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Chapter

Lithium Recovery from Brines Including Seawater, Salt Lake Brine, Underground Water and Geothermal Water

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Abstract

Demand to lithium rising swiftly as increasing due to its diverse applications such as rechargeable batteries, light aircraft alloys, air purification, medicine and nuclear fusion. Lithium demand is expected to triple by 2025 through the use of batteries, particularly electric vehicles. The lithium market is expected to grow from 184,000 TPA of lithium carbonate to 534,000 TPA by 2025. To ensure the growing consumption of lithium, it is necessary to increase the production of lithium from different resources. Natural lithium resources mainly associate within granite pegmatite type deposit (spodumene and petalite ores), salt lake brines, seawater and geothermal water. Among them, the reserves of lithium resource in salt lake brine, seawater and geothermal water are in 70–80% of the total, which are excellent raw materials for lithium extraction. Compared with the minerals, the extraction of lithium from water resources is promising because this aqueous lithium recovery is more abundant, more environmentally friendly and cost-effective.

Keywords: thermodynamics, lithium energy, lithium recovery, adsorption, precipitation, membrane process

1. Introduction

Lithium and its compounds are widely used in manufactured glass, ceramics, greases, batteries, refrigerants, chemical reagents and other industries. World lithium reserves are about 14 million tons, mostly 70–80% is stored in salt lake brine, geothermal water and solid lithium contained in lithium ore. Currently, many researchers are turning their attention to 2600 billion tons of lithium-containing seawater, which is about 15,000 times more than solid lithium ores [1].

Figures for lithium resources and reserves differ considerably accordingly to the source, although there is a unanimous agreement that lithium resources in brine are much larger than those in hard rock [2–6]. The most recent figures from the US Geological Survey indicate total lithium resources (brine + hard rock) to be 54.1 million tons [5]. Approximate minimum and maximum hard rock lithium resources were reported at 12.8 and 30.7 million tons, respectively; while brine field data were reported as 21.3 and 65.3 million tons, respectively, for minimum and maximum estimates [3].

Lithium has various uses, but its abundance in nature is only 0.0018% [7]. The use of lithium on ceramics enriched with Li^6 is up to 15% for use in the production of tritium [8, 9]. In addition, enriched Li^6 is very expensive, what is commensurate with the value of gold. Consequently, it is necessary to extract and recycle lithium from the waste of solid breeding materials. Hence widespread use of lithium in various spheres, many studies have been conducted to extract lithium from various sources.

Lithium demand is expected to grow continuously and dramatically in the coming years as different types of lithium batteries are the most promising candidates for powering electric or hybrid vehicles [10, 11]. Lithium batteries include both current technologies such as lithium-ion and growing battery technologies such as lithium-sulfur or lithium-air [12–15].

Lithium demand is projected to increase by ~60% from 102,000 to 162,000 tonnes of lithium carbonate equivalent in the next 5 years, with battery applications taking a huge percentage of this growth [16, 17]. It was reported that the present lithium resource in continental and Salar brines is roughly 52.3 million tons of lithium equivalent, mainly in Argentina, Chile and Bolivia, from which 23.2 million tons can be extracted [18]. From the other side, lithium from mineral resources is 8.8 million tons, where there are huge deposits in the United States, Russia and China. Evans estimated lithium reserves and recoverable resources at 29.79 million tons [19].

Meanwhile, the general public mainly associates lithium batteries with portable electronics and electric and hybrid vehicles, large storage capacity lithium batteries are also a lead candidate for a possible energy storage solution for the electric grid, intelligent network, etc. Batteries with large capacity are needed to store green energy, wind, that is, sun and waves, all this by their nature intermittent sources of energy [20–30]. Nowadays battling to achieve a greater percentage of green energy, high-capacity batteries or energy banks are mandatory. Basically, if in the near future we want our energy matrix to be highly dependent on renewable energy, energy banks will be needed to provide continuous energy to the grid, during the time these intermittent energy sources are either off or not working completely (no wind, no waves, at night) [20–22]. After all, on its own of the energy source, high-capacity batteries are also an alternative for storing energy during periods of low demand, allowing this excess energy to be re-injected into the grid at high demand peaks [24].

Currently, lithium is relatively not expensive (a ton of Li_2CO_3 is about 15,000 USD), the market shows that, its price is rising with increasing demand [25].

In China, lithium prices have risen about 300% since 2016, and contract prices for existing manufacturers have risen to more than 16,000 USD per tonne.

Because of the exhaustion of lithium ores, recent studies have shown recovery of lithium from seawater, brine and geothermal water. Production of lithium from water resources has become more important due to its wide availability, ease of process and cost-effectiveness compared with its production from various resources [26].

Many methods for extracting lithium from seawater, brines and geothermal water have been reported [27]: solvent extraction, including precipitation, liquid-liquid extraction, selective membrane separation, electrodialysis, ion exchange adsorption, etc. [28–34]. Of these methods, the most attention was paid to ion exchange adsorption methods based on lithium-ion sieves because of their good lithium-ion selectivity and high adsorption properties [35–37]. From the point of view of cost and efficiency, extraction of lithium ions from solutions by ion exchange adsorption is an important method [38].

Various methods of removing lithium from water have been proposed in recent years. In their midst, adsorption has been proven to be a perfect way to extract lithium, offering significant benefits, such as availability, lower cost, profitability, efficiency and easy operation. For lithium removal, various Li adsorbent materials

have previously been reported, including metal oxides, clay minerals, silicotitanates and zirconium phosphate. The main attention of the researchers was focused on the adsorbents of titanium-lithium ion sieves [39–43] manganese-lithium ion sieves [44–50] and aluminum salts [51, 52]. Adsorbents of aluminum salts [52] showed stable and high selectivity for Li^+ with lithium absorption of only 2–3 mg g^{-1}. By Chitrakar et al. [53] nanoscale H_2TiO_3 was synthesized by solid-phase reaction and its adsorption capacity with lithium reached 32 mg g^{-1} [41]. Tang et al. and Zhang et al. were synthesized H_2TiO_3 using different raw materials [41, 42]. Wang et al. synthesized lithium-enriched β-Li_2TiO_3 with a maximum lithium absorption of 76.7 mg g^{-1} in LiOH alkali solution [43]. Despite the fact the maximum absorption of Li^+ adsorbent H_2TiO_3 from the lithium-enriched solution has reached 76.7 mg g^{-1}, the high cost of synthesis and loss of dissolution of the titanium ion is still an obstacle. Chitrakar et al. by hydrothermal reaction synthesized $Li_{1.6}Mn_{1.6}O_4$ and with 52 mg g^{-1} Li^+ adsorption capacity [48]. By Xiao et al. synthesized spinel-structured hydrogen oxides of manganese, the saturated adsorption capacity of which was up to 42 mg g^{-1} [54]. 1-D MnO_2 was synthesized with a maximum adsorption capacity reaching 46.34 mg g^{-1} in LiOH solution (C_0 = 35 mg L^{-1}) [50]. In this case, the dismutation reaction during etching can lead to distortion of the lattice and dissolution of manganese, which will violate its cyclicality.

In addition to lithium and magnesium, the treated salt lake brines may contain significant concentrations of potassium, sodium and boron. Zhou et al. compared the competitive sequences for several cations using TBP/$FeCl_3$ in MIBK as the extractant [55–57]. However, quantitative correlations for competing for ion extractions, which are crucial in industrial design, were not reported.

The review is devoted to the extraction of lithium from brines, marine and geothermal waters, the collection of different methods of lithium extraction from water resources, which makes it possible to compare different methods that determine the optimal path for further research. Moreover, scientists around the world are challenged to find a way to extract lithium from water resources that are environmentally friendly, highly selective, economical, time-efficient and easy to process.

2. Lithium extraction

Lithium is comparatively abundant on the earth's crust, being the affluent 25th more element [58]. More than 150 minerals contain lithium, in solid sediments, in geothermal waters, in many continental brines and in seawater. The concentration of lithium in seawater is very low, with an average of 0.17 ppm [3, 59]. The change in concentration from 1 to 100 ppm shows geothermal waters around the world [2, 4]. Although lithium deposits in all of the above forms are widespread throughout the world, only a very few are large enough and/or concentrated to potentially allow their exploitation. Several high-grade lithium minerals and brines are the only ones currently manufacturing at lithium extraction [2–4].

Interest in the recycling of lithium batteries has grown in recent years. However, recycling is still not economically attractive if compared with the mining of the raw materials [60]. Facilities for recycling are now available in the USA, Canada, Belgium, Germany and Japan. However, lithium availability from recycling is insignificant as compared with mined raw materials [61].

Figures for lithium resources and reserves differ considerably accordingly to the source, although there is unanimously agreement that lithium resources in brine are much larger than those in hard rock [2–4, 6]. The latest data from the U.S. Geological Survey show that total lithium resources (brine + hard rock) are 54.1 million tons. It was reported that the minimum and maximum reserves of lithium

in hard rocks were 12.8 and 30.7 million tons, respectively; while the brine field data were reported as 21.3 and 65.3 million tons, respectively, for the minimum and maximum evaluation [3].

3. Lithium resources

In contradistinction to the uses of lithium, it is necessary to discuss the question of responsibility for Li from a variety of sources. The economic efficiency of lithium is found in minerals, clays and brines. High-grade lithium ores and brines are the current sources for all commercial lithium manufacture. **Figure 1(a)** demonstrates the distribution of lithium over different resources. The figure shows that continental brine is the largest resource (59%) for lithium, followed by solid rock (25%). **Figure 1(b)** demonstrates the spread of lithium across countries. The largest of the studied lithium deposits are in Bolivia and Chile. **Figure 1(c)** demonstrates the distribution of lithium production across countries. The main producers and exporters of lithium ores are Chile and Australia. Chile and China have huge resources of lithium ore. Canada, Russia, Serbia and Congo (Kinshasa) have lithium ores of about 1 million tons each, and equal reserve for Brazil is total 180,000 tons [62].

It is estimated that the earth's crust contains an average of about 0.007% lithium. In nature, lithium does not occur freely, but it occurs in small quantities in almost all magmatic breeds and the ocean, in seawater, in the waters of many mineral springs. Of the approximately 20 known minerals containing lithium, only 4, that is, Lepidolite ($KLi_{1.5}Al_{1.5}[Si_3O_{10}][F,OH]_2$), Spodumene ($LiO_2{\cdot}Al_2O_3{\cdot}4SiO_2$), Petalite ($LiO_2{\cdot}Al_2O_3{\cdot}8SiO_2$) and Amblygonite ($LiAl[PO_4][OH,F]$) are known to occur in quantities sufficient for commercial interest as well industrial importance [63–66]. The spodumen ($LiAlSi_2O_6$) mineral is the most significant industrial lithium ore mineral. Minerals of lithium also exist as cookeite as ($LiAl_4(Si_3Al)O_{10}(OH)_8$) in fine hydrothermal veins of quartz. Taeniolite ($KLiMg_2\ Si_4O_{10}F_2$) is present in veins of smoky quartz in recrystallized novaculite, in manganese deposits the appearance of Lithiophorite ((Al, Li) $Mn^{4+}O_2(OH)$) is noted. Pegmatites, Taeniolite, Lithiophorite and Cookeite are considered to be economically inefficient sources of lithium [67–69]. A large part of the lithium is extracted from brine or seawater has a high concentration of lithium carbonate. In the earth's crust, there are brines called continental brines/subsurface brines are the main source for the production of lithium (lithium carbonate). The literature reports that lithium is also present in seawater at about 0.17 mg L^{-1}. Lithium is found in significant quantities in oil well brines and geothermal waters. These sources of brine and seawater are considered less expensive than mining from rocks such as spodumene, lepidolite, amblygonite and petalite containing lithium.

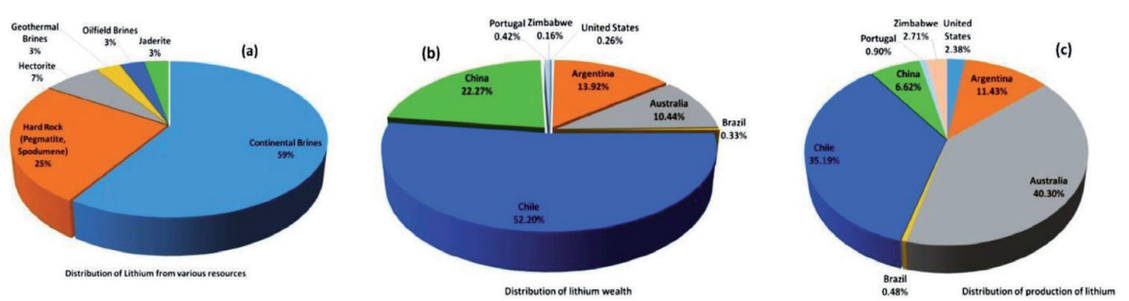

Figure 1.
The distribution of lithium (a) different natural resources, (b) worldwide distribution, (c) the number of producers around the world.

4. Lithium extraction from various resources

4.1 Lithium extraction from brine

Extracting lithium from brine is an important potential resource. When considered from an economic and scientific perspective, the following points are important to consider lithium recovery from brine: (1) suitability of pond soil and admissibility of the area for solar evaporation; (2) the concentration of lithium in brine; (3) the ratio of alkali metals and alkaline earth elements to lithium and (4) the complexity of the phase chemistry. The resources of brines containing lithium can be divided into three types: evaporative, geothermal and oilfield brines. In the process of evaporation of the brine about 50% of the original natural brine, lithium remains in the residual brine. This expression has been ascribed to the retention of lithium by precipitated salts. Residual brine is highly loaded with Mg^{2+} as compared with K^{+} and Na^{+}, this makes it difficult to extract lithium from this residual brine [70].

The extraction of lithium from brine does not correspond to any general regularity since each process is specific depending on the composition of the brine field. Typical lithium production technology used for lithium extraction by Outotec®, where different methods such as precipitation, solvent extraction and flotation were used (**Figure 2**). Lithium extraction by Outotec® uses a lithium carbocation process to produce lithium [71]. Various lithium separation and purification methods have been reported in the literature, which is discussed below. By Chagnes and Swiatowska the general technological scheme of lithium production from brine and seawater is proposed [72]. In this method, liquid-liquid extraction, ion exchange, electrodialysis and adsorption are important hydrometallurgical processes necessary to concentrate lithium before production [72]. **Table 1** discusses and summarizes the extraction of lithium from both brine and synthetic brine in various ways.

4.2 Recovery of lithium from brine by precipitation

Pelly et al., Epstein et al. and Kalpan et al. it has been reported that lithium recovery as precipitation of lithium aluminate from Dead sea brine and final brine [73–75]. Pelly et al. have reported, it is necessary to control the pH of the brine through dilution to achieve 90% extraction efficiency end brine and Dead sea brine [73]. As indicated, the optimal pH should be in the range of 6.6–7.2 For Dead sea brine and 6.8–7.0 for end brine. The optimum reaction time should be 3 hours at room temperature. $AlCl_3{\cdot}6H_2O$ (30–40 g L^{-1}) was added to the brine. The negative effect was given by higher temperature, but better yields were obtained at room temperature and the yield decreased with increasing temperature [73]. The importance of extracting lithium from the Dead sea by precipitation as lithium aluminate followed by liquid-liquid extraction to separate lithium from aluminum with economic evaluation was reported [74]. Kaplan et al. reported on the process of extracting lithium by lithium aluminate from Dead sea brine by precipitation [75]. A small amount of lithium, which is mainly present as LiCl, was precipitated as a lithium aluminate precipitate using ammonia and aluminum salt at room temperature. Although subsequent reduction processes both by dissolving lithium in sulfuric acid and followed by precipitation with calcium chloride lithium were reduced as alum [75]. An et al. reported on the process of extracting lithium from brine collected in Salar de Uyuni, Bolivia. Mg and Ca were extracted from the brine as $Mg(OH)_2$ and gypsum ($CaSO_4{\cdot}2H_2O$) using sulfate and lime. Both CAO and MgO were extracted using oxalic acid followed by firing using residual Ca and Mg. In the end, by heating at 80–90°C lithium was recovered in the form of Li_2CO_3.

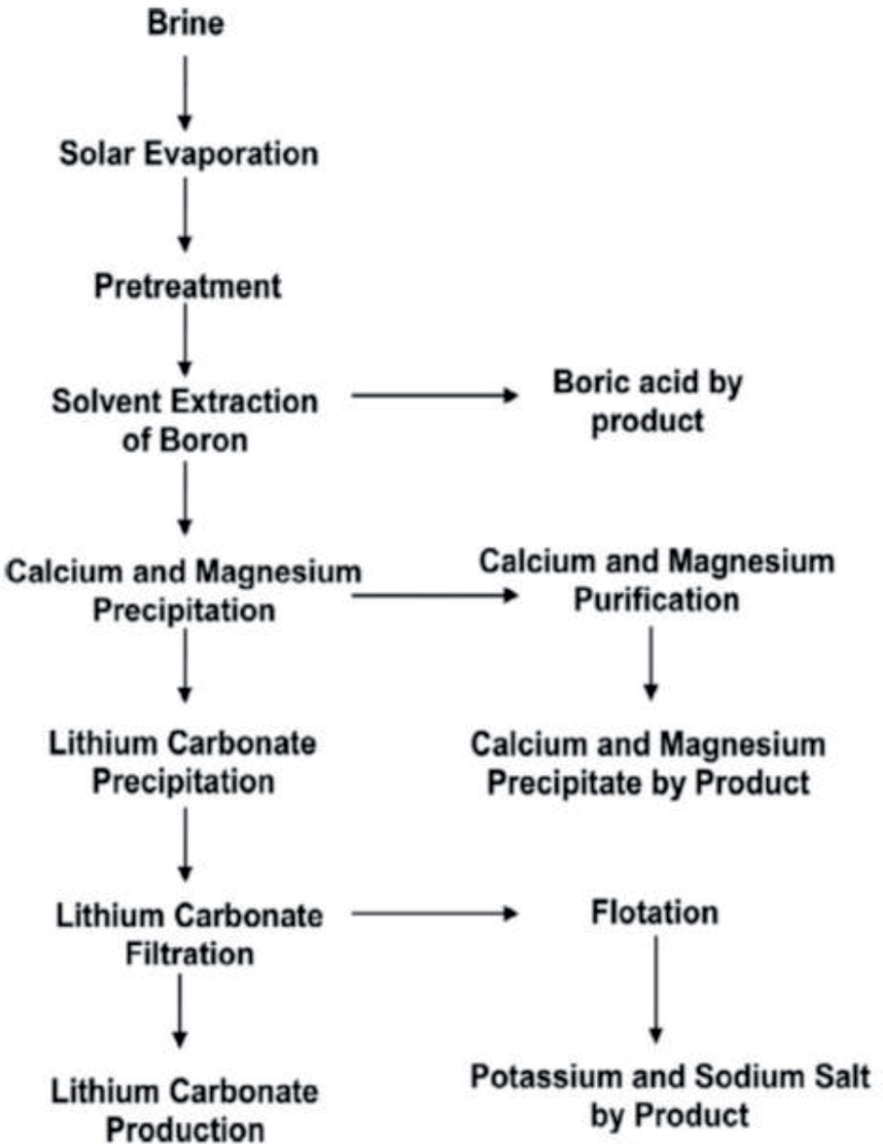

Figure 2.
Outotec lithium production technology from brine. Reproduced with permission from Outotec.

As a result of precipitation processes with a high content of pure (99.55%) and crystalline Li_2CO_3 were reduced [93].

4.3 Ion-exchange method of lithium recovery from brine

Through the use of a specially made resin/aluminates composite/inorganic ion exchanger, from brine lithium can be recovered productively. Bukowski et al. reported through a process of carbocation and ion exchange an extract of pure LiCl from brines containing higher levels of $CaCl_2$ and $MgCl_2$ [77]. Three different ion exchange resins Y80-N Chemie AG (Chemie AG Bitterfeld-Wolfen)), TP207 resin (Bayer AG), (MC50 resin, (Chemie AG Bitterfeld-Wolfen) for lithium extraction from synthetic brine were investigated. As a result of the conducted researches, it is established that it is possible to clean LiCl solutions with Y 80 resin at room temperature and with TP 207 resin at 50°C [77]. Hui et al. synthesis of H_2TiO_3 ion exchanger and extraction of lithium from the brine of natural gas wells have been reported [76]. Ion exchanger H_2TiO_3 was synthesized from Li_2CO_3 and TiO_2 or precipitation of LiOH and TiO_2 followed by calcination at 400–800°C. Ion exchanger H_2TiO_3 provided high selectivity for Li^+ at an exchange capacity of Li^+ 25.34 mg g^{-1} in mixtures

Resources	Process	Reagents	Mechanism	Reference
End brine and Dead Sea brine	Precipitation	Lithium aluminate	Precipitaion	[73]
Dead Sea brine	Precipitation	Lithium aluminate	Precipitaion	[74]
Dead Sea brine	Precipitation	Lithium aluminate	Precipitaion	[75]
Salar de Uyini, Bolivia	Precipitation		Precipitaion	[76]
Dead Sea brine	Gel permeation chromatography	Polyacrymidegel, Bio-Gel P-2 and Blue Dextran 2000	Column chromatography	[77]
From other alkali metal	Reversed phase chromatography	Polytetrafluroethylene tribytyle phosphase (TBP), dibenzoylmethane (DBM) and trioctylephosphine oxide (TOPO)	Column chromatography	[76]
Seawater, hydrothermal water	Column chromatography	Titanium (IV) antimonate cation exchanger (TiSbA)	Column chromatography	[78]
Synthetic brine	Chelating resins	MC50 resin, TP207 resin, Y80-N Chemie AG	Ion exchange	[79]
Brine of natural gas wells	Inorganic ion exchanger	H_2TiO_3 ion exchanger	Ion exchange	[80]
Salt Lake brine	Inorganic ion exchanger	H_2TiO_3 ion exchanger	Ion exchange	[81]
Synthetic brine	Liquid-liquid extraction	n-Butanol		[82]
Synthetic brine	Liquid-liquid extraction	2-Ethyle-1,3-hexanediol, isoamyle alcohol, di-isopropyl ether, diethyl ether		[83]
Brine	Liquid-liquid extraction	With tributyl phosphate (TBP)		[84]
Brine	Liquid-liquid extraction	Heptofluorodimethyloctunedione, peniafluorodimeihylhepiunedione, trifluorodimethylhexanedione, dibenzoylmethane and tetrameihylheptonedione		[85]

Resources	Process	Reagents	Mechanism	Reference
Salt Lake brine	Ionic liquid liquid-liquid extraction	-Butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]-imide, 1-ethyl-3-methyl-imidazolium bis[(trifluoromethyl)-sulfonyl]-imide and 1-butyl-3-methylimidazolium hexafluorophosphate		[86]
Brine	Ionic liquid liquid-liquid extraction	1-Alkyl-3-methylimidazolium-based ionic liquids (ILs), in which the alkyl chain lengths were 4-butyl (C4), 5-pentyl (C5), 6-hexyl (C6), 7-heptyl (C7), 8-octyl (C8) or 9-nonyl (C9)		[87]
Salt Lake brine	Ionic liquid liquid-liquid extraction	1-Octyl-3-methyl-imidazolium hexafluorophosphate and tributyl phosphate (TBP)		[88]
Salt Lake brine	Ionic liquid liquid-liquid extraction	Bis(trifluoromethylsulfonyl) imide in TBP		[88]
Brine	Electro-electrodialysis	Bipolar membranes		[89]
Salt Lake brine	Membrane electrolysis	Bipolar membranes		[93]
Dead Sea brine	Solvent impregnated membrane	Solvent-polymeric membranes (2-ethylhexyl)-diphenyl phosphate		[66]
Brine	Desalination	Nanofiltration membrane		[91]
Salt Lake brine	Desalination	Nanofiltration (NF90 membrane XLE membrane)		[92]

Table 1.
Recovery of lithium from brines by various processes.

of alkaline earth metal and an alkali metal. From brine ion exchanger H_2TiO_3 showed 97% exchange rate and 98% elution rate for Li^+ [76]. Chitrakar et al. reported with the same H_2TiO_3 ion exchanger extract lithium from Salt lake brine. Adsorption of lithium ions by H_2TiO_3 ion exchanger according to Langmuir model having exchange capacity for Li^+ 25.34, 32.6 mg g^{-1} at pH 6.5 from brine was reported [53].

4.4 Liquid-liquid method of lithium recovery from brine

Many studies have provided my traditional liquid-liquid extraction and liquid-liquid extraction by ionic liquids (ILs) have been reported for lithium extraction from brine. Gabra et al. using synthetic solutions of nbutanol containing different amounts of lithium, potassium, calcium and sodium chloride, a laboratory-scale of LiCl extraction process were developed. A method for lithium reduction for separation and LiCl reduction is proposed, derived from distribution coefficients, separation coefficients and the presentation of McCabe-Thiel results. According to this method, 99.6% purity of LiCl can be restored [78]. Liquid-liquid extraction of lithium from brines by alcohol such as isoamyl alcohol and n-butanol, combined with precipitation of the lithium-aluminum complex reported by Bukowski et al. The amount of LiCl extraction from brine at pH 5.4 with different alcohol follow the order: 2-ethyl-1,3-hexanediol > isoamyl alcohol > di-isopropyl ether > diethyl ether and can extract 32.8, 25.2, 11.4, 9.1% lithium, respectively, along with Na, Mg and Ca. Lithium extraction was also studied using a binary mixture of the above compounds in a 1:1 ratio at a pH of 5.4. 2-ethyl-1,3-hexanediol mixed with isoamyl alcohol is suitable for 90% LiCl reduction as well as suppression of metal co-extraction [79]. Zhou et al. reported the extraction of lithium from brine sources using tributyl phosphate (TBP) in three different diluents [55]. Three salt solutions ($ZnCl_2$, $FeCl_3$ and $CrCl_3$) were selected as co-extractors to investigate the possibility of extracting lithium metal from brine sources. The method of liquid-liquid extraction equilibrium of lithium with tributyl phosphate (TBP) in methylisobutyl ketone (MIBC), TBP in kerosene and TBP in 2-octanol was analyzed. In liquid–liquid extraction, lithium equilibrium is investigated by $FeCl_3$ solution as a co-extractor. The results showed that the extraction efficiency followed the sequence: TBP/2-octanol < TBP/kerosene < TBP/MIBK. It was significantly larger than the TBP/2-octanol system than the TBP/MIBK and TBP/kerosene systems for lithium recovery [55]. A method for extracting lithium from neutral brines using beta-diketone and trioctyl phosphine oxide in benzene was patented by Baldwin and Seeley [80]. The mechanism of extraction was discussed in more detail with scientists [81].

4.5 Liquid-liquid extraction using ionic liquid method to extract lithium from brine

Unlike traditional liquid-liquid extraction, ionic liquid extraction is considered not only as a solvent but also as a co-extraction reagent. Gao et al. reported the extraction of lithium from salt lake brine using tri-isobutyl phosphate in ionic liquid and kerosene [82]. Three ionic liquids (ILs) have been reported, that is, 1-ethyl-3-methyl-imidazolium-bis[(trifluoromethyl)-sulfonyl]-imide, 1-butyl-3-methylimidazolium-bis[(trifluoromethyl)-sulfonyl]-imide and 1-butyl-3-methylimidazolium-hexafluorophosphate with triisobutyl phosphate (TIBP) and kerosene for ion recovery lithium from salt lake brine. The results show that the best selective lithium extraction was obtained using IL 1-ethyl-3-methylimidazole bis[(trifluoromethyl)-sulfonyl] imide. Under optimal extraction conditions, the one-stage efficiency of lithium ion extraction was 83.71% and the one-stage distillation efficiency was 85.61% at 1.0 mol L^{-1} HCl in 1.0 mol L^{-1} NaCl as a stripping

agent at (O/A) = 2 [82]. Also, lithium extraction from brine is performed using imidazolium-containing ionic liquids with varying alkyl chain lengths in a series of ionic liquids based on 1-alkyl-3-methylimidazolium (ILs), in which the alkyl chain lengths are 4-butyl (C_4), 5-pentyl (C_5), 6-hexyl (C_6), 7-heptyl (C_7), 8-octyl (C_8) or 9-nonyl (C_9), in the presence of tri-isobutyl phosphate (TIBP) and kerosene systems presented by Gao et al. [83]. Studies have shown that the shorter the alkyl chain length of imidazolibased ILs, the higher the lithium recovery efficiency. Optimal lithium extraction can be achieved using ionic liquids based on n-butyl (C_4) based on 1-alkyl-3-methylimidazoline (ILs). With a single contact of extraction and distillation, the efficiency of lithium extraction under optimal conditions was 74.14 and 86.37%, respectively. And the optimal condition was ionic liquids based on N-butyl-3-methylimidazole: TIBP: kerosene = 1:8:1 (vol/vol), pH = 5.0, O/A = 2.0 at the extraction stage using 1 mol L^{-1} HCl at O/A = 3 at the distillation stage [83]. Separation of lithium and magnesium from Salt lake brine by liquid-liquid extraction using ILs containing tributyl phosphate, reported Chenglong et al. [84, 85]. Tributyl phosphate (TBP), ILs and 1-octyl-3-methylimidazolium hexafluorophosphate, respectively, were used as the extraction medium and extractant for lithium extraction from Salt lake brine. The most suitable conditions for the extraction of this system were the ratio of TBP/ILs at 9/1(vol), O/A at 2:1. The pH of the brines of salt lakes is maintained constant. The obtained data show that the efficiency of single-stage extraction of lithium and magnesium was 80.64 and 5.30%, respectively. The total extraction efficiency of 99.42% was achieved by three-stage countercurrent extraction. With a one-stage method of removing lithium and magnesium, the efficiency was at A/O phase ratio of 298.78 and 99.15%, respectively, at 80°C. Provisional result showed that ILs has the potential to replace volatile organic solvents in liquid-liquid recovery of lithium cations [84]. At room temperature, ionic liquid solvent extraction of lithium cations using TBP was reported by Chenglong et al. The authors used TBP against the widely used ILs bis(trifluoromethylsulfonyl) imide and quantitative reduction of lithium [85].

4.6 Membrane process of extraction of lithium from brine

The extraction of lithium from brine by membrane method is a relatively modern and novel technology reported by various authors, which are discussed below. Through electroelectrodialysis with bipolar membranes, the production of lithium hydroxide from brines has been reported by Jiang et al. [86]. In a laboratory-scale process, a sequentially configured electro-electrodialysis with a bipolar membrane was installed with a permutation of the conventional electrodialysis stack. Standard electrodialysis stacks were reconfigured using five cation exchange membranes and four anion exchange membranes. With conventional electrodialysis and Na_2CO_3, through preconcentrating and precipitating brine, respectively, 98% pure Li_2CO_3 powder can be recovered. The authors investigated the influence of current density and raw material concentration on the production of lithium hydroxide (LiOH). Cost-effective was electro-electrodialysis with bipolar membranes at a current density of 30 mA/cm^2 and a feed concentration of 0.18 MPa. Jiang et al. argued that the process is environmentally friendly and cost-effective [86]. The extraction of lithium from salt lake brine by membrane electrolysis was reported by Liu et al. [87]. Different technological parameters are optimized: the distance between the anode and the cathode, the initial concentration of lithium in the analyte, the electrolyte temperature, the electrolysis time and the surface density of the active substrate. The electrode demonstrates a remarkable Li^+ 38.9 mg g^{-1} exchange capacity and an analyte pH value below 8.00 at optimal conditions [87]. Extraction of lithium from Dead sea brine by membrane separation using an ion-exchange hybrid

process reported by Jagur-Grodzinski and Schori [88]. Lithium cations can be selectively permeated by solvent-polymer membranes. Better selectivity of Li^+ transport by Mg^{2+} and Ca^{2+} gave membranes with (2-ethylhexyl)-diphenyl phosphate. No significant changes in membrane permeability and selectivity were observed during the 6 months of operation. Preliminary concentration of lithium and subsequent selective separation of lithium by membrane and ion exchange fusion were described by Jagur-Grodzinski and Schori. The expediency of lithium separation by combination of ion exchange process and membrane is substantiated [88]. The processes of concentration and separation of lithium from brine by reverse osmosis, nanofiltration was used. Sun et al. reported the isolation of lithium and magnesium from brine using a desalination nanofiltration membrane [89]. Magnesium lithium rejection rate was estimated by optimizing various operational parameters such as pressure, supply water temperature, pH and Mg^{2+} to Li^+ ratio. Lithium extractions from salt lake brine using RO and NF processes have also been investigated. Studies show that the separation of magnesium and lithium was strongly dependent on the operating pressure, Mg^{2+}/Li^+ ratio and pH [89]. Lithium recovery from salt lake brine has been reported using NF and a low-pressure RO membrane by Somrani et al. [90]. Lithium selective membrane NF90 compared with XLE with low-pressure reverse osmosis membrane. For Li^+ extraction, the NF90 membrane is more efficient than the XLE on the low pressure RO membrane due to its higher permeability to clean water and 0.1 m NaCl solution. A lower critical pressure (Pc = 0) and higher selectivity were obtained at a low operating transmembrane pressure (<15 bar) between monovalent cations (40%). Nf90 membrane showed 100% magnesium rejection in the initial step separation from dilute brine (15% for Li^+, 10 times dilution). An 85% separation between Mg^{2+}/Li^+ was achieved in the final. Lithium can easily be separated by dialysis from the solution [90].

5. Lithium extraction from seawater

In the near future, to meet the needs of the world community in lithium, the ocean is considered the most important and promising resource for lithium [66]. It is reported that the total amount of lithium reserves in the oceans is approximately 2.6×10^{11} t [91]. Lithium extraction from hydromineral sources is carried out on a semi-industrial and industrial scale in the USA from salt lakes [66, 92, 94, 95], in Japan from thermal waters [96, 97], in Israel from the Dead sea [66, 73]. The extraction of lithium metal from geothermal and brine has also been studied in Russia, Germany, Bulgaria and Korea [98]. Typically, lithium is extracted from seawater by these two processes: (1) co-precipitation and extraction process and (2) ion exchange and sorption process.

Various methods have emerged with the development of technology, such as liquid-liquid extraction, a membrane process is used to extract lithium from seawater **Table 2**. The process of lithium extraction from both brine and synthetic brine has been considered and generalized through various processes such as liquid–liquid extraction, ion exchange and sorption, co-deposition and membrane processes.

5.1 Co-precipitation method for extracting lithium from seawater

Like other methods, it has not received wide application the extraction process of lithium recovery and extraction by co-precipitation. For lithium recovery, an important problem is the presence of higher concentrations of alkali and alkali metals in seawater. The alkali metal group has a very similar parameter, which creates problems for lithium recovery. The problems associated with lithium recovery from

seawater and terrestrial hydromineral resources are very similar [66]. To extract lithium from seawater, various reagents such as potassium, iron sulfates and aluminum hydroxides, are successfully used to co-precipitate lithium [66, 96]. To obtain lithium concentrate, the dissolution of the co-precipitate after an ion exchange process is used. A hydrometallurgical process for extracting lithium from seawater using an adsorption process with a manganese oxide adsorbent followed by a deposition process reported by Um and Hirato [99]. By this method, at a temperature of (25–90°C), $MgCl_2$ and $CaCl_2$ from seawater were precipitated as $Mg(OH)_2$ and $Ca(OH)_2$. Using the NaOH, pH was managed between 7 and 14 with an initial concentration of $CaCl_2$, $MgCl_2$ and $MnCl_2$ (10 and 100 mmol/dm^3). Followed by the second stage Li_2CO_3 was recovered through carbonation using Na_2CO_3 by neutralization using HCl [99].

Resources	Process	Reagents	Mechanism	Reference
Seawater	Precipitation	Na_2CO_3 + HCl	Precipitation	[99]
Seawater	Adsorption	k-MnO_2 adsorbent	Sorption	[100]
Seawater	Adsorption	$Al(OH)_3$ layer	Sorption	[101]
Seawater	Adsorption	(HMnO) ion-sieve (microporous)	Sorption	[102]
Seawater	Adsorption	k-MnO_2	Sorption	[103]
Seawater	Adsorption	MnO_2	Sorption	[104]
Seawater	Adsorption	HMnO	Sorption	[105]
Seawater	Adsorption	Nanostructure MnO_2 ion-sieve	Sorption	[18]
Seawater	Adsorption	MnO_2 adsorbent	Sorption	[106]
Seawater	Adsorption	$H_{1.6}Mn_{1.6}O_4$	Sorption	[48]
Seawater	Liquid-liquid extraction	Cyclohexane and tri-octyloxyphosphine		[101, 107]
Seawater	Liquid-liquid extraction	Thenoyltrifluoroacetone (TTA) and TOPO		[108]
Seawater	Membrane process	Mixed matrix nanofiber as a flow-through membrane	Adsorption	[102]
Seawater	Membrane process	Inorganic adsorbent containing polymeric membrane	Adsorption	[103]
Seawater	Membrane process	Inorganic adsorbent containing polymeric membrane	Adsorption	[109]
Seawater	Membrane process	Recyclable composite nanofiber adsorbent	Adsorption	[110]
Seawater	Membrane process	Li ionic superconductor functioning as a Li separation membrane	Dialysis	[111]
Seawater	Membrane process	Ionic liquid membrane	Electrodialysis	[112, 113]
Seawater	Membrane process	Membrane distillation and crystallization	Osmotic and vacuum configuration	[114]
Seawater	Membrane process	Mixed matrix nanofiber as a flow-through membrane	Adsorption	[115]

Table 2.
Recovery of lithium from seawater by various processes.

5.2 Ion exchange and sorption method for extracting lithium from seawater

Although various mega-industries are interested in extracting lithium from seawater in the present decade, extracting lithium from seawater has become increasingly attractive to researchers over several years through ion exchange and sorption. Several alternative methods of lithium extraction from seawater using ion-exchange after solar evaporation and fractional crystallization of NaCl, KCl and $CaSO_4$ are also proposed. According to this method, organic and inorganic sorbents are similar to the compounds used to extract lithium. Reports explaining this method are discussed below. Obtained by treating a Dowex-1 type microporous anion exchanger with a lithium-selective aluminum-containing resin with a saturated solution of ammonia, $AlCl_3$, and finally a solution of lithium halide before heating to produce a composite matrix of the microcrystalline resin $LiX{\cdot}2Al(OH)_3$ is an example of such products that have been patented in the United States [66, 116, 117]. High selectivity for lithium extraction was synthesized with sorbents based on antimony, tin, dioxides based on titanium and zirconium [118], mixed oxides of titanium and iron, titanium and chromium, titanium arsenate and magnesium and thorium [66]. To extract lithium from seawater, only manganese oxide-based cation exchange yields effective results in a wide range of lithium-selective ion exchange materials. Russian scientists use manganese oxide and mixed oxides of manganese and aluminum, known as ISM-1 and ISMA-1, respectively, to reduce lithium [66, 119]. For Li^+ in mixtures of alkali metal and alkali metal ions, the H_2TiO_3 ion exchanger resulted in high selectivity. Achieving the exchange capacity of Li^+ was 25–34 mg g^{-1}. High selectivity for lithium cations by synthetic inorganic materials of titanium (IV) antimonate cation exchanger (TiSbA) ion exchange has been reported by Abe et al. Recovery of lithium cations from hydrothermal water as well as seawater can be successfully applied. Using the periodic method, the effect of K^+, Mg^{2+} and Ca^{2+} cations on the adsorption of lithium cations on TiSbA has been reported by Abe et al. They showed that lithium adsorption decreases significantly with increasing concentrations of K^+, Mg^{2+} and Ca^{2+} cations. Lithium from the sea and hydrothermal water is enriched through TiSbA columns. To separate lithium cations from seawater and hydrothermal water TiSbA exchanger potentially be reused. With HNO_3 solution as the eluent, the adsorbed lithium can be eluted [120].

Selective extraction of lithium from seawater using two sequential ion exchange processes has been reported by Nishihama et al. [100]. By bench chromatographic operation with adsorbent k-MnO_2, lithium was concentrated from seawater, which has a 33% lithium recovery efficiency. A combination of ion exchange using resin and solvent impregnated resin is carried out lithium purification from the concentrated liquor of the reference unit. The cleaning process consists of the removal of divalent metal ions with a strong acid cation exchange resin accompanied by the removal of Na^+ and K^+ with b-diketone/TOPO impregnated resin; finally, the reduction of Li^+ as Li_2CO_3 precipitates using a saturated solution $(NH_4)^{2-}CO_3$. According to the method, the concede was 56%, and the cleanness was 99.9% [100]. Takeuchi reported on a new method of extracting lithium from seawater, also supported [101]. At a temperature of 50°C, almost 70% for lithium ion recovery is achieved in a periodic mode with a high selectivity of the $Al(OH)_3$ layer [101].

Several authors have reported that the extraction of lithium from seawater by sorption/desorption is a fairly common process, which is discussed below [108]. Many studies based on manganese oxide sorbate are used for the sorption/desorption of lithium from seawater. Japanese scientists have developed a sorbet based on hydrated c-oxides of manganese and mixed oxide of manganese and magnesium [102, 103]. By Ooi et al. lithium extraction from seawater using manganese oxide ion sieve (HMnO) was investigated. Maximum (7.8 mg g^{-1}) absorption of lithium

HMnO from seawater was achieved [102]. A study using ISMA-1 sorbents to extract lithium from seawater shows the following information: (1) The Li^+ cation distribution ratio is 4×10^4. (2) Sorbents are easily regenerated by nitric acid. (3) They exhibit a high capacity for lithium cations of about 20 mg/m. (4) Lithium concentrates containing up to 1 g L^{-1} of lithium can be achieved under optimal conditions. A two stage scheme for obtaining Li_2CO_3 from seawater using this information of a pilot plant with a capacity of 3 m^3 of seawater per hour has been developed and presented [66]. ISMA-1 sorbents provide higher chemical stability, but manganese oxide degradation associated with ion exchange remains the most serious drawback for their large-scale application in the lithium reduction process. A Japanese researcher developed a composite material by introducing a fine powder k-MnO_2 with spinel structure into polyvinyl chloride to improve the kinetic properties of manganese oxide sorbents [121]. Sorbents ISM and ISM-1, synthesized in Russia, are also a composite material obtained using a polymer binder [66, 119]. In Korea, it has also been reported to recover lithium from seawater using an ion exchange type of manganese oxide adsorbent. To recover dissolved lithium in seawater a highly efficient ion exchange adsorbent was prepared according to their method. A highly efficient ion exchange type adsorbate was synthesized as a result of the solid state reaction of Li_2CO_3 and $MgCO_3$. The ion sieve is formed after treatment of seawater with adsorbate, which is reduced by acid treatment. The lithium-ion sieve was produced by 3 cycles of 0.5 m HCl treatment with 24 h/cycle stringing, which shows 25.7 mg L^{-1} lithium absorption from artificial seawater [98]. Extraction of lithium from seawater by manganese oxide ion-sieve reported by Liu et al. The most promising method of industrial application was considered to be the extraction of lithium from seawater by adsorption using manganese oxide-ion sieves [104]. The sorption properties of HMnO in seawater and wastewater have been studied by Park et al. [105]. Lithium recovery from lake Urmia by the MnO_2 ion sieve, where more than 90% lithium recovery can be achieved, was reported by Zandevakili et al. [122]. Wajima et al. studied the adsorption behavior of lithium from seawater using the adsorbent manganese oxide [106]. In studies using a pseudo-second-order kinetic model, a higher adsorption Kinetics of lithium cations in seawater was observed [106]. Reduction of lithium from seawater using manganese oxide adsorbent synthesized from $Li_{1.6}Mn_{1.6}O_4$ precursor studied by Chitrakar et al. Manganese oxide adsorbent $LiMnO_2$ was synthesized from $H_{1.6}Mn_{1.6}O_4$ at 400°C by hydrothermal and reflux method. $H_{1.6}Mn_{1.6}O_4$ was synthesized from precursor $Li_{1.6}Mn_{1.6}O_4$. The sufficiently effective adsorbent can absorb lithium up to 40 mg g^{-1} from seawater [48].

5.3 Liquid-liquid extraction method of recovery of lithium from seawater

Scientists reported that liquid-liquid lithium extraction from seawater and liquid-liquid extraction are considered a potential process for extracting lithium from seawater. The use of liquid-liquid extraction to extract lithium from seawater is very limited, but the separation, purification and extraction of lithium by liquid-liquid extraction have been considered by several authors [81]. On the basis of the reference liquid-liquid extraction of lithium from seawater discussed below.

Scientists have used several extractants, such as primary alcohol C_3-C_5 and aliphatic alcohol C_6-C_8, to extract lithium from seawater, but the most effective and promising is Isobutanol. Japanese scientists have developed the most interesting method of extraction and in fact the most modern technology [107, 115]. In these methods, lithium is first extracted with cyclohexane and trioctyloxyphosphine, then the lithium reacts with hydrochloric acid and potassium phosphate, followed by lithium precipitation. The product obtained by this method has a purity of more

than 95%. Synergistic extraction of lithium from seawater using a TTA-TOPO mixture has been reported by Harvianto et al. [123]. About 93% of the lithium can be recovered by TTA-TOPO. With acidic solutions, the lithium ion can be easily removed, but the removal efficiency decreases with increasing pH of acidic solutions. The type of acid does not affect the stripping efficiency. Similarly, by liquid-liquid extraction, 65% of lithium can be extracted from seawater, in the liquid-liquid extraction process, a magnesium ion is precipitated in advance. The recovery efficiency of lithium ions is negated by other metal ions in seawater [123].

5.4 Membrane process recovery of lithium from seawater

In recent years a number of authors have studied lithium recovery using different types of membranes. The membrane process of lithium reduction is a fairly advanced process that is gaining the attention of various researchers around the world.

Polysulfone (PSf)-based mixed matrix nanofiber dispersed with particulate lithium ion sieves as a flow-through membrane Li^+ absorber has developed by Park et al. A mixed matrix of electro-spinning nanofibers was prepared by thermal annealing, where lithium-ion sieves were activated by acid pickling as $Li_{0.67}H_{0.96}Mn_{1.58}O_4$ or MO. PSF based mixed matrix nanofiber effectively improved Li^+ selectivity. At minimal trans-membrane pressure, the mixed matrix nanofiber membranes were very permeable to water. By supporting the dynamic adsorption capacity of Li^+ mixed matrix nanofibers, the shorter adsorption–desorption cycle time (24 h) was successfully controlled by continuous streaming operations. In a small volume of acid solution, Li^+ enrichment was successfully achieved by repeated desorption of Li^+ [115]. Recovery of lithium from seawater using an inorganic adsorbent containing a polymer membrane reservoir system, reported Chung et al. To extract lithium from seawater, Chung et al. used three different membranes: a PSf nonwoven membrane, a PSF nonwoven composite membrane and a Kimtex® composite membrane.

The proposed system has the advantage of direct application in the seawater eliminates the use of a pressurized flow system [124]. The proposed system can have a direct application in seawater using a pressure flow system. In addition, lithium extraction from seawater using an inorganic adsorbent containing a polymer membrane has been reported by Umeno et al. Lithium recovery from seawater desalination retentate using composite poly(acrylonitrile) nanofibers with $H_{1.6}Mn_{1.6}O_4$ (HMO) lithium ion sieves was reported by Park et al. [110]. To obtain nanofibers, HMO/PAN dope solutions in N,N-dimethylformamide (DMF) with different HMO loads were used, and nanofibers were obtained by electrospinning. For efficient lithium extraction from seawater desalination retentate the material may be a potential membrane (Park et al.) [110]. The use of poly(vinyl chloride) (PVC) membrane adsorbent spinel-type manganese oxide by solvent exchange reported by Umeno et al. Poly(vinyl chloride) was dissolved in DMF solution, then lithium manganese oxide (spinel type) was mixed with DMF to obtain a suspension. The cured PVC film was prepared by applying a suspension to a thin film and immersed in water. To extract lithium obtained as a membrane type adsorbent the membrane was treated with HCl solution. Lithium extraction has been reported to be highly dependent on the method of preparation [109]. Hoshino reported on the recovery of lithium by dialysis and electrodialysis of seawater [111–113]. Selective extraction of lithium from seawater under laboratory conditions was investigated by electrodialysis using an ionic liquid (PP13-TFSI) impregnated with a membrane. The lithium recovery process was developed using

a membrane process [112, 113]. Lithium extraction from seawater was selectively achieved by dialysis using a lithium ion superconducting membrane. For appropriate industrial lithium mass production applications, the dialysis process can be energy efficient and easily scalable [111]. Recovery of lithium by membrane desalination followed by crystallization was reported by Quist-Jensen et al. [114]. Extraction of lithium chloride and comparison of membrane crystallization in direct contact, vacuum and osmotic configuration were carried out. In their environment, the necessary supersaturation for crystallization was achieved for the simultaneous production of pure water and lithium by vacuum-membrane distillation [114].

6. Lithium ion-sieve effect

In 1971, ion-sieve oxides were first prepared by Volkhin et al. [125] since ion-sieve oxides have received increasing attention in the last few decades due to the special properties and performance as metal ions [126–130]. To extract specific metal ions with effective ion-sieve characteristics, ion-sieve oxides are fine adsorbents. Ion-sieve oxide adsorbents are obtained from corresponding precursors containing ions of the target metal. Characteristically, precursors are stable molecular structures, even if target ions are removed from their crystal sites, free crystal sites can still be retained. Thus, the resulting free crystal regions can only contain ions whose ionic radii are less than or equal to the radii of the target ions. In fact, only lithium ions can re-enter the free spaces of lithium ion sieves because lithium has the smallest ionic radius among all metal ions.

The study shows that only lithium ions can be adsorbed when LISs are placed in aqueous solutions containing different kinds of metal ions. **Figure 3** shows how LIS works. The main stage is the formation of LIS with hydrogen filled state [LIS (H)] by removing lithium ions from the lithium filled state [LIS (Li)], principally through Li-H ion exchange, then the adsorption isolation of lithium ions LIS from Li^+-containing solutions based on the steric effect. The spent LIS (H) is then regenerated to form LIS (Li) by adsorption of lithium ions. In General, the process can be called "LIS effect" [131–135].

7. Lithium ion-sieve

In fact, two types of chemical elements can be used, such as LISs, lithium manganese oxide type (LMO type) and lithium titanium oxide type (LTO type). LMO-type LISs are the most popular selective lithium adsorbents at present because of superior lithium absorption abilities, magnificent regeneration performance and high lithium selectivity. In addition, the extraction of lithium from aqueous solutions has recently improved significantly through the use of electrochemical methods. However, the LISs type suffers from the dissolution of manganese in aqueous solutions, which in industrial conditions can lead to serious water contamination. In this regard, LISs type LTO can overcome this problem, can be easily removed from the aqueous solution, and titanium compounds are not harmful to the aquatic environment [136–138]. In addition, LTO-type LISs has much more stable molecular structures due to the high energy of the titanium-oxygen bond compared with LMO-type LISs. But when an electrical potential is applied LISs of type LTO have limited use in extracting lithium from an aqueous solution. This restriction may prevent future industrial use of LISs type LTO. Thus, LMO-type and LTO-type LISs have their own unique benefits and

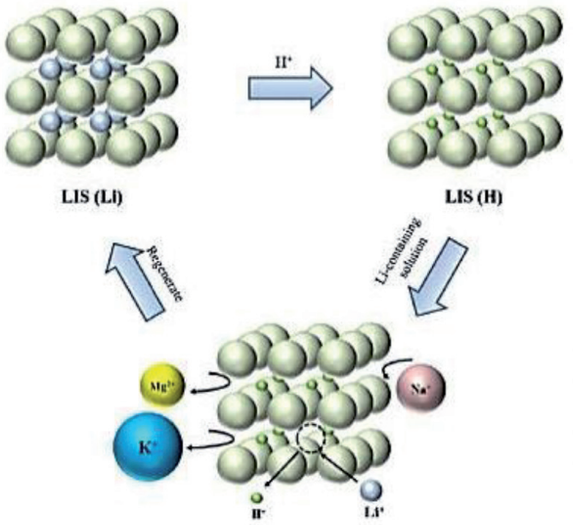

Figure 3.
Schematic representation of LIS process.

problems. Therefore future research to meet large scale industrial applications may focus on minimizing their respective disadvantages.

7.1 Lithium recovery by LMO type lithium-ion sieves

7.1.1 Study of ternary phase diagram of Li-Mn-O

With research [44], several LMO-type LISs have been well developed by many scientists [48]. As a rule, their precursors demonstrate a spinel structure. Because of multiple valence states of manganese, several lithium manganese oxides with different crystal structures can be formed. At 25°C, the phase diagram Li-Mn-O shows the isothermal cross-section **Figure 4** [139–143].

In the blue area in **Figure 4a**, the stoichiometric spinel phase defect is defined by the triangle Mn_3O_4·$Li_4Mn_5O_{12}$·λ-MnO_2. Using the general formula $Li_xMn_{3-x}O_4$ ($0 \leq x \leq 1.33$), one can imagine the stoichiometric spinel phases lying on the bond between Mn_3O_4 and $Li_4Mn_5O_{12}$. According to the general formula $Mn_{3-x}O_4$ ($0 \leq x \leq 1$) defective spinels of manganese oxides located between Mn_3O_4 and λ-MnO_2 are presented. In accordance with the general formula Li_2O·$yMnO_2$ ($y > 2.5$), the defect of lithium-manganese-oxide spinel is expressed and the communication line lies between $Li_4Mn_5O_{12}$ and λ-MnO_2. At this point, in $LiMn_2O_4$·$Li_2Mn_4O_9$·$Li_4Mn_5O1_2$ the blue triangle in **Figure 4b** is the active area for preparing the precursors of LMO-type LISs. Therefore, it is possible to obtain high Li-Mn precursors such as $Li_5Mn_4O_9$ and $Li_7Mn_5O_{12}$ in principle, implying that high Li^+ capacity LISs may be obtained in the future.

Currently, only a few LMO-type LIS precursors with high Li^+ adsorption capacities such as λ-MnO_2, MnO_2·$0.31H_2O$ and MnO_2·$0.5H_2O$, which are derived from $LiMn_2O_4$, $Li_4Mn_5O_{12}$ and $Li_{1.6}Mn_{1.6}O_4$, respectively, were prepared. As shown in **Figure 5**, a phase diagram consisting of additional proton-type manganese oxides depending on the valence state of manganese, molar Li/Mn and H/Mn ratios constructed by Chitrakar et al. [47].

As shown in the figure, LIS precursors of the LMO-type can be classified into two types of reactions and are represented in two perpendicular planes: the vertical plane represents the redox reaction region, and the horizontal plane represents the ion exchange region. **Table 3** mainly summarizes their main properties for the absorption of lithium from aqueous solutions.

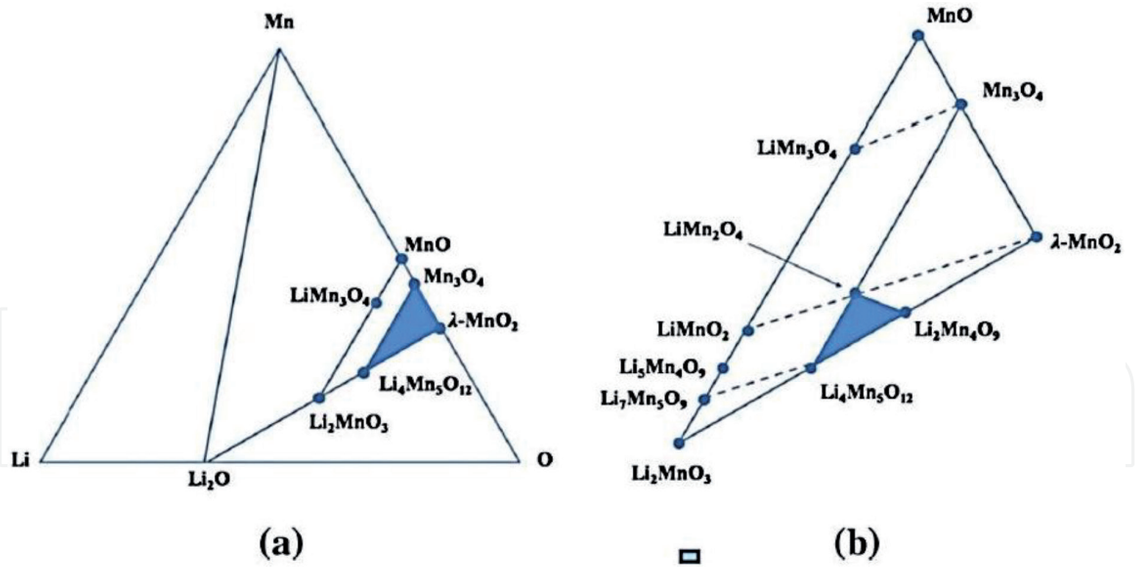

Figure 4.
(a) An isothermal cross section of the Li-Mn-O phase diagram at 25°C and (b) an expanded region of the Li-Mn-O phase diagram.

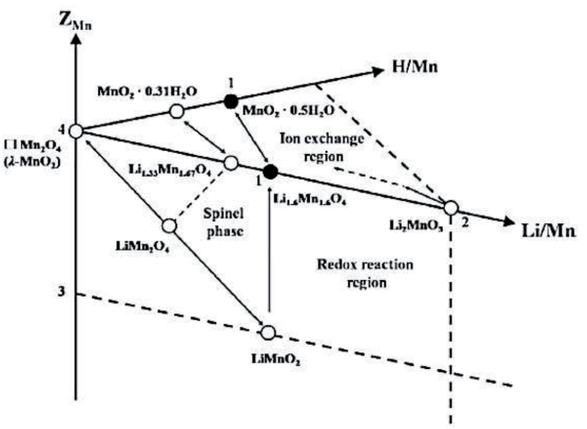

Figure 5.
Phase diagram of LMO and their delithiated products [47]. Reproduced from Ref. [47].

7.1.2 The spinel structure of the precursors of LMO

Inevitably, the chemical properties depend on the chemical structures to be determined, so the extraction of lithium by LMO precursors is explained by their peculiar chemical structure. Actually, all synthesized precursors of LMOs have spinel structures [144–152]. Among these, the $LiMn_2O_4$ structure is the most representative one, as shown in **Figure 6**.

Spinel $LiMn_2O_4$ has a cubic crystal structure that belongs to the spatial group *Fd3m*. The structure shows that the tetrahedron's 8a sites occupy lithium ions. At a molar ratio of 1:1, Mn^{3+} and Mn^{4+} ions are randomly distributed over 16d sites of octahedra, and oxygen anions occupy 32e sites of the face-centered cubes. Accordingly, the formula $(Li)_{8a}[Mn(III)Mn(IV)]_{16d}O_4$ can be represented by spinels $LiMn_2O_4$, which can be described by the general spinel formula (AB_2O_4). From other side, the $LiMn_2O_4$ unit cell can be viewed as a complex cubic structure: oxygen atoms are 32 and 16 manganese atoms occupy half of the octahedral pore (16d), while the other half of the sections (16c) are free. Here are 8 of the lithium atoms occupy 1/8 of tetrahedral interstices plot (8a). Li^+ can intercalate/deintercalate in three-dimensional networks of free octahedral and octahedral gaps along the

Materials		Li^+ uptake capacity	Regenerations	Li^+ selectivity	Ref.
Precursors	**Ion sieves**				
$LiMn_2O_4$	λ-MnO_2	16.9 mg g^{-1} (LiCl solution, pH = 9.19)	—	Equilibrium distribution (Kd): $Li^+ \gg Ca^{2+} > Mg^{2+} > K^+ > Na^+$	[140]
1D nano $LiMn_2O_4$	1D nano λ-MnO_2	ca. 20 mg g^{-1} (10 mmol L^{-1} LiCl solution, pH = 10.1)	—	K_d: $Li^+ \gg Ca^{2+} > Mg^{2+} > Na^+ > K^+$	[141]
$Li_4Mn_5O_{12}$	MnO_2–$0.4H_2O$	39.6 mg g^{-1} (10 mmol L^{-1} LiCl solution, pH = 10.1)	The Li^+ adsorption capacity of the spherical ion sieve after 55 cycle's adsorption-desorption was 0.4 mmol g^{-1}	The adsorption capacities of other ions were almost zero except for Mg^{2+}; the ratio of Mg/Li was reduced to less than 1 from 746	[54]
$Li_4Mn_5O_{12}$	$H_4Mn_5O_{12}$	49.6 mg g^{-1} (0.1 mol L^{-1} LiCl + LiOH solution)	—	K_d: $Li^+ \gg Mg^{2+} > Ca^{2+} > K^+ > Na^+$	[142]
$Li_{1.}6Mn_{1.6}O_4$	MnO_2-$0.5H_2O$	42.1 mg g^{-1} (initial Li^+ concentration 10 mmol L^{-1}, pH = 10.1)	The Li^+ adsorption capacity reduces from 4.08 mmol g^{-1} to 3.62 mmol g^{-1} after six times	K_d: $Li^+ \gg Mg^{2+} > Na^{2+} > K^+ > Ca^+$	[45]
$Li_{1.6}Mn_{1.6}O_4$	MnO_2-$0.5H_2O$	40.9 mg g^{-1} (seawater)	The Li^+ adsorption capacity is 35.4 mg g^{-1}, and Li^+ desorption rate still reaches 96% at the second cycle operation	K_d: $Li^+ \gg Cg^{2+} > K^+ > Mg^{2+} > Na^+$	[48]
$Li_{1.5}Mn_2O_4$	$H_{1.5}Mn_2O_4$	ca. 15.3 mg g^{-1} (pH = 8.1)	—	400 times higher conc. of Li^+ could be achieved while most of Na^+ remains in artificial seawater that contains 10 ppm of Li^+ and 10,000 ppm of Na^+ by chromatographic separation	[135]
$Li_{1.51}Mn_{1.63}O_4$	$H_{1.36}Li_{0.07}Mn_{1.65}O_4$	34.07 mg g^{-1} (pH = 12.01)	—	—	[140]
$Li_{1.57}Mn_{1.65}O_4$	$H_{1.39}Li_{0.01}Mn_{1.65}O_4$	ca. 37 mg g^{-1} (pH = 12)	—	—	[143]

Table 3.
Classification for some LMO type LISs.

8a-16c-8a-16c channel, what is the structural basis of Li^+ intercalation/deintercalation in $LiMn_2O_4$ spinel [145].

The 1:2 ratio shows a spinel $LiMn_2O_4$ of the two metal cations Li and Mn; although the stoichiometric proportion may be somewhat weakened in some circumstances. For example, in **Figure 7** it is shown that manganese ions in 16d sites can be replaced by lithium ions without changing the entire crystal framework.

Since more lithium ions can be extracted or inserted, the corresponding LIS of the substituted precursor $Li_{1.33}Mn_{1.67}O_4$ (or $Li_4Mn_5O_{12}$) is theoretically a higher lithium capacity than λ-MnO_2. Ammundsen et al. [148] the results of neutron diffraction studies of the lithium reinsertion process are given only for tetrahedral sites and not for octahedral sites, which indicates that the lithium extraction/insertion reaction can be expressed by the equation below:

$$(Li)\,[Li_{0:33}\,Mn_{1:67}]\,O_4 + H^+ \leftrightarrow (H)\,[Li_{0:33}\,Mn_{1:67}]\,O_4 + Li^+ \qquad (1)$$

Another typical lithium-rich precursor to LMO is $Li_{1.6}Mn_{1.6}O_4$ (or $Li_2Mn_2O_5$), which are relevant LIS is $MnO_2{\cdot}0.5H_2O$. Among all available manganese, LISs $MnO_2{\cdot}0.5H_2O$ has the highest theoretical lithium capacity (*ca*. 72.3 mg g^{-1}). With this composition, the ratio of cations and anions (4:5) differs from that of typical spinel compounds (3:4), meaning that additional lithium ions are likely to be found in interstitial regions of the spinel structure with a single-digit arrangement [143]. Chitrakar et al. [47] proposed three hypothetical models through a preliminary Rietveld analysis, since there is still no published structural model for $Li_{1.6}Mn_{1.6}O_4$: (1) $(Li)_{8a}[Li_{0.2}]_{16c}[Li_{0.4}Mn_{1.6}]_{16d}O_4$ site at the of 16c model with excess Li; (2) a $(Li)_{8a}[Li_{0.5}Mn_{1.5}]_{16d}O_{3.75}$ model with oxygen deficiency and (3) a hexagonal lattice model with cation deficiency $(Li_{0.8}\square_{0.2})_{3b}(Mn_{0.8}\square_{0.2})_{3a}O_2$ (the "□" are the free areas in the spinels). The modulation results showed that all models traced the X-ray peaks of the heat-treated sample, but the third model (a hexagonal lattice with a deficit of cations) accurately traced the relative intensity of the X-ray peaks. By Ariza et al. [147] showed that X-ray absorption spectroscopy of $Li_{1.6}Mn_{1.6}O_4$ samples does not result in the complete displacement of the manganese absorption edge after lithium extraction/reintroduction. In addition, the structural arrangement and oxidation state of manganese remained unchanged during lithium extraction and re-administration, confirming the ion exchange mechanism for lithium extraction and re-administration. Thus, there is still some disagreement on the crystal structure of $Li_{1.6}Mn_{1.6}O_4$. Possible future research by scientists should focus on this issue to link the development of LIS to the excellent absorption properties of lithium.

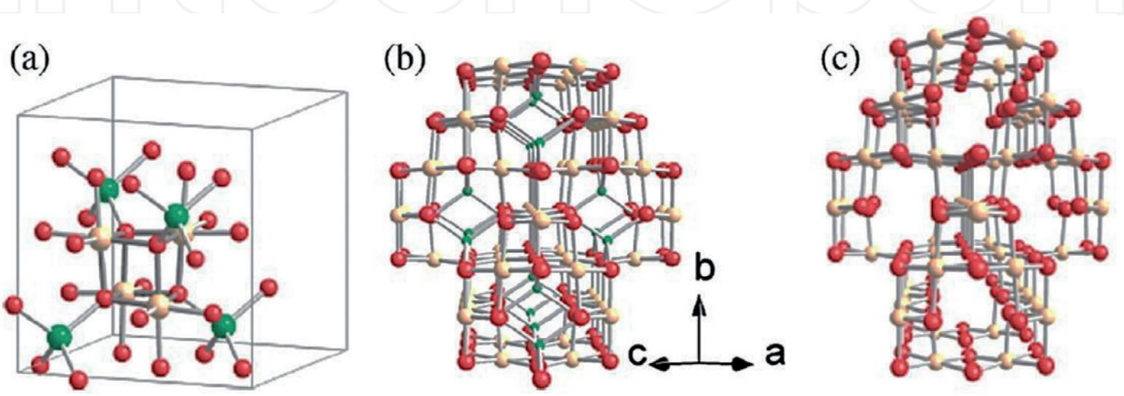

Figure 6.
Promising type (a) cubic core in spinel unit cell $LiMn_2O_4$, (b) $LiMn_2O_4$ of extended three-dimensional frame structure and (c) λ-MnO_2 with voids after Li ions removal. Green, pink and red represent Li, Mn and O atoms, respectively [146].

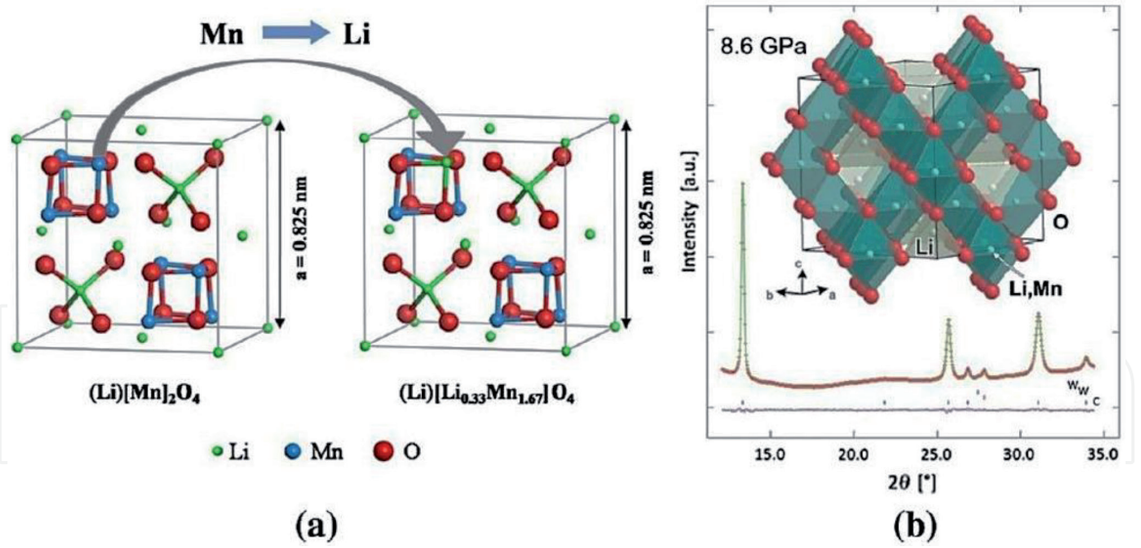

Figure 7.
(a) Cubic spinel lithium manganese oxide quadrants were comparison and (b) recorded under the 8.6 GPa. C, cubic spinel phase (spatial group Fd3m); W, tungsten strip model of polyhedral structure and structure refinement by Rietveld X-ray diffraction powder sample for $Li_{1.33}Mn_{1.67}O_4$ (or $Li_4Mn_5O_{12}$).

7.1.3 The doping modification

Because of the specific configuration of the 3d electron orbit, t_{2g}^3-e_g^1, Mn^{3+} can cause the Jahn-teller effect, which can cause severe distortions in the octahedral structure of MnO_6. This distortion will be accompanied by a decrease in LMO stability and a decrease in the efficiency of the intercalation/deintercalation process of Li^+ [153–157]. Much more seriously in industrial operations dissolving large amounts of manganese in water can lead to water contamination. Consequently, some alloying modifications have been proposed to replace Mn^{3+} with other metal ions, which is more efficient.

In the field of lithium-ion batteries, a wide variety of cation substitution (including Co^{2+}, Ni^{2+}, Cr^{3+}, Mg^{2+}, Al^{3+}, Fe^{3+} and ions of rare earth element) has been applied to inhibit capacity fading and improve electrochemical performance [158–183]. Analogously, modifications of LIS by doping with metal ions to improve the absorption properties of lithium in aqueous solutions are proposed. The effect of $Li_mMg_xMn(III)_yMn(IV)_zO_4$ ($0 \leq x \leq 0.5$) on the dissolution of manganese within acid treatment, the results showed that the adsorption capacity of lithium and the chemical stability of protonated samples increased with the mg/MN ratio studied by Chitrakar et al. [181]. Mild chemical method of Mg^{2+} doped lithium-manganese spinel synthesized by Tian et al. [36]. During the periodic experiment, it was found that the sorption of Li^+ showed a high pH and a dependence profile of the initial concentration. In addition, kinetic experiments have shown that the adsorption process followed by a pseudo-second-order model. Li^+ extraction process in both compound $LiMg_{0.5}Mn_{1.5}O_4$ spinel and $LiZn_{0.5}Mn_{1.5}O_4$ spinel studied by Feng et al. [182, 183]. Discovered that the extraction and insertion of Li^+ are topotaxically through ion exchange mechanisms. In addition, with $LiAlMnO_4$ and $LiFeMnO_4$ spinel Li^+ extraction/insertion reactions in the aqueous phase, also follow the ion exchange mechanisms tested by Liu et al. [184]. $LiM_xMn_{2-x}O_4$ spinel series (M = Ni, Al, Ti; $0 \leq x \leq 1$) and comparison of their lithium reduction properties in aqueous solutions prepared by Ma et al. [185]. Studies have shown that $LiAl_{0.5}Mn_{1.5}O_4$ spinels exhibit relatively high Li extraction coefficient and relatively low Mn and Al extraction coefficients when treated with acid, and

$LiNi_{0.5}Mn_{1.5}O_4$ and $LiTi0_{.5}Mn_{1.5}O_4$ spinels do not exhibit satisfactory Li^+ extraction and adsorption properties because of substantial cell contraction or expansion. By Chitrakar et al. Sb-doped LMO spinel was synthesized for the first time [186]. Samples received $Li_{1.16}Sb(V)_{0.29}Mn(III)_{0.77}Mn(IV)_{0.77}O_4$ was a well-crystallized spinel-type structure, in the following order of affinity K < Na ≪ Li and exchange capacity reaching 5.6 mmol g^{-1} for Li^+. In a subsequent study, a series of Li-Sb-Mn composite oxides with various Sb/Mn molar ratios by solid-state reactions obtained by Ma et al. [187]. Studies have shown that the molar ratio Sb/Mn of composite oxides Li-Sb-Mn is a decisive factor in the identification of their structure and extraction-adsorption properties Li^+. Hereinafter, the acid-treated composite spinel oxide Li-Sb-Mn with a molar ratio Sb/Mn of 0.05 showed in lithium solution a high adsorption capacity of Li^+ 33.23 mg g^{-1}. By Chitrakar et al. the ion-exchange property of iron-doped lithium manganese oxides $Li_{1.33}Fe_xMn_{1.67-x}O_4$ (x = 0.15, 0.30 and 0.40) in Bolivian brine was studied [38]. Studies have shown that the adsorbent with a Fe/Mn ratio of 0.1, obtained by calcining the precursor at 450°C, has the highest extractability of lithium with HCl solution. Finally, from crude brine at a final pH of 2.0, the adsorbent showed lithium absorption of 18.1 mg g^{-1} with an increase in absorption to 28 mg g^{-1} at a final pH of 7.2 after adding 1 mol L^{-1} NaOH l-1 solution to the crude brine.

Study of the description of the LMO-doped spinels, it is obvious that doping modifications can effectively improve the adsorption properties of lithium. Nevertheless, little attention has been paid to refining LIS compared with the great progress of ion-doped manganese oxide spinels in the field of electrochemistry. At present, just several studies of LISs doped with a single metal have been studied. Lithium adsorption property of multicharged ions doped LISs, including several cation-doped, several anion-doped and cation-anion-doped LISs in aqueous solution, still an untouched area for research. Early research of numerous ion-doped $LiMn_2O_4$ showed high capacity retention, high discharge capacity, and lithium ion batteries good cycling performance. This is due to the fact that multiple ions doped $LiMn_2O_4$, have increased structural stability [188–197]. Besides, as cathodes, co-doping has a synergistic effect on increasing the cyclic durability of materials, which can for single ion-doped $LiMn_2O_4$ discourage all factors responsible for capacity loss [198–201]. Similarly, it has been convincingly shown that multiple ion doping has a beneficial effect on improving the regeneration efficiency and absorption capacity of lithium LISs in aqueous solutions. Prospective studies should focus on the synergistic effects of different ions on the reductive properties of lithium.

7.2 About LTO-type LISs

There are currently two categories of LTO-type LISs: layered structure H_2TiO_3 and spinel structure $H_4Ti_5O_{12}$. Albeit the amount of LTO-type LISs is confined, there is great potential to develop these green lithium adsorbents for application in the industry, avoiding water pollution.

7.2.1 Study of layered H_2TiO_3 LISs

The chemical structure of layered H_2TiO_3 is shown in **Figure 8**. From the layered precursor Li_2TiO_3 a layered H_2TiO_3 is obtained. One can better describe as $Li[Li_{1/3}Ti_{2/3}]O_2$ the crystal structure of this precursor; precisely, when metal atoms are placed in octahedral voids the structure can be represented as cubic close packed oxygen atoms. In the structure of Li_2TiO_3 two types of layers form Li and Ti. The first layer (Li) is inhabited only by lithium atoms, while the other layer ($LiTi_2$) occupies Li 1/3 and

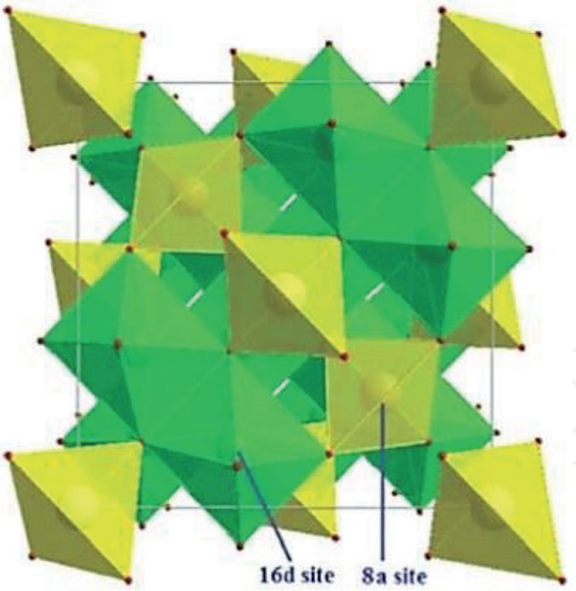

Figure 8.
Crystal structure of $Li_4Ti_5O_{12}$ (yellow tetrahedra represent lithium, and green octahedra represent disordered lithium and titanium) [39]. Reproduced from Ref. [39].

Ti 2/3. In fact, in the structure of Li_2TiO_3, lithium ions in the layers make up 75% of the total amount of lithium, while the surviving 25% are in layers ($LiTi_2$) [53].

Accordingly, whole lithium ions are changed by protons in the layered structure of H_2TiO_3. Accordingly, in early studies, some researchers believed that the structure of H_2TiO_3 was converted from layered Li_2TiO_3 by topotactic substitution of lithium ions by protons. The authors explore the composition of H_2TiO_3 by reviewing the variation among Li_2TiO_3 and H_2TiO_3 and modeling the XRD patterns of $H_xLi_{2-x}TiO_3$ ($0 \leq x \leq 2$), they pointed out that a structure with a layered double hydroxide type with a sequence of $3R_1$ oxygen layers is more acceptable for H_2TiO_3, and H_2TiO_3 can be described as laying charge-neutral metal oxyhydroxide plates [$(OH)_2OTi_2O(OH)_2$] [202]. In advanced research, requires additional experimental testing to confirm the well-honed structure.

In 1988, Onodera et al. first obtained Li_2TiO_3 [203], many kinds of research have been conducted on its electrochemical application [204–208] and in the degradation of pollutants the photocatalytic applications [209–211]. Chitrakar et al. investigated the behavior of ion exchange in salt lake brines [53]. While the rate of adsorption of lithium was relatively slow (it took 1day to reach equilibrium at room temperature), at pH 6.5 the capacity of the Li^+ can reach up to 32.6 mg g^{-1}, that is among the adsorbents of lithium the greatest value is studied in an acidic solution. Besides, H_2TiO_3 has been found to be able to efficiently absorb lithium ions from Na^+, K^+, Mg^{2+} and Ca^{2+} containing competitive cations in brine. With ionic radii exceeding Li^+ (0.074 nm), it is not possible to introduce sites into the LTO adsorbent, since exchange sites have radii sizes Na^+ (0.102 nm), K^+ (0.138 nm) and Ca^{2+} (0.100 nm), which do not allow adsorption due to the large size of the ionic radii. Although the ionic radius of Mg^{2+} (0.072 nm) is close to the ionic radii of Li^+, dehydration of magnesium ions requires high energy to enter the exchange nodes, since the free hydration energy for Mg ($\Delta G^0_h = -1980$ kJ mol^{-1}) is four times greater than for Li ($\Delta G^0_h = -475$ kJ mol^{-1}) [212]. In addition, the Li-Mg separation ratio reached 102.4 on the 8th adsorption cycle, that in salt lake brines represents the excellent separation of Li^+ and Mg^{2+} found by Shi et al. [40]. In designing the orthogonal test, the maximum absorption of lithium by H_2TiO_3 reached 57.8 mg g^{-1} at the optimal state studied by He et al. [213].

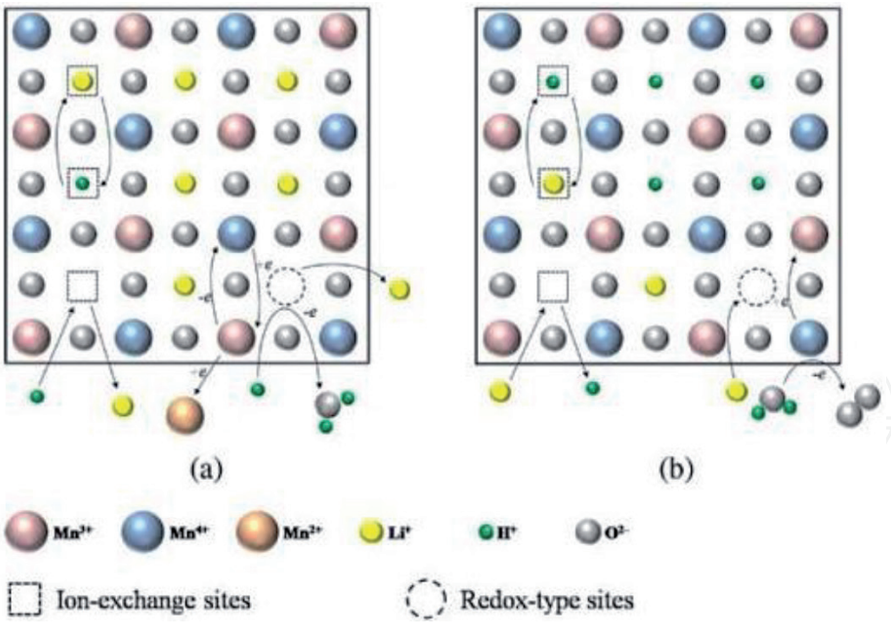

Figure 9.
Schematic representation in spinel manganese oxides by the composite mechanism (a) Li^+ extraction reactions and (b) Li^+ insertion reactions.

7.2.2 Study of spinel titanium oxides

The LTO-type LISs represent the different types of spinel titanium oxides that are derived from spinel precursors $Li_4Ti_5O_{12}$. In the field of lithium-ion batteries, spinel $Li_4Ti_5O_{12}$ is seen as one of the most promising future anode candidates for large-scale lithium-ion batteries used for hybrid electric vehicles or power electric vehicles. Through high efficient due to high potential during charge and discharge of about 1.55 V (vs. Li/Li^+), good cycle property and good heat resistance and security [214–216]. There is great potential for the development of spinel $Li_4Ti_5O_{12}$ in the extraction of lithium from aqueous solutions. High capacity lithium has on LIS ($H_4Ti_5O_{12}$) and due to stronger Ti–O bond cycling performance is better than that of manganese-type LISs. Withal, $Li_4Ti_5O_{12}$ has an identical chemical structure like $Li_4Mn_5O_{12}$ (**Figure 9**).

Nevertheless, as far as we know, there are currently very limited reports on the property of extracting lithium from $H_4Ti_5O_{12}$. A three-dimensionally ordered precursor to nano $Li_4Ti_5O_{12}$ using colloidal PMMA crystal matrices developed by Dong et al. [217]. High selectivity for Li^+, 56.81 mg g^{-1} showed corresponding ion sieve and good stability to acid. LISs $H_4Ti_5O_{12}$ with nanotube morphology synthesized by an ordinary two-stage hydrothermal process presented a lithium capacity of 39.43 mg g^{-1} in a 120 mg L^{-1} in lithium solution reported by Moazeni et al. [39].

8. Conclusions

Lithium is one of the rarest metals with various applications and the demand for lithium will increase with the ever-increasing use of electric and electronic devices and hybrid electric vehicles.

Therefore, the search for ways to obtain lithium from water sources suitable for the production of lithium compounds is a serious and very important problem.

Various methods have been given in the literature for lithium recovery from brines, seawater and geothermal water: including precipitation, solvent extraction, selective membrane separation, liquid-liquid extraction, ion exchange adsorption, electro dialysis and so on.

The recovery of lithium by the absorption method shows promising results for future production. Because of the adsorption method, evaporation, crystallization process can be avoided. That is why it is necessary to develop and recommend a technically and economically feasible, environmentally friendly and sustainable process.

Scientists and manufacturers are faced with the task to solve several problems: the ion sieve has a relatively low ion exchange capacity and weak stability; lithium absorption reaches from 16 to 26–28 mg g^{-1}, the theoretical adsorption capacity is 54 mg g^{-1}; dissolution of sorbents. Weight loss was observed in almost all compositions; low stability during cycling; the appearance of secondary waste in the regeneration of acids; the process takes a long time.

To solve this problem, scientists of the world have carried out many scientific works to improve the stability of sorbents, increase the absorption capacity, selectivity, acceleration of sorption time, for this purpose, many methods were used, including organic chemicals, synergies, binders, various composites. But none of them makes it possible to industrialize the method of lithium adsorption. That is why there is still a goal to find ways to improve the method of lithium adsorption. Lithium adsorption extraction may be an alternative option to meet future demand, energy sustainability, environment and circular economy.

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