



A review on advances in direct lithium extraction from continental brines: Ion-sieve adsorption and electrochemical methods for varied Mg/Li ratios

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ABSTRACT

The unbalanced supply and demand of lithium (Li) has elevated the urge for its extraction owing to the accelerated surge of battery and electric vehicle (EV) industries to meet the carbon emission reduction target. As the cost of extracting Li from brine is typically 30–50% lower than conventional hard-rock sources, this work intends to critically analyze the evolution of direct lithium extraction (DLE) methods employed in Salt Lake brine with various magnesium/lithium (Mg/Li) mass ratios whereas the lithium brine concentration (LBC) methods seek to concentrate the Li brine and eliminate contaminants without isolating the Li from the brine. Solvent extraction, precipitation, adsorption, membrane technology, and electrochemical extraction are the developed methods for Li extraction from Salt Lake brine. This review focuses on the mechanism, workflow, and comparative analysis of different methods. Moreover, recent technological advancements to handle the high Mg/Li ratio, such as modification of adsorption using ion sieves, liquid-membrane electrodialysis, and efficient multicomponent doping electrode materials, have also been discussed in depth. Although it was previously believed that solvent extraction was only feasible for low Mg/Li ratio brines, it has recently been commercially applied for high Mg/Li ratio brines in China. Precipitation is more ecology-friendly and economically favorable because of its low cost. Li extraction from brines with high Mg/Li ratios also shows promising performance using aluminate (Al) precipitants and novel Mg precipitants. However, during Mg precipitation, there is a significant loss of Li. On the other hand, in the cost-effective adsorption method, aluminium salt adsorbents are industrially used, yet low adsorption capacities limit their application. Recently, ion-exchange methods have gained popularity, as ‘Li sieves’ exhibit remarkable selectivity and adsorption towards Li-ions and are effective at high Mg/Li ratios. Powdered ionic sieves have low fluidity and solution permeability despite their strong affinity and adsorption capacity. Membrane technology is promising because of the benefits of improved energy consumption, simple controls, high separation rates, and the continuity of the process, yet as an emerging technology, its commercial viability is not proven. Nevertheless, a coupled “adsorption-membrane” technique has been developed and used in China for Salt Lake brines with low Li grades. Furthermore, exceptional selectivity, low energy demand, and minimal impact on the environment of electrochemical methods make Li extraction from brine promising. Being a recent technology, there is ample scope for improving electrode materials and understanding the process

Abbreviations: Li, Lithium; Li⁺, Lithium ion Ion; Mg, Magnesium; Mg²⁺, Magnesium Ion; Mg/Li ratio, Magnesium/Li ratio; DLE, Direct Li Extraction; LBC, Lithium Brine Concentration; LIB, Lithium-Ion Batteries; EV, Electric Vehicle; Cl, Chlorine; Cl[−], Chloride Ion; USGS, United States Geological Survey; Li₂O, Lithium Oxide; Li₂CO₃, Lithium Carbonate; LCE, Lithium Carbonate Equivalent; LiOH, Lithium Hydroxide; LIS, Lithium ion-sieves; Na₂SO₄, Sodium Sulphate; MgSO₄, Magnesium Sulphate; Na₂CO₃, Sodium Carbonate; AlCl₃, Aluminium Chloride; LDH, Layered Double Hydroxide; MDC, Membrane Distillation Crystallization; CaO, Calcium Oxide; LiHCO₃, Lithium Bicarbonate; ME, Membrane Extraction; NF, Nano Filtration; ED, Electrodialysis; FO, Forward Osmosis; NaCl, Sodium Chloride; KCl, Potassium Chloride; LiCl, Lithium Chloride; EIP, Electrochemical Ion Pump; MnO₂, Manganese Oxide; Mn, Manganese; Ti, Titanium; LMO, Lithium Manganese Oxide; LTO, Lithium Titanium Oxide; HCl, Hydrochloric Acid; NaHCO₃, Sodium Bicarbonate; mm, Milli Metre; mmol/g, Milli Mole per Gram; PVC, Poly Vinyl Chloride; PAM, Polyacrylamide; AABs, Alpha-Alumina Beads; PVA, Poly Vinyl Alcohol; Sol-gel method, Solution-Gel Method; 3D, Three Dimensional; PAA, Peroxyacetic Acid; μm, Micrometre; Sb/Mn, Antimony/Manganese; Fe, Iron; NiHCF, Nickel Hexacyanoferrate; LEC, Lithium Extraction Capacity; EC, Energy Consumption; PP, Product Purity; LFP, Lithium-Iron-Phosphate; NCM, Nickel-Cobalt-Manganese; Ag, Silver; DIW, Deionized Water; EDD, Electron Density Difference; PPy, Polypyrrole; CDI, Capacitive Deionization; ESIX, Electrochemical Switching Ion Exchange; BPMD, Bipolar Membrane Electrodialysis; RO, Reverse Osmosis; TRL, Technology Readiness Level; EV, Eclectic Vehicle; mt, Metric Ton; ppm, Parts per Million; \$, U.S. Dollar; g/L, Gram per Litre; mg/g, Milligram per Gram; KJ/mol, Kilo Joule per Mole; pH, Potential of Hydrogen; °C, Degree Celsius; V, Volt.

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mechanism and cell configuration. Lastly, perspectives on the future Li extraction from brines are conferred in this article. By combining the methods (i.e., adsorption and ion exchange, membrane technology, and electrochemical process), the growth potential exists for an efficient, cost-effective, green, and sustainable extraction technology for Li from Salt Lake brine with a high Mg/Li ratio.

1. Introduction

Lithium (Li) is a crucial energy commodity and an essential strategic asset for the twenty-first century's transition to a clean-energy economy. This lightest metallic element has broad applications in Li-ion batteries (LIB) and nuclear fusion, being the heat-transmitting media [1,2]. The accelerated growth of EV and grid-based energy storage businesses causes an acute demand for Li in the battery industry [3,4]. Due to this increasing demand and being 30–50% less expensive in production than conventional hard-rock sources, the urge for Li recovery from Salt Lake brine has gained the utmost attraction [5]. Fig. 1 (a) presents the production profile of Li, where it can be found that there is a 21.5% increase in worldwide production of Li from the year 2021 to 2022. Moreover, there has been a massive change in pattern in the use of Li from the year of 2010 to the year of 2021, and two-thirds of the current Li use is in rechargeable Li-ion batteries (e.g., portable electronic devices, EVs, and grid-based energy storage) as presented in Fig. 1 (b) [6–8].

Clays, minerals, seawater, and brines all contain trace amounts of Li. Continental brines are the most abundant (almost 60% [10]) of these primary resources, followed by hard rock resources (e.g., spodumene, petalite, and lepidolite). Salt Lake brine accounts for 62.6% of the

world's Li supply, while 37.4% comes from hard rock minerals [11]. Li extraction from Salt Lake brines is becoming increasingly competitive with mining for Li in ore deposits. Hence, the industry is shifting its focus from ores to brines [1,3,12]. According to the USGS of 2022, the world's Li reserve is 26,050,000 t [8]. Fig. 2 (a) shows the concentration of Li resources, and Fig. 2 (b) presents the country-wise distribution of Li worldwide. Furthermore, it is worth noting that over 48% of the present Li carbonate (Li_2CO_3) equivalent (LCE) output is derived from Salt Lake brines, with Chile and Argentina accounting for the majority, namely around 40%. In addition, it is worth noting that the Li deposits in Chile, Bolivia, and Argentina collectively account for over 58% of the global Li reserves. Hence, these three countries comprising the “Li triangle” are pertinent in facilitating the necessary increase in production within the near and intermediate timeframes [13]. According to the Scopus database, from 1963 to 2000, only 824 articles were published on Li extraction. Fig. 3 shows the publication trend on the mentioned topics within the timeframe of January 2001 to December 2023, where a rapid increase is observed from 2019 to 2023.

Although the ocean has a vast Li reserve of around 231.4 trillion tonnes, currently, it is not economically viable to recover Li from salt-water due to its low concentration in seawater of approximately 0.178 mg/L [14]. However, in most cases, Salt Lake brine has a higher Li concentration (250 to 1600 mg/L [1,12]) than seawater. Geothermal power plants produce geothermal brines as waste products. Li^+ can be extracted from heated saline deposits transported to the surface, although there are considerable hurdles due to the deposits' complex chemistry, high temperature, and high salinity [15]. Brine deposits in oil fields are typically found at depths >1000 m. Traditional Li extraction processes from brine deposits, such as precipitation, are impractical outside arid areas, even though the Li^+ content in these brines (500–700 ppm) is favorable [16]. Concurrently, due to its environmental and economic benefits, the spent LIB is emerging as a secondary Li resource [17,18]. The increased use of LIBs is projected to enhance recycling rates. As a result, much effort has been expended in developing legislation, methods, and technology to recover and regenerate used LIBs [19,20].

There have been numerous studies on the worldwide extraction of Li from various Li resources. Widely used methods of extraction from Li-bearing ores are calcination and roasting [21], chlorination [22], and acid/alkaline digestion [23]. The most economically significant hard rocks are granite pegmatites, which typically include the Li-carrying mineral spodumene with a potential Li_2O content of 8%. Typically, Li run-of-mine ore has 1%–2% Li_2O (~20% spodumene), whereas a Li concentrate ready to be used to produce Li_2CO_3 typically contains 6%–7% Li_2O (~80% spodumene) after processing [24]. It is possible to obtain a Li concentrate by crushing mined ore, separating the Li-minerals via floatation, roasting at 1050 °C, treating with sulfuric acid, and finally re-roasting at 200 °C. Leaching, liquid-solid separation, impurity elimination by precipitation, and ion exchange are all steps in transforming the Li concentrate into Li_2CO_3 or $\text{LiOH}\cdot\text{H}_2\text{O}$.

The average cost of production for eleven different hard rock mines is \$2540 per metric ton of Li carbonate equivalent (LCE) [24]. However, this is the price paid for the mining concentrate to make Li_2CO_3 and LiOH . The cost to process mining concentrate into battery-grade forms varies from \$2000 to \$2500 per metric ton of Li concentration and bulk chemistry [24]. Moreover, Li extraction from ore resources infects the environment by inevitably impairing the soil, polluting the water bodies, contaminating the air, and thus adversely impacting the nearby biodiversity [25].

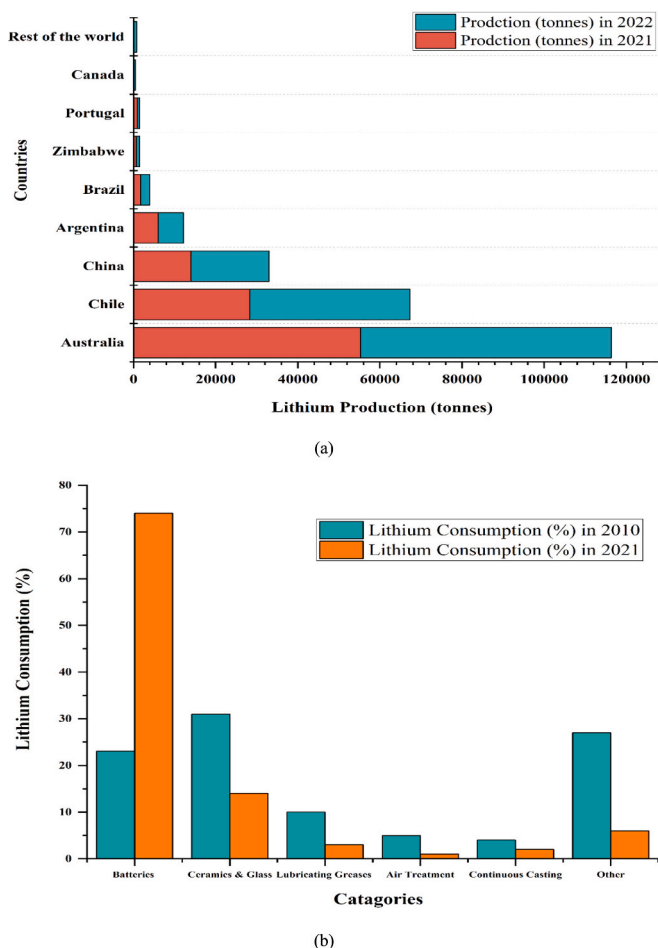
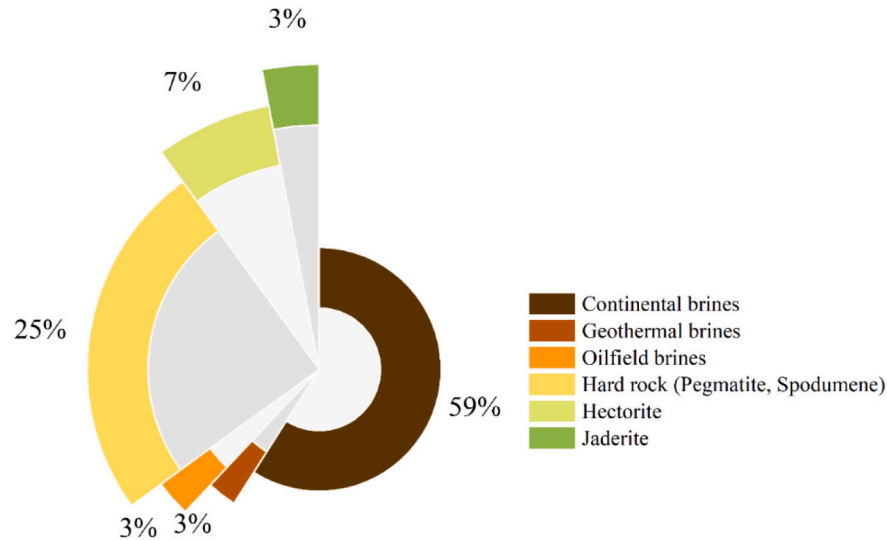


Fig. 1. Lithium (a) production (excluding the United States) and (b) consumption profile [9].

Li extraction from brine is 30–50% less expensive than from conventional hard rock sources [5]. Modern approaches to Li extraction are becoming more eco-friendly. Extremely salty brines can be found in oil fields and geothermal or continental resources. Solvent extraction, precipitation, adsorption, and electrochemical extraction are just some of the DLE methods developed in recent decades to combat the rapid depletion of hard rock Li ores. Moreover, membrane extraction (ME), nanofiltration (NF), electrodialysis (ED), membrane distillation (MD), and membrane distillation and crystallization (MDC) are some LBC methods which have been investigated quite intensively in the recent past. The use of membrane-based LBC process are more efficient and have less of an effect on the environment than older methods like evaporation ponds and thus achieve the transition towards decarbonized

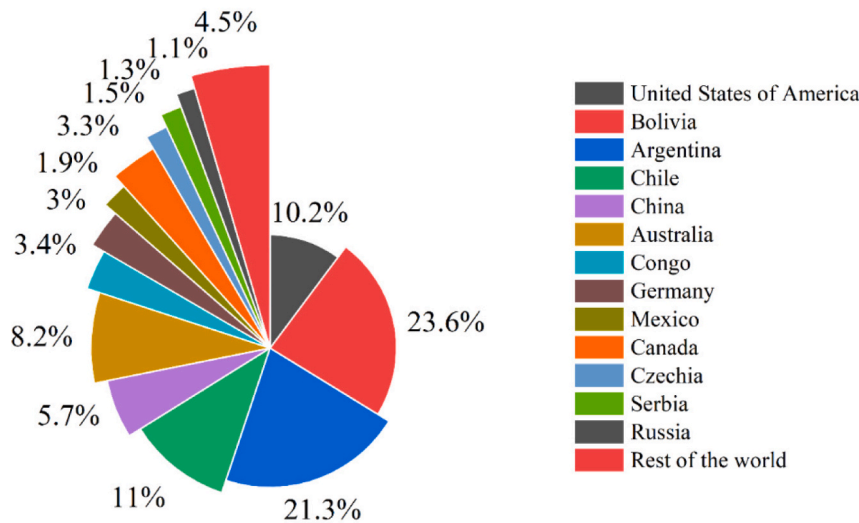
world [26]. Selective Li extraction from brine is the primary goal of DLE operations, with subsequent steps leading to the production of finished Li products. Separating or removing Li from the brine efficiently is the goal of this kind of technology. In contrast, the LBC operations aim to remove impurities and concentrate the Li brine without separating the Li from the brine, allowing the subsequent generation of final Li products. In this respect, LBC operations are analogous to evaporation ponds, except that the former recovers water instead of losing it. Minimization of the loss of brine-containing water is the primary objective in both scenarios [13].

In the current practice of Li extraction from brine using the evaporative method, the first phase pumps brine from subsurface reservoirs. When brines are deposited into substantial shallow exterior ponds,



Lithium Resources

(a)



Lithium Reserve of the World

(b)

Fig. 2. Lithium (a) resources and (b)worldwide reserve [8].

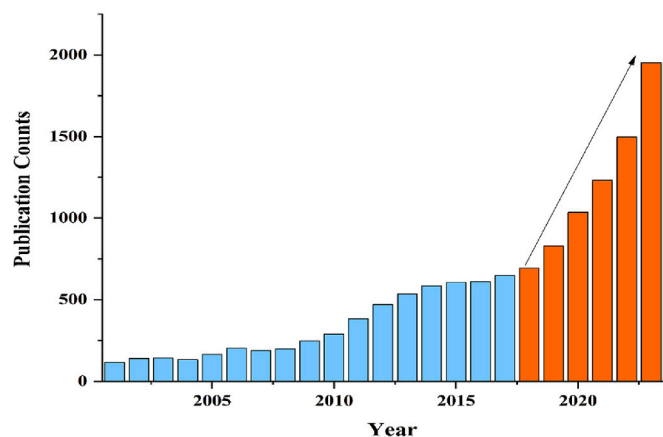


Fig. 3. Publication counts on lithium extraction from brines from the Scopus database.

sunlight, and wind speed up evaporation, causing >90% of the water content to be lost. Once saturation is reached, the concentration of LiCl rises steadily as additional cation salts crystallize in the ponds. The concentrated brines then go through a refining plant where Li_2CO_3 is crystallized as the end product. Freshwater and chemicals are required at various production stages (i.e., dissolved CaO to precipitate Mg^{2+} , added Na_2CO_3 to remove borates, and washed Li_2CO_3 crystals) [27,28].

The developed methods for Li extraction from Salt Lake brine, including solvent extraction, precipitation, adsorption, membrane technology, and electrochemical extraction. Due to its low cost and high product yield, solvent extraction, known as “liquid-liquid extraction,” is a promising approach for Li recovery from brine [28]. However, several organic extractant systems have been studied for their potential to cause environmental damage during solvent extraction [29]. Precipitation, being relatively simple and commercially favorable, still requires further research to elevate energy consumption and eradicate the adverse effects of using chemicals on the surroundings. However, the adsorption method’s poor adsorption stability and ion exchangers prevent its widespread usage in industrial settings, even though it is the most effective method for Li extraction. [30]. Besides, the membrane method provides improved energy consumption, simple controls, and process continuity. Yet, these successes are at the laboratory scale, which hasn’t reached the pilot test [1].

Electrochemical methods have great potential for Li extraction from natural brines because of their exceptional selectivity, low energy demand, and minimal environmental impact. More work needs to be done to increase the field applicability of Li by enhancing its capacity for storage, cyclic stability, and ion preference [31]. The incorporation of the ion-exchange method and adsorption method is gaining popularity because of the exceptional selectivity and greater affinity of ‘Li sieves’ towards Li-ions, making them highly effective even at low Li concentrations [28]. Powdered ionic sieves have low fluidity and solution permeability despite their strong affinity and adsorption capacity [31]. Additionally, newer efforts have begun investigating LBC techniques which can boost the efficacy of DLE procedures when used in tandem with them. By eliminating contaminants in subsequent steps, LBC techniques aim to concentrate Li brine without actually isolating the Li from the brine.

This article provides a comprehensive overview of the most up-to-date methods for extracting Li from natural brines, with an intensive focus on electrochemical techniques and ion-sieve adsorption. Moreover, the materials for the electrode, configuration of the cell, process mechanism for electrochemical, and Li deintercalation/intercalation mechanism for ion-sieve methods are also analyzed at length. This study lays the groundwork for determining the most pressing issues regarding the widespread application of Li recovery from natural brines, especially

Salt Lake brine.

2. DLE methods for lithium extraction from Salt Lake brine

Based on the composition of chemicals, Salt Lake brines can be categorized into four broad categories such as carbonate (CO_3^{2-}), sodium sulphate (Na_2SO_4), magnesium sulphate (MgSO_4), and chloride (Cl^-), where carbonate brines are low in Mg/Li ratio, and the rest are high in Mg/Li ratio. Table 1 presents the average Mg/Li ratio of these four significant types of brine. As a result, carbonate brines have proven to be the most cost-effective and long-term Li^+ extraction materials for use in the more conventional evaporation and precipitation processes [32,33]. Commercial Li production from Salt Lake brines has been standardized on the solar evaporation-precipitation method [34,35]. Despite substantial attempts to reduce Li losses, optimize operations, and mitigate ecosystem impacts, the hunt for more novel ways with lower capital costs and enhanced ecological and economic viability has become an extrusive tendency. Several new methods are discussed below that potentially significantly improve Li recovery from brines.

2.1. Solvent extraction

Hydrometallurgy’s liquid-liquid extraction first came into existence in the late 1940s for the separation of uranium, but it has since developed into a commercially viable process for the separation of several metals, including Li. Multiple studies have been published on the processes involved in the neutral extraction, ionic liquid extraction, synergistic solvent extraction system, and crown ether system for separating Li from brines. Solvent extraction is commercially viable when Li is high in ratio [36]. Being highly selective for Li, ionic liquids can process brine with a high Mg/Li ratio due to their low volatility, nonflammability, tunable viscosity, and excellent thermal stability.

The general workflow of solvent extraction is presented in Fig. 4. Please note that all the flowcharts from Fig. 4 to Fig. 8 in the article follow the same color code. Input items are represented by light blue, output items by dark blue (except for the final Li solution, which is an output item and has been represented by light green to keep it distinguished from other output items), and processes are denoted by light purple. Moreover, spent brine (i.e., leftover solution after Li extraction processes, which typically contain reduced lithium concentrations and various other dissolved salts) reinjection is also incorporated in these flowcharts. Fig. 4 shows that the contaminant ions remain in the liquid phase. At the same time, Li-ions are transported to the natural state after Salt Lake brine is recovered. Li is then re-extracted from the organic phase into the aqueous phase through stripping experiments. At the same time, the organic phase is recycled for further use in the extraction procedure. After evaporating the Li-rich solution, the pure Li solution is obtained, and the dissolved impurities are eliminated using precipitation. In the next step, the Li-rich solution is evaporated to get a pure Li solution after the dissolved contaminants have been eliminated via precipitation. Lastly, Li is precipitated as Li_2CO_3 by adding the precipitating agent, Na_2CO_3 . Solvent extraction offers some clear benefits over current lithium extraction methods. Solvent extraction allows for the selective extraction of lithium from Salt Lake brines in a single step, even when there are many impurities present, such as Mg, Na, K, and B. The method is also known for its simple process flow, low cost, reduced

Table 1
Types of brine defined by Mg/Li ratio.

Brine type	Average Mg/Li ratio (>10 is high, and ≤ 10 is low.)
Carbonate	1.5
Sodium Sulphate	24.6
Magnesium Sulphate	151.2
Chloride	324.5

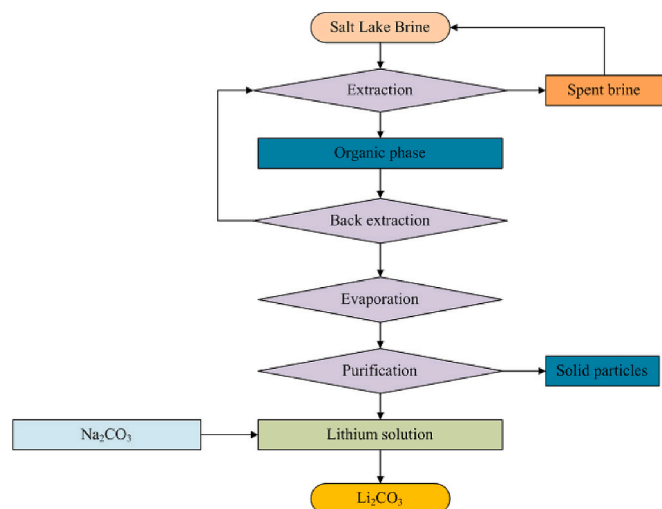


Fig. 4. Workflow diagram of a primary solvent (liquid-liquid) extraction method of lithium recovery (redrawn from [38]).

freshwater consumption, and minimal solid waste generation [37].

Recovering Li from seawater and other solutions using strong acid cation-exchange resins has been attempted as far back as the 1970s, as Meshram et al. noted [39]. The selectivity of organic ion exchange resins for Li ions was found to be poor in early experiments [39–41]. Although strong acid cation exchangers such as AmberSep™ G26H Resin are capable of removing Li from water, ordinary resins are not useful for Li extraction due to Li's poor affinity for ion-exchange resins compared to other cations [40,42]. Ion-exchange resins can be treated with inorganic, Li-selective sorbents to improve selectivity [40,43].

To selectively extract Li ions, several researchers have explored creating organic polymers. This selectivity is accomplished by an ion-imprinting method that incorporates reactive or chelation sites inside tailored steric structures. To facilitate the removal of Li from geothermal brines, researchers like Ventura et al. created a nanocomposite sorbent comprised of Li-imprinted polymeric resins and molecular sieve nanoparticles [44,45]. Crosslinking and polymerization of metal chelates are used to develop metal-imprinted polymer beads. Because of the memory effect produced during production, these beads are employed as selective solid sorbents to extract specific metal ions from brines. The size and geometry of the holes created in the polymers and the ligand affinity affect the selectivity for metal ions [44].

Materials Research LLC is working on producing new polymers imprinted with Li to recover Li from geothermal brines and other essential materials [15]. Despite their many ongoing endeavors, they have yet to release any commercially available items [15,44]. In order to create lithium carbonate from geothermal brine, one project entails expanding the sorbent's production capacity and testing the system in a mobile pilot study. The study's experiments may use artificial and real geothermal brines. The project's goals are to develop expertise in managing a large-scale facility, modify the process in light of lessons gained, revise energy and material balances, and improve the economics of the process [15].

Researchers such as Lu et al. engineered polymers embedded with Li and crown ether structures to separate Li from sodium and potassium ions selectively [46]. Li was adsorbed to crown ether sites in these polymers and held while other ions were allowed to pass through the barrier. Other ion-imprinted polymers for Li adsorption also used crown ether moieties [47]. Saboe et al. used a chromatographic procedure to isolate Li from brine with an organic sorbent as the stationary phase [48]. A stationary phase with zwitterionic properties was employed, while brine and freshwater served as the mobile phase. The zwitterionic group worked as a trap for Li and other salts due to the ions' dissimilar affinities, allowing for their separation. The Van der Waals radius,

charge, and solubility of the salts all had a role in the rate of separation [48].

Apart from the advantages of this process, separation is difficult when components with related chemical and physical properties in the solution exist, such as Mg and Li. Organic polymerization occurs when there are <80% neutral organic phosphorus extractants in the organic phase, leading to organic loss and environmental pollution and thus lowering the process's efficiency [38]. Besides, it had high capital expenditures and was very difficult to utilize on a large scale. However, the Qinghai Qaidam Xinghua Li Salt Company has used solvent extraction to economically treat brines with a high Mg/Li ratio and set up a high-purity lithium chloride manufacturing facility in Dachaidan Salt Lake, Qinghai, and is projected to handle 20,000–25,000 tons of Li chloride per year from 2025 [49].

2.2. Precipitation

Precipitation-based technologies are economically appealing because of their low cost and simple operation. Using aluminium chloride (AlCl₃) at the proper pH and temperature, several scientists have reported the first successful attempts to isolate Li as LiAlO₂ from dead sea brine [50,51]. Aluminate precipitation is more ecology-friendly and has demonstrated excellent recovery of Li from brines with high Mg/Li ratios. Furthermore, an 86% extraction efficiency and a maximum capacity of 37.86 mg/g were achieved in a single step during lithiation in a study by Jayanthi et al. in 2023. The researchers used amorphous aluminium hydroxide in a liquid-solid lithiation reaction, followed by acid-free delithiation and relithiation procedures [52]. Novel Mg precipitants show promise for Li extraction from brines with high Mg/Li mass ratios. The extensive precipitation process suggested by Wang et al. reported a 91% yield and 99.7% pure Li₂CO₃, in addition to the nearly complete elimination of Mg [28].

A multi-step precipitation procedure was also used to precipitate Li as Li₂CO₃ in brine. For low Mg/Li ratios (<10), carbonate precipitation is commonly employed [53,54], wherein Mg is first precipitated via CaO, and then Li is precipitated as Li₂CO₃ by adding Na₂CO₃. For crude Li₂CO₃ with a low Mg/Li ratio, carbonization precipitation precipitates Li as LiHCO₃. To obtain a high purity of Li₂CO₃, a mixture of carbonate and carbonization precipitation is also used. Li is often extracted using either Al precipitation or Mg precipitation processes when the Mg/Li ratio is high, as it is in most naturally occurring brine deposits. Researchers have demonstrated that Mg can be isolated from high-Mg/Li brines by combining integrated and multi-step precipitation and isolation processes.

As seen in Fig. 5, Wang et al. introduced a method for selective Mg and Li recovery involving various ways and chemicals [55]. However, increasing the temperature to induce precipitation is not just high in energy consumption but also challenging to implement in terms of logistics, mainly when the brine is located at a higher altitude. There is a significant loss of Li during Mg precipitation, ranging from 20% to 30%. Increasing energy efficiency and eliminating the adverse effects of chemical additions on the environment will require more study. Advancement in Li extraction via the precipitation method is summarized in Table 2.

2.3. Adsorption

Adsorption has developed into a promising alternative approach for retrieving Li from brines. This process is very cost-effective and easy for large-scale use. Adsorbents with high ion recognition and screening capability, such as ion-sieve oxides, help extract particular metal ions. The exceptional selectivity and adsorption of 'Li sieves' towards Li-ions makes them highly effective even at low Li concentrations, typical of most naturally occurring brines, and has contributed to the rise in popularity of ion-exchange techniques [28]. Powdered ionic sieves have low fluidity and solution permeability despite their strong affinity and

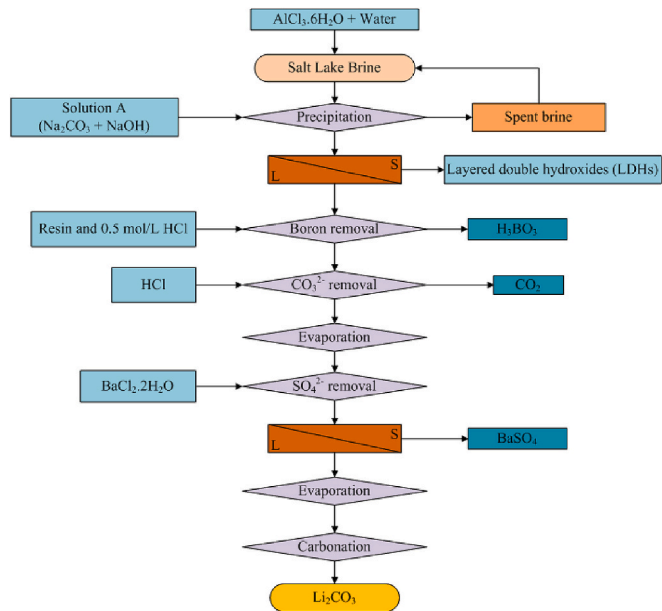


Fig. 5. Workflow diagram of a precipitation method of lithium recovery (redrawn from [55]).

adsorption capacity [31].

Adsorption techniques use Li-selective adsorbents to separate and extract Li from Salt Lake brine containing a high Mg/Li ratio. Fig. 6 depicts the adsorption technique used to recover Li. The adsorption substance is the main factor in this technique. The first need for the material employed in Li adsorption is structural integrity, both in the high-salinity Salt Lake brine system and the robust acid elution system. Mainly, it needs to be flexible enough to meet the shifting mechanical demands of the adsorption process and variations in brine temperature.

For the successful Li extraction from high-salinity, complex-composition Salt Lake brine deposits, the adsorption material must have excellent preference and adsorption ability for Li. Adsorbents for aluminium salts and Li ions (based on either manganese (Mn) or titanium (Ti)) have been the primary focus of study up to this point in time. Adsorption capability is reduced due to ion channel obstruction and adsorbent dissolution. Furthermore, achieving a good elution process is also a significant challenge for its application. Aluminium salt adsorbents are industrially used, yet low adsorption capacities limit their application. Furthermore, the theoretical adsorption capacity is significantly higher than the actual adsorption capacity. An adequate granulation process and enhanced adsorption capacity are necessary in the context of industrial use of ion sieve adsorbents. Moreover, a detailed discussion of recent advances in ion-sieve adsorption is described in section 5.1.

2.4. Electrochemical method

Alkali metal and alkaline earth metal ions complicate isolating Li salt from brine. Due to their exceptional preference, ecological friendliness, and low energy use, it was established that Li ions could be successfully extracted from brine and seawater using electrochemical methods.

Fig. 7 presents the conceptual workflow diagram of the electrochemical method. The versatility of electrochemical Li extraction is one of its main benefits. Adjusting the treatment parameters allows the most effective management of varying brine compositions and concentrations. In laboratory settings, electrochemical methods utilizing ion pumping within mixing entropy cells and intercalation battery cathode materials have proven to be rapid and efficient. These approaches offer sustainable solutions for recovering Li from natural brine and recycling old batteries [66]. More work needs to be done to increase the field

Table 2
Summary of Li extraction from brine using the precipitation method.

Resources	Mg/Li Ratio	Methods and Reagents	Li Recovery (%)
Brine containing Li	<10	Carbonate precipitation (CaO and Na ₂ CO ₃)	- [54]
Damxungcuo Salt Lake brine	2.25	Two-stage carbonate precipitation (Ca(OH) ₂ , NaOH, C ₂ H ₂ O ₄ , and carbonate)	- [53]
Zabuye Salt Lake Alkaline Salt Lake brine	0.23	Carbonization precipitation (-)	72.91 [56]
Urmia lake brine	-	Phosphate precipitation (-)	77 [33]
Oil field brine	325.8	Al precipitation (AlCl ₃ .H ₂ O and NaOH)	76.4 [57]
Uyuni Salar brine	4.96	Al precipitation (AlCl ₃ and NaOH)	75.6 [58]
Uyuni Salar brine	21.2	Mg precipitation (NaOH and C ₂ H ₂ O ₄)	70–90 [59]
Uyuni Salar brine	23.33	Mg precipitation (Na ₂ CO ₃ and C ₂ H ₂ O ₄)	>70 [60]
Uyuni Salar brine	19.88–22.89	Mg precipitation (CaO, Na ₂ CO ₃ and Na ₂ C ₂ O ₄)	/ [61]
Taijinar Salt Lake brine	19.22	Mg precipitation (AlCl ₃ .6H ₂ O, Na ₂ CO ₃ , NaOH, HCl, and BaCl ₂ .2H ₂ O)	91 [55]
Yiliping Salt Lake brine	60	Fractional crystallization (NaOH and Na ₂ CO ₃)	/ [33]
Mg-S subtype brine	>40	B-Li co-precipitation (Sulfate and HCl or H ₂ SO ₄)	80–90 [33]
Qarhan Salt Lake brine	17.14	Co-precipitation (NH ₃ .H ₂ O and Na ₂ SiO ₃ .9H ₂ O)	- [62]
Natural brine	55	Mg precipitation (Na ₂ CO ₃)	- [33]
Natural brine	≥48	Mg precipitation (NH ₃ and NH ₄ HCO ₃)	95 [33]
Natural brine	≥20	Mg precipitation (NaOH and surfactants)	85–93 [33]
Natural brine	>19	Co-precipitation (Rare earth elements, quaternary NH ₃ salt, and water glass)	- [33]
Synthetic brine	260	Al precipitation (AlCl ₃ .H ₂ O and KOH)	73 [63]
Synthetic brine	20	Al precipitation (Al powder and NaCl)	78.3 [29]
Synthetic brine	495.9	Mg precipitation (Na ₂ CO ₃ and (NH ₄) ₂ C ₂ O ₄)	>80 [64]
Synthetic brine	-	Al precipitation (Al–Ca alloy and NaCl)	94.6 [65]

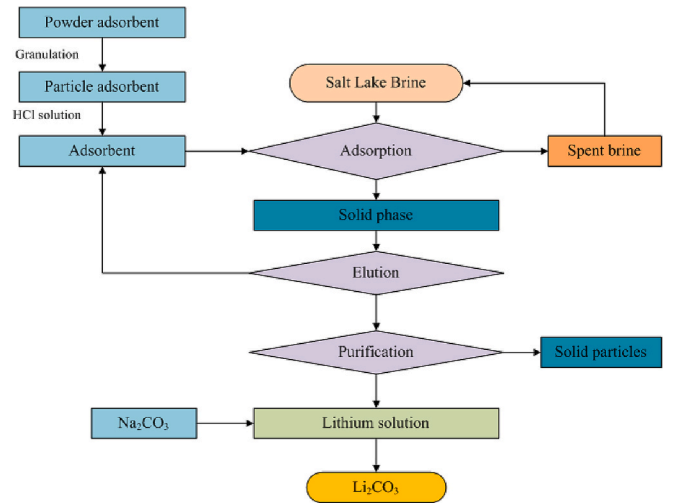


Fig. 6. Workflow diagram of a primary adsorption method of lithium recovery (redrawn from [38]).

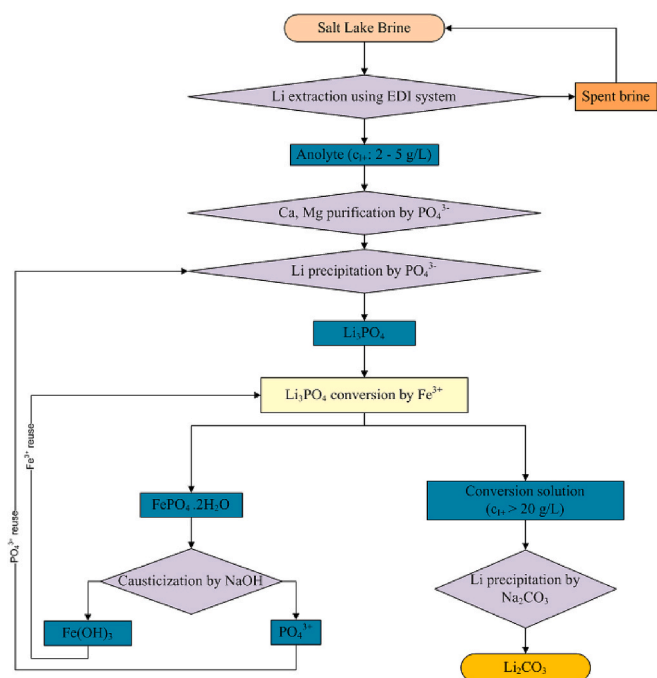


Fig. 7. Workflow diagram of a primary electrochemical method of lithium recovery (a concept from [67]).

applicability of Li by enhancing its capacity for storage, cyclic stability, and ion preference [31].

For Li extraction, Kanoh et al. were the pioneers of the electrochemical method [68]. Using a variety of metal chloride solutions, they investigated the system in which MnO_2 served as the working electrode. The working electrode in an electrochemical ion pump (EIP) exhibits the unique characteristics of ion-sieves. The device's electrochemical insertion showed remarkable efficiency and significant applicability in Li extraction from brines. The primary goal of selective EIP is to recover Li^+ from brine through extraction. Even though electrochemical Li extraction shows promise, the most crucial component is the availability of electrodes with desirable qualities such as superior preference, competing Li capacity, durability, and energy efficiency. Many researchers are working to enhance electrochemical Li extraction devices, and the most current discoveries are discussed in the latter portion of 5.2.5.

3. Brief overview of LBC methods for lithium extraction from Salt Lake brine

Significant developments in membrane-based Li extraction technologies, currently categorized under LBC, have been reported in recent years [69–72]. Some of these approaches can be categorized into nanofiltration (i.e., pressure-driven) and electrodialysis (i.e., electrical potential-driven). These methods combine mobility and affinity to make membranes that selectively separate ions, intending to make Li extraction easier. Future studies should focus heavily on fundamental and engineering solutions for Li extraction from high Mg/Li ratio brine, as this is a particularly challenging brine type with valuable metal deposits.

This technology is promising because of the benefits of improved energy consumption, simple controls, high separation rates, and the continuity of the process. Jiang et al. reported a cost-effective and environmentally friendly bipolar membrane electrodialysis process, where Li_2CO_3 was obtained in powder form (98% purity) using a Na_2CO_3 precipitation treatment [73]. Even though the nanofiltration process proved successful in laboratory testing, it failed during the pilot test. Therefore, it is still an emerging technology that has yet to become commercially viable [1]. Selective recovery of Li over Mg is made

difficult by the high Mg/Li ratio in brine.

Fig. 8 shows the basic workflow of Li extraction from the Salt Lake brine with a high Mg/Li ratio. After using sequential evaporation to enrich Li in brine, the enriched brine is pumped for solar-powered evaporation to precipitate NaCl. The brine's Li concentration can be enriched to as much as 4–5 g/L through evaporation after the KCl production stage. The membranes in ME reduce solvent loss, making liquid-liquid extraction and ME effective methods for separating and enriching Li in a single step. Oftentimes, the resultant product is LiCl_2 . It is possible to separate Mg^{2+} and Li^+ via adsorption, electrodialysis, nanofiltration, or any combination of these three methods. The additional concentration of the Li-rich brine is achieved by using FO, RO, evaporation ponds, or a combination of these methods. The addition of Na_2CO_3 causes the generation of Li_2CO_3 to conclude. Table 3 presents the process stages of the Li extraction technologies based on membranes.

Nanofiltration is a widely used technique to extract Li from sea water, Salt Lake, and geothermal brine sources. The method employs steric hindrance and the Donnan exclusion mechanism to separate Li^+ . This technology is fully mature and has a separation factor of 2.6–10.4 for Li^+ over Mg^{2+} . While it has a low carbon footprint, it is hindered by issues like membrane fouling, high capital expenditure (CapEx), and operational expenditure (OpEx) [89–91]. Besides, supported liquid membrane utilizes solvent-impregnated membrane for selective ion transportation, achieving >95% Li extraction from seawater or geothermal brine with a low carbon footprint and high selectivity. However, it has limitations, such as organic solvent leakage and the need for chemical reagents for desorption [92,93]. Additionally, an ion-imprinted membrane can selectively adsorb ions by chelating to extract Li from seawater or geothermal brine. This laboratory-stage technology provides a separation factor of Li^+ over Na^+ , K^+ , Ca^{2+} , and Mg^{2+} of 4–51 and adsorption capacity of 4–50 mg/g. Although this method has high selectivity, diminutive adsorption ability and heavy reliance on chemical reagents for desorption hinder subsequent stage development [94,95]. Moreover, the ion-sieve membrane utilizes a selective adsorption mechanism to extract Li ions from seawater or geothermal brine

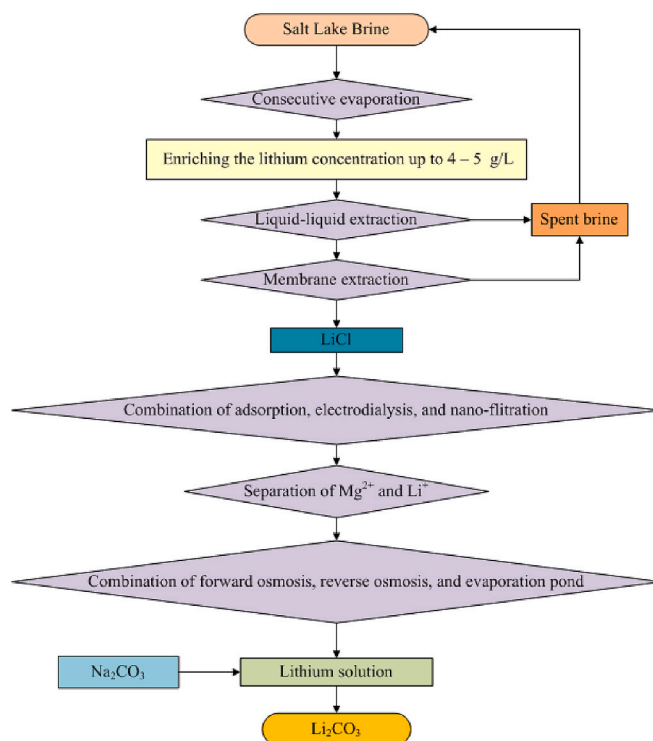


Fig. 8. Workflow diagram of a primary membrane method of lithium recovery (a concept from [71]).

Table 3
Lithium extraction technologies based on membranes.

Process Stage	Membrane Technology	Driving Force	Expected Characteristics
Separation	Membrane with integrated Li-ion sorbents [74,75]	Concentration	1. Superior cycle stability and Li ⁺ adsorption capability 2. Powder loss and pressure drops are minimal, and the powder may be successfully recycled 3. Reduced energy use and minimal impact on ecosystems
	Electrodialysis [76–78]	Electric-driven	1. Superb current efficiency and perm-selectivity 2. Reduced power requirements and a negatively charged solid layer 3. Skin and membrane matrices have a strong attraction to one another
	Nanofiltration [79,80]	Hydraulic pressure	1. Superior hydrophilicity and permeability selectivity 2. Positivity charged, low-cost, and low-resistance
Concentration	Forward osmosis [81,82]	Osmotic pressure	1. Low acceptance and hydrophilicity 2. Low structure parameters and moderate mechanical strength
	Reverse osmosis [83,84]	Hydraulic pressure	1. Strong repulsion and flux 2. High mechanical strength 3. Low energy consumption and resistance
Separation & Concentration	Membrane distillation [85,86]	Vapor pressure	1. A low-priced, highly water-repellent membrane 2. Scaling and wetting resistance
	Membrane extraction [87,88]	Concentration	1. Connective porous membranes with a high ion flux 2. High stacking density and resilience to solvents

through intercalation. This experimental technology in the lab demonstrates a selectivity for Li⁺ over Na⁺, K⁺, Ca²⁺, and Mg²⁺ ranging from 99 to 5312, coupled with an adsorption capacity varying between 10.3 and 27.8 mg/g. The ion-exchange membrane has high selectivity and adsorption capacity but requires chemical reagents for desorption and can experience inorganic particle leakage [96,97].

Membrane distillation and membrane crystallization technology are used to extract Li from seawater, Salt Lake brine, and geothermal brine. This method uses a hydrophobic membrane to generate a vapor pressure gradient. It has been successfully implemented on a pilot scale with a recovery rate of over 73%. MD is a thermal-based separation process that uses a hydrophobic membrane to separate water vapor from a liquid phase. Thus, this leaves behind the concentrated brine solution. The driving force for this process is the vapor pressure difference across the membrane, which is maintained by creating a temperature gradient between the feed solution and the permeate side [69,98]. To enhance freshwater recovery and concentrate the brine further, MDC combines the principles of membrane distillation with crystallization. This process also utilizes a hydrophobic membrane to separate water vapor from the brine. However, in MDC, the concentrated brine from MD is further cooled to induce crystallization of salts, typically Li salts in the context of Li extraction from Salt Lake brines. The crystallization process further reduces the volume of the brine and increases the concentration of lithium salts, facilitating their recovery [98,99]. Recovering freshwater from spent brine in Li extraction from Salt Lake brines is made effective via membrane-based LBC technologies like MD and MDC using various energy sources [69,100]. On the other hand, NF and ED methods are used in various sectors, including water treatment and desalination. However, these methods are rarely used to recover freshwater from the spent brine during Li extraction from Salt Lake brines [85]. However, issues related to membrane wetting caused by fouling and salt separation remain a critical concern [101,102]. Selective Electrodialysis is a technology that uses electrical potential difference as a driving force to extract Li ions from seawater, Salt Lake brine, and geothermal brine. It has advanced to a pilot-scale implementation with a recovery rate of over 95%. This technology is eco-friendly and has a high selectivity of monovalent ions. However, it still faces some limitations, like membrane fouling and high energy costs, especially with increasing salinity [103,104]. Besides, permselective exchange membrane capacitive deionization uses electrostatic adsorption to extract Li from seawater, Salt Lake, and geothermal brine. This high-efficiency and eco-friendly technology is still in the laboratory stage and has recovered over 83%. Nonetheless, low desorption efficiency remains a limitation of this method [105,106].

4. Comparative analysis of lithium extraction methods

Table 4 summarizes the comparative analysis of Li extraction methods regarding energy consumption, cost, high Mg/Li ratio relevancy, scalability, environmental impact, economic viability, separation efficiency, and their significant setbacks.

5. Recent advancement in ion-sieve adsorption and electrochemical methods

5.1. Ion-sieve adsorption

Because of their low cost, efficiency, limited energy usage, and ecological friendliness, ion-exchange technologies are growing in popularity. Since its synthesis in 1971, ion-sieve oxide has been the subject of increasing interest because of its unusual properties and powerful adsorption abilities [116,117]. An inorganic substance known as an ion-sieve adsorbent is prepared by first adding template ions to an inorganic substance via a redox or ion-exchange reaction and then heating the chemical to obtain the compound oxide. Eluent flushes the template ions out of the crystal, leaving behind empty sites. Therefore, the inorganic material with regular crystal sites developed could only accommodate ions with a smaller or equal ionic radius to the target ion. Template ions can effectively adsorb target ions despite the presence of other ions due to their screening and memory effects. An ion-sieve effect is another name for this phenomenon. This process is represented in Fig. 9.

5.1.1. Li ion-sieve (LIS)

Li extraction from brine while leaving behind the other alkali and alkaline-earth metal ions, a Li-ion sieve (LIS) is utilized. The approach is advantageous due to its low toxicity, excellent selectivity, remarkable regeneration performances, and high Li absorption capacity [119–121]. This approach, which entails the systematic design and manufacture of mesoporous materials with extremely selective Li-ion active sites, is thriving even at low concentrations of Li, which are typical of natural brines [109,122]. Adsorbents made of Mn and Ti have attracted much interest recently due to their potential to extract Li from brine selectively. Spinel Li—Mn oxide (LMO) outperforms Li—Ti oxide (LTO) in adsorption capacity and Li selectivity. In contrast, LTO boasts lengthy recyclability and negligible dissolving loss. There are some other inorganic hydrous oxide ion sieves, such as LiSbO₃, LiNbO₃, LiMg_{0.5}Mn_{1.5}O₄, LiAlMnO₄, and LiFeMnO₄ [123–125]. Table 5 presents the adsorption capacity of various adsorbents. Ion-sieve issues include but are not limited to metal dissolution, filtration particle fragmentation, capture of fragmented particles, expensive cleaning and regeneration procedures,

Table 4
Comparison of lithium extraction methods.

Contents	Solvent Extraction	Precipitation	Adsorption	Membrane	Electrochemical
Energy consumption	Low in energy consumption, however, organic polymerization causes a reduction in process efficiency [38]	Minimal energy usage [107]	Minimal energy usage [1].	Minimal energy consumption among all other methods with improved energy consumption, simple controls, high separation rates, and the continuity of the process [1,73,107]	Low energy consumption [31]
Cost	High capital expenditures [1]	Relatively low-cost and straightforward [50,51]	Low initial cost yet high operating cost method [107]	Mostly cost-effective, but high costs associated with manufacturing and regenerating different membranes [71,107]	Not very cost-effective
Relevancy for high Mg/Li ratio	Production costs would be too high when the Mg/Li ratio is too high [36].	Generally, it is not suitable for high Mg/Li ratios, yet excellent Li recovery was shown using aluminate and novel Mg precipitants from brines with high Mg/Li ratios [28,108].	Even at low Li concentrations, Li-ion-sieve shows excellent selectivity and adsorption towards Li-ions [109].	Selective recovery of Li over Mg is nevertheless hindered by the brine's high Mg/Li ratio [71].	Good response in terms of high Mg/Li ratio [110,111]
Scalability	Limited to laboratory-scale study due to technical and cost constraints [1]	Precipitation necessitates raising the temperature, which is energy-intensive and challenging on a wide scale [33]	Accessible for large-scale use [1]	Although the nanofiltration process is successful in laboratory testing, it failed in the pilot test due to its low resistance [1,71].	Yet to be proven in the pilot scale and large-scale implementation [31,111]
Environmental impact	During organic polymerization, environmental pollution occurs [38].	Ecology friendly. However, using chemical additives makes it harsh on the environment [33,112].	Environment-friendly	Environmentally friendly bipolar membrane electro dialysis process [73]	Environment-friendly [31]
Economic viability	Currently unsuitable for industrial use [38]	Commercially favorable [33]	Aluminium salt adsorbents are industrially used, yet low adsorption capacities limit their application [47]. High separation efficiency than other methods [1]	Emerging technology but yet to be commercially viable [71,85]	It still needs to be proven in commercial viability [111,113].
Separation efficiency	Separation is difficult when components with related chemical and physical properties in the solution exist, such as Mg and Li [38,114].	Almost all of the Mg was eliminated, and the yield was 91%, while the purity of the Li_2CO_3 was 99.7% [28].		High separation rates [1]	Highest separation efficiency among other methods [31,115]
Major setbacks	Low separation efficiency and scalability issues	Significant loss of Li ranging from 20% to 30% [55]	A significant discrepancy exists between the theoretical and actual adsorption capacity of adsorbent dissolution throughout the elution process [47].	Scalability and high Mg/Li ratio [1,71]	More work needs to be done to increase the field applicability of Li by enhancing its storage capacity, cyclic stability, and ion selectivity [31].

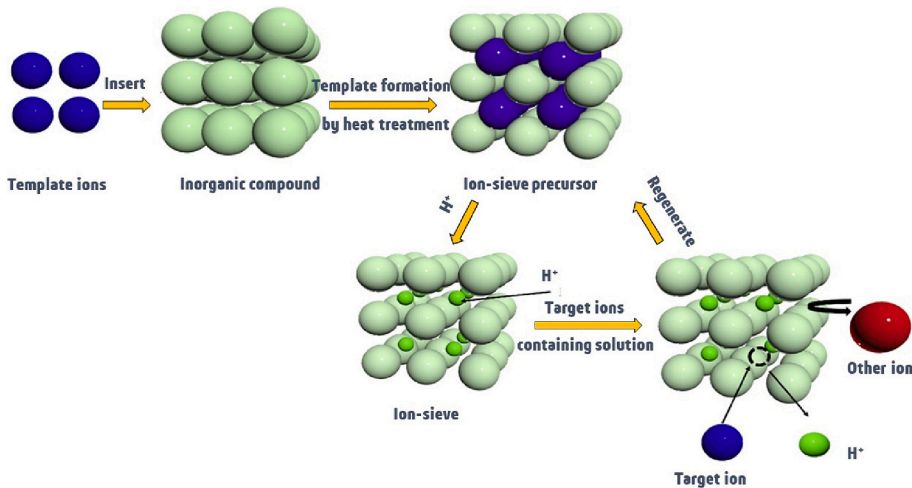


Fig. 9. Atomic depiction of ion-sieve preparation and its effect [118].

Table 5

Adsorption performance of adsorbents used for Li recovery [7].

Adsorbents	Li Source	Condition	Adsorption Capacity (mg/g)
Spherical Poly Vinyl Chloride (PVC) MnO ₂	Brine	–	23.46
λ-MnO ₂	Brine	72 h at pH 13	30.9
MnO ₂ ·0.5H ₂ O	Brine	pH 10	39.6
MnO ₂ ·0.5H ₂ O	Li-enriched seawater	–	37
Granular H ₄ Mn ₅ O ₁₂	Salt Lake brine	–	17.2
Porous H ₄ Ti ₅ O ₁₂ nanofibers	Simulated brine	–	59.1
Li _{1.33} Mn _{1.67} O ₄	Natural brine	–	>50
Li ₄ Ti ₅ O ₁₂ nanotubes	Brine	–	39.43
Yolk-shell structured C@Li ₄ Ti ₅ O ₁₂	Brine	12 h at pH 13.1 with a specific surface area of 185.66 m ² /g	28.46
H ₂ TiO ₃	Salt Lake brine	–	24.5
H ₂ TiO ₃	Brine	2 g/L Li ⁺ , at 30 °C for 24 h	76.7
H ₂ TiO ₃	High Mg/Li ratio brine	pH 8.8 at 25 °C for 24 h	36.34
Layered H ₂ TiO ₃	Salt Lake brine	–	32.7
Layered H ₂ TiO ₃	Simulated brine	–	40
Iron doped H ₂ TiO ₃	Brine	pH 8.8 at 25 °C for 24 h	34.8
H ₂ TiO ₃ loaded on ceramic foams	Brine	24 h	21
H ₂ TiO ₃ loaded on ceramic foams	Brine	8 h	33.35
Iron doped LiMn ₂ O ₄	Brine	pH 11 for 24 h	30.6
Nanocrystal MnO ₂	Brine	–	16.86
Nanostructure MnO ₂	Salt Lake brine	120 h at 30 °C	62.46

and diminished adsorption capacity due to ion channel obstruction.

5.1.2. Lithium manganese oxide & Lithium titanium oxide

5.1.2.1. LMO. Higher Li affinity is seen in polymorphic forms of Mn (i.e., α, β, γ, λ), and the most favorable Li extraction efficiency is found in -MnO₂ [126,127]. Most LMO ion sieves can be produced by subjecting the respective LMO compounds to an acidic treatment. Sol-gel, hydrothermal, and solid-state processes are all used to make the precursors [34,128]. Furthermore, the efficiency and architectures of the ion sieves are determined by the morphology of the predecessors. High selectivity capacity and unique memory are made possible by the spinel lattice structure of Li-ion sieves. There are two characteristics of the exchange sites' memory impact. Li⁺ has an ionic radius of 0.074 nm, but Na⁺, K⁺, and Ca²⁺ cannot replace them at the exchange site because their ions have a larger ionic radius [129]. The other attribute is the approximate energy of dehydration (ΔG_h[°]), where Mg²⁺ ((ΔG_h[°])_{Mg} = −1980 KJ/mol) having a similar ionic radius of 0.072 nm of Li⁺ ((ΔG_h[°])_{Li} = −475 KJ/mol), yet it can't take the spot of Li⁺ due to the higher energy of dehydration [129].

To create delithiated oxide or Li_{1.6}Mn_{1.6}O₄, Chitrakar et al. used LiMnO₂ as a precursor. Li was extracted from seawater over the course of three days, with a capacity of 40 mg/g and a recovery of over 80% [119]. With just a little NaHCO₃ and HCl, the same results might be produced in just one day. The comparison of the theoretical and practical adsorption capacities of various LMO forms is shown in Table 6.

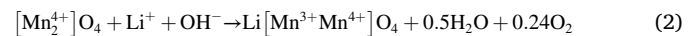
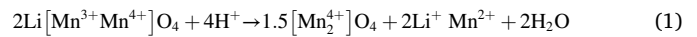
Unlike the typical framework, a Li-Mn-O framework can keep its cubic spinel structure even as Li⁺ is inserted and removed. The extraction mechanism of LMO is shown in Eqs. 1–4.

Table 6

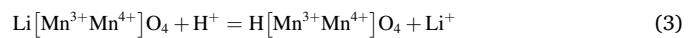
Comparison of the adsorption capacities of various LMO types.

Precursors	Ion-sieves	Theoretical adsorption (mg/g)	Experimental adsorption (mg/g)
LiMn ₂ O ₄	λ-MnO ₂	39.9	1.1 (seawater) [119]
Li _{1.33} Mn _{1.67} O ₄	MnO ₂ ·0.3H ₂ O	59.5	25 (seawater) [119]
			19 (brine) [130]
			63 (brine) [131]
			39.9 (LiCl solution) [132]
			39.3 (LiCl solution) [120]
Li _{1.67} Mn _{1.67} O ₄	MnO ₂ ·0.5H ₂ O	72.8	37 (seawater) [119]
			40 (seawater) [133]
			37.6 (LiCl solution) [10]
			42.4 (LiCl solution) [134]
			28.6 (brine) [134]
			22 (brine) [135]

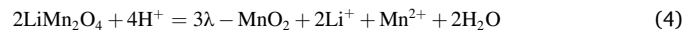
Redox [136].



Ion exchange [137,138].



Surface disproportionation [139].



The dissolution of LMO is the biggest problem, which may create severe water pollution that hinders the field application of LMO. A weak metal-oxygen link makes LMOs chemically unstable, making them challenging to produce and regenerate. Adding metal dopants may enhance adsorbents' stability and Li extraction efficiency.

5.1.2.2. LTO. LTO overcomes the dissolution problem of LMO. The LTO-type LIS had a far more stable molecular structure due to the high Ti—O bond energy. The LTO-type LIS has a much lower Li adsorption rate than the LMO-type LIS. Furthermore, when an electrical potential was applied, this adsorbent was not very helpful in recovering Li from an aqueous solution.

Currently, two types of LTO type LIS are available, such as layered H₂TiO₃ and spinel H₄Ti₅O₁₂. Although LTO-type LISs are in short supply, there is a significant opportunity to advance the development of these water-safe industrial green Li adsorbents. For layered structures, the intercalation/deintercalation mechanism of Li is more straightforward, and layered H₂TiO₃ provides higher selectivity towards Li⁺ than other cations. The selectivity sequence is given in Eq. 5 [38]. The ion-exchange mechanism of LTO is presented in Eqs. 6 and 7 [7]. H₂TiO₃ LIS exhibits excellent Li extraction capacity and adsorption capacity reduction of 10% or less after 100 or more cycles [140].



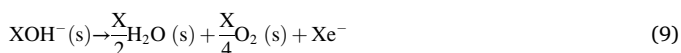
Spinel Ti oxides are another kind of LIS in the LTO family produced from spinel Li₄Ti₅O₁₂ precursors. There is much promise for developing the spinel Li₄Ti₅O₁₂ in Li recovery from aqueous solutions. The stronger Ti—O bond in the analogous LIS (H₄Ti₅O₁₂) results in a larger Li capacity and improved cycle performance than Mn-type LISs. Furthermore, the molecular structure of Li₄Ti₅O₁₂ is identical to that of Li₄Mn₅O₁₂. The Li extraction ability of spinel H₄Ti₅O₁₂ has been the

subject of very few published studies. Traditional solid adsorbents tend to clump together, reducing their adsorption efficiency. The issue was resolved using a series of porous fibrous Ti-based Li-ion sieves prepared via electrospinning and subsequent calcination. The high adsorption capacity of 59.1 mg/g at 25 °C can be attributed to the porous structure promoting Li intercalation/deintercalation [141].

A good adsorbent quality was shown by Li–Al double-layered hydroxide in Li recovery [142–144]. A 7.27 mg/g adsorption capacity was observed for Li/Al double-layered hydroxides produced via coprecipitation in natural Salt Lake brine. After 12 adsorption/desorption cycles, the adsorption capacity is still >7 mg/g, and the Li⁺/Mg²⁺ selectivity is still up to 125 [142]. This adsorption capacity was much lower than that of LMO, but LTO was a good option for the adsorbent since it was inexpensive to produce, easy to fabricate, and did not require the presence of acid or base to undergo regeneration. Jayanthi et al. studied the delithiation of (Li–Al–X) LDHs produced and dried under various circumstances (where X = Cl[−], OH[−], and SO₄^{2−}). Their findings show that post-drying circumstances, anion choice, and interlayer water concentration greatly affect LDH stability [145].

5.1.3. Lithium intercalation/deintercalation mechanisms

5.1.3.1. Redox Mechanism. In 1981, Hunter showed that the intercalation/deintercalation of Li in LiMn₂O₄ was a pair of redox reactions [136]. In this reaction, Mn III is disproportioned in an acidic environment. This process transforms only the surface Mn III into Mn II and Mn IV. λ-MnO₂, which has the most favorable Li extraction efficiency, is obtained from Mn IV with a tetrahedral position of 8a vacant. The cathodic reaction of MnO₂ at an alkaline electrode follows a mechanism similar to that postulated by Kozawa in 1966. [146]. Li-ion mobility and electron mobility in the λ-MnO₂ structure are both unrelated. Alternating Mn III and Mn IV distribution in spinel structure make electron migration possible. Ooi et al. in 1989 divided the Li intercalation process into two steps, which have been described in Eqs. 8 & 9 [147].



In the above equations, X represents the fraction of solid-state Mn atoms replaced by inserted Li atoms. This is meant to symbolize the particle's exterior. The reduction of Mn IV to Mn III and the incorporation of Li into the tetrahedral void in the λ-MnO₂ framework are depicted in Eq. 8. As seen in Eq. 9, surplus positive charge is transferred to the surface of λ-MnO₂ while hydroxide ions undergo oxidation in the aqueous phase. The redox mechanism helps explain why Li-ion sieves lose some adsorption capacity when reused. However, the redox mechanism does not account for the rise of ion sieves' adsorption capacity as solution pH increases.

5.1.3.2. Ion-exchange mechanism. Shen et al. 1986 proposed intercalation/deintercalation of Li in LMO type LIS following the reaction below in Eq. 10 [139].



In contrast to the redox mechanism, this proposes that the tetrahedral sites at position 8a in LMO type LIS are protonated (i.e., hydrogen atom to another molecule) to transfer a proton rather than empty. In 2003, Koyanaka et al. analyzed the link between the composition and adsorption capacity of different spinel MnO₂ compounds. They demonstrated that the adsorption capacity of Li-ion was directly related to the hydrogen ion concentration [148]. According to these findings, MnO₂'s selective adsorption ability is due to the ion exchange interaction between Li-ions and protons rather than the ion-sieve effect. Crystalline Mn III and Mn IV sites are unaffected by the Li⁺/H⁺ ion exchange, as demonstrated by this process. Ion sieves' adsorption capacity

increases as solution pH rises, and this mechanism can explain the reason.

5.1.3.3. Composite mechanism. The composite mechanism is based on the redox and ion exchange mechanism. In 1991, Ooi et al. categorized Li insertion sites into three types: redox-type sites, Li⁺ specific and nonspecific ion-exchange sites for a better comprehension of Li insertion sites [149]. Depending on the preparation method, each site's relative abundance can vary. The most important factor influencing the formation of the insertion site is the oxidation state of Mn in the heat treatment precursor. Feng et al. 1992 inferred that the spinel precursor with trivalent Mn provides a redox site, whereas if it contains only tetravalent Mn, it gives an ion-exchange site [150]. The formation of ion-exchange sites occurs at temperatures below 500 °C, while redox sites occur at higher temperatures. However, this composite mechanism is too complex to validate experimentally despite its ability to explain the intercalation/deintercalation of LMO theoretically.

5.1.4. LMO formulation

The industry does not use LMO in its standard powder form because of the recovery problem following Li⁺ adsorption and the large amounts of powder required. It has a significant energy requirement in column operation as well. Therefore, understanding LMO forming methods requires detailed investigation. Three conventional methods of LMO formulation, such as granulation, membrane formation, and foaming, have been discussed below.

5.1.4.1. Granulation. The organic polymers in LMO powders link to generate microspheres of varying diameters. This makes ion-sieve mechanically robust and flexible for use in industrial column applications. The adsorption capacity of ion sieves reduces after granulation because the active sites are covered. Xiao et al. in 2012 constructed a 2–3.5 mm-diameter spherical PVC-MnO₂ ion sieve [151]. The adsorption capacity, selectivity, and regeneration performance of this type of adsorbent were all superior. The interparticle diffusion mechanism governs the Li adsorption by estimating the pore diffusion and mass transfer coefficients. Spherical PVC-MnO₂ is a good candidate for the industrial application of Li extraction from Salt Lake brine and seawater.

The granulated polyacrylamide (PAM) MnO₂ ion-sieve developed by Xiao et al. has a diameter of 0.3–0.7 mm. The experiment demonstrated that Li's highest equilibrium adsorption capacity was 2.68 mmol/g at 30 °C [151]. Hong et al. in 2015 immobilized the adsorption of alpha-alumina beads (AABs) to extract Li. When tested for Li⁺ adsorption capacity in seawater, this composite material performed admirably (8.87 mg/g), retaining <2% of its initial capacity after 15 use cycles [152]. In 2018, Hong et al. developed an intensely porous, surface-optimized LMO/Al₂O₃ composite [153]. This material's increased surface area and porous structure allowed it to display the same Li⁺ adsorption capacity as the related powder. However, the crystallinity of the LMO spinel structure was reduced by an excessive amount of Al₂O₃, leading to Mn dissolution during regeneration.

5.1.4.2. Membrane formation. In contrast to granulated adsorbents, membrane adsorbents offer the advantage of convenient construction for adsorption modules through stacking or winding membranes. The design is robust enough for uninterrupted use in an industrial setting. Being costly, complicated, and not environmentally friendly, membrane formation has its disadvantages. Spinel Mn oxide membranes were created by Umeno et al. in 2022, and the membrane precursors with varying amounts of PVC and LMO were studied [96]. The outer surface area was shown to be crucial in regulating the adsorption rate, and a linear relationship between LMO content and adsorption rate was found.

Umeno et al. developed a novel adsorption cell that uses a membrane-type adsorbent to achieve parallel seawater flow. Li extraction from seawater natural flow benefited from this. A set of PVC-

$\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$ compounds was produced by Zhu et al. in 2014 [74]. They proposed to prepare the membrane with 10 wt% of PVC and 15 wt % of $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$. Based on the results of these tests, it appears that membrane-type adsorbent can be recycled for several Li recovery cycles without suffering from appreciable adsorption capacity loss.

5.1.4.3. Foaming. Foaming has better mechanical qualities, higher Li selectivity, and higher regeneration efficiency than other methods. However, its adsorption capability is much lower than that of the powders. Foam's components, in particular, gradually degrade with repeated adsorption due to its flimsy internal skeleton. Polyurethane templates were used by Ma et al. to create LMO foam in 2011 [154]. Their findings demonstrated the presence of a uniform 3D interpretive network in the foam-type adsorbent, which had a Li adsorption ability of 1.4 mg/g in salt water. However, after multiple adsorption cycles, the pith support and nanoparticles become disorganized and produce harmful environmental byproducts.

In 2012, Han et al. combined foaming drops in oil with agar gelation to create LMO's spherical ion-sieve foams with a final size of a few millimeters [155]. The maximum Li adsorption capacity could increase to 3.4 mg/g in seawater. After 5 adsorption cycles, the retention of adsorption capacity was almost 95%. The flexible LMO/PVA composite foam was developed by Nisola et al. in 2015 [156]. PVA acted as a binder and support, and its high hydrophilicity made it an ideal material for enhancing adsorbents' kinetic characteristics. Li could be extracted from secondary sources using this material without the need for any further energy-intensive operations. Nonetheless, it has a similar problem of lower material strength to other foam-type adsorbents.

5.1.5. LMO type LIS synthesis

Predominantly, precursor preparation and acid treatment are the two main steps in synthesizing LMO-type LIS. Precursors are often obtained in a single procedure, however, $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ requires two stages, including heat treatment. This sub-section discusses the preparation of precursors, acid treatment, and doping modification in detail.

5.1.5.1. Precursors preparation. The adsorption capability of LMO-type LIS relies significantly on the mechanism of its precursors. The crystal-line structure of the finished goods, and by extension, the adsorbent's ability to be regenerated, is influenced by the relative amounts of Li and Mn in the starting materials. Precursor synthesis can be described in the soft chemical and solid phase synthesis methods. Table 7 presents some common types of LIS precursors and their preparation methods.

5.1.5.1.1. Soft chemical synthesis method. This process involves dissolving soluble Li and Mn compounds in water to create atomic mixes of essential components. Different methods for preparing LIS precursors use soft chemical synthesis methods such as sol-gel, hydrothermal, molten-salt, and other methods. These methods have been discussed below.

(i) Sol-gel Method

Nanoparticles with excellent purity and uniform phase distribution can be prepared using this technology. Raw ingredients are dispersed in an agglomerated solution to create a gel with a continuous 3D network structure. When the right conditions are met, the result is an aerogel. To produce optimal crystallization of precursors, beginning components are combined at the atomic scale in a multi-component system.

Spinel LiMn_2O_4 powders were produced by the sol-gel technique by Sun et al. in 1997 [157]. It is predicted that the sol-gel method, when applied to acetates containing peroxyacetic acid (PAA), can produce the same outcomes as the solid-state reaction with substantially less heat and time. Seyedahmadian et al. in 2013 created the LiMn_2O_4 using citric acid as a chelating agent by sol-gel method and investigated the influence of the condition of pH, starting components on the structure,

Table 7
Common precursors and their metal sources with the preparation method [118].

Precursors	Metal Sources	Preparation Method
LiMn_2O_4	$\text{Li}_2\text{CO}_3 + \text{MnO}, \text{MnO}_2 \text{ \& } \text{Mn}_3\text{O}_4$	Solid phase method
	$\text{Li}_2\text{CO}_3 + \text{MnO}_2$	Rheological phase-assisted microwave method
	$\text{LiNO}_3 + \text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Sol-gel method
	$\text{LiCl} + \text{MnO}_2$	Molten-salt method
	$\text{LiNO}_3 + \text{MnSO}_4$	Co-precipitation method
	$\text{LiNO}_3, \text{Li}_2\text{CO}_3, \text{LiOH}, \text{LiCl} + \text{Y-MnOOH}$	Molten-salt method
	$\text{CH}_3\text{COOLi} + \text{Mn}(\text{CH}_3\text{COO})_2$	Microemulsion method
	$\text{Li}(\text{CH}_3\text{COO}) \cdot 4\text{H}_2\text{O} + \text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Spray-drying method
	$\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O} + \text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$	Sol-gel method
	$\text{CH}_3\text{COOLi} + \text{Mn}(\text{NO}_3)_2$	Solid phase method
$\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$	$\text{LiNO}_3 + \beta\text{-}, \text{Y-MnO}_2$	Solid phase method
	$\text{LiOH} \cdot \text{H}_2\text{O} + \text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Sol-gel method
	$\text{Y-MnOOH} + \text{LiOH}$	Hydrothermal method
	$\text{KMnO}_4 + \text{MnCl}_2 + \text{LiOH}$	Hydrothermal method
$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	$\text{LiOH} + \text{Mn}(\text{NO}_3)_2$	Hydrothermal method
	$\text{LiOH} + \text{Mn}_2\text{O}_3$	Hydrothermal method
	$\text{Y-MnOOH} + \text{LiOH}$	Microwave hydrothermal method
	$\text{LiOH} + \text{Mn}(\text{NO}_3)_2$	Microwave hydrothermal method
$\text{Li}_4\text{MnO}_{12}$	$\text{LiOH} + \text{Mn}(\text{NO}_3)_2$	Hydrothermal method
$\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$	$\text{LiOH}, \text{Li}_2\text{CO}_3 + \text{MnCO}_3$	Solid phase method
$\text{Li}_x\text{Mn}_2\text{O}_4$	$\text{MnO}_2, \text{Mn}_2\text{O}_3, \text{MnO} + \text{LiOH}, \text{Li}_2\text{CO}_3$	Sol-gel method

solvents, calcination temperature, the molar ratio of citric acid to metal ions, calcination temperature, morphology and purity of oxides and found that optimum pH was around $4 \leq \text{pH} \leq 6$ and molar ratio of the chelating agent as 1 [158]. Spinel ($\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) was made using a simple sol-gel technique by Chu et al. [159]. They blended a specific stoichiometric ratio of $\text{LiOH} \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in DIW by incorporating citric acid into the solution at 75 °C and adding ammonia to get the pH down to 6.5. (A stoichiometric mixture is an ideal mixture of fuel and oxidizer, which doesn't contain the excess remaining (i.e., the total consumption of fuel and O_2 in the air) after the combustion.)

(ii) Hydrothermal Method

Hydrothermal processing allows for uniform mixing of raw materials with less effort and expense due to its user-friendliness and lack of specialized machinery. It also has a unique homogeneous nucleation mechanism, which helps to create a new compound by this method [160]. In 2000, Chitrakar et al. calcined hydrothermally synthesized orthorhombic LiMnO_2 to produce $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [119]. The interrelated ion sieve ($\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$) provided a theoretically maximum Li adsorption capacity of 72.8 mg/g.

Changing the operating parameters of hydrothermal processes yields different morphologies, such as nanorods, nanowires, cubic forms, and spheres, that have a wide range of effects on adsorption behavior. LiMn_2O_4 with a diameter of $<0.2 \text{ }\mu\text{m}$ was synthesized by Xiao et al., and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, using Li-brinessite ultrafine fiber as a precursor, was prepared by Zhang et al. [134,161]. Due to its own heating mechanism, the microwave thermal process can address the issues of insufficiently uniform temperatures and prolonged reaction times. Using Y-MnOOH and LiOH at 120 °C, Chitrakar et al. in 2002 synthesized semi-crystalline orthorhombic LiMnO_2 [162]. In contrast to the more common cubic shape, the shape of the resulting sample is needle-like.

(iii) Molten-Salt Analysis and Other Methods

Ceramic materials with high product purity, easy operation, and

reactivity to high-concentration reactants can be obtained using this technique [163]. However, some safety risks have hampered the large-scale industrial implementation of this method. Using molten salts with a low melting point as reactants and solvents, scientists developed LMO-type LIS precursors between 1999 and 2010 [164–167].

Single crystals of octahedral LiMn_2O_4 and orthorhombic LiMn_2O_4 in the form of tubes and rods were produced by Yang et al. [165]. Helan et al. employed a eutectic mixture of LiCl and MnO_2 salt to create LMO powders [164]. The superior physical qualities of the manufactured good make this a practical and affordable option for wide-scale deployment.

Wu et al. produced spinel LiMn_2O_4 using a spray drying method, resulting in finely distributed particles with narrow distribution and excellent crystallization [168]. Co-precipitation of Li and Mn in stoichiometric proportions from LiNO_3 and MnSO_4 using stearic acid in tetra methylammonium hydroxide was utilized by Nagash et al. to create LiMn_2O_4 [169]. Sinha et al. prepared submicron size- LiMn_2O_4 by microemulsion method where particle size was bound to be <200 nm [170].

5.1.5.1.2. Solid phase synthesis method. In order to make LMO-type LIS precursors, Li and Mn salt are typically mixed in precise stoichiometric ratios, and then the mixture is calcined at an appropriate temperature for a proper period of time. Li_2CO_3 and several Mn oxides (i.e., MnO , MnO_2 & Mn_3O_4) were combined by Hunter et al. to create LiMn_2O_4 at 850°C temperature in the air [136].

By heating a eutectic mixture (which is defined as the definite composition of at least two solid components that undergo a phase transition to a liquid state at an appropriate temperature) of $\text{CH}_3\text{COOLi} + \text{Mn}(\text{NO}_3)_2$, Takada et al. were able to make well-crystallized powder of $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ [171]. At a temperature of 400°C , Yang et al. used LiNO_3 and Mn sources (i.e., β -, γ - MnO_2) H^+ from Li-brinssite Mn oxides hollandite to obtain $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ spinel [172].

Spinel $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ was developed by Chitrakar et al. by heating orthorhombic LiMnO_2 , -MnOOH or Mn_2O_3 , and $\text{LiOH.H}_2\text{O}$ to 400°C in the air from a lower crystallization temperature of 120°C by steam operation [173]. Similarly, the adsorption capability of the LIS $\text{MnO}_2.0.5\text{H}_2\text{O}$ is 33 mg/g.

However, in cases of uniform contact and insufficient raw materials, the resulting products are enormous and unevenly distributed, necessitating a lengthy reaction time and increased energy expenditure. The standard solid phase process is simple and easy to apply. To overcome these shortcomings, auxiliary methods are used. Highly scattered stoichiometric and non-stoichiometric $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel was synthesized by Kosava et al. from various Mn compounds (i.e., MnO_2 , Mn_2O_3 , MnO) and Li compounds (i.e., LiOH , $\text{LiOH.H}_2\text{O}$, Li_2CO_3) by a mechanochemical method [174]. The study unveiled that temperature and Li concentration significantly impacted the composition and lattice constant of the final products.

Improvements in both reaction duration and effectiveness during preparation can be attributed to the use of microwave combustion. In 2008, Cui et al. used rheological phase-assisted microwave synthesis to speed up the practice of LiMn_2O_4 [175]. Pure LiMn_2O_4 spinel powder was synthesized at 750°C , and the resulting powders were more homogeneous in shape and size than those produced using more traditional solid-phase samples.

5.1.5.2. Acid treatment. Ion sieves are generated by subjecting the precursors to an acid treatment. The standard acid treatment removes Li while the spinel structure is preserved. Eq. 11 explains the process reaction.



There is no denying that Mn dissolves in acid. Mn dissolution rate was 4% for MnO_2 produced by Shen et al. and 2% for $\text{MnO}_2.0.3\text{H}_2\text{O}$ synthesized by Xiao et al., both in 0.5 mol/L HCl solution [130,139].

Using a 3% Mn dissolving rate, Wang et al. synthesized $\text{MnO}_2.0.5\text{H}_2\text{O}$ [10]. The dissolution of Mn poses a danger to the environment and shortens the lifespan of the adsorbent by destroying the spinel structure.

Gao et al. prepared $\text{MnO}_2.0.5\text{H}_2\text{O}$ and proposed the mechanism of Mn dissolution [176]. Trivalent Mn loses one electron in the bulk phase, but tetravalent Mn can pick it up from the surface in an acidic environment. After absorbing enough electrons, tetravalent Mn dissolves simultaneously as bivalent Mn.

5.1.5.3. Doping modifications. The LMO stability is diminished, and the efficiency with which Li-ions can intercalate because of the Jahn-Teller effect (loss of symmetry and energy in a non-linear molecular system is caused by geometric distortion) caused by Mn^{3+} , which renders the octahedral MnO_6 structure to be deformed [177,178]. The breakdown of Mn is likewise greatly accelerated. Doping adjustments proposing the replacement of Mn^{3+} with other metal ions have been presented as a solution to this problem. Octahedral complexes are notorious for displaying this Jahn-Teller effect-based distortion, in which two axial bonds can be shorter or longer than those of the equatorial bonds.

Doping variations with divalent metals have received increased attention. Li^+ extraction reactions in $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel were studied by Feng et al., who discovered that Li extraction and insertion occurred via an ion exchange type mechanism [124]. Spinel Li-Sb-Mn oxides were created by Chitrakar et al. through the ageing of precipitates formed through the reactions of an aqueous mixture of Mn(II)Sb(V)Cl with $(\text{LiOH} + \text{H}_2\text{O}_2)$ solution, after which hydrothermal treatment was performed at a temperature of 120°C [123]. The exchangeability of Li^+ of the $\text{Li}_{1.16}\text{Sb(V)}_{0.29}\text{Mn(III)}_{0.77}\text{Mn(IV)}_{0.77}\text{O}_4$ reached 5.6 mmol/g.

By using a typical solid phase process, Ma et al. could generate a variety of Li-Sb-Mn composite oxides [179]. The structure, Li extraction, and adsorption capability of this Li-Sb-Mn oxide were highly dependent on the Sb/Mn molar ratio. With an Sb/Mn molar ratio of 0.5 , Li adsorption capacity in acid-treated spinel Li-Sb-Mn oxide was 33.23 mg/g. The Mg(III) doped spinel LMO was synthesized by Tian et al. using a soft-chemical synthesis strategy [180]. This adsorbent has an adsorption capability of 37.4 mg/g, and even after four cycles, the Li content was still $>95\%$.

Chitrakar et al. explored Mg-doped Mn oxides on Mn dissolution during acid treatment and found that Mg-doped samples restrained the Mn dissolution to a great extent [181]. Stability, Li extraction, and adsorption capacity in aqueous solution were studied by Ma et al. for series spinel $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (where $\text{M} = \text{Ni}, \text{Al}, \text{Ti}$, and $0 \leq x \leq 1$) [125]. During acid treatment, the Li extraction ratio in $\text{LiAl}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was high, but the Mn and Al extraction ratios were low, leading to a material with superior Li^+ adsorption capability in the following investigations. Due to significant cell expansion and contraction, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiTi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ failed to exhibit desirable Li extraction and adsorption characteristics.

By heating carbonates of Li and Mn with nitrates of Fe in the air, Chitrakar et al. were able to produce iron-doped liquid metal oxide $\text{Li}_{1.33}\text{Fe}_x\text{Mn}_{1.67-x}\text{O}_4$ [182]. The researchers discovered that when the Fe/Mn ratio rose, the amount of manganese extracted from the HCl solution dropped. The maximum Li extraction with HCl solution was seen with a Fe/Mn ratio of 0.1 after calcining the precursor at 450°C . However, the mechanism of doping modifications on adsorbent regeneration ability requires attention for further research.

5.2. Electrochemical method

Using an electrochemical process for Li extraction has great promise for enhancing traditional methods. According to E. J. Calvo, ion-pumping mixing entropy cells and electro dialysis are used in the electrochemical extraction of Li [66].

A direct correlation exists between the efficiency and capacity of Li extraction, the design of electrochemical cells, and the development of

electrode materials in Li recovery systems. Recent developments in electrode materials and efficiencies in electrochemical extraction systems are the focus of this section.

5.2.1. Electrode materials

One electrode material for inserting Li and another for capturing negative ions are theoretically required for efficient electrochemical extraction of Li from seawater/brine.

Table 8 summarizes the common electrode materials. Previously Li iron phosphate (LiFePO_4) (i.e., $\text{LiFePO}_4/\text{FePO}_4$; $\text{LiFePO}_4/\text{Ag}$) and Li manganate (LiMn_2O_4) (i.e., $\lambda\text{-MnO}_2/\text{Ag}$; LMO/Zn ; $\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$; $\lambda\text{-MnO}_2/\text{AC}$; $\text{LiMn}_2\text{O}_4/\text{Ppy}$) had been used as cathode material [111].

However, in recent studies, it has been found that in terms of capacity and cycling stability, multicomponent doping Li cathode shows better performance. Nickel hexacyanoferrate (NiHCF), which is typically employed as a counter electrode or anode material, is used to prevent the passage of cations other than Li ions. LMO was used as a Li capture electrode, whereas NiHCF was used as a Li repulsive electrode, and Palagonia ran tests on the system with varying component and flow rates. Fig. 10 shows that NiHCF allows using seawater and Atacama

Table 8
Summary of electrode materials.

Electrode materials	Summary
$\text{LiFePO}_4/\text{FePO}_4$	LiFePO_4 solution has an insertion capacity of 41.26 mg/g at 1 V, which is 93.78% of its theoretical value.
$\text{LiFePO}_4/\text{Ag}$	In a simulated brine (converted from Na-rich solution (Li: Na = 1:100) to Li-rich solution (Li: Na = 5:1), it has an energy consumption (EC) of 144 Wh/Kj Li. However, this one needs better performance in terms of cost and stability.
$\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$	Using simulated brine, $\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ has an EC of 18 Wh/mol Li^+ and Li extraction capacity (LEC) of 22 mg/g, whereas the usage of simulated concentrated seawater has an EC of 18.6 Wh/mol Li^+ and LEC of 21 mg/g.
$\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Ag}$	In a simulated brine, $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Ag}$ has an EC of 2.6 Wh/mol Li^+ , LEC of 10.83 mg/g, and product purity (PP) of 96.4%.
$\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_4/\text{Ag}$	Using simulated brine, $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_4/\text{Ag}$ has an EC of 1.32 Wh/mol Li^+ , 8.74 mg/g LEC, and product purity (PP) of 98.14%.
$\lambda\text{-MnO}_2/\text{Ag}$	Using simulated brine, $\lambda\text{-MnO}_2/\text{Ag}$ has an EC of 3.07 Wh/mol Li^+ , LEC of 10.1 mg/g, and product purity (PP) of 99%.
$\text{LiNi}_{0.038}\text{Mo}_{0.012}\text{Mn}_{1.95}\text{O}_4/\text{Ni}_{0.038}\text{Mo}_{0.012}\text{Mn}_{1.95}\text{O}_4/\text{AC}$	Using simulated brine, $\text{LiNi}_{0.038}\text{Mo}_{0.012}\text{Mn}_{1.95}\text{O}_4/\text{Ni}_{0.038}\text{Mo}_{0.012}\text{Mn}_{1.95}\text{O}_4/\text{AC}$ has an EC of 7.91 Wh/mol Li^+ , LEC of 14.4 mg/g, and product purity (PP) of 97.2%.
$\text{Ppy}/\text{Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4/\text{AC}$	Using simulated brine, $\text{Ppy}/\text{Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4/\text{AC}$ has an EC of 1.41 Wh/mol Li^+ , LEC of 12.84 mg/g, and product purity (PP) of 97.37%.
$\lambda\text{-MnO}_2/\text{BiOCl}/\text{Ppy}$	Using simulated brine, $\lambda\text{-MnO}_2/\text{BiOCl}/\text{Ppy}$ has an EC of 1.007 Wh/mol Li^+ and LEC of 10.88 mg/g.
$\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$	Using Salt Lake brine, $\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ has an EC of 1.41 Wh/mol Li^+ and LEC of 12.84 mg/g.
$\lambda\text{-MnO}_2/\text{LiMn}_2\text{O}_4/\text{Pt}$	Using simulated brine, $\lambda\text{-MnO}_2/\text{LiMn}_2\text{O}_4/\text{Pt}$ has an EC of 23.38 Wh/mol Li^+ and LEC of 75.06 mg/g.
LMO/Zn	As a negative electrode, Zn is relatively cost-effective, with a large extraction capacity and stable redox.
$\text{LiMnO}_2/\text{Ppy}$	Using simulated brine, $\text{LiMnO}_2/\text{Ppy}$ has an LEC of 37.55 mg/g. After over 200 cycles, the EC is 5–10 Wh/mol Li^+ , and the recovery efficiency is almost 50%.

brine instead of clean water in recovery solutions. [183].

Compared to the existing manufacturing technology, this method has the potential to significantly shorten the time needed to generate a high-purity Li-rich solution. Aside from experimental studies, simulation studies on improving the electrode materials, analysis of the process mechanism, and cell configuration will be critical in supporting the commercialization of Li extraction by electrochemistry.

5.2.2. Cell configuration

From research to production, electrochemical Li extraction relies largely on cell arrangement. Three types of intermittently operating cells exist: the 2-electrode cell (without membrane), the 2-electrode cell with membrane, and the 3-electrode cell. There are a lot of potential uses for the flow electrode design in selective electrochemical recovery systems for Li recovery [184].

5.2.2.1. Two electrodes cell (without membrane). Battistel et al. initially charged the electrode by submerging it in a Li-rich brine [106]. At first, a negative current was delivered to the cathode, causing the LFP to absorb the Li^+ in the brine and the Ag electrode to absorb the Cl^- . The counter-current in the recovery solution released the accumulated ions that replaced the brine in the second and third phases. Finally, fresh brine was added to the recovery solution, and the recovery process was restarted. In reality, the procedure for Li extraction involved switching the key and the current direction. This whole scenario has been illustrated in Fig. 11.

5.2.2.2. Two electrodes cell (with membrane). In the electrolytic cell, a constant voltage was used for Li extraction and insertion by Kim et al. in 2018 [185]. The first stage involved the incorporation of Li^+ ions from the source solution into the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ negative electrode; the second step involved the liberation of Li^+ ions from the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ electrode into the recovery solution. The negative electrode used in the first step will be the positive electrode in the second step, and the positive electrode employed in the first step will be the negative electrode in the second step. This method could be used to concentrate Li in a recovery solution after it has been removed from the source solution. Li ions from the brine are adsorbed onto LMO during the discharge process, while chloride ions pass through the exchange membrane and out the opposite side. In order to maintain charge conservation, Zn is also oxidized to Zn ions. The Li-ions are transferred from the LMO to the solution during the charging process, which involves converting the brine to a recovery solution. This whole scenario has been illustrated in Fig. 12.

5.2.2.3. Three electrodes cell. Including a reference electrode in the early phases of a novel electrochemical system is prudent. Using Ag/AgCl as a standard, Lee et al. in 2018 developed an NCM/Ag three-electrode system [186]. The system has no upper voltage limit, and a built-in battery circulator powers the current (± 1). In the first step, Cl^- is retained on the Ag electrode while Li^+ enters the NCM lattice thanks to applying a negative current to the brine. After a predetermined time has passed, the LiCl receiver is inserted after the electrode component is briefly submerged in DIW to flush out any leftover brine. As shown in Fig. 13, the second stage in extracting Li^+ from NCM in LiCl solution involves desorbing Cl^- from Ag.

5.2.3. Materials simulation

Li deintercalation behavior in the olivine system was described in 2008 by Delmas et al. Cooperative structural distortion results from Li deintercalation, which oxidizes Fe^{2+} ions to Fe^{3+} with high charges in the Fe—O bond lengths and O—O bond distances in FeO_6 octahedral [187]. In 2019, Zhang et al. employed density functional theory calculations to illustrate the interplay between the electronic conductivity, ionic conductivity, and ion preference of a $\lambda\text{-MnO}_2$ /graphene composite [188].

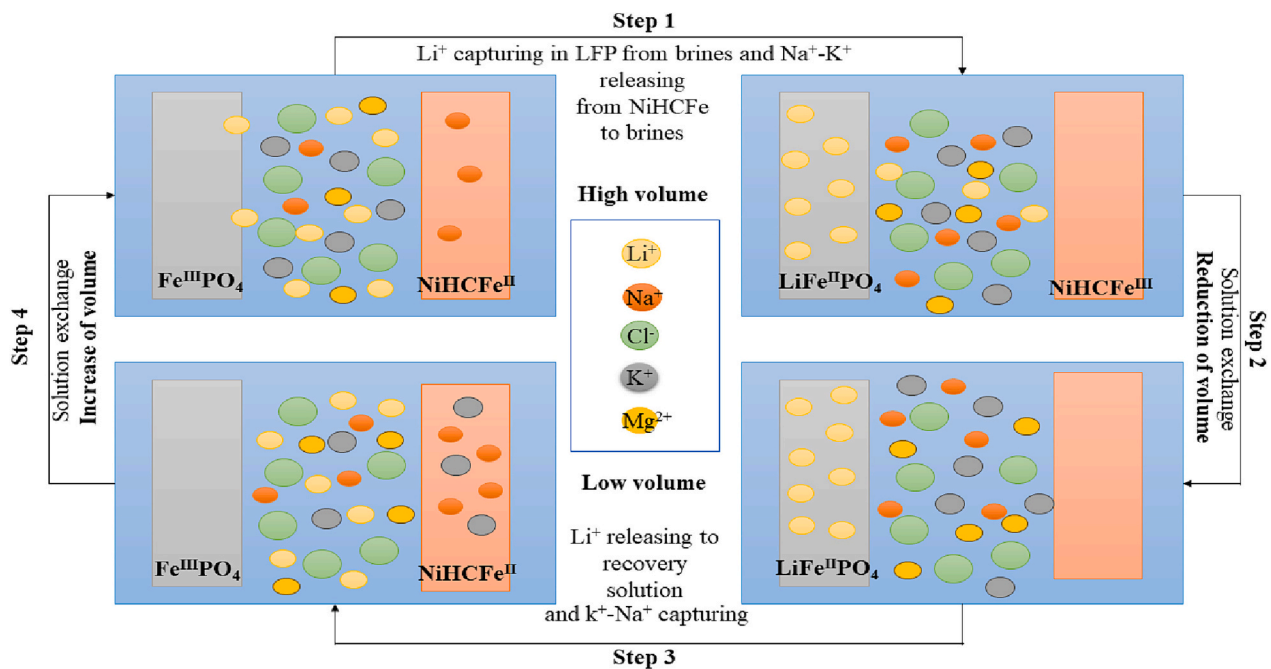


Fig. 10. Recovery of Li from saltwater using lithium iron phosphate (LFP) electrodes [115].

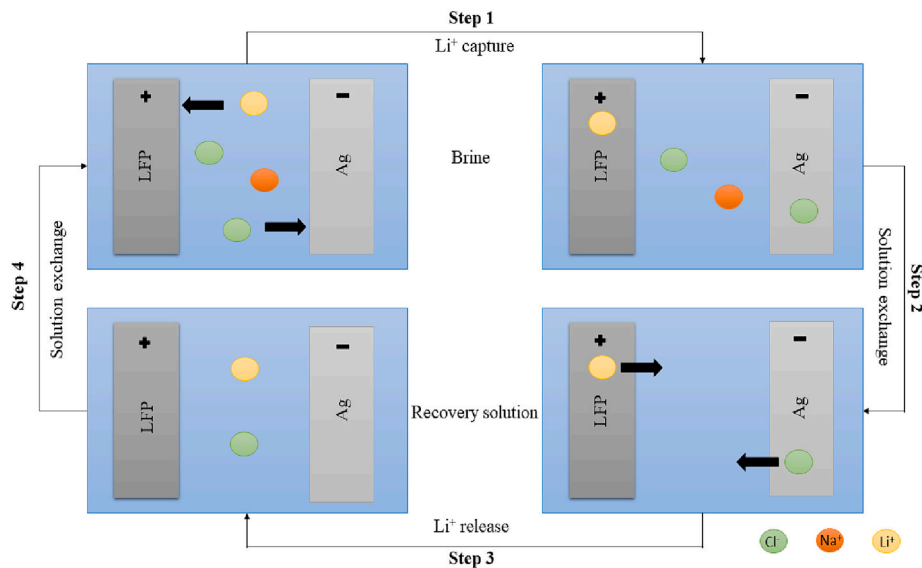


Fig. 11. Recovering lithium with an electrochemical method using the LFP-Ag system [106].

The first principle technique was used by Xiong et al. to investigate the characteristics of LiFePO_4 cathode material in 2014. Electron density differential (EDD) and bond ordering are computed for LiFePO_4 to illustrate the impact of the chemical backbone [189]. The reactor features a pair of porous packed bed electrodes separated by an electrolyte-filled porous insulating membrane. There are current collectors on both porous electrodes, and the electrolyte flows in from the bottom of the reactor and out the top.

The Li extraction apparatus has a cell voltage of <1 V, as Xiong et al. used polypyrrole (Ppy) as an anion-selective counter electrode instead of a carbon electrode [189]. Two different ways of running the reactor were considered. Both the LMO/AC and LMO/Ppy systems were available. Then, the capacitive electrode and Li insertion materials were replicated by applying a steady current to the LMO's positive electrode and grounding the capacitive electrode's right end. Using the first-

principle approach, one may foretell the microscopical course of Li intercalation. Some crucial theoretical supports for subsequent experimental synthesis can be provided by gaining a firm grasp on the connection between structures and properties throughout this dynamic process.

5.2.4. Process mechanism

Salt capture via the Ag/Ag process in a Prussian blue derivative required less energy than selective exchange via the ion intercalation reaction in a 2016 study by Trocoli R. et al. [115]. When the theoretical calculation was compared to the experimental results, they found that they were congruent with each other regarding the dynamics.

In 2018, Marchini et al. used the adsorption model of Li-ion intercalation to introduce the steps of embedding the $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel lattice, which include Li-ion transport, de-solvation, and adsorption [190].

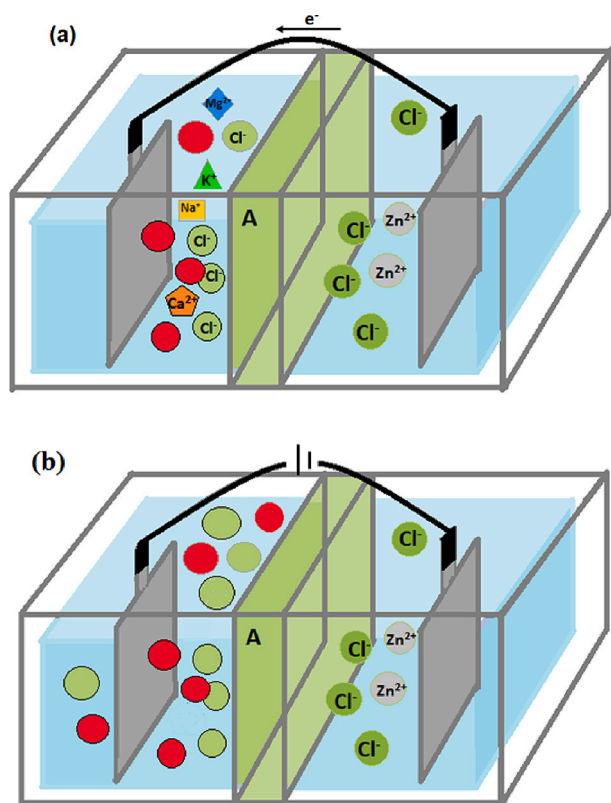


Fig. 12. The LMO-Zn system for electrochemical lithium recovery [185].

Solvated Li-ion migration towards the spinel oxide surface, hydration water loss, ad-ion tetrahedral site adsorption, and electron transfer to the Mn(IV) surface ions are all accounted for in this model. Li ions diffuse throughout the crystal and accumulate at the electrode during the phase transition between intercalation stages. In tandem with this motion, the spinel's tetrahedral sublattice undergoes an additional insertion.

The model of Li-ion transfer reaction at the interface of $\text{Li}_x\text{Mn}_2\text{O}_4/\text{brine}$ and $\text{Li}_x\text{Mn}_2\text{O}_4/\text{LiCl}$ solution can be used to forecast the practical use of new electrode materials using electrochemical impedance. Furthermore, Romero et al. 2018 attempted to construct and scale up the packed bed reactor efficiently by thoroughly comprehending the potential profiles and the distribution of ionic species within the reactor [113]. By employing the Nernst-Planck equation and the battery intercalation model, they developed an electrochemical reactor for Li

extraction from brine. This research illuminated the importance of reactor design in the broader context of industrial applications.

5.2.5. Continuous operation

Considering the operational simplicity and energy economy of continuous operation, the electrochemical extraction of Li from seawater/brine could be scaled up for industrial use. The NMMO/AC hybrid supercapacitor created by Zhao et al. in 2019 is seen in Fig. 14 [111,191]. In a cube-shaped electrolytic cell, they created a two-electrode system made up of $\text{SPCE}/\text{Ni}_{0.03}\text{Mo}_{0.01}\text{Mn}_{1.96}\text{O}_4$ and an AC electrode. Li-ions were introduced into the NMMO lattice during the discharge step of the operation, and anions were trapped on the AC electrode surface using a steady current of -2.25C -rate. In the charging process, 30 mM of the receiving solution replaced the feed solution. A positive current, applied at a rate of 2.25C , facilitated the removal of Li^+ ions. The extraction efficiency of up to 14.4 mg/g per cycle was achieved in artificial brine using only 7.91 Wh/mol Li^+ [191].

Table 9 summarizes the performance index and the pertinent parameters. The benefits of utilizing batch operation with three electrodes become evident primarily in the initial phases of a new electrochemical system. This is because the availability of accurate and stable potential data assists in uncovering the dynamics of the reaction.

The core of a batch operation with a two-electrode, membrane-less cell is a single cell and two electrodes. Therefore, cell design and exploration of operating parameters are straightforward. However, when the brine composition becomes complex, its selectivity and working life are reduced, which can be overcome using a membrane. However, by alternating between a DC positive and a DC negative electrolyte, as well as a Li-inserted electrode and a counter electrode, the extraction and recovery of Li^+ ions were achieved. Continuous extraction and recovery can be attained by permanently putting electrodes in a cell and utilizing a flow-regulating device. Due to their convenience and efficiency, continuous operations are desirable in large-scale industrial processes.

5.2.6. Development of operation mechanisms of electrochemical extraction

Several electrochemical techniques, such as electro-sorption technology, electrochemical switching ion exchange, ionic pump, and rocking chair battery system, have recently been developed for Li extraction. In this article, we'll examine the various approaches in depth.

5.2.6.1. Electro-sorption technology. Adsorption of dissolved salt or other charged substances onto the surface of a charged electrode is the basis of electro-sorption technology, also known as capacitive deionization (CDI), a new approach for purifying and desalinating water.

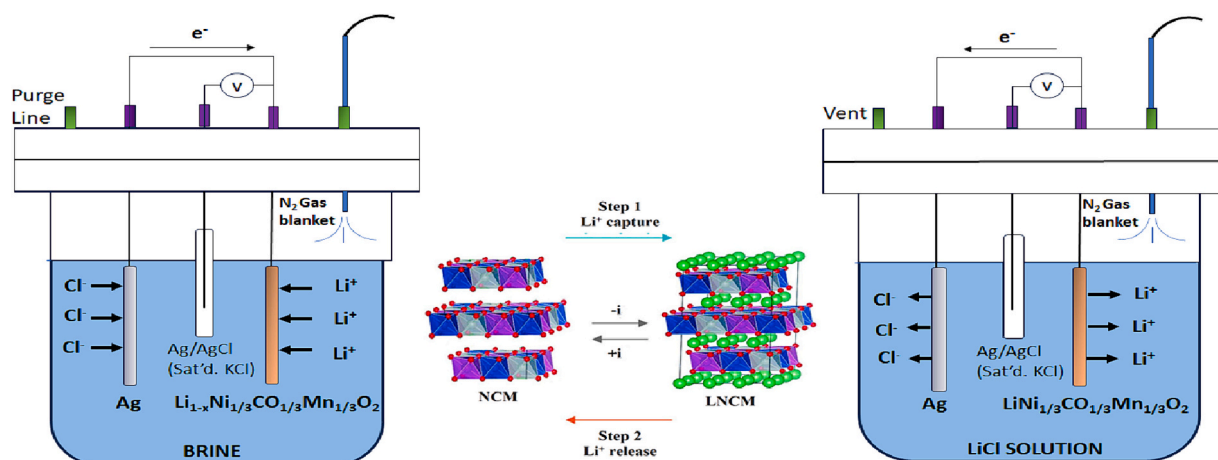


Fig. 13. Schematic representation of the electrochemical technique for recovering Li^+ using NCM/Ag [186].

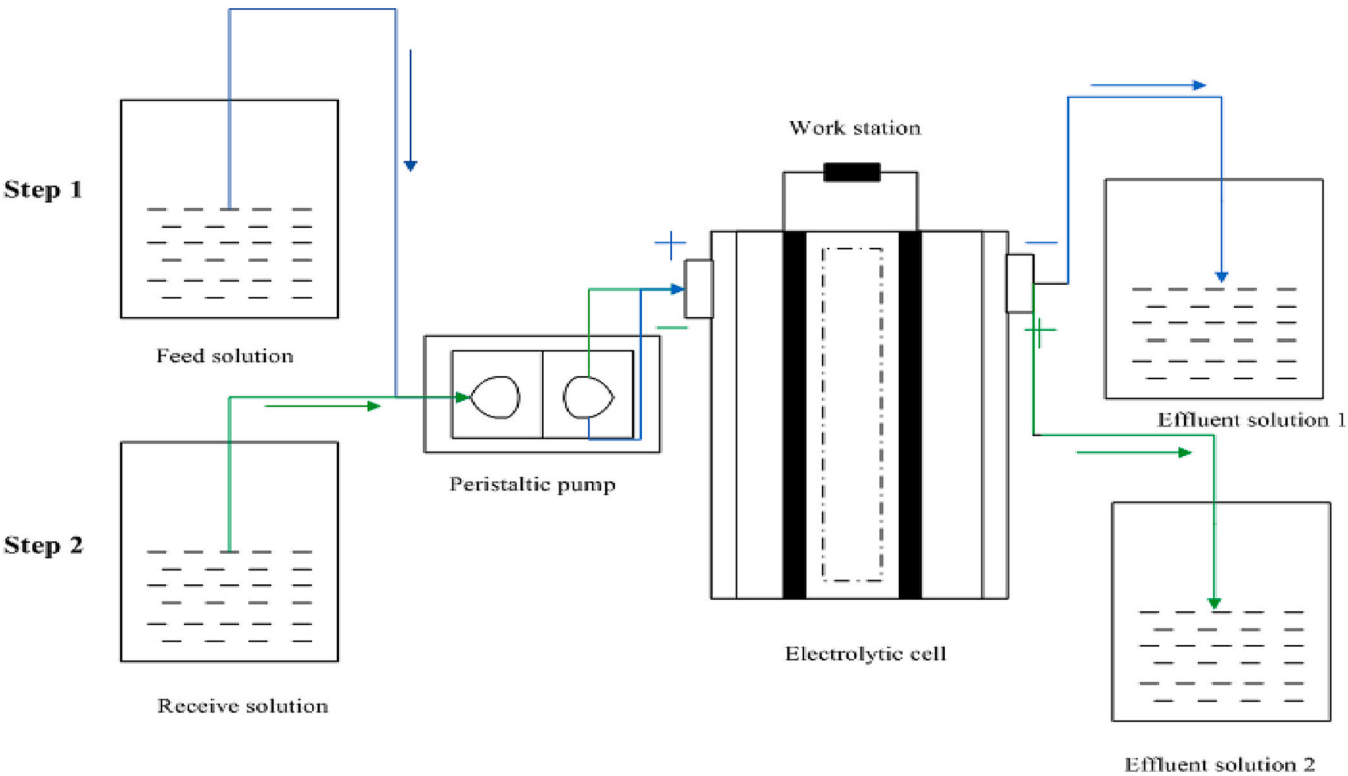


Fig. 14. Schematic diagram of a continuous process of electrochemical method [191].

Table 9
Specific lithium extraction parameters in published articles [111].

Electrode materials	Source solution	W (W.h.mol ⁻¹ Li ⁺)	K _{Li/Mg} α _{Li-Mg}	Capacity retention rate/n cycles	Coulomb efficiency (%)
LFP/Ag	Natural brine	1	—	—	94.3
LFP/FePO4	220 mg/L LiCl	2.8	K116	—	—
LFP/Ag	Artificial brine	8.7	—	—	—
LFP/NiHCF	Atacama brine	6.3	—	73%/100	—
LMO/Zn	Natural brine	4.5	—	87%/20	98.5
λ-MnO ₂ /Ag	1 M LiCl	3.07 Wh/g _{Li}	—	—	—
λ-MnO ₂ /Ag	Simulated desalination brine	3.58	K101	—	—
λ-MnO ₂ /NiHCF	Atacama brine	18	α74.03	—	97
LMO/Li1 – xMn2O4	Simulated brine	18.6	α98.17	—	97
LMO/Li1 – xMn2O4	Simulated concentrated seawater	4.2	—	96%/50	97
λ-MnO ₂ /AC	Atacama brine	4.14	—	91%/100	—
λ-MnO ₂ film electrode/AC	0.03 M LiCl	5–10	—	50%/200	—
LMO/Ppy	Natural brine	2.6	α42.87	96%/20	99
NCM/Ag	Simulated brine	7.91	—	90.8%/30	98
NMMO/AC	Simulated brine				

Electric double layers are formed when the two electrodes are charged, and positively charged cations and particles move towards the cathode and remain adsorbed there using the parallel capacitor principle. At the anode's surface, anions experience similar processes. Adsorption of ions or charged particles can be reversed, and a fresh adsorption-desorption cycle can commence when the two electrodes are subjected to a voltage of the opposite sign or an open circuit, respectively. An efficient battery system based on EST has been developed to extract Li from high Na/Li brine, as shown in Fig. 11.

5.2.6.2. *Electrochemical switching ion exchange.* When combined with other electrochemical techniques, electrochemical switching ion exchange (ESIX) technology can provide separations with high ion selectivity and reversibility. The ESIX procedure requires an electrode that is electrically active and has been coated with an ion ESIX layer. As presented in Fig. 15, the ESIX membrane responds rapidly to an applied

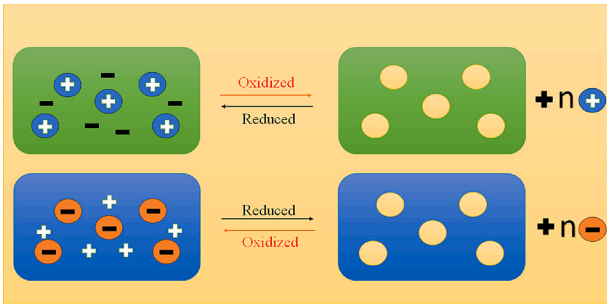


Fig. 15. Schematic diagram of electrochemical switching ion exchange process.

electrochemical potential by absorbing and releasing the target ions.

Cations move from the solution into the ESIX film when a cathodic potential is supplied, as illustrated in Eq. 12. Moreover, Eq. 13 shows that when X⁻ is reoxidized, the cation leaves the ESIX film and moves into the solution.



To extract Li-ions from a dilute solution, Wang et al. developed a vacuum-filtered $H_{1.6}Mn_{1.6}O_4$ /rGO hybrid ESIX film [192]. Additionally, a new Ppy and CU-MOF (Metal-Organic Frameworks) electroactive composite film was fabricated and tested using in-situ coordinated unipolar pulse electro-erosion [193]. Besides, λ - MnO_2 /BiOCl@Ppy, and λ - MnO_2 /rGO/Ca-Alginate, and other ESIX membranes were also utilized to select Li^+ from solutions [194,195].

5.2.6.3. Ionic pump. Li-ion extraction from liquid solutions is made possible by a novel technology called an electrochemical Li ionic pump, which uses an ion exchange membrane.

Applying a voltage to the system enables the electrostatic separation of Li-ions and counter-ions in the solution, which are then collected by the positive and negative electrodes. Reversing the potential releases the trapped Li ions and counter-ions back into the electrolyte, rejuvenating the electrodes.

As seen in Fig. 10, R. Trocoli et al. have proposed using the abundant and environmentally beneficial $KNiFe(CN)_6$ to replace the precious metal currently utilized in the Li extraction from solutions [115]. The electrochemical ionic pump process entails the following four actions: In step a) the Li capture electrode undergoes selective intercalation of Li-ions from the feed electrolyte, while in step b) the recovered solutions are traded in for the feed solutions, step c) oxidizes the $LiFe(II)PO_4$, liberating the Li^+ that was previously trapped in the first step, and step d) reduces the $NiHCF(III)$, capturing cations from the recovered solution. The recovered Li^+ concentration and purity can be improved through cycling.

5.2.6.4. Rocking chair battery system. The Li-ions in a rocking chair battery are charged and discharged by intercalation and deintercalation between the positive and negative electrodes. To illustrate the extreme reversibility of the rocking chair movement of the Li ions, Li^+ is selectively caught from the seawater in the cathode chamber and discharged to the anode chamber. Both electrodes in this electrochemical system are either utterly saturated with Li or completely deficient in Li. The electrode in its saturated condition, known as the anode, is always maintained in the recovery solution. In contrast, the electrode in its deficient state, known as the cathode, is always held in the source solution. Li may be extracted by creating electric fields between the electrodes in

different orientations. Fig. 16 depicts Xu et al.'s LMO cathode-based rocking chair technology [196]. Furthermore, $LiFePO_4/FePO_4$ electrodes may selectively recover Li from Salt Lake brines.

6. Challenges and environmental impact of DLE from brine

As of 2022, eight commercially operational facilities produce Li compounds from continental brines, seven of which use evaporitic technology [197]. During the process, >90% of the water content is lost, and over 90% of salts, except LiCl, crystallize and are treated as waste [197,198]. Concerns have been raised about the impact of this approach on the water balance and biodiversity of salt lakes. The unquestionable necessity of sustaining Li production in the “Li triangle” nations within the energy transition framework is evident. However, both Argentina and Chile have several regulatory hurdles in implementing the existing evaporative Li processing technology [199,200]. These challenges raise concerns over the possible environmental impact, preservation of endemic species, residents' well-being, and governance effectiveness [201–205].

Li in salt lakes is mainly in brine, aqueous solutions characterized by high concentrations of dissolved salts, including NaCl, KCl, LiCl, and $MgCl_2$. The brines undergo several unit processes to create LCE. The subsequent segment demonstrates that the current processing method used for Li extraction from Salt Lake brines considers the loss of approximately 85–95% of the brine's water content due to evaporation [197]. This loss is comparable to 200–1400 m³ of water per metric ton of Li in the recovered brine [99]. In recent years, there has been a notable occurrence of this phenomenon in arid regions that have been impacted by the worldwide issue of water shortage. This has resulted in heightened conflict between residents and corporations involved in Li extraction [206]. Hence, Li production in the “Li triangle” has several potential dangers that may impact the global Li supply in the following years.

The “ong-term feasibility and sustainability of these new Li recovery technologies remain a significant problem despite the promising results reported thus far. The biggest issue with all of the Li recovery methods is what to do with all the leftover used brine. Almost all previous studies ignore this point, and it is commonly believed that the brine should be disposed of in subsurface aquifers or the Salt Lakes [207].

Freshwater can be extracted from MD and MDC and used for different purposes, such as irrigation and industrial processes. The remaining concentrated brine, which has a higher concentration of lithium, can be further processed to extract lithium. These methods result in high freshwater recovery rates, which reduces water consumption and minimizes environmental impact. Compared to traditional thermal processes for brine concentration, MD and MDC are relatively energy-efficient [98,208,209]. However, NF membranes have a lower rejection rate for monovalent ions (e.g., Na^+ and Cl^-) compared

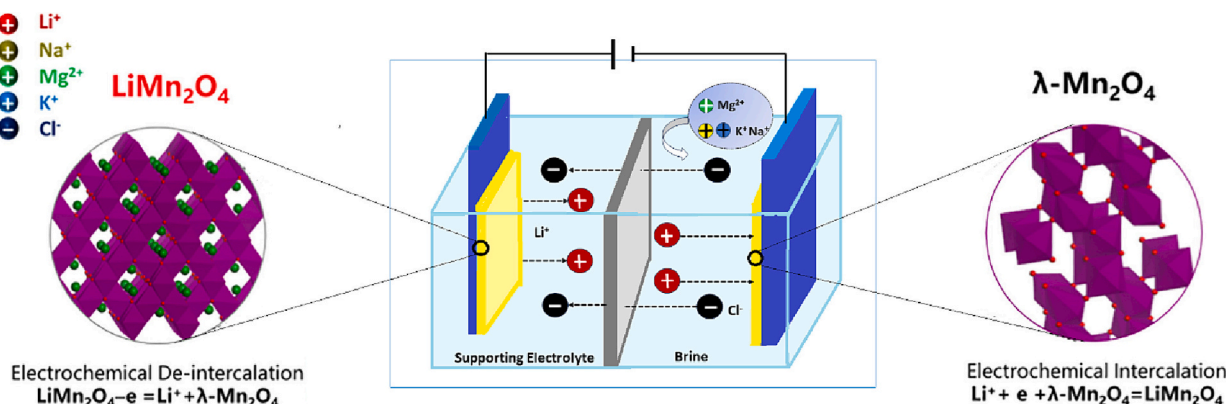


Fig. 16. Skeleton of electrolytic cell for Li extraction from brine using $LiMn_2O_4/Li_{1-x}Mn_2O_4$ [196].

to divalent ions (e.g., Ca^{2+} and Mg^{2+}), which means that they may not remove all dissolved ions from brine to produce freshwater effectively. On the other hand, ED relies on the application of an electric field to drive ions through ion-selective membranes. While it can effectively separate ions, the process is energy-intensive and may not be efficient for recovering freshwater from highly concentrated brines. In summary, although NF and ED are valuable membrane-based processes for different applications, they are not typically used for recovering

freshwater directly from spent brine in Li extraction from Salt Lake brines due to their limited effectiveness in highly concentrated brine environments and their relatively low freshwater recovery rates compared to processes like MD and MDC [85,210].

Some unique sustainability issues arise with these Li recovery techniques. For example, the precipitation method requires much freshwater as an eluent. Still, a steady supply of so much water could not be sustainable in the long run, depending on the drought-prone locations

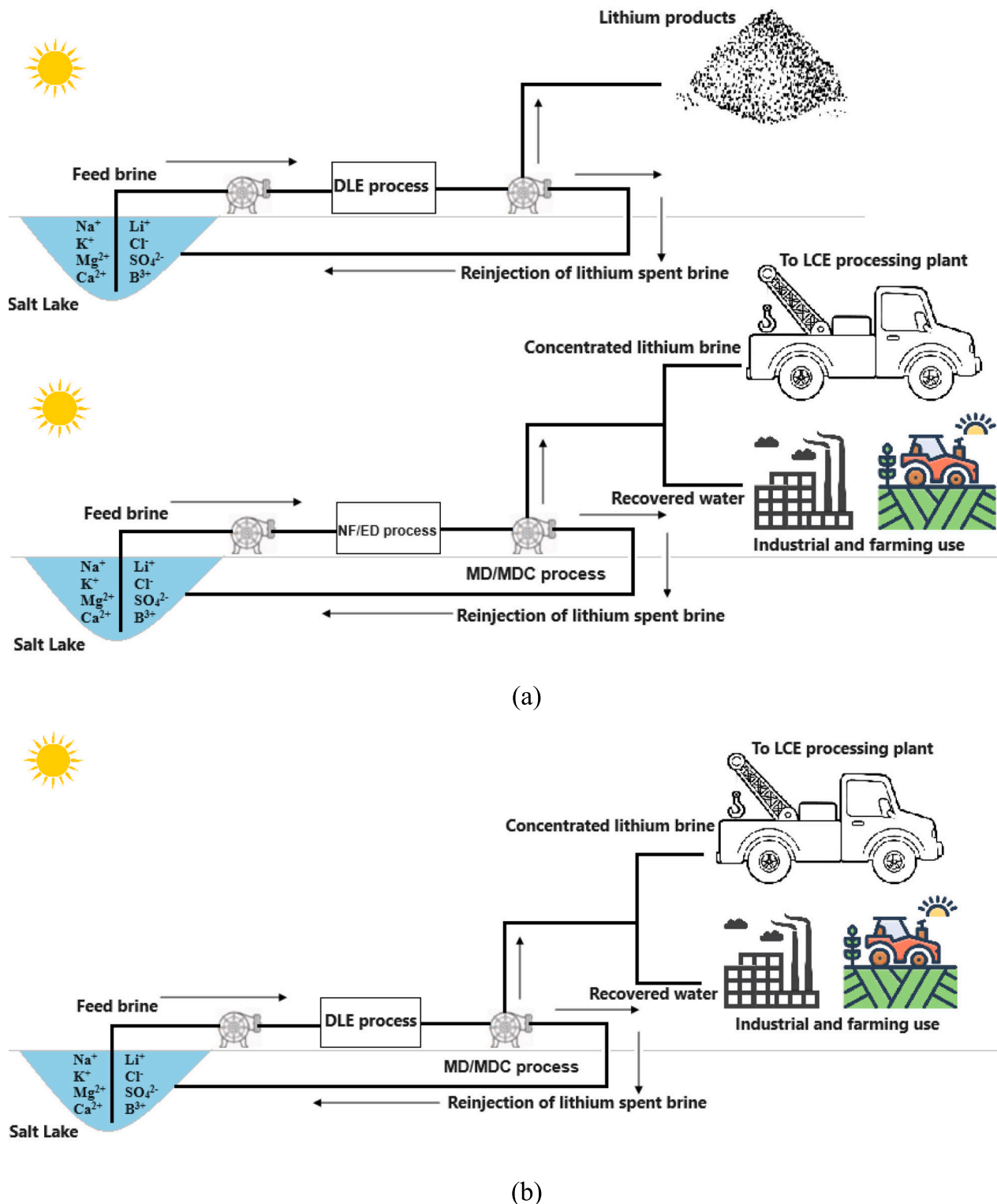


Fig. 17. (a) Brine management in DLE and LBC methods [13], (b) incorporation of DLE and LBC brine management system.

[197]. The large amounts of organic solvent and ionic liquids typically wasted during solvent extraction are a significant environmental risk. The membrane-based approaches are comparably advantageous due to their high Li production; however, their essential energy consumption renders the process unsustainable at an industrial scale. Most naturally occurring brines fall into the low- to medium-Li concentration range, which suffers the abovementioned problems [69].

Additionally, water shortages have been exacerbated by the excessive extraction of Li from natural brine. As a result of the severe water shortages in certain areas, there has been significant discussion on whether or not brine should be classified as a “water” or “mineral” [211]. Since the brine from reverse osmosis (RO) desalination plants is being utilized to produce water and Li simultaneously, this problem can be solved by using the brine as a source of Li recovery. Meanwhile, the potential for reinjecting the Li-depleted brines is one reason why using non-evaporative technology for Li extraction can reduce the amount of water lost in aquifers [197]. However, this can make things worse by diluting the brine sources with Li-depleted brine, making the problem harder to solve in the first place.

DLE methods are designed to prevent water loss to the atmosphere by recycling the treated brine back into Salt Lake. In this regard, the aim of LBC processes is similar to that of evaporation ponds, but LBC processes focus on recovering or preventing water loss. However, DLE methods have limited flexibility regarding water management because they require the return of all the spent brine. As previously mentioned, no available public research or studies currently explore the potential effects of reintroducing 100% brine-treated water back into Salt Lake [197]. Two commercial implementations of DLE procedures are active now. The first one is in the Hombre Muerto Salt Lake of Argentina, and the second is in the Chaerhan Salt Lake of China [26,197]. Both examples contain readily available details regarding the recycling of used brine. It would appear that just a small percentage of the extracted brine in the Argentinian example is treated at the DLE stage, with the remainder of the brine being processed using the more traditional evaporation pond procedure. Hence, it is imperative to establish a precise framework outlining the specific location for the disposal of the spent brine (i.e., surface or injection), the method of return (e.g., utilizing pumping wells, dispersion), and setting volume limits. This is crucial to prevent potential adverse effects on the chemical quality of aquifers, geotechnical stability of the Salt Lake, endemic biodiversity, and overall water balance. Furthermore, it is essential to consider the distinct geochemical and geological characteristics of each Salt Lake during this process.

The combination of DLE and LBC technologies is unexplored but could offer advantages in Li extraction efficiency, freshwater production, and spent brine management [99]. Fig. 17 (a) presents the current brine management system of DLE and LBC [13], while Fig. 17 (b) shows the proposed integration of these two technologies. Additional research on energy consumption and brine management will be essential to evaluate the potential environmental impact, even though this approach offers inherent advantages in terms of versatility.

Numerous researchers and technologists suggest the reinjection of spent brines, but there are concerns that this process could dilute a valuable resource [197,212,213]. To name a few hydrologic implications, the reinjection procedure can potentially change the physical and chemical properties of the groundwater and the pore-water pressures [214]. Induced seismicity is another major concern in brine reinjection. Locals in Southern California were understandably alarmed by a string of earthquakes in April 2023 close to the Salton Sea (where multiple fault lines including the San Andreas run through). Researchers and residents suspect nearby geothermal and lithium mining operations are to blame [215]. In geothermal fields, for instance, reinjection wells tend to interfere rapidly with production wells in about 80% of cases [216]. While brine reinjection in Salt Lake basins could be a viable option, more practical knowledge needs to be available, and there is a risk that it could disrupt the layered stratigraphic structure of these basins [197].

Examining the diverse geological formations of each deposit individually is crucial as it is necessary to effectively evaluate the risks and benefits associated with reinjection processes. It should be noted that spent brines may contain chemical species not native to Salt Lake due to the leaching of active materials from DLE setups or altered pH levels, which may impact the surrounding ecosystems. Additionally, on cycling, many adsorbents or electrodes slowly dissolve in brines, while solvent solubility in brines up to 200 ppm has been reported [198]. It is imperative to consider advanced technologies for desalinating hypersaline brines as an alternative to reinjection, which may come with a higher cost [27,114,217].

Incorporating costly materials and devices into modern Li recovery systems drives the initial investment compared to more traditional evaporative approaches. Most modern adsorbents are not commercially available, and their synthesis is less time- and energy-consuming; however, even for the low Li brines, the adsorption method has proven highly efficient regarding Li recovery and selectivity. Several studies have shown that ‘Li sieves’ made from non-stoichiometric LMO are effective Li adsorbents. However, they can only be synthesized in tiny quantities in the lab, and their widespread use currently needs to be more expensive to be practical. Adequate adsorption and the presence of other elements in significant concentrations make it necessary to use more advanced adsorbents to achieve acceptable purity levels [218]. High equipment costs further restrict the scalability of membrane-based approaches. The current market demand and pricing of Li products often do not justify initial expenditures in ion-exchange membranes and the advanced design of the ED and BPMED systems. Also, significant operational costs are incurred over the lifetime of all membrane-based Li recovery systems due to membrane scaling, which causes a continual drop in flux [219]. In the event electrochemical approaches for Li recovery are hindered by high material costs due to limited adsorption of Li by the working electrode [197]. Most cutting-edge Li recovery technologies are economically not feasible for widespread use, according to a thorough techno-economic analysis conducted by Albo et al. [220].

Owing to the low Li concentration in seawater brine, the operational cost of modern Li recovery technologies is projected to be much greater than the conventional evaporative procedures. It is predicted that the cost to produce Li from seawater is \$80 per kg of product, but the cost to build Li using Salt Lake brine as feed is only \$2. Positive results for NF have ranged from about \$5 to \$7, which is still relatively high [221]. In the case of membrane distillation crystallization (MDC), Jensen et al. in 2016 reduced the operational cost to \$2.18; nonetheless, the expensive initial investment and ongoing operating expenses remain significant obstacles [208]. So far, selective ED has yielded the best results (\$1.3), but further improvements are anticipated once the necessary infrastructure is built and pretreatment procedures are implemented [222].

China has played a pivotal role in developing and deploying several cutting-edge technologies for Li recovery at both the pilot and commercial scales, allowing for the successful extraction of Li from Salt Lake and geothermal brines. Since these brines contain a relatively high concentration of Li, they are ideal for use with these techniques. As a result of the deficient Li concentration in saltwater, current technologies for Li recovery from seawater brine are both expensive and energy-intensive. However, this is where the vast majority of the world’s Li reserves are stored. Due to the fact that most of these techniques have yet to be shown outside of a lab, they require further study to advance to a higher technology readiness level (TRL).

A critical technological impediment to wider deployment is high energy usage, and it has been suggested that increasing the utilization of alternative energy sources can be one solution. Before brine recovery technologies can be used widely, they each have unique requirements that must be met. Their long-term stability and regeneration ability present a practical problem in adsorption and the presence of other cations, especially in large amounts. Since the membrane and electrochemical systems are so energy-dependent on feed salinity, building more flexible systems that can accommodate variations in salinity is

essential.

Most DLE technologies require more energy than evaporative conventional lithium extraction, and their cost analysis and optimization processes are rarely reported [194,223]. Energy demands are often documented solely for the crucial DLE step, neglecting pre-processing, post-processing stages, and additional equipment. For instance, in an electrochemical ion-pumping process, the mechanical energy utilized for pumping solutions through electrochemical cells was found to be 300 times higher than the energy needed to drive the electrochemical reactions [224,225]. Besides, the calculation of electrical work is usually limited to what is required for an electrochemical process. [223,226,227]. Although the energy value of an individual step holds importance, it represents only a lower limit. Due to the partial reporting of energy needs, making accurate comparisons becomes impossible.

Recognizing the significance of pre-processing as a vital step in DLE is crucial, particularly when dealing with substantial brine volumes. Research investigating the efficiency of Li Manganese Oxide (LMO) as a Li^+ adsorbent revealed that heating brine from 10 °C to 80 °C significantly enhanced Li^+ adsorption efficiency from 15% to 70%. This increase in efficiency contributed to a higher separation efficiency from other cations [228]. Other ion exchange resins also show improved absorption efficiency at higher brine temperatures [229]. However, heating brine volumes on the order of 21,000 m³ daily to approximately 80 °C led to considerable operational cost increases. When analyzing the overall process, it is essential to consider brine heating as an energy input. It is worth noting that in the case of continental brines, most deposits are located at high altitudes and latitudes where the average annual horizontal global solar irradiation values exceed 2000 kWh/m². [230]. These values rank among the highest on Earth, making these locations ideal for solar energy harvesting. While installing photovoltaic cells or solar-concentrating power capacity increases the initial capital cost of mining projects, significantly reducing operational expenses in the long run.

Additionally, oceanic brine, another lithium source, faces obstacles to the widespread adoption of new technologies due to the low amount of lithium present in it. However, seawater RO brine, significantly richer in Li by volume than saltwater, presents a promising opportunity for high-yield Li recovery by applying cutting-edge methods. Nearly 141 m³ day of seawater RO brine is produced and dumped back into the oceans around the world [231]. Based on preliminary estimations, approximately 42 tons of Li are returned to the oceans daily in seawater RO brine [232]. In order to proficiently extract Li and other valuable minerals from saltwater RO brine, cutting-edge technology must be implemented without delay. Several additional undesirable minerals are also concentrated in the seawater RO brine, making selective Li recovery more challenging. To address this, existing water desalination technologies require comprehensive revision, with particular attention paid to pretreatment procedures. Desalination processes can be adjusted so that freshwater and Li (and possibly other valuable elements like Co and U) are the principal products, bringing the 'waste-to-wealth' concept to the industry.

7. Conclusion & prospect

Given the exponential rise in the price and demand for Li as the portable electronics and EV industry boom, immediate attention to long-term Li recovery from other resources is necessary to maintain supply and demand balance in the future markets. Large quantities of Li can be found in seawater, and rising marine pollution from desalination brine discharge presents another compelling argument for the possible use of cutting-edge Li recovery technologies. Due to extended cycle times and geographical variability, traditional evaporative Li recovery technologies based on Salt Lakes and geothermal brine will likely need help to keep up with rising Li demand. LMO-type LIS is a novel, efficient, environmentally friendly, cost-effective adsorbent with excellent growth and application prospects in ion-sieve adsorption. Additionally,

the adsorption process boasts superior safety, reliability, and efficiency compared to traditional approaches. The introduction of LMO-type LIS will reduce the worldwide demand for this scarce resource. Nano-structured LMO precursors have been developed using a soft-chemical strategy to increase the adsorbent's selectivity, adsorption capacity, and adsorption efficiency. Future research should center on $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$, as it can theoretically adsorb more than many other LMO-type LIS. Precursors with a greater Li/Mn molar ratio require either the development of novel technologies or an exploration of a compromise between the advantages and disadvantages of various methods for composite synthesis based on traditional methodologies. Commercial Li extraction necessitates the development of increasingly complicated electrode materials, which have become more complex as Li deposits have become scarcer. If new anode materials are constantly being developed, the overall efficiency of Li recovery could potentially exceed current performance levels. Despite concerns about cyclic stability, new electrode materials that are both inexpensive and environmentally safe, with innovative, user-friendly designs, will allow for more prominent scaled-up applications. LIS's adsorption/desorption behavior is poorly understood, therefore, more fundamental research is needed, including adsorption kinetics, isothermal adsorption performance, Mn dissolution, and the Li intercalation/de-intercalation process. The LMO forming process is now a significant barrier preventing LMO-type LIS from being used in widespread industrial settings. Decreased adsorption ability and absorption efficiency are relative to raw powder, necessitating optimizing the forming procedure. Furthermore, the promising electrochemical extraction method still requires improved electrode materials, an understanding of the in-depth process mechanism, and cell configuration. Li insertion capacity and electrode material life-cycle were used to evaluate the overall efficacy of Li extraction. Crystal collapse is more likely to occur in electrode materials with a high Li-insertion capacity because their lattice expansion is more apparent. This behavior is more likely observed in fresh brine with corrosive ions. There is a suggestion to develop electrode materials with more stable structures or, alternatively, adjust the surface of Li-rich cathodes to strike a proper balance between capacity and cycle stability. Moreover, when designing the electrochemical extraction cell, it's crucial to consider the kinetics of a specific electrode reaction in an authentic brine system. This accounts for the varying ion compositions in brines from different Salt Lakes or seawater sources. As a result, a thorough knowledge of the mechanisms of interfacial intercalation and deintercalation of Li in specific conditions would be beneficial. After that was established, other parameters, such as electrode spacing, plate surface area, membrane preference in the cell, and so on, could be calculated. Another distant difficulty is the amplification impact during the scale-up phase for actual industrialization. In addition, continuous operation is likely to be more efficient. However, particular operational factors, such as DC potential, feed flow rate, and recovered solution cycles, must be addressed to achieve better performance.

CRediT authorship contribution statement

Muhammed Rashik Mojid: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kyung Jae Lee:** Writing – review & editing, Supervision, Software, Resources, Project administration, Funding acquisition, Conceptualization. **Jiahui You:** Writing – review & editing, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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