Due to the ubiquitous presence of lithium-ion batteries in portable applications, and their implementation in the transportation and large-scale energy sectors, the future cost and availability of lithium is currently under debate. Lithium demand is expected to grow in the near future, up to 900 ktons per year in 2025. Lithium utilization would depend on a strong increase in production. However, the currently most extended lithium extraction method, the lime-soda evaporation process, requires a period of time in the range of 1–2 years and depends on weather conditions. The actual global production of lithium by this technology will soon be far exceeded by market demand. Alternative production methods have recently attracted great attention. Among them, electrochemical lithium recovery, based on electrochemical ion-pumping technology, offers higher capacity production, it does not require the use of chemicals for the regeneration of the materials, reduces the consumption of water and the production of chemical wastes, and allows the production rate to be controlled, attending to the market demand. Here, this technology is analyzed with a special focus on the methodology, materials employed, and reactor designs. The state-of-the-art is reevaluated from a critical perspective and the viability of the different proposed methodologies analyzed.

1. Introduction

Although lithium has been used as a raw material in various production sectors, such as glass, ceramics, and aluminum, in the last two decades its importance has raised due to the spread of Li-ion batteries in portable devices, electromobility, and large-scale energy storage.[1,2] Lithium production grew steadily year after year passing from 16.4 thousand metric tons of contained Li at the beginning of the 20th century to 39.3 in 2016 (Figure 1). It doubled in roughly 16 years. However, from 2016 on, the production sky-rocketed reaching 85 thousand metric tons in 2018, more than double the amount of two years before. Although the large increase in production, the price for battery grade lithium carbonate doubled passing from 8650 to 17000 $ per metric ton in the same time span (Figure 1). This followed the large increase in electric-vehicle fleet which passed from 3.1 million vehicles in 2017 to more than 5 millions in 2018.[3]

Still, due to the envisaged expansion of these technologies, Li demand is expected to grow further in the near future, up to 900 ktons per year by 2025 (three times higher than 2018).[8] with a consequent increase of its price, which has already doubled in the last two years.[9,10] Global sources of Li are mainly divided into ores and brines. Various published reviews describe the extraction methods from ores,[11,12] which require several hydrometallurgical steps. It is reported that the production cost of Li from minerals is around twice the one from brines.[12] Moreover, according to some estimations, the brine sources are approximately double than the mineral ones.[13] Taking into account only the amount of Li needed for powering electric...
vehicles, it is predicted that in the next 20 years Li market request will require from twice up to six times the capability of its mineral sources.\textsuperscript{[14]}

Although Australia spodumene mining in 2018 represents the largest producer of lithium, more than 45% of all identified resources are located in the so-called “Lithium Triangle,” a geographic area at the borders of Chile, Bolivia, and Argentina,\textsuperscript{[4,15]} rich of salt lakes with Li concentrations from 220 to 3800 mg L\textsuperscript{−1}.\textsuperscript{[16,17]} The current process for the extraction of Li is an evaporation-based technology, called the lime-soda evaporation process. This method consists of pumping the brine from the lake into some large open-air shallow tanks, where the brine concentration goes from 300 to 5000 ppm in Li by means of solar evaporation. Meanwhile, most of the unwanted cations spontaneously precipitate. Species that do not precipitate during the evaporation must be removed with post chemical treatments, depending on the type and amount of species. For example, magnesium cations are eliminated through a precipitation step with lime, and borates are instead removed through liquid–liquid extraction. Once a high concentrated Li solution is reached, Li\textsubscript{2}CO\textsubscript{3}, the final product in the market, is obtained by precipitation thanks to the addition of sodium carbonate.\textsuperscript{[12,18]}

This process has low costs and high profits, but it has also many disadvantages. First, it is very slow, as it is based on solar evaporation. The required time span between the pumping of brine and the Li carbonate production is about 1–2 years. It is reported that the Li global production capacity from brine by means of lime-soda evaporation is 120.5 ktons per year,\textsuperscript{[12]} which will be soon exceeded by the market demand.\textsuperscript{[8]} Second, it consumes an enormous amount of water. The production of one ton of Li\textsubscript{2}CO\textsubscript{3} requires the evaporation of half a million liters of brine.\textsuperscript{[12]} This problem is exacerbated by the fact that most of the brine lakes are located in desert areas. Moreover, since the process is based on solar evaporation, its efficiency and rate strongly depend on weather conditions, such as rainfall and wind.\textsuperscript{[19]} Finally, a large amount of waste is produced as a consequence of the chemical treatments that follow the initial evaporation.

Therefore, alternative methods of Li extraction have attracted great attention in the last 20 years. The mining of valuable metals (not just Li, also other like Co, Au, Ag, U…) from seawater,\textsuperscript{[20–22]} minerals,\textsuperscript{[23]} spent,\textsuperscript{[18,24,25]} and brines\textsuperscript{[12,18,23,26,27]} have been summarized in a considerable number of reviews in recent years. Several methods like evaporation, adsorption, precipitation, extraction with solvents or chelating materials, chromatography, and electro dialysis have been described as possible alternatives to extract lithium from brines. Among these techniques, it is worth mentioning the precipitation of Li from brines as aluminate by adding aluminum salts;\textsuperscript{[20,29]} the adsorption
on Li selective materials, such as MnO₂,[30,31] Li₁.₆Mn₁.₆O₄,[32] H₂TiO₃,[33,34] and H₁.₆Mn₁.₆O₄,[35] and the liquid–liquid extraction with various organic solvents such as diethyl ether or alcohols.[16–38] In general, these methods have good selectivity and recovery yield, but they often require prior brine treatment to improve the efficiency, such as modification of brine pH. Moreover, postprocesses, involving the use of large volumes of chemicals, are needed for regenerating the active materials. Despite the emerging interest of electrochemical methods for Li recovery, this technology has been briefly mentioned in two general reviews.[12,26] He et al.[26] described 11 references while Wu et al. just mentioned one article based on spent.[39]

As Garret[16] described, a large variety of brines in terms of Li and other components can be found in brines. A purity of lithium as high as possible would be the best case scenario for electrochemical extraction, however in most of the brines this is not the case, and the lithium purity is relatively low. One of the main advantages of electrochemical recovery is its versatility, which allows handling brines with different components and concentrations by changing the electrochemical input. It has been efficiently proven with solutions with concentrations ranging from 0.5 to 18 230 mg L⁻¹.[16] Some papers[40] have even suggested that the electrochemical extraction could exploit sea water as source solution, with a Li concentration as low as 0.17 mg L⁻¹. Such a source is attractive for its abundance and availability. The target of exploiting sea water seems to be beyond the practical feasibility. Rather, the technique can be applied to concentrated sea water brines that are widely available as by-products from salterns and desalination plants; such source solutions have a Li concentration around or above 7 mg L⁻¹. Thus the main target of electrochemical techniques is the exploitation of sources in the range of 7–350 mg L⁻¹, which also include widely available geothermal sources and water obtained as a by-product of gas and oil extraction. Herein, we summarize and analyze from a critical point of view the last advances in the electrochemical methods employed for the lithium extraction from sources in this range of concentrations.

2. Li Extraction by Electrochemical Methods

At the early 1990s, Kanoh et al. carried out for first time an electrochemical capture of Li cations from a source solution into a battery material.[41,42] The capturing process was based on intercalation of Li, which is the most spread working mechanism of rechargeable Li-ion batteries. They used spinel λ-MnO₂ as working electrode and a Pt wire as the counter electrode, on which the oxygen or hydrogen generation took place. However, this method has the disadvantage that water splitting, a high cost process, is occurring in parallel to the lithium recovery. The capturing and release processes can be summarized as

\[
2\lambda-MnO_2 + Li^+ + 3/2H_2O \rightarrow LiMn_2O_4 + 1/4O_2 + H_3O^+ \quad (1)
\]

\[
LiMn_2O_4 + H_2O^+ \rightarrow 2\lambda-MnO_2 + 1/2H_2 + H_2O \quad (2)
\]

In 2012, inspired by the so-called “desalination battery” and “mixing entropy battery,”[43,44] Pasta et al. proposed to capture together with lithium ions also the anions, chlorides, through the following capture and release steps (see Figure 2)

\[
FePO_4 + LiCl + Ag \rightarrow LiFeO_4 + AgCl \quad (3)
\]

\[
LiFePO_4 + AgCl \rightarrow FeO_4^2- + Ag + LiCl \quad (4)
\]

Figure 2. a,b) Li recovery from brines by using λ-MnO₂ as a Li⁺-capturing electrode and Ag as a Cl⁻-capturing electrode (a) or NiHCF as Li exclusion electrode (b). a,b) Adapted with permission.[47] Copyright 2016, Wiley-VCH.

Recently, this technology was renamed with the term electrochemical ion pumping.[40,45–51] It is clear that the electrochemical ion pumping requires less energy, as it involves only entropic terms and minimizes the enthalpic ones, connected with the breaking and formation of chemical bonds.
Other possible configurations based on the concept of the electrochemical ion pumping involve the use of lithium-excluding counter electrodes, which then work through the following capture and release steps:

\[
\text{FePO}_4 + \text{LiCl} + \text{M}_\text{NiFe(CN)}_6 \rightarrow \text{LiFeO}_4 + \text{M}^+ \text{Cl}^- + \text{MNiFe(CN)}_6 \quad (5)
\]

\[
\text{LiFePO}_4 + \text{KNiFe(CN)}_6 + \text{KCl} \rightarrow \text{FeO}_4^+ + \text{LiCl} + \text{K}_2\text{NiFe(CN)}_6 \quad (6)
\]

By using the lithium-exclusion method, the thermodynamic energy cost is even lower, because it does not involve any more the mixing entropy energy, but only a small amount of energy related to the difference in solvation of the lithium and the cation \(M^+\).

In general, the electrochemical ion pumping consists of four steps (Figure 2): i) in the first step, Li cations from a feed electrolyte, an artificial brine, are selectively intercalated in a Li-capturing electrode by applying a current; ii) in the second step, the solution is exchanged with a recovery solution where Li will be released; iii) in the third step, the Li cations are released into the recovery solution, by switching the current direction; and iv) in the fourth step, the Li brine is flushed again in the cell and the cycle can start from the beginning. The Li concentration and purity of the recovery solution increase by repeating the cycles.

Other similar methods incorporated an anion exchange membrane (AEM) between the two compartments of the reactor (Figure 3). The electrodes employed and steps required are equivalent to those described above but in this case the charge neutrality of this system is balanced by the transfer of anions through the AEM. These two methodologies can be modified by the substitution of the faradaic type electrodes by capacitive materials, but in such case, this technique is closer to electroassisted adsorption methods than electrochemical ion pumping processes. Finally, electrodialysis was employed for the recovery of Li from different sources (brines and seawater). It based on the use of a selective membrane through which only the \(\text{Li}^+\) ions permeates. The electrodes employed were commonly metal pieces without intercalation or selectivity properties.

The main advantage of all these methods is that the driving force for the capture of lithium is the application of the current, meaning that no other chemical species are needed to regenerate the active material. Although the capacity of the battery materials is not much different from the one of the adsorption materials used in the past (around 30–35 mg g\(^{-1}\)), the time required for capturing the same amount of Li is much lower than in the adsorption process. This is again a direct consequence of the application of the current to the electrode, which enhances the capturing rate of Li. On the other hand, the porosity and hygroscopic properties of the materials limits the final Li concentration, as the solution adsorbed into the electrodes will mix at each cycle with the enriched Li solution. However, this problem can be limited by flushing and utilizing a cell design with small dead volumes and a compact electrode stack.

Here, we focus on Li recovery methods based on faradaic electrodes. Their higher selectivity compared to capacitive and electrodialysis techniques, superior recovery rates than adsorption process, and greater versatility (most of the materials employed for Li-ion batteries could also be employed for these recovery processes) have made them much more attractive for the scientific community as manifested by the continuously growing number of publications dedicated to them, especially in recent years.

### 3. Evaluation of the Li Recovery Methods

Once the different Li recovery methods based on Li-ion selective electrodes are described, we also need to address the different methodologies employed for their evaluation as a recovery process. The Li-ion selectivity toward other cations (also named cocations) of the Li-capturing electrode (\(\alpha_{\text{Li}}\)) gives an idea of how much Li-ion could be incorporated from the brine source without cointercalating other cations and it has been calculated as the ratio of concentration of Li (\(C_{\text{Li}}\)) and the concentration of a secondary cations (\(C_{M}\), mainly Na\(^+\), K\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\)) after one full recovery cycle in the recovery solution:[45–48,60,61]

\[
\alpha_{\text{Li}} = \frac{C_{\text{Li}}}{C_{M}}
\]

It is directly dependent on the concentrations of cocation in the recovery solutions and indirectly dependent on the concentrations of ions in the brine source. Higher concentrations of cocations would cause an increment of cointercalation of cocation and a decrease of the value of \(\alpha_{\text{Li}}\). This implies that for a proper evaluation of the viability of Li recovery methods, source...
solutions with similar concentrations to brines should be used. This methodology has a critical limitation: in order to compare different studies using the same Li-capturing electrode, source and especially recovery solutions have to be similar, which is not often the case in literature. The Li selectivity has also been calculated as the ratio of the distribution coefficients (\(K_D\)) of Li-ion with respect to other cation (\(K_{D_m}\)) from the brine solution to the electrode material\(^{[62,63]}\)

\[
\alpha_{Li} = \frac{K_{D_{Li}}}{K_{D_m}} \tag{8}
\]

Meanwhile, the distribution coefficients (\(K_D\)) were determined based on the insertion capacity (\(Q_f\)) of the lithium-capturing electrode with respect to all cations

\[
K_D = \frac{Q_f}{C_f} \tag{9}
\]

where \(Q_f\) is calculated based on the initial (\(C_0\)) and final (\(C_f\)) concentration of the cation in the brine with a known volume (\(V_f\)) and mass of material (\(m\))

\[
Q_f = \frac{(C_0 - C_f)}{m} V_f \tag{10}
\]

Although the insertion capacity of the material, a parameter that allows comparing these methodologies with liquid–liquid extraction, is correctly determined (moles of Li-ion exchanged per gram of active material), its use to evaluate the selectivity of the material gives rise to some practical problems. In fact, while \(Q_f\) for lithium can be easily calculated because a great variation in lithium concentration in the brine can be expected, the same does not hold true for the other cations. A very small fraction of their total amount is removed during capturing, giving rise to large errors in the calculation of \(Q_f\). If \(Q_f\) were to be determined from the concentrations in the recovery solution, care should be taken in the assumption of whether intercalation/deintercalation processes for all the cations are totally reversible, which is often not the case.

Another key parameter to evaluate the effectiveness of a Li recovery method is associated with the purity of the recovery solution through \(A_{Li}\), the total selectivity coefficient

\[
A_{Li} = \frac{C_{Li}}{\sum C_M} \tag{11}
\]

where \(C_M\) is the concentration of any cation in solution, including Li. Equation (11) is related to Equation (7) through a sum of inverses. In order to reach an efficient industrial chemical treatment and production of \(\text{Li}_2\text{CO}_3\), solutions with purities as high as 99% are required. Both Equations (7) and (11) are directly calculated from the analysis of the recovery solution and hide the effect of concentrations in the brine solution on the recovery. The separation coefficient or separation factor, SF, of Li-ion to a relative cation M can be calculated from the ratio of their molar concentrations at the recovery and source solutions

\[
SF = \left(\frac{C_{Li}}{C_M}\right)_r / \left(\frac{C_{Li}}{C_M}\right)_f \tag{12}
\]

This factor represents the improvement of the Li concentration by the recovery process and it is equivalent to a comparison of Li purity in the recovery and source solutions. Although SF gives a straightforward idea of how many times the recovery cycle should run in series before reaching the desired purity, it still strongly depends on the characteristic of the brine solution.

The main drawback of the electrochemical methods is the need for electricity for the extraction process that is not necessary in the case of the lime-soda evaporation process. The energy required per mole of recovered Li is given by the ratio of the circular integral of the voltage profile with respect to the charge (\(W\)) and the amount of Li-ion in the recovery solution

\[
W = \frac{\Delta E dq}{V C_{Li}} \tag{13}
\]

In an equivalent manner, when a constant voltage was applied the energy has been calculated as follow

\[
E_{sec} = \frac{M_{Li} U \int_{t_0}^{t_f} I(t)dt}{3.6 E_{w} w} \tag{14}
\]

where \(E_{sec}\) is the energy consumption (Wh mol\(^{-1}\)), \(M_{Li}\) is the molar mass of Li (g mol\(^{-1}\)), \(U\) is the voltage applied (V), \(I\) is the current during the process (A), \(t\) is the reaction time (s), \(E_{w}\) is the extraction capacity of the Li, and \(w\) is the effective mass of the electrode.\(^{[64]}\) This value must be as small as possible to make this methodology competitive with the current extraction methods. Additionally, the mechanical energy required for moving the electrodes or the hydraulic energy for pumping the brine and the recovery solution has to be added (see Section 6).

The coulombic efficiency is described as the percentage of the current applied that is effectively used to extract Li-ion and it is expressed as follow

\[
\eta_{Li} = \frac{FE_{w} V}{Q} \times 100 \tag{15}
\]

where \(F\) is the Faraday constant, \(V\) the volume of the recovery cell, and \(Q\) the total charge flow during the Li extraction step. It has also been estimated from

\[
\eta_{Li} = \frac{F \cdot E_{w} \cdot w}{10 M_{Li} \int_{t_0}^{t_f} I(t)dt} \times 100 \tag{16}
\]

The efficiency is especially affected by two parameters: firstly, how selective is the capturing material, (an electrode that intercalates a large amount of unwanted cation or provides secondary reactions would display a low coulombic efficiency); secondly, the intrinsic reversibility of Li-ion intercalation reaction (if a part of the lithium remains trapped into the crystal structure of the electrode it will not be transferred to the recovery solution). The coulombic efficiency is commonly measured in batteries also as the ratio of the discharging and charging capacities. Its evolution with the number of cycles is not in general studied in the lithium recovery process although it plays a critical role in the potential...
applicability of the process. Finally, the concentrations of the feed solution differ largely between studies, this makes difficult the comparison between publications. It would be of great advantage if the scientific community could reach an agreement on the use of a standardized brine for analyzing the lithium recovery properties of a novel material, mainly the selectivity (we propose here a solution mimicking the Atacama brine, see brine 2 in Table 5).

4. Li Intercalation Electrodes

The materials employed heretofore as lithium recovery electrodes are common to those utilized as cathode electrodes in Li-ion batteries, which ensure their capacity of extracting/inserting lithium. Their Li-ion (de-)insertion mechanisms, theoretical and practical capacities, reduction/oxidation potentials or even the different methodologies required to improve their electrochemical performance has been studied in detail. Extensive knowledge of their properties has made them the ideal candidate as a lithium-selective electrode owing to the fact that, in principle, the same parameters that rule their performances as Li-ion cathode materials would be favorable for their use as Li-selective electrodes.

4.1. Olivine LiFePO$_4$/FePO$_4$

Lithium iron phosphate (LiFePO$_4$, LFP) is a common material for the cathode of Li-ion batteries. Introduced in the 1990s [65] it has ordered olivine structure (Figure 4) shown by the characteristic XRD peaks [10,66–71]. It possesses 1D diffusion channels that grant facile Li ion insertion into octahedral sites with a formal reaction

$$\text{FePO}_4 + \text{Li}^+ + e^- \leftrightarrow \text{LiFeO}_4 \quad (17)$$

Its use in aqueous Li-ion batteries was already suggested in 2006 [66] and makes it a preferential candidate for the electrochemical recovery of Li from natural solutions. Also, Li intercalation reaction shows remarkable stability in water solution as shown by Zhao et al. [72] (Figure 5).

Its use for Li recovery was first proposed by Pasta et al. [45] They showed that iron phosphate could selectively recover Li from a 5 M NaCl solution. Li concentration was between 0.5 and $50 \times 10^{-3}$ M, which gave an initial ration Li/Na of 1/100, 1/1000, and 1/10 000. The intercalation electrode was made of carbon-coated iron phosphate, carbon black, poly(vinylidene fluoride) slurry supported on a carbon cloth electrode similarly to Li-ion battery electrodes. They employed a three-electrode setup for the intercalation step and they concentrated the Li into a 200 µL recovery solution, in both cases using a silver slurry electrode counter electrode, all the experiments were performed at a current density of 0.5 mA cm$^{-2}$. The final compositions of the recovery solutions are shown in Table 1. The authors could reach a ratio Li:Na equal to 5:1 in the case of $50 \times 10^{-3}$ M LiCl and a selectivity $\alpha_{\text{Li}}$ above 500 in all cases.

They found that although the process is theoretically energetically spontaneous, the energy was consumed due to the losses connected with the solution resistance and with the kinetics of the electrodes. Nevertheless, the electrochemical recovery of Li was energetically more efficient than what suggested by Kanoh et al. [42] A similar setup was used by Trócoli et al. [46] who also studied the influence of other cations and of the current density on the recovery cycle. Their results are summarized in Tables 2 and 3 and show that in 0.1 M equimolar solutions of Li with other cations the selectivity was above 240 for Na and K, but only 34 for...
Mg. However, the selectivity went above 15 000 in the case of 5 mA cm\(^{-2}\) in artificial brine resembling the composition of the Salar de Atacama, Chile. At low current density (0.05 mA cm\(^{-2}\)) all the selectivity coefficients were well above 60 000, while they went to 916 for Mg and 58 for Na at the highest current density (5 mA cm\(^{-2}\)). However, although the maximal selectivity was found at 0.05 mA cm\(^{-2}\), the coulombic recovery efficiency was only 68%. This was due to the lengthy duration of the experiment compared to higher current densities, which made oxygen reduction unavoidable. On the other hand, the coulombic efficiency was 92.9% in the case of 0.5 mA cm\(^{-2}\) and decreased one more time in the case of 5 mA cm\(^{-2}\) as an effect of the coin-tercalation of the other cations.

Trócoli et al. also improved the original recovery method changing the C1-capturing counter electrode with an ion-exchange one, but still keeping iron phosphate as Li-interca-lating material\cite{46,48}. They showed that this strategy leads to higher selectivity and purity at the expense of higher energy consumption. Further details on this secondary electrode are reported in Section 5.4.

Zhao et al.\cite{72} studied the behavior of an iron phosphate electrode in solutions with different cations using two LFP electrodes and an ion exchange membrane (see Section 5.5 for details). In their first study, they focused on a solution with Li and magnesium where the Li concentration was 220 mg L\(^{-1}\) (31.7 \(\times\) 10\(^{-3}\)) and a ratio of Mg/Li between 10 and 60 weight ratio (2.8 to 17.1 molar ratio)\cite{72}, mimicking the compositions of some salt lakes in West China. All the experiments were performed through potentiostatic control. They employed an anion exchange membrane, similar to Figure 3, but in this case with two iron phosphate electrodes, one in the brine solution and one in the recovery solution. The electrodes were prepared from carbon-coated iron phosphate similarly to Pasta et al.\cite{45}.

They observed that in Mg solution the anodic peak in the cyclic voltammetry of iron phosphate disappears and that there is no cathodic peak, while in mixed Mg-Li solution the anodic peak decreases and the cathodic peak shift positively. Interestingly, in real brine solutions, LiFePO\(_4\) would stabilize its performances retaining 87% of its initial intercalation capacity after 30 cycles (Figure 6). By recovery tests, they observed that LFP could show 94% of its theoretical capacity in a solution containing only Li, but it would lose circa 20% of this capacity when also Mg\(^{2+}\) was present in solution. Besides, they observed that during the deintercalation step in the recovery solution Li\(^+\) was released first and Mg\(^{2+}\) came later. Operation at lower cell voltage (0.8 V) showed better performance in terms of selectivity. Their final selectivity was \(K_{Li,Mg} = 12\), however since Mg\(^{2+}\) deintercalated after Li\(^+\) their selectivity could be twice as high if the recovery would be interrupted earlier.

A similar study was extended to Na\(^+\) and K\(^+\)\cite{73}. The authors observed that in a cyclic voltammetry using a Na\(^+\) solution, the cathodic peak moved 400 mV more negative and the anodic peak split in two. However, in a K\(^+\) solution, they did not observe any peak, suggesting that the intercalation of Na\(^+\) is possible, but more hindered than that of Li\(^+\), contrary to that of K\(^+\), which does not happen. Recently, olivine Na iron phosphate (NaFePO\(_4\)) has been proposed as Na-intercalation electrode. The material was obtained by electrochemical displacement from LiFePO\(_4\)\cite{74–76}. This implies that at certain conditions Na\(^+\) could be incorporated in the structure.

Through optimization of the cell voltage, the authors could pass from a weight ratio of 493 Mg/Li and 16.7 Na/Li (141 and 5 molar ratio) to a final ratio of 0.3 and 0.19 for Mg and Na, respectively (0.085 and 0.057 molar ratio). This gives a selectivity ratio \(\alpha_{Na} = 1640\) and \(\alpha_{Li} = 87.9\), in contrast to previous studies where \(\alpha_{Na}\) was in general lower than \(\alpha_{Li}\). Further studies on the cell voltage showed that the optimal voltage is

| Table 1. Concentrations of Li\(^+\) and Na\(^+\) in the recovery solutions. Adapted from ref. [45]. |
|-----------------|-------------------|-----------------|
| Initial [Li]/[Na] | Li\(^+\) in recovery solution [\(\times 10^{-3}\) v] | Na\(^+\) in recovery solution [\(\times 10^{-3}\) v] |
| 1/100 | 115 | 21 |
| 1/1000 | 52 | 91 |
| 1/10 000 | 27 | 103 |

| Table 2. Selectivity values of LiFePO\(_4\) versus different cations. Adapted from ref. [46]. |
|-----------------|-----------------|-----------------|
| Current [mA cm\(^{-2}\)] | \(\alpha_{Na}^{Li}\) | \(\alpha_{K}^{Li}\) | \(\alpha_{Mg}^{Li}\) |
| 0.05 | 17 469 143 | 65|190 |
| 0.5 | 20 10 | 127 286 | 205 |
| 5 | 58 | 66 857 | 916 |

Through optimization of the cell voltage, the authors could pass from a weight ratio of 493 Mg/Li and 16.7 Na/Li (141 and 5 molar ratio) to a final ratio of 0.3 and 0.19 for Mg and Na, respectively (0.085 and 0.057 molar ratio). This gives a selectivity ratio \(\alpha_{Na} = 1640\) and \(\alpha_{Li} = 87.9\), in contrast to previous studies where \(\alpha_{Na}\) was in general lower than \(\alpha_{Li}\). Further studies on the cell voltage showed that the optimal voltage is

![Typical CV curves of LiFePO\(_4\)/FePO\(_4\) obtained in brine. Reproduced with permission.\cite{72} Copyright 2013, Elsevier.](image-url)
0.25 V and repeated recovery cycling could bring the final concentration of Li in the recovery solution to $6.23 \times 10^{-3}$ M.[77]

Kim et al. use a FePO$_4$ electrode coupled with a I$^-$/I$_3^-$ counter electrode to recover Li from a simulated artificial seawater solution.[78] They did not perform a full recovery, but they focused on the intercalation step and they found that a mussel-inspired polydopamine coating of the electrode increased the amount of Li recovered. Based on elementary analysis of the electrodes’ material, they estimated that the selectivity improved by a factor of 20. Based on the atomic ratio in the electrodes’ material they got a selectivity ratio $\frac{Na}{Li} = 263$ without polydopamine coating, which is similar to that reported by Pasta et al. ($\frac{Na}{Li} = 548$ for Li/Na ratio of 1/100), although made in 5 M NaCl, and a selectivity ratio $\frac{Na}{Li} = 4300$ with the polydopamine coating. Differently than in the previous cited attempts, Intaranont et al. proposed to recover Li$^+$ through the chemical reaction of iron phosphate directly in solution[79]

$$2 \text{Li}^+ + 2\text{FePO}_4 + 2\text{S}_2\text{O}_8^{2-} \leftrightarrow \text{S}_2\text{O}_8^{2-} + 2\text{LiFePO}_4$$  \hspace{1cm} (18)

where thiosulfate was used as a mild, water-soluble reducing agent. The reaction was conducted for 24 h. Although this method is not strictly an electrochemical approach but requires the use of chemical reagents, we included because of the use of iron phosphate. Subsequently, Li could be recovered from Li iron phosphate through oxidation with potassium persulfate

$$2\text{LiFePO}_4 + \text{K}_2\text{S}_2\text{O}_8 \leftrightarrow 2\text{FePO}_4 + \text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4$$  \hspace{1cm} (19)

A summary of all the results for LiFePO$_4$ is reported in Table 4.

### 4.2. Spinel LiMn$_2$O$_4$\textendash MnO$_2$

LiMn$_2$O$_4$ forms a spinel structure (Fd3m group), with a cubic close-packed array in which oxygen ions occupy the 32 sites, Mn ions are located in the octahedral 16d sites and Li ions are in the tetrahedral 8a sites (Figure 7).

Since Thackeray et al. in the early 1980s[81] proposed this spinel oxide as an intercalation cathode for Li-ion batteries, a tremendous effort has been overtaken in order to overcome its drawbacks, mainly Mn dissolution in the electrolyte and poor electronic conductivity. Morphology and particle size control, surface modification, and doping have been the main methodologies studied.[82–84] LiMn$_2$O$_4$ (LMO) is commonly

![LiMn$_2$O$_4$ Crystal Structure](https://isicad.org/short27858.png)
employed in blended cathodes for rechargeable automotive batteries because of its low cost and excellent rate capability.\(^{85,86}\) Li ion can be inserted in the \(\lambda\)-MnO\(_2\) cubic phase by a topto-
tactic insertion reaction with isotropical expansion of the cell to form LiMn\(_2\)O\(_4\).\(^{87}\) The characteristic two peaks in the I versus V profile in cyclic voltammetry (CV) and the two plateaus observed in constant current measurements (Figure 8) are attributed to the occupancy by Li\(^+\) of two sets of nonequivalent 8a sites with a transition composition close to Li\(_{0.5}\)Mn\(_2\)O\(_4\) (reaction 20)

\[
2\lambda\cdot\text{MnO}_2 + 0.5\text{Li}^+ + 0.5\text{e}^- \leftrightarrow \text{Li}_0.5\text{Mn}_2\text{O}_4
\]

(20)

Recently LiMn\(_2\)O\(_4\) has also been used as a cathode electrode in aqueous rechargeable Li-ion batteries,\(^{88-97}\) and in hybrid dual metal ion rechargeable batteries that face the same issues as in Li recovery technologies such as coinstitution of ions and blocking of adsorption sites.\(^{98,99-103}\) These problems were already anticipated in the pioneering articles of Kanoh et al.\(^{41,42}\) where the electrochemical performance of LiMn\(_2\)O\(_4\) in aqueous media and its application for the recovery of Li\(^+\) from geothermal water was analyzed. They used a three elec-
trodes cell with \(\lambda\)-MnO\(_2\) as Li\(^+\) selective electrode, calomel, and Pt-wire were employed as reference and counter electrodes, respectively. The properties of Pt as a counter electrode as well as the rest of the materials utilized as counter electrodes are evaluated in Section 5. By measuring the equilibrium potential of the Pt/\(\lambda\)-MnO\(_2\) electrode in LiCl solution with and without NaCl or KCl, Kanoh et al. concluded that among the tested ions, \(\lambda\)-MnO\(_2\) responds only to Li\(^+\) and the redox insertion/extraction takes place for Li\(^+\) ions and not for other alkali metals ions. A first selectivity coefficient of Li\(^+\) against Na\(^+\) or K\(^+\) was calculated by the fixed interference method (method 1), with values of log \(K_{\text{Li,Na}}^{\text{int}} = -4.8\) against Na\(^+\) and log \(K_{\text{Li,K}}^{\text{int}} = -4.6\) and K\(^+\), the smaller the value of \(K_{\text{Li,Na}}^{\text{int}}\) the greater the material selectivity. Kanoh et al. calculated superior selectivity toward Na\(^+\) than toward K\(^+\). In addition, the selectivity toward H\(^+\) (\(K_{\text{H,K}}^{\text{int}} = +1.9\)) was evaluated from the potential versus pH curve., \(\lambda\)-MnO\(_2\) responds to H\(^+\) as well as to Li\(^+\) but the influence of H\(^+\) is negligible between pH 5 and 9 in a solution with a Li\(^+\) concentration above 1 \(\times\) 10\(^{-3}\) M. The possible cointercalation of H\(^+\) is in general not considered in the Li\(^+\) recovery studies because the average pH of lake brines, the main Li source, is around 7. However, there are some Li sources with pH values above or below the optimal range, like Zabuye Cake Lake Brine (pH = 10.3–11.13), East Pacific Rise deep-ocean thermal (pH = 3.5) or Salton Sea (pH = 4.6–5.5).\(^{16}\) In addition, the cointercalation of H\(^+\) should be considered when high current rates are used, as the limited Li\(^+\) diffusion in diluted solution and in the \(\lambda\)-MnO\(_2\) structure could favor the cointercalation of H\(^+\).

To evaluate the effect of the coexisting cations in the source solution, Kanoh et al. analyzed by atomic absorption spectroscopy (AAS) the composition of the electrodes after the Li\(^+\) uptake process. They indicated that the CV (not shown in the article) in a mixed solution of LiCl plus alkaline earth metal chlorides were almost the same as that in pure LiCl solution. However, an inhibition effect was observed. These divalent cations blocked the Li\(^+\) insertion in the \(\lambda\)-MnO\(_2\), with up to 55% less Li\(^+\) uptake. The contradictory results between CV and AAS are at least controversial. They claimed that the inhibition effect by alkaline earth metal ions was stronger than that by alkali metal ions\(^{41}\) because of their stronger adsorption on the electrode surface by electrostatic interaction or surface complex formation. The Li\(^+\) recovery process from geothermal water did not show the typical profile of CV measurements. The authors attributed this electrochemical behavior to the presence of silicate ions that interfere with the Li\(^+\) insertion/extraction by the adsorption on the surface of the \(\lambda\)-MnO\(_2\). Silicates and alkaline earth metal ions are commonly founded in brine solutions,\(^{16}\) their effect in the recovery process has not been reevaluated since these pioneering works of Kanoh et al. in the early 1990s. The possible inhibition of Li\(^+\) capturing by Na\(^+\), a main component of brine lakes, has been recently evaluated by Calvo et al.\(^{49,104,105}\) and Palagonia et al.\(^{106}\) in their first study they analyzed the surface chemistry of a LiMn\(_2\)O\(_4\) thin film prepared by pulsed laser deposition (PLD).

One of the main challenges of working with Li containing compounds in PLD is the nonstoichiometric transfer of Li.\(^{88,89,92,93,107-112}\) The laser ablation of a mixed target containing light Li and a heavier metal, such as Mn, will always lead to Li deficiency materials.\(^{113}\) To overcome this obstacle a customized target with Li excess (+15%) is commonly prepared.\(^{92,93,114,115}\) In the description of the PLD thin film deposited by Calvo et al. there are no indications about any compensatory action to solve the Li nonstoichiometric transfer.
Unfortunately, there were no XRD or Rutherford backscatter spectroscopy measurements to corroborate the stoichiometric of the LMO prepared. The possible formation of a Li deficiency thin film and the associated impurities, mainly Mn$_2$O$_3$, could jeopardize the conclusion obtained. In addition, the authors indicated that the thicknesses of the thin films were estimated between 100 and 250 nm, but they did not normalize the electrochemical measurements by the thickness or mass (even more complicated to estimate). This makes very challenging the comparison between samples because the electrochemical performance of a thin film is clearly controlled by its thicknesses.

The authors claim that the shift to higher potentials observed between CV measurements (see Figure 9) of LMO in Jujuy’s brine ($0.18 \text{ m LiCl, 5 m NaCl, 0.11 m MgCl}_2, 0.28 \text{ m KCl, 0.1 m B}$) and in $0.1 \text{ m LiNO}_3$ is related to a kinetic effect due to Na-ion coadsorption on the oxide surface. However, according to the Nernst equation, the difference of concentrations causes a shift of 15 mV, which should be also considered. On the contrary, Kim et al. reported a small shift in just one of the reduction peaks by the addition of $1.8 \text{ m NaCl to 0.1 m LiCl electrolytes.}$

The article of Calvo et al. included a detailed XPS study of the surface of the electrode at different state of charge in the presence or absence of NaCl that evidenced the evolution of the surface from Mn$^{III}$ to Mn$^{IV}$ following the deintercalation of Li$^+$ from the structure. Similar Mn 3p peak XPS signals were obtained for pure LiCl solution and mixture with NaCl. The Na 1s XPS peak was dependent of the Na concentration in the electrolyte. From these data, the authors concluded that the competition between Li and Na cations adsorbed would influence the rate of Li$^+$ intercalation. From chronocoulometry measurements, superior diffusion coefficient ($D_{Li^+}$) for LMO was obtained for pure LiCl solution ($8.4 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$) than for mixture with NaCl ($6.0 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$). In subsequent articles Marchini et al. corroborated the findings of Kanoh et al.: LMO, prepared by deep coating onto Pt sheet, does not intercalate Na$^+$. They confirmed by XPS of LMO electrodes cycled 55 times the absence of a solid electrolyte interphase as well as the low dissolution of Mn in the electrolyte, just 0.17% of the initial amount. Since upon the reduction of a LMO electrode in $0.1 \text{ m NaCl electrolyte by applying 0.6 V for 1 h, Li}^+$ was absent, the authors concluded that the appearance of Na cations on the surfaces is accompanied by the appearance of Mn (III) due to the electrochemical reduction of the surface given by the applied potential. Na$^+$ ions in the surface compensate the positive charge in the surface Mn (IV) to Mn(III) reduction. However, there is the doubt if the same process is happening when Li$^+$ is present in the electrolyte: the Li$^+$ inserted balances the Mn valence and in fact, it has been reported that at high temperature ($55 ^\circ \text{C}$) a Li rich surface is formed causing the dissolution of Mn. Additionally, the authors studied the CV of a LMO carried out before and after cycling the electrode in a $0.1 \text{ m NaCl}$. After the cycling in NaCl, the integral current in the CV dropped by 50% with respect to the initial charge, not recovered even after 10 cycles. The authors suggested that Na$^+$ cations block the Li$^+$ adsorption sites causing this effect. However, an XRD study to corroborate this theory, dismissing the degradation of the spinel phase, was not provided.

Marchini et al. continued the study of the effect of the coadsorption of Na$^+$ by an impedance analysis of LMO in pure $0.2 \text{ m LiCl aqueous solutions, mixtures with different concentrations of NaCl and brine solutions at different polarization potentials.}$ The Nyquist plots exhibited only one semicircle since there is no formation of SEI. The uncompensated electrolyte solution resistance decreases with increasing the salt concentration and the charge transfer resistance increases with the NaCl concentration in agreement with the blocking effect of Na proposed. Xu et al. compared the use of a self-supported $\lambda$-MnO$_2$ electrode with traditional powder-based electrodes in Li recovery from brines. The fabrication of the $\lambda$-MnO$_2$ electrode implies a four steps process: cathodic deposition of Mn(OH)$_2$ on Pt, aerobic oxidation to Mn$_3$O$_4$, hydrothermal lithiation to LiMn$_2$O$_4$ and finally potentiostat transformation to $\lambda$-MnO$_2$. Values of thicknesses and/or masses were not provided. A strong polarization was observed when the LMO electrodes were voltammetry cycled with steps above 1 mV s$^{-1}$, as well as the classic two plateaus profile during constant current measurements were lost for currents over 50 mA g$^{-1}$. The low observed kinetics could be attributed to the lack of electron conductive additive and/or carbon coating, which have been proved of a great need for semiconductor materials.

Higher efficiencies in both Li releasing and extraction were observed for self-supported electrodes mainly because of the poor electrochemical performance of the powder based electrode. In fact, 60% of theoretical capacity and 25% of capacity fade after 100 cycles. An optimized electrode can clearly overcome these values. The changes in Li$^+$ concentration from a...
source solution (200 ml, initially containing $3 \times 10^{-3}$ M of LiCl, NaCl, KCl, MgCl$_2$, and CaCl$_2$) clearly showed a preferential Li$^+$ uptake, with reduction of Li concentration of $1 \times 10^{-3}$ M, $1 \times 10^{-3}$ M of Mg and negligible variation of other cations after 40 cycles. The concentration of Li increased in the recovery solution ($10 \times 10^{-3}$ M LiCl) to $25.4 \times 10^{-3}$ M after 100 cycles, equivalent to 3.52 mg of Li per cycle, the absence of mass load of the electrode hinders the normalization of this value and its comparison with literature. Additionally, the concentrations of the cations in the source solutions, $3 \times 10^{-3}$ M equimolar LiCl-Mn$_{1.3}$Cl$_{0.7}$ solutions, are far from the values found in brine lakes.$^{[147]}$

Du et al. analyzed the effect of coating $\lambda$-MnO$_2$ with polypyrrole (PPy) doped with polystyrenesulfonate (PSS), to form $\lambda$-MnO$_2$/PPy/PSS, in the Li$^+$ uptake capacity.$^{[118]}$ For the fabrication of the electrode, a pulse potential method was applied on a Pt quartz crystal or carbon felt electrode just 34.1 mA g$^{-1}$ after 200 cycles. These low retentions and capacities provided are considerably worse than other reported $\lambda$-MnO$_2$ based methods.$^{[47,105]}$ The poor electrochemical performance also affected the recovery efficiency, which resulted in only 50%, and the voltage profiles, where the two classic plateaus were merged into a slope, indicative of poor kinetics. The authors highlighted the need for washing the electrode surfaces between the extraction and recovery steps that would avoid the presence of adsorbed ions in the recovery solutions. Despite its significance, this simple step has been ignored (or nonmentioned) in most of Li recovery studies.

Lee et al. reported about the use of the $\lambda$-MnO$_2$–Ag battery for the Li recovery from simulated Atacama Brine solution ($0.21$ m Li$^+$, $3.3$ m Na$^+$, $0.46$ m K$^+$, $0.4$ m Mg$^{2+}$, $7.75 \times 10^{-3}$ m Ca$^{2+}$, $0.17$ m SO$_4^{2-}$, $4.5$ m Cl$^-$, $0.6 \times 10^{-3}$ m Br$^{-}$).$^{[59]}$ The authors observed the adsorption of Mg$^{2+}$ by simple immersion of the electrode, however, this was not transferred to the recovery solution. The washing of electrodes between steps was not mentioned. An increment in Li$^+$ concentration of $18 \times 10^{-3}$ m was reached after 4 operation cycles with a minimum increment of other cations ($1 \times 10^{-3}$ m Na$^+$). There are no data of mass load of the electrodes ($3 \times 3$ cm) and the capacities provided were not normalized by the mass, so it is not possible to know what percentage of the theoretical capacity of LMO was employed. The classic two plateaus in the voltage profile related to the (de-) intercalation of Li$^+$ in the spinel structure were clearly observed when 1 m LiCl was used as electrolyte, but it was less evident in Atacama brine. The commercial LMO employed probably does not fulfill the requirements of an optimized LMO material in terms of nanometric scale and porosity.$^{[120]}$

Cao et al. have recently reported the extraction of Li from simulated brine of Taijinair Lake (Qinghai, China), which has a very high Mg/Li ratio of 14.46 by the use of a polyline/Li$_2$Mn$_3$O$_4$ cell.$^{[124]}$ The authors employed a commercial LMO material that provided around 100 mAh g$^{-1}$ for at least 100 cycles at slow current densities (0.1 mA cm$^{-2}$). However, the specific charge dramatically decreased with the increment of the rate, reaching values of 65 mAh g$^{-1}$ at 2.0 mA cm$^{-2}$.

Figure 10. a,b) TEM images of $\lambda$-MnO$_2$/PPy/PSS with different magnifications; the inset is the electron diffraction pattern. c) Cyclic voltammogram and weight-change curve of the $\lambda$-MnO$_2$/PPy/PSS hybrid film in 0.5 mol L$^{-1}$ LiCl solution at a scan rate of 50 mV s$^{-1}$. a–c) Reproduced with permission.$^{[118]}$ Copyright 2016, Royal Society of Chemistry.
This capacity fade was attributed to the low concentration of Li in the brine electrolyte, which leads to serious concentration polarization for the Li insertion reaction. The concentration of Li increased up to $35 \times 10^{-3}$ m after 4 recovery cycles meanwhile the K and Mg increments were negligible. However, the Na concentration raised to $5 \times 10^{-3}$ m obtaining a final recovery solution with a purity of 87.5%. The authors suggested 3 mmol L$^{-1}$ of Li as the lowest concentration limit for a selective extraction, under this value, both Li and Na were released with similar concentrations.

Recently, we have optimized a Li recovery process from brines by using an electrochemical ion-pumping method based on a stoichiometric $\lambda$-MnO$_2$ with a morphology composed of nanoparticles (50–100 nm) fused to form a porous structure.[47,125] Two different counter electrodes were employed, Ag and NiHCF, their effect in the recovery process is analyzed in detail in Section 5. The selectivity of the optimized $\lambda$-MnO$_2$ was evaluated by capturing cations from an artificial brine containing equimolar concentration of LiCl and other chloride salts, releasing them in pure water, and measuring (by ICP-MS) the concentration of cations released in the recovery solution. The selectivity (Equation (1)), calculated as coefficient of Li$^+$ concentration and the concentration of secondary cations (Na$^+$, K$^+$, or Mg$^{2+}$), gave values of $K_{\text{Li/Na}} = 36.6$, $K_{\text{Li/K}} = 30$, and $K_{\text{Li/Mg}} = 315$, at least 23.6% higher than reported in Kim and Lee articles.[59,126] This clearly evidence the positive effect of nanosize and porosity of synthesized LMO. The high selectivity toward Mg$^{2+}$ would allow the use of optimized $\lambda$-MnO$_2$ in brines with high contents of magnesium, such as those of Salar de Uyuni.[18] The method allowed increasing the purity from 4.13% to 96.2% in a single step. A study of the effect of the current rate was also reported. It is not possible to accelerate the intercalation process because of the low Li$^+$ concentration in brines and the limiting diffusion current is quickly reached (see engineering part, Section 6). However, the time for the recovery step, releasing Li$^+$ from the spinel structure, could be reduced without affecting the voltage profile, Li selectivity, efficiency, and Li purity.

The reduction of time has the penalty of an increment of energy consumption. On the other hand, a comparison of the stability of LMO and LFP were reported, with a considerable lower capacity fade for the spinel structure than for the olivine type (Figure 11). The article does not include values of insertion capacity, milligrams of Li$^+$ recovered per gram of LMO, that complicates the comparison with other recovery methods, nevertheless, these values can be calculated from the efficiency and capacities showed (Table 5).

Kim et al.[61] also analyzed the effect of the current rate in the Li recovery process from industrial wastewater based on $\lambda$-MnO$_2$ and boron-doped diamond (BDD) as Li recovery and counter electrodes, respectively. The role of BDD is reported in Section 5.5. They observed a reduction of the recovery capacities from 62% of the theoretical values to 20.6% with the increment of the current applied, from 100 mA g$^{-1}$ (C/1.5) to 500 mA g$^{-1}$ (3.3 C). The author attributed these losses to the depletion of Li$^+$ at the electrode surface, however because of the relatively high concentration of Li$^+$ in the wastewater ($276.5 \pm 1.7 \times 10^{-3}$ m), the limiting diffusion current, in the range of 27 mA–24.5 C, was considerably higher than the applied current. Commercial LMO was employed that could jeopardize the electrochemical performance of the electrode.

The alternative Li recovery method proposed by Zhao et al.[64] halfway between a battery process and electrolysis based on the introduction of a monovalent selective permeable membrane between electrodes (Figures 3 and 15), was applied to Li$_{1+x}$MnO$_4$ and LiMn$_2$O$_4$ materials. The position of the electrodes was interchanged between every step to continuously increase and decrease the Li$^+$ concentration in the recovery solution ($50 \times 10^{-3}$ m NaCl) and source solution ($50 \times 10^{-3}$ m LiCl + 50 mL KCl), respectively. The insertion and extraction capacities were dependent on the potential applied. When 1.2 V was used, the highest potential employed, the value reached 34.31 mg g$^{-1}$, 92.68% of the theoretical one. The current efficiency was always above 97%, however, the energy consumption reached up to 33.05 Wh mol$^{-1}$, around 8–10 times more than for battery methods based on $\lambda$-MnO$_2$. When the effect of coinserter of other cations (Na$^+$, Mg$^{2+}$, Ca$^{2+}$, K$^+$) was analyzed, the author observed lower separation coefficients than in previous studies on $\lambda$-MnO$_2$, with extremely low value for Mg and suggested the insertion of Mg$^{2+}$ in the spinel structure, contrary to previous studies where the intercalation of Mg$^{2+}$ was very limited.[47,59,119,127] The recovery process was also evaluated using a diluted artificial brine as a source solution, with concentrations ten times lower than those found in Atacama brine. With the goal of reducing the presence of cointercalated cation, a potential of just 0.6 V was applied to extract Li$^+$, causing the partial use of the electrode material and consequently reducing the capacity. Lower extraction capacities of Li$^+$ and higher coextractions of Mg$^{2+}$ and Na$^+$ were obtained, however, the values of separation coefficients were considerably higher than those for mixture solution of LiCl + KCl (that showed better extraction coefficients).

Kim et al.[60] also used a selective membrane to separate the Li$^+$ intercalation electrode ($\lambda$-MnO$_2$) from the counter (Zn). A solution mimicking the composition of Atacama brine and 0.1 m CaCl$_2$ was used as Li$^+$ sources and recovery solutions respectively. The selectivity of the method was lower than in previous

![Figure 11. Evolution of the capacity upon cycling of LFP and $\lambda$-MnO$_2$ in Atacama brine as electrolyte. The empty and full symbols indicate the discharge and charge processes, respectively. Adapted with permission.[47] Copyright 2017, Wiley-VCH.](image-url)
studies. The authors were not able to explain the reason. We think that the lack of washing the electrodes between steps could be the cause of this lower selectivity. In addition, a crossover of zinc ions (3%) through the membrane reduced the purity. On the other hand, the author attributed the decrease of the selectivity observed with the increment of the current rate to the cointercalation of cations, on the contrary, we ascribed these poorer values of selectivity to the lower amount of Li\(^+\) captured, as observed also by Kim et al., i.e., the lower the numerator of the ratio the lower the value of selectivity. We did not detect a higher concentration of Na\(^+\) or K\(^+\).

In a hypothetic commercial reactor for Li\(^+\) recovery, a continuous flow of the source and recovery solution would be required to optimize the extraction process. Palagonia et al.\(^{[106]}\) studied the effect of the hydrodynamic flow, from 0.1 to 10 mL min\(^{-1}\), in electrolytes containing cations concentrations equivalent to those found in Atacama brine, ten times diluted as well as in solution with LiCl concentrations up to \(10 \times 10^{-3}\) M. The design of the reactor and the hydraulic energy required to extract one mole of Li are commented in Section 6. A clear increment of the practical capacity, equivalent to the amount of Li\(^+\) captured-released, was observed when the transport of Li was enhanced by advection through a forced flow (Figure 12). It is worth to mention that the flow did not have an effect in the oxidation step of LiMn\(_2\)O\(_4\) (lithium release), all the oxidation plateaus occurred at the same potential, but had a tremendous influence in the reduction process (lithium capturing).

The authors observed that the determining step of the capturing process in these low concentrated solutions was the transport of ions in the liquid phase, thus the convection improves the amount of captured Li\(^+\). Nevertheless, flowing the electrolyte through the electrodes is not enough to reach the maximum capacity because the Li\(^+\) transport in the smallest pores remains controlled by the sole diffusion. The influence of the Na\(^+\) in the recovery process was evaluated by cycling the electrodes in solutions with fixed concentration of LiCl (\(5 \times 10^{-3}\) M) and various concentrations of NaCl (up to 5 M). On the contrary to the studies of Calvo et al.\(^{[49,104,105]}\) where the polarization of oxidation and reduction was reported, a clear polarization was just observed for the reduction process with practically equivalent oxidation potential for all NaCl concentrations, similar to the one described by Kim et al.\(^{[61]}\) In addition, the effect of the NaCl concentration was minimized by the increment of the flow rate employed.

Kim et al.\(^{[126]}\) also applied a flow of 1 mL min\(^{-1}\) for a Li\(^+\) recovery process based on 4-MnO\(_3\), activated carbon, and an anion exchange membrane placed between the spacer and the activated carbon to prevent the insertion of cations into the pores of the activated carbon electrode. Static measurements were not reported. The concentration of Li\(^+\) in an equimolar solution (\(30 \times 10^{-3}\) M Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\)) changed 5.94 and 5.56 \(\times 10^{-3}\) M during the recovery and release step, respectively, and variations of less than \(1 \times 10^{-3}\) M were observed for the rest of the cations. The authors also extracted Li\(^+\) from the Atacama brine solution by repeating three times the cycle. The authors observed that at each cycle the concentration of lithium in the recovery solution was increased by \(20 \times 10^{-3}\) M, meanwhile, the concentrations of cations increased by \(1 \times 10^{-3}\) M after three cycles. Data about the evolution of concentration during extraction from Atacama brine were not shown. A summary of all the results for LiMn\(_4\) is reported in Table 5.

4.3. Spinel LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\)

Manganese spinel can be site doped by Ni to form LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) (LNMO). This material can be cycled at higher potentials, and it is characterized for high discharge capacity and two plateaus at around 4.7 and 3.7 V versus Li (1.45 and 0.45 V vs Ag/AgCl) ascribed to the Ni\(^{2+}/\text{Ni}^{3+}\) and Mn\(^{3+}/\text{Mn}^{4+}\)}
redox couples and simultaneous Li\textsuperscript{+} extraction from and insertion to 8a and 16c sites, respectively.\[^{128}\] The voltage of the first plateau exceeds the electrochemical window of water and it cannot be employed for the Li recovery process. Chung et al.\[^{129}\] studied the use of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} spinel material as a Li recovery electrode. It has been reported that the stoichiometric LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} has a cubic, primitive structure (P4\textsubscript{3}3\textbar 2), while nonstoichiometric LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}\textsubscript{–δ} has a normal face-centered spinel structure (Fd-3m).\[^{128,130}\]

The diffraction measurements provided in the article of Chung et al.\[^{129}\] showed Fd-3m space group symbol, so the crystal structure of the material analyzed was actually nonstoichiometric LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}\textsubscript{–δ}. The authors optimized the extraction of lithium in terms of current rate employed and step duration. The limited utilization of the material (the redox pair Ni\textsuperscript{2+}/Ni\textsuperscript{4+} was not employed) caused that the maximum capacity did not overcome the 34% of the theoretical value. The system optimally operated at 1.05C with steps of 20 min reaching a lithium purity of 98.14\% and energy consumption of 1.29–1.44 Wh mol\textsuperscript{–1}.

### 4.4. Layered LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2}

LiNi\textsubscript{x}Co\textsubscript{1−x}Mn\textsubscript{2}O\textsubscript{4} (NCM) family, characterized for high discharge capacity, moderate voltage platform, low cost, and low environmental toxicity, has also been considered as

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### Table 5. Characteristic parameters of the lithium recovery methods based on LiMn\textsubscript{2}O\textsubscript{4}.

| Counter electrode | Feed [x 10\textsuperscript{–3} m] | Recovery [x 10\textsuperscript{–3} m] | \(a_{\text{Li}}^{\text{Na}}\) | \(a_{\text{Li}}^{\text{Mg}}\) | \(a_{\text{Li}}^{\text{K}}\) | Absorption capacity [mg g\textsuperscript{–1}] | Energy [Wh mol\textsuperscript{–1}] | Increment CLi\textsuperscript{+} cycle\textsuperscript{–1} [x 10\textsuperscript{–3} m] | Efficiency [%] | Purity |
|------------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------------------------|----------------|-------|
| Pt               | 500 LiCl                        | –4.8\[^{a}\]                   | –4.6\[^{a}\]    | 31.8\[^{a}\]    | 14.1              | 0.25            | 82–92           |                               |                 |       |
| Pt               | Geothermal                      | 22                             |                 |                 |                 |                 |                 |                               |                 |       |
| Ag               | 30 Cl; X = Li, Na, K, Mg, Ca     | 10 LiCl                        |                 |                 |                 |                 |                 |                               |                 |       |
| Pt               | 4.3 Li, 4.3 Na                  | 4.3 LiCl                       |                 |                 |                 |                 |                 |                               |                 |       |
| PPy              | Brine 1 = 5000 Na, 280 K, 110 Mg, 14 B | Brine                          |                 |                 |                 |                 |                 |                               |                 |       |
| C                | Brine 1                          | Brine 1                        |                 |                 |                 |                 |                 |                               |                 |       |
| Pt               | Brine 1                          | Brine 1                        |                 |                 |                 |                 |                 |                               |                 |       |
| PPy              | Brine 1                          | 25 LiCl                        |                 |                 |                 |                 |                 |                               |                 |       |
| Ag               | 30 Cl; X = Li, Na, K, Mg, Ca     | 30 LiCl                        |                 |                 |                 |                 |                 |                               |                 |       |
| Ag               | 42 Li, 108 K, 793 Na, 74 Mg      | 91.2 CaCl\textsubscript{2}     | 29.6\[^{a}\]    | 7100\[^{a}\]    | 177.5\[^{a}\]   | 26              | 4.1             | 29                            | 92.7            | 96.2  |
| NiHCF            | Brine 2                          | 156.3 KCl                      | 57.6\[^{a}\]    | 1633\[^{a}\]    | 1.63\[^{a}\]    | 25.4            | 3.5             | 56                            | 71.1            | 61.3  |
| LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}/membrane | 50 KCl                       | 321\[^{a}\]                    | 74.03\[^{a}\]   | 118.38\[^{a}\]  |                 | 22              | 17.98           | 89.45                        |                 |       |
| LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}/membrane | 330 Na, 40 Mg, 7.7 Ca, 21 Li | 384\[^{a}\]                    | 98.17\[^{a}\]   | 113.99\[^{a}\]  |                 | 21              | 18.61           | 86.43                        |                 |       |
| Zn/membrane      | Brine 4                          | 100 KCl                        | 6.3             | 18              |                 |                 |                 |                               |                 |       |
| Boron doped diamond | Waste water                     | 100 K\textsubscript{2}PO\textsubscript{4} | 88.4\[^{a}\]—1st | 77.6\[^{a}\]—5th | 22.7 (1st cycle) | 9.94            | 60.45           | 30                            | 98.9—1st       | 77.6—5th |
| Activated carbon | 30 Cl; X = Li, Na, K, Mg, Ca     | 30 LiCl                        | 29.6\[^{a}\]—4th | 29.6\[^{a}\]—4th | 29.6\[^{a}\]—4th | 4.2             | 5.56            | ≥90                          | 80\[^{a}\]      |       |
| PANI             | Taijinair Lake                  | 30 ClC                         | 25\[^{a}\]       | 3.95            | 8.75             |                 |                 |                               |                 |       |

\[^{a}\]Fixed interference method; Section 4.2; \[^{b}\]Method 2; Equation (1); \[^{c}\]Method 3; Equation (2); \[^{d}\]Not directly reported in the article: calculated from data; \[^{e}\]Obtained from capacities values or % capacities given (the efficiency was considered when it was provided).
promising cathode candidates for Li-ion batteries.[131,132] Specifically, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ adopts a rhombohedral α-NaFeO$_2$ structure (R$3\bar{m}$) with consecutively alternating [MO$_2$]$^-$ (M = Ni, Co, Mn) and Li$^+$ layers (Figure 14).[133,134] During charge/discharge, only Ni$^{2+}$ and Co$^{3+}$ are electrochemically active. Mn$^{4+}$ is beneficial for the stability of the crystal structure, reducing Mn dissolution and Jahn–Teller distortion.[135] Chung et al. studied LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (LNCM) as a Li recovery electrode and Ag as a counter electrode.[136] The authors evaluated the effect of the current rate, from 0.56 C to 2.88 C, in 30 × 10$^{-3}$ m equivmolar of mixed cation solution (Li, Na, Mg, K, and Ca) without cutoff potential limits and stopped the measurements after 20 min of applied current. The C-rates and percentage of specific capacity provided were calculated based on the practical capacity reported in the literature for aqueous batteries (93 mA h g$^{-1}$).[136] instead of using the theoretical capacity of LNCM (275 mA h g$^{-1}$). Superior selectivities were obtained for $i = \pm 0.5$ mA, reaching values from 130 (vs Mg) to 415 (vs Ca) and energy consumption of 8.22 Wh mol$^{-1}$ Li$. The authors modified the time limit of the measurements from 10 to 30 min ($i = \pm 0.5$ mA) and surprisingly found not just lower purities for $t > 20$ min, ascribed to the coin-\-\-\-\-\-calation of cations different than Li$, but also at times $<20$ min. The authors hypothesized that at these short times Li$^+$ intercalation probably occurred only at the surface of NCM. Hence, other M$^{3+}$ was able to compete with Li$. The values of salt concentrations were not shown, just the ratio between them. The recyclability of the NCM/Ag system in a solution with a composition similar to Salar de Uyuni was also evaluated at 0.5 mA and limited to 20 min. Li concentration raised of 0.61 × 10$^{-3}$ m per cycle, with a selectivity toward other cations equal to 68 (Na$^+$), 76 (Mg$^{2+}$), 203 (K$^+$), and 610 (Ca$^{2+}$), and a purity of 96.40%.

A deeply comparison of the described material as Li selective electrode is hindered by the extreme discrepancy between the analysis conditions, nevertheless some pros and cons could be highlighted. The studies of LNMO and NMC are limited in number. LNMO suffers of a low value of maximum theoretical extraction capacity (12.66 mg g$^{-1}$) owing to the incompatibility of the redox couple Ni$^{2+}$/Ni$^{4+}$ with the stability window of water. On the contrary, NMC offers the highest theoretical value (71.95 mg g$^{-1}$). however its Li-selectivity and consequently the purity of the recovery solution, were the lowest among the studied materials. LFP and LMO showed generally excellent selectivity toward Na and K, yet LMO apparently showed superior values toward Mg than LFP. Just one article has analyzed the stability upon long-medium cycling (≥100 cycles) of the LFP and LMO materials in brine solutions.[47] The specific charge of LFP swiftly decreased whereas LMO was stable up to 100 of cycles, however, the well-known low stability of LMO electrode in Li-ion batteries is expected to happen in Li recovery system upon cycling. Equivalent methodologies than those employed to improve the Li-ion electrodes (surface coating, doping...) could improve their performances. Other parameters like energy consumption, increment of concentration per cycle or efficiency are critically dependent on the experimental conditions and their comparison is unfeasible, which clearly manifest the need of a standardization in the methodology.

5. Counter Electrodes

Research efforts have been mainly focused on the study and development of materials able to intercalate selectively Li. However, the electrochemical recovery of Li would require an efficient and inexpensive secondary electrode, which we will name in the following “counter electrode.” The methodology employed for Li extraction would also affect the nature of the counter electrode.

5.1. Platinum

In their pioneering works, Kanoh et al. employed a Pt wire or sheet as the counter electrode.[41,42] This material was also selected as a counter electrode in some recent publications.[118,119] Pt does not react with Li or other ion contained in the Brine lakes so the oxidation and reduction of water occur during the extraction and recovery steps, respectively. In addition to the high cost of this noble metal, the electrochemical potential of these reactions causes an increment in the energy required for the process, thus preventing its commercial use (see Table 5). Furthermore, the local evolution of the pH close to the electrode’s surface, as a consequence of
the water oxidation or reduction, can produce the precipitation of dissolved ions.

5.2. Silver

Silver has been a widespread alternative to Pt. In spite of its cost that would preclude its commercial use, Ag has been extensively employed because of its easy preparation and reactivity with Cl\(^-\), one of the main components of Brine lakes, to form AgCl. The potential versus time profile of this reaction is a plateau, allowing the utilization of an Ag/AgCl electrode simultaneously as counter and pseudoreference electrode, especially interesting for cell working with volume in the range of hundreds of microliters. However, it should be noted that in solutions with high chloride concentration the solubility of AgCl is enhanced by the presence of soluble complexes.\(^{[138]}\)

5.3. Electroactive Polymers

Calvo et al. implemented the use of polypyrrole (PPy) as counter electrode for the Li recovery process. The anion doping and undoping were confirmed by cyclic voltammetry (~0.8 to 0.4 V vs Ag/AgCl) in an Atacama brine and the simultaneous electrochemical quartz crystal microbalance measurements.\(^{[49,50,104,105]}\) Polypyrrole has been extensively studied as a component of Li-ion batteries. However, it is generally considered to be difficult to n-dope PPy hence its use as a negative electrode in rechargeable batteries is unlikely.\(^{[139]}\) Thus, research efforts were essentially concentrated on the utilization of polypyrrole as positive electrodes in batteries. On the contrary, Wu et al.\(^{[123]}\) reported the doping and undoping of Li ions of PPy anode electrode at average redox potential of ~0.23 V versus Ag/AgCl in saturated Li\(_2\)SO\(_4\) solution. The authors claim that the doping and undoping of PPy with anions happens at higher potential, at 0.28 and 0.9 V Ag/AgCl, that contradicts previous findings by Marchina et al.\(^{[49]}\) Such discrepancy could be attributed to differences in the PPy preparation and measurement conditions.

Recently, Cao et al. showed the use of nanowire of polyaniline (PANI) as counter electrode by the p-doping/dedoping processes with reversible uptake/release of Cl\(^-\) in the potential range of 0.2–0.7 V versus Ag/AgCl.\(^{[124]}\) The material provided a reversible capacity of 77.6 mAh g\(^-1\) after 100 cycles in 1 M LiCl aqueous solution, corresponding to 78% capacity retention and coulombic efficiencies close to 100%. Owing to the abundant presence of different cations in the brine, a specific study of the electrochemical performance of PPy and PANI in such a solution would be of great interest.

5.4. Prussian Blue Analogues

Recently, a new family of open-framework materials with the Prussian blue (PB) crystal structure has been studied as candidates for positive electrodes in Na, K, or Zn ion batteries.\(^{[140–144]}\) The insertion of Na is strongly favored in Prussian blue materials compared to that of Li.\(^{[145]}\) Taking advantage of this higher affinity of PB toward Na than Li, nickel hexacyano ferrate (NiHCF) has been proposed as a Li exclusion electrode in electrochemical Li recovery,\(^{[47,48,106]}\) as described already in the Introduction.

Trócoli et al. demonstrated the higher affinity of NiHCF toward Na than Li by its electrochemical reduction in an equimolar solution of LiCl–NaCl. NiHCF inserted 17 mol of Na per mol of Li.\(^{[48]}\) The use of a Li exclusion electrode requires the presence of counter cations different than Li in the recovery solution to be incorporated during the releasing step and keep the electroneutrality of the solution. This methodology permits the utilization of seawater or brine water as recovery solution, thus reducing the consumption of freshwater, which is typically a scarce element in Li production sites. However, obtaining highly pure Li solutions is more challenging with this process than with the others. The purity depends not only on the selectivity of the Li intercalation electrode but also on the presence of counter cations. Their concentrations must be optimized to a value that would allow its complete removal during the recovery process. On the other hand, it has been also theoretically and experimentally demonstrated that there is a considerable difference in energy consumption because of the use of Li exclusion electrodes. This methodology implies a smaller thermodynamic contribution to the energy consumption, but a greater influence of the limiting current density on the kinetic energy consumption. On the contrary, superior Li recovery capacity and efficiency at all used current densities were reported.\(^{[61]}\)

5.5. Other Counter Electrodes

Yoon et al. reported the use of BDD as an oxidant-generating counter electrode to recover Li and decompose organic pollutants simultaneously from battery recycling wastewater.\(^{[61]}\) BDD shifts the oxygen evolution reaction at around 2.2 V versus Ag/AgCl, promote the formation of hydroxyl radicals (OH\(^-\)), persulfates (S\(_2\)O\(_8^2-\)), and sulfate radicals (SO\(_4^{2-}\)) and the oxidation of the organic pollutant. By direct and indirect oxidation, the dissolved organic carbon content was reduced by 65%. However, the use of BDD would considerably increase the energy required for the Li recovery as a consequence of the high oxidation potential, up to 4.1 V versus Ag/AgCl when a high current was applied. Additionally, the role of the BDD electrode during the reduction process is unknown.

Kim et al. proposed to enclose a Pt counter electrode in an acetonitrile solution containing the I\(^-\)/I\(^3-\) redox couple and separated by the rest of the solution by a separator.\(^{[78]}\) The migration of cations from this solution would compensate for the intercalation of Li in the iron phosphate (similarly as step 1 of Figure 2). However, no attempt for a full recovery of lithium was shown (step 2–4 of Figure 2) and further details were not given.

The division of the electrochemical cell into two slots by the introduction of an anion exchange membrane with monovalent selective permeability permits the utilization of the spinel Li\(_{1-x}\)Mn\(_2\)O\(_4\) or LiFePO\(_4\) as counter electrode\(^{[64,72,73,77]}\) as well as Zn metal\(^{[60]}\) or activated carbon with a high specific area (Figures 3 and 15).\(^{[63]}\) All these systems have in common that
the Li intercalation is compensated by the transfer of anions, mainly $\text{Cl}^{-}$, through the membrane. Although this strategy offers great flexibility it also suffers from the inevitable high ionic resistance of the membrane, with consequent high energy losses.

6. Electrochemical Reactor Designs

Most of the works described hitherto were focused on the technique development, by investigating the performances of the materials in terms of selectivity and capacity. In these works, the process was performed in two different cells, one for the capturing and the other for the release step, manually moving the electrodes from a cell to the other to perform the entire cycle. In view of an industrial application, it is necessary to design a reactor where both steps can be performed.

Recently, researchers have focused on the design of suitable cell geometries to run the process in one reactor. The limitation on the performances of such reactors is linked to the amount of source solution that is retained in the cell (in the tubes, in the electrodes, in the separators and others) after the capturing step, which represents a dead volume that dilutes the final Li enriched solution. This effect can be reduced by using a reactor design with a compact electrode stack that limits the dead volumes and allows removing the source solution residuals from the cell as much as possible, before the injection of the recovery solution. A typical reactor used in salt removal operation is the packed bed reactor\cite{146–148} where the electrodes are pressed to each other as much as possible to minimize the unwanted dead volume.

Two kinds of packed bed reactor configurations have been used for the extraction of Li from brine, namely, a flow-by and a flow-through electrodes configuration (Figure 16). In the first configuration, the flow passes between anode and cathode and its direction is parallel to the electrodes. In the second one, the flow passes through the electrodes, and its direction is perpendicular to them. The two configurations are schematically represented in Figure 16 for a single cell, where the blue arrows showing the flow direction.

In general, the flow-through electrodes configuration is preferred to the flow-by design, due to its higher compactness, that allows minimizing the distance between the electrodes, reducing the ohmic drops and the cell volume.\cite{149} Moreover, in the flow-through electrodes design, the electrolyte is pumped through the porous matrix of the electrodes, adding a convective flow along the thickness of the electrode stack, which improves the mass transport in the pores. On the other hand, the hydraulic resistance in a flow-by configuration can be lower than in flow-through. These two configurations have recently raised the attention of the researchers because they allow to capture Li from more diluted brine than the currently used ones ($0.5$–$70$ mg L$^{-1}$), thanks to the circulation of the electrolyte inside the reactor, that improves the transport of Li cations from the liquid to the solid during the capturing step. Kim et al.'\cite{126} have proposed a hybrid supercapacitor system in a flow-through electrodes reactor for Li recovery, using $\lambda$-MnO$_2$ as Li-capturing electrode and activated carbon to capture chlorine ions. The electrodes were placed inside a cylindrical reactor on the top of the other in a sandwich configuration, with the flow passing through them. The system captured Li cations from synthetic Atacama brine and released them in 9 mL of recovery solution, reaching a final concentration of circa $90 \times 10^{-3}$ m.

A flow-through electrodes configuration of the reactor was used by Palagonia et al.\cite{106} to extract Li from diluted brine ($7$–$70$ mg L$^{-1}$). Such sources are relatively widespread, including geothermal waters, brines produced in salt-works, and the wastewaters from gas and oil extraction wells. In the proposed reactor, $\lambda$-MnO$_2$ was used as capturing electrode and NiHCF as a cation-exchange electrode. The active materials were hand-painted on a conductive porous substrate (carbon cloth) and the electrodes were separated by a filter paper. The electrodes were pressed against each other, and the active areas faced the inlet flow of the reactor so that the electrolyte could pass through them. The electrical contact was created by means of graphite rods passing in the substrate of each electrode, as shown in Figure 17.

The authors studied the influence of the flow rate on the captured amount of Li per unit of solid (capacity). It has been observed that the capacity increased with the flow rate until a maximum value, after which it kept constant. The maximum capacity occurred at a “saturation flow rate” and it depends on the Li brine concentration. Specifically, it increases with
the concentration, reaching around 95% of the total electrode capacity at \(10 \times 10^{-3} \text{ mol} \).\(^{[126]}\) Nevertheless, the saturation flow rate can be lowered by decreasing the applied current, thus the hydraulic energy required for pumping the electrolyte is reduced by slowing down the capturing process.\(^{[106]}\) Moreover, by decreasing the current, the capacity of the process at low concentration increases due to the reduced mass transport overpotential.\(^{[106]}\) The operative current can be therefore chosen as a trade-off between high capacity, high capturing rate, and low hydraulic energy. By extracting Li from \(1 \times 10^{-3} \text{ mol} \) LiCl brine at 0.2 mA cm\(^{-2}\), it is possible to reach a capacity equal to 18.4 mg g\(^{-1}\), and around 95% of Li is captured from the source solution. This value of capacity is higher than the one obtained with conventional adsorption processes (circa 10 mg g\(^{-1}\)).\(^{[106]}\) Moreover, the capturing rate is 9 mg g\(^{-1}\) h\(^{-1}\), which is much higher than the capturing rate obtained with the adsorption process from brines with similar concentration (0.5 mg g\(^{-1}\) h\(^{-1}\)).\(^{[150]}\)

The influence of the porous electrode structure on the process efficiency was also investigated. It was observed that the capture efficiency of the flow-through electrodes reactor improved by creating a more compact structure with smaller active pores. This was obtained by increasing the mass loading on the carbon substrate. This expedient increased the hydraulic resistivity of the electrodes stacks due to the lower permeability of the electrodes, but on the other hand, it was fundamental to obtain higher capacity and a higher amount of Li transferred per cycle.

The flow-by electrodes configuration was used by Kim et al.\(^{[151]}\) for extracting Li from diluted brine (2–3 times concentrated seawater), using \(\lambda\text{-MnO}_2\) as Li-capturing electrode and Ag as Cl-capturing electrode. The electrodes were cut in rounded shape (50 mm of diameter), placed in the reactor one on the top of the other and separated by a nylon spacer in a filter press configuration. The \(\lambda\text{-MnO}_2\) electrode had a hole in the middle that allowed the electrolyte to flow and to flood transversally the space between the two electrodes. By using this reactor, a recovery solution of \(190 \times 10^{-3} \text{ mol} \) and 99% purity of LiCl was obtained in two cycles. The applied current, chosen as a compromise between high capacity and high capturing rate, was 10 \(\mu A \text{ cm}^{-2}\), corresponding to 10.1 mg g\(^{-1}\) day\(^{-1}\) of captured Li. These results further demonstrate that the electrochemical capturing from very diluted brine is efficient only at low current densities. In fact, by tuning the flow rates, higher current can be applied speeding up the process, as the convective flow inside the porous electrode influences positively the Li transport in the pores, when the process is run in a flow-through electrodes configuration.\(^{[106]}\)

7. Energy and Material Cost Analysis

Lithium extraction requires both electrical energy, for driving the electrochemical process, and mechanical energy, for pumping the liquids through the cell. In literature, the evaluation of energy consumption is typically limited to the former, through Equation (13). However, a thorough study of a flow-through reactor\(^{[106,152,153]}\) highlighted that the pumping energy is the main contribution to the energy consumption and that it must be taken into consideration during the optimization of the reactor operation.

7.1. Electrical Energy Consumption

The electrical energy consumption \(W\) has been already defined by Equation (13). It can be divided into two contributions, the reversible and irreversible energies, \(W_{\text{rev}}\) and \(W_{\text{irr}}\), respectively

\[
W = W_{\text{rev}} + W_{\text{irr}}
\]  

(21)

The \(W_{\text{rev}}\) term equals the variation of the free energy of the solutions due to the ion pumping, and can be theoretically calculated\(^{[31,153]}\) from thermodynamic data. The term \(W_{\text{irr}}\) accounts for the nonreversible processes, such as ohmic drop, charge transfer, and diffusion overpotential (for mathematical modeling of such phenomena in a similar electrochemical system.\(^{[155]}\)

Two schemes for the electrochemical ion pumping were compared in terms of energy consumption. LiFePO\(_4\) was used as selective lithium capturing electrode and two different counter electrodes were tested, one based on Ag/AgCl silver/silver chloride reaction (Cl capturing) and the other based on
ion intercalation reaction in a Prussian Blue derivative (Li exclusion electrode).[31] The authors showed theoretically and experimentally, that salt capturing and selective exchange methods were not only differing in the used materials yet as well in the energy consumption. The theoretical calculation predicted a larger thermodynamic contribution in the energy consumption in the case of the selective exchange method with respect to the salt capturing. These calculations also predicted a great influence of the current density employed on the kinetic energy consumption, small and similar for the two methods at low current density, but higher when the current density in step 1 and 3 is increased to 5 mA cm~2 especially for the salt capturing method. Experimentally, similar concentrations of lithium in the recovery solution were observed for the salt capturing and selective exchange lithium recovery methods, however, the selective exchange method showed superior lithium recovery capacity and efficiency at all used current densities. The experimental energy consumption was much larger than the theoretical values predicted, which were connected only to the resistance of the electrolyte and the diffusion of the reacting and produced species, evidencing that the largest contribution to the kinetic energy consumption is connected to the surface overvoltage.

An evaluation of the electrical energy consumption has been thoroughly performed for a flow-through setup,[106] with LMO and NiHCF electrodes. The evaluation was carried out for the capture stage[152] and for the whole process (capture plus release).[153] With optimized working parameters, the reactor was able to extract more than 90% of the lithium present in a 1 × 10^{-3} m LiCl source solution.[152]

The whole process (capture plus release) was analyzed,[154] in which a reactor with small dead volume was designed and studied. Several cycles of capture/release were performed, by capturing from a source solution with 1 × 10^{-3} m of LiCl and releasing it into 5 mL of recovery solution, initially composed by 100 × 10^{-3} m KCl. Table 6 shows the K+ and Li+ concentrations in the recovery solution upon cycles: the measured values are the experimental concentrations detected with inductively coupled plasma–optical emission spectrometry (ICP-OES), while the calculated values are the concentrations evaluated from the circulated charge, assuming a Coulombic efficiency equal to one. The discrepancy was due to the back-mixing and to a Coulombic efficiency less than one. The actual values were correctly fitted by taking into account a back-mixing of 1.4% of the recovery solution volume and Coulombic efficiency values of 0.8 and 0.94 for and (de)intercalation respectively.

The total W_{e,j} was evaluated from the experimental data,[153] so that the contributions W_{irr} could be calculated.[154]

In Figure 18, W_e, W_{rev} and W_{irr} are reported; in this graph, they are normalized by lithium number moles transferred in each cycle.

The total electrical energy required for the whole sequence of cycles is

\[ W_T = \sum_j \frac{W_{e,j}N_j}{N_{tot}} \]  

where j is the cycle number, N_j are the lithium moles transferred at each cycle, and N_{tot} are the total transferred moles. W_T for the experiment reported in ref. [154] was 6.1 Wh mol^{-1}. It was noticed that the use of NaCl rather than KCl in the recovery solution affects the reversible work needed by the extraction: by using KCl, 85% of energy is spared. A related result, for the case of anions, was discussed in the LMO/polypyrrole system,[155] in that case, the whole process could take place spontaneously when the concentration of the anions in the source solution was much higher than the concentration of lithium.

### 7.2. Pumping Energy

The hydraulic pumping energy \( W_p \) is calculated as[106]

\[ W_p = R_p \Gamma_s T \]  

| Cycle number | \[\text{Li}^+\]_{measured} [mM] | \[\text{Li}^+\]_{calculated} [mM] | \[\text{K}^+\]_{measured} [mM] | \[\text{K}^+\]_{calculated} [mM] |
|--------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1st          | 16.8                            | 19.24                           | 101.7                           | 101.7                           |
| 2nd          | 29.4                            | 35.7                            | 86.01                           | 86.3                            |
| 3rd          | 40.45                           | 51.8                            | 67.9                            | 68                              |
| 5th          | 61.6                            | 80.5                            | 44.38                           | 38.8                            |
| 7th          | 80.9                            | 108                             | –                               | –                               |
| 9th          | 100.9                           | –                               | 0.7                             | –                               |

Table 6. Evolution of the Li+ and K+ concentrations in the recovery solution upon cycling. The measured values are the estimated concentrations by means of the Faraday law with Coulombic efficiency equal to 1. The data in the table are taken form ref. [153].
Table 7. Variation of the hydraulic energy per unit of mole required during the capturing process with the concentration of lithium in the source solution and the cost of pumping as a percentage with respect to the income of the final process in a non-optimized reactor. The data in the table are taken from ref. [106].

| Li concentration [mM] | Hydraulic energy [kWh mol⁻¹] | % relative cost of pumping |
|----------------------|-----------------------------|--------------------------|
| 1                    | 50                          | 140                      |
| 2                    | 10.5                        | 105                      |
| 5                    | 1.8                         | 18                       |
| 10                   | 0.4                         | 3                        |
| 40                   | 0.018                       | 0.18                     |

where Γ is the volumetric flow, R is the hydraulic resistance of the cell, and T is the duration of the process, see ref. [106] for the measurement technique.

In Ref. [106], the pumping energy consumption was evaluated in a non-optimized reactor, for various concentrations of lithium in the source solution. The results are reported in Table 7. Additionally, Table 7 reports the cost of pumping as a percentage of the price of the corresponding extracted lithium carbonate (24 € kg⁻¹); this evaluation is performed by considering a typical pump with efficiency 80% (ratio between ideal pumping energy and energy consumption) and with the price of electricity equal to 0.097 € kWh⁻¹, typical of a medium-sized industrial plant located in Germany.[156] Using a source solution with a low concentration of lithium chloride made the process less economically convenient.

In ref. [154], the improved reactor design allowed the pumping energy to be decreased down to 1.9 kWh mol⁻¹ for the extraction from 1 mM solution. In this situation, the pumping energy consumption widely exceeded the required electric energy (6.1 Wh mol⁻¹ [154]), which could be neglected in the total cost evaluation. From these data, it was estimated that the pumping energy cost for extracting lithium from 1 mM brine is around 30% of the lithium price; thus, the process is economically sustainable also at this small lithium concentration. From Table 7, it can be noticed that the pumping energy roughly decreases with the square of the concentration of the source solution: at higher concentrations, lower cost is expected. Moreover, the pumping costs can be further decreased by optimization of the cycles and of the porous structure of the electrode.

7.3. Cost of Materials

The evaluation of the cost of a plant (CAPEX and OPEX) is outside the scope of the present review and has not been discussed in the literature, due to the relatively low technological readiness level of the technology. However, it is possible to discuss the cost of the electrode materials. The theoretical capacities of LMO and NiHCF are ≈60 and 120 mAh g⁻¹, respectively. These values can be translated into mass ratios between the mass of active material and the mass of captured lithium per cycle; the results are 91 and 63, respectively. From the typical market costs of the two materials, we evaluate a ratio in the range of 8–30 between the cost of the active materials and the value of produced lithium per cycle (prices of lithium carbonate in 2016). This cost must be considered as part of the OPEX, since the materials must be substituted periodically. This evaluation thus says that the OPEX cost for the substitution of active materials is smaller than the value of produced lithium if the materials are able to withstand at least 8–30 cycles. Although the literature still does not provide a reliable evaluation of material stability under working conditions, the results in the literature[47] suggest that this should be likely.

8. Conclusion and Final Remarks

There is not an established protocol to evaluate the properties of electrochemical lithium recovery methods. Tables 5 and 6 summarize the main properties of the Li⁺ recovery studies reported so far using LiFePO₄ or λ-MnO₂. It is clear that there is not a homogeneity in what are the key parameters of the process and even the procedure to calculate some parameters differ between authors, so a standardization is required for a proper comparison, especially in the case of LFP where half of the studies employed different methods to quantify the lithium recovery or did not provide a complete recovery process, giving rise to much more heterogeneous results compared to those for LMO. We encourage researchers to include at least the seven parameters described in these tables: selectivity; absorption capacity; energy consumption; increment concentration per cycle; efficiency and purity. In addition, we stress the need of analyzing the performance of the recovery method using one feed solution with concentrations equivalent to those found in natural brines. It would be of great advantage if the scientific community could agree in the use of a standard concentration (we propose here Atacama brine).

The selectivity toward Na⁺, generally the main cation in the Li⁺ sources, plays a critical role to understand the potential capacity of Li selective materials. Even when similar selectivity is expected for equivalent materials (mainly λ-MnO₂ and LiFePO₄), the different synthesis route employed, the doping level, the presence or not of a coating, the porosity and particle size, all play a critical role in the electrochemical performance of the electrode, similar to what observed in Li-ion batteries, and is one of the main causes of the observed divergences. A similar case is the selectivity toward Mg²⁺. This component of Li source hinders the exploitation of numerous brine lakes, therefore measuring the capacity of the material to discriminate between these cations is decisive. In spite of their important role, the selectivity is calculated just in 55% (Na) and 27% (Mg) of the recovery methods when λ-MnO₂ was employed as Li selectivity electrode and 89% (Na) and 66.7% (Mg) in the case of LiFePO₄. Another parameter highly dependent on the synthesis route is the absorption capacity. A superior electrochemical performance will imply higher absorption capacities. We think that values over 32 mg g⁻¹ (λ-MnO₂) or 40 mg g⁻¹ (LiFePO₄) should be critically considered. Such values correspond to capacities above 120 and 150 mAh g⁻¹, which are the values obtained in optimized lithium-ion batteries.

On the other hand, for the conversion to Li₂CO₃, the purity of the recovery solution must reach values of 99%. However,
this parameter is not generally reported in the literature, thus preventing the evaluation of the viability of the Li\(^{+}\) recovery method presented. Additionally, concentrations of Li in the range of 0.7 \(\mu\) are required before its utilization for the synthesis of Li\(_2\)CO\(_3\). The current methodologies are far from these values, but could reach them by the repetition of the recovery cycles. However, there is an enormous discrepancy between methods and their capacity to increase the concentration by several repetitions. When microliters are used in the recovery solution, around 10–15 repetitions would permit to reach the desired concentration, on the contrary for reactors with volume in the range of 20–40 mL an unfeasible number of cycles, 2500–3000, would be needed.

In general, just the energy consumption in an intercalation-deintercalation cycle is considered for Li\(^{+}\) extraction. It is reported in 44% and 73% of the works for LiFePO\(_4\) and Li-MnO\(_2\), respectively. Nevertheless, the energy required to pump in/out the solution should not be ignored. Therefore, methods that require a lower number of repetitions will also have a reduced energy cost. In addition, the reported energies are based on the initial recovery cycle, but the depletion of Li in the feed solution and increment of concentration in the recovery solution by repetitive cycling could increase these values.

Other key parameters that affect energy consumption are the counter electrode employed and the nature of the source and recovery solutions. For a proper evaluation of the potential applicability of the recovery method, a source solution based on concentrations reported in typical Li sources (brine lakes, wastewater, geothermal water) must be used, but just 55% of the studies include this analysis. Finally, the efficiency will have a tremendous impact on the cost of the extraction process. Values close to those reported for Li-ion batteries, 99.9%, will be difficult to obtain because of the conditions found in Li sources are less favorable than in batteries. However, values above 90% have already been reported.

Regarding the counter electrodes, new materials have been recently demonstrated as alternatives to Pt and Ag, which were used in almost half of the reported works, but there is still room for improvement and a better understanding of their properties in brines is still needed. Another key parameter poorly studied in literature is the stability of the materials in the brine, focusing most of the studies on the first cycle or on a few initial cycles (less than 5).

From the point of view of the reactor design, Li extraction from brine has been efficiently performed in packed bed reactors with flow-by or flow-through configurations. Both designs have advantages and disadvantages. A trade-off between the parameters governing the process (current, flow rate, mass loading) has to be made to find the optimal conditions (capacity and capturing rate) of Li extraction from brine in the electrochemical reactors.

An optimization of different parameters like range of potential, cell voltage, applied current, mass loading, current collector, as well as the nature of the recovery solution or the crystallographic and morphological properties of the electrodes (porosity, particle size, coating) as well as researching of novel electrodes materials will be required for the improvement of the performances of the methods and consequently reduction of the Li production time and cost.

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### Conflict of Interest

The authors declare no conflict of interest.

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brine, electrochemical methods, lithium extraction, lithium recovery, sustainable mining

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