



## OPEN ACCESS

## EDITED BY

Costas Tsouris,  
Oak Ridge National Laboratory (DOE),  
United States

## REVIEWED BY

Yang Zhang,  
Qingdao Institute of Bioenergy and  
Bioprocess Technology (CAS), China  
Eunhyea Chung,  
Seoul National University, South Korea

## \*CORRESPONDENCE

Olivia Murphy,  
om66@cornell.edu

## SPECIALTY SECTION

This article was submitted to Sustainable  
Process Engineering,  
a section of the journal  
Frontiers in Chemical Engineering

RECEIVED 01 August 2022

ACCEPTED 10 November 2022

PUBLISHED 30 November 2022

## CITATION

Murphy O and Haji MN (2022), A review  
of technologies for direct lithium  
extraction from low Li<sup>+</sup> concentration  
aqueous solutions.  
*Front. Chem. Eng.* 4:1008680.  
doi: 10.3389/fceng.2022.1008680

## COPYRIGHT

© 2022 Murphy and Haji. This is an  
open-access article distributed under  
the terms of the [Creative Commons  
Attribution License \(CC BY\)](https://creativecommons.org/licenses/by/4.0/). The use,  
distribution or reproduction in other  
forums is permitted, provided the  
original author(s) and the copyright  
owner(s) are credited and that the  
original publication in this journal is  
cited, in accordance with accepted  
academic practice. No use, distribution  
or reproduction is permitted which does  
not comply with these terms.

# A review of technologies for direct lithium extraction from low Li<sup>+</sup> concentration aqueous solutions

Olivia Murphy\* and Maha N. Haji

Symbiotic Engineering and Analysis Laboratory, Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY, United States

Under the Paris Agreement, established by the United Nations Framework Convention on Climate Change, many countries have agreed to transition their energy sources and technologies to reduce greenhouse gas emissions to levels concordant with the 1.5°C warming goal. Lithium (Li) is critical to this transition due to its use in nuclear fusion as well as in rechargeable lithium-ion batteries used for energy storage for electric vehicles and renewable energy harvesting systems. As a result, the global demand for Li is expected to reach 5.11 Mt by 2050. At this consumption rate, the Li reserves on land are expected to be depleted by 2080. In addition to spodumene and lepidolite ores, Li is present in seawater, and salt-lake brines as dissolved Li<sup>+</sup> ions. Li recovery from aqueous solutions such as these are a potential solution to limited terrestrial reserves. The present work reviews the advantages and challenges of a variety of technologies for Li recovery from aqueous solutions, including precipitants, solvent extractants, Li-ion sieves, Li-ion-imprinted membranes, battery-based electrochemical systems, and electro-membrane-based electrochemical systems. The techno-economic feasibility and key performance parameters of each technology, such as the Li<sup>+</sup> capacity, selectivity, separation efficiency, recovery, regeneration, cyclical stability, thermal stability, environmental durability, product quality, extraction time, and energy consumption are highlighted when available. Excluding precipitation and solvent extraction, these technologies demonstrate a high potential for sustainable Li<sup>+</sup> extraction from low Li<sup>+</sup> concentration aqueous solutions or seawater. However, further research and development will be required to scale these technologies from benchtop experiments to industrial applications. The development of optimized materials and synthesis methods that improve the Li<sup>+</sup> selectivity, separation efficiency, chemical stability, lifetime, and Li<sup>+</sup> recovery should be prioritized. Additionally, techno-economic and life cycle analyses are needed for a more critical evaluation of these extraction technologies for large-scale Li production. Such assessments will further elucidate the climate impact, energy demand, capital costs, operational costs, productivity, potential return on investment, and other key feasibility factors. It is anticipated that this review will provide a solid foundation for future research commercialization efforts to sustainably meet the growing demand for Li as the world transitions to clean energy.

## KEYWORDS

low Li concentration aqueous extraction, aqueous lithium extraction, direct lithium extraction, DLE technology review, sustainable lithium recovery, lithium resources, critical minerals, seawater extraction

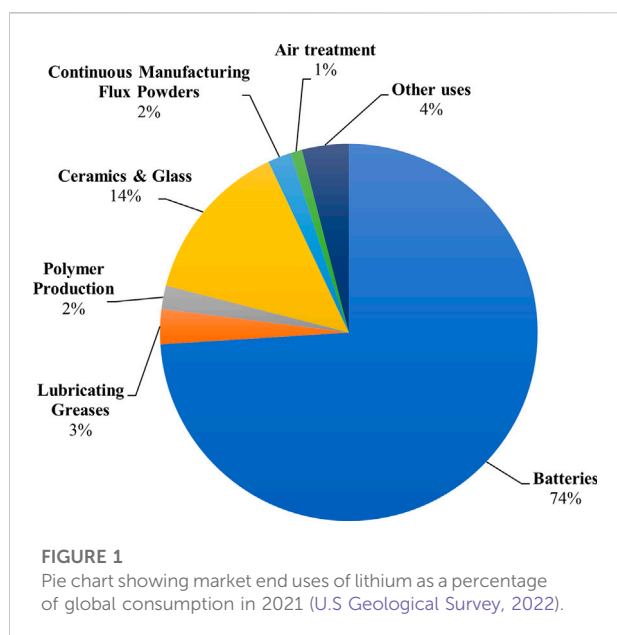
## 1 Introduction

Lithium (Li) is a fundamental metal for manufacturing batteries, ceramics, glass, lubricants, and flux powders, and air treatment processes (Zhang et al., 2019)). Figure 1 shows the predominant market end uses of Li in 2021. Before the 1970s, Li was a considerably obscure mineral commodity. However, it has experienced exponential growth in production in recent years. The annual Li mine production by country in 1970, 2000, and 2021 are provided for comparison in Figure 2. Yearly global Li production has expanded from an estimated 3,700 metric tons (MT) in 1970 to over 100,000 MT in 2021, a record high (USGS, 2017; U.S Geological Survey, 2022). This growth can be attributed to Li's crucial role in the global energy transition. The most prevalent application for Li is in rechargeable lithium-ion batteries for renewable energy storage and electric vehicles. In addition to existing use in Li-ion batteries, Li might also experience growing demand from the hydrogen fuel sector, given that it can be converted to tritium, a potential fuel source for next-generation fuel reactors.

In 2021, international annual electric vehicle sales more than doubled to 6.6 million cars, or 9% of the international car market. This increase in sales is almost triple the global market share in 2019 (IEA, 2022). Summarily, electric vehicles were responsible for the total net growth of global car sales in 2021 (IEA, 2022). Of the 6.6 million cars, 4.7 million (71%) were Battery Electric Vehicles (BEVs), and 1.9 million (29%) were Plug-in Hybrid

Electric Vehicles (PHEVs) (Irle, 2022). The typical lithium-ion battery capacities for BEVs and PHEVs are estimated to be 25 and 9 kWh, respectively (Vikström et al., 2013). Furthermore, it is estimated that 160 g of Li can supply one kWh of battery capacity (Kushnir and Sandén, 2012). Therefore, the estimated Li requirement for a BEV and PHEV is four and 1.4 kilograms, respectively. Applying these estimations, the 4.7 million BEVs and 1.9 million PHEVs required roughly 18,800 and 2,700 MT of Li, respectively. This combined mass equates to almost 22% of global Li production in 2021. Accordingly, the global consumption of Li in 2021 was estimated to be 93,000 MT, a 22% increase from 70,000 MT in 2020 (U.S Geological Survey, 2022). By 2030, the global Li demand is expected to exceed 2 Mt, with batteries accounting for 95% of this demand (Azevedo et al., 2018; U.S Geological Survey, 2022). In response, many countries are now prioritizing the development of technologies for low-cost Li extraction to combat impending supply shortages and price hikes. Technologies that enable extraction from low Li<sup>+</sup> concentrated aqueous solutions are the leading edge of these development efforts.

Traditionally, Li has been mined from the Li-bearing minerals lepidolite, petalite, and spodumene contained in pegmatite formations. Lepidolite (K(Li, Al)<sub>3</sub>(Al, Si, Rb)<sub>4</sub>O<sub>10</sub>(F, OH)<sub>2</sub>), contains 3.58% Li content. It is no longer a major mining ore due to its high fluorine content. Petalite (LiAlSi<sub>4</sub>O<sub>10</sub>), contains 2.09% Li content. Its high iron content and low thermal expansion rate make it ideal for glass and ceramics, but it is also used for EV and battery storage applications. Of the three minerals, spodumene (LiAl(SiO<sub>3</sub>)<sub>2</sub>), has the highest Li content at 3.73% (Vikström et al., 2013). Its treatment chain can be completed in roughly 5 days and is consistently productive (Grosjean et al., 2012). The traditional sulfuric acid method for extracting Li from spodumene ores has a percent yield between 85% and 90% and a percent recovery of 60%–70% (Ellestad and Leute, 1950; Grosjean et al., 2012; Dessemond et al., 2019). However, the pegmatite formations spodumene is contained in are challenging to mine given their hardness and occurrence in difficult-to-reach belt deposits (Grosjean et al., 2012; Kesler et al., 2012). Additionally, the treatment process requires high-energy-demanding furnaces, pit-digging machines, and rock-crushing machines. Ultimately, these machines, the dust produced from excavation, and the concentrated chemicals used for processing cause environmental damage and pose health and safety risks (Aral and Vecchio-Sadus, 2008; Grosjean et al., 2012). These drawbacks to Li recovery from terrestrial mining and the rapid depletion of Li ores have led to the innovative practice of recovering Li from salt lake brines, or Direct Lithium



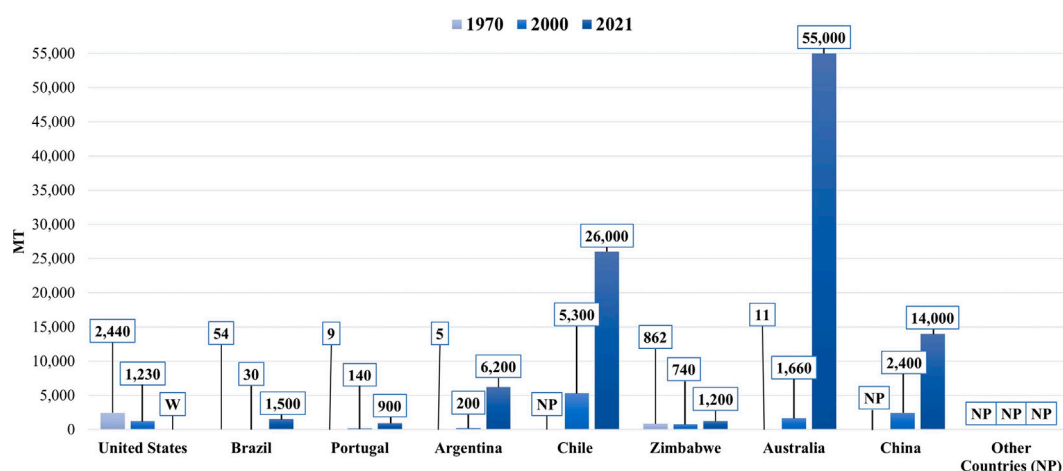


FIGURE 2

A bar chart showing the annual lithium production by country in 1970, 2000, and 2021. Note that the countries labeled with “NP” reported no data that year. Additionally, the United States withheld (W) its production data in 2021 (U.S Geological Survey, 2022; Mohr et al., 2012).

Extraction (DLE). As of 2021, the worldwide Li reserves from ores and brines total an estimated 22 Mt. Salt lake brines account for almost 80% of this total (Zhang et al., 2019). It is important to note that the geographical distribution of these reserves is very uneven (see Figure 3) (U.S Geological Survey, 2022). More than half of the world’s Li reserves are found in the “ABC Triangle,” a phrase coined for the South American countries of Argentina, Bolivia, and Chile (Grosjean et al., 2012). The remaining resources are concentrated in Australia (25%) and China (7%) (U.S Geological Survey, 2022).

New development in DLE technologies has garnered renewed interest in seawater extraction. Although the  $\text{Li}^+$  concentration is low at 0.1–0.2 ppm, seawater contains nearly 230 Gt of  $\text{Li}^+$ , making it a potentially inexhaustible extraction source (Yang et al., 2018). Additionally, seawater’s abundance eliminates many of the geopolitical concerns surrounding land-based reserves because, essentially, any country with access to the ocean has the opportunity to strengthen its Li supply chain with seawater extraction (Månberger and Johansson, 2019; Kalantzakos, 2020). While the  $\text{Li}^+$  content in salt lake brines and seawater is vast, and extraction from these resources has the potential to be more sustainable than terrestrial mining, many technological challenges must be mitigated before these resources can be considered comprehensive solutions for the impending Li shortage (Graham et al., 2021; Kelly et al., 2021; Chordia et al., 2022). The main challenges facing DLE to date are the extraction technology’s  $\text{Li}^+$  selectivity, separation efficiency, recovery, and lifetime.

This paper reviews technology used for  $\text{Li}^+$  extraction from salt lake brine and seawater, or low  $\text{Li}^+$  concentration aqueous solutions. First, brine and seawater are classified according to their content. Subsequently, key advantages and challenges of the

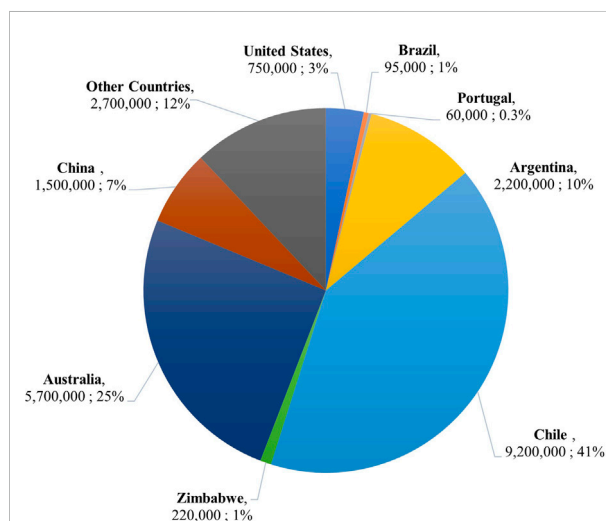


FIGURE 3

Pie chart showing lithium reserves by country as a percentage of the total world-wide reserves in 2021 (U.S Geological Survey, 2022).

precipitation, solvent extraction, ion sieve adsorption, ion-imprinted membrane (IIM) extraction, and electrochemical extraction technologies are detailed. The  $\text{Li}^+$  adsorption capacity, selectivity, separation efficiency, recovery, regeneration, cyclical stability, thermal stability, environmental durability, product quality, extraction time, optimal pH value, and specific energy consumption are also highlighted when provided. The adsorption capacity is the maximum amount of  $\text{Li}^+$  that can be absorbed by the technology. Selectivity is the technology’s ability to exclusively select  $\text{Li}^+$  or other desired ions over competing ions present in the solution. The separation

efficiency is a measure of the quality of  $\text{Li}^+$  separation from the solution achieved by the technology. It is measured by the ratio of the  $\text{Li}^+$  concentrate removed from the solution feed stream to the initial  $\text{Li}^+$  concentration in the solution. Furthermore, the recovery is the amount or percentage of pure Li product obtained after extraction and additional treatment processes, if any. Regeneration refers to the number of times the technology can be regenerated using a treatment process without significant losses in recovery. The cyclical stability indicates the number of times a technology can be reused before there are major losses in recovery. Thermal stability indicates the operating temperature(s) at which the technology achieves optimal performance. Environmental durability refers to the number of times the technology can be reused with minimal physical degradation. The product quality is the percent purity of the Li product recovered. The extraction time is the duration required to remove  $\text{Li}^+$  and recover the Li product. The pH value is the recommended solution pH for optimal  $\text{Li}^+$  extraction and recovery. Finally, the specific energy consumption is the total energy used to produce a unit weight of Li product. The review concludes with recommendations for enhancements and future research pathways of technologies for DLE from low  $\text{Li}^+$  concentration aqueous solutions.

## 2 Classification of aqueous lithium extraction resources

Brines are excessively saline solutions found in continental, geothermal, and oil field deposits. The worldwide distribution of these brine types spans continental basins (58%), geothermal brines (3%), and oil field brines (3%) (USGS, 2017). Geothermal brines are byproducts of geothermal energy production activities. These heated saline deposits can be pumped to the surface for  $\text{Li}^+$  extraction, but their complex chemistry, high salinity, and high temperature ( $> 100^\circ\text{C}$ ) are significant challenges for extraction (Stringfellow and Dobson, 2021). Oil field brine deposits generally occur at depths greater than one kilometer (km). Although the  $\text{Li}^+$  concentration in these brines is optimal (500–700 ppm), conventional extraction methods, such as precipitation, are infeasible for those located in non-arid climates (Bradley and McCauley, 2013; USGS, 2017). Finally, continental basins, also known as salt lakes, are the most prevalent  $\text{Li}^+$  brine deposits. These deposits are pools of saline groundwater that have been enriched with Li from the Earth's crust (USGS, 2017). Arid climates with immense sun exposure promote the formation of these deposits, as is the case in the ABC Triangle. However, the ionic concentrations of brines are diverse due to varying regional characteristics, seasons, and evaporation rates per deposit. To date, salt lakes are the most conventional aqueous solutions for  $\text{Li}^+$  extraction.

Both salt lakes and seawater possess complex concentrations of chlorine ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), nitrate ( $\text{NO}_3^-$ ), bicarbonate ( $\text{HCO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ) and other ions, albeit seawater at lower concentrations. On average, the total dissolved solids in brines range from 170,000 to 330,000 ppm, compared to 500 to 30,000 ppm in seawater (Flexer et al., 2018; Moran, 2018). The same disparity is observed in their relative  $\text{Li}^+$  concentrations. Salt lake  $\text{Li}^+$  concentrations typically range from 54 to 1,600 ppm, compared to a range of 0.1–0.2 ppm in seawater (Yaksic and Tilton, 2009). Although the  $\text{Li}^+$  content of salt lakes is generally three orders of magnitude higher than seawater, both resources are low  $\text{Li}^+$  concentration solutions: the concentration of  $\text{Li}^+$  is meager relative to the concentrations of the major ions ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ ) in both solutions. Table 1 provides the total reserves,  $\text{Li}^+$  content, and principal  $\text{Li}^+$  mass ratios for various salt lakes and oceans. Lake Zabuye, Salar de Atacama, Salar de Uyuni, Salar del Hombre Muerto, Smackover Formation, and the Great Salt Lake are currently large-scale DLE project sites. The remaining salt lakes and oceans listed have lower  $\text{Li}^+$  concentrations and are prime candidates for DLE using the technologies reviewed in this paper, given their ionic compositions.

Salt lake brines can generally be classified into four main types based on their composition: carbonate ( $\text{CO}_3^{2-}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), magnesium sulfate ( $\text{MgSO}_4$ ), and chloride ( $\text{Cl}^-$ ) (Qinghai Institute of Salt Lakes, 2019). The first four salt lakes listed in Table 1 highlight the variation in ionic concentration across the four different brine types. Ultimately, the ionic concentrations of the different brine types and seawater impact the extraction technology's performance. The aqueous solution's  $\text{Mg}^{2+}$  to  $\text{Li}^+$  mass ratio ( $\text{Mg}^{2+}/\text{Li}^+$ ) is a crucial example. A study on the major ionic concentrations of 74 salt lakes in the Qinghai-Tibetan Plateau revealed that the average  $\text{Mg}^{2+}/\text{Li}^+$  ratios for carbonate, sodium sulfate, magnesium sulfate, and chloride brines are 1.5, 24.6, 151.2, and 324.5 respectively (Li et al., 2019b). Comparatively, the average  $\text{Mg}^{2+}/\text{Li}^+$  ratio of seawater is 7,340. Saline waters with an  $\text{Mg}^{2+}/\text{Li}^+$  ratio equal to or below ten ( $\leq 10$ ) are classified as low –  $\text{Mg}^{2+}/\text{Li}^+$ , while those with  $\text{Mg}^{2+}/\text{Li}^+$  greater than ten ( $> 10$ ) are classified as high- $\text{Mg}^{2+}/\text{Li}^+$ . (Heidari and Momeni, 2017). Therefore, seawater and sodium sulfate, magnesium sulfate, and chloride brines are high –  $\text{Mg}^{2+}/\text{Li}^+$ , low  $\text{Li}^+$  concentration solutions. Conversely, carbonate brines are low –  $\text{Mg}^{2+}/\text{Li}^+$ , high  $\text{Li}^+$  concentration solutions. These brine classifications are summarized in Table 2. Carbonate brine types have been the most economical and sustainable  $\text{Li}^+$  extraction resources for traditional evaporation and precipitation extraction methods due to their low –  $\text{Mg}^{2+}/\text{Li}^+$  mass ratios and higher  $\text{Li}^+$  concentrations relative to the other solutions (Li et al., 2019b; Zhang et al., 2019). However, the emergence of the specialized precipitants, solvents, Li-ion sieves, Li-imprinted membranes, and electrochemical systems examined in this review may improve the feasibility of extraction from high –  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration solutions. Further detail on how ionic

TABLE 1 Major ionic concentration and competing ion mass ratios of select salt lakes and oceans.

Resource	Location	Reserves (Mt)	Li <sup>+</sup> (mg/L)	Cl <sup>-</sup> (g/L)	Na <sup>+</sup> (g/L)	SO <sub>4</sub> <sup>2-</sup> (g/L)	Mg <sup>2+</sup> (g/L)	K <sup>+</sup> (g/L)	HCO <sub>3</sub> <sup>-</sup> (g/L)	Mg <sup>2+</sup> /Li <sup>+</sup>	Ca <sup>2+</sup> /Li <sup>+</sup>	Na <sup>+</sup> /Li <sup>+</sup>	K <sup>+</sup> /Li <sup>+</sup>	pH	Refs
Dongtai Lake (Magnesium Sulfate)	QTP China	1	141	187	332	18	6	4	0	43	0	2,355	28	7.75	o
Lexiewudan Lake (Chloride)	QTP China	0.06	103	54	30	1	1	2	0	10	19	291	19	8.2	f,o
Yibu Chaka (Sodium Sulfate)	QTP China	NP	43	43	34	17	1	1	0	23	0	791	23	8.2	o,p
Lake Zabuye (Carbonate)	QTP China	1.5	970	156	130	39	0	41	0	0	0	134	42	9.2	f,i,j,n,o
Salar de Atacama	Chile	9	2,100	119	51	38	12	24	NP	6	0	24	11	8.68	i,j,n,s,v
Salar de Uyuni	Bolivia	21	960	190	91	21	20	17	NP	21	3	95	17	6.4	i,j,n,v
Salar del Hombre Muerto (Well)	Argentina	1.2	504	151	92	8	0.79	6	NP	2	1	183	11	8	g,j,n
Lake Frome	Australia	0.75	14	173	116	14	1	0.370	0.11	76	42	8,593	27	6.5	e,j
Dead Sea	Israel	5.4	20	224	33	0.350	52	8	0	2,580	930	1,670	395	6.2	i,k,m,n
Great Salt Lake	UT, United States	0.53	18	72	41	8	4	2	0.47	222	11	2,283	133	7.95	i,l,n,v
Salton Sea	CA, United States	0.32	215	128	46	0.10	0.02	13	NP	0	106	215	58	5.2	i,j,n,y
Smackover Formation	AK, United States	0.75	174	172	67	0.45	3.5	3	0	20	198	385	16	5.35	c,t
Arctic Ocean	-	-	0.26	0.04	0.03	0.01	0.004	0.001	NP	15	77	115	5	8.1	b
Atlantic Ocean	-	-	0.17	19	10.8	0.9	1.3	0.40	0.03	7,588	2,353	63,353	2,353	8	a,t,u
Pacific Ocean	-	-	0.19	19	10.7	2.7	1.3	0.40	0.14	6,760	2,135	55,693	2083	7.5	t,w,x
Arabian Gulf (Indian Ocean)	-	-	0.18	19	12.0	3.2	1.5	0.46	0.16	8,296	2,125	65,130	2,522	8	h
Caspian Sea	-	-	0.21	5.4	3.2	3.0	0.73	0.08	0.22	3,486	1,638	15,219	400	8	q,r
Red Sea	-	-	0.26	155	93	0.84	0.76	1.87	0.14	2,916	19,656	354,389	7,137	8.1	d,t

Note. Data is from Angino and Billings (1966)<sup>a</sup>, Brown et al. (2020)<sup>b</sup>, Collins (1974)<sup>c</sup>, Craig (1969)<sup>d</sup>, Draper and Jensen. (1976)<sup>e</sup>, Gao et al. (2016)<sup>f</sup>, Godfrey et al. (2013)<sup>g</sup>, Gouda et al. (1993)<sup>h</sup>, Grosjean et al. (2012)<sup>i</sup>, Gruber et al. (2011)<sup>j</sup>, Jamal and Khzaee (2019)<sup>k</sup>, Jones et al. (2009)<sup>l</sup>, Katz et al. (2009)<sup>m</sup>, Li et al. (2019b)<sup>n</sup>, Li et al. (2019b)<sup>o</sup>, Li et al. (2006)<sup>p</sup>, Millero and Chetirkin. (1980)<sup>q</sup>, Pouraghabar et al. (2021)<sup>r</sup>, Schmidt et al. (2019)<sup>s</sup>, Steiner et al. (2022)<sup>t</sup>, Summerhayes and Thorpe. (1996)<sup>u</sup>, Sun et al. (2021)<sup>v</sup>, Takeuchi (1980)<sup>w</sup>, Voutchkov (2010)<sup>x</sup>, Williams and McKibben. (1989)<sup>y</sup>.

TABLE 2 Classification of the four major brine types according to  $Mg^{2+}/Li^+$  mass ratio.

Brine Concentration	High $Mg^{2+}/Li^+$ ( $> 10$ )	Low $Mg^{2+}/Li^+$ ( $\leq 10$ )	Avg. $Mg^{2+}/Li^+$ Mass Ratio
Carbonate		✓	1.5
Sodium Sulfate	✓		24.6
Magnesium Sulfate	✓		151.2
Chloride	✓		324.5

concentration impacts each extraction technology will be provided in the subsequent sections.

### 3 Traditional lithium extraction

The evaporation, purification, and reactive crystallization, or precipitation,  $Li^+$  extraction method is credited as the first technology investigated and applied in industrial applications. The  $Li^+$  concentration of naturally occurring salt lake brines is too low for cost-effective extraction without a pre-enrichment process (Vikström et al., 2013; Flexer et al., 2018). Consequently, solar energy is used to evaporate, and therefore, concentrate the  $Li^+$  in the brine after it is pumped from the salt lake into large evaporation ponds. The optimal conditions for this process are an arid climate, consistent, unidirectional winds, low salt water permeability, and low rainfall. This evaporitic enrichment process takes several months as the brine is cycled continuously through a series of ponds that increase in salt saturation. When lithium chloride ( $LiCl$ ) concentration in the evaporation pond reaches approximately 6,000 ppm, the brine is pumped to a recovery pond. The ion salts that do not spontaneously precipitate, such as boron, calcium, magnesium, and sulfate, must be removed with chemical treatments. Lime ( $Ca(OH)_2$ ) is added to the brine to remove the  $Mg^{2+}$  as magnesium hydroxide ( $Mg(OH)_2$ ) and remove sulfate as calcium sulfate ( $CaSO_4$ ) via single-replacement and acid-base neutralization reactions, respectively. The remaining brine is treated with sodium carbonate ( $Na_2CO_3$ ) to remove residual  $Ca^{2+}$  as  $CaCO_3$  through a single-replacement reaction. Additionally, the brine reaches critical supersaturation after  $Na_2CO_3$  is introduced, and  $Li_2CO_3$  crystallization begins. The crystal nuclei begin to form and grow as crystal ions spread and deposit on the  $Li_2CO_3$  nuclei surfaces. The  $Li_2CO_3$  nuclei grow into precipitated particles that aggregate into larger particles (Zhao et al., 2019). The final product is a chemically stable, odorless, white powder. Typically, the initial  $Li_2CO_3$  product is dissolved and re-precipitated until battery-grade purity (99.5 wt%) is reached (Flexer et al., 2018). The final product is then used as a precursor for the Li compounds utilized for the cathodes and electrodes of Li-ion batteries. However,  $Li_2CO_3$  can also be converted into other industrial salts or treated to yield pure Li metal.

This  $Li^+$  extraction method is the most conventional and economical method to date, primarily due to its use of solar energy for the  $Li^+$  enrichment process. Additionally, the chemicals added for each ion salt precipitation step and the production infrastructure afford low initial investment and operation costs. However, there are significant drawbacks associated with this extraction method. While  $Li_2CO_3$  extraction from brine has lower life-cycle greenhouse gas (GHG) emissions than ore mining, the initial product quality is much lower (Kelly et al., 2021).  $Li_2CO_3$  produced from terrestrial extraction achieves an initial purity close to 99% wt. Conversely, additional processing is required to achieve comparable purity with conventional brine extraction, where initial product purity ranges from 50 to 80% wt (Zhang et al., 2019). Furthermore, the chemicals used for precipitation and the waste produced by this process have raised many socio-environmental concerns (Anlauf, 2016; Liu et al., 2019; Dorn et al., 2020). There is a threat of  $Li_2CO_3$  and sodium carbonate leaching into the environment and contaminating the soil, air, and freshwater supply of surrounding communities (Agusdinata et al., 2018). Similarly, large amounts of waste are produced during precipitation and generally left to accumulate on the margins of the ponds. A salt lake with an annual production rate of 18,000 MT will produce approximately  $2 \times 10^7$  tons of waste, which translates to a land area of 10 km<sup>2</sup> (Flexer et al., 2018). Therefore, practical resource, waste, and land-use management strategies are of utmost priority and should be developed in tandem with Li production expansion efforts. Further investigation into the potential impacts on human health and native biodiversity is also a critical component of expansion efforts.

The economy of traditional Li extraction from low  $Li^+$  concentration aqueous solutions is highly dependent on four key factors: 1) land and climate suitability; 2) production life cycle time; 3) the brine's natural  $Li^+$  concentration; and 4) the mass ratio of competing ions to  $Li^+$  (i.e.,  $Mg^{2+}/Li^+$  mass ratio). Producing Li from brine is an intricate process because productivity is driven by environmental factors that are impossible to control and increasingly more difficult to predict due to the disruptive influence of climate change on historical weather patterns. Consequently, a single extraction facility can experience variations in production speed and

efficiency throughout the year (Perez de Solay, 2017). This production instability is especially concerning, given that 12–24 months are required to enrich the brine for Li recovery alone. Consequently, traditional Li<sup>+</sup> extraction is uneconomical for solutions with concentrations less than 30 ppm. For reference, Salar de Atacama has one of the world's highest Li<sup>+</sup> concentrations (2,100 ppm) and evaporation rates (3,200 mm/year), and the Li<sup>+</sup> enrichment process ranges from 12 to 18 months. Finally, the Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio is perhaps the most critical consideration for determining application feasibility. High amounts of Mg<sup>2+</sup> slow the evaporation process and prevent LiCl formation, the first step to Li<sub>2</sub>CO<sub>3</sub> production. Additionally, excessive Mg<sup>2+</sup> causes precipitant overconsumption, further contributing to precipitation efficiency challenges and increasing operational costs. Therefore, the traditional Li<sup>+</sup> extraction method is economically infeasible for aqueous solutions with high Mg<sup>2+</sup>/Li<sup>+</sup> mass ratios (> 10). However, most brines and seawater are classified as high Mg<sup>2+</sup>/Li<sup>+</sup> aqueous solutions (see Table 1). This conundrum has motivated the development of the subsequent technologies highlighted in this review.

## 4 High Mg<sup>2+</sup>/Li<sup>+</sup> precipitant extraction

High Mg<sup>2+</sup>/Li<sup>+</sup> precipitants continue to leverage traditional precipitation extraction's most advantageous aspects: a solar-powered Li<sup>+</sup> enrichment process (optional), low-cost chemical agents, and easy industrialization. Their extraction mechanism is identical: the precipitants are added to the aqueous extraction solution to generate supersaturation *via* chemical reactions. Once the extraction solution reaches critical supersaturation, the metal ions present (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) can be crystallized in sequence so that the competing metal complexes are removed and a high purity Li complex is the final product. However, unlike traditional precipitants, they have effectively extracted Li<sup>+</sup> from high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration solutions. Additionally, their selectivity rates are comparable to or higher than the average selectivity rates achieved by traditional precipitants. The main challenges facing high Mg<sup>2+</sup>/Li<sup>+</sup> precipitants are their sensitivity to precipitant dosage (precipitant to target ion molar ratio), pH, temperature, and very high competing ion concentrations. These factors directly impact the technology extraction efficiency, the recovery and quality of the Li products, and potential co-products. Similarly to traditional precipitants, high operational costs stemming from precipitant overconsumption, and pollution from process waste are potential challenges. Therefore, extensive experimentation is required to establish productive to optimal ranges for each precipitant performance factor and substantiate their technological feasibility. Ultimately, their technological advantages combined with the opportunity to co-precipitate additional products for commercial resale indicate that high Mg<sup>2+</sup>/Li<sup>+</sup>

precipitants are promising for Li<sup>+</sup> extraction from high Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio brines. However, further experimentation is needed to determine the feasibility of solely using these precipitants for Li extraction from seawater. To date, high Mg<sup>2+</sup>/Li<sup>+</sup> precipitants have been paired with ion exchange technologies for seawater extraction (Um and Hirato, 2014). Table 3 provides the aqueous solution, Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio, recovery, thermal stability, products, product quality, extraction time, and optimal pH for various high Mg<sup>2+</sup>/Li<sup>+</sup> precipitants.

### 4.1 Aluminate precipitation method

The aluminate precipitation method has demonstrated excellent performance in Li<sup>+</sup> recovery from high Mg<sup>2+</sup>/Li<sup>+</sup> aqueous solutions in experiments dating back to 1960 (Goodenough, 1960; Goodenough and Stenger, 1961; Kaplan, 1963; Pelly, 1978; Epstein et al., 1981; Isupov et al., 1999; Hamzaoui et al., 2007; Hamzaoui et al., 2008; Yang et al., 2013; Li et al., 2015; Heidari and Momeni, 2017; Liu et al., 2018). Epstein et al. (1981) precipitated Li<sup>+</sup> from the dead sea as lithium aluminate (LiAlO<sub>2</sub>), used a liquid-liquid extraction technique to separate the Li<sup>+</sup> from the Al<sup>3+</sup>. Similarly, Kaplan (1963) recovered Li<sup>+</sup> through LiAlO<sub>2</sub> precipitation from dead sea brine. Typically, an aluminum salt (AlCl<sub>3</sub> · H<sub>2</sub>O) and sodium hydroxide (NaOH) are added to the salt lake brines instead of lime and sodium carbonate. The amorphous aluminum hydroxide (Al(OH)<sub>3</sub>) created by this mixture selectively precipitates Li<sup>+</sup>. Lithium aluminate precipitate (LiCl<sub>2</sub>·2Al(OH)<sub>3</sub>·H<sub>2</sub>O) is produced, and the Li<sup>+</sup> in the precipitate is expelled by manipulating the solution pH: the Li<sup>+</sup> is released from the precipitate in acidic and alkaline conditions Zhang et al. (2019). Experimental studies with synthetic brine report that the optimal values for Al/Li, mixing time, pH, and temperature are 4.7, 3 h, 7.2, and 25°C, respectively (Hamzaoui et al., 2007; Hamzaoui et al., 2008). The highest Li percent recovery achieved with these parameters is 73%. However, the actual recovery in natural brine systems decreased to 60%. This reduction in Li recovery is attributed to brine impurities, such as boron, and variable environmental conditions (Pauwels et al., 1995). The challenges associated with this particular precipitation method are the sensitivities to Al<sup>3+</sup>/Li<sup>+</sup> ratio, mixing time, and the solution pH at ambient temperatures.

Furthermore, Heidari and Momeni (2017) conducted experimental studies on Li recovery from Urmia lake using lithium aluminate. An aluminum salt, aluminum chloride (AlCl<sub>3</sub>·6H<sub>2</sub>O), and NaOH were used to co-precipitate Li<sup>+</sup> from two Urmia Lake water samples. The first sample had a Li<sup>+</sup> concentration of 0.038 ppm and an approximated Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio of 326. The second sample had a Li<sup>+</sup> concentration of 0.055 ppm and an approximated Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio of 207.

TABLE 3 High Mg<sup>2+</sup>/Li<sup>+</sup> precipitant extraction from salt lake brines, simulated brines, and seawater.

References	Precipitation method	Reagents	Solution	Mg <sup>2+</sup> /Li <sup>+</sup> Mass Ratio	Recovery	Thermal stability	Product	Product quality	Ext. Time	pH
Hamzaoui et al. (2007)	Aluminum	Al(OH) <sub>3</sub>	Tunisian Brine	260	60%	25 °C	LiAlO <sub>2</sub>	-	3 h	7
Pelly (1978)	Aluminum	Al(OH) <sub>3</sub>	Dead Sea Brine	2,580	90%	-	LiAlO <sub>2</sub>	-	3 h	6.6–7.2
Heidari and Momeni. (2017)	Aluminum	Al(OH) <sub>3</sub>	Urmia Lake	325.8	76.4%	30 °C	Li <sup>+</sup>	-	3 h	7.5
Li et al. (2015)	Aluminum	Al-Ca alloy	Salt Lake Brine	-	94.6%	70 °C	LiCl-Al(OH) <sub>3</sub> H <sub>2</sub> O	-	1 h	-
Goodenough, (1960)	Aluminum	Al(OH) <sub>3</sub>	Chloride Brine	324.5	82%	25 °C	LiCl	-	-	6.4
Goodenough and Stenger (1961)	Aluminum	Al(OH) <sub>3</sub>	Chloride Brine	324.5	91%	120–130°C	LiCl	-	1.5 h	-
Isupov et al. (1999)	Al-LDH	LADH-Cl	Natural Brine	-	93–96%	-	LiCl	5–7 g/L	-	3–8
Paranthaman et al. (2017)	Al-LDH	LDH	Geothermal Brine	-	91%	95°C	LiCl	-	-	6
An et al. (2012)	Co-Precipitate	Ca(OH) <sub>2</sub> , Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Na <sub>2</sub> CO <sub>3</sub>	Salar de Uyuni Brine	21	90% Li <sup>+</sup> , 98.98% Mg <sup>2+</sup> , 71.43% B	80–90°C	Li <sub>2</sub> CO <sub>3</sub>	99.55%	1 h	11.3
Xu et al. (2009)	Co-Precipitate	NH <sub>3</sub> , NH <sub>4</sub> HCO <sub>3</sub> , NaOH	Salt Lake Brine	-	98% Mg <sup>2+</sup> , 95% Li <sup>+</sup>	25 °C	Li <sub>2</sub> CO <sub>3</sub>	-	20–30 min	12
Tran et al. (2013)	Co-Precipitate	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> , NaOH	Salar de Uyuni Brine	21	80% Ca <sup>2+</sup> , 95% Mg <sup>2+</sup> , 35% Li <sup>+</sup> , K <sup>+</sup>	20–22°C	MgC <sub>2</sub> O <sub>4</sub> , CaC <sub>2</sub> O <sub>4</sub> , Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	99.5%	1 h	3–5.5

Therefore, both samples are high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration aqueous solutions. The first step in the extraction process involved adding and dissolving AlCl<sub>3</sub>·6H<sub>2</sub>O into the water samples. Next the alkaline reagent, NaOH, was added to increase the pH and form the precipitant, Al(OH)<sub>3</sub>. The Li<sup>+</sup> ions present in the solution were then absorbed into the Al(OH)<sub>3</sub>. Finally, the Li<sup>+</sup> was desorbed from the solid phase using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The maximum Li recovery from both samples occurred at a pH of 7.5. The sample with the highest Li<sup>+</sup> concentration, 0.055 ppm, had a percent recovery of 76.4%, whereas the sample with 0.038 ppm Li<sup>+</sup> concentration had a percent recovery of 71%. These Li percentages of recovery are comparable to those achieved by traditional precipitants from salt lakes with Li<sup>+</sup> concentrations three to four orders of magnitude higher than the two samples tested. Also, the high Mg<sup>2+</sup>/Li<sup>+</sup> mass ratios did not impact either sample's Li<sup>+</sup> adsorption or desorption process. Therefore, this technology is promising for Li<sup>+</sup> extraction from seawater, and other brines with Li<sup>+</sup> concentrations less than 30 ppm. The main challenges for Li<sup>+</sup> extraction *via* this precipitant are the sensitivities to ambient temperature, pH, and initial Li<sup>+</sup> concentration. Heidari and

Momeni (2017) indicate Li<sup>+</sup> adsorption is reduced when temperatures exceed 30 °C. Furthermore, the amphoteric properties of the Al(OH)<sub>3</sub> surface groups only enhance the Li<sup>+</sup> adsorption capacity when the pH is in the 7 to 8 range (Zymon and Kurbiel, 1986). Finally, the efficiency of the Li<sup>+</sup> adsorption process improves with increasing Li<sup>+</sup> concentration, as seen in the percent recovery of the two samples. This finding suggests that an Li<sup>+</sup> pre-concentration step will be required to improve the feasibility of this precipitant for large-scale Li production from aqueous solutions with very high Mg<sup>2+</sup>/Li<sup>+</sup> mass ratios and seawater.

## 4.2 Aluminum layered double hydroxide chloride precipitation method

Isupov et al. (1999) used a sorbent synthesized from aluminum hydroxide and the chloride of the double hydroxide of lithium and aluminum (LADH-Cl) to precipitate and extract Li<sup>+</sup> from natural brine. The reusable sorbent demonstrated Li percent recovery ranging from 93% to 96%



and an LiCl product quality of 5–7 g/l. Paranthaman et al. (2017) developed a similar lithium aluminum layered double hydroxide chloride (Al-LDH) sorbent for Li<sup>+</sup> extraction using a three-stage, bench-scale column extraction process. The aluminum Al-LDH (Li:Al ratio 1:3) sorbent selectively precipitated LiCl from geothermal brine with an initial Li<sup>+</sup> concentration of 360 ppm. The Mg<sup>2+</sup>/Li<sup>+</sup> ratio of the brine is unreported. In the column extraction process three solutions, the initial brine, intermediate wash (NaCl + LiCl), and final strip solution (purely LiCl), are fed into the column extractor. From there, two computer-operated pinch valves are used to cycle the column extractor through three steps: 1) loading the lithium sorbent with the LiCl present in the brine; 2) washing the sorbent to remove any unwanted ions that are trapped; 3) a final washing of the sorbent to desorb the LiCl ions.

The Al-LDH extraction technology demonstrated an approximated percent recovery of 91% and a high selectivity of Li<sup>+</sup> compared to competing ions Na<sup>+</sup> and K<sup>+</sup> at 47.87 and 212 selectivity, respectively. The only chemical agents required for this process are NaCl and LiCl, and their low cost contributes to the economy of this technology. Additionally, the load-wash-elution cycle does not produce secondary waste, an important consideration for environmental contamination and land use. Although the sorbent composition and column extraction technique could be further optimized to improve selectivity, capacity, and competing ion removal, this novel sorbent technology is a promising solution for Li extraction from aqueous solutions with high competing ion to Li<sup>+</sup> ratios.

### 4.3 Magnesium Co-precipitation method

The high concentrations of Mg<sup>2+</sup> present in salt lake brines and seawater have motivated investigations into the potential economic benefits of Mg and Li co-precipitation extraction from aqueous solutions. Mg and its compounds are essential to the global agricultural, insulation, automotive, food, pharmaceutical, chemical industries. The International Magnesium Association estimates global Mg production exceeds 429,000 MT annually, with steady increases attributed to the demand for Mg<sup>2+</sup> alloys in the automobile industry (Tran et al., 2013). On average, seawater contains about 1,300 ppm of Mg<sup>2+</sup>, and the estimated global resource of Mg bearing brines and bitters is in the billions of tonnes. Therefore, a co-extraction technology that efficiently harvests Li and Mg from these abundant aqueous resources is of high economic value.

Quintero et al. (2020) explored the use of oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) for Mg<sup>2+</sup> and Ca<sup>2+</sup> precipitation before Li<sup>+</sup> precipitation. The recovery of these competing divalent ions before Li<sup>+</sup> improves the efficiency of Li<sup>+</sup> selectivity and produces high-quality calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>) and magnesium oxalate (MgC<sub>2</sub>O<sub>4</sub>). They achieved a 90% Ca<sup>2+</sup> removal rate and a maximum yield of 88% for the solid Li<sup>+</sup>

and Mg<sup>2+</sup> products, lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) and magnesium hydroxide (Mg(OH)<sub>2</sub>), respectively. The Ca<sup>2+</sup> extraction yield was obtained by adding oxalic acid and sodium hydroxide (NaOH) (5 M) to the Li-enriched refined brine and then allowing a 2 h lapse at room temperature. The Oxalic Acid/Ca was added until a molar ratio of 6:1 was achieved. A NaOH/Oxalate molar ratio of 3:3:1 was used to lower the extraction solution pH into a 0–1 range. The Li<sub>2</sub>CO<sub>3</sub>/Mg(OH)<sub>2</sub> was then co-precipitated by adding 5M NaOH and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The Mg<sup>2+</sup> was precipitated with NaOH, then Na<sub>2</sub>CO<sub>3</sub> was used to precipitate the Li<sub>2</sub>CO<sub>3</sub>.

Technologies that remove and co-precipitate competing ions (Mg<sup>2+</sup> and Ca<sup>2+</sup>) from high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration aqueous solutions demonstrate high Li<sup>+</sup> yield and extraction efficiency rates. Additionally, their co-production of saleable products, such as magnesium hydroxide, present a lucrative opportunity to sustainably supply the industrial demand for these co-products and Li. Overall, they present a more efficient and sustainable crystallization process than what is used in traditional precipitation extraction. The main drawback of this technology is the sensitivity to pH and the concentration of competing ions during the co-precipitation processes. If the concentration of these ions is not controlled, they become impurities that decrease the co-precipitation efficiency and quality of the co-products. More authors have explored the use of oxalic acid to remove or co-precipitate competing ions in high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration aqueous solutions. An et al. (2012) used calcium hydroxide and sodium oxalate in a two-step precipitation process to recover > 90% of battery quality (99.55%) Li<sub>2</sub>CO<sub>3</sub>, 98.98% of Mg<sup>2+</sup>, and 71.43% of boron from Salar de Uyuni brine. Xu et al. (2009) developed a two-stage ammonia and ammonia bicarbonate co-precipitation process to remove 98% of Mg<sup>2+</sup> and recover 95% of Li<sup>+</sup>. Finally, Tran et al. (2013), Tran et al. (2016) explored the co-precipitation of magnesium oxalate and magnesium carbonate from Salar de Uyuni brine and achieved 99.5% and 99.6% purity, respectively.

## 5 Solvent extraction

Solvent extraction, also called liquid-liquid extraction (LLE), is a method used to separate compounds according to their relative solubilities into two immiscible liquid phases, an organic phase, and an aqueous phase. An organic phase containing the solvent is added to the aqueous Li solution to form organic Li<sup>+</sup> complexes and equilibrate coexisting metals (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>). The Li<sup>+</sup> complexes and some residual impurity metals are transferred to the organic phase. However, most impurity metals remain in the Li<sup>+</sup> depleted aqueous solution, or raffinate. The organic phase containing the extracted Li<sup>+</sup> complexes is scrubbed to remove the remaining impurities. The scrubbed organic phase is stripped, typically with an acid, to remove the Li<sup>+</sup> in a highly concentrated strip liquor.

TABLE 4 Li<sup>+</sup> solvent extraction from salt lake brines, simulated brines, and seawater.

References	Solvent type	Solution	Mg <sup>2+</sup> /Li <sup>+</sup> Mass Ratio	Selectivity	Extraction efficiency	Recovery	Thermal stability	Regeneration	Extraction time	pH
Torrejos et al. (2016)	Chelating Acidic	Simulated Brine		1954 Na <sup>+</sup> , 138 K <sup>+</sup>	72.8%	100%, 0.1 HCl	50°C	5 cycles	10 min	12
Xiong et al. (2022)	Chelating Acidic	Simulated Brine		68.09 Ca <sup>2+</sup> , 24.53 K <sup>+</sup> , 16.32 Na <sup>+</sup> , 3.99 Mg <sup>2+</sup>	7%		20°C		30 min	
Huang et al. (2018)	Chelating Polymer	Simulated Brine		6.34 Ca <sup>2+</sup> , 8.91 K <sup>+</sup> , 5.83 Na <sup>+</sup> , 4.75 Mg <sup>2+</sup>		91.8%	25°C	5 cycles	3 h	6
Li et al. (2019a)	Chelating	Simulated Brine	1,000	50 Li <sup>+</sup> /Na <sup>+</sup> , 84.6 Li <sup>+</sup> /K <sup>+</sup> , 157 Li <sup>+</sup> /Ca <sup>2+</sup>	1.1 mol/mol	85%		6 cycles	10 min	
Bai et al. (2020)	Chelating Polymer	Simulated Brine		12.3 Ca <sup>2+</sup> , 3.10 K <sup>+</sup> , 9.06 Na <sup>+</sup> , 3.79 Mg <sup>2+</sup>	4.43 mg/g	4.08 mg/g	25°C	5 cycles	2 h	6
Harvianto et al. (2016)	Chelating Neutral	Seawater			93%	65%		3 cycles	80 min	2–4
Zhou et al. (2011)	Acidic Neutral	LiCl	94.8		98%		25°C		10 min	
Shi et al. (2018)	Acidic Neutral	Salt Lake Brine		23,521.4 Li <sup>+</sup> /Mg <sup>2+</sup> , 563.8 Li <sup>+</sup> /H <sub>3</sub> BO <sub>3</sub>	96%	28 g/L	25°C	25 cycles	4 h	4.7
Su et al. (2022)	Acidic Neutral	Salt Lake Brine	22		80%	100%	20°C		50 min	0.86
Bai et al. (2022)	Ionic Liquid	Simulated Brine	274		98%	98%	25°C	6 cycles	20 min	
Wang et al. (2018)	Ionic Liquid	Salt Lake Brine	16	74.86 Li <sup>+</sup>	91%		25°C		30 min	5
Wang et al. (2018)	Ionic Liquid	Salt Lake Brine	16	71.29 Li <sup>+</sup>	88%		25°C		30 min	5
Wang et al. (2018)	Ionic Liquid	Salt Lake Brine	16	51.27 Li <sup>+</sup>	88%		25°C		30 min	5
Wang et al. (2018)	Ionic Liquid	Salt Lake Brine	16	44.68 Li <sup>+</sup>	84%		25°C		30 min	5
Wang et al. (2018)	Ionic Liquid	Salt Lake Brine	16		37%		25°C		30 min	5

Finally, the Li<sup>+</sup> stripped organic phase is regenerated and recycled to the extraction stage (Bang Mo, 1984; Butt et al., 2022). Cation exchange is the driving mechanism for the extraction, scrubbing, and stripping stages, and acid-base neutralization is the driving mechanism for the organic phase regeneration stage (Shi et al., 2018). This extraction process is typically stand-alone and does not require the pre-concentration of Li<sup>+</sup> in the aqueous solution. Additionally, solvent extraction can achieve any concentration factor up to the saturation limit compared to other DLE technologies. However, like precipitation, solvent extraction generates high volumes of harmful waste during the scrubbing and stripping stages. Additionally, the corrosive nature of the

solvents and process solutions point to equipment and environmental damages under continuous operating conditions. Finally, the most significant barrier to the techno-economic feasibility of solvents for low Li<sup>+</sup> concentration solutions is their high cost compared to present-day industrial Li<sup>+</sup> precipitants and solvents, which are ineffective for low Li<sup>+</sup> concentration solutions. Table 4 provides the aqueous solution, Mg<sup>2+</sup>/Li<sup>+</sup> mass ratio, selectivity, extraction efficiency, recovery, thermal stability, regeneration, Li product, extraction time, and optimal pH value for several solvents. Note that the extraction efficiency is the percentage of the Li<sup>+</sup> solute that moves from the brine to the extraction solution.

TABLE 5 Li<sup>+</sup> selective crown ethers.

Crown ether	Selectivity order	Li <sup>+</sup> /Na <sup>+</sup>
14-crown-4	Li <sup>+</sup> ≫ Na <sup>+</sup> > (No K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> )	20
Benzo-14-crown-4	Li <sup>+</sup> > Na <sup>+</sup> > K <sup>+</sup> , Rb <sup>+</sup> (No Cs <sup>+</sup> )	4.7
15-crown-4	Li <sup>+</sup> > Na <sup>+</sup> > K <sup>+</sup> > Cs <sup>+</sup> > Rb <sup>+</sup>	3.5
13-crown-4	Li <sup>+</sup> > Na <sup>+</sup> > K <sup>+</sup> , Rb <sup>+</sup> > Cs <sup>+</sup>	2.3
Benzo-12-crown-4	Li <sup>+</sup> > Na <sup>+</sup> > K <sup>+</sup> > Rb <sup>+</sup> > Cs <sup>+</sup>	1.8
12-crown-4	Li <sup>+</sup> > Na <sup>+</sup> > K <sup>+</sup> > Rb <sup>+</sup> ≥ Cs <sup>+</sup>	1.7

## 5.1 Chelating extractants

Several studies have investigated chelating extractants, such as crown ether (CE) and its ether derivative for Li<sup>+</sup> extraction. Their polydentate structure encourages Li<sup>+</sup> selectivity. Extraction using these ethers follows Pearson's hard-soft-acid-base (HSAB) principle. The principle asserts that soft acids prefer to bond with soft bases, and hard acids prefer to bond with hard bases. The hard acids possess tiny, highly charged, non-polarizable acceptor atoms. Conversely, softer acids have larger atoms with a lower charge. Also, the bond between the hard acids and bases is dominated by electrostatic interactions, and the bonds between soft acids and bases are covalent. Applying these principles to Li<sup>+</sup> extraction, CEs that use ether oxygens, a hard base species, as donor atoms easily bond with hard acid, alkali metal cations such as Li<sup>+</sup> (Lowry and Richardson, 1987; Pearson, 1990). Li<sup>+</sup> separation efficiency depends on the cavity size of the CE or the CE derivative, especially when competitive ions such as Na<sup>+</sup> and Mg<sup>2+</sup> are present in the extraction solution. The most Li<sup>+</sup> selective CEs are listed in Table 5 (Bartsch et al., 1985).

While the selectivity of CEs is competitive, even for high Mg<sup>2+</sup>/Li<sup>+</sup> ratio solutions, the commercial use of Li<sup>+</sup> extraction using CEs has been limited due to the high costs of the ethers and ether derivatives (Hamilton, 1984; Swain, 2016). Additionally, the influence of their underlying extraction mechanisms on the base metal extraction process is not well understood (Swain, 2016). A final consideration is the severely polluting and corrosive nature of the chemical agents used in solvent extraction that ultimately reduce the lifetime of the process equipment. These factors have contributed to the delay in commercializing this solvent extraction technology. However, the development of more economical CEs could bridge this gap. Future developmental efforts should focus on the three critical factors for CE Li extractability: 1) the structure and size of the CE ring; 2) the basicity of the pendent phenolic group (PPG); 3) the geometry between the CE center and the PPG (Katayama et al., 1985).

## 5.2 Acidic extractants

There are two classes of acidic extractants for liquid-liquid metal extraction: organophosphorus acids and carboxylic

acids. Both acids extract Li<sup>+</sup> from aqueous solutions by cation exchange (Peppard et al., 1958). This extraction process is facilitated by increasing the aqueous solution pH. Conversely, the Li<sup>+</sup> stripping or elution process is triggered by increasing the acidity of the aqueous stripping solution (Xie et al., 2014). To date, acidic solvents have typically been used to extract rare earth and heavy rare earth metals from aqueous solutions, with organophosphorus acids being the more conventional and efficient acid class for extraction (Safarwali et al., 2016). Their characteristically high target ion selectivity and separation efficiency have prompted investigations into their use for aqueous Li<sup>+</sup> extraction. However, the best separation and extraction performance has been achieved by a mixture of acidic and solvating extractants (Chen and Wu, 2000). The oxygen atoms in solvating extractants enable the aqueous solution molecules to be incorporated into the Li<sup>+</sup> coordination sphere to form an extractable solvated complex (Fuks and Majdan, 2000; Roundhill, 2001). Hano et al. (1992) demonstrated this synergy in a foundational experiment investigating Li recovery from geothermal brine using organophosphorus acid and solvating extractants. Di-2-ethylhexyl-phosphoric acid (D2EHPA) and 2-ethylhexyl-phosphoric acid 2-ethylhexyl ester (MEHPA) were the extractant agents, and tri-n-butylphosphate (TBP) or tri-n-octylphosphine-oxide (TOPO) were the solvating extractants. The geothermal brine samples used in the experiments were hot spring water collected from Yamaga and Hazama, Japan.

The Yamaga water Na<sup>+</sup>/Li<sup>+</sup> and Mg<sup>2+</sup>/Li<sup>+</sup> ratios are ~301 and ~4. The Hazama water Na<sup>+</sup>/Li<sup>+</sup> and Mg<sup>2+</sup>/Li<sup>+</sup> ratios are ~184 and ~11, respectively. The Hazama water samples are high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration aqueous solutions. The percent of Li<sup>+</sup> extracted from the Yamaga water samples for D2EHPA and MEHPA were 42.5% and 42.2%, respectively. The percent Li<sup>+</sup> extraction from the Hazama water samples for D2EHPA and MEHPA were 52% and 5.2%, respectively. The TOPO additive did not affect extraction behavior. However, the TBP additive increased Li<sup>+</sup> extraction in all cases. Li<sup>+</sup> extraction percentages for the Yamaga water samples with additive, or D2EHPA + TBP and MEHPA + TBP, were 52.6% and 47.6%, respectively. Similarly, the extraction percentages for the D2EHPA + TBP and MEHPA + TBP Hazama water samples were 88.3% and 11.7%, respectively. D2EHPA and MEHPA demonstrated high selectivity of Li<sup>+</sup> ions over Na<sup>+</sup> and K<sup>+</sup>. However, Ca<sup>2+</sup> and Mg<sup>2+</sup> had a greater affinity for the acidic extractants and demonstrated extraction percentages greater than 91% (excluding Ca<sup>2+</sup>) from the MEHPA and MEHPA + TBP Hazama water samples. D2EHPA + TBP demonstrated the highest extraction performance overall. In a similar study, (Jang et al., 2017), used D2EHPA and TBP to recover Li<sup>+</sup> from oilfield brine in two phases. In the first phase, 94.4% of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions were removed by D2EHPA. In the second phase, D2EHPA and TBP recovered Li at a 41.2% extraction rate. The total amount of Li recovered was 30.8%.

The results from these experiments indicate that combining acidic extractants D2EHPA and MEHPA and neutral extractants (TBP) is ideal for Li<sup>+</sup> extraction from aqueous solutions with minimal divalent ion (Mg<sup>2+</sup> and Ca<sup>2+</sup>) concentrations such as the Salar de Atacama and Lake Zabuye brines. The use of these solvents for Li extraction from high Mg<sup>2+</sup>/Li<sup>+</sup> and Na<sup>+</sup>/Li<sup>+</sup> seawater is infeasible because Li<sup>+</sup> is too dilute. However, these extractants could be leveraged as pre-separation agents that remove the competing divalent ions (Mg<sup>2+</sup> and Ca<sup>2+</sup>) before an additional selectivity process is used to extract the remaining Li<sup>+</sup> ions from solutions with exorbitant competing ion to Li<sup>+</sup> mass ratios. Many other authors have investigated other organophosphoric extractants and TBP for aqueous Li<sup>+</sup> extraction in recent years (Torrejos et al., 2015; Nguyen and Lee, 2018; Su et al., 2022).

### 5.3 Ionic liquid extractants

Ionic Liquids (ILs) are organic compounds comprised of ions with melting points at or below room temperature (25°C). They have many advantageous solvent properties, including high thermal stability, selectivity, and separation efficiency, but marginal volatility (Mori et al., 2015; Patil et al., 2015; Rama et al., 2015). These properties have garnered the interest of researchers working to develop augmented solvents for metal ion extraction. Traditionally, conventional molecular extractants have been combined with ILs that contain fluorinated anions because their immiscible properties facilitate the formation of hydrophobic complexes with the metal ions for extraction. However, extraction with fluorinated ILs leads to hydrofluoric acid contamination, limiting the reuse of ILs for continuous extraction.

Shi et al. (2017) investigated the use of two non-fluorinated ionic liquids (ILs), tetrabutylammonium bis(2-ethylhexyl)-phosphate ([N<sub>4444</sub>][DEHP]) and tetraoctylammonium bis(2-ethylhexyl)-phosphate ([N<sub>8888</sub>]) for aqueous Li<sup>+</sup> extraction. These novel ILs, or functionalized ionic liquids (FILs), were prepared *via* ion exchange and neutralizing reactions. The Li<sup>+</sup> extraction performance of the DEHP-type FILs was tested using a multi-metal-ion solution that contained Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. Both FILs preferred the alkali metal with the smallest ionic radius and the highest surface charge density. Therefore, Li<sup>+</sup> had the leading electrostatic interactions and formed the most stable species with the FILs' [DEHP]<sup>-</sup> anions. Additionally, the initial Li<sup>+</sup> stripping percentage of 90% increased with the number of stripping stages, and complete Li<sup>+</sup> stripping occurred after four stages with minimal reduction in the FILs' extraction efficiency. Overall, the [N<sub>4444</sub>][DEHP] FILs demonstrated higher extraction efficiencies than [N<sub>8888</sub>][DEHP] at 92% and 83%, respectively, due to the increased steric hindrance associated with longer alkyl chains. Bai et al. (2022) investigated the synergy of a phosphate-based ionic

liquid ([N<sub>1888</sub>][P<sub>507</sub>]) and a neutral extractant + acidic ion compound system (TBP + FeCl<sub>3</sub>) for Li<sup>+</sup> extraction from high Mg<sup>2+</sup>/Li<sup>+</sup> brine. At optimal extraction parameters, 97% of the Li<sup>+</sup> solute could be stripped from the solvent. Additionally, an initial extraction efficiency of 61% was achieved after the first extraction-stripping-extraction cycle and rose above 70% for the five remaining cycles.

[N<sub>4444</sub>][DEHP] and [N<sub>8888</sub>][DEHP] FILs show promising continuous Li extraction efficiency from aqueous solutions containing competing monovalent ions (Na<sup>+</sup> and K<sup>+</sup>). Both FILs outperformed DEHPA, a popular acidic extractant (Shi et al., 2017). However, further investigation into the performance of these FILs in the presence of competing divalent ions such as Mg<sup>2+</sup> is needed to determine the feasibility of extraction from brines, seawater, and any other high Mg<sup>2+</sup>/Li<sup>+</sup>, low Li<sup>+</sup> concentration solutions. Conversely, the novel ([N<sub>1888</sub>][P<sub>507</sub>]) + TBP + FeCl<sub>3</sub> extractant system demonstrated promising Li<sup>+</sup> separation and extraction from high Mg<sup>2+</sup>/Li<sup>+</sup> salt lake brine. Unfortunately, there is a potential trade-off between separation and extraction efficiency: increasing the concentration of ([N<sub>1888</sub>][P<sub>507</sub>]) increases Li<sup>+</sup> separation efficiency but causes slight reductions in the extraction efficiency. Further experimentation with extraction solutions similar to those of salt lake brines or seawater would provide more insight into the feasibility of ILs for these applications. In recent years, more authors have studied the performance of other FILs in either salt lake brines or high Mg<sup>2+</sup>/Li<sup>+</sup> aqueous solutions (Gao et al., 2016; Wang et al., 2018; Zante et al., 2019; Bai et al., 2020; Bai et al., 2021; Olea et al., 2022).

### 6 Lithium-ion sieve adsorption

Ion sieve adsorbents are inorganic materials containing template ions that are introduced into an inorganic compound by redox or an ion exchange reaction. A heating process is then used to obtain the compound oxide. After the compound oxide is formed, an eluent is used to remove the target ions from their crystal positions while retaining the vacancy sites on the crystal. The resulting sieve extracts Li<sup>+</sup> *via* two adsorption mechanisms: physisorption driven by electrostatic interaction and chemical adsorption *via* ion exchange (Xu et al., 2019). Hence, the target ions can only be obtained in these crystal sites if the ionic radii are similar to the ionic radii of the template ion. Additionally, the material tends to have a higher selectivity for ions that form the best crystal configuration. As a result, the template ions create a reliable selection effect, allowing for the adsorption of target ions even if multiple ions are present in the solution. This process is known as the "ion-sieve effect" (Weng et al., 2020).

One critical techno-economic challenge facing ion sieves is their tendency to disintegrate during adsorption/desorption cycling. This loss is caused by biofouling and the hydrochloric

acid treatments used for the  $\text{Li}^+$  desorption process. Both sources of loss reduce the adsorption capacity, selectivity, and separation efficiency of the ion sieve during cycling. Consequently, operational costs are driven up because more sieve is needed to compensate for these losses, and Li-ion sieve synthesis is expensive (Hu et al., 2022). Additionally, hydrochloric acid is generally the recovery solution used for sieves and its caustic nature raises concerns for environmental pollution. A final drawback is the extraction lead time. Typically, extraction using ion sieves takes days to complete. (Chung et al., 2008; Chitrakar et al., 2014).

Despite the drawbacks, ion sieves demonstrate high  $\text{Li}^+$  adsorption, selectivity, and cycle stability. Also, the sieves can be regenerated and reused, albeit with some loss after each cycle. More importantly, the adsorption capacity is not impacted by the presence of competing ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Na}^{2+}$ , and  $\text{Mg}^{2+}$ . The passive nature of the extraction process is conducive to low initial investment and operation costs. Lastly, in addition to superior selectivity and separation efficiency, Li-ion sieves demonstrate higher theoretical uptake capacity. This feature is particularly desirable for  $\text{Li}^+$  extraction from high  $\text{Mg}^{2+}/\text{Li}^+$  solutions with  $\text{Li}^+$  concentrations below 30 ppm.

## 6.1 $\text{Li}^+$ manganese oxide-type lithium-ion sieves

Manganese dioxide exists in many different crystalline structures:  $\alpha$ - $\text{MnO}_2$ ,  $\beta$ - $\text{MnO}_2$ ,  $\gamma$ - $\text{MnO}_2$ , and  $\lambda$ - $\text{MnO}_2$ . While each structure demonstrates a strong affinity for  $\text{Li}^+$ , the spinel-type hydrous manganese oxides,  $\lambda$ - $\text{MnO}_2$ , are the top performers (Voinov, 1982; Chitrakar et al., 2000a; Chitrakar et al., 2000b; Liu et al., 2019). This top performance is attributed to the spinel structure of the  $\lambda$ - $\text{MnO}_2$  ion sieve precursor,  $\text{Li}^+$  manganese oxide ( $\text{LiMn}_2\text{O}_4$ ). The template spinel formula is  $(\text{AB}_2\text{O}_4)$ , where the divalent cations, A, occupy eight tetrahedral voids, the trivalent ions, B, occupy 16 octahedral voids, and the oxygen anions, O, occupy the 32 face-centered cube lattice points (Hill et al., 1979). Therefore, the ratio of A: B: O is 8: 16: 32, which can be reduced to 1: 2: 4, or the conventional spinel formula.

As it relates to spinel  $\text{LiMn}_2\text{O}_4$ , the  $\text{Li}^+$  cations occupy the eight tetrahedral voids, manganese (III) and manganese (IV) occupy the 16 octahedral voids, and the oxygen anions occupy the 32 face-centered cube lattice points. The manganese ions have octahedral coordination with the oxygen anions, and the  $\text{MnO}_6$  octahedra share edges that create a three-dimensional host for the  $\text{Li}^+$  guest cations. Furthermore, the  $\text{Li}^+$  tetrahedral voids are located the furthest away from the manganese octahedral voids of the interstitial tetrahedra and octahedra. Consequently, each  $\text{Li}^+$  tetrahedron face is matched with an octahedral void (Xu et al., 2016). This combination of structural features inhibits easy Li-ion exchange without changing crystalline structure during

reversible  $\text{Li}^+$  intercalation. Additionally, the Mn-O framework remains stable after desorption/regeneration with an acidic treatment (Wang et al., 2008; Wang et al., 2014).

The  $\text{LiMn}_2\text{O}_4$  precursor has low  $\text{Li}^+$  adsorption capacity and stability. The maximum adsorption capacities achieved from seawater and salt lake brine are 1.1 and 30.9 mg/g, respectively (Chitrakar et al., 2000b; Wang et al., 2014). However, the stoichiometric proportion between Li: Mn can be altered to increase the theoretical  $\text{Li}^+$  capacity of LMO-type LISs (Xu et al., 2016). Chitrakar et al. (2000b) used a hydrothermal method to synthesize  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  and cubic  $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$ , which achieved  $\text{Li}^+$  adsorption capacities of 25 and 37 mg/g from seawater and salt lake brine, respectively. The highest recorded  $\text{Li}^+$  adsorption capacities for  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  from seawater and salt lake brine are 54.7 and 63 mg/g, respectively (Zandevakili et al., 2014; Ryu et al., 2016). Additionally, the highest recorded  $\text{Li}^+$  adsorption capacities for  $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$  from seawater and salt lake brine are 40 and 28 mg/g, respectively (Chitrakar et al., 2001; Xiao et al., 2013). Currently,  $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$  has the highest theoretical adsorption capacity at 72.8 mg/g. However,  $\text{Li}_{1.67}\text{Mn}_{1.67}\text{O}_4$  requires a two-step preparation process compared to the one-step required for the other precursors. Consequently,  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  are more economical for industrial  $\text{Li}^+$  extraction applications at this time. Table 6 provides the adsorption capacity, cyclical stability, thermal stability, environmental durability, extraction time, and optimal pH of various LMO-type LISs used for  $\text{Li}^+$  extraction from salt lake brines, simulated brines, and seawater.

The main challenges facing LMO-type LISs for large-scale, industrial  $\text{Li}^+$  extraction applications are the residual impacts of the precursor acid treatments. These acid treatments reduce the LMO-type adsorbent stability, adsorption capacity, and durability and cause environmental pollution. While the acid effectively removes most of the  $\text{Li}^+$  without disrupting the precursor crystalline structure, it simultaneously causes manganese to dissolve with each successive treatment (Shen and Clearfield, 1986; Wang et al., 2009; Xiao J. L. et al., 2015; Gao et al., 2018; Weng et al., 2020). The dissolution of the Mn is attributed to the Jahn Teller effect induced by trivalent manganese ( $\text{Mn}^{3+}$ ). The octahedral  $\text{MnO}_6$  structure becomes increasingly distorted, reducing the stability, adsorbent capacity, and durability, and causing considerable water pollution (Jin et al., 2018; Weng et al., 2020). To combat this dissolution phenomenon, many authors have experimented with replacing the  $\text{Mn}^{3+}$  with: divalent cobalt ( $\text{Co}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ), and magnesium ( $\text{Mg}^{2+}$ ); trivalent chromium ( $\text{Cr}^{3+}$ ), aluminum ( $\text{Al}^{3+}$ ), and iron ( $\text{Fe}^{3+}$ ); and, other rare-earth ions (Malyovanyi et al., 2003; Ein-Eli et al., 2005; Eftekhari et al., 2006; Wu et al., 2007; Iqbal and Ahmad, 2008; Amaral et al., 2010; Sakunthala et al., 2010; Wu et al., 2010; Helan et al., 2011; Xu et al., 2011; Xu et al., 2016). LMO-type precursors doped with  $\text{Fe}^{3+}$ , antimony Sb(v), and  $\text{Al}^{3+}$  demonstrated the highest  $\text{Li}^+$  extraction capacity with minimal Mn dissolution. However, ascertaining the optimal

TABLE 6 Li<sup>+</sup> LMO-Type LIS extraction from salt lake brines, simulated brines, and seawater.

References	Precursor	Ion sieve	Solution	Mg <sup>2+</sup> / Li <sup>+</sup> Mass Ratio	Adsorption capacity	Cyclical stability	Thermal stability	Envi. Durability	Ext. Time	pH
Chitrakar et al. (2000b)	LiMn <sub>2</sub> O <sub>4</sub>	λ-MnO <sub>2</sub>	Seawater		39.9 mg/g (Theoretical), 1.1 mg/g (Practical)		22°C	1.5% Mn Loss	144 h	8.1
Chitrakar et al. (2000b)	Li <sub>1.33</sub> Mn <sub>1.67</sub> O <sub>4</sub>	MnO <sub>2</sub> ·0.31H <sub>2</sub> O	Seawater		59.5 mg/g (Theoretical), 25.5 mg/g (Practical)		22°C	< 1.5% Mn Loss	144 h	8.1
Chitrakar et al. (2000b)	Li <sub>1.67</sub> Mn <sub>1.67</sub> O <sub>4</sub>	MnO <sub>2</sub> ·0.5H <sub>2</sub> O	Seawater		73 mg/g (Theoretical), 37mg/g (Practical)		22°C	< 1.5% Mn Loss	144 h	8.1
Xiao et al. (2015a)	Li <sub>4</sub> Mn <sub>5</sub> O <sub>12</sub>	PAM-MnO <sub>2</sub>	Qarhan Brine	264	19 mg/g	30 cycles	30°C		48 h	10.1
Xiao et al. (2015a)	Li <sub>4</sub> Mn <sub>5</sub> O <sub>12</sub>	MnO <sub>2</sub> ·0.4H <sub>2</sub> O	Qarhan Brine	446	39 mg/g, 2.8 mg/g (> 55 cycles)	55 cycles	30°C	2% Mn Loss	48 h	10.1
Zhang et al. (2009)	Li <sub>4</sub> Mn <sub>5</sub> O <sub>12</sub>	β-MnO <sub>2</sub>	LiCl		46 mg/g		30°C	0.28 mg/g Mn Loss	72 h	10.1
Zandevakili et al. (2014)	Li-Mn-O	λ-MnO <sub>2</sub>	Urmia Lake Brine	325.8	63 mg/g, 62 mg/g (> 3 cycles)	3 cycles	30°C	1% Mn Loss	120 h	11
Wang et al. (2009)	Li <sub>1.51</sub> Mn <sub>1.63</sub> O <sub>4</sub>	H <sub>1.36</sub> Li <sub>0.07</sub> Mn <sub>1.65</sub> O <sub>4</sub>	LiCl		33.3 mg/g		25°C	1% Mn Loss	48 h	12
Wang et al. (2009)	Li <sub>1.57</sub> Mn <sub>1.65</sub> O <sub>4</sub>	H <sub>1.41</sub> Li <sub>0.01</sub> Mn <sub>1.65</sub> O <sub>4</sub>	LiCl		37.6 mg/g		25°C	1% Mn Loss	48 h	12
Chitrakar et al. (2012)	Li <sub>1.33</sub> Mn <sub>1.67</sub> O <sub>4</sub>	H <sub>1.33</sub> Mn <sub>1.67</sub> O <sub>4</sub>	Bolivian Brine	22	30 mg/g, 27 mg/g (10 cycles)	10 cycles, 45% Recovery		0.5% Mn Loss (Cycles 1–4) 0.3% Mn Loss (Cycles 5–10)	24 h	6.6
Chitrakar et al. (2012)	Li <sub>1.6</sub> Mn <sub>1.6</sub> O <sub>4</sub>	H <sub>1.6</sub> Mn <sub>1.6</sub> O <sub>4</sub>	Bolivian Brine	22	32 mg/g, 27 mg/g (10 cycles)	10 cycles, 54% Recovery		0.5% Mn Loss (Cycles 1–4) 0.3% Mn Loss (Cycles 5–10)	8 h	6.6
Ryu et al. (2016)	Li <sub>1.33</sub> Mn <sub>1.67</sub> O <sub>4</sub>	LMO Chitosan	Seawater	~8,530	54.65 mg/g, 46.5 mg/g (3 cycles)	3 cycles, 96% Recovery	20°C	~9.2% Mn Loss (3rd Cycle)	72 h	6.6

molar ratio between the doping ions and Mn is critical for achieving a high Li<sup>+</sup> adsorption capacity. Further investigation is needed into improving the cyclical stability and practical ion exchange capacity of Li-Mn-O precursors for large-scale Li production.

## 6.2 Lithium titanium oxide-type lithium-ion sieves

At present, there are two classifications for LTO-type LISs: layered H<sub>2</sub>TiO<sub>3</sub> and spinel H<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. The structure of H<sub>2</sub>TiO<sub>3</sub> is attributed to the layered structure of the Li<sub>2</sub>TiO<sub>3</sub> precursor that is synthesized to create the LIS. Similarly, the spinel structure of H<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is derived from the spinel structure of its precursor, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. Compared to LMO-type LISs, LTO-type LISs

demonstrate high adsorption capacities, with marginal Ti loss. The main advantage of these LISs is that they are more ecologically friendly because titanium ions are environmentally benign and easy to remove from liquids (Xu et al., 2016; Gopinath et al., 2020). Unlike Mn, the Ti valence ions remain stable during permeation and adsorption. Consequently, LTO-type LISs demonstrate higher theoretical adsorption capacity and better recyclability for continuous extraction (Marthi et al., 2021). Additionally, the Ti-O bonds present in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> provide anti-acidic properties: an especially compelling feature for extraction from seawater and salt lake brines. The main drawback of LTO-type LISs is that they demonstrate slower Li<sup>+</sup> adsorption rates than LMO-type LISs (Chitrakar et al., 2014). Table 7 provides the adsorption capacity, cyclical stability, thermal stability, environmental durability, extraction time, and optimal pH of various LTO-type LISs

TABLE 7 Li<sup>+</sup> LTO-Type LIS extraction from salt lake brines, simulated brines, and seawater.

References	Precursor	Ion sieve	Solution	Mg <sup>2+</sup> /Li <sup>+</sup> Mass Ratio	Adsorption capacity	Cyclical stability	Thermal stability	Environmental Durability	Ext. Time	pH
He et al. (2015)	Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	LiOH		57.8 mg/g	5 cycles	60°C	25–30 mg/g, ≤ 5 cycles	8 h	6.5
Chitrakar et al. (2014)	Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	Salar de Uyuni Brine	18	32.6 mg/g	2 cycles	60°C	32.6 mg/g, ≤ 2 cycles	24 h	6.5
Limjuco et al. (2016)	Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	Seawater	~8,530	30 mg/g	5 cycles	30°C	~30 mg/g ≥ 5 cycles	24 h	7
Lawagon et al. (2016)	Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	LiOH + LiCl		94.5 mg/g	5 cycles	30°C	~94.5 mg/g ≤ 5 cycles, < 0.5% Ti Loss	12 h	11
Wang et al. (2019)	Mo-doped Li <sub>2</sub> TiO <sub>3</sub>	Mo-Ti-0.15(H)	LiOH	35	78 mg/g	6 cycles	30°C	~78.8 mg/g ≤ 6 cycles	48 h	8.8
Wang et al. (2016)	β-Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	LiOH		76.7 mg/g		30°C		24 h	5–7
Moazeni et al. (2015)	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	H <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	LiCl		39.4 mg/g		30°C		120 h	9.17
Shi et al. (2013)	Li <sub>2</sub> TiO <sub>3</sub>	H <sub>2</sub> TiO <sub>3</sub>	LiOH		39.8 mg/g	8 cycles	60°C	0.17% Ti Loss ≤ 8 cycles	192 h	

used for Li<sup>+</sup> extraction from salt lake brines, simulated brines, and seawater.

### 6.2.1 H<sub>2</sub>TiO<sub>3</sub> lithium ion sieves

The crystal structure of Li<sub>2</sub>TiO<sub>3</sub> can be represented as a cubic close packing of oxygen atoms with metal atoms placed in the octahedral voids. Li<sup>+</sup> and Ti<sup>4+</sup> form two layers. The first layer is solely composed of Li atoms, and the second is composed of 2/3 Ti atoms and 1/3 Li atoms. The crystal structure is formed by successive stacks of oxygen, lithium, and titanium/lithium layers (e.g., O/Li-Ti/O/Li/O) that conform to the C2/c space group symmetry (Watanabe et al., 2020). This crystal formation of Li<sub>2</sub>TiO<sub>3</sub>, also known as monoclinic β-phase Li<sub>2</sub>TiO<sub>3</sub>, achieves nearly complete Li extraction (100%) to form monoclinic H<sub>2</sub>TiO<sub>3</sub> when treated with acid at comparatively low temperatures (700°C). Two other phases of Li<sub>2</sub>TiO<sub>3</sub> exist, α-phase and γ-phase, but the β-phase is the most promising for aqueous Li extraction. The α-phase has lower thermal stability and will transform into β-phase when exposed to temperatures above 300°C. Alternatively, γ-phase only achieves 50% Li<sup>+</sup> extraction (Chitrakar et al., 2014).

Chitrakar et al. (2014) investigated the Li<sup>+</sup> ion exchange reaction of H<sub>2</sub>TiO<sub>3</sub> in brine collected from Salar de Uyuni, Bolivia. H<sub>2</sub>TiO<sub>3</sub> demonstrated initial adsorption of 26 mg/g within 1 h and reached equilibrium after 24 h. A Li<sup>+</sup> adsorptive capacity of 32 mg/g was achieved, reaching equilibrium after 8 h. The high concentrations of competing monovalent (Na<sup>+</sup> and K<sup>+</sup>) and divalent (Mg<sup>2+</sup> and Ca<sup>2+</sup>) ions present in the brine did not impact the Li<sup>+</sup> selectivity. Finally, after elution with an HCl solution, H<sub>2</sub>TiO<sub>3</sub> demonstrated a Li<sup>+</sup> adsorptive capacity of 31.4 mg/g, 98% of the initial capacity reported. Zhang et al. (2016) prepared H<sub>2</sub>TiO<sub>3</sub> using a sol-gel process and tested its Li<sup>+</sup> adsorption performance from LiOH and LiCl + NaOH

solutions. The maximum Li<sup>+</sup> adsorption capacities from the LiOH and LiCl + NaOH solutions were 27.4 and 24.1 mg/g, respectively. They found that alkaline pH values and higher initial Li<sup>+</sup> concentrations yield higher adsorption capacities.

While the theoretical adsorption capacity of H<sub>2</sub>TiO<sub>3</sub> LISs is higher than most LMO-type LISs, the practical adsorption capacity demonstrated after recovery from brine or seawater is often lower (Dai et al., 2021). Authors have explored the use of doping to potentially increase the adsorption capacity of LISs (Chitrakar et al., 2014; Wang et al., 2019; Qian et al., 2021a; Qian et al., 2021b). Dai et al. (2021) tested the adsorption performance of Al-doped H<sub>2</sub>TiO<sub>3</sub> using a LiCl solution. A maximum adsorption capacity of 32.1 mg/g was achieved, with the adsorption capacity remaining at 29.3 mg/g after five HCl elution cycles. The undoped H<sub>2</sub>TiO<sub>3</sub> achieved a maximum of 29.73 mg/g. Although there was no major improvement in adsorption capacity, the Al-doped H<sub>2</sub>TiO<sub>3</sub> demonstrated favorable adsorption selectivity and solubility resistance. Additionally, the dissolution of Ti after multiple regenerations was marginal (2.53%). Further investigation into doping materials and other capacity-increasing processes is recommended to improve the feasibility of H<sub>2</sub>TiO<sub>3</sub> LISs for Li<sup>+</sup> extraction from high Mg<sup>2+</sup>/Li<sup>+</sup> and low Li<sup>+</sup> concentration aqueous solutions. The chemical stability, cyclical stability, and eco-friendliness of H<sub>2</sub>TiO<sub>3</sub> LISs signal their potential to surpass LMO-type LISs if their adsorption capacity is significantly improved.

### 6.2.2 H<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> lithium ion sieve

In the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel structure, Ti atoms occupy 5/6 of the 16 days octahedral voids, Li atoms occupy the remaining 16 days octahedral voids, and oxygen atoms occupy the 32e voids

(Ohzuku et al., 1995). The resulting  $[\text{Li}_{1/3}\text{Ti}_{5/3}]^{16d}\text{O}_4$  framework features face shared tetrahedral and octahedral interstitial Li-ion positions in the lattice that create three-dimensional connections for Li-ion migration. In addition to creating stronger Ti-O bonds, this spinel structure enables easy migration of  $\text{Li}^+$  ions for recovery and elution with minimal Ti dissolution (Ouyang et al., 2007). Consequently,  $\text{H}_4\text{Ti}_5\text{O}_{12}$  LISs have higher  $\text{Li}^+$  capacity and greater cyclical stability than LMO-type LISs (Xu et al., 2016). Furthermore, a preliminary study of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  for  $\text{Li}^+$  recovery from Salar de Atacama brine and seawater revealed that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has high  $\text{Li}^+$  selectivity for aqueous solutions with high concentrations of H and  $\text{Na}^+$ . Consequently,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is predicted to be one of the most promising LIS precursors for large-scale  $\text{Li}^+$  extraction from brine and seawater (Snydacker et al., 2018).

Gu et al. (2016) studied the ion exchange properties and selectivity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  for Li recovery from a LiOH solution.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was prepared by a solid-state reaction of  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  then treated with nitric acid to form the  $\text{H}_4\text{Ti}_5\text{O}_{12}$  LIS. The LISs demonstrated excellent  $\text{Li}^+$  selectivity of 145.7 mg/g, with only a moderate reduction of 5.5% after three recovery/elution cycles. Wei et al. (2020) synthesized  $\text{H}_4\text{Ti}_5\text{O}_{12}$  nanofibers (P-HTO-NF) for Li recovery from simulated brine water ( $\text{Li}^+$  40 mg/L,  $\text{Na}^+$  241 mg/L,  $\text{K}^+$  443 mg/L,  $\text{Mg}^{2+}$  501 mg/L,  $\text{Ca}^{2+}$  535 mg/L). The P-HTO-NF demonstrated an adsorption capacity of 59.1 mg/g, which is 93% of the theoretical capacity. Adsorption equilibrium occurred within 30 min. Also, the equilibrium distribution coefficient for  $\text{Li}^+$  was two orders of magnitude higher than the coefficients of the competing ions, indicating an extraordinary  $\text{Li}^+$  selectivity. Finally, the LIS demonstrated excellent cyclical stability, with capacity remaining at 86.5% after six cycles. Similarly, Zhao B. et al. (2020) explored using  $\text{H}_4\text{Ti}_5\text{O}_{12}$  sheets in place of the traditional powder adsorbent to recover Li from Lagoco Salt Lake samples and simulated brine. While the adsorption capacity was not as competitive at 21.57 mg/g, 96.84% of the initial adsorption capacity was retained after four cycles.

$\text{H}_4\text{Ti}_5\text{O}_{12}$  LISs have demonstrated superior  $\text{Li}^+$  selectivity, adsorption capacity, chemical stability, and cyclical stability after multiple adsorption/elution cycles from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration aqueous solutions. The main challenge facing the commercialization of  $\text{H}_4\text{Ti}_5\text{O}_{12}$  LISs is their novelty. Few experiments have explored the performance of this sieve in traditional powder form, and the limited studies of alternative morphologies have remained at the bench scale. Further performance testing of  $\text{H}_4\text{Ti}_5\text{O}_{12}$  LISs for recovery from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration aqueous solutions is needed.

## 7 Lithium-ion imprinted membrane extraction

Ion-imprinted membranes (IIMs) are the combined product of membrane separation and ion-imprinting techniques.

Membrane separation is a highly efficient technique that utilizes pores to filter and selective permeability to separate substances in aqueous solutions (Malliga et al., 2020). These aqueous solutions are driven through the membrane by a concentration, pressure, or potential gradient. Furthermore, ion-imprinting is a bio-inspired technique that mimics the “lock and key” interaction between natural receptors and ligands (Lu et al., 2019). During the ion imprinting process, polymeric matrices are loaded with artificial ionic recognition sites complementary to the template ion’s size and shape (Ertürk and Mattiasson, 2017). Protonation is then used to remove the template ions, leaving the recognition sites open for target ion adsorption. In summary, IIMs leverage the functionality provided by both technologies and can selectively separate and detect target ions *via* ion-selective recognition (Lu et al., 2019). Additionally, these membranes can be modified with interlayers or imprinted with nanomaterials that prevent membrane fouling, a major challenge for all membrane extraction technologies (He et al., 2022; Sun et al., 2022). Similarly, the antifouling properties suggest that the standard feed solution pretreatment required for most membrane technologies may not be required for IIMs. Li-IIMs’ high separation efficiency, selectivity, low energy consumption, easy operation, and unique antifouling properties have prompted recent investigations into its feasibility for  $\text{Li}^+$  extraction from low  $\text{Li}^+$  aqueous solutions. Table 8 provides the selectivity, rebinding capacity, thermal stability, regeneration, cyclical stability, specific energy consumption, extraction time, and optimal pH of various IIMs used for  $\text{Li}^+$  extraction from simulated brines. Note that the rebinding capacity is the degree to which the Li-ions in the aqueous solution can bind, detach, and rebind to the IIMs  $\text{Li}^+$  recognition sites.

The most significant challenges facing the commercialization of IIMs for industrial scale, aqueous  $\text{Li}^+$  extraction are pH sensitivity, temperature dependence, extraction time, and the ratio of template ions, ligands, and functional monomers (Lu et al., 2019). The pH value is generally the determining factor for IIM ion selectivity. When the pH value is too low, protons compete with target ions for binding sites, decreasing the membrane’s adsorption capacity. Increasing the pH value can reduce this competition. Ultimately, the pH value can be adjusted to trigger  $\text{Li}^+$  adsorption/desorption and, therefore, potential membrane regeneration for continuous extraction. However, extensive experimentation is required to identify the pH values that optimize  $\text{Li}^+$  adsorption/desorption rates without destroying the IIMs ion recognition sites. The optimal pH value varies across IIM technologies. Furthermore, IIMs demonstrate enhanced adsorption capacities at higher temperatures. Consequently, passive  $\text{Li}^+$  extraction from seawater and salt brines with cooler temperatures or extraction during winter months may be economically infeasible. Similar to the pH value, additional experimentation is required to identify an extraction time that maximizes recovery



TABLE 8 Li<sup>+</sup> IIM extraction from simulated brines.

References	Membrane	Solution	Selectivity	Rebinding capacity	Thermal stability	Regen	Cyclical stability	Sp. Energy consumption	Ext. Time	pH
Yu et al. (2020)	PDMS-PDA	LiCl	1.71 Na <sup>+</sup> , 4.56 K <sup>+</sup> , 3.80 Rb <sup>+</sup>	50.87 mg/g	20°C	43.94 mg/g (4th cycle)	4 cycles		3 h	3
Liu et al. (2020)	High-selective Multilayered	Li Acidic Solution	4.20 Na <sup>+</sup> , 4.11 K <sup>+</sup> , 4.13 Mg <sup>2+</sup> , 4.30 Al <sup>3+</sup> , 4.28 Fe <sup>3+</sup>	16.40 mg/g	25°C	95.88% (5 cycles)	5 cycles	-0.2 V	80 min	1
Lu et al. (2018)	PDMS-PDA 12-crown-4	Simulated Brine	1.85 Na <sup>+</sup> , 2.07 K <sup>+</sup>	27.55 mg/g		90.3% (5 cycles), 88.1% (10 cycles)	10 cycles		3 h	9

without damaging the IIMs. Extended elution periods do not guarantee higher percent recovery. Finally, the ratio of templates to ligands to functional monomers dictates the number of effective binding sites on the membrane. Therefore, research that identifies the optimal ratio of templates to ligands to functional monomers, which varies according to the materials used to prepare the IIMs, is critical to adsorption capacity and overall performance. Addressing these performance challenges will significantly improve the techno-economic feasibility of Li-IIMs, especially compared to other membrane extraction technologies that are subject to fouling and require pretreated extraction solutions.

## 7.1 High-selective multilayered Li<sup>+</sup>-imprinted membranes

Lu et al. (2018) developed and tested High-selective Li-Ion-Imprinted Membranes (Li-IIMs) with enhanced hydrophilicity and stability for aqueous Li<sup>+</sup> extraction. Polyether sulfone membranes (PMs) were selected for their high porosity, high-pressure resistance, and high stability. PMs have also demonstrated satisfactory performance in other ion separation experiments (Maheswari et al., 2012; Mortaheb et al., 2014). Synthetic polydopamine (PDA) layers were synthesized on the surface of the PMs to enhance interfacial adhesion for the attachment of the ion-imprinted polymers. Additionally, silicon dioxide nanoparticles (SiO<sub>2</sub>) were added to the PMs surface to enhance their hydrophilicity and stability. Finally, 12-crown-4 ether and Li<sup>+</sup> ions were imprinted on the PMs' surfaces to create the adsorption cavities and ion recognition sites, respectively. The Li-IIMs demonstrated high relative selectivity with coefficients of 1.85 and 2.07 for Li<sup>+</sup>/Na<sup>+</sup> and Li<sup>+</sup>/K<sup>+</sup>, respectively. The permselectivity (separation efficiency) factors were also high, with coefficients of 7.39 and 9.86 for Na<sup>+</sup>/Li<sup>+</sup> and K<sup>+</sup>/Li<sup>+</sup>, respectively. The rebinding (adsorption) capacity reached a maximum of 90.3% of initial binding after five cycles of

adsorption/desorption with a slight decline to 88.1% after ten cycles.

While the Li-IIMs demonstrated excellent performance, experiments with aqueous solutions that more closely resemble the ionic concentration of salt lake brine and seawater should be investigated. Even salt lakes with higher Li<sup>+</sup> concentrations, like Salar de Atacama (2,100 ppm), have Na<sup>+</sup>/Li<sup>+</sup> and K<sup>+</sup>/Li<sup>+</sup> ratios greater than 10:1, as compared to the 1:1 concentration used in the Lu et al. (2018) experiments. In 2021, Ding et al. (2022) developed and tested a novel high-selective ion imprinted polymer (sans membrane) for Li<sup>+</sup> extraction lake Zabuye brine samples. The technology achieved a maximum adsorption capacity of 1.1 mg/g. While this is promising for green Li<sup>+</sup> extraction from carbonate type, low Mg<sup>2+</sup>/Li<sup>+</sup> brines, experiments that investigate the performance of these ion-imprinted technologies in high Mg<sup>2+</sup>/Li<sup>+</sup> aqueous solutions are needed.

## 7.2 PDMS-PDA Li<sup>+</sup> -imprinted membranes

Yu et al. (2020) investigated the use of polydimethylsiloxane-polydopamine (PDMS-PDA) Li-IIMs for rapid, high-efficiency recovery of Li from seawater. A powerfully adhesive PDA layer with numerous functional groups was synthesized on the PDMS membrane surface *via* the self-polymerization of dopamine to improve hydrophilicity. Carboxyl groups were then grafted onto the PDA functionalized substrate per the hydrolysis of succinic anhydride. The carboxyl-modified PDMS membranes were further modified to construct ester-modified membranes. The calix [4] arene ligand and Li-ions were used to create the absorption cavities and ion recognition sites, respectively. Finally, EDTA removed the template Li-ions from the prepared Li-IIMs.

The PDMS-PDA Li-IIMs demonstrated high thermal stability, with their rebinding capacity decreasing marginally with increasing temperatures. Similarly, the modified

membranes were stable in acidic and alkaline conditions. However, the pH significantly impacted rebinding capacity; a pH of 3.0 was identified as the optimal value. Furthermore, a  $\text{Li}^+$  rebinding capacity of 51 mg/g was achieved. The PDMS-PDA Li-IIMS demonstrated high relative selectivity with coefficients of 1.71, 4.56, and 3.80 for  $\text{Na}^+/\text{Li}^+$ ,  $\text{K}^+/\text{Li}^+$ , and  $\text{Rb}^+/\text{Li}^+$ , respectively. The permselectivity factors for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$  were approximately 2.52, 2.8, and 3.03, respectively. Finally, the PDMS-PDA Li-IIMS showed high adsorption/desorption cycle durability. Four successive regeneration cycles were completed over 10 days, and the rebinding capacities remained almost unchanged.

PDMS-PDA Li-IIMS demonstrated excellent performance overall and appear to be a viable technology for  $\text{Li}^+$  extraction from seawater. However, similar to the High-selective Li-IIMS developed by (Lu et al., 2018), investigations with aqueous solutions that simulate the ionic concentrations in seawater are recommended. Also, the cost and specific energy consumption implications for the stirring required to elute  $\text{Li}^+$  on an industrial scale should be further explored to determine the techno-economic feasibility of this technology.

## 8 Electrochemical Lithium capturing systems

Electrochemical Li capturing systems (ELiCSs) use electricity to drive ion-separation processes for  $\text{Li}^+$  extraction. There is a proportional relationship between the total charge storage of the systems electrode and the amount of  $\text{Li}^+$  extracted from an aqueous feed solution. The basic configuration of an ELiCS consists of an external power supply, electrodes, and an aqueous electrolyte, in this case, brine or seawater (Soffer and Folman, 1972; Kim et al., 2018; Yoon et al., 2019). Electrochemical technologies are particularly interesting for extraction from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentrations solutions because they are environmentally sustainable and have demonstrated excellent recovery capacities, scalability, cycling efficiency, reversibility, and selectivity (Hoshino, 2013a; Lee et al., 2013; Kim et al., 2015; Yoon et al., 2019; Zhang et al., 2019; Zhao et al., 2020b; Srimuk et al., 2020). Additionally, electrochemical technologies can easily integrate energy recovery techniques that utilize the salinity gradient of the aqueous feed solutions to generate energy Zhang X. et al. (2021). Their characteristic high extraction efficiency and low environmental impact suggest that ELiCSs are more techno-economically feasible for  $\text{Li}^+$  extraction from low  $\text{Li}^+$  concentration solution than precipitants or solvents. However, the main disadvantages that must be addressed are their potentially high energy consumption due to process inefficiencies and high material costs Zhang Y. et al. (2021).

ELiCSs generally belong to one of three categories: battery-based (BB), membrane enhanced battery-based (MEBB), or

electro-membrane-based (EMB) (Zavahir et al., 2021). BB ELiCSs use at least one faradic electrode to capture  $\text{Li}^+$  from aqueous solutions. The faradic electrode(s) capture Li-ions *via* conversion reaction or intercalation over the bulk of the electrode's materials. They have greater storage capacity,  $\text{Li}^+$  selectivity, and capacitance but slower removal rates than non-faradic (capacitive) electrodes (Patrice et al., 2014; Yoon et al., 2019). The MEBB ELiCSs augment the battery-based configuration with an anion exchange membrane (AEM) for Li recovery. In the rocking chair configuration, the AEM splits the electrochemical cell into a cathode and an anode chamber that contain one  $\text{Li}^+$  intercalating electrode each. In the redox configuration, there is one intercalating electrode and one redox couple electrode. Continuous Li recovery is achieved by swapping the positions of the  $\text{Li}^+$  "capture" and "release" electrodes. Finally, the EMB, or electro dialysis configurations, have a series of AEM and cation exchange membranes (CEM) sandwiched between two faradic electrodes. Electric potential drives the  $\text{Li}^+$  through the CEMs towards concentrating compartments (Zavahir et al., 2021). Further information about the performance, advantages, and challenges of prominent ELiCSs is provided in subsequent sections.

### 8.1 ESIX membrane

The electrochemically switched ion exchange system (ESIX), first proposed by the Pacific Northwest National Laboratory, is a battery-based ELiCS (when employed for Li capture). In the ESIX process, an electroactive ion exchange film is deposited onto a high surface area electrode. The redox reactions that drive ion uptake and elution are directly controlled by adjusting the electric potential of the film. A cathodic potential can be applied to intercalate  $\text{Li}^+$  into the film for Li recovery from an aqueous solution. This intercalation is driven by the film's need to maintain charge neutrality. Conversely, when an anodic potential is applied, the film is oxidized, and Li is released from the film (Sukamto et al., 1998). Essentially, the ESIX combines electrochemistry and ion exchange to provide a Li recovery process with high selectivity and reversibility. Also, the ESIX utilizes a faradic and a capacitive electrode, the combined benefits of which bridge the performance gaps in conventional battery and capacitor-based recovery systems.

Adjustments to the conventional ESIX electrode configuration must be made to circumvent the mass transport challenges associated with Li recovery from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration aqueous solutions. An array of smaller electrodes with higher surface areas arranged into working and counter electrode pairs can be employed for recovery instead of a large, singular electrode (Joo et al., 2020; Zavahir et al., 2021). Additionally, keeping the volume of the recovered solution low is mandatory for obtaining a high Li-concentrated final product (Joo et al., 2020; Zavahir et al.,

TABLE 9 Li<sup>+</sup> ESIX (electrode) extraction from salt lake brines, simulated brines, and wastewater.

References	Electrode materials	Solution	Mg <sup>2+</sup> /Li <sup>+</sup> Mass Ratio	Selectivity	Current efficiency	Regeneration	Adsorp. Capacity	Recov.	Sp. energy consumption	Product quality	Ext. time
Kanoh et al. (1991)	λ-MnO <sub>2</sub> -Pt	LiCl		only Li <sup>+</sup>		85%		97%			
Lee et al. (2013)	λ-MnO <sub>2</sub> /Ag	Simulated Seawater	1.9		92.7%	87% (≥ 4 cycles)			0.14 Wh/g Li <sup>+</sup>	91.8%	1 h
Kim et al. (2019)	λ-MnO <sub>2</sub> /Ag	Simulated Brine	2,107				7.34 mg/g		3.07 Wh/g Li <sup>+</sup>	99%	~18 h
Kim et al. (2015)	λ-MnO <sub>2</sub> /AC	Salar de Atacama Brine	6		> 90%			96%	0.60 Wh/g Li <sup>+</sup>	91.8%	1 h
Trócoli et al. (2017)	λ-MnO <sub>2</sub> /NiHCF	Simulated Brine	≪ 1	1.63 K <sup>+</sup> , 57.6 Na <sup>+</sup> , 1,633 Mg <sup>2+</sup> ,	79.9%			71.05%	0.52 Wh/g Li <sup>+</sup>	96.2%	~8 h
Liu et al. (2019)	λ-MnO <sub>2</sub> /LiM <sub>2</sub> O <sub>4</sub>	Simulated Brine				57.1% (≥ 30 cycles)	24.3 mg/g				2 h
Kim et al. (2018)	LMO/BDD	Industrial Wastewater		88.4 Na <sup>+</sup> ,		44% (5 cycles)	22.7 mg/g		8.71 Wh/g Li <sup>+</sup>	~98%	1 h
Missoni et al. (2016)	LMO/Ppy	Natural Brine				50% (200 cycles)		56%	0.72–1.44 Wh/g Li <sup>+</sup>		
Zhao et al. (2020c)	LMO/Ppy/Al <sub>2</sub> O <sub>3</sub>	Simulated Brine	5.2			91.7% (30 cycles)	12.8 mg/g	91.7%	0.2 Wh/g Li <sup>+</sup>	97.4%	40 min
Trócoli et al. (2014)	LiFePO <sub>4</sub> /Ag	Simulated Brine	116		92.9%				0.4 Wh/g Li <sup>+</sup>	97.9%	1 h
Trócoli et al. (2015)	FePO <sub>4</sub> /NiHCF	Salar de Atacama Brine	6						1.25 Wh/g Li <sup>+</sup>	97.9%	24 h

2021). The  $\text{Li}^+$  selectivity of the ESIX depends on the selectivity of the electrode materials. Several working and counter electrode materials have been tested to identify the best candidates for Li recovery from low concentration solutions:  $\lambda\text{-MnO}_2/\text{Pt}$  (Kanoh et al., 1991; Kanoh et al., 1993; Kim et al., 2019; Liu et al., 2019);  $\lambda\text{-MnO}_2/\text{Ag}$  (Lee et al., 2013; Xu et al., 2018; Kim et al., 2019; Joo et al., 2020);  $\lambda\text{-MnO}_2$ -activated carbon (AC) (Kim et al., 2015);  $\lambda\text{-MnO}_2/\text{NiHCF}$  (Trócoli et al., 2017);  $\lambda\text{-MnO}_2/\text{LiMn}_2\text{O}_4$  (Liu et al., 2019); LMO/Boron Doped Diamond (BDD) (Kim et al., 2018); LMO/Polypyrrole (Ppy) (Marchini et al., 2016; Missoni et al., 2016); LMO/Ppy/ $\text{Al}_2\text{O}_3$  (Zhao et al., 2020c);  $\text{LiFePO}_4/\text{Ag}$  (Trócoli et al., 2014); and,  $\text{FePO}_4/\text{NiHCF}$  (Trócoli et al., 2015). When applied for Li recovery from simulated brine, natural brines, and multi-ion solutions, the specific energy consumption for these electrode variations ranged from 1.4 kWh/kmol to 18.5 kWh/kmol. The AC counter electrode demonstrated a high Li recovery of 14.4 mg/g for a 25 min cycle, so it is recommended for all ESIX systems (Zhao et al., 2020d; Zavahir et al., 2021). Furthermore, the  $\lambda\text{-MnO}_2$  and LMO working electrodes demonstrate the highest adsorption capacities at 10 mg/g and 30 mg/g, respectively. Table 9 provides the selectivity, current efficiency, regeneration, adsorption capacity, recovery, specific energy consumption, product quality and extraction time of various ESIX working/counter electrode materials used for  $\text{Li}^+$  extraction from salt lake brines, simulated brines, and wastewater. Note that the current efficiency is a measure of how efficiently the electrodes transfer the charges driving the electrochemical extraction of  $\text{Li}^+$ .

A major challenge facing ESIX for industrial operation is the flushing process needed to exchange the source solution for the recovery solution. Pure water, a precious resource, is required for flushing to prevent cross-contamination of the two solutions. Consequently, this process poses a considerable threat to process efficiency and sustainability. Furthermore, this batch operation is less efficient than other continuous mode technologies, such as electrodialysis (Zavahir et al., 2021). Additionally, the reported energy consumption for ESIX can be misleading because it is typically calculated using metrics from the first cycle only, which results in underestimated projections for total energy consumption over many cycles. Finally, as mentioned previously, maintaining a low recovery solution is critical to the quality of the Li recovered. At the bench level, recovery solutions at the  $\mu$  scale require around five enrichment cycles. Therefore, the solution enrichment process at the commercial level can be expected to exceed 1,000 cycles (Zavahir et al., 2021). Further investigation into the practical energy consumption and sustainability of ESIX for Li recovery from brine and seawater is needed. A special focus on the solution flushing process and finding an alternative for

pure water is recommended. In this vein, Trócoli et al. (2017) have developed a promising ion-pumping process that employs a  $\lambda\text{-MnO}_2/\text{NiHCF}$  working/counter electrodes for  $\text{Li}^+$  recovery. No chemical reactants are required, the electrodes are recyclable, and most importantly, only a small volume of water is required.

## 8.2 Electrodialysis

Electrodialysis (ED) is an electrochemical membrane separation process that utilizes an ion-selective membrane and an electric potential gradient for ion separation from aqueous solutions (Gurreri et al., 2020). A typical electrodialysis cell comprises an alternating series of AEMs and CEMs between a cathode and an anode (Gmar and Chagnes, 2019). In the electrodialysis process for  $\text{Li}^+$  extraction, electric force drives  $\text{Li}^+$  ions in the feed solution from the positive side of the cell (cathode) to the negative side (anode) through an ion  $\text{Li}^+$  selective membrane. As a result,  $\text{Li}^+$  is concentrated on one side of the cell. Additional treatments are required to obtain the metallic or solid Li compounds dissolved in the  $\text{Li}^+$  enriched water. Similarly to other membrane technologies, ED systems require the feed solution to be pretreated so that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and other metals that cause membrane fouling can be removed prior to  $\text{Li}^+$  extraction (Wang et al., 2022). However, compared to other membrane technologies such as nanofiltration, ED systems have higher recovery rates, lower energy consumption, and higher  $\text{Li}^+/\text{Mg}^{2+}$  separation factors (Gmar and Chagnes, 2019).

ED systems are classified according to the attributes of their ion exchange membranes (IEMs): selective electrodialysis (SED) utilizes IEMS that have high selectivity for monovalent ions; bipolar membrane electrodialysis (BMED) utilizes bipolar IEMS; and finally, ion liquid membrane electrodialysis (ILMED) which employs liquid ion membranes (Zavahir et al., 2021). While ED technologies are already used for industrial hydrometallurgical processes to recover Li from industrial brines, ore concentrates, and spent LIBs, their use for recovery from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration solutions has been limited (Campione et al., 2018; Gmar and Chagnes, 2019). Table 10 provides the applied voltage, selectivity, current efficiency, separation efficiency, recovery, and specific energy consumption of various ED membranes for  $\text{Li}^+$  extraction from salt lake brines, simulated brines, and seawater.

### 8.2.1 Selective electrodialysis

SED employs monovalent anion exchange membranes (MAEMs) and monovalent cation exchange membranes (MCEMs) to transport the monovalent anions ( $\text{Cl}^-$ ) and cations ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) through the MAEMs and MCEMs and to the anode and cathode, respectively. The divalent anions ( $\text{SO}_4^{2-}$ ) and cations ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) are rejected by the MAEMs and MCEMs (Lambert et al., 2006; Zhang et al., 2012; Reig et al.,

TABLE 10 Li<sup>+</sup> ED extraction from salt lake brines, simulated brines, and seawater.

References	Classification	Solution	Mg <sup>2+</sup> / Li <sup>+</sup> Mass Ratio	Li <sup>+</sup> concentration	Applied voltage	Selectivity	Current efficiency	Separation efficiency	Recovery	Sp. energy consumption
Nie et al. (2017)	SED	LiCl·H <sub>2</sub> O, MgCl <sub>2</sub> (Low Li <sup>+</sup> )	18.9	4.86 g/L	20 V	10.4 Li <sup>+</sup>	8.7%		90.5%	0.01 kWh/m <sup>3</sup>
Nie et al. (2017)	SED	LiCl·H <sub>2</sub> O, MgCl <sub>2</sub> (High Li <sup>+</sup> )	150	6.94 g/L	6 V	27.5 Li <sup>+</sup>			70%	
Nie et al. (2017)	SED	Salt Lake Brine	21.4	5.55 g/L	20 V	9.9 Li <sup>+</sup>				22.3 kWh/m <sup>3</sup>
Ji et al. (2017)	SED	Simulated Brine	60	6.94 g/L	5 V	12.5 Li <sup>+</sup>		7%	72.5%	1.4 kWh/m <sup>3</sup>
Chen et al. (2018)	SED	Simulated Brine	20.8	0.14 g/L	5 V	65 Li <sup>+</sup>	51.5%		77.5%	0.05 kWh/m <sup>3</sup>
Chen et al. (2018)	SED	Simulated Brine		0.14 g/L	5 V	7.8 Li <sup>+</sup>	41.5%		76%	0.73 kWh/m <sup>3</sup>
Ji et al. (2018)	SED	Simulated Brine	20	0.14 g/L	6 V	6.4 Li <sup>+</sup>			67.7%	0.2 kWh/m <sup>3</sup>
Guo et al. (2018)	SED	Seawater	16	0.14 g/L	7 V		~1.2%			16 kWh/m <sup>3</sup>
Guo et al. (2018)	SED	Salt Lake Brine	36	34.7 g/L	10 V		47%		76.5%	4.86 kWh/m <sup>3</sup>
İpekçi et al. (2020)	BMED	Lithium Bromide Solution		0.28 g/L	25 V				73%	3.2 kWh/m <sup>3</sup>
İpekçi et al. (2018)	BMED	Lithium Bromide Solution		0.35 g/L	30 V			94.7%	62%	7.9 kWh/m <sup>3</sup>
Hoshino (2013a)	ILMED	Seawater		3.4 · 10 <sup>-4</sup> g/L	2 V				22.2%	
Hoshino (2013b)	ILMED	Seawater		3.4 · 10 <sup>-4</sup> g/L	2–3 V			63%		
Liu et al. (2020)	ILMED	Simulated Brine	347	0.97 g/L	2 V		65%			0.76 kWh/m <sup>3</sup>
Zhao et al. (2020e)	ILMED	Brine	694	0.97 g/L	3 V					0.9 kWh/m <sup>3</sup>

2018). As a result, the monovalent ions are enriched in a concentrate chamber as they migrate from the dilute chamber.  $\text{Na}_2\text{CO}_3$  is added to the concentrate chamber exit flow to form  $\text{Li}_2\text{CO}_3$ . SED has demonstrated high permselectivity and retention of monovalent and divalent ions, respectively, in experiments that tested high  $\text{Mg}^{2+}/\text{Li}^+$  brines and seawater for aqueous Li recovery (Ji et al., 2017; Nie et al., 2017; Guo et al., 2018; Ji et al., 2018). They also require little pretreatment for recovery. Increasing the applied voltage increases SED Li recovery and specific energy consumption (SEC). The recovery performance of SED is critically sensitive to the concentration of divalent ions in the feed solution, specifically, the  $\text{Mg}^{2+}/\text{Li}^+$  and  $\text{Na}^+/\text{Li}^+$  mass ratios due to their influence on separation efficiency. SED demonstrated higher selectivity of  $\text{Li}^+$  in solutions that had higher  $\text{Mg}^{2+}/\text{Li}^+$  mass ratios and lower selectivity at higher  $\text{Na}^+/\text{Li}^+$  mass ratios (Nie et al., 2017; Chen et al., 2018; Ji et al., 2018). Finally, the SEC for SED recovery from  $\text{Li}^+$  is more efficient for salt lake brines than seawater due to their higher ionic strength and mass ratios (Zavahir et al., 2021). However, a Li percent recovery of 80% was achieved from seawater at 9 V after 120 min (Guo et al., 2018). To improve the feasibility of SED for salt lake brines and seawater, MCEMs with higher selectivity for  $\text{Li}^+$  in solutions with high  $\text{Na}^+$  and  $\text{K}^+$  concentrations. Investigation of more selective materials, temperatures, pH levels, and membrane preparation techniques is recommended. However, SED still offers the advantages of environmental sustainability, high separation efficiency, and high Li recovery compared to other extraction technologies.

## 8.2.2 Bipolar membrane electro dialysis

BMED employs a bipolar membrane (BM) comprising a cation-exchange layer, an anion-exchange layer, and a hydrophilic interface layer (Huang and Xu, 2006; Li et al., 2016; Gmar and Chagnes, 2019). When an electric field is applied to the BM, the water molecules in the hydrophilic layer separate into hydrogen ( $\text{H}^+$ ) and hydroxide ( $\text{OH}^-$ ) ions. Simultaneously, anions passing through the AEM are combined with  $\text{H}^+$ , and cations passing through the CEM are combined with  $\text{OH}^-$ . The resulting acidic and basic solutions are enriched in corresponding recovery compartments (Mani, 1991). The acidic and basic recovery compartment streams can be treated with precipitants to produce  $\text{LiOH}$  and other valuable co-products (Bazinet et al., 1998; Jiang et al., 2014; Xue et al., 2015; Gmar and Chagnes, 2019).

Similar to SED, BMED demonstrates higher Li recovery at higher voltages. However, the ion leakage induced by higher voltages reduces Li recovery, so finding an optimum applied voltage is critical. Furthermore, BMED is very promising for Li recovery from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration solutions (Bunani et al., 2017b; Gmar and Chagnes, 2019). Compared to the other ED processes, it has the highest average  $\text{Li}^+$  recovery range (60%–98%), lowest average extraction time (20–120 min),

and the lowest SEC range (3–19 kWh/kmol) (Bunani et al., 2017a; Bunani et al., 2017b; İpekçi et al., 2018; İpekçi et al., 2020). Also, BMED is ecologically friendly, requiring no chemical reagents for recovery (e.g., lime or sodium carbonate). The production of a basic and acidic recovery stream provides an economic opportunity to co-recover other industrial minerals, such as boron (Jiang et al., 2014; Yang et al., 2014; Hwang et al., 2016; Bunani et al., 2017a; Bunani et al., 2017b; Chen et al., 2022).

The main drawback of BMED is the sensitivity to high ion concentrations. The BM permselectivity is significantly reduced due to the Donnan exclusion phenomena wherein salt leaks through the membrane into the Li product (Tanaka, 2015; Venugopal and Dharmalingam, 2016; Pärnamäe et al., 2021). The BM's high cost and thermal instability have also contributed to the limited use of BMED for aqueous mineral recovery. A pretreatment to reduce initial concentration is required for optimal performance. Despite its disadvantageous aspects, BMED has demonstrated higher chemical stability, mechanical stability, current efficiency, permselectivity, durability, and lower electrical resistance and voltage drop than the conventional ED processes for Li recovery. Many authors are already exploring ways to improve BMED performance, such as decreasing the AEM thickness, combining BMs with MAEMS and MCEMs, and appending catalysts layers to the BMs (Wilhelm et al., 2001; Manohar et al., 2017; Wang et al., 2017; Chen et al., 2021).

## 8.2.3 Ionic liquid membrane electro dialysis

ILMED comprises two ion exchange membranes separated by an ionic liquid membrane (ILM). As previously mentioned, Ionic liquids (ILs) are unique liquids that have garnered attention as negligible vapor pressure alternatives to traditional organic solvents. Perhaps the most attractive feature of ILs for ED Li recovery is that they can be customized with pre-selected characteristics such as high thermal stability, moisture stability, and ion selectivity, by careful selection of the cation and anion (Seddon et al., 2000; Seddon et al., 2002; Deetlefs et al., 2006; Zavahir et al., 2021). ILMs have successfully been used for critical and heavy metals from aqueous solutions (Chen and Chen, 2016; Makanyire et al., 2016; Zante et al., 2019; Imdad and Dohare, 2022). The high permselectivity, separation efficiency, and low energy consumption demonstrated in previous studies support the integration of ILMs into the ED process for Li recovery from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration solutions.

When employing ILMED for Li recovery, the ILM must be sealed with a coat for durability and efficient recovery. After sealing novel, ion liquid impregnated organic membranes (IL-I-OM) with Nafion N-324, Hoshino (2013b) found that the membrane's durability increased, the concentration of  $\text{Li}^+$  in the cathode increased by 5.94%, and the recovery of Li from seawater increased up to 22.2%. In addition to fortifying the IL-I-OM, the Nafion N-324 coating sealed the inside the IL-I-OM, resulting in an increase in  $\text{Li}^+$  concentration at the minimum voltage (2 V) and Li recovery. Similarly, in Hoshino (2013a), two CEMs were used to seal

the ends of the IL-I-OM. To test selectivity, the CEMs employed were only permeable to the competing cations present in the seawater ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ). The divalent cations were successfully separated from the monovalent cations and enriched in the cathode compartment. The  $\text{Li}^+$  was retained in the anode compartment, and a maximum separation efficiency of 63% was achieved. Other experiments explored the impacts of high  $\text{Mg}^{2+}/\text{Li}^+$  mass ratios and voltage on ILMED SEC and Li recovery (Zhao Z. et al., 2020; Liu et al., 2020). Liu et al. (2020) observed a 99.5% reduction in the brine  $\text{Mg}^{2+}/\text{Li}^+$  mass ratio after 12 h at 20°C and 3 V. Also, a minimum SEC of 16 Wh/g  $\text{Li}^+$  was achieved, compared to the 40 Wh/g  $\text{Li}^+$  for typical ED processes.

Zante et al. (2019) found that for an IL-TBP ILMED adding equimolar sodium carbonate and sodium hydrogen carbonate to the feedstream could reduce the loss of IL and extend the lifetime of the ILM. IL-TBP ILMED achieved a maximum extraction efficiency of 80%, and high selectivity for  $\text{Li}^+$  over  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , even when the competing ions were present in high concentrations. Despite their limited application, ILMED demonstrates high  $\text{Li}^+$  selectivity and competing monovalent and divalent ion separation efficiency at low voltages. The main challenges facing the commercialization of ILMED for industrial-scale Li recovery from aqueous solutions are the flux drops in membrane stability and the dissolution of IL to the feedstream after short periods of (2 days) of continuous use (Ma et al., 2000; Zante et al., 2019). Further investigation into treatments or mechanisms that minimize the loss of IL is needed to improve the feasibility of ILMED for recovery from brines and seawater.

## 9 Conclusion

The exponential growth in demand for the world's exhaustible Li supply signals an impending shortage unless we expand current extraction resources to include high  $\text{Mg}^{2+}/\text{Li}^+$  mass ratio and low  $\text{Li}^+$  concentration aqueous solutions such as seawater and most brines. Several technologies, including high  $\text{Mg}^{2+}/\text{Li}^+$  precipitants, novel solvent extractants, Li-ion sieves, Li-ion-imprinted membranes, and electrochemical Li capturing systems, have been identified for  $\text{Li}^+$  extraction from these resources. However, each technology has unique challenges that have limited their application beyond bench-scale experiments. High  $\text{Mg}^{2+}/\text{Li}^+$  precipitants leverage low reagent costs and passive extraction, but an  $\text{Li}^+$  enrichment step is required for feasibility. The high cost and low manufacturability combined with the associated environmental concerns make most novel solvent extractants infeasible for seawater, or most salt-lake brines. In contrast, LMO-type and LTO-type ion sieves are very promising for  $\text{Li}^+$  extraction from high  $\text{Mg}^{2+}/\text{Li}^+$  and low  $\text{Li}^+$  concentration solutions. However, the powder morphology of the adsorbents reduce their durability and efficiency for continuous extraction. Li-IIMs leverage a unique combination of membrane separation technology and target ion-imprinting that achieves high rebinding capacity, selectivity, and recovery, but low specific energy

consumption. The main challenges facing their commercialization are their sensitivity to pH, temperature, extraction time, and ion-recognition sites. Finally, ELICs demonstrate great potential for extracting  $\text{Li}^+$  from solutions with high competing ion to  $\text{Li}^+$  ratios with their characteristically high separation and extraction efficiency. Their main challenges are operating cost, high energy demand, and very high competing ion to  $\text{Li}^+$  mass ratios.

A techno-economic analysis and life cycle assessment for each of the extraction technologies reviewed is needed. Both of these activities will further elucidate the climate impact, energy demand, operational costs, capital costs, productivity, and potential ROI for large scale projects using these technologies. Additionally these benchmarks can be used to develop pathways that move these technologies from bench-scale experiments to continuous demonstrations, and eventual pilot-scale systems. A recommended pathway is further exploration of the synergies between these technologies. The literature suggests that a strategic combination of two or more of the technologies reviewed can mitigate their individual challenges.

## Author contributions

OM and MH contributed to the conceptualization of the manuscript. OM conducted the literature review and prepared the manuscript. OM and MH contributed to reviewing and revising the manuscript; All authors have read and agreed to the published version of the manuscript.

## Funding

This work is supported by the John Colman Family, The Alfred P. Sloan Foundation (Grant No: G-2019-11435), the National GEM Consortium, and in part by a New Frontier Grant from Cornell University's College of Arts and Sciences.

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

## Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

## References

- Agusdinata, D. B., Liu, W., Eakin, H., and Romero, H. (2018). Socio-environmental impacts of lithium mineral extraction: Towards a research agenda. *Environ. Res. Lett.* 13, 123001. doi:10.1088/1748-9326/aae9b1
- Amaral, F. A., Bocchi, N., Brocenschi, R. F., Biaggio, S. R., and Rocha-Filho, R. C. (2010). Structural and electrochemical properties of the doped spinels Li<sub>1.05</sub>Mn<sub>0.02</sub>Mn<sub>1.98</sub>O<sub>3.98</sub>N<sub>0.02</sub> (M=Ga<sup>3+</sup>, Al<sup>3+</sup>, or Co<sup>3+</sup>; N=S<sub>2</sub> or F) for use as cathode material in lithium batteries. *J. Power Sources* 195, 3293–3299. doi:10.1016/j.jpowsour.2009.12.002
- An, J. W., Kang, D. J., Tran, K. T., Kim, M. J., Lim, T., and Tran, T. (2012). Recovery of lithium from Uyuni salar brine. *Hydrometallurgy* 117–118, 64–70. doi:10.1016/j.hydromet.2012.02.008
- Angino, E. E., and Billings, G. K. (1966). Lithium content of sea water by atomic absorption spectrometry. *Geochimica Cosmochimica Acta* 30, 153–158. doi:10.1016/0016-7037(66)90104-9
- Anlauf, A. (2016). “Greening the imperial mode of living? Socio-ecological (in) justice, electromobility, and lithium mining in Argentina,” in *Fairness and justice in natural resource politics* (England, UK: Routledge), 176–192.
- Aral, H., and Vecchio-Sadus, A. (2008). Toxicity of lithium to humans and the environment—A literature review. *Ecotoxicol. Environ. Saf.* 70, 349–356. doi:10.1016/J.ECOENV.2008.02.026
- Azevedo, M., Campagnol, N., Hagenbruch, T., Hoffman, K., Lala, A., and Ramsbottom, O. (2018). *Lithium and cobalt—a tale of two commodities*. Brussels, Belgium: McKinsey and Company: Metals and Mining, 1–25.
- Bai, R., Wang, J., Wang, D., Cui, J., and Zhang, Y. (2022). Recovery of lithium from high Mg/Li ratio salt-lake brines using ion-exchange with NaNTf<sub>2</sub> and TBP. *Hydrometallurgy* 213, 105914. doi:10.1016/j.hydromet.2022.105914
- Bai, R., Wang, J., Wang, D., Zhang, Y., and Cui, J. (2021). Selective separation of lithium from the high magnesium brine by the extraction system containing phosphate-based ionic liquids. *Sep. Purif. Technol.* 274, 119051. doi:10.1016/j.seppur.2021.119051
- Bai, X., Dai, J., Ma, Y., Bian, W., and Pan, J. (2020). 2-(Allyloxy) methylol-12-crown-4 ether functionalized polymer brushes from porous PolyHIPE using UV-initiated surface polymerization for recognition and recovery of lithium. *Chem. Eng. J.* 380, 122386. doi:10.1016/j.cej.2019.122386
- Bang Mo, K. (1984). Membrane-based solvent extraction for selective removal and recovery of metals. *J. Membr. Sci.* 21, 5–19. doi:10.1016/S0376-7388(00)83060-4
- Bartsch, R. A., Czech, B. P., Kang, S. I., Stewart, L. E., Walkowiak, W., Charewicz, W. A., et al. (1985). High lithium selectivity in competitive alkali metal solvent extraction by lipophilic crown carboxylic acids. *J. Am. Chem. Soc.* 107, 4997–4998. doi:10.1021/ja00303a030
- Bazinot, L., Lamarche, F., and Ippersiel, D. (1998). Bipolar-membrane electro dialysis: Applications of electro dialysis in the food industry. *Trends Food Sci. Technol.* 9, 107–113. doi:10.1016/S0924-2244(98)00026-0
- Bradley, D., and McCauley, A. (2013). *A preliminary deposit model for lithium-cesium-tantalum (LCT) pegmatites*, 6. United States: USGS.
- Brown, K. A., Williams, W. J., Carmack, E. C., Fiske, G., François, R., McLennan, D., et al. (2020). Geochemistry of small Canadian arctic rivers with diverse geological and hydrological settings. *J. Geophys. Res. Biogeosci.* 125, e2019JG005414. doi:10.1029/2019JG005414
- Bunani, S., Arda, M., Kabay, N., Yoshizuka, K., and Nishihama, S. (2017a). Effect of process conditions on recovery of lithium and boron from water using bipolar membrane electro dialysis (BMED). *Desalination* 416, 10–15. doi:10.1016/j.desal.2017.04.017
- Bunani, S., Yoshizuka, K., Nishihama, S., Arda, M., and Kabay, N. (2017b). Application of bipolar membrane electro dialysis (BMED) for simultaneous separation and recovery of boron and lithium from aqueous solutions. *Desalination* 424, 37–44. doi:10.1016/j.desal.2017.09.029
- Butt, F. S., Lewis, A., Chen, T., Mazlan, N. A., Wei, X., Hayer, J., et al. (2022). Lithium harvesting from the most abundant primary and secondary sources: A comparative study on conventional and membrane technologies. *Membranes* 12, 373. doi:10.3390/membranes12040373
- Campione, A., Gurreri, L., Ciofalo, M., Micale, G., Tamburini, A., and Cipollina, A. (2018). Electro dialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications. *Desalination* 434, 121–160. doi:10.1016/j.desal.2017.12.044
- Chen, J., and Wu, Z. (2000). Solvation extraction by amines and synergistic solvation extraction with neutral or acidic extractants. *Mineral Process. Extr. Metallurgy Rev.* 21, 49–87. doi:10.1080/08827500008914165
- Chen, L., and Chen, J. (2016). Asymmetric membrane containing ionic liquid [A336] [P507] for the preconcentration and separation of heavy rare earth lutetium. *ACS Sustain. Chem. Eng.* 4, 2644–2650. doi:10.1021/acssuschemeng.6b00141
- Chen, Q.-B., Ji, Z.-Y., Liu, J., Zhao, Y.-Y., Wang, S.-Z., and Yuan, J.-S. (2018). Development of recovering lithium from brines by selective-electro dialysis: Effect of coexisting cations on the migration of lithium. *J. Membr. Sci.* 548, 408–420. doi:10.1016/j.memsci.2017.11.040
- Chen, Q.-B., Wang, J., Liu, Y., Zhao, J., Li, P.-F., and Xu, Y. (2021). Sustainable disposal of seawater brine by novel hybrid electro dialysis system: Fine utilization of mixed salts. *Water Res.* 201, 117335. doi:10.1016/j.watres.2021.117335
- Chen, T., Bi, J., Zhao, Y., Du, Z., Guo, X., Yuan, J., et al. (2022). Carbon dioxide capture coupled with magnesium utilization from seawater by bipolar membrane electro dialysis. *Sci. Total Environ.* 820, 153272. doi:10.1016/j.scitotenv.2022.153272
- Chitrakar, R., Kanoh, H., Makita, Y., Miyai, Y., and Ooi, K. (2000a). Synthesis of spinel-type lithium antimony manganese oxides and their Li<sup>+</sup> extraction/ion insertion reactions. *J. Mat. Chem.* 10, 2325–2329. doi:10.1039/B002465L
- Chitrakar, R., Kanoh, H., Miyai, Y., and Ooi, K. (2000b). A new type of manganese oxide (MnO<sub>2</sub>·0.5H<sub>2</sub>O) derived from Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> and its lithium ion-sieve properties. *Chem. Mat.* 12, 3151–3157. doi:10.1021/cm0000191
- Chitrakar, R., Kanoh, H., Miyai, Y., and Ooi, K. (2001). Recovery of lithium from seawater using manganese oxide adsorbent (H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>) derived from Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>. *Ind. Eng. Chem. Res.* 40, 2054–2058. doi:10.1021/ie000911h
- Chitrakar, R., Makita, Y., Ooi, K., and Sonoda, A. (2014). Lithium recovery from salt lake brine by H<sub>2</sub>TiO<sub>3</sub>. *Dalton Trans.* 43, 8933–8939. doi:10.1039/C4DT00467A
- Chitrakar, R., Makita, Y., Ooi, K., and Sonoda, A. (2012). Selective uptake of lithium ion from brine by H<sub>1.33</sub>Mn<sub>1.67</sub>O<sub>4</sub> and H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>. *Chem. Lett.* 41, 1647–1649. doi:10.1246/cl.2012.1647
- Chordia, M., Wickerts, S., Nordelöf, A., and Arvidsson, R. (2022). Life cycle environmental impacts of current and future battery-grade lithium supply from brine and spodumene. *Resour. Conservation Recycl.* 187, 106634. doi:10.1016/J.RESCONREC.2022.106634
- Chung, K. S., Lee, J. C., Kim, W. K., Kim, S. B., and Cho, K. Y. (2008). Inorganic adsorbent containing polymeric membrane reservoir for the recovery of lithium from seawater. *J. Membr. Sci.* 325, 503–508. doi:10.1016/J.MEMSCI.2008.09.041
- Collins, A. G. (1974). Geochemistry of liquids, gases, and rocks from the Smackover Formation.
- Craig, H. (1969). *Geochemistry and origin of the red sea brines bt - hot brines and recent heavy metal deposits in the red sea: A geochemical and geophysical account*. Berlin, Heidelberg: Springer Berlin Heidelberg, 208–242. doi:10.1007/978-3-662-28603-6\_22
- Dai, X., Zhan, H., Qian, Z., Li, J., Liu, Z., and Wu, Z. (2021). Al-doped H<sub>2</sub>TiO<sub>3</sub> ion sieve with enhanced Li<sup>+</sup> adsorption performance. *RSC Adv.* 11, 34988–34995. doi:10.1039/D1RA06535A
- Deetlefs, M., Seddon, K. R., and Shara, M. (2006). Predicting physical properties of ionic liquids. *Phys. Chem. Chem. Phys.* 8, 642–649. doi:10.1039/B513453F
- Desmond, C., Lajoie-Leroux, F., Soucy, G., Laroche, N., and Magnan, J.-F. (2019). Spodumene: The lithium market, resources and processes. *Minerals* 9, 334. doi:10.3390/min9060334
- Ding, T., Wu, Q., Nie, Z., Zheng, M., Wang, Y., and Yang, D. (2022). Selective recovery of lithium resources in salt lakes by polyacrylonitrile/ion-imprinted polymer: Synthesis, testing, and computation. *Polym. Test.* 113, 107647. doi:10.1016/j.polymertesting.2022.107647
- Dorn, F. M., Ruiz Peyré, F., and Peyré, F. R. (2020). Lithium as a strategic resource: Geopolitics, industrialization, and mining in Argentina. *J. Lat. Am. Geogr.* 19, 68–90. doi:10.1353/lag.2020.0101
- Draper, J. J., and Jensen, A. R. (1976). The geochemistry of Lake Frome, a playa lake in South Australia. *BMR J. Aust. Geol. Geophys.* 1, 83–104.
- Eftekhari, A., Moghaddam, A. B., and Solati-Hashjin, M. (2006). Electrochemical properties of LiMn<sub>2</sub>O<sub>4</sub> cathode material doped with an actinide. *J. Alloys Compd.* 424, 225–230. doi:10.1016/j.jallcom.2005.10.088
- Ein-Eli, Y., Urian, R. C., Wen, W., and Mukerjee, S. (2005). Low temperature performance of copper/nickel modified LiMn<sub>2</sub>O<sub>4</sub> spinels. *Electrochimica Acta* 50, 1931–1937. doi:10.1016/j.electacta.2004.09.002
- Ellestad, R. B., and Leute, K.-M. (1950). *Method of extracting lithium values from spodumene ores*. US2516109A.
- Epstein, J. A., Feist, E. M., Zmora, J., and Marcus, Y. (1981). Extraction of lithium from the dead sea. *Hydrometallurgy* 6, 269–275. doi:10.1016/0304-386X(81)90044-X



- Ertürk, G., and Mattiasson, B. (2017). Molecular imprinting techniques used for the preparation of biosensors. *Sensors* 17, 288. doi:10.3390/s17020288
- Flexer, V., Baspineiro, C. F., and Galli, C. I. (2018). Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. *Sci. Total Environ.* 639, 1188–1204. doi:10.1016/j.scitotenv.2018.05.223
- Fuks, L., and Majdan, M. (2000). Features of solvent extraction of lanthanides and actinides. *Mineral Process. Extr. Metallurgy Rev.* 21, 25–48. doi:10.1080/08827500008914164
- Gao, A., Sun, Z., Li, S., Hou, X., Li, H., Wu, Q., et al. (2018). The mechanism of manganese dissolution on Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> ion sieves with HCl. *Dalton Trans.* 47, 3864–3871. doi:10.1039/C8DT00033F
- Gao, D., Guo, Y., Yu, X., Wang, S., and Deng, T. (2016). Extracting lithium from the high concentration ratio of magnesium and lithium brine using imidazolium-based ionic liquids with varying alkyl chain lengths. *J. Chem. Eng. Jpn. / JCEJ.* 49, 104–110. doi:10.1252/jcej.15we046
- Gmar, S., and Chagnes, A. (2019). Recent advances on electro dialysis for the recovery of lithium from primary and secondary resources. *Hydrometallurgy* 189, 105124. doi:10.1016/j.hydromet.2019.105124
- Godfrey, L. V., Chan, L. H., Alonso, R. N., Lowenstein, T. K., McDonough, W. F., Houston, J., et al. (2013). The role of climate in the accumulation of lithium-rich brine in the Central Andes. *Appl. Geochem.* 38, 92–102. doi:10.1016/j.apgeochem.2013.09.002
- Goodenough, R. D. (1960). Recovery of lithium, United States. Available at: <https://patents.google.com/patent/US2964381A>.
- Goodenough, R. D., and Stenger, V. A. (1961). Recovery of lithium from lithium aluminate complex. United States US2980497A, 2, 980, 497.
- Gopinath, K. P., Madhav, N. V., Krishnan, A., Malolan, R., and Rangarajan, G. (2020). Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. *J. Environ. Manag.* 270, 110906. doi:10.1016/j.jenvman.2020.110906
- Gouda, V. K., Banat, I. M., Riad, W. T., and Mansour, S. (1993). Microbiologically induced corrosion of UNS N04400 in seawater. *Corrosion* 49, 63–73. doi:10.5006/1.3316036
- Graham, J. D., Rupp, J. A., and Brungard, E. (2021). Lithium in the green energy transition: The quest for both sustainability and security. *Sustainability* 13, 11274. doi:10.3390/su132011274
- Grosjean, C., Herrera Miranda, P., Perrin, M., and Poggi, P. (2012). Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. *Renew. Sustain. Energy Rev.* 16, 1735–1744. doi:10.1016/j.rser.2011.11.023
- Gruber, P. W., Medina, P. A., Keoleian, G. A., Kesler, S. E., Everson, M. P., and Wallington, T. J. (2011). Global lithium availability. *J. Ind. Ecol.* 15, 760–775. doi:10.1111/j.1530-9290.2011.00359.x
- Gu, L., Sun, X.-L., Zhou, W., Ren, D.-H., Qiu, D., Gu, Z.-G., et al. (2016). Ion exchange properties and lithium isotopes selectivity of H<sub>0.36</sub>La<sub>0.55</sub>Ti<sub>0.3</sub>O<sub>3</sub>, H<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. *J. Radioanal. Nucl. Chem.* 307, 973–983. doi:10.1007/s10967-015-4239-6
- Guo, Z.-Y., Ji, Z.-Y., Chen, Q.-B., Liu, J., Zhao, Y.-Y., Li, F., et al. (2018). Prefractionation of LiCl from concentrated seawater/salt lake brines by electro dialysis with monovalent selective ion exchange membranes. *J. Clean. Prod.* 193, 338–350. doi:10.1016/j.jclepro.2018.05.077
- Gurreri, L., Tamburini, A., Cipollina, A., and Micale, G. (2020). Electro dialysis applications in wastewater treatment for environmental protection and resources recovery: A systematic review on progress and perspectives. *Membranes* 10, 146. doi:10.3390/membranes10070146
- Hamilton, A. D. (1984). *5.21 - crown ethers and cryptands*. Oxford: Pergamon, 731–761. doi:10.1016/B978-008096519-2.00127-2
- Hamzaoui, A. H., Hammi, H., and M'nif, A. (2007). Operating conditions for lithium recovery from natural brines. *Russ. J. Inorg. Chem.* 52, 1859–1863. doi:10.1134/S0036023607120091
- Hamzaoui, A. H., Jamoussi, B., and M'nif, A. (2008). Lithium recovery from highly concentrated solutions: Response surface methodology (RSM) process parameters optimization. *Hydrometallurgy* 90, 1–7. doi:10.1016/j.hydromet.2007.09.005
- Hano, T., Matsumoto, M., Ohtake, T., Egashiri, N., and Hori, F. (1992). Recovery of lithium from geothermal water by solvent extraction technique. *Solvent Extr. Ion Exch.* 10, 195–206. doi:10.1080/07366299208918100
- Harvianto, G. R., Kim, S.-H., and Ju, C.-S. (2016). Solvent extraction and stripping of lithium ion from aqueous solution and its application to seawater. *Rare Met.* 35, 948–953. doi:10.1007/s12598-015-0453-1
- He, G., Li, Z., Liu, Y., Liu, M., Zhu, C., Zhang, L., et al. (2022). A novel lithium ion-imprinted membrane with robust adsorption capacity and anti-fouling property based on the uniform multilayered interlayer. *Desalination* 539, 115973. doi:10.1016/j.desal.2022.115973
- He, G., Zhang, L., Zhou, D., Zou, Y., and Wang, F. (2015). The optimal condition for H<sub>2</sub>TiO<sub>3</sub>-lithium adsorbent preparation and Li<sup>+</sup> adsorption confirmed by an orthogonal test design. *Ionics* 21, 2219–2226. doi:10.1007/s11581-015-1393-3
- Heidari, N., and Momeni, P. (2017). Selective adsorption of lithium ions from Urmia Lake onto aluminum hydroxide. *Environ. Earth Sci.* 76, 551. doi:10.1007/s12665-017-6885-1
- Helan, M., Berchmans, L. J., Syamala Kumari, V. S., RaviSankar, R., and Shanmugam, V. M. (2011). Molten salt synthesis of LiGd<sub>0</sub> 01Mn<sub>1</sub> 99O<sub>4</sub> using chloride-carbonate melt. *Mater. Res. Innovations* 15, 130–134. doi:10.1179/143307511X12998222918958
- Hill, R. J., Craig, J. R., and Gibbs, G. V. (1979). Systematics of the spinel structure type. *Phys. Chem. Min.* 4, 317–339. doi:10.1007/BF00307535
- Hoshino, T. (2013a). Development of technology for recovering lithium from seawater by electro dialysis using ionic liquid membrane. *Fusion Eng. Des.* 88, 2956–2959. doi:10.1016/j.fusengdes.2013.06.009
- Hoshino, T. (2013b). Preliminary studies of lithium recovery technology from seawater by electro dialysis using ionic liquid membrane. *Desalination* 317, 11–16. doi:10.1016/j.desal.2013.02.014
- Hu, H., Guo, J., Liu, M., Li, Y., Wu, B., Xiong, L., et al. (2022). Preparation and characterization of high-stability lithium ion-sieves with aluminosilicate framework. *Hydrometallurgy* 213, 105929. doi:10.1016/j.hydromet.2022.105929
- Huang, C., and Xu, T. (2006). Electro dialysis with bipolar membranes for sustainable development. *Environ. Sci. Technol.* 40, 5233–5243. doi:10.1021/es060039p
- Huang, W., Liu, S., Liu, J., Zhang, W., and Pan, J. (2018). 2-Methylol-12-crown-4 ether immobilized PolyHIPEs toward recovery of lithium(i). *New J. Chem.* 42, 16814–16822. doi:10.1039/C8NJ01961D
- Hwang, C. W., Jeong, M. H., Kim, Y. J., Son, W. K., Kang, K. S., Lee, C. S., et al. (2016). Process design for lithium recovery using bipolar membrane electro dialysis system. *Sep. Purif. Technol.* 166, 34–40. doi:10.1016/j.seppur.2016.03.013
- IEA (2022). *Global EV Outlook 2022 Securing supplies for an electric future*. Paris, France: OECD, 221.
- Imdad, S., and Dohare, R. K. (2022). A critical review on heavy metals removal using ionic liquid membranes from the industrial wastewater. *Chem. Eng. Process. - Process Intensif.* 173, 108812. doi:10.1016/j.cep.2022.108812
- İpekçi, D., Altok, E., Bunani, S., Yoshizuka, K., Nishihama, S., Arda, M., et al. (2018). Effect of acid-base solutions used in acid-base compartments for simultaneous recovery of lithium and boron from aqueous solution using bipolar membrane electro dialysis (BMED). *Desalination* 448, 69–75. doi:10.1016/j.desal.2018.10.001
- İpekçi, D., Kabay, N., Bunani, S., Altok, E., Arda, M., Yoshizuka, K., et al. (2020). Application of heterogeneous ion exchange membranes for simultaneous separation and recovery of lithium and boron from aqueous solution with bipolar membrane electro dialysis (EDBM). *Desalination* 479, 114313. doi:10.1016/j.desal.2020.114313
- Iqbal, M. J., and Ahmad, Z. (2008). Electrical and dielectric properties of lithium manganate nanomaterials doped with rare-Earth elements. *J. Power Sources* 179, 763–769. doi:10.1016/j.jpowsour.2007.12.115
- Irle, R. (2022). Global EV sales for 2021.
- Isupov, V. P., Kotsupalo, N. P., Nemudry, A. P., and Menzeres, L. T. (1999). "Aluminium hydroxide as selective sorbent of lithium salts from brines and technical solutions," in *Adsorption and its applications in industry and environmental protection*. Editor A. Dąbrowski (Amsterdam, Netherlands: Elsevier), 120, 621–652. doi:10.1016/S0167-2991(99)80567-9
- Jamal, A., and Khzahee, M. (2019). The influence of the dead sea water decline on the concentration changes of lithium and strontium trace elements.
- Jang, E., Jang, Y., and Chung, E. (2017). Lithium recovery from shale gas produced water using solvent extraction. *Appl. Geochem.* 78, 343–350. doi:10.1016/j.apgeochem.2017.01.016
- Ji, P.-Y., Ji, Z.-Y., Chen, Q.-B., Liu, J., Zhao, Y.-Y., Wang, S.-Z., et al. (2018). Effect of coexisting ions on recovering lithium from high Mg<sup>2+</sup>/Li<sup>+</sup> ratio brines by selective-electro dialysis. *Sep. Purif. Technol.* 207, 1–11. doi:10.1016/j.seppur.2018.06.012
- Ji, Z.-y., Chen, Q.-b., Yuan, J.-s., Liu, J., Zhao, Y.-y., and Feng, W.-x. (2017). Preliminary study on recovering lithium from high Mg<sup>2+</sup>/Li<sup>+</sup> ratio brines by electro dialysis. *Sep. Purif. Technol.* 172, 168–177. doi:10.1016/j.seppur.2016.08.006

- Jiang, C., Wang, Y., Wang, Q., Feng, H., and Xu, T. (2014). Production of lithium hydroxide from Lake Brines through electro-electrodialysis with bipolar membranes (EEDBM). *Ind. Eng. Chem. Res.* 53, 6103–6112. doi:10.1021/ie404334s
- Jin, Y., Jiang, Q., Zhao, Y., alAnthuvan Rajesh, J., and Min, B.-K. (2018). IOP conference series: Earth and environmental science LiMn<sub>2</sub>O<sub>4</sub> microspheres as high-performance cathode materials for Li-ion batteries you may also like controllable fabrication of CoMn<sub>2</sub>O<sub>4</sub> microflowers and microspheres as high-performance lithium ion battery anode material cubic spinel AB<sub>2</sub>O<sub>4</sub> type porous ZnCo<sub>2</sub>O<sub>4</sub> microspheres: Facile hydrothermal synthesis and their electrochemical performances in pseudocapacitor. *IOP Conf. Ser. Earth Environ. Sci.* 108, 22011. doi:10.1088/1755-1315/108/2/022011
- Jones, B. F., Naftz, D. L., Spencer, R. J., and Oviatt, C. G. (2009). Geochemical evolution of great Salt Lake, Utah, USA. *Aquat. Geochem.* 15, 95–121. doi:10.1007/s10498-008-9047-y
- Joo, H., Kim, S., Kim, S., Choi, M., Kim, S.-H., and Yoon, J. (2020). Pilot-scale demonstration of an electrochemical system for lithium recovery from the desalination concentrate. *Environ. Sci. Water Res. Technol.* 6, 290–295. doi:10.1039/C9EW00756C
- Kalantzos, S. (2020). The race for critical minerals in an era of geopolitical realignments. *Int. Spectator* 55, 1–16. doi:10.1080/03932729.2020.1786926
- Kanoh, H., Ooi, K., Miyai, Y., and Katoh, S. (1993). Electrochemical recovery of lithium ions in the aqueous phase. *Sep. Sci. Technol.* 28, 643–651. doi:10.1080/01496399308019512
- Kanoh, H., Ooi, K., Miyai, Y., and Katoh, S. (1991). Selective electroinsertion of lithium ions into a platinum/lambda.-manganese dioxide electrode in the aqueous phase. *Langmuir* 7, 1841–1842. doi:10.1021/la00057a002
- Kaplan, D. (1963). Process for the extraction of lithium from dead sea solutions. *Isr. J. Chem.* 1, 115–120. doi:10.1002/ijch.196300021
- Katayama, Y., Nita, K., Ueda, M., Nakamura, H., Takagi, M., and Ueno, K. (1985). Synthesis of chromogenic crown ethers and liquid-liquid extraction of alkali metal ions. *Anal. Chim. Acta* 173, 193–209. doi:10.1016/S0003-2670(00)84957-0
- Katz, A., Starinsky, A. A., Katz, A., and Starinsky, A. A. (2009). Geochemical history of the dead sea. *Aquat. Geochem.* 15, 159–194. doi:10.1007/s10498-008-9045-0
- Kelly, J. C., Wang, M., Dai, Q., and Winjobi, O. (2021). Energy, greenhouse gas, and water life cycle analysis of lithium carbonate and lithium hydroxide monohydrate from brine and ore resources and their use in lithium ion battery cathodes and lithium ion batteries. *Resour. Conservation Recycl.* 174, 105762. doi:10.1016/j.resconrec.2021.105762
- Kesler, S. E., Gruber, P. W., Medina, P. A., Keoleian, G. A., Everson, M. P., and Wallington, T. J. (2012). Global lithium resources: Relative importance of pegmatite, brine and other deposits. *Ore Geol. Rev.* 48, 55–69. doi:10.1016/j.OREGEOREV.2012.05.006
- Kim, S., Joo, H., Moon, T., Kim, S.-H., and Yoon, J. (2019). Rapid and selective lithium recovery from desalination brine using an electrochemical system. *Environ. Sci. Process. Impacts* 21, 667–676. doi:10.1039/C8EM00498F
- Kim, S., Kim, J., Kim, S., Lee, J., and Yoon, J. (2018). Electrochemical lithium recovery and organic pollutant removal from industrial wastewater of a battery recycling plant. *Environ. Sci. Water Res. Technol.* 4, 175–182. doi:10.1039/C7EW00454K
- Kim, S., Lee, J., Kang, J. S., Jo, K., Kim, S., Sung, Y.-E., et al. (2015). Lithium recovery from brine using a λ-MnO<sub>2</sub>/activated carbon hybrid supercapacitor system. *Chemosphere* 125, 50–56. doi:10.1016/j.chemosphere.2015.01.024
- Kushnir, D., and Sandén, B. A. (2012). The time dimension and lithium resource constraints for electric vehicles. *Resour. Policy* 37, 93–103. doi:10.1016/j.resourpol.2011.11.003
- Lambert, J., Avila-Rodriguez, M., Durand, G., and Rakib, M. (2006). Separation of sodium ions from trivalent chromium by electro-dialysis using monovalent cation selective membranes. *J. Membr. Sci.* 280, 219–225. doi:10.1016/j.memsci.2006.01.021
- Lawagon, C. P., Nisola, G. M., Mun, J., Tron, A., Torrejos, R. E. C., Seo, J. G., et al. (2016). Adsorptive Li<sup>+</sup> mining from liquid resources by H<sub>2</sub>TiO<sub>3</sub>: Equilibrium, kinetics, thermodynamics, and mechanisms. *J. Industrial Eng. Chem.* 35, 347–356. doi:10.1016/j.jiec.2016.01.015
- Lee, J., Yu, S.-H., Kim, C., Sung, Y.-E., and Yoon, J. (2013). Highly selective lithium recovery from brine using a λ-MnO<sub>2</sub>-Ag battery. *Phys. Chem. Chem. Phys.* 15, 7690–7695. doi:10.1039/C3CP50919B
- Li, E., Kang, J., Ye, P., Zhang, W., Cheng, F., Yin, C., et al. (2019a). A prospective material for the highly selective extraction of lithium ions based on a photochromic crowned spirobenzopyran. *J. Mater. Chem.* 7 (6), 903–907. doi:10.1039/C8TB02906G
- Li, Q., Fan, Q., Wang, J., Qin, Z., Zhang, X., Wei, H., et al. (2019b). Hydrochemistry, distribution and formation of lithium-rich brines in salt lakes on the Qinghai-Tibetan plateau. *Miner. (Basel)*. 9, 528. doi:10.3390/min9090528
- Li, T., Tan, H., and Fan, Q. (2006). Hydrochemical characteristics and origin analysis for the underground brines in west quaidam basin. *J. Salt Lake Res.* 14, 26–32.
- Li, Y.-h., Zhao, Z.-w., Liu, X.-h., Chen, X.-y., and Zhong, M.-l. (2015). Extraction of lithium from salt lake brine by aluminum-based alloys. *Trans. Nonferrous Metals Soc. China* 25, 3484–3489. doi:10.1016/S1003-6326(15)64032-8
- Li, Y., Shi, S., Cao, H., Wu, X., Zhao, Z., and Wang, L. (2016). Bipolar membrane electro-dialysis for generation of hydrochloric acid and ammonia from simulated ammonium chloride wastewater. *Water Res.* 89, 201–209. doi:10.1016/j.watres.2015.11.038
- Limjoco, L. A., Nisola, G. M., Lawagon, C. P., Lee, S.-P., Seo, J. G., Kim, H., et al. (2016). H<sub>2</sub>TiO<sub>3</sub> composite adsorbent foam for efficient and continuous recovery of Li<sup>+</sup> from liquid resources. *Colloids Surfaces A Physicochem. Eng. Aspects* 504, 267–279. doi:10.1016/j.colsurfa.2016.05.072
- Liu, G., Zhao, Z., and He, L. (2020). Highly selective lithium recovery from high Mg/Li ratio brines. *Desalination* 474, 114185. doi:10.1016/j.desal.2019.114185
- Liu, W., Agusdinata, D. B., and Myint, S. W. (2019). Spatiotemporal patterns of lithium mining and environmental degradation in the Atacama Salt Flat, Chile. *Int. J. Appl. Earth Observation Geoinformation* 80, 145–156. doi:10.1016/j.jag.2019.04.016
- Liu, X., Zhong, M., Chen, X., and Zhao, Z. (2018). Separating lithium and magnesium in brine by aluminum-based materials. *Hydrometallurgy* 176, 73–77. doi:10.1016/j.hydromet.2018.01.005
- Lowry, T., and Richardson, K. (1987). *Mechanism and theory in organic chemistry*. New York, United States: Harper & Row.
- Lu, J., Qin, Y., Wu, Y., Meng, M., Yan, Y., and Li, C. (2019). Recent advances in ion-imprinted membranes: Separation and detection via ion-selective recognition. *Environ. Sci. Water Res. Technol.* 5, 1626–1653. doi:10.1039/C9EW00465C
- Lu, J., Qin, Y., Zhang, Q., Wu, Y., Cui, J., Li, C., et al. (2018). Multilayered ion-imprinted membranes with high selectivity towards Li<sup>+</sup> based on the synergistic effect of 12-crown-4 and polyether sulfone. *Appl. Surf. Sci.* 427, 931–941. doi:10.1016/j.apsusc.2017.08.016
- Ma, P., Chen, X. D., and Hossain, M. D. M. (2000). Lithium extraction from a multicomponent mixture using supported liquid membranes. *Sep. Sci. Technol.* 35, 2513–2533. doi:10.1081/SS-100102353
- Maheswari, P., Prasannadevi, D., and Mohan, D. (2012). Preparation and performance of silver nanoparticle incorporated polyethersulfone nanofiltration membranes. *High. Perform. Polym.* 25, 174–187. doi:10.1177/0954008312459865
- Makanyire, T., Sanchez-Segado, S., and Jha, A. (2016). Separation and recovery of critical metal ions using ionic liquids. *Adv. Manuf.* 4, 33–46. doi:10.1007/s40436-015-0132-3
- Malliga, P., Bela, R. B., and Shanmugapriya, N. (2020). *Chapter 5 - conversion of textile effluent wastewater into fertilizer using marine cyanobacteria along with different agricultural waste*. Amsterdam, Netherlands: Elsevier, 87–111. doi:10.1016/B978-0-12-817951-2.00005-5
- Malyovanyi, S. M., Andriiko, A. A., and Monko, A. P. (2003). Synthesis and electrochemical behavior of Fe-doped overstoichiometric LiMn<sub>2</sub>O<sub>4</sub>-based spinels. *J. Solid State Electrochem.* 8, 7–10. doi:10.1007/s10008-003-0414-8
- Månberger, A., and Johansson, B. (2019). The geopolitics of metals and metalloids used for the renewable energy transition. *Energy Strategy Rev.* 26, 100394. doi:10.1016/j.esr.2019.100394
- Mani, K. N. (1991). Electro-dialysis water splitting technology. *J. Membr. Sci.* 58, 117–138. doi:10.1016/S0376-7388(00)82450-3
- Manohar, M., Shukla, G., Pandey, R. P., and Shahi, V. K. (2017). Efficient bipolar membrane with protein interfacial layer for optimal water splitting. *J. Industrial Eng. Chem.* 47, 141–149. doi:10.1016/j.jiec.2016.11.025
- Marchini, F., Rubi, D., del Pozo, M., Williams, F. J., and Calvo, E. J. (2016). Surface chemistry and lithium-ion exchange in LiMn<sub>2</sub>O<sub>4</sub> for the electrochemical selective extraction of LiCl from natural Salt Lake Brines. *J. Phys. Chem. C* 120, 15875–15883. doi:10.1021/acs.jpcc.5b11722
- Marthi, R., Asgar, H., Gadikota, G., and Smith, Y. R. (2021). On the structure and lithium adsorption mechanism of layered H<sub>2</sub>TiO<sub>3</sub>. *ACS Appl. Mat. Interfaces* 13, 8361–8369. doi:10.1021/acsami.0c20691
- Millero, F. J., and Chetirkin, P. V. (1980). The density of Caspian Sea waters. *Deep Sea Res. Part A. Oceanogr. Res. Pap.* 27, 265–271. doi:10.1016/0198-0149(80)90017-5
- Missoni, L. L., Marchini, F., del Pozo, M., and Calvo, E. J. (2016). A LiMn<sub>2</sub>O<sub>4</sub>-poly pyrrole system for the extraction of LiCl from natural brine. *J. Electrochem. Soc.* 163, A1898–A1902. doi:10.1149/2.0591609jes
- Moazeni, M., Hajipour, H., Askari, M., and Nusheh, M. (2015). Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents. *Mater. Res. Bull.* 61, 70–75. doi:10.1016/j.materresbull.2014.09.069

- Mohr, S. H., Mudd, G. M., and Giurco, D. (2012). Lithium resources and production: Critical assessment and global projections. *Minerals* 2 (1), 65–84. doi:10.3390/min2010065
- Moran, S. (2018). *Chapter 6 - clean water characterization and treatment objectives*. Oxford, United Kingdom: Butterworth-Heinemann, 61–67. doi:10.1016/B978-0-12-811309-7.00006-0
- Mori, T., Takao, K., Sasaki, K., Suzuki, T., Arai, T., and Ikeda, Y. (2015). Homogeneous liquid–liquid extraction of U(VI) from HNO<sub>3</sub> aqueous solution to betainium bis(trifluoromethylsulfonyl)imide ionic liquid and recovery of extracted U(VI). *Sep. Purif. Technol.* 155, 133–138. doi:10.1016/j.seppur.2015.01.045
- Mortaheb, H., Moghadasi, M., and Garmsiri, M. (2014). “Synthesis of porous polyether sulfone ion-exchange membrane, investigation on its properties and characterizations,” in *The 8th International Chemical Engineering Congress & Exhibition, 2014-02-24* (Kish, Iran).
- Nguyen, T., and Lee, M. (2018). A review on the separation of lithium ion from leach liquors of primary and secondary resources by solvent extraction with commercial extractants. *Processes* 6, 55. doi:10.3390/pr6050055
- Nie, X.-Y., Sun, S.-Y., Song, X., and Yu, J.-G. (2017). Further investigation into lithium recovery from salt lake brines with different feed characteristics by electro dialysis. *J. Membr. Sci.* 530, 185–191. doi:10.1016/j.memsci.2017.02.020
- Ohzuku, T., Ueda, A., and Yamamoto, N. (1995). Zero-strain insertion material of Li<sub>1/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> for rechargeable lithium cells. *J. Electrochem. Soc.* 142, 1431–1435. doi:10.1149/1.2048592
- Olea, F., Durán, G., Díaz, G., Villarroel, E., Araya-López, C., Cabezas, R., et al. (2022). Ionic liquids for the selective solvent extraction of lithium from aqueous solutions: A theoretical selection using COSMO-RS. *Minerals* 12, 190. doi:10.3390/min12020190
- Ouyang, C. Y., Zhong, Z. Y., and Lei, M. S. (2007). *Ab initio* studies of structural and electronic properties of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel. *Electrochem. Commun.* 9, 1107–1112. doi:10.1016/j.elecom.2007.01.013
- Paranthaman, M. P., Li, L., Luo, J., Hoke, T., Ucar, H., Moyer, B. A., et al. (2017). Recovery of lithium from geothermal brine with lithium–aluminum layered double hydroxide chloride sorbents. *Environ. Sci. Technol.* 51, 13481–13486. doi:10.1021/acs.est.7b03464
- Pärnamäe, R., Mareev, S., Nikonenko, V., Melnikov, S., Sheldeshov, N., Zabolotskii, V., et al. (2021). Bipolar membranes: A review on principles, latest developments, and applications. *J. Membr. Sci.* 617, 118538. doi:10.1016/j.memsci.2020.118538
- Patil, A. B., Pathak, P. N., Shinde, V. S., Alyapyshev, M. Y., Babain, V. A., and Mohapatra, P. K. (2015). A novel solvent system containing a dipicolinamide in room temperature ionic liquids for actinide ion extraction. *J. Radioanal. Nucl. Chem.* 305, 521–528. doi:10.1007/s10967-015-4028-2
- Patrice, S., Yury, G., and Bruce, D. (2014). Where do batteries end and supercapacitors begin? *Science* 343, 1210–1211. doi:10.1126/science.1249625
- Pauwels, H., Brach, M., and Fouillac, C. (1995). Study of Li<sup>+</sup> adsorption onto polymeric aluminium (III) hydroxide for application in the treatment of geothermal waters. *Colloids Surfaces A Physicochem. Eng. Aspects* 100, 73–82. doi:10.1016/0927-7757(95)03185-G
- Pearson, R. G. (1990). Hard and soft acids and bases—The evolution of a chemical concept. *Coord. Chem. Rev.* 100, 403–425. doi:10.1016/0010-8545(90)85016-L
- Pelly, I. (1978). Recovery of lithium from dead sea brines. *J. Appl. Chem. Biotechnol.* 28, 469–474.
- Peppard, D. F., Mason, G. W., Driscoll, W. J., and Sironen, R. J. (1958). Acidic esters of orthophosphoric acid as selective extractants for metallic cations—Tracer studies. *J. Inorg. Nucl. Chem.* 7, 276–285. doi:10.1016/0022-1902(58)80078-0
- Perez de Solay, M. (2017). Oroco bre limited: Severe weather affects operations.
- Pouraghabarar, M., Taleshi, S., and Chaichi, M. J. (2021). Determination of lithium abundances in seawater in the southern coast of the caspian sea and river estuaries. *J. Mar. Sci. Technol.* 19, 66–72. doi:10.22113/jmst.2018.109755.2088
- Qian, F., Guo, M., Qian, Z., Zhao, B., Li, J., Wu, Z., et al. (2021a). Enabling highly structure stability and adsorption performances of Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> by Al-gradient surface doping. *Sep. Purif. Technol.* 264, 118433. doi:10.1016/j.seppur.2021.118433
- Qian, F., Zhao, B., Guo, M., Wu, Z., Zhou, W., and Liu, Z. (2021b). Surface trace doping of Na enhancing structure stability and adsorption properties of Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> for Li<sup>+</sup> recovery. *Sep. Purif. Technol.* 256, 117583. doi:10.1016/j.seppur.2020.117583
- Qinghai Institute of Salt Lakes (2019). About salt lakes.
- Quintero, C., Dahlkamp, J. M., Fierro, F., Thennis, T., Zhang, Y., Videla, Á., et al. (2020). Development of a co-precipitation process for the preparation of magnesium hydroxide containing lithium carbonate from Li-enriched brines. *Hydrometallurgy* 198, 105515. doi:10.1016/j.hydromet.2020.105515
- Rama, R., Rout, A., Venkatesan, K. A., Antony, M. P., and Vasudeva Rao, P. R. (2015). Extraction behavior of americium(III) in benzoylpyrazolone dissolved in pyrrolidinium based ionic liquid. *Sep. Sci. Technol.* 50, 150615133350006–150615133352169. doi:10.1080/01496395.2015.1050109
- Reig, M., Vecino, X., Valderrama, C., Gibert, O., and Cortina, J. L. (2018). Application of electro dialysis for the removal of as from metallurgical process waters: Recovery of Cu and Zn. *Sep. Purif. Technol.* 195, 404–412. doi:10.1016/j.seppur.2017.12.040
- Roundhill, D. M. (2001). *Extraction of metals from soils and waters*. Berlin, Germany: Springer Science & Business Media.
- Ryu, T., Haldorai, Y., Rengaraj, A., Shin, J., Hong, H.-J., Lee, G.-W., et al. (2016). Recovery of lithium ions from seawater using a continuous flow adsorption column packed with granulated chitosan–lithium manganese oxide. *Ind. Eng. Chem. Res.* 55, 7218–7225. doi:10.1021/acs.iecr.6b01632
- Safarali, R., Yaftian, M. R., and Zamani, A. (2016). Solvent extraction-separation of La(III), Eu(III) and Er(III) ions from aqueous chloride medium using carbamoyl-carboxylic acid extractants. *J. Rare Earths* 34, 91–98. doi:10.1016/S1002-0721(14)60583-4
- Sakunthala, A., Reddy, M. V., Selvasekarapandian, S., Chowdari, B. V. R., and Selvin, P. C. (2010). Synthesis of compounds, Li(MMn<sub>11/6</sub>)O<sub>4</sub> (M=Mn<sub>1/6</sub>, Co<sub>1/6</sub>, (Co<sub>1/12</sub>Cr<sub>1/12</sub>), (Co<sub>1/12</sub>Al<sub>1/12</sub>), (Cr<sub>1/12</sub>Al<sub>1/12</sub>)) by polymer precursor method and its electrochemical performance for lithium-ion batteries. *Electrochimica Acta* 55, 4441–4450. doi:10.1016/j.electacta.2010.02.080
- Schmidt, A., Mestmäcker, F., Brückner, L., Elwert, T., and Strube, J. (2019). Liquid-liquid extraction and chromatography process routes for the purification of lithium. *Mater. Sci. Forum* 959, 79–99. doi:10.4028/www.scientific.net/MSF.959.79
- Seddon, K. R., Stark, A., and Torres, M.-J. (2000). Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* 72, 2275–2287. doi:10.1351/pac200072122275
- Seddon, K. R., Stark, A., and Torres, M.-J. (2002). “Viscosity and density of 1-Alkyl-3-methylimidazolium ionic liquids,” in *Clean solvents* (Washington, United States: American Chemical Society), 4–34. 819 of ACS Symposium Series. doi:10.1021/bk-2002-0819.ch004
- Shen, X.-M., and Clearfield, A. (1986). Phase transitions and ion exchange behavior of electrolytically prepared manganese dioxide. *J. Solid State Chem.* 64, 270–282. doi:10.1016/0022-4596(86)90071-X
- Shi, C., Jing, Y., Xiao, J., Wang, X., Yao, Y., and Jia, Y. (2017). Solvent extraction of lithium from aqueous solution using non-fluorinated functionalized ionic liquids as extraction agents. *Sep. Purif. Technol.* 172, 473–479. doi:10.1016/j.seppur.2016.08.034
- Shi, D., Zhang, L., Peng, X., Li, L., Song, F., Nie, F., et al. (2018). Extraction of lithium from salt lake brine containing boron using multistage centrifuge extractors. *Desalination* 441, 44–51. doi:10.1016/j.desal.2018.04.029
- Shi, X.-c., Zhang, Z.-b., Zhou, D.-f., Zhang, L.-f., Bai-zhen, C., and Yu, L.-l. (2013). Synthesis of Li<sup>+</sup> adsorbent (H<sub>2</sub>TiO<sub>3</sub>) and its adsorption properties. *Trans. Nonferrous Metals Soc. China* 23, 253–259. doi:10.1016/S1003-6326(13)62453-X
- Snydacker, D. H., Hegde, V. L., Aykol, M., and Wolverton, C. (2018). Computational discovery of Li–M–O ion exchange materials for lithium extraction from brines. *Chem. Mat.* 30, 6961–6968. doi:10.1021/acs.chemmater.7b03509
- Soffer, A., and Folman, M. (1972). The electrical double layer of high surface porous carbon electrode. *J. Electroanal. Chem. Interfacial Electrochem.* 38, 25–43. doi:10.1016/S0022-0728(72)80087-1
- Srimuk, P., Su, X., Yoon, J., Aurbach, D., and Presser, V. (2020). Charge-transfer materials for electrochemical water desalination, ion separation and the recovery of elements. *Nat. Rev. Mat.* 5, 517–538. doi:10.1038/s41578-020-0193-1
- Steiner, Z., Landing, W. M., Bohlin, M. S., Greaves, M., Prakash, S., Vinayachandran, P. N., et al. (2022). Variability in the concentration of lithium in the indo-pacific ocean. *Glob. Biogeochem. Cycles* 36, 6–7. doi:10.1029/2021GB007184
- Stringfellow, W. T., and Dobson, P. F. (2021). Technology for the recovery of lithium from geothermal brines. *Energies* 14, 6805. doi:10.3390/EN14206805
- Su, H., Tan, B., Zhang, J., Liu, W., Wang, L., Wang, Y., et al. (2022). Modelling of lithium extraction with TBP/P507–FeCl<sub>3</sub> system from salt-lake brine. *Sep. Purif. Technol.* 282, 120110. doi:10.1016/j.seppur.2021.120110
- Sukamto, J. P. H., Lilga, M. L., and Orth, R. K. (1998). Electrically switched cesium ion exchange. *Tech. rep.*, United States. doi:10.2172/1118
- Summerhayes, C. P., and Thorpe, S. A. (1996). *Oceanography: An illustrated guide*. New York, United States: John Wiley, 165–181. *Chapter 11*.
- Sun, D., Zhou, T., Lu, Y., Yan, Y., Liu, C., and Che, G. (2022). Ion-imprinted antifouling nanocomposite membrane for separation of lithium ion. *Korean J. Chem. Eng.* 39, 2482–2490. doi:10.1007/s11814-022-1176-2

- Sun, Y., Wang, Q., Wang, Y., Yun, R., and Xiang, X. (2021). Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine. *Sep. Purif. Technol.* 256, 117807. doi:10.1016/j.seppur.2020.117807
- Swain, B. (2016). Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: A review. *J. Chem. Technol. Biotechnol.* 91, 2549–2562. doi:10.1002/jctb.4976
- Takeuchi, T. (1980). Extraction of lithium from sea water with metallic aluminum. *J. Nucl. Sci. Technol.* 17, 922–928. doi:10.1080/18811248.1980.9732675
- Tanaka, Y. (2015). *17 - bipolar membrane electrodialysis*. Amsterdam: Elsevier, 369–392. doi:10.1016/B978-0-444-63319-4.00017-1
- Torresos, R. E. C., Nisola, G. M., Park, M. J., Beltran, A. B., Seo, J. G., Lee, S.-P., et al. (2015). Liquid-liquid extraction of lithium using mixed ion carrier system at room temperature ionic liquid. *Desalination Water Treat.* 53, 2774–2781. doi:10.1080/19443994.2014.931534
- Torresos, R. E. C., Nisola, G. M., Song, H. S., Han, J. W., Lawagon, C. P., Seo, J. G., et al. (2016). Liquid-liquid extraction of lithium using lipophilic dibenzo-14-crown-4 ether carboxylic acid in hydrophobic room temperature ionic liquid. *Hydrometallurgy* 164, 362–371. doi:10.1016/j.hydromet.2016.05.010
- Tran, K. T., Han, K. S., Kim, S. J., Kim, M. J., and Tran, T. (2016). Recovery of magnesium from Uyuni salar brine as hydrated magnesium carbonate. *Hydrometallurgy* 160, 106–114. doi:10.1016/j.hydromet.2015.12.008
- Tran, K. T., Van Luong, T., An, J.-W., Kang, D.-J., Kim, M.-J., and Tran, T. (2013). Recovery of magnesium from Uyuni salar brine as high purity magnesium oxalate. *Hydrometallurgy* 138, 93–99. doi:10.1016/j.hydromet.2013.05.013
- Trócoli, R., Battistel, A., and LaMantia, F. (2015). Nickel hexacyanoferrate as suitable Alternative to Ag for electrochemical lithium recovery. *ChemSusChem* 8, 2514–2519. doi:10.1002/cssc.201500368
- Trócoli, R., Battistel, A., and Mantia, F. L. (2014). Selectivity of a lithium-recovery process based on LiFePO<sub>4</sub>. *Chem. Eur. J.* 20, 9888–9891. doi:10.1002/chem.201403535
- Trócoli, R., Erinmwingbovo, C., and LaMantia, F. (2017). Optimized lithium recovery from brines by using an electrochemical ion-pumping process based on  $\lambda$ -MnO<sub>2</sub> and nickel hexacyanoferrate. *ChemElectroChem* 4, 143–149. doi:10.1002/celec.201600509
- Um, N., and Hirato, T. (2014). Precipitation behavior of Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, and Mn(OH)<sub>2</sub> from CaCl<sub>2</sub>, MgCl<sub>2</sub>, and MnCl<sub>2</sub> in NaOH-H<sub>2</sub>O solutions and study of lithium recovery from seawater via two-stage precipitation process. *Hydrometallurgy* 146, 142–148. doi:10.1016/j.hydromet.2014.04.006
- U.S. Geological Survey (2022). *Mineral commodity summary - lithium carbonate*. United States: U.S Geological Survey.
- USGS (2017). "Lithium. U.S. Geological Survey professional paper 1802-K," in *Critical mineral resources of the United States—economic and environmental geology and prospects for future supply* (United States: USGS), 1, 34.
- Venugopal, K., and Dharmalingam, S. (2016). Composite ion exchange membrane based electrodialysis cell for desalination as well as acid and alkali productions 3.
- Vikström, H., Davidsson, S., and Höök, M. (2013). Lithium availability and future production outlooks. *Appl. Energy* 110, 252–266. doi:10.1016/j.apenergy.2013.04.005
- Voinov, M. (1982). MnO<sub>2</sub>: Structure and activity. *Electrochimica Acta* 27, 833–835. doi:10.1016/0013-4686(82)80204-1
- Voutchkov, N. (2010). Introduction to reverse osmosis desalination - a SunCam online continuing education course. doi:10.13140/RG.2.2.13908.60801
- Wang, C., Zhai, Y., Wang, X., and Zeng, M. (2014). Preparation and characterization of lithium  $\lambda$ -MnO<sub>2</sub> ion-sieves. *Front. Chem. Sci. Eng.* 8, 471–477. doi:10.1007/s11705-014-1449-3
- Wang, H., Ding, F., Jin, G., Li, C., and Meng, H. (2017). Ultra-thin graphene oxide intermediate layer for bipolar membranes using atomizing spray assembly. *Colloids Surfaces A Physicochem. Eng. Aspects* 520, 114–120. doi:10.1016/j.colsurfa.2017.01.041
- Wang, J., Yue, X., Wang, P., Yu, T., Du, X., Hao, X., et al. (2022). Electrochemical technologies for lithium recovery from liquid resources: A review. *Renew. Sustain. Energy Rev.* 154, 111813. doi:10.1016/j.rser.2021.111813
- Wang, L., Meng, C. G., Han, M., and Ma, W. (2008). Lithium uptake in fixed-pH solution by ion sieves. *J. Colloid Interface Sci.* 325, 31–40. doi:10.1016/j.jcis.2008.05.005
- Wang, L., Meng, C. G., and Ma, W. (2009). Study on Li<sup>+</sup> uptake by lithium ion-sieve via the pH technique. *Colloids Surfaces A Physicochem. Eng. Aspects* 334, 34–39. doi:10.1016/j.colsurfa.2008.09.050
- Wang, S., Li, P., Cui, W., Zhang, H., Wang, H., Zheng, S., et al. (2016). Hydrothermal synthesis of lithium-enriched  $\beta$ -Li<sub>2</sub>TiO<sub>3</sub> with an ion-sieve application: Excellent lithium adsorption. *RSC Adv.* 6, 102608–102616. doi:10.1039/C6RA18018C
- Wang, S., Zhang, M., Zhang, Y., Zhang, Y., Qiao, S., and Zheng, S. (2019). High adsorption performance of the Mo-doped titanium oxide sieve for lithium ions. *Hydrometallurgy* 187, 30–37. doi:10.1016/j.hydromet.2019.05.004
- Wang, X., Jing, Y., Liu, H., Yao, Y., Shi, C., Xiao, J., et al. (2018). Extraction of lithium from salt lake brines by bis[(trifluoromethyl)sulfonyl]imide-based ionic liquids. *Chem. Phys. Lett.* 707, 8–12. doi:10.1016/j.cplett.2018.07.030
- Watanabe, A., Matsunaga, T., Abulikemu, A., Shimoda, K., Yamamoto, K., Uchiyama, T., et al. (2020). Structural analysis of imperfect Li<sub>2</sub>TiO<sub>3</sub> crystals. *J. Alloys Compd.* 819, 153037. doi:10.1016/j.jallcom.2019.153037
- Wei, S., Wei, Y., Chen, T., Liu, C., and Tang, Y. (2020). Porous lithium ion sieves nanofibers: General synthesis strategy and highly selective recovery of lithium from brine water. *Chem. Eng. J.* 379, 122407. doi:10.1016/j.cej.2019.122407
- Weng, D., Duan, H., Hou, Y., Huo, J., Chen, L., Zhang, F., et al. (2020). Introduction of manganese based lithium-ion Sieve-A review. *Prog. Nat. Sci. Mater. Int.* 30, 139–152. doi:10.1016/j.pnsc.2020.01.017
- Wilhelm, F. G., Pünt, I., van der Vegt, N. F. A., Wessling, M., and Strathmann, H. (2001). Optimisation strategies for the preparation of bipolar membranes with reduced salt ion leakage in acid-base electrodialysis. *J. Memb. Sci.* 182, 13–28. doi:10.1016/S0376-7388(00)00519-6
- Williams, A. E., and McKibben, M. A. (1989). A brine interface in the Salton Sea Geothermal System, California: Fluid geochemical and isotopic characteristics. *Geochimica Cosmochimica Acta* 53, 1905–1920. doi:10.1016/0016-7037(89)90312-8
- Wu, H. M., Belharouak, I., Abouimrane, A., Sun, Y.-K., and Amine, K. (2010). Surface modification of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> by ZrP<sub>2</sub>O<sub>7</sub> and ZrO<sub>2</sub> for lithium-ion batteries. *J. Power Sources* 195, 2909–2913. doi:10.1016/j.jpowsour.2009.11.029
- Wu, H. M., Tu, J. P., Chen, X. T., Li, Y., Zhao, X. B., and Cao, G. S. (2007). Effects of Ni-ion doping on electrochemical characteristics of spinel LiMn<sub>2</sub>O<sub>4</sub> powders prepared by a spray-drying method. *J. Solid State Electrochem.* 11, 173–176. doi:10.1007/s10008-005-0082-y
- Xiao, J.-L., Sun, S.-Y., Wang, J., Li, P., and Yu, J.-G. (2013). Synthesis and adsorption properties of Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> spinel. *Ind. Eng. Chem. Res.* 52, 11967–11973. doi:10.1021/ie400691d
- Xiao, J. L., Sun, S. Y., Song, X., Li, P., and Yu, J. G. (2015b). Lithium ion recovery from brine using granulated polyacrylamide-MnO<sub>2</sub> ion-sieve. *Chem. Eng. J.* 279, 659–666. doi:10.1016/j.cej.2015.05.075
- Xiao, J., Nie, X., Sun, S., Song, X., Li, P., and Yu, J. (2015a). Lithium ion adsorption-desorption properties on spinel Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> and pH-dependent ion-exchange model. *Adv. Powder Technol.* 26, 589–594. doi:10.1016/j.apt.2015.01.008
- Xie, F., Zhang, T. A., Dreisinger, D., and Doyle, F. (2014). A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* 56, 10–28. doi:10.1016/j.mineng.2013.10.021
- Xiong, Y., Ge, T., Xu, L., Wang, L., He, J., Zhou, X., et al. (2022). A fundamental study on selective extraction of Li<sup>+</sup> with dibenzo-14-crown-4 ether: Toward new technology development for lithium recovery from brines. *J. Environ. Manag.* 310, 114705. doi:10.1016/j.jenvman.2022.114705
- Xu, H., Xu, L., Chen, B.-z., Shi, X.-c., and Yang, X. (2009). Separating technique for magnesium and lithium from high Mg/Li ratio salt lake brine. *J. Central South Univ. Sci. Technol.* 40, 36–40.
- Xu, N., Li, S., Guo, M., Qian, Z., Li, W., and Liu, Z. (2019). Synthesis of H<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> nanotubes lithium ion sieve and its adsorption properties for Li<sup>+</sup> from aqueous solution. *ChemistrySelect* 4, 9562–9569. doi:10.1002/slct.201901764
- Xu, W., Yuan, A., Tian, L., and Wang, Y. (2011). Improved high-rate cyclability of sol-gel derived Cr-doped spinel LiCr<sub>0.5</sub>Mn<sub>2.5</sub>O<sub>4</sub> in an aqueous electrolyte. *J. Appl. Electrochem.* 41, 453–460. doi:10.1007/s10800-011-0255-6
- Xu, X., Chen, Y., Wan, P., Gasem, K., Wang, K., He, T., et al. (2016). Extraction of lithium with functionalized lithium ion-sieves. *Prog. Mater. Sci.* 84, 276–313. doi:10.1016/j.pmatsci.2016.09.004
- Xu, X., Zhou, Y., Feng, Z., Kahn, N. U., HaqKhan, Z. U., Tang, Y., et al. (2018). A self-supported  $\lambda$ -MnO<sub>2</sub> film electrode used for electrochemical lithium recovery from brines. *ChemPlusChem* 83, 521–528. doi:10.1002/cplu.201800185
- Xue, S., Wu, C., Wu, Y., Chen, J., and Li, Z. (2015). Bipolar membrane electrodialysis for treatment of sodium acetate waste residue. *Sep. Purif. Technol.* 154, 193–203. doi:10.1016/j.seppur.2015.09.040
- Yaksic, A., and Tilton, J. E. (2009). Using the cumulative availability curve to assess the threat of mineral depletion: The case of lithium. *Resour. Policy* 34, 185–194. doi:10.1016/j.resourpol.2009.05.002
- Yang, H. J., Li, B., Chai, X. L., and Li, W. (2013). Studies on the interaction mechanism between lithium chloride and amorphous Al(OH)<sub>3</sub>. *Adv. Mat. Res.* 634–638, 126–129. doi:10.4028/www.scientific.net/AMR.634-638.126
- Yang, S., Zhang, F., Ding, H., He, P., and Zhou, H. (2018). Lithium metal extraction from seawater. *Joule* 2, 1648–1651. doi:10.1016/j.joule.2018.07.006

- Yang, Y., Gao, X., Fan, A., Fu, L., and Gao, C. (2014). An innovative beneficial reuse of seawater concentrate using bipolar membrane electrodialysis. *J. Membr. Sci.* 449, 119–126. doi:10.1016/j.memsci.2013.07.066
- Yoon, H., Lee, J., Kim, S., and Yoon, J. (2019). Review of concepts and applications of electrochemical ion separation (EIONS) process. *Sep. Purif. Technol.* 215, 190–207. doi:10.1016/j.seppur.2018.12.071
- Yu, C., Lu, J., Dai, J., Dong, Z., Lin, X., Xing, W., et al. (2020). Bio-inspired fabrication of Ester-functionalized imprinted composite membrane for rapid and high-efficient recovery of lithium ion from seawater. *J. Colloid Interface Sci.* 572, 340–353. doi:10.1016/j.jcis.2020.03.091
- Zandevakili, S., Ranjbar, M., and Ehteshamzadeh, M. (2014). Recovery of lithium from Urmia Lake by a nanostructure MnO<sub>2</sub> ion sieve. *Hydrometallurgy* 149, 148–152. doi:10.1016/j.hydromet.2014.08.004
- Zante, G., Boltoeva, M., Masmoudi, A., Barillon, R., and Trébouet, D. (2019). Lithium extraction from complex aqueous solutions using supported ionic liquid membranes. *J. Membr. Sci.* 580, 62–76. doi:10.1016/j.memsci.2019.03.013
- Zavahir, S., Elmakki, T., Gulied, M., Ahmad, Z., Al-Sulaiti, L., Shon, H. K., et al. (2021). A review on lithium recovery using electrochemical capturing systems. *Desalination* 500, 114883. doi:10.1016/j.desal.2020.114883
- Zhang, L., Zhou, D., Yao, Q., and Zhou, J. (2016). Preparation of H<sub>2</sub>TiO<sub>3</sub>-lithium adsorbent by the sol-gel process and its adsorption performance. *Appl. Surf. Sci.* 368, 82–87. doi:10.1016/j.apsusc.2016.01.203
- Zhang, Q. H., Li, S. P., Sun, S. Y., Yin, X. S., and Yu, J. G. (2009). Lithium selective adsorption on 1-D MnO<sub>2</sub> nanostructure ion-sieve. *Adv. Powder Technol.* 20, 432–437. doi:10.1016/j.apt.2009.02.008
- Zhang, X., Zhao, W., Zhang, Y., and Jegatheesan, V. (2021a). A review of resource recovery from seawater desalination brine. *Rev. Environ. Sci. Biotechnol.* 20, 333–361. doi:10.1007/s1157-021-09570-4
- Zhang, Y., Hu, Y., Wang, L., and Sun, W. (2019). Systematic review of lithium extraction from salt-lake brines via precipitation approaches. *Miner. Eng.* 139, 105868. doi:10.1016/j.mineng.2019.105868
- Zhang, Y., Paepen, S., Pinoy, L., Meerschaeft, B., and Van der Bruggen, B. (2012). Selectrodialysis: Fractionation of divalent ions from monovalent ions in a novel electrodialysis stack. *Sep. Purif. Technol.* 88, 191–201. doi:10.1016/j.seppur.2011.12.017
- Zhang, Y., Sun, W., Xu, R., Wang, L., and Tang, H. (2021b). Lithium extraction from water lithium resources through green electrochemical-battery approaches: A comprehensive review. *J. Clean. Prod.* 285, 124905. doi:10.1016/j.jclepro.2020.124905
- Zhao, B., Guo, M., Qian, Z., Li, J., Wu, Z., and Liu, Z. (2020a). The adsorption behavior of lithium on spinel titanium oxide nanosheets with exposed (114) high-index facets. *Dalton Trans.* 49, 14180–14190. doi:10.1039/D0DT02960B
- Zhao, C., Zhang, Y., Cao, H., Zheng, X., Van Gerven, T., Hu, Y., et al. (2019). Lithium carbonate recovery from lithium-containing solution by ultrasound assisted precipitation. *Ultrason. Sonochemistry* 52, 484–492. doi:10.1016/j.ultrsonch.2018.12.025
- Zhao, X., Feng, M., Jiao, Y., Zhang, Y., Wang, Y., and Sha, Z. (2020b). Lithium extraction from brine in an ionic selective desalination battery. *Desalination* 481, 114360. doi:10.1016/j.desal.2020.114360
- Zhao, X., Jiao, Y., Xue, P., Feng, M., Wang, Y., and Sha, Z. (2020c). Efficient lithium extraction from brine using a three-dimensional nanostructured hybrid inorganic-gel framework electrode. *ACS Sustain. Chem. Eng.* 8, 4827–4837. doi:10.1021/acssuschemeng.9b07644
- Zhao, X., Li, G., Feng, M., and Wang, Y. (2020d). Semi-continuous electrochemical extraction of lithium from brine using CF-NMMO/AC asymmetric hybrid capacitors. *Electrochimica Acta* 331, 135285. doi:10.1016/j.electacta.2019.135285
- Zhao, Z., Liu, G., Jia, H., and He, L. (2020e). Sandwiched liquid-membrane electrodialysis: Lithium selective recovery from salt lake brines with high Mg/Li ratio. *J. Membr. Sci.* 596, 117685. doi:10.1016/j.memsci.2019.117685
- Zhou, Z., Qin, W., and Fei, W. (2011). Extraction equilibria of lithium with tributyl phosphate in three diluents. *J. Chem. Eng. Data* 56, 3518–3522. doi:10.1021/je200246x
- Zymon, W., and Kurbiel, J. (1986). "Application of previously precipitated active aluminium hydroxide (AAH) for removal of refractory substances from wastewater," in *Chemistry for protection of the environment 1985*. Editors L. Pawlowski, G. Alaerts, and W. Lacy (Amsterdam, Netherlands: Elsevier), 29, 345–353. doi:10.1016/S0166-1116(08)70951-8