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# Direct lithium extraction (DLE) methods and their potential in Li-ion battery recycling

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ABSTRACT

Lithium (Li) supply from secondary sources (e.g. batteries) will play a critical role in easing the demand from primary production (brines and minerals). To meet ambitious Li recycling targets from electric vehicle (EV) Li-ion batteries (LIBs) imposed by the European Union, it is imperative to develop innovative recycling processes at an accelerated pace. Direct Lithium Extraction (DLE) methods have been developed to produce Li from brines. Herein we assess the application of various DLE technologies to extract Li from recycling streams of EV LIBs. Technical aspects and suitable initial solute concentration ranges of several DLE methods namely solvent extraction, ion-exchange resins, sorbents, membranes, and electrochemical ion pumping have been mapped. After this, an optimum pre-treatment route of the EV LIB recycling process has been chosen by estimation of Li recoveries and losses through different combinations of dry and wet crushing followed by froth flotation for anode and cathode separation. Pyrolyzing the whole cells/modules followed by dry crushing and flotation was found to be the most ideal process which can minimize Li losses during pre-treatment. Furthermore, the estimation of concentrations, compositions, and volumes of streams for the downstream hydrometallurgical process is done to identify Li-containing streams where DLE can be used, and suitable technologies have been highlighted. The incorporation of DLE has the potential to minimize Li losses in the recycling process. However, various DLE methods may be required to recover Li in different steps, with nanofiltration and reverse osmosis, selective ion-exchange resins, and solvent extraction being the most promising options.

## 1. Introduction

Lithium-ion batteries (LIBs) are critical for decarbonizing the mobility sector, serving as efficient green energy storage devices. This has led to their rapid adoption in electric vehicles (EVs). The EV market is anticipated to expand to approximately 130 million vehicles worldwide by 2030, coinciding with around 11 million tons of LIBs expected to reach the end-of-life (EOL) [1]. This surge in demand for LIBs is projected to increase the demand for lithium (Li) from 0.5 to up to 3.2 million tons from 2022 to 2040 [1,2], respectively, making supply from secondary sources (recycled materials) critical. Li reserves in the form of brines and minerals (spodumene, lepidolite, petalite, and amblygonite [3]) are concentrated in a few countries namely Chile, Australia, China, and Argentina holding major reserves [2]. Around 52 % of primary Li production came from Australia (minerals), Chile 25 % (brines), Argentina 13 % (brines), and China 6 % (brine and minerals) in 2021 [4]. The uneven distribution of Li reserves deems it necessary to secure supply from secondary sources with spent EV LIBs as the major source. The current global recycling rate of LIBs is estimated to be $<$ 5 % [1,5]. According to a recent European Commission report the EOL recycling input rate (supply into production from EOL products only) of Li in 2023 was 0 % [6]. This is mainly attributed to low volumes of spent materials and inefficient recycling processes. To mitigate this European Union (EU) has enacted a new directive imposing Li recycling targets of 50 % and 80 % in 2027 and 2031 from batteries, respectively, and a minimum of 6 % recycled Li in new batteries by 2031 [7]. The ambitious recycling targets call for accelerated development and up-scaling of recycling processes. Thus, we investigate the application of Direct Lithium

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Extraction (DLE), used in primary Li production, to extract Li from recycling streams of LIBs to ease the burden on primary Li supply.

Several studies have been published on Li extraction from primary resources using DLE, Table 1. Stringfellow et al. [8] discussed various DLE technologies in detail and presented their potential to recover Li from geothermal brines. They also urged for commercial scale testing for further development of processes. Vera et al. [9] evaluated the environmental impact of conventional evaporative processes of Li production from brines and compared them with DLE processes. They suggested monitoring the environmental impact of both evaporative processes and DLE-based technology, even though the latter consumes less fresh water and other resources. Meng et al. discussed the conventional practices for Li recovery from brines, ores, and LIBs [3]. Recently, Farahbakhsh et al., [10] in their review, recommended employing DLE for Li production from evaporation brines, brine pumping, and hard rock ores. They also discussed the possibility of DLE application to recover Li from batteries, but the potential of different technologies available to extract Li from the recycling stream of LIBs was not critically evaluated. Moreover, several DLE technologies have already been applied for Li recovery from recycling streams but there is a need to critically assess and evaluate the available materials with respect to recycling streams which differ from brines in many aspects such as pH, composition, concentration, among others. Li brines are rich in magnesium, sodium, calcium, and potassium with high salinity while the recycling streams are dominated by nickel (Ni), manganese (Mn), cobalt (Co), iron (Fe), copper (Cu), aluminum (Al) etc. as the competing ions. By focusing solely on the recovery of Li from recycling streams of EV LIBs, this review can provide concise recommendations on materials and processes as well as identify materials that can potentially recover Li from such streams but have not been investigated as of now.

**Table 1**
Overview of recent studies on DLE

| Focus area | Brief summary | Ref. |
|---|---|---|
| DLE | Discussed the potential of different DLE methods and materials to recover Li from geothermal brines with possible improvements. | [8] |
| DLE | Evaluated the environmental impact of evaporative processes of Li production from brines and compared them with DLE processes. | [9] |
| Production from different sources | Industrial Li production processes from ores, brines, and spent LIBs were reviewed. The production from LIBs was mainly focused on commercial recycling processes. | [3] |
| DLE from brines | Reviewed DLE technologies and recommended employing DLE for Li production from different sources. Briefly discussed the possibility of DLE application to recover Li from batteries. | [10] |
| DLE from geothermal brines | Reviewed different DLE technologies with a focus on sorbents. | [11] |
| Primary production | Compared the impact of Li production from open pit mining, evaporation in ponds, and DLE on water and society. | [12] |
| Extraction from salt lake brines | Reviewed different technologies and advances in Li production from salt lake brines. | [13] |
| Production from seawater, brines and lakes | Reviewed the established and emerging technologies and identified the bottlenecks. | [14] |
| Production from seawater and brines | Briefly discussed Li production from ores. The extraction from seawater and brines using different technologies was critically evaluated. | [15] |
| DLE from geothermal brines | Reviewed different DLE technologies to find suitable candidates for extraction from geothermal brines in Indonesia. | [16] |
| DLE from salt lake brines | Critically reviewed adsorbents for DLE from salt lake brines with a focus on structure, extraction mechanisms, performance, limitations, and challenges. | [17] |
| DLE | Reviewed the Li extraction from oilfield brines using metal oxide sorbents. | [18] |
| Extraction from salt lakes | Identified solvent extraction as an environmentally friendly technology and reviewed different extraction systems for Li extraction from salt lakes. | [19] |
| Extraction from salt lake brines | Different technologies to extract Li from high $Mg^{2+}$ brines were reviewed. | [20] |
| Extraction from brines | Membrane-based technologies for Li extraction from brines were reviewed. | [21] |
| Extraction from brines | Application of nanofiltration membranes for Li extraction is critically reviewed and commercial applications are also briefly discussed. | [22] |
| Extraction from brines | Reviewed different electrochemical lithium ion pumping systems for Li recovery from primary sources. | [23] |
| DLE | Extraction from brines with a focus on sorbents and electrochemical methods. | [24] |
| DLE from battery recycling streams | • Critical review and evaluation of DLE technologies with a focus on the chemistry of LIB recycling streams<br>• Estimation of concentration and composition of Li containing streams in the EV LIB recycling process<br>• Recommendations to investigate different DLE technologies and materials to extract Li from such streams | **This work** |

In this study, the application of DLE to recover Li from EV LIBs recycling streams has been investigated. First, the DLE concept has been introduced followed by an extensive literature review of different processes and materials which have been critically evaluated on their limitations to recover Li from the later devised EV LIBs recycling process. Furthermore, different pre-treatment routes of a recycling process for spent EV LIBs have been explored with a focus on dry & wet crushing and froth flotation for graphite separation from black mass. The most optimal pre-treatment route has been chosen by calculating Li recoveries and losses through their combinations. This is followed by the estimation of concentration, composition, and volumes of streams throughout the downstream hydrometallurgical recycling process. Finally, the optimal DLE materials and processes have been proposed to recover Li from different streams of the devised recycling process. This study will give impetus for researchers and industries trying to optimize Li recycling yields by recovery and valorization of Li from different waste/feed streams and provide a basis for further investigation of the application and development of DLE methods in LIB recycling.

## 2. Direct lithium extraction (DLE)

Li recovery from brines is conventionally conducted by stepwise concentration and impurity removal by precipitation in solar evaporation ponds, the final product being a concentrated lithium chloride (LiCl) solution. Such a process is resource-intensive in water and reagent consumption (acids, bases, precipitating reagents, etc.), with a production time of up to 2 years [8,9]. To mitigate the low concentration in ponds DLE technologies (Fig. 1a) have been gaining interest in recent years. DLE processes employ different materials/mechanisms to selectively isolate Li from other ions present in the brine. Such processes can rely on several mechanisms including solvent extraction, adsorption, ion exchange, membrane or electrochemical processes, Fig. 1b-g [8,9]. The preference of most commercial materials to bind di- and trivalent metal ions over monovalent Li ions complicates this separation, highlighting the need for specific chemistry and properties of materials. Herein we discuss the most promising processes and materials with a focus on selectivity, cycling performance, and limitations. Several reviews have been reported on DLE from brines [3,8–10], Table 1, but as the composition and concentration of LIB recycling streams are different compared to brines, an evaluation of their adaptability for specifically Li extraction from LIB recycling streams is needed.

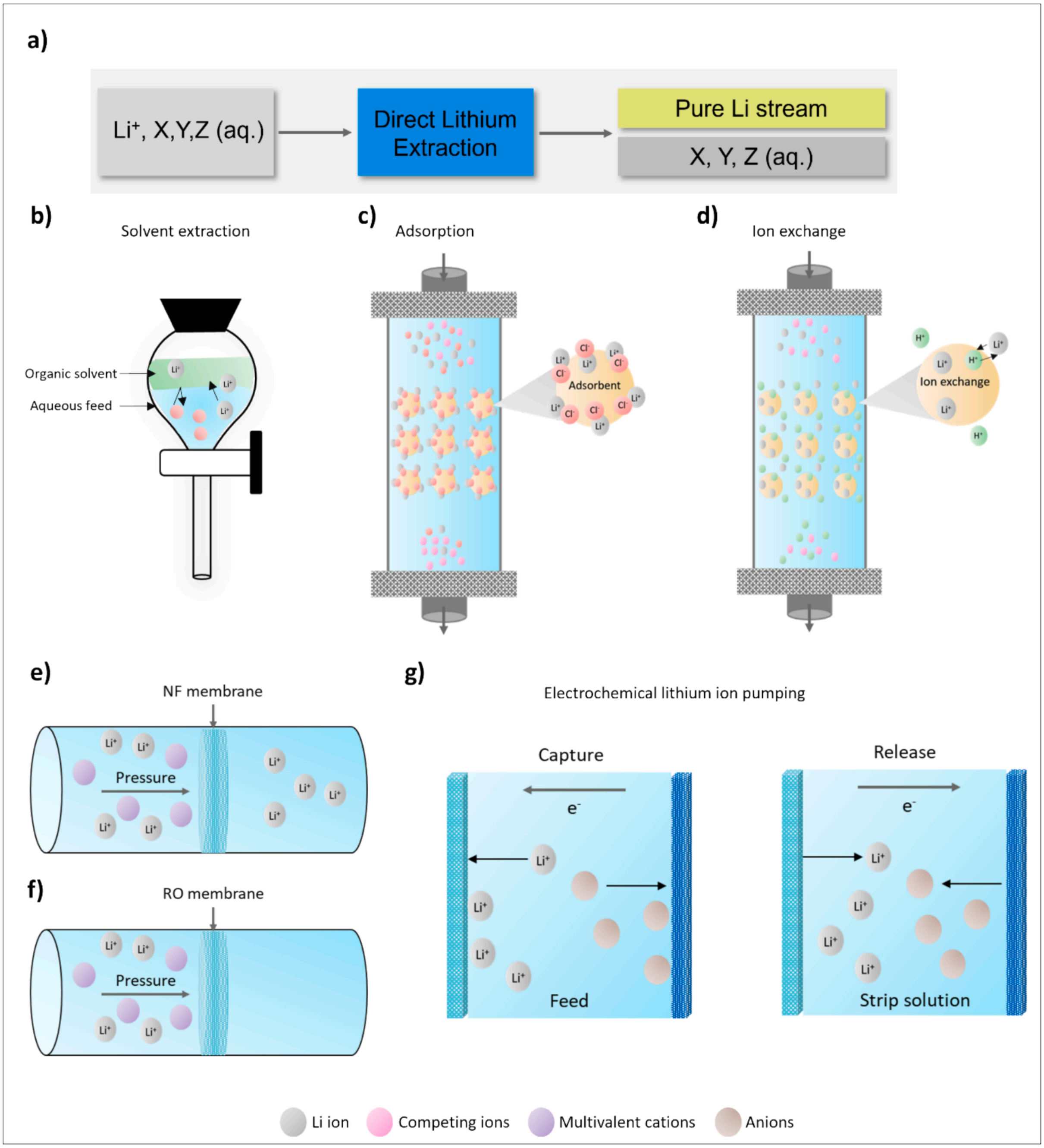


**Fig. 1.** Schematic of a) Direct lithium extraction (DLE) b) solvent extraction c) adsorption d) ion exchange e) nanofiltration f) reverse osmosis g) electrochemical ion pumping process.

### 2.1. Solvent extraction

Solvent extraction is a mass transfer unit operation based on the distribution of solute between two phases which are immiscible with each other (liquid–liquid extraction). The phase containing a species of interest with competing ions (usually aqueous) is mixed with the other phase (usually organic) which selectively extracts the species of interest. The extracted ions are stripped using an acid e.g., hydrochloric acid. Solvent extraction has been extensively studied for extracting Li from seawater and brines and we review the rigorously investigated solvents with possible industrial applications.

Synergistic solvent extraction of Li from brines with β-diketones + neutral extractants has been reported to selectively extract $Li^+$ over $Na^+$ in alkaline pH 8–12 with the prerequisite of removal of multivalent cations such as $Ca^{2+}$ and $Mg^{2+}$. Some of the β-diketones investigated are benzoyl-1,1,1-trifluotoacetone (HBTA), thenoyltrifluoroacetone (TTA), 4,4,4 Trifluoro-1-phenyl-1,3-butanedione (TPB), dibenzoylmethane (HDBM), with neutral extractants such as tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO), in diluents such as kerosene, etc. [8,25–29]. Pranolo et al. [26] reported a commercial extractant system of 0.4 M LIX 54 (β-diketone derivative) + 0.2 M Cyanex 923 (trialkyl phosphine oxide) in ShellSol D70 achieving a $Li^+/Na^+$ separation factor of 1100–1500 at pH 11. Furthermore, iron (III) chloride and TBP in kerosene has been reported to selectively extract Li from brines and LIB recycling streams at the expense of high $Cl^-$ concentration > 6 mol/L [30–33]. Ji et al. [32] added *N, N* –bis(2-ethylhexyl)-3-oxobutamide in TBP and $FeCl_3$ extraction system for which they reported a separation factor of $Li^+$ and $Mg^{2+}$ of

450. Wesselborg et al. [30] succeeded in extracting Li over Ni and Co using 80 % TBP + 20 % kerosene with $Fe^{3+}/Li^+$ ratio of 1.3 achieving separation factor of $Li^+$ over Ni and Co of 2825 and 854, respectively, in acidic pH. This confirmed the selectivity of solvent towards $Li^+$ in the presence of multivalent cations. However, the use of concentrated acid ~ 6 mol/L HCl during stripping to prevent Fe loss from the organic phase is a major challenge to overcome for $FeCl_3$/TBP solvent system [30,34]. Recently, crown ethers have been gaining interest in extracting Li, but they are still limited to lab-scale studies due to complex synthesis processes and low extraction efficiencies [8,25,35–38]. Some other solvent systems and ionic liquids have also been reported to extract Li from different streams, but these are still in the early stages of development [32,39–43]. Table S1 in supplementary information (SI) summarizes the different solvent extraction publications to extract Li, including information about feed stream composition, separation efficiency and selectivity.

### 2.2. *Ion exchange resins and inorganic sorbents (ion exchange and adsorption)*

The following section discusses ion exchange resins and inorganic sorbents in detail. The relevant literature is also summarized in Table S2.

#### 2.2.1. *Ion exchange resins*

Ion exchange resins generally consist of specific functional groups stabilized in a polymer matrix and were investigated for Li recovery from seawater as early as 1970 [8,44]. The cationic resins have exchangeable cations replaced with Li ions during loading. However, it has been reported that most commercial organic ion-exchange resins lose their selectivity towards $Li^+$ in the presence of competing cations ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, among others) due to the higher affinity of resins towards them [8,44,45]. Arroyo et al. [45] investigated Li extraction from a LiCl solution and real brine sample using three commercial ion exchangers namely Lewatit K2629 (sulfonic, $H^+$ form), TP 207 (chelating, iminodiacetic acid, $Na^+$ form) and TP 208 ($Na^+$ form) which were eluted with 4 M HCl. They reported > 95 % retention from solutions containing only $Li^+$ for all the resins but it decreased considerably in the real brine samples [45]. In another report, 30 commercial ion exchange resins were tested to extract Li from LiCl solution with only sulfonate, iminodiacetate, and aminomethylphosphonate resins successfully extracting Li but the selectivity was poor when tested in a synthetic brine feed solution [44]. Therefore, ion exchange resins must be altered to improve their selectivity. This is possible by imprinting them with Li selective sorbents also called ion imprinted polymers (IIP). The selectivity in IIPs mainly arises from the generation of specific Li containing sites during the imprinting process from which Li is eluted with a dilute acid before application in brines [8,46]. A Li imprinted polymer using crown ether have been reported to achieve $Li^+$ selectivity of 50.88 and 42.38 over $Na^+$ and $K^+$, respectively [47]. In another report week acid cation exchange resins with carboxyl, carbonyl, phosphorus oxygen double bonds and sulfur oxygen double bonds have been demonstrated to efficiently isolate Li achieving high concentration of Li (up to 29 g/L) after elution by controlling the amount of acid [48,49]. Furthermore, ion sieve type resins maintained more than 80 % selectivity for Li in high $Mg^{2+}/Li^+$ brines for 500 cycles [50]. However, the preparation of IIP is usually complex and complicated [51]. An alternate simple way to improve the selectivity is to impregnate the resins with Li selective extractants. During this process the extractant is adsorbed onto the porous structure of the resin materials which is called solvent impregnated resin (SIR) [51,52]. A β-diketone and trioctylphosphine oxide impregnated resin has been reported to efficiently isolate $Li^+$ over $Na^+$ and $K^+$ which was eluted with 1 M HCl [53,54]. The SIRs suffer from poor cycling as the extractant tends to be lost from the porous support over extended use needing further stabilization [51]. Summarizing, ion exchange resin can be a promising technology if the resin properties are modified to improve Li selectivity. They can also minimize the need for post Li up-concentration processes as a high concentration of Li can be achieved during elution by controlling the amount of concentrated acid.

#### 2.2.2. *Inorganic sorbents*

Sorption based DLE encompasses materials that can either exhibit adsorption or ion exchange properties for Li extraction. In adsorption processes, solute is intercalated onto the surface of an adsorbent from an aqueous solution which is eluted with fresh water e.g., aluminum-based sorbents[10,11], Fig. 1c. While in ion exchange, an insoluble solid material exchanges cation or anion with the species of interest in aqueous solution e.g. manganese and titanium based sorbents [10,11], Fig. 1d. Inorganic crystalline solids, e.g. various aluminum hydroxides (AlOH), aluminum oxides (AlOx), lithium manganese oxides (LMO), lithium titanium oxides (LTO), lithium iron phosphate (LFP) are proven to be selective Li sorbents, among others [8,11].

*2.2.2.1. Al-based.* Aluminum hydroxides are generally used as Li selective sorbents with lithium aluminum layered double hydroxides (Li-Al-LDH) as the most promising material [10,55]. Li-Al-LDH can be represented by the general formula $LiX.2Al(OH)_3{\cdot}nH_2O$, Fig. 2a, where X is an anion e.g. $Cl^-$ and n represent the number of $H_2O$ [56]. They have octahedral voids between a two-dimensional aluminum hydroxide layer where Li is intercalated, also responsible for their selectivity, with anion e.g., $Cl^-$ adsorbed simultaneously for charge neutrality [56]. Although their adsorption capacity is lower (typically < 10 mg/g) compared to Mn, Ti, and Fe type sorbents they have achieved technology readiness level (TRL) of 9 mainly due to their excellent cycling performance and reagent friendly process as they can be eluted and regenerated with only water [10,56–58]. The sorbent tends to dissolve below pH 6 and can be eluted with fresh water thus negating the dissolution which is prominent in case of elution with acids [57]. The dissolution loss of LDH in low pH rules them out for capturing Li from acidic waste streams. Al-based sorbents have been reported to efficiently reduce $Mg^{2+}/Li^+$ ratio of 284–301.58 in the Qarhan Salt Lake brine to 0.4–0.43 with an adsorption capacity of 6–7.26 mg/g [58,59]. However, Li-Al-LDH sorbents need high salinity, optimum temperature (typically 45–95 °C), and a minimum Li concentration of 100 mg/L for effective adsorption [55]. Another Al-based Li adsorption process is the precipitation of aluminum hydroxide ($Al(OH)_3$) on which Li is adsorbed [56]. This is achieved by adding an aluminum salt such as aluminum chloride to the brine and adjusting the pH with an alkali which results in the precipitation of aluminum hydroxide containing an appreciable amount of adsorbed Li. However, such sorbents need acids during the elution process [60,61].

*2.2.2.2. Lmos.* In addition to being used as cathode material in LIBs, LMOs are gaining interest as sorbents to capture Li due to their selectivity and sorption capacity. They act as ion sieves which is related to the memory effect, prohibiting entry of other ions in hydrated or dehydrated forms, with $Li^+/H^+$ occupying the tetrahedral sites of spinel-type LMOs while Mn occupies octahedral [62,63]. While the Li sorption mechanism is still debatable, it is proposed to be an ion exchange between $Li^+$ and $H^+$ or a redox reaction (under acidic conditions) where Mn III is reduced to soluble Mn II leaving sites for Li intercalation or a combination of both (composite) [10,56,63]. The loss of sorbent material occurs during elution with acids due to the reduction of Mn to Mn II species which can be dissolved into the eluate. The theoretical sorption capacities of three LMO sorbents namely $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$ and $Li_{1.6}Mn_{1.6}O_4$ are 39.9, 59.5, and 72.8 mg/g, respectively, Fig. 2b-c [56,62]. The theoretical sorption capacity increases with increasing Li/Mn ratio and depends on the crystal structure of spinels. Granulation of sorbent is done for continuous operation on a commercial scale which usually results in a decrease of uptake. Chitosan granulated $Li_{1.33}Mn_{1.67}O_4$ exhibited Li uptake of 8.98 – 11.4 mg/g from seawater containing 25——30 mg/L of

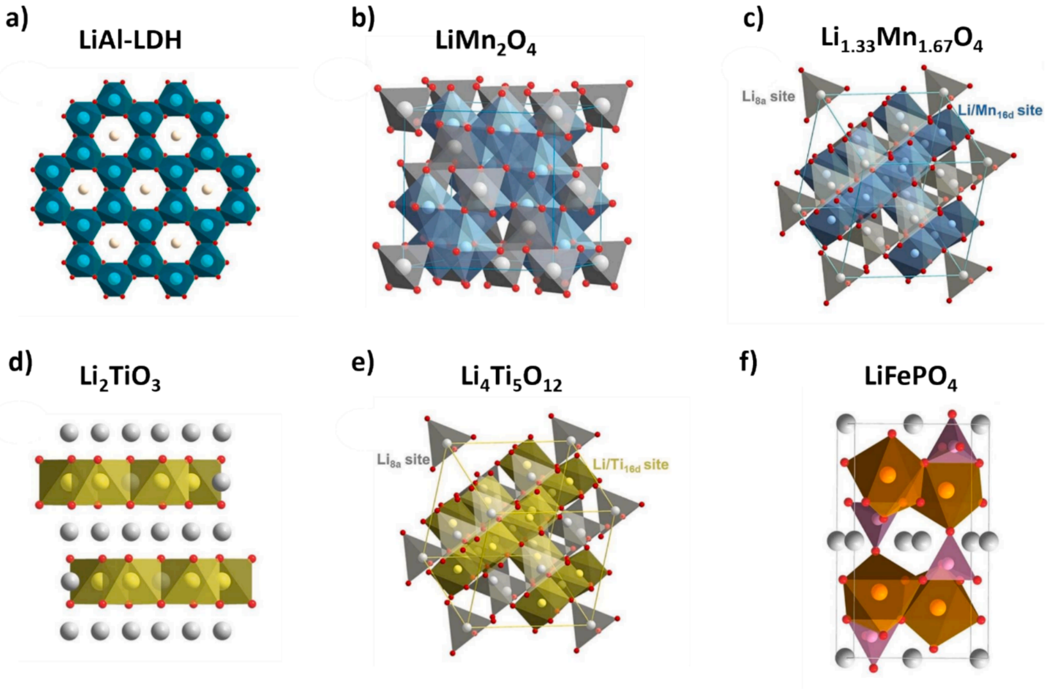


**Fig. 2.** Structure of different metal-based sorbents a) LiAl −LDH, b-c) LMO, d-e) LTO, f) LFP, where gray, green, yellow, blue, orange, violet, red and white spheres represent the Li, Al, Ti, Mn, Fe, P, O and H atoms, respectively, reproduced with permission from [17].

Li in ~ 24—72 hrs at pH ~ 12 reaching extraction efficiencies of > 90 % [64,65]. The adsorption uptakes observed are significantly less than the theoretical capacity of the sorbent. This can be attributed to the low initial concentration of Li with sorption uptake increasing to 54.65 mg/g with an initial Li concentration of 360 mg/L within 72 hrs [66]. The dissolution of active material from chitosan granulated sorbent was reduced to 9.2 % after three cycles during acid treatment [66] and the selectivity factor of $Li^+$ over $Na^+$, $K^+$ and $Ca^{2+}$ reached ~ 70, 51, and 87, respectively [64]. In addition to chitosan, other types of materials are also used for granulation/foaming [67–69]. However, the major challenge with LMOs remains the dissolution as Mn II and slow kinetics prohibiting its commercial application.

### 2.2.2.3. *Ltos.*

LTO sorbents are gaining interest due to their improved stability over LMO and eco-friendliness [20]. Similar to LMOs their selectivity arises from the memory effect in the structure which allows the de-/insertion of Li ions while rejecting others due to varying ionic radius or dehydration energy (steric hindrance) [10,56,63]. LTO sorbents can have a spinel or layered structure depending on the type of precursors i.e., $Li_4Ti_5O_{12}$ and $Li_2TiO_3$, respectively, (Fig. 2d-e) with the former having better cycling performance and the latter has improved selectivity for $Li^+$ over $Mg^{2+}$ reaching 4783 with 36.3 mg/g capacity [56,63,70,71]. B-$Li_2TiO_3$ has been reported to possess a high theoretical capacity of 142.9 mg/g of which 76.7 mg/g was achieved experimentally from a LiOH solution containing 2 g/L $Li^+$ [72]. Spinel $Li_4Ti_5O_{12}$ nanotubes showed even higher practical adsorption uptake of 160.6 mg/g in 24hrs from a LiCl solution with 2000 mg/L $Li^+$. The high uptake was attributed to the significantly higher surface area of nanotubes e.g., 115.4 $m^2/g$ [73]. The uptake decrease/vary considerably in the presence of competing ions when sorbent is granulated (reduced sorption sites on the surface) with low initial Li concentration and the process of production of sorbent. For example, the separation factor of $Li^+$ over $Na^+$, $K^+$ and $Ca^{2+}$ of ~ 297, 521 and 273, respectively, was achieved with an uptake of 12.84 mg/g at 328.15 K in 12hrs employing $Li_2TiO_3$ granulated using polyvinyl chloride with 25 mg/L initial Li [74]. The Li sorption mechanism is attributed to ion exchange, redox reaction, and composite already explained for LMOs previously [10]. In general, research shows LTOs have at least the same efficiency as LMOs regarding the sorption of Li ions from aqueous solution however kinetics are comparatively slower [8]. Even though LTOs have already been tested at a lab scale more research is needed to commercialize them.

### 2.2.2.4. *Lfps.*

LFP is one of the most commercialized cathode materials for EV LIBs alongside NMC cathodes [75]. They have also been employed to capture Li from brines as a sorbent. Olivine LFP sorbents, Fig. 2f, can capture Li by a redox reaction involving oxidation producing heterosite iron phosphate which then reversibly captures Li ions when reduced [11,44,76]. The process uses oxidation and reducing agents, which can increase the cost, but they benefit from better kinetics and selectivity over other inorganic sorbents. High sorption capacities of ~ 46 mg/g is reported with the extraction of $Na^+$, $K^+$ and $Mg^{2+}$ less than 4 mg/g, $Li^+/Na^+$ selectivity factor of 2541 and fast equilibrium time of 1.5–3 hrs [44,76]. However, iron dissolution becomes significant, up to 20 %, during sorption in acidic conditions at pH 4 [44]. Xiaong et al. [77] reported exceptional selectivity of $Li^+$ over $Na^+$, $K^+$ and $Mg^{2+}$ of 8704, 2460 and 6864, respectively, with an uptake of 9.13 mg/g in 20 mins, reaching 90 % extraction. The low uptake of Li could be attributed to the low initial concentration which was 0.1 g/L [77] and a high $Na^+$ concentration of 82.34 g/L. The Li concentration is much lower compared to others [44]. LFPs have also been applied in electrochemical cells to selectively capture Li. However, more research is needed to explore suitable reagents and continuous operation to commercialize them.

## 2.3. *Membranes*

Membranes are barriers that allow the transport of certain species from one fluid to another across them. They benefit from their modular design, ease of integration, and environmentally friendly process due to less use of reagents during operation. However, membrane technologies having TRL above 7 are mostly used for DLE pre- or post-treatment. The dominant membrane technologies are nano, micro, and ultrafiltration

[10]. Nanofiltration (NF) membranes allow monovalent ions to pass while prohibiting the flow of multivalent. This can be used to separate $Li^+$ over divalent ions such as $Mg^{2+}$ and $Ca^{2+}$ but the separation of monovalent ions such as $Na^+$ and $K^+$ needs further processing [8,78–81]. The mass transfer through NF membranes is governed by Donnan exclusion, steric hindrance, and dielectric exclusion [10,80,82]. The dilution of bines might become necessary in case of high salinity to reduce osmotic pressure [11,78,82]. Reverse osmosis (and pervaporation) is not considered a DLE method, but it is highly effective in up-concentrating a $Li^+$ solution or rejecting water. Even though reverse osmosis is an energy-intensive process, it offers higher water recovery efficiency, more flexibility, reduced time consumption, and a smaller footprint than other methods e.g., evaporation in ponds [8,83]. Membrane technologies that can be regarded as viable DLE options, such as supported liquid membranes (SLM), ion imprinted membranes, ion-selective membranes, etc., are in an early stage of development [10]. SLM is a promising technology employing a membrane suspended in a hydrophobic Li selective organic solvent, which separates the aqueous feed and strip solutions, achieving $Li^+/Na^+$ separation factor of ~ 400 [25,84]. However, several challenges, such as solvent degradation, leakage, and stability, need further exploration. Ion imprinted membranes incorporate adsorbing units such as crown ethers (e.g., 12C4) along with functional monomer and crosslinking agents during the polymerization process for better selectivity performance [36,38,85–87]. Electrodialysis processes separate cations and anions which travel across respective ion-selective membranes, under an electric field. Recently, selective electrodialysis has shown improved separation of $Li^+/Mg^{2+}$ due to the incorporation of a monovalent selective ion exchange membrane [86,88–90]. In summary, a combination of several membrane technologies might be necessary for complete DLE applications, with membrane fouling and energy consumption being the major challenges to overcome [78,91,92]. The membrane processes for DLE applications are summarized in Table S3 including membrane types, feed stream composition, selectivity, performance, and cycles.

### 2.4. Electrochemical lithium-ion pumping (ELIP)

ELIPs comprise an external electric field, Li selective electrode (sorbents such as LMO and LFP), and often an ion-exchange membrane. During the extraction process, a certain external voltage is applied, and Li and counter anion in the feed are captured by the respective positive and negative electrodes, Fig. 1g. These ions are released when voltage is reversed in the recovery solution, thus generating the electrode material for the next cycle [23,93]. ELIPs can generally be divided into five electrochemical systems, namely: (1) **water split** (Fig. 3a) where an active electrode captures/releases $Li^+$ with a water split reaction on the counter electrode, (2) **salt capturing** (Fig. 3b) which captures/releases $Li^+$ and anion (e.g. $Cl^-$) on respective electrodes without water splitting reaction, (3) **rocking chair** (Fig. 3c) which involves reciprocating motion of $Li^+$ between electrodes divided by an anion exchange membrane,

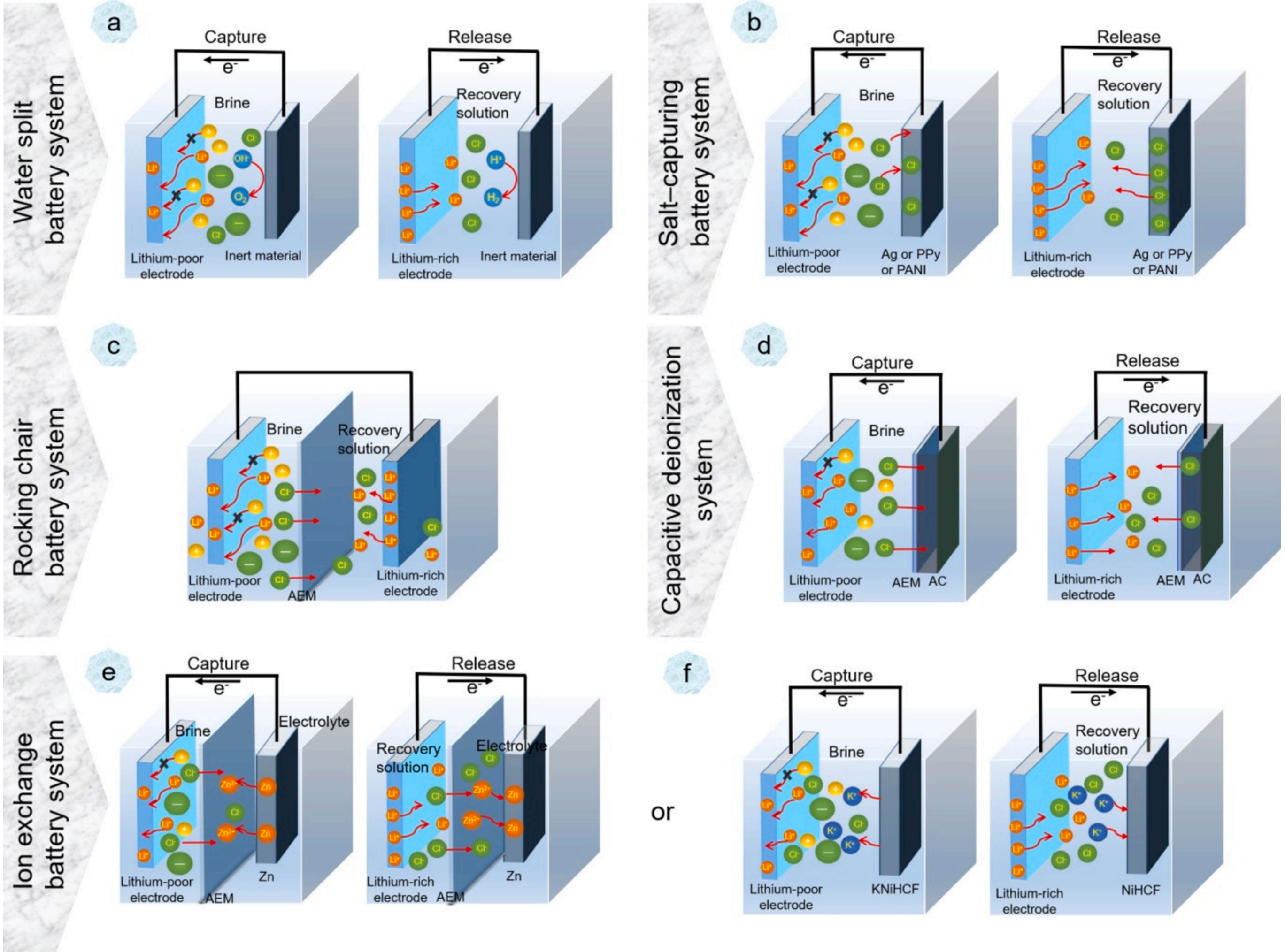


**Fig. 3.** Principles of different ELIPs battery system a) water split, b) salt capturing, c) rocking chair, d) capacitive deionization system, e and f), ion exchange. reprinted with permission from [23].

(4) **membrane capacitive deionization system** (Fig. 3d) incorporates Li intercalation in selective electrode with a cation exchange membrane while anion passes through anion exchange membrane and captured, and finally (5) **ion exchange** (Fig. 3e-f) involving replacement of $Li^{+}$ in the solution with ions from counter electrodes of similar electric charge e.g. $Zn^{2+}$ [23,93]. The Li selective electrodes are made from conventional cathode materials such as LMO and LFP, sometimes doped to improve performance [94–99]. Jang et al. utilized an LMO electrode for the first time to capture Li from the industrial LIB leachate of pH 2.1, achieving a separation factor of Li/Ni of approximately 90 [100]. Although ELIP has already been demonstrated at a pilot scale, achieving product purity of 88 % [101] they are still at a very early stage of development often requiring a high amount of electrolyte (TRL 3–4) [9,10]. Future research should be focused on standardized protocols and operating conditions. Some of the relevant literature reports exploring ELIPs have been summarized in Table S4.

### 2.5. Technological mapping of DLEs

The literature presented about the DLE methods in the aforementioned sections is condensed in a high-level overview in Table 2. The shortlisted DLE methods with the most efficient materials/technologies have also been presented. In addition, several companies/industries offering DLE technology/materials are summarized in Table S5.

Furthermore, an attempt has been made to combine all the gathered information to visualize and compare the strengths and weaknesses of the different DLE methods on nine parameters, shown in Fig. 4 (superior performance away from the center). These parameters have been chosen by extensively reviewing the literature presented in previous sections and SI Table S1--4 and the mapping has been done accordingly. However, it must be mentioned that, besides having significant objective indicators of the categories, summarizing and generalizing one DLE method is hard by itself due to them being also dependent on other parameters (e.g. feed solution, different planned recycling steps and others). Therefore, there is a certain portion of subjective views included in the categorization by the authors. The parameters include the cost of material, Li extraction/sorption efficiency, kinetics, recyclability or cyclic stability, ease of integration into an existing process, technical maturity, $Li^{+}/Na^{+}$ selectivity, energy consumption, and environmental impact ($CO_2$ footprint, water consumption, land use, waste generation, etc.). In the following, the strengths, and drawbacks of all DLE methods are explained concisely.

Solvents (Fig. 4a): They show fast kinetics and a high selectivity between monovalent ions, which is very important to separate $Li^{+}$ and $Na^{+}$. This, combined with their well-established technical maturity, makes them efficient as many commercial solvents are available. However, the cost of material and lower rates of recyclability, compared to ion exchange resins and sorbents, could make them not so ideal from an economic and environmental point of view, Table S1.

Ion-exchange resins (Fig. 4b): Ion-exchange resins, together with inorganic sorbents, have the highest form of technical maturity and there are already resins available for commercial use on the market. Selectivity between monovalent ions is a little worse than for solvents, but, depending on the material and Li concentration in the solution, they are reported to work well. However, the selectivity in the presence of di-trivalent ions is poor. Kinetics are generally slower, leading to lower efficiency. However, recyclability is higher as well as the cost of material and energy consumption is lower, which makes them more environmentally and economically friendly, Table S2.

Inorganic sorbents (Fig. 4c): Aluminum based sorbents with physical adsorption as the mechanism are not mapped here due to the need of high salinity for their application. Since LIBs recycling streams generally have low salinity compared to brines, explained earlier, that's why they have been omitted here. Other inorganic sorbents show somewhat similar characteristics to ion-exchangers resins, just mainly a tradeoff between cost of material, better Li selectivity in the presence of multivalent ions, and poor recyclability (dissolution of active material occurs during elution). They can be used to extract Li from low-concentration feed solutions, Table S2.

**Table 2**
Overview of different DLEs (the limitations and improvements needed for materials is summarized in the respective subsections)

| Process | Pros | Cons |
|---|---|---|
| **Solvent extraction** (β-diketones + Neutral extractants) | • Effective to separate Li and Na<br>• Can be recycled<br>• Can be used to up-concentrate Li, working pH 8-12, extraction time <30 mins | • Not recommended when divalent ions exist in solution<br>• High capital and operational cost<br>• Complex operation |
| **Ion exchange resins** | • Cleanliness of process<br>• More environmental friendly (less energy consumption compared to membranes)<br>• Can up-concentrate Li using acids during elution<br>• Good cyclic performance | • Long(er) time spans for reaching equilibrium<br>• Poor selectivity of Li over di-trivalent cations<br>• High energy cost for recovering material<br>• Need chemical treatment for recovery |
| **Inorganic sorbents** (LMO, LTO, LFP) | • High separation efficiency<br>• High selectivity and recovery<br>• High product quality<br>• Cleanliness of process<br>• Can be used in streams with low(er) Li concentration<br>• More environmental friendly (less energy consumption compared to membranes)<br>• Different forms, mainly powder at beginning | • Long(er) time spans for reaching equilibrium<br>• Depended on good preparation. Influences the degree of crystallinity and regeneration ability<br>• Loss of active material (more the smaller the sorbent)<br>• Need chemical treatment for recovery<br>• Often low or unknown durability/recyclability |
| **Membranes** (Nanofiltration, reverse osmosis) | • High separation efficiency<br>• High selectivity for divalent cations<br>• Modular design -> promising for large-scale applications<br>• Preprocessing step used for the feed stream<br>• Relatively eco-friendly operation (low footprint) | • Very low selectivity between monovalent cations<br>• Membrane fouling<br>• Often chemical reagent needed for desorption<br>• High investment and operating costs<br>• Leakage of inorganic particles possible for some<br>• Efficiency and selectivity can go down after few cycles |
| **Electrochemical**(Ion pumping) | • Low to no amount of chemicals/chemical waste (strong acids)<br>• High Li removal capacities<br>• High efficiency<br>• Flexible operation modes = better control of Li production rates | • Electrochemical processes need to operate under a current flow, high energy consumption<br>• Very often information like removal, recovery, uptake, duration, selectivity, energy consumption and/or purity of the final solution not (completely) given in most studies |

Membranes (Fig. 4d): NF and reverse osmosis are mapped here (cannot be considered as DLE methods). They are easy to integrate into a process because very often they are already delivered as finished modules or module packs. Also, they show fast kinetics and even though the costs of material and energy consumption are relatively high, they are often considered environmentally friendly as during operation no chemicals are needed. The main challenge is their cyclability (fouling, clogging) and their low selectivity between monovalent ions (NF), which makes them inefficient for such feeds. Although, they could be

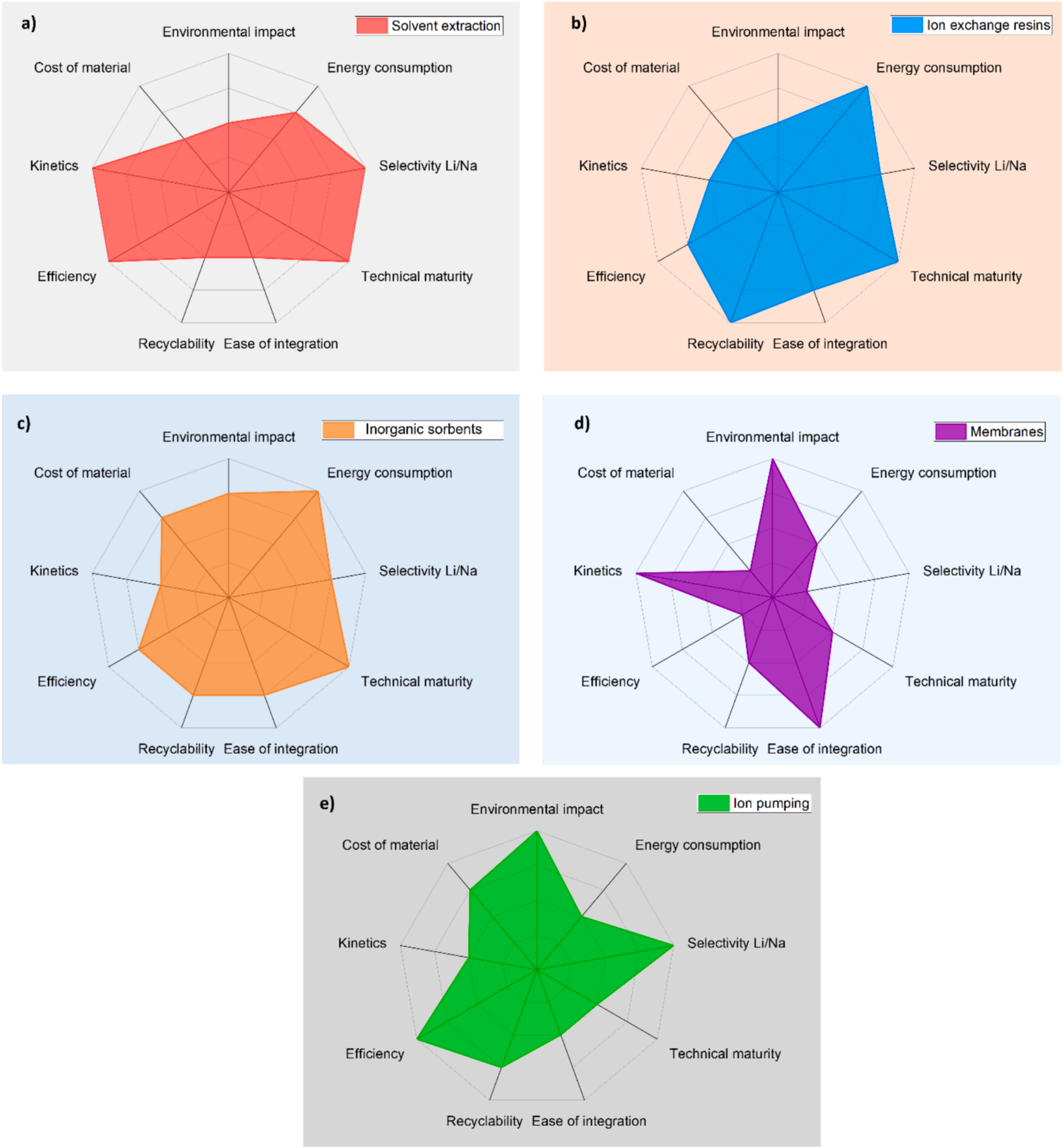


**Fig. 4.** Technological mapping of different DLE methods a) solvent extraction b) ion exchange resins c) inorganic sorbents d) membranes and c) ELIPs.

used efficiently for up-concentrating Li or rejecting water, Table S3.

Electrochemical ion pumping (Fig. 4e): These methods are very selective between monovalent ions. Most systems are relatively robust and operate stably over several cycles, which makes them efficient for battery recycling processes in that regard. Also, the cost of the material is low due to the longevity of the material and little to no use of chemicals during the ELIP process, but water consumption can be high [9]. Furthermore, they can be energy intensive as one study reported ∼ 300 folds more energy demand to only pump the solutions through cells compared to reactions [9], which makes them worse from an economic point of view. The TRL levels of ELIPs being a relatively new method is low and therefore ease of integration is low or unknown, Table S4.

Since several DLE methods can be used to extract Li from a certain stream it is vital to identify the most optimal choice regarding the ease of process operation. The recommendations based on the initial Li concentration in the feed solution are presented in Fig. 5 and are based on the reported literature, Table S1-4. Fig. 5 shows the most suitable ranges for different DLE methods for efficient operation. These recommendations fall under the category of Principle 4 which is **Maximize Mass, Energy, space, and Time Efficiency** from The Twelve Principles of Circular Hydrometallurgy, and are adapted to our process by keeping the fundamentals same as suggested by Kentish et al., and Binnemans et al., [102,103]. It should be mentioned here that all these processes can be and have been used outside their recommended range of initial

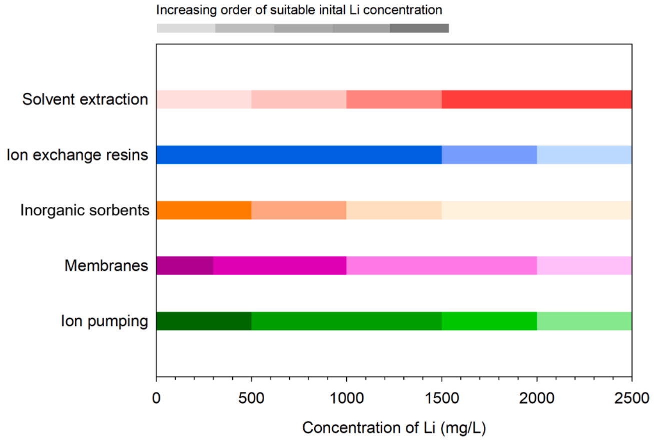


**Fig. 5.** Suitable initial Li concentration range of different DLEs.

solute concentrations. Generally, solvent extraction is preferred when the solute concentration is high in the feed stream, and this can also be verified by some of the studies that reported the use of this process for Li extraction [26–28,30,104]. This technology is not recommended when the solute concentration is low because of high aqueous/organic phase ratios leading to loss of the organic phase due to entrainment [102,103]. Ion exchange resins and inorganic sorbents are used when the solute concentration is low. We have recommended a higher operational range for ion-exchange resins [44,45,48,49] compared to sorbents (~500 mg/L [44,57,58,60,61,64–66,74]) as the former can be easily packed in the columns. This can also be true for inorganic sorbents when granulated with an organic backbone, considerably increasing the volume of sorbent increasing equipment sizes and decreasing uptake. Furthermore, inorganic sorbents are susceptible to leakage during elution with acids which makes them less favorable to use at higher solute concentrations. In such feed solutions the desirable case would be to get a higher concentration of Li after elution using concentrated acids which can be obtained using ion-exchange resins and solvent extraction processes thus minimizing the use of post up-concentration processes [26–28,30,48,104]. The membrane technology recommended here is reverse osmosis and nanofiltration (only to separate monovalent and divalent ions). They are recommended to be used when the solute concentration is very low to up-concentrate and pretreatment of feed streams in terms of separating multivalent ions [78,81–83]. Electrochemical ion pumping is an emerging technology, and distinct conditions need to be evaluated in future research. However, based on existing literature, a favorable solute concentration range is recommended [94,96–99]. This range can also be broad but in those cases, it would need to outcompete more mature technologies such as solvent extraction. To summarize, a suitable choice of DLE method can offer fast kinetics, high extraction capacities, less process complications, improved economy (capital and operational), and efficient plant operation.

The insights gained after mapping technological aspects and suitable initial concentration of Li for different DLE methods allow us to investigate their potential to recover Li from recycling streams. To do that it is essential to know the composition and concentration of such streams. In the following section, we identify the Li flow through the pre-treatment process of recycling EV LIBs and the downstream hydrometallurgical process from which Li is finally recovered.

## 3. Recycling routes to recover Li from EV LIBs

EV LIBs are discarded when they reach around 80 % of the state of health [105]. These LIBs may find other applications e.g., stationary energy storage in power plants, and eventually need to be recycled. A typical LIB cell consists of the cathode (lithium nickel manganese cobalt oxide (NMC), and others), anode (graphite, and others), electrolyte (lithium hexafluorophosphate ($LiPF_6$) in carbonate-based solvents, etc.,), separator (polypropylene, and others), and current collectors (Al or Cu metal). The cathode and anode further contain conductive additives (carbon black, and others) and binders (polyvinylidene fluoride (PVDF) etc.,). The battery cells are packed in modules which are further assembled to form a battery pack. After reaching the end of life a battery pack needs to be discharged, dismantled, crushed, and sorted to get a powder called black mass (BM). The process adopted to produce BM influences downstream hydrometallurgical processing to recover metal values and is explained here [106–108].

### 3.1. *Discharging and dismantling*

The first step in the recycling process is discharging the spent EV battery packs either by connecting it to a load, chemical discharge e.g., in a NaCl solution, or by cryogenic freezing [106]. Residual charge in the batteries is a potential safety hazard which deems it necessary to discharge them efficiently [106]. The next step is the dismantling of battery packs to recover casings, plastics, and cables. This could be done up to module or cell level depending on the process flowsheet. Dismantling is typically done manually because of the different shapes and sizes of battery packs from different manufacturers containing cylindrical, prismatic, and pouch cells among others [106].

### 3.2. *Crushing and sorting*

The next step is crushing and sorting of batteries. Crushing can be done in an inert atmosphere known as dry crushing or in a brine solution called wet crushing, Fig. 6 [109].

#### 3.2.1. *Dry crushing*

In dry crushing battery cells or modules are broken up into individual fractions. The electrodes are freed from the current collector foils. The electrolyte solvents are removed in a drying step which may use vacuum and heat. The electrolyte Li salts remain with the solid fractions. The dry fragments are easy to handle during the recycling process. An overview of a typical industrial pretreatment process based on dry crushing to produce BM is shown in Fig. 7. After discharging, dismantling, crushing, and drying a first air classification is carried out in a zig-zag-sifler which separates the particles based on their density concentrating Al 74.3 %, steel 13.8 %, copper 5 %, among others, in the light fraction while electrode particles are recovered in heavy products. This is followed by the sieving of particles after a second crushing step and 97 % BM (cathode active material (CAM) and graphite) are collected with particle sizes below 500 μm. Finally, a second air classification is carried out to concentrate 97.8 % of the separator in the light fraction while Cu and Al are recovered in the heavy product. The BM obtained is further processed by hydro or pyrometallurgical methods or their combination [106]. The Li loss in such a process occurs during the loss of electrode material in different fractions which can amount to 10–14 % [110] and Li deposited and penetrated in the separator.

Zhang et al. [110] further optimized the dry crushing of LIB cells by pyrolysis treatment of electrode scraps at 500 °C followed by crushing and reported shorter crushing times with effective liberation of electrode particles from the current collector foils. They reported a significant decrease in crushing loss of ~ 10 % for Ni, Mn, Co, and Li for pyrolytic electrode scrap compared to raw electrode sheets. This decrease in crushing loss is attributed to the removal of binder which is burned off at an optimum temperature of ~ 500 °C aiding in the liberation of electrode particles from the collector foils.

#### 3.2.2. *Wet crushing*

In this type of crushing whole battery pack, module, or individual cells are crushed in an aqueous or brine solution which can dissipate heat due to salt acting as a conducting medium. Since the whole feed

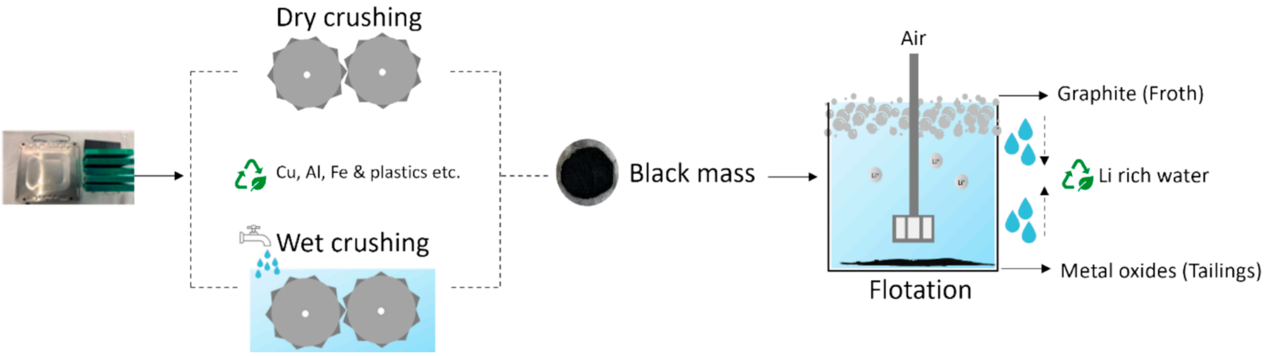


**Fig. 6.** Pre-treatment routes of recycling EV LIBs.

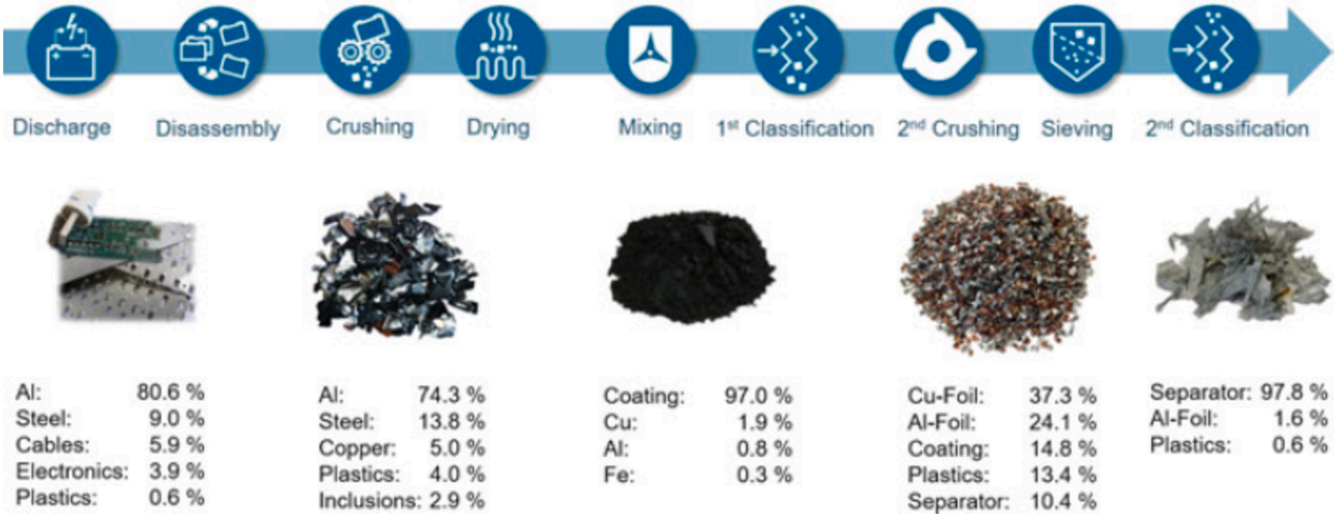


**Fig. 7.** An example of industrial pre-treatment process of BM production from EV LIBs, reprinted with permission from [106].

material is submerged potential fire hazards can be avoided due to a reduced supply of oxygen. Furthermore, the dissolution of $LiPF_6$ can form aqueous HF which can be converted into insoluble products such as calcium fluoride if the crushing is done in a calcium hydroxide solution [111]. However, this process generates an aqueous stream containing Li which then needs to be treated [109]. Li from the electrolyte can dissolve according to reaction (1) [106]. Furthermore, some dead Li deposited and penetrated in the separator (~18 μg/mg of separator [112]), and anode (~16 % [113,114]) can also be dissolved and needs to be recovered. If a basis of 2 $m^3$ brine/$m^3$ [111] feed of LIBs is considered and wet crush a 25 kg [107] module of dimensions 79 mm * 302 mm * 665 mm [107] comprised of cylindrical cells with the composition shown in Fig. 8 the water required is calculated to be 31.73 L. The calculated concentration of Li in crushing water can amount to 3.5 g/L (Appendix S1 in SI): where 0.36 g/L $Li^+$ arises from the dissolution of electrolyte i.e., 1 M $LiPF_6$ (density 1.27 g/mL in ethylene carbonate), 2.64 g/L $Li^+$ from anode considering 16 % Li (basis [113,114]) is deposited and penetrated, and 0.50 g/L $Li^+$ from separator ((basis 18 μg/mg [112]) which otherwise will be lost in dry crushing (Fig. 7) amounting to 3 % (calculated) of the total Li in the module.

On the other hand, wet crushing makes the separation of materials difficult as they stick together, extensive cleaning of equipment is required and more impurities concentrate in the BM due to the scouring effect of water [109]. Zhang et al [109] compared dry and wet crushing and concluded that for selective crushing characteristics dry crushing should be preferred.

$$LiPF_6 + H_2O = LiF + 2HF + POF_3 \tag{1}$$

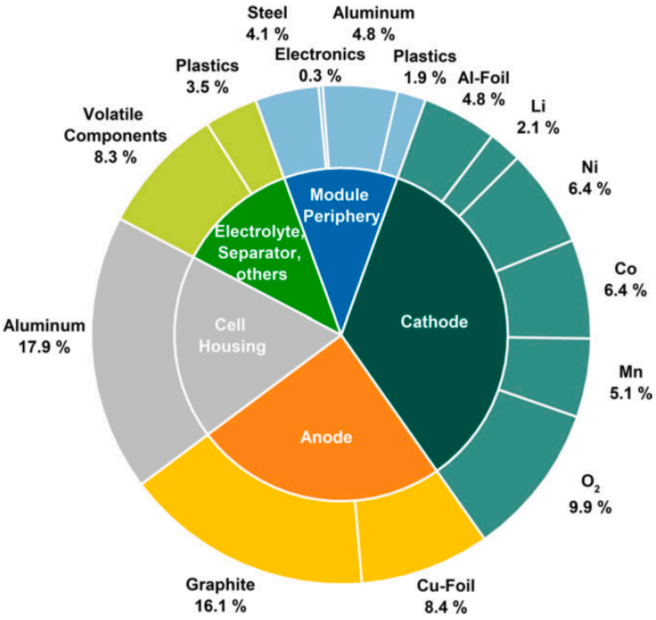


**Fig. 8.** Composition of a typical NMC 111 module, reprinted with permission from [106].

### 3.3. Froth flotation

The BM produced after crushing and sorting can be subjected to froth flotation to separate graphite and CAM. This process separates particles by their surface wettability. Air is bubbled through a flotation cell which causes the hydrophobic graphite particles to attach and rise to the top as froth. Meanwhile, hydrophilic metal oxides from the cathode are collected from the tailings at the bottom, Fig. 6 [113,115–118]. In a study by Yu et al. [115], cathode and anode sheets from LCO-type batteries were crushed, sieved to 0.074 mm, and subjected to grinding flotation. Electrode materials were grinded to improve the hydrophobicity of particles by removing the coating of binder and other organics. They reported 97.19 % and 82.57 % of grade and recovery rates of 49.32 % and 73.56 % of LCO and graphite, respectively. However, significant electrode material loss occurred due to incomplete removal of organic coatings.

Salces et al. [113] proposed a thermal treatment before the flotation process to simultaneously recover Li and graphite. The thermal treatment burns off the binder coating and improves the recovery and product grades in flotation. The LIB cells were pyrolyzed at 500 °C for 1hr in $N_2$ atmosphere followed by shredding and sieving and underwent flotation at 8 wt% pulp density. The concentration of Li after 1st, 2nd, and 3rd cycle of water reuse was around 1100 mg/L, 2020 mg/L, and 2600 mg/L which corresponded to 45 %, 43 %, and 25 %, respectively, recovery of Li. There was no appreciable increase in Li concentration after 3rd cycle likely due to saturation of the solution with respect to Li. The source of Li was related to the carbothermic reduction of metal oxide during pyrolysis, Li from the anode, and leftover Li from the electrolyte. The main impurity incorporated in the solution was Al which reached a maximum concentration of 70 mg/L after 3rd cycle. The increased concentration of ions can negatively affect the flotation process due to increased water viscosity, reduced froth stability, water drainage, and recovery by water entrainment. However, they suggested that the graphite recovery (85 %) and grade (75 %) were reduced by only 1–2 % in the case of Li-rich water rendering it not significant.

Verdugo et al. [116] further investigated the effect of Li-ion on flotation process. They performed a case study where froth flotation of roasted BM (case 1) and water washing the BM before flotation (case 2) were investigated. They studied pure NMC cathode, a semi-synthetic mixture mimicking a liberated LIB cell, and BM from spent LIBs. The Li concentration in water for different feed materials was reported. Li concentration in the case of spent mixed BM was 2572.82 mg/L and when this BM was washed prior to flotation the concentration reduced to 648.83 mg/L which also indicates that solution reaches saturation with regards to Li during the 1st washing. The separation efficiency in flotation experiments between electrode materials was higher in the case of spent-mixed washed BM ~ 87 % with 648.83 mg/L of $Li^+$ compared to spent mixed unwashed which showed lower separation efficiency of 66 % with $Li^+$ 2572.82 mg/L in flotation water. However, the flotation kinetics are fast in experiments with high Li concentrations. They correlated the lower separation efficiencies with higher Li concentration and froth stability arguing that oxide recovery in graphite concentrate increases when water entrainment is the main mechanism of recovery [116].

### 3.4. Estimation of Li recovery and losses for different pre-treatment routes of LIBs recycling

The choice of routes to produce BM from spent EV LIBs influences the downstream processing. For example, a pyrolyzed BM can be subjected to froth flotation to separate CAM and graphite while a BM that is only crushed without any thermal or chemical treatment to remove the binder coating from electrode particles cannot. However, pyrolysis treatment of LIB cells or modules followed by dry crushing could minimize the crushing losses due to the complete liberation of electrode particles from the collector foils, and the resulting BM could be suitable for flotation. To verify this, the Li recovery and loss based on different combinations of pre-treatment options of dry and wet crushing & sorting (C&S) followed by froth flotation has been calculated with reference to Li content in an NMC 111 module (25 kg [107]) of the composition shown in Fig. 8. Four process routes have been considered and the results are displayed in Fig. 9 while the calculations are shown in Appendix S2 in SI.

- **Process 1:** Dry C&S followed by flotation
- **Process 2:** Wet C&S followed by flotation
- **Process 3:** Pyrolysis of whole module followed by dry C&S and flotation
- **Process 4:** Wet C&S followed by pyrolysis of the BM and flotation

The Li loss in dry C&S (Process 1) was calculated based on the findings of Zhang et al. [110] who compared the metal loss during C&S of pyrolyzed and unpyrolyzed electrode material and reported around 2 % and 9 % loss of Li in fraction < 200 μm. Thus, by calculation the total loss during C&S in process 1 amounts to 12 % of which 9 % is lost in coarse fractions and 3 % lost in separator (deposited and penetrated Li) calculated in the section on wet crushing. The flotation of such BM is challenging because of the organics coating on the electrode materials during C&S. The material separation efficiency in this step has been based on the findings of Yu et al. [115] who employed grinding flotation to increase the hydrophobicity of particles by removing the organics coating. To achieve higher grade and recovery rate of electrode material they employed two flotation steps and reported 49.32 % and 73.56 % recovery rate of graphite and cathode material, respectively. The recovery rate of cathode material could be higher because of two flotation steps. For the sake of simplicity and to reduce the number of streams we have considered only one flotation step in our calculations and the separation efficiency between electrode materials has been kept at 50 % and pulp density of 40 g/L in flotation as reported by Yu et al [115]. The results in process 1 indicate that from 88 % Li, after flotation around 14 % is dissolved in flotation water (calculated from own water leaching data reported by Saleem et al. [119] for unpyrolysed BM), 37 % is recovered in tailings which can be further processed by hydrometallurgical process and 37 % is lost in froth. The Li in froth can also be recovered by acid leaching or a second flotation step but this will increase the cost, and the poor flotation separation efficiency builds a stronger case against flotation of this type of BM. The maximum Li recovered during process 1 could go up to 51 % (there could be additional losses in the downstream processing) while around 49 % is lost which is attributed to C&S and loss in the froth. Thus, the combination of processing steps in process 1 can lead to significant losses if such a BM is subjected to flotation.

Process 2 incorporates wet C&S prior to flotation. A significant amount of Li can be recovered in crushing water which can amount to 20.7 % compared to Li in an NMC111 module of the composition shown in Fig. 8. The breakdown of Li contribution sources in crushing water is explained in the section on wet crushing. The crushing loss of Li can amount to around 7 % calculated based on the findings of Zhang et al. [110]. Leftover Li in the BM before flotation amounts to around 72.3 % which is then floated according to conditions explained in process 1, [115]. Even though most of Li is recovered from electrolyte, separator, and anode in crushing water there could still be some leftover Li dissolution in the flotation water. Considering the concentration of Li in the flotation water of 0.25 g/L [119,120], around 13.9 % Li is recovered in flotation water while the remaining goes to hydrometallurgy and in the froth. Although wet crushing in Process 2 reduces the overall Li loss such a BM will still not be suited for flotation because of organics coatings on the electrode particles thus higher losses in froth.

Process 3 includes the pyrolysis of the whole module prior to dry crushing followed by flotation. Pyrolysis in an inert atmosphere (~600 °C) has been widely reported in the literature which not only

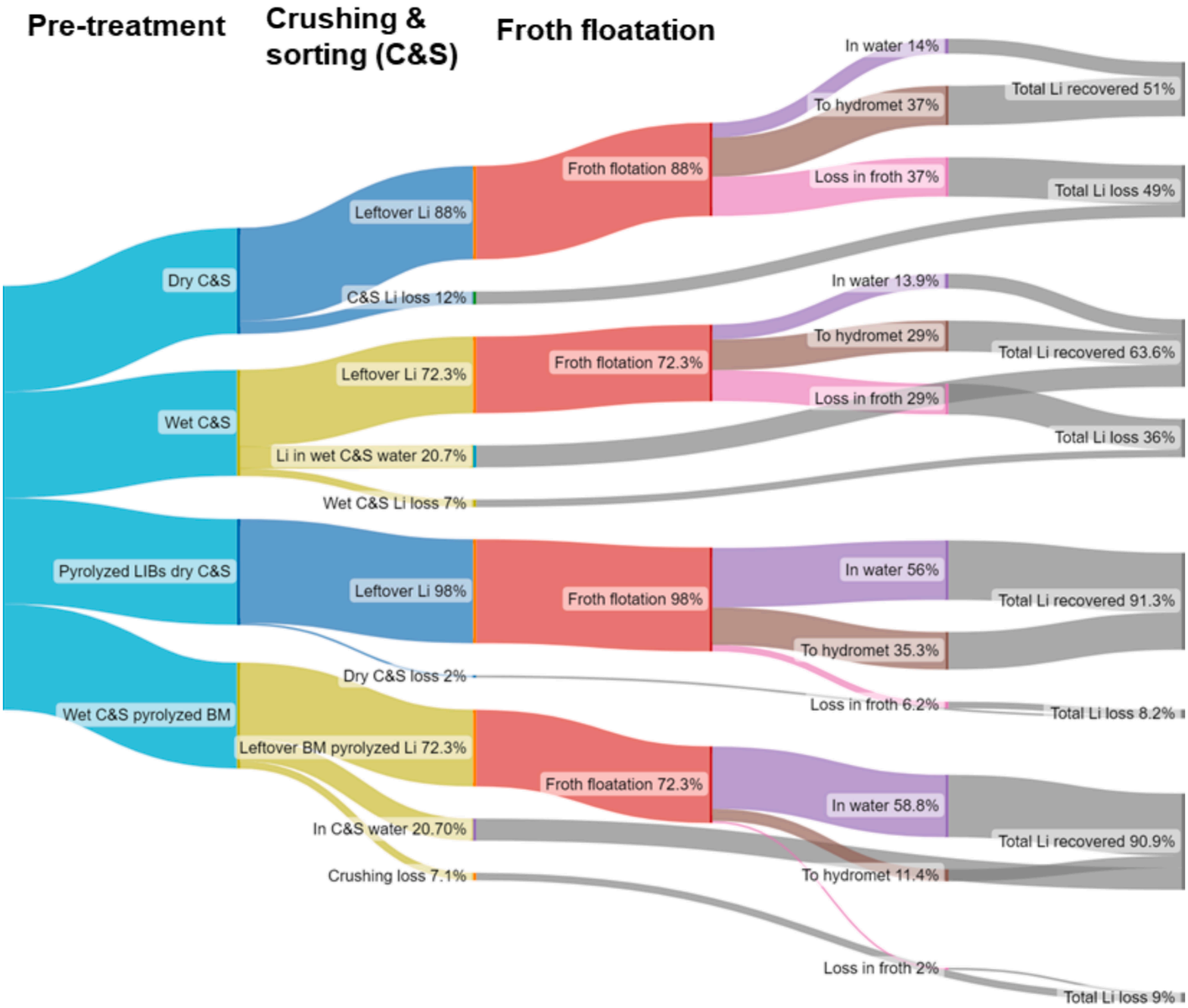


**Fig. 9.** Calculation of Li flow through different pre-treatment routes of a EV LIB recycling process.

valorizes electrode particles from current collector foils by decomposing the binder (~450 °C) but also phase transforms the cathode material into $Li_2CO_3$, Ni, and respective transition metal oxides [121,122]. The Li can then be recovered by water leaching the BM after crushing. The additional advantage of pyrolyzing the whole LIB module or cell is a supplementary source of $CO_2$ which aids in the carbothermic reduction of metal oxides provided by the decomposition of the separator which otherwise is removed in dry C&S prior to BM pyrolysis [122]. The C&S loss in process 3 is calculated to be only 2 % from the data provided by Zhang et al. [110]. They further floated this BM and reported around 85 % recovery of metal oxide in the tailings with the S/L ratio of 40 g/L. Additionally, the pyrolysis of LIBs transforms Li in the BM into water-soluble phase specifically $Li_2CO_3$. The Li concentration in the flotation water can amount to around 1.05 g/L (own water leaching data reported by Saleem et al. [119] for pyrolyzed BM) representing around 56 % compared to Li in an NMC 111 module of composition shown in Fig. 8. The Li content in froth and tailings is calculated based on the aforementioned separation data from Zhang et al. [110] and corresponds to around 6.2 % and 35.3 %, respectively. Choosing a lower S/L ratio in flotation can allow for greater Li recovery in flotation water, although this will result in an increased volume of this stream. The maximum recovery of Li in this process can go up to 91.3 % (there might be additional losses in the downstream processing), and major losses occur in the froth. Those can be minimized by a second flotation step at a higher S/L or mild acid treatment to keep the cost at a minimum.

Finally, Process 4 starts with wet C&S of the module followed by pyrolysis of the BM (<200 μm fraction). The Li content in crushing water and crushing loss in this process is similar to Process 2 and has been calculated in the same way. However, the flotation separation efficiency and Li in flotation water have been calculated in the same way as Process 3 due to the pyrolysis of BM. In this process, the major loss occurs in C&S at around 7 % followed by a loss in froth i.e., 2 %. The maximum cumulative recovery of Li in different steps can amount to 90.9 % while the losses are 9 %.

To summarize, Process 3 and 4 offer the maximum recovery of Li with Process 3 giving minimum crushing loss. Although Li loss in froth is slightly higher for Process 3 compared to 4 the number of aqueous streams is less in Process 3 and dry fractions are easier to handle in a recycling process compared to wet. Thus, Process 3 was chosen for further optimization and estimation of concentrations, composition, and volumes of all the streams in a hydrometallurgical BM recycling process.

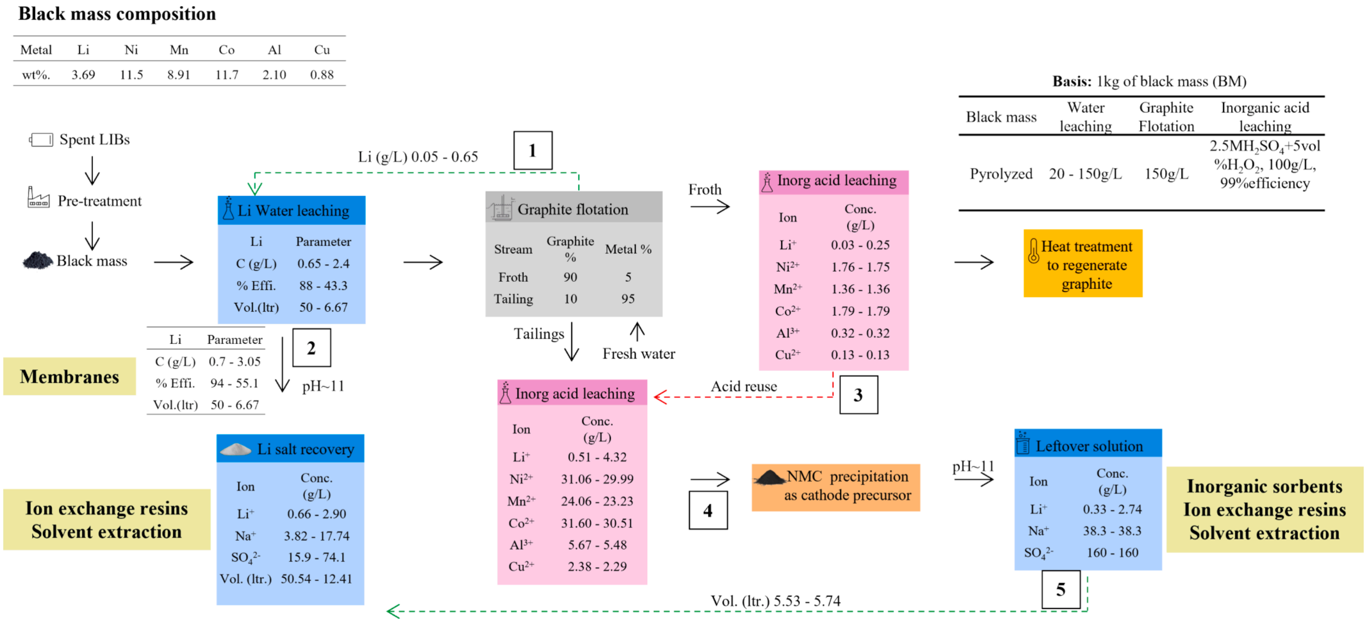
### 3.5. Hydrometallurgical recycling process of LIBs

Process 3 from the previous section was selected for the estimation of concentrations, compositions, and volume of streams with a basis of 1 kg of BM to be recycled, shown in Fig. 10, calculations shown in Appendix S3 in SI. The BM composition was taken from Schwich et al. [121] who pyrolyzed the whole battery cells followed by dry C&S. A similar type of pretreatment was applied to the BM by Verdugo et al. [116] who investigated the simultaneous recovery of Li and graphite in flotation. In addition, we thoroughly investigated optimum water leaching conditions on a similar type of BM in our previous work [119]. The water leaching step was added before flotation as suggested by Verdugo et al. [116]. It has been calculated at two S/L ratios of 20 g/L (concentration data taken from [123]) and 150 g/L (concentration data taken from [116]) while the flotation has been calculated at 150 g/L (conditions and concentration taken from [116]). They are set up in a way that fresh water is added in the flotation step which is then used to wash a fresh batch of BM in the water leaching step. The froth is subjected to mild acid leaching to recover leftover metal oxide from the flotation step. The tailings are leached by the combination of sulfuric acid and hydrogen peroxide using the conditions and efficiency data reported by [124]. After the removal of impurities (Fe, Al, Cu), nickel manganese cobalt hydroxide has been co-precipitated with the leftover stream containing Li$^+$ and Na$^+$ [125]. The total Li loss has been kept at 10 % in impurity removal and NMC precipitation combined, and 5 M NaOH has been used in the calculation for the pH adjustment and a 50 % increase in the volume of the inorganic acid leachate has been assumed to reach pH 11 [125].

The Li concentration after water leaching and flotation combined (stream 2) reached 0.7 g/L and 3.05 g/L reaching leaching efficiencies of 94 % and 55.1 % with a total volume of 50 L and 6.67 L at S/L ratio of 20 g/L and 150 g/L in water leaching, respectively. A significant amount of Li (94 %) can be leached at a lower S/L ratio of 20 g/L but at the expense of around 7.5 times the water used at a higher S/L ratio. Pyrolyzed BM gives pH ~ 11 in the water with a major impurity of Al (~70——320 mg/L [113,119]) which can be minimized if the pH of the water is adjusted and kept at 10 (~5mg/L [119]). The concentration of Li after inorganic acid leaching of froth and tailings combined reached 0.51——4.32 g/L (stream 4) which is justifiable as around 94 % of Li is already removed during water leaching and flotation in the former compared to the latter only 55.1 %. Although the concentration of metals in inorganic acid leaching is calculated at 100 g/L S/L ratio two levels of concentration are obtained due to two S/L ratios used in the water leaching step. After pH adjustment to remove impurities and precipitate NMC at pH 11 with 5 M NaOH a 50 % increase in volume has been considered with a 10 % loss of Li in these steps [125]. The leftover stream (5) is rich in Na$^+$ and SO$_4^{2-}$ with Li concentration ranging from 0.33-2.74 g/L with a volume of 5.53–5.74 L. This stream can be processed separately or combined with Li rich stream after water leaching and flotation (stream 2) as shown under Li salt recovery in Fig. 10. Li-containing streams are shown in blue blocks in Fig. 10 with major impurities of Na$^+$ and SO$_4$ $^{2-}$ in the stream after NMC precipitation and only Li after water leaching and flotation. In the following section, the application of DLE will be explored to recover Li from these streams.

#### 3.5.1. DLE to recover Li from recycling streams

There are two Li-containing streams after water leaching and NMC precipitation (stream 2 and 5, respectively), Fig. 10. These streams can also be combined with Na$^+$ and SO$_4^{2-}$ ions as major impurities. We recommend to up-concentrate (by rejecting water) Li after flotation and water leaching (stream 2) using membranes (nanofiltration and reverse osmosis). Although reverse osmosis is a mature technique it has not been rigorously investigated for DLE purposes [23]. This will improve the overall water efficiency and will offer a simpler process. In addition, the salinity in this stream is low compared to real brines (up to 500 g/L [9,82,83]) which should reduce membrane fouling and prolong life. After NMC precipitation (stream 5), Na$^+$ is the major impurity, and Li$^+$ can be isolated using inorganic sorbents, ion exchange resins, or solvents. It should be noted that although the concentration of Li$^+$ in this stream can be as low as 0.33 g/L, reverse osmosis and nanofiltration membranes are not recommended here for up-concentration. This is primarily due to the high salinity resulting from the presence of Na$^+$ and SO$_4^{2-}$. The choice of these processes/materials should depend on the concentration recommendations in Fig. 5. It should be mentioned that ion exchange resins and solvents are more resistant to acids during elution compared to metal-based sorbents. This can minimize the use of post up-concentration process as a controlled amount of concentrated acids (e.g. 2–3 M HCl) can be used during elution to get equally concentrated Li solutions [26–28,30,48,104]. Moreover, an attempt can be made to extract Li after inorganic acid leaching (stream 4) using FeCl$_3$



**Black mass composition**

| Metal | Li | Ni | Mn | Co | Al | Cu |
|---|---|---|---|---|---|---|
| wt%. | 3.69 | 11.5 | 8.91 | 11.7 | 2.10 | 0.88 |

**Basis:** 1kg of black mass (BM)

| Black mass | Water leaching | Graphite Flotation | Inorganic acid leaching |
|---|---|---|---|
| Pyrolyzed | 20 - 150g/L | 150g/L | 2.5MH$_2$SO$_4$+5vol %H$_2$O$_2$, 100g/L, 99%efficiency |

Li Water leaching

| Li | Parameter |
|---|---|
| C (g/L) | 0.65 - 2.4 |
| % Effi. | 88 - 43.3 |
| Vol.(ltr) | 50 - 6.67 |

Graphite flotation

| Stream | Graphite % | Metal % |
|---|---|---|
| Froth | 90 | 5 |
| Tailing | 10 | 95 |

Inorg acid leaching (3)

| Ion | Conc. (g/L) |
|---|---|
| Li$^+$ | 0.03 - 0.25 |
| Ni$^{2+}$ | 1.76 - 1.75 |
| Mn$^{2+}$ | 1.36 - 1.36 |
| Co$^{2+}$ | 1.79 - 1.79 |
| Al$^{3+}$ | 0.32 - 0.32 |
| Cu$^{2+}$ | 0.13 - 0.13 |

Stream 2

| Li | Parameter |
|---|---|
| C (g/L) | 0.7 - 3.05 |
| % Effi. | 94 - 55.1 |
| Vol.(ltr) | 50 - 6.67 |

Inorg acid leaching (4)

| Ion | Conc. (g/L) |
|---|---|
| Li$^+$ | 0.51 - 4.32 |
| Ni$^{2+}$ | 31.06 - 29.99 |
| Mn$^{2+}$ | 24.06 - 23.23 |
| Co$^{2+}$ | 31.60 - 30.51 |
| Al$^{3+}$ | 5.67 - 5.48 |
| Cu$^{2+}$ | 2.38 - 2.29 |

Li salt recovery

| Ion | Conc. (g/L) |
|---|---|
| Li$^+$ | 0.66 - 2.90 |
| Na$^+$ | 3.82 - 17.74 |
| SO$_4^{2-}$ | 15.9 - 74.1 |
| Vol. (ltr.) | 50.54 - 12.41 |

Leftover solution

| Ion | Conc. (g/L) |
|---|---|
| Li$^+$ | 0.33 - 2.74 |
| Na$^+$ | 38.3 - 38.3 |
| SO$_4^{2-}$ | 160 - 160 |

**Fig. 10.** Estimation of composition, concentration, and volumes of streams with basis of 1 kg pyrolyzed BM and recommendations to employ suitable DLE technology to recover Li from them.

and tributyl phosphate solvent system in kerosene which has been demonstrated to reach high separation factors of Li over Ni and Co [30]. However, this may result in a loss of NMC metals during pH adjustments and will complicate the system. In addition, more research is needed to extract Li over NMC metals as only limited literature is found with complicated extraction systems. Combining the two Li-containing streams (2 and 5) the concentration becomes favorable for ion-exchange resins and solvent extraction.

## 4. Conclusion and outlooks

In this study, the application of DLE to extract Li from LIB recycling streams has been assessed by reviewing the literature. First, DLE methods such as solvent extraction, ion exchange resins, metal-based sorbents (adsorption and ion exchange), membranes, and electrochemical lithium-ion pumping have been reviewed extensively. These DLE methods were rated on nine different parameters based on the technical aspects of these processes and materials. In addition, recommendations on when to use certain types of DLE methods at specific Li concentrations in the feed stream were made. This was followed by the selection of an optimized EV LIBs recycling process by reviewing the literature. The pretreatment options for recycling LIBs were investigated and different crushing (dry and wet) methods were compared followed by separation of anode and cathode materials with froth flotation. The Li loss in various combinations of these three processes was calculated and it was found that pyrolyzing the whole cells or modules followed by dry crushing and flotation could be the most ideal process route to minimize Li losses compared to others. This was due to the valorization of electrode materials from the current collector foils minimizing crushing loss, reduction of CAM so that Li could be easily leached by water washing the BM or dissolve into flotation water, and burning of separator aiding in carbothermic reduction as an additional $CO_2$ source. This was followed by the calculation of process streams for hydrometallurgical processing downstream using the chemistry of a pyrolyzed BM from the literature. The Li-containing streams were identified, and their concentration, compositions, and volumes were calculated by employing necessary parameters from reported literature (e.g. leaching efficiencies, concentrations, S/L ratio) with the basis of 1 kg of pyrolyzed BM.

It was found that the incorporation of DLE could minimize Li losses in the process. However, various DLE methods may be required to recover Li in different steps of the recycling process. An economic evaluation of Li recovery from these streams using suitable DLE methods should be done. Even though recommendations to use different DLE methods based on calculated streams in the recycling process have been cited from the literature it is proposed to validate them experimentally, especially nanofiltration and reverse osmosis membranes, sorption with Mn, Ti, and Fe-based sorbents, ion exchange resins, and solvent extraction with β-diketones + neutral extractants. It is proposed as future work to validate the pyrolysis process followed by dry crushing and finally the whole hydrometallurgical process. The validation part can be complex and lengthy but the necessary conditions for each unit process and operation have been extensively specified in this study to provide a starting point.

## Declaration of competing interest

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

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.131315.

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