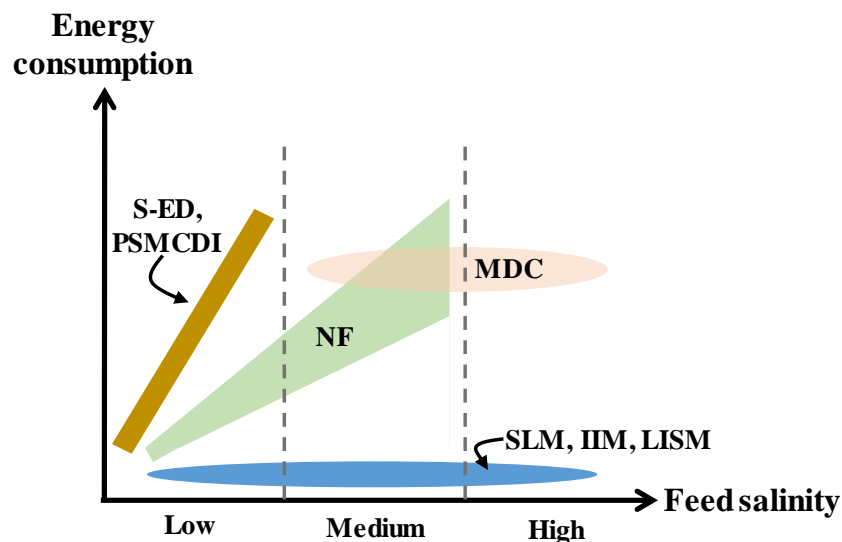


Fig. 8. Illustrations of the relationships between energy consumption and feed salinity in S-ED, PSMCDI, MDC, NF, SLM, IIM and LISM.

An overview of the energy consumption and the feed salinity in S-ED, PSMCDI, MDC, NF, SLM, IIM, and LISM is shown in Fig. 8. In general, the energy consumption of the adsorption/desorption membrane processes, including SLM, IIM, and LISM, was the lowest among the various membrane processes. Nevertheless, large-scale applications of these membrane processes are prohibited by their high cost. NF is more attractive for

low-to-medium feed salinity (less than 35,000 mg L⁻¹ TDS) because of its mature technology and moderate energy consumption. Nevertheless, NF is not economically viable in desalting high-salinity brine, because of the rapid increase in energy consumption with an increase in the feed salinity. A generally linear dependence of the energy consumption on the feed water salinity applies in electrically driven technologies (PSMCDI and S-ED), which are only suitable for low feed salinity. In contrast, the energy consumption of the thermal-driven technology of MDC is nearly independent of the feed salinity, which renders this technology more attractive in dealing with high feed salinity. Unfortunately, the desorption process leads to a serious capacity loss because of the oxidising agents or acids used as the desorption reagents. In addition, the selectivity of the adsorbents for lithium cannot reach 100%. This problem leads to the use of additional selective precipitated methods to specifically remove the competing mineral. More importantly, unlike the other membrane-based processes, these processes cannot produce desalted water and need to be combined with NF/RO, leading to a reduction of the revenue.

4. Outlook

NF as a mature technology has been facing major challenges, including its long-term stability and cost-saving operation in large-scale systems. Therefore, the study on the use of NF membranes in lithium recovery should be focused on the process optimisation to achieve the goals of low energy, low fouling tendency, and minimised equipment size. For instance, the membrane pre-treatment could be adopted for inhibiting membrane fouling, thereby reducing the operating costs. Technique that can provide accurate non-invasive and online monitoring of membrane fouling to timely clean membrane need to be developed [55, 115, 116]. Additionally, the further development of antifouling NF membranes is needed, as well as that of membranes with a high selectivity to separate monovalent and divalent ions.

MDC could effectively recover lithium along with water purification because of its unique mass transfer characteristics. However, membrane fouling and the related wetting phenomena restrict its widespread application. To solve these problems, the fabrication of a super-hydrophobic membrane with anti-fouling properties is the key to preventing wetting and mitigating membrane fouling. Meanwhile, the optimisation of the MD configuration and the enhancement of mass and heat transfer are key factors for the reduction in energy consumption. As a mature technology, future studies should be focused on the accomplishment of full-scale applications.

Further, the lithium extraction processes involving SLM, IIM and LISM have not been successfully used in the industry because of the inefficient lithium adsorption/desorption cycle. These processes suffer from the low efficiency of lithium recovery. Future work should focus on the development of novel lithium separation membranes with higher lithium selectivity and better economic applicability.

More importantly, to intensify the ion-exchange rates of Li^+ in the adsorbent layer, an electric driving force could be used to enhance the efficiency of the lithium recovery system. Hence, the electrical drive technologies involving PSMCDI and S-ED have attracted considerable attention. Unfortunately, they still face some technical and economic barriers, mainly their relatively low production efficiency and the high investment capital required during the industrial-scale applications. The development of a cost-effective cation-exchange membrane with oxidation tolerance for high lithium-ion selectivity remains a challenge for further study. The electrode design is also a key to improving the performance of the PSMCDI technology. More efforts should be focused on developing new porous and cost-effective counter-electrodes for the reduction of the cost and the enhancement of the lithium recovery efficiency and regeneration performance. In particular, some fundamental research has been actively encouraged to obtain a deep understanding of the mechanisms of

lithium intercalation/de-intercalation and the lithium adsorption/desorption behaviour in a PSMCDI system, and grasp the mechanisms of the permselectivity between the lithium and the co-ions through the establishment of transport modeling.

The membrane technologies discussed above have demonstrated their capacity to advance lithium extraction by either increasing the lithium concentration factors, such as NF, MDC, and S-ED, or increasing the lithium selectivity, such as PSMCDI, SLM, IIM, and LISM. The highly selective adsorption processes involving SLM, IIM, and LISM, and the electrical drive technologies, including PSMCDI and S-ED, are effective strategies to capture the diluted Li^+ from seawater. The selective enrichment of the lithium from the concentrated mixed brines in less time is of considerable significance in the lithium-rich salt-lake brines. NF, MDC, and S-ED are therefore more suitable for the salt-lake brines. All the membrane-based technologies can be applied for lithium recovery from geothermal water because of the moderate salinity and lithium concentration.

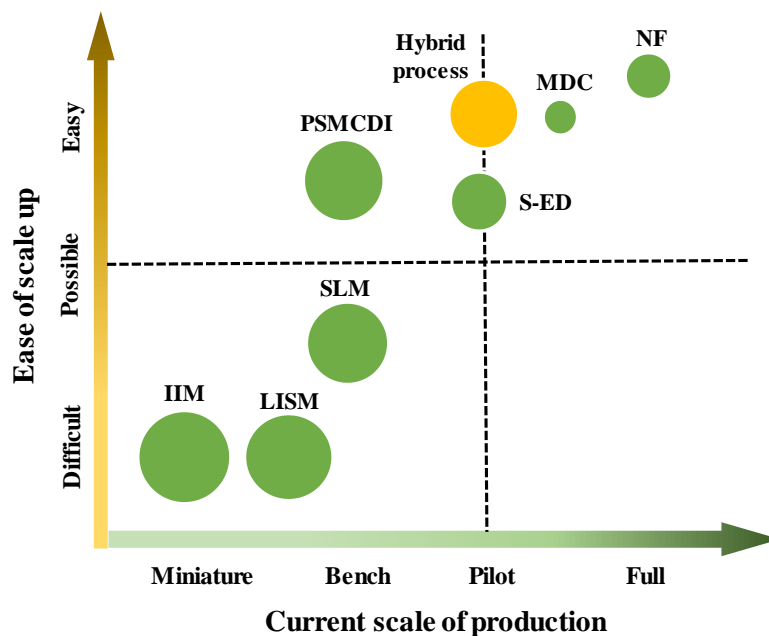


Fig. 9. Comparison of the performance and commercial viability of membrane-based lithium-recovery technologies on the basis of the current scale of production (horizontal axis), the ease of scale up (vertical axis) and selectivity towards lithium (size of the symbol).

While each technology has clearly demonstrated its own merits and limitations, Fig. 9 compares these different membrane-based technologies on the basis of three key parameters: the current scale of production (horizontal axis), the ease of scale up (vertical axis) evaluated by considering the technical stability as well as the production cost, and the selectivity towards lithium (size of the symbol). As shown in this figure, the upper-right quadrant of the chart denotes the technologies that have already been commercialised or are close to commercialisation, whereas the lower-left quadrant of the chart denotes the technologies that are still far away from commercialisation (Fig. 9). The upper left quadrant indicates that although the relevant technologies are still at the bench-scale development, they are relatively easy to scale up. For example, a practical PSMCDI separation system is easily established for lithium extraction by selecting suitable battery materials as the positive and negative electrodes. Notably, the hybrid membrane processes, which complement each other accordingly to maximize the overall efficiency of lithium recovery, are highly encouraged. For instance, a hybrid MDC-LISM process was used for lithium recovery from low temperature geothermal brines [114]. A high recovery of lithium of 74% from brine was achieved using an NF-MDC hybrid system (Fig. 10) [14, 65, 68]. More importantly, this hybrid system could also simultaneously produce desalted water. In addition, the coupling NF membrane in the S-ED or the PSMCDI process presented high demineralisation rates, exhibiting notably excellent separation performances of divalent and monovalent ions [117–118]. The integration of membrane technologies is regarded as a promising strategy for increasing the lithium recovery from brine [79, 101, 119, 120].

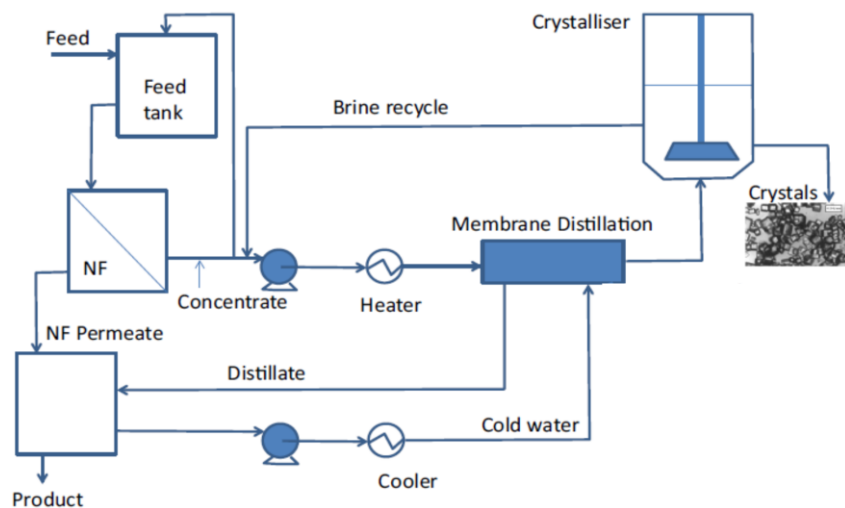


Fig. 10. Typical diagram of the NF-MDC hybrid unit for minerals recovery system (the concentrate from NF is fed into the MDC system). Figure obtained from reference [65] with copyright permission from Springer Nature.

In other words, scaling up to a large-scale plant is the ultimate goal for all of these membrane technologies. Researchers should thus be sought out to assist the optimisation of the process so that correct operating procedures are used to provide both sufficient extraction and membrane longevity.

5. Conclusions

The potential membrane-based technologies to recover lithium from water resources were critically reviewed. Based on the different separation mechanisms of these membrane technologies, a further improvement of lithium recovery can be undertaken in the following four directions:

- (1) As a commercially available membrane process for lithium extraction, NF should focus on the cost reduction through system optimisation and membrane improvement with an enhanced antifouling property and a high selectivity of the monovalent/divalent ions.
- (2) Membrane distillation crystallization, driven by the vapour pressure difference, is

capable of achieving a high concentration factor and recovery. Membrane wetting/fouling and the purification of valuable salts from the produced mixed minerals are two major barriers for its widespread application in lithium extraction.

- (3) The lithium adsorption/desorption methods involving supported liquid membranes, ion-imprinted membranes and ion-sieve membranes can extract lithium from a low-concentration source by selective adsorption and quantitative desorption. Although these membrane adsorption technologies are technically feasible, the reduction of capital and operating costs is still a significant challenge for their commercial application.
- (4) The electrically driven technologies involving permselective exchange membrane capacitive deionisation, and particularly selective electrodialysis, are the most promising approaches in the near future. Future research should emphasise not only on the improvements of the cation-exchange membrane/electrodes with high lithium selectivity but also on the ion transport mechanism and the interplay between ions in electrodialysis.

Further development of membranes with high selectivity of lithium is crucial for all the membrane-based processes and should therefore be prioritised. Furthermore, comprehensive optimisation of these single or hybridised membrane-based processes in lithium extraction should be performed considering the energy demand, system stability, operating costs, and product quality.

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Fig. 1. (a) Distribution of global lithium end-uses in various applications in the year of 2016, and (b) global lithium production in the years from 2010 to 2025. Part (a) and Part (b) of the figure were obtained from references [3–4], respectively, with copyright permissions from Elsevier.

Fig. 2. Schematic diagram of separation principle of a supported liquid membrane. Figure obtained from reference [31] with copyright permission from Elsevier

Fig. 3. Schematic diagram of the procedure for the preparation of IIMs for selective adsorption of Li^+ : (i) fabrication of the PVDF/GO hybrid membranes; (ii) PDA coating on PVDF/GO substrate as the anchor for loading imprinted sites; (iii) immobilization of 12-Crown-4-ether on the membrane surface. Figure obtained from reference [53] with copyright permission from the Royal Society of Chemistry.

Fig. 4. Schematic illustration of the PSf based mixed matrix nanofibers membrane with lithium ion sieves: (i) preparation of lithium ion sieves particles; (ii) preparation of mixed LMO/PSf electrospun nanofibers; (iii) activation of mixed LMO/PSf membrane. Figure obtained from reference [63] with copyright permission from Elsevier.

Fig. 5. Schematic diagram of the MDC system. Figure obtained from reference [67] with copyright permission from Elsevier.

Fig. 6. Schematic illustration of (a) conventional ED stack and (b) BMED stack for recovering lithium. Figure obtained from reference [81] with copyright permission from ACS Publications.

Fig. 7. Schematic illustration of PSMCDI lithium recovery system of (a) adsorption and (b) desorption processes. Figure obtained from reference [100] with copyright permission from Elsevier Publications.

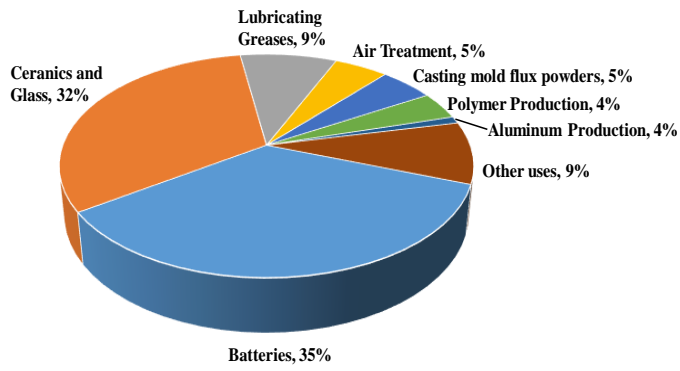
Fig. 8. Illustrations of the relationships between energy consumption and feed salinity in S-ED, PSMCDI, MDC, NF, SLM, IIM and LISM.

Fig. 9. Comparison of the performance and commercial viability of membrane-based lithium-recovery technologies on the basis of the current scale of production (horizontal axis), the ease of scale up (vertical axis) and selectivity towards lithium (size of the symbol).

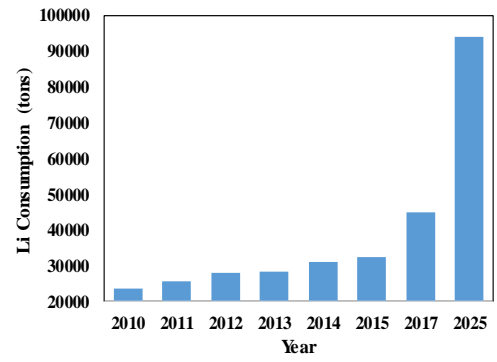
Fig. 10. Typical diagram of the NF-MDC hybrid unit for minerals recovery system (the concentrate from NF is fed into the MDC system). Figure obtained from reference [65] with copyright permission from Springer Nature.

Fig. 1

(Li et al.)



(b)



(b)

Fig. 2

(Li et al.)

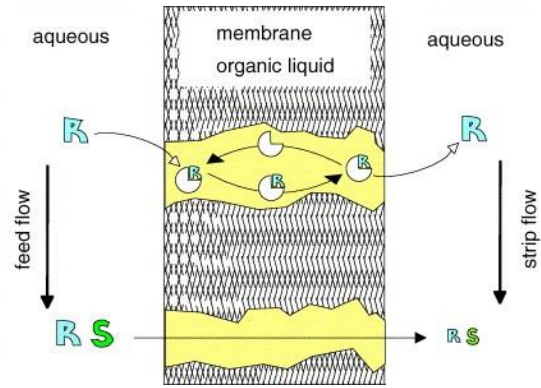


Fig. 3

(Li et al.)

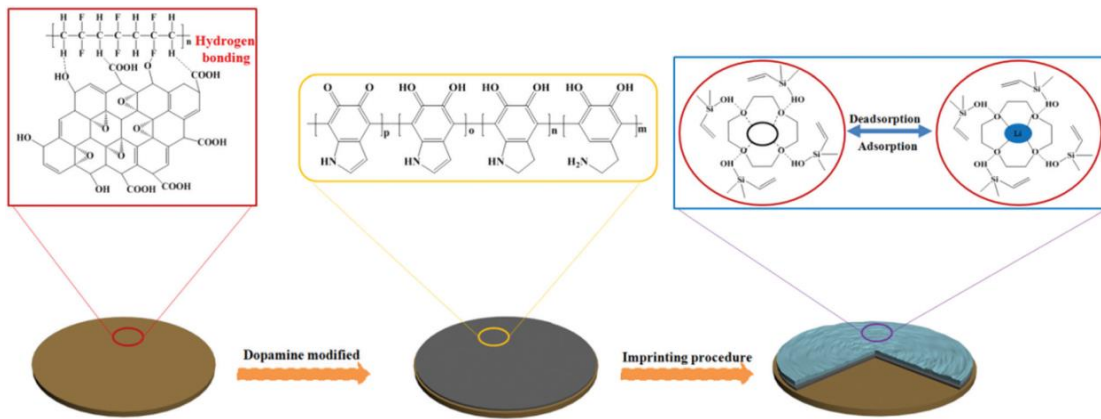


Fig. 4

(Li et al.)

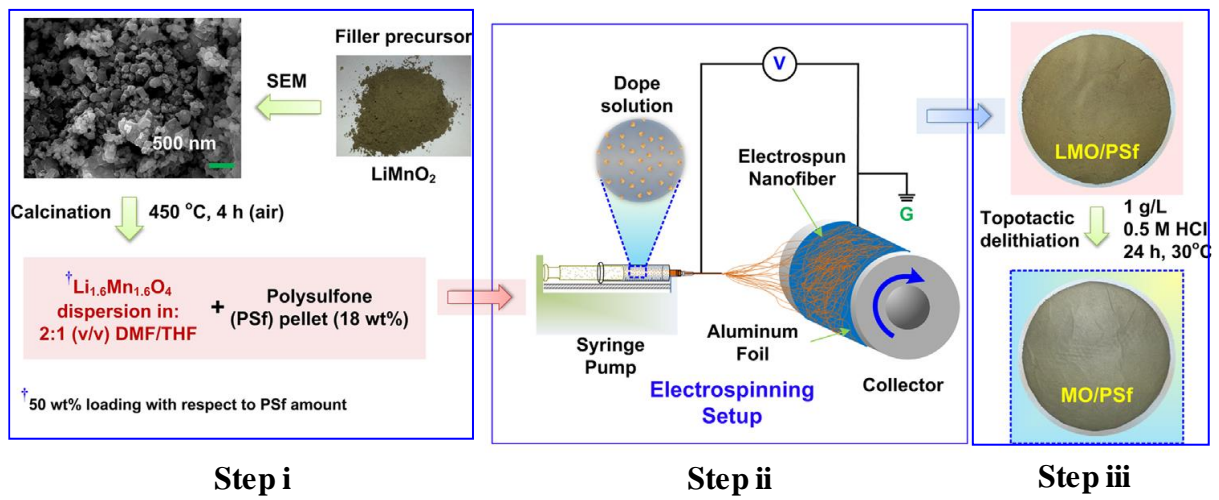


Fig. 5

(Li et al.)

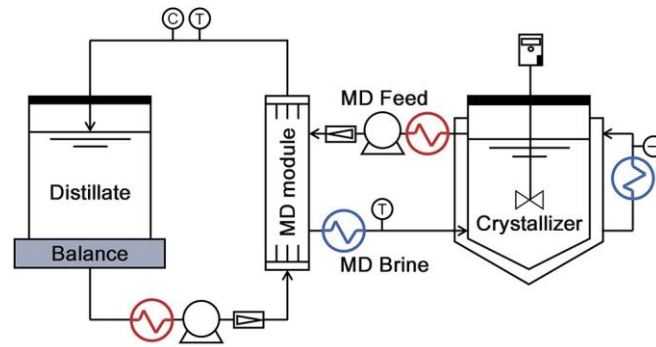
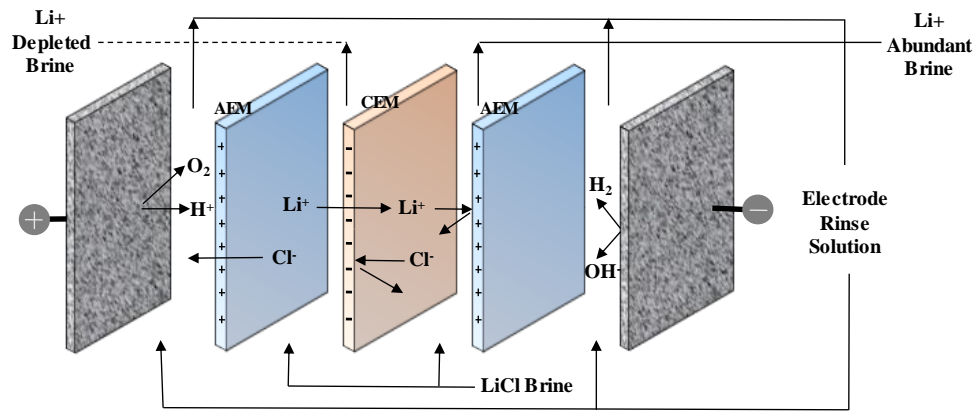
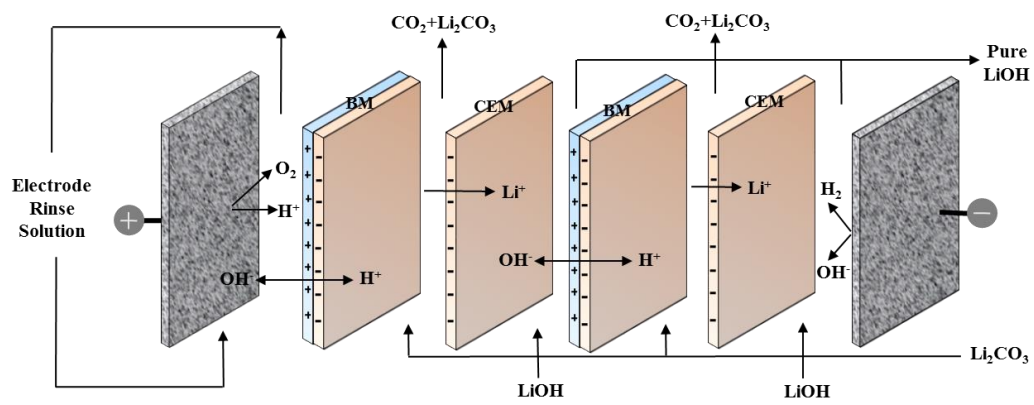


Fig. 6

(Li et al.)



(a)



(b)

Fig. 7

(Li et al.)

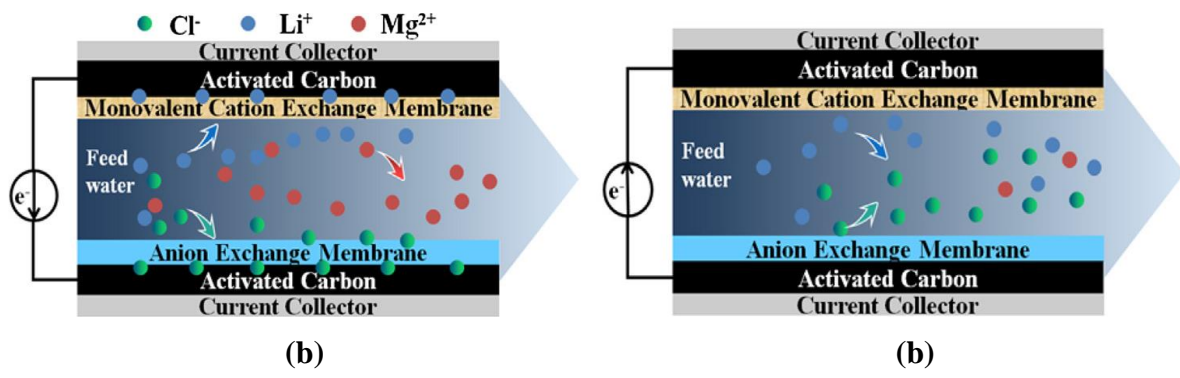


Fig. 8

(Li et al.)

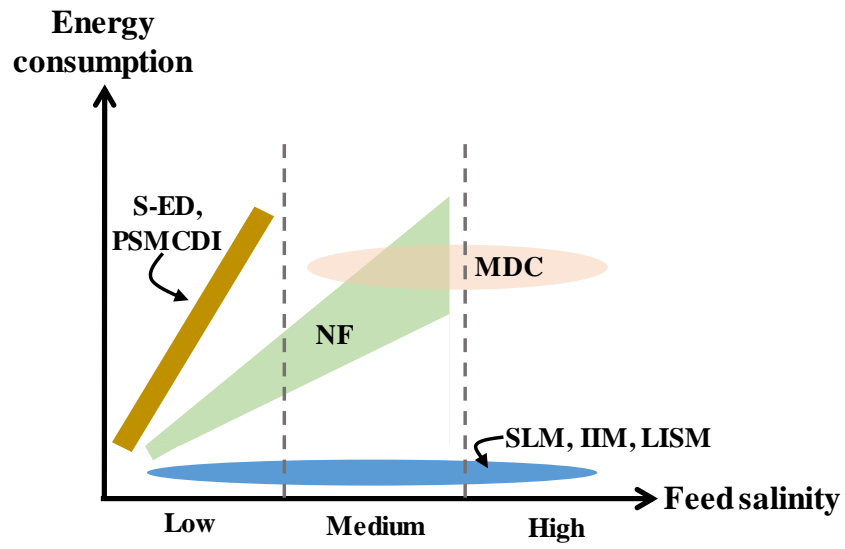


Fig. 9

(Li et al.)

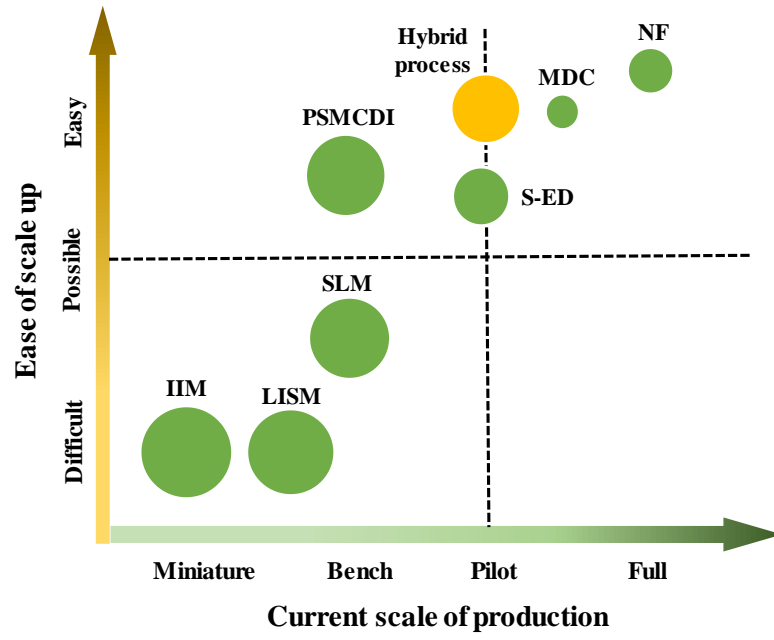
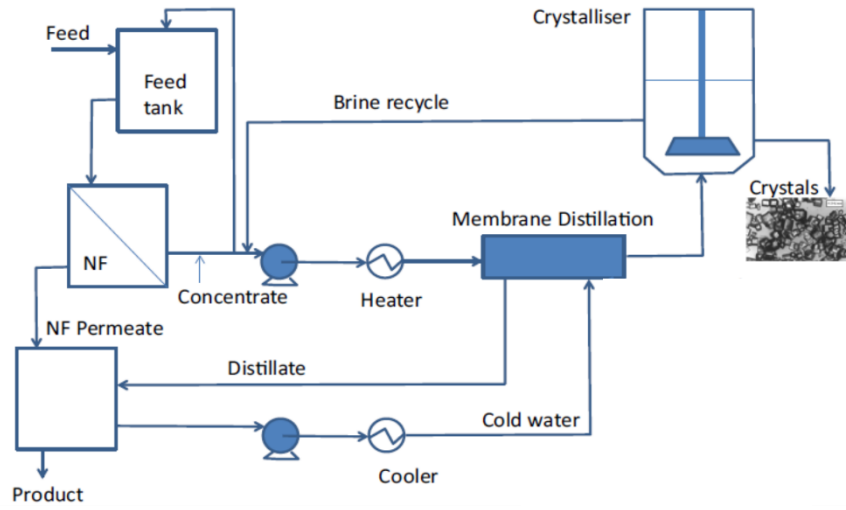


Fig. 10

(Li et al.)



Graphical abstract

