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Lithium Recovery from Aqueous Resources and Batteries: A Brief Review

A review of the methods to produce lithium and approaches to recycling from end-of-life lithium-ion batteries

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The demand for lithium is expected to increase drastically in the near future due to the increased usage of rechargeable lithium-ion batteries (LIB) in electric vehicles, smartphones and other portable electronics. To alleviate the potential risk of undersupply, lithium can be extracted from raw sources consisting of minerals and brines or from recycled batteries and glasses. Aqueous lithium mining from naturally occurring brines and salt deposits is advantageous compared to extraction from minerals, since it may be more environmentally friendly and cost-effective. In this article, we briefly discuss the adsorptive behaviour, synthetic methodology and prospects or challenges of major sorbents including spinel lithium manganese oxide (Li-Mn-O or LMO), spinel lithium titanium oxide (Li-Ti-O or LTO) and lithium aluminium layered double hydroxide chloride ($LiCl{\cdot}2Al(OH)_3$). Membrane approaches and lithium recovery from end-of-life LIB will also be briefly discussed.

1. Introduction

Due to the accelerated expansion of the LIB industry, the global demand for lithium is expected to increase significantly with an annual growth rate of 8.9% through 2019 to 49,350 metric tonnes (1–3). The estimated global lithium end-use applications are summarised in **Table I**. Batteries used in portable electronics, hybrid cars and electric vehicles consume ~35% of the total lithium market share. The ceramics and glass sector with a ~32% market share is the second highest consumer of lithium. Primary lithium resources are from pegmatites, continental brines and geothermal brines, and the secondary resources are from clays and seawater (4). Lithium carbonate (Li_2CO_3), which is the major commercial lithium product, is

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Table I List of Estimated Global Lithium End-Use Applications[a]

Applications	Market share, %	Products
Batteries – portable electronics; hybrid cars; electric vehicles; grid storage applications	35	Li_2CO_3; LiOH; Li metal; lithium hexafluorophosphate ($LiPF_6$) electrolyte salts; lithium chloride (LiCl); Li alloys; lithium cobalt oxide ($LiCoO_2$); and other Li electrode compositions
Ceramics and glass	32	Spodumene – $LiAl(SiO_3)_2$; Li_2CO_3
Lubricants and greases	9	LiOH
Air treatment; continuous casting mould flux powders; polymer production; primary Al production	5; 5; 4; 1	Li organometallics; Li metal; LiCl; lithium aluminium hydride ($LiAlH_4$); butyl lithium; lithium citrate
Other uses such as in medicine as antidepressants, bipolar disorder	9	Li compounds

[a] Summarised from (5, 9, 10)

mostly prepared through mining, extracting and treating spodumene ores and salt lake brines (4). Lithium carbonate is losing market share to lithium hydroxide (LiOH), which is increasingly favoured for LIB cathode applications (2). Currently, two brine operations in Chile and a spodumene operation in Australia account for the majority of global lithium production (5).

Extraction from brines would be advantageous relative to extraction from ores, since it is more environmentally friendly and cost-effective (6). It is estimated that the lithium production cost from salt lake brines is US$2–3 kg^{-1}, whereas that from the ores or spodumene is US$6–8 kg^{-1} (4). The major lithium-containing brine resources around the world are listed in **Table II**. The lithium concentration of brines ranges from 100–1000 mg l^{-1}, whereas average lithium concentration present in seawater is merely 0.17 mg l^{-1} (4). Therefore, salt lake and geothermal brines are the most promising aqueous resources for industrial scale lithium extraction (7). In fact, a majority of lithium is currently produced through solar evaporation, followed by the removal of impurities through precipitation. However, this method is time consuming (usually 18–24 months) and requires large land areas. Besides, the presence of excessive cations such as sodium, potassium, calcium and magnesium plus chloride ions in the brines makes it challenging to obtain a high purity product.

Finally, the rechargeable LIB industry has expanded significantly with the maturation of clean and sustainable energy technologies. A short review on the recovery of lithium and other valuable metals from end-of-life LIBs are discussed in Section 5.

2. Recovery of Lithium from Brines by Adsorption and Ion Exchange

Spinel Li-Mn-O, spinel Li-Ti-O and $LiCl{\cdot}2Al(OH)_3$ have been identified as potential sorbents for lithium extraction from aqueous resources. In the section below, we discuss these sorbents including their synthetic methods, structures, adsorption mechanisms, morphologies and adsorption or ion exchange capacities from different aqueous resources.

2.1 Lithium Manganese Oxides (Li-Mn-O)

Spinel-type Li-Mn-O are attractive candidates for commercial lithium extraction owing to their high capacity and superior selectivity towards lithium. Li-Mn-O are synthesised as precursor materials, from which the ion sieves are obtained by replacing the Li^+ with H^+. Li-Mn-O can be synthesised *via* various methods including solid state reaction, sol-gel, hydrothermal or reflux, yielding different particle sizes and morphologies, which lead to different ion exchange capacities of the lithium de-intercalated sorbents. In general, the Li-Mn-O precursors can be expressed by the formula $(Li)[Li_xMn_{2-x}]O_4$, where A-site (mostly Li) and B-site (Li and/or Mn) represent 8*a* tetrahedral and 16*d* octahedral sites

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Table II World Brine Compositions[a,b]

Source	Li, wt%	Na, wt%	Mg, wt%	K, wt%	Ca, wt%
Clayton Valley, USA	0.0163	4.69	0.019	0.4	0.045
Salton Sea, USA	0.01–0.04	5.00–7.00	0.07–0.57	1.30–2.40	2.26–3.9
Salar de Atacama, Chile	0.157	9.1	0.965	2.36	0.045
HombreMuerto, Argentina	0.068–0.121	9.9–10.3	0.018–0.14	0.24–0.97	0.019–0.09
Salar de Uyuni, Bolivia	0.0321	7.06	0.65	1.17	0.0306
Searles Lake, USA	0.0054	11.8	–	2.53	0.0016
Great Salt Lake, USA	0.0018	3.70–8.70	0.5–0.97	0.26–0.72	0.026–0.036
Dead Sea, Israel	0.0012	3.01	3.09	0.56	1.29
Sua Pan, India	0.002	6	–	0.2	–
Bonneville, USA	0.0057	8.3	0.4	0.5	0.0057
Zabuye, China	0.0489	7.29	0.0026	1.66	0.0106
Taijinaier, China	0.031	5.63	2.02	0.44	0.02

[a] Adapted from (8, 9)

[b] Please note only cations with high concentrations are provided in addition to Li

(10), and the acid treated ion sieves have a general formula of $MnO_2{\cdot}xH_2O$. The primary Li uptake mechanism for the spinel-type sorbents is the Li^+/H^+ exchange, in which the Li^+ can be intercalated/de-intercalated into the octahedral interstices, with an intact spinel structure (11). Furthermore, the Li^+ can be cycled in and out freely within a relatively wide range of Li:Mn molar ratios (12, 13), resulting in several common manganese oxide precursors including $LiMn_2O_4$ (10, 12, 14–18), $Li_{1.6}Mn_{1.6}O_4$ (11, 19–26) and $Li_{1.33}Mn_{1.67}O_4$ (19, 27–32). Desorption/regeneration of the spinel-type sorbents requires contacting the sorbents with acid.

Table III lists the ion exchange properties of the lithium ion sieves derived from Li-Mn-O with various Li:Mn molar ratios. The lithium extraction capacity depends on various parameters including the synthetic condition of the precursor materials (20, 33), actual Li:Mn molar ratio (33), temperature and pH of the contact solution (22). Therefore, the reported ion exchange behaviour of a given sorbent can vary between different research groups. To date, the maximum ion exchange capacity of the manganese oxide is 54.65 mg g^{-1} which was realised recently in $Li_{1.33}Mn_{1.67}O_4$ synthesised from Li_2CO_3 and $MnCO_3$ (30). The as-prepared $Li_{1.33}Mn_{1.67}O_4$ powders were mixed with a chitosan binder and extruded into cylinder-shaped material (chitosan–LMO, diameter of 0.7 mm). The extraction was carried out in a column system with seawater flowing at room temperature. Nevertheless, the nano-sized $Li_{1.33}Mn_{1.67}O_4$ prepared by a gel process exhibited a slightly lower lithium uptake of 28.2 mg g^{-1} from artificial seawater (31). In fact, $Li_{1.33}Mn_{1.67}O_4$ prepared from different precursors exhibited different lithium uptake even though the synthetic method and temperature are exactly the same (27). A comparative study showed that ion sieves derived from $Li_4Mn_5O_{12}$ ($Li_{1.33}Mn_{1.67}O_4$) exhibited a higher capacity compared to those derived from $LiMn_2O_4$ (46.6 mg g^{-1} *vs.* 23.9 mg g^{-1}) (10).

$LiMn_2O_4$ related ion sieve has a relatively lower ion exchange capacity and weak stability due to the Jahn-Teller distortion with cycling. The MnO_2 preparation was first reported in 1981 *via* treating $LiMn_2O_4$ with acid (34). It was further confirmed in 1984 that lithium can be cycled in and out of the $[Mn_2]O_4$ framework over a wide range of x to form $Li_{1-x}Mn_2O_4$ (12). The acid treated ion sieve MnO_2 obtained from $LiMn_2O_4$ nanowire exhibited an ion exchange capacity of ~16.8 mg g^{-1} from LiCl solutions (15). In later years, the same research group synthesised $LiMn_2O_4$ nanorods (15–20 nm in diameter and several micrometers in length) *via* a one-step soft chemistry method, and the related ion sieve showed a slightly higher extraction capacity of 20.5 mg g^{-1} from LiCl solutions (14).

$Li_{1.6}Mn_{1.6}O_4$ related ion sieve $MnO_2{\cdot}0.5H_2O$ has an overall relatively high capacity, which is attributed to the availability of strong acidic sites

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Table III List of Some Common Li-Mn-O Precursors Synthesised Under Different Conditions

Precursors	Synthesis	Morphology	Solution	Capacity, mg g^{-1}	Ref.
$H_{1.33}Mn_{1.67}O_4$ $H_{1.6}Mn_{1.6}O_4$	–	–	pH = 6.6	27–30	(19)
$Li_{1.33}Mn_{1.67}O_4$	400°C using lithium nitrate ($LiNO_3$) as a flux from different precursors	Various	–	47.1 (optimum)	(27)
	Low-temperature solid-phase reaction (673 K)	Nanorod	Mixed solution with Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} of 10.0 mmol l^{-1}	46.6	(10)
	A combination of hydrothermal reaction and solid-phase calcinations	Spherical with 2–3.5 mm in diameter, polyvinyl chloride (PVC)-manganese(IV) oxide (MnO_2)	LiCl, pH = 10.1	23.5	(35)
	Tartaric acid gel process with lithium acetate (CH_3COOLi) and $Mn(CH_3COO)_2{\cdot}4H_2O$	Nano	Artificial seawater	28.2	(31)
	Solid state	Cylinder-shaped, chitosan-LMO granules diameter of 0.7 mm	Seawater through a column setup packed with chitosan-LMO, room temperature, pH = 6.6	54.7	(30)
	Modelling a column system	–	–	–	(28)
$LiMn_2O_4$	Controlled low-temperature hydrothermal synthesis	Nanowire with 5 nm diameter and 400 nm in length	LiCl, pH = 9.19	16.8	(15)
	Manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2$), LiOH and hydrogen peroxide (H_2O_2) mixed solution at 383 K for 8 h	MnO_2 nanorods with 15–20 nm in diameter	LiCl (10.0 mmol l^{-1} Li^+), pH = 10.1	20.5	(14)
	High-temperature calcinations (1003 K)	Nanorod	Mixed solution with Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} of 10.0 mmol l^{-1}	23.9	(10)
Molar Mn/Li = 1.125 $Li_{1.6}Mn_{1.6}O_4$	Citrate method	Meso- or macroporous foam	Lithium-enriched salt lake brine (pH = 6; main metallic ions: Li^+ 237 mg l^{-1}, Na^+ 3591 mg l^{-1}, K^+ 3118 mg l^{-1} and Mg^{2+} 109 g l^{-1})	1.5	(36)
	Sol-gel with $Mn(NO_3)_2$ and LiOH	One-dimensional (1D) nanowire	Saltern bittern, pH = 10	10.5	(21)

Continued

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Precursors	Synthesis	Morphology	Solution	Capacity, mg g^{-1}	Ref.
Molar Mn/Li = 1.125	Calcination of lithium manganese dioxide ($LiMnO_2$) which was made by hydrothermal and reflux methods	Materials prepared by the reflux method was less crystalline as compared to the hydrothermal method	Seawater (0.17 mg l^{-1} Li^+)	40	(20)
$Li_{1.6}Mn_{1.6}O_4$ $Li_{1.16}Sb_{0.29}Mn_{1.54}O_4$	Calcination of $LiMnO_2$ which was made by a hydrothermal method using manganese(III) oxide (Mn_2O_3) and LiOH	Particle size 100–300 nm	Simulated brine (270 mg l^{-1} Li^+), 50°C, pH = 5.35	27.2	(22)
	Calcination of $LiMnO_2$ which was made by a hydrothermal method using potassium permanganate ($KMnO_4$), manganese(II) chloride ($MnCl_2$) and LiOH	Particle size ≤200 nm	LiCl (69.4 mg l^{-1} Li^+, with the presence of Na^+, K^+, Ca^{2+} and Mg^{2+}), pH = 10.1	42.1	(24)
	Calcination of $LiMnO_2$ which was made by a controlled redox precipitation using manganese(II) hydroxide ($Mn(OH)_2$), LiOH and ammonium persulfate ($(NH_4)_2S_2O_8$)	Particle size ≤200 nm	Qarhan salt lake brine (179 mmol l^{-1} Li^+, 15,190 mmol l^{-1} Na^+, 13,729 mmol l^{-1} K^+, 429 mmol l^{-1} Ca^{2+}, 80,125 mmol l^{-1} Mg^{2+})	26.9	(25)
	Wet chemistry and hydrothermal at 120°C		LiCl enriched seawater (5 mg l^{-1} Li^+)	40	(37)

inside the solid (20). $Li_{1.6}Mn_{1.6}O_4$ is relatively difficult to synthesise, usually by calcination of $LiMnO_2$ in O_2 at an appropriate temperature ($8LiMnO_2 + 2O_2 \rightarrow 5Li_{1.6}Mn_{1.6}O_4$). To date, the highest reported ion exchange capacity is 42.1 mg g^{-1} (6.06 mmol g^{-1}) from LiCl solution at a pH of 10.1 (24). However, the lithium uptake of the same sorbent from salt lake brine dropped to 28.3 mg g^{-1} (4.08 mmol g^{-1}) and was further reduced to 25.1 mg g^{-1} after six cycles (24). In addition, the ion exchange capacity increases with increasing stacking fault concentrations in the precursor $LiMnO_2$ (24, 38). $Li_{1.6}Mn_{1.6}O_4$ prepared by the hydrothermal method showed a slightly higher lithium uptake and cycling stability than that prepared by the reflux method (20). Lithium extractive materials prepared with $LiOH{\cdot}H_2O$ and manganese(II) carbonate ($MnCO_3$) usually have higher Li^+ ion exchange capacity than materials prepared with Li_2CO_3 and $MnCO_3$, and an ascending trend was found in Li^+ uptake with increasing Li:Mn molar ratio (33). Furthermore, the extraction capacity of $Li_{1.6}Mn_{1.6}O_4$ in simulated brines (270 mg l^{-1} Li^+) increases with increasing temperature (30–50°C) and increasing pH values (1–12) (22). The high selectivity for lithium ions was confirmed, with high separation coefficients of $\alpha_{Li/Mg} = 109.5$, $\alpha_{Li/Na} = 220.7$, $\alpha_{Li/K} = 125.5$ (22).

In addition, there have been studies on ion sieves derived from antimony (37), Mg (39, 40) and Fe (41) doped Li-Mn-O. The ion exchange capacity (from Li^+ enriched seawater) of ion sieves derived from $Li_{1.16}Sb_{0.29}Mn_{1.54}O_4$ reached 40 mg g^{-1} (37). Mg-doped spinel Li-Mn-O ion sieve exhibited an optimum ion exchange capacity of 37.4 mg g^{-1} from LiCl solution (200 mg l^{-1} Li^+, pH = 12) (39). Nevertheless, $MgMn_2O_4$ exhibited a small ion exchange capacity (from seawater) of 8.5 mg g^{-1} and the equilibrium time is 96 hours, indicating a slow ion exchange (42).

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In summary, Li-Mn-O ion sieves exhibited a high ion exchange capacity and high selectivity for lithium ions from various aqueous resources. The acid generated during lithium uptake can be recycled for regenerating the sorbents. This could potentially reduce the cost of the acid consumption itself. However, the dissolution of Mn^{2+} during the regeneration process with acid degrades the ion exchange capacity and results in a poor cycling stability. This key issue seriously limits Li-Mn-O's potential for upscaling. Further studies are needed to improve the stability during cycling to realise a stable ion exchange capacity. Simplicity of the regeneration process is also desirable.

2.2 Lithium Titanium Oxides (Li-Ti-O)

Titanium-based spinel oxides share most of the advantages with the manganese-based spinel oxides, with an addition of being more environmentally friendly, as the titanium is an earth abundant element, is stable and does not dissolve in acid. In particular, metatitanic acid (H_2TiO_3) has been considered as an emerging environmentally friendly sorbent for lithium extraction from aqueous resources. The precursor lithium titanate (Li_2TiO_3) was first synthesised in 1988 and various synthesis methods are now available in the literature, including solid-state reaction (43–47), hydrothermal (48) and sol-gel (49, 50).

Debate persists about the crystal structures of Li_2TiO_3 and H_2TiO_3, in which Chitrakar *et al.* (43) indexed both compounds as monoclinic with a space group *C*2/*c*, but later Yu *et al.* (51) pointed out that H_2TiO_3 should be more reasonably indexed with the $3R_1$ space group with an LDH structure. Typically, layered H_2TiO_3, derived from a layered Li_2TiO_3 precursor upon treatment with HCl solution, will go through ion exchange with lithium ions from the geothermal brines at a pH >7 to form Li_2TiO_3 ($H_2TiO_3 + 2LiOH \rightarrow Li_2TiO_3 + 2H_2O$). Lithium can be recovered from Li_2TiO_3 by treating with HCl solution ($Li_2TiO_3 + 2HCl \rightarrow H_2TiO_3 + 2LiCl$). The theoretical ion exchange capacity of H_2TiO_3 is up to 142.9 mg g^{-1} (48), whereas the highest experimental ion exchange capacity so far is 94.5 mg g^{-1} (46). This is actually the maximum achievable capacity, as only 75% of the H^+ occupied ion exchange sites in H_2TiO_3 are exchangeable with Li^+ (44). **Table IV** summarises the adsorptive behaviours of H_2TiO_3 synthesised under different conditions from various research groups.

It was first demonstrated in 2014 that H_2TiO_3 exhibits an extremely high selectivity toward lithium ions in the sodium bicarbonate ($NaHCO_3$)-added salt brine and the ion exchange capacity reached 32.6 mg g^{-1} at a pH of 6.5 (43). However, the ion exchange rate is slow, taking 24 hours to get to equilibrium. This work has since stimulated great efforts investigating the ion exchange behaviour of this emerging ion sieve (44–49, 52, 53). The isotherm of H_2TiO_3 exhibited a Langmuir type behaviour, following the pseudo-second-order rate model (45, 46). The ion exchange capacity of H_2TiO_3 increases with increasing Li^+ concentration and decreasing pH values of the aqueous resources (46, 49). Specifically, the ion exchange capacity of H_2TiO_3 increased from 11.26 to 31.27 mg g^{-1} when initial concentration of Li^+ was increased from 500 to 2500 ppm (pH = 13.46) (49). To further elucidate the effects of other factors on the ion exchange capacity of H_2TiO_3, a comprehensive orthogonal test with five factors (pre-calcination temperature, Li:Ti molar ratio, reaction temperature, ion exchange temperature, Li^+ concentration) was performed (52). The highest ion exchange capacity of 57.8 mg g^{-1} is achieved under the optimum conditions: Li^+ concentration = 4.0 g l^{-1} (highest among the tested), ion exchange temperature = 60°C (highest among the tested), molar ratio of Li:Ti = 2.2, reaction temperature = 650°C, pre-calcination temperature = 25°C. To make H_2TiO_3 more economically efficient, low-grade titanium slag was used as the starting material and the optimal capacity reached 27.8 mg g^{-1} (47).

$Li_4Ti_5O_{12}$ is one of the common anode materials used in LIB (54) and the related $H_4Ti_5O_{12}$ is a common ion sieve for lithium extraction from aqueous solutions. $H_4Ti_5O_{12}$ derived from $Li_4Ti_5O_{12}$ nanotubes (~70 nm in diameter) exhibited an ion exchange capacity of 39.43 mg g^{-1} from LiCl solution (120 mg l^{-1} Li^+, pH = 9.17). In summary, H_2TiO_3 is an attractive sorbent for selective lithium extraction with superior advantages including high ion exchange capacity, high selectivity, high stability, environmental friendliness and economic efficiency. However, it is still at the laboratory scale, partly due to the acid requirement during the regeneration process, which produces secondary wastes.

2.3 Lithium Aluminium Layered Double Hydroxide Chloride

While the Li-Mn-O and Li-Ti-O sorbents have attracted significant attention from academia, $LiCl{\cdot}2Al(OH)_3.xH_2O$ (referred to as Li/Al LDH) is an attractive candidate for application in large scale

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Table IV List of the Adsorptive Properties of H_2TiO_3 Synthesised Under Different Conditions

Synthesis Method	Ion sieve morphology	Solution	Capacity, mg g^{-1}	Ref.
Solid state	Uniform particle, 1–2 μm	LiOH (694.1 mg l^{-1} Li^+)	39.8	(45)
Solid state	Plate like particles with average diameter of 100–200 nm	Li enriched salt lake brine (1630 mg l^{-1} Li^+, collected from Salar de Uyuni, Bolivia) added with sodium bicarbonate ($NaHCO_3$), pH = 6.5	32.6	(43)
Solid state using titanium dioxide (TiO_2) and $LiOH{\cdot}H_2O$	–	LiOH (2.0 g l^{-1} Li^+), 25°C	39.2	(44)
Sol-gel	Particles size ranges from 20–70 nm	LiOH (4.0 g l^{-1} Li^+), 60°C	Optimum 57.8	(52)
Low grade Ti, solid state	100–300 nm	LiOH (2.0 g l^{-1} Li^+)	27.8	(47)
Solid state 700°C	Plate-like particle, 100–300 nm	LiOH+LiCl	94.5	(46)
Solid state	H_2TiO_3 mixed with poly(vinyl alcohol) (PVA) matrix, porous composite foam	Seawater pH = 7.64	30.3	(53)
Solid state from $LiOH{\cdot}H_2O$ and TiO_2	Plate-like particle	LiOH (2.0 g l^{-1} Li^+)	76.7	(48)
Sol-gel using CH_3COOLi and $Ti(OC_4H_9)_4$	60–80 nm	LiOH (4.0 g l^{-1} Li^+)	Optimum, 27.4	(49)

industrial plants due to its various advantages, including low cost, environmental friendliness and easy regeneration. Li/Al LDH materials have a general formula $[LiAl_2(OH)_6]^+B^-{\cdot}nH_2O$, where B = Cl, Br. They are crystallised in hexagonal symmetry with the Li^+ located in the vacant octahedral sites within the aluminium hydroxide ($Al(OH)_3$) layer (55). The $[LiAl_2(OH)_6]^+$ layers are separated by water molecules and hydroxide ions (55). Li/Al LDHs can be synthesised by intercalating the Li^+ (in the form of LiCl, LiOH, lithium sulfate (Li_2SO_4)) into aluminium hydroxides, which are in the form of naturally occurring minerals such as gibbsite (α-$Al(OH)_3$) or bayerite (β-$Al(OH)_3$) (55–59). Recently, alternative synthetic routes such as a solvent-free mechanochemical method have been demonstrated (60, 61).

To the best of our knowledge, there exist limited articles in the literature discussing the adsorptive properties of Li/Al LDH. It was first discovered to be a selective sorbent for lithium extraction by Dow Chemical Inc in 1980 (62). The synthesis method was later modified, leading to an increase in the molar fraction of LiX in $LiX/Al(OH)_3$ from 0.2 to 0.33 (63). Commercial granular Li/Al LDH (atomic ratio Li:Al ~0.38) was used in a large scale column system packed with 25 tonnes of sorbent for selective lithium extraction from magnesium-containing brines for more than 200 cycles, demonstrating the good stability of this sorbent (64). Li/Al LDH has a good selectivity for LiCl (the form of Li salts in brine and seawater) compared to other cations, because the distance between $Al(OH)_3$ layers is at the nanoscale such that only ions with small radii can be intercalated (64). Even though the ionic radii of Mg^{2+} (0.074 nm) and Li^+ (0.068 nm) are close, the large polarisability of the Li–Cl bond as compared to the Mg–Cl bond still makes this sorbent Li^+ selective (64).

Simbol Inc, USA (65) developed a column system packed with Li/Al LDHs for the extraction of lithium salts from geothermal brines sourced from the Salton Sea, California, USA. The geothermal brine has a bulk composition of about 260 ppm Li^+, 63,000 ppm Na^+, 20,100 ppm K^+, 33,000 ppm Ca^{2+} and other ions (65). The Li/Al LDHs Simbol Inc prepared have a high Li:Al atomic ratio of up to 0.5, which maximises the number of lithium sites available in the layered structure for the intercalation and de-intercalation of lithium from a brine solution

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(65). Note that this invention of extraction process is applicable to geothermal brine as well as other brine sources. Recently, Li *et al*. demonstrated safe LIB using $Li_4Ti_5O_{12}$ (LTO) electrode materials prepared from Li_2CO_3 extracted from geothermal brine solutions using Li/Al LDH sorbents with good cyclability (65). These demonstrations provide a promising way for making low cost, large scale LTO electrode materials for energy storage applications. In summary, $LiCl{\cdot}2Al(OH)_3{\cdot}xH_2O$ is an attractive candidate to be applied in large scale plant for extraction of lithium salts from various brines. A detailed study on this sorbent regarding the isotherms is still needed.

3. Recovery of Lithium from Brines by Membranes

Membrane processes offer several advantages compared to conventional processes, such as lower energy requirements and capital investments, simple and easy to operate systems, smaller footprints, ease of scalability and many other specific application related advantages. For example, in sorbent based separations in packed and fluidised bed systems, there is a significant pressure drop and loss of sorbent particles. However, both these limitations can be eliminated by the fabrication of mixed matrix membranes including Li^+ selective sorbent. Although there is an increasing interest in membrane based Li^+ recovery processes, there are only limited published reports discussing techniques such as nanofiltration (2, 5, 21, 66–69), electrolysis (70–72), electrodialysis (73–76), dialysis (74), membrane solvent extraction (77–79) and membrane type adsorbents or mixed matrix membranes (80–84). The summary of these studies is provided in **Table V**.

The first study on the application of nanofiltration for the recovery of lithium from brines used a spiral-wound Desal-5 DL 2540C membrane (GE Osmonics), which showed a 61–67% retention of the Mg^{2+}, while Li^+ passed through the membrane, giving a Li^+/Mg^{2+} separation factor of 3.5 (66). A Desal-DK membrane (GE Osmonics) showed a Li^+/Mg^{2+} separation factor ranging between 2 to 3.2 depending upon the feed Li^+ and Mg^{2+} concentration and their ratio (5, 68). The higher operating pressure, lower pH and higher feed Li^+:Mg^{2+} ratio improved the separation (68). The relative Li^+ separation performance of nanofiltration-NF90 (Dow) and low pressure reverse osmosis-XLE (Dow) membranes was evaluated with salt lake brine (2). NF90 membrane appeared more efficient, showing 100% Mg^{2+} rejection compared to only 15% for Li^+, which was attributed to its higher hydraulic permeability to pure water and 0.1 M sodium chloride (NaCl) solution, and its lower critical pressure. Recently, novel positively charged polyamide composite nanofiltration membranes were fabricated by the interfacial polymerisation of DAPP and TMC and supported on PAN ultrafiltration hollow fibre membrane (21). The advantage of using hollow fibre compared to the mostly reported flat-sheet configuration is that the hollow fibres have high packing density, lower energy and maintenance cost and easy fabrication of the modules. The rejection order of this composite hollow fibre membrane was magnesium chloride ($MgCl_2$) > magnesium sulfate ($MgSO_4$) > NaCl ≥ LiCl (21).

Functionalisation of the positively charged membrane (fabricated by interfacial polymerisation of TMC and BPEI supported on polyetherimide sheets) with EDTA showed good separation performance with a Li^+/Mg^{2+} separation factor of ~9.2. This was attributed to the tendency of EDTA to form complexes with the divalent cations. It was suggested that the combination of Donnan exclusion, dielectric exclusion and steric hindrance governed the mass transport inside the nanofiltration membranes. Furthermore, it was also indicated that when membrane pore size is close to the ionic radius, steric hindrance plays a significant role in the separation (21, 66, 67).

An electrolysis method employing the typical anion exchange membranes (MA-7500, SYBRON and American IONAC®) and lithium iron phosphate ($LiFePO_4$)/iron(III) phosphate ($FePO_4$) electrodes was investigated for the extraction of Li^+ from salt lake brines (70–72). The effect of different parameters on the Li^+ extraction performance was studied. At optimised operating conditions, electrodes exhibited a noteworthy Li^+ exchange capacity of 38.9 mg g^{-1} (72).

Recovery of lithium from seawater was also demonstrated by an electrodialysis based technique, which uses organic membranes impregnated with an ionic liquid (73, 75). The separation of lithium was mainly achieved based on its relatively lower or higher permeation rates compared to other cations. However, it was suggested that the poor durability of the ionic membrane is a major issue preventing long-term lithium recovery (74). The applied voltage, feed velocity, feed Li^+:Mg^{2+} ratio and pH significantly influenced the Li^+/Mg^{2+} separation factor (76).

Supported liquid membranes (SLMs) have also attracted interest, borrowing selectivity from

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Table V Summary of Reported Studies of Lithium Extraction Using Membrane Processes

Mechanism or separation process	Lithium source	Membrane system	Separation factor	Ref.
Nanofiltration	Salt lake brine	Spiral-wound Desal-5 DL 2540C, spiral-wound Desal DK (GE Osmonics, USA); NF90 and XLE (Dow, USA); Spiral-wound DK-1812 (Suntar Membrane Tech, China), DL-2540; 1,4-bis(3-aminopropyl)piperazine (DAPP) and trimesoyl chloride (TMC) polymerised on the polyacrylonitrile (PAN) hollow fibre; ethylenediaminetetraacetic acid (EDTA) functionalised TMC and branched polyethyleneimine (BPEI)	Li^+/Mg^{2+}: 2–42	(2, 5, 21, 66–69)
Electrolysis, electrodialysis, dialysis	Salt lake brine, seawater	Anion exchange MA-7500 (SYBRON); Selemion™ CMV with ionic liquid TMPA-TFSI; Gore-Tex® impregnated with ionic liquid (PP13-TFSI); Li ion conductive glass-ceramics (Ohara Inc, Japan), ACS (Anion exchange) and CIMS (Cation exchange) (ASTOM, Japan)	Highly selective recovery of Li^+, Li^+/Mg^{2+}: 12–77	(72–76)
Membrane solvent extraction	Geothermal water, salt lake brine	α-acetyl-*m*-dodecylacetophenone (LIX54) and tri-*n*-octylphosphine oxide (TOPO) in kerosene embedded in Celgard® 2500 membrane; tributylphosphate (TBP) + $FeCl_3$ in kerosene with polyethersulfone (PES) and sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) blend; TBP + iron(III) chloride ($FeCl_3$) in kerosene with poly(ethylene-co-vinyl alcohol) (EVAL)	>90% extraction of Li^+ in 2 h, high Li^+ selectivity	(77–79)
Grotthuss	Binary mixtures of Na^+, K^+ and Mg^{2+} with Li^+*	PSS threaded HKUST-1 metal-organic framework (MOF)	Li^+/Na^+: 35, Li^+/Mg^{2+}: 1815	(80)
Sorption	Seawater, geothermal brine	$Li_{1.33}Mn_{1.67}O_4$/PVC, $Li_{1.33}Mn_{1.67}O_4$ encapsulated in polysulfone (PSf)/Kimtex, $Li_{1.33}Mn_{1.67}O_4$/PSf/PAN mixed matrix (nanofibre), LDH-polyvinylidene fluoride (PVDF)/PVDF hollow fibres	>90% Li^+ recovery, complete Li^+ selectivity	(81–85)

the incorporated solvent extraction reagents. Ma *et al.* (77) reported the first study on the extraction of lithium from geothermal water with the SLM technique. A mixture of extractants consisting of LIX54 (the main component is α-acetyl-*m*-dodecylacetophenone) and TOPO were immobilised in the Celgard® 2500 membrane having 37–48% porosity. The SLM showed 95% extraction of Li^+ in just 2 hours; however, it exhibited stable performance for only up to 72 hours before the flux dropped drastically. The decreased stability was attributed to the pressure difference over the membrane sheet, the solubility of the liquid membrane in the adjacent solutions and emulsion formation of the liquid membrane in aqueous solutions (77).

To improve the stability of the SLM for Li^+ extraction, a nanoporous ion exchange membrane was fabricated by blending PES with sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) as a extractant stabiliser (79). With PES/SPPESK blend membrane and TBP and $FeCl_3$ mixed in kerosene as an extractant, Li^+ extraction was performed both in a single-stage extraction and a sandwiched membrane extraction contactor system. The best Li^+ extraction performance was obtained at a PES:SPPESK ratio of 6:4 and a polymer concentration of 30 wt%. However, these membranes had limited stability in benzene and toluene despite being stable in kerosene (78, 79). To further improve the stability of the membrane with different solvents, EVAL membranes were

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fabricated. These membranes showed exceptional stability in Li^+ extraction with TBP/$FeCl_3$/kerosene for about 1037 hours. This higher stability was attributed to the unique structure of EVAL, consisting of both hydrophobic ethylene and hydrophilic vinyl alcohol units (78).

In a recent study, novel polystyrene sulfonate (PSS) incorporated HKUST-1 MOF membranes were fabricated for Li^+ recovery from brines through an *in situ* lithium confinement process (80). These MOF membranes showed exceptionally good performance in Li^+ recovery with separation selectivities (molar) of 35, 67 and 1815 over Na^+, K^+ and Mg^{2+}, respectively. It was established that the perm-selectivity followed a trend of $Li^+ > Na^+ > K^+$, which was determined by the corresponding binding affinities of these cations to the sulfonate groups. The transportation of Li^+ through the membrane is proposed to be governed by the Grotthuss mechanism, wherein the charge is transported by the coordinated hopping of Li^+ between sulfonate groups of PSS threaded through the cavities of HKUST-1 (80). Another successful membrane-type adsorbent of spinel manganese oxide ($H_{1.33}Mn_{1.67}O_4$) was prepared by a solvent exchange method using PVC as a binder (81). This membrane-type adsorbent has an uptake capacity of 10.6 mg g^{-1} Li^+ from seawater (0.17 mg l^{-1} Li^+).

A membrane reservoir system with encapsulated $Li_{1.33}Mn_{1.67}O_4$ in PSf and Kimtex (Korea Non-woven Tech Ltd, South Korea) was tested for Li^+ recovery from seawater. The Kimtex based systems showed best results with ~84% Li^+ recovery in one day due to the easy wetting and water penetration in the reservoir (82). The $Li_{1.6}Mn_{1.6}O_4$-PSf/PAN-based composite mixed matrix nanofibres as a flow through membrane Li^+ absorber was highly permeable to water under minimal trans-membrane pressure (83, 84). The balance between kinetic and dynamic Li^+ adsorption capacity could be obtained at optimal seawater and membrane contact time (84).

Bhave *et al.* (85) have fabricated novel LDH (LIS)/Kynar®-PVDF mixed matrix membranes supported on PVDF hollow fibres (Arkema Inc, France) for Li^+ recovery from geothermal brines. Due to the high temperature of the geothermal brines, robust membranes are required to operate at temperatures up to 95°C. Preliminary results showed the potential of these membranes to obtain a high lithium separation factor with nearly complete rejection of other monovalent and divalent cations in the brine solution. The selective sorption/diffusion of Li^+ and back-extraction into the strip is carried out simultaneously, eliminating the need to employ a separate step for Li^+ recovery.

In summary, although there are many published reports on membrane-based separation processes for lithium extraction, the technology is currently at the laboratory scale with significant potential for further development and process scale-up in the future.

4. Recovery of Lithium from Brines by Other Methods

There have been reports of lithium extraction using other methods such as precipitation and solvent extraction. The precipitation method was used to extract lithium from the Dead Sea in 1981 (86). Later a two-stage precipitation process was developed to extract Li_2CO_3 from brines collected from Salar de Uyuni, Bolivia (700–900 mg l^{-1} Li^+) (8). Solvent extraction has been widely used to extract metals from the aqueous phase due to the simplicity of the equipment and operation. In fact, it was applied to extract lithium from aqueous solutions of alkali metal salts as early as 1968 (87). The extraction of Li^+ ions into the organic phase is associated with the cation exchange mechanism. Various solvents including tri-*n*-butyl phosphate (88), ionic liquid added 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) mixed with tri-*n*-butyl (89) and so on, have been reported for lithium extraction. Organophosphorus ligands in the presence of ammonia were tested for lithium extraction, in which the highest extraction percentages in the presence of H-PHO, H-PHI and H-BIS ligands were 43.2%, 45.7% and 90.0%, respectively (90).

5. Recovery of Lithium from Recycled Lithium-Ion Batteries

A rechargeable LIB mainly comprises a lithium-containing oxide cathode, an anode, an organic electrolyte and a separator. **Table VI** lists the chemical composition of a typical LIB. The cathode is usually made of $LiCoO_2$, lithium nickel dioxide ($LiNiO_2$) and lithium manganese(III,IV) oxide ($LiMn_2O_4$) and the anode is typically graphite. Aluminium and copper are used as current collectors. The recoverable materials from an end-of-life battery include aluminium, copper, LiOH or Li_2CO_3, cobalt oxide, nickel oxide and manganese oxide. There have been a number of articles in the literature focused on recovery of metals such as cobalt, lithium and nickel from spent LIBs (91–95).

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Table VI Chemical Composition of a Typical LIB[a]

Component	wt%
$LiCoO_2$	27.5
Steel/Ni	24.5
Cu/Al	14.5
Carbon	16
Electrolyte	3.5
Polymer	14

[a] Adapted from (95)

Processes to recycle LIBs were first developed for the sake of environmental considerations, since the waste is usually flammable and toxic. It can also achieve some economic benefits as driven by the prices of cobalt and possibly lithium, though they fluctuate drastically depending on their availability.

Figure 1 presents a flow sheet of a typical hydrometallurgical process, which is the most common process to recover lithium from spent LIBs. The whole procedure involves physical and chemical processes to complete the following steps:

(a) pretreatment of the spent LIBs – dismantling the cells, thermal treatment and mechanochemical process
(b) dissolution and leaching of metals from the cathode material with hydrochloric acid (HCl), bioleaching
(c) separation of lithium and other metals *via* solvent extraction, chemical precipitation and electrochemical process (96–99).

For example, a three-step process (100) was developed to recover cobalt and lithium from the cathode materials:

(a) leaching of the cathode materials with HCl
(b) separation of cobalt from lithium with solvent extraction
(c) precipitation of lithium as carbonate.

Employing the same technique, with organic citric acid as the leachant, 90% cobalt and 100% lithium were recovered from end-of-life LIBs (101). Alkaline solution was used to leach the battery's internal substances followed by dissolving the residue in sulfuric acid (H_2SO_4) solution, yielding Li_2CO_3 (102). The effect of different parameters such as the concentration of the leachant H_2SO_4, temperature, pulp density and reductant H_2O_2 concentration on the leaching of the waste was investigated (103). An optimum condition of pulp density, 100 g l^{-1}, 2M H_2SO_4, 5 vol% of H_2O_2, with a leaching time of 30 min and a temperature of 75°C, was identified (103). Very recently, several methods to recover lithium and other high value metals such as cobalt from spent LIB have been reported (104–110). From both the viewpoints of environmental friendliness and economic benefits, recovery of lithium from spent LIB is desirable. Nevertheless, most of the recycling processes are still at laboratory scale and much effort needs to be directed into this area. In addition, safety precautions should be emphasised when LIB are dismantled.

Summary and Outlook

Aqueous lithium mining of continental brines appears to be a promising approach to realise economically

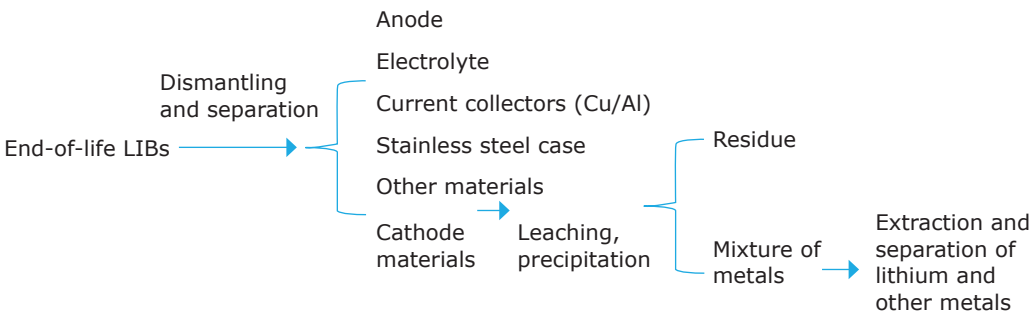

Fig. 1. Flow sheet of a typical recycling process for spent LIBs

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and environmentally attractive lithium production. Extraction from seawater would be relatively costly due to the extremely low lithium concentration of 0.17 ppm, though it would be of interest in coastal countries that have neither mineral nor continental brine resources. Alternatively, brines such as salt lake brines or geothermal brines serve as a rich resource. However, evaporation is a slow process that takes up to 24 months and the final products usually have low purity, whereby sorbents and membranes are effective alternatives. The spinel-type sorbents exhibit excellent ion exchange capacity and high selectivity, although the regeneration process could be expensive. On the other hand, $LiCl{\cdot}2Al(OH)_3$ offers moderate capacity, but this material has other advantages such as low cost and easy regeneration, which are essential for industrial applications. Further research needs to be carried out to better control the defects of the spinel precursor materials. Alternative methods such as solvent extraction could be used to extract lithium from salt lake brines or geothermal brines. The need for large quantities of lithium domestic supply in the USA remains a key priority, for example. Scale-up trials are essential to realise industrial operations to meet the US domestic demand. This requirement justifies continued investment in the extraction of critical lithium from salt lake and geothermal brines. In addition, recovery of lithium from recycled LIB needs a major investment in the near future.

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