



One-Step Solvometallurgical Process for Purification of Lithium Chloride to Battery Grade

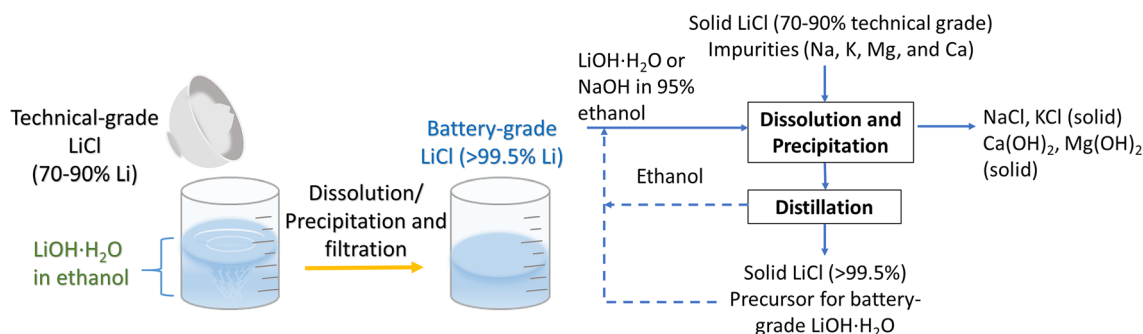
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Abstract

The use of lithium in manufacturing of lithium-ion batteries for hybrid and electric vehicles, along with stringent environmental regulations, have strongly increased the need for its sustainable production and recycling. The required purity of lithium compounds used for the production of battery components is very high (> 99.5%). In this work, a solvometallurgical process that exploits the differences in solubility between LiCl and other alkali and alkaline-earth chlorides and hydroxides in ethanolic solutions has been investigated for the purification of LiCl to battery grade at room temperature. A closed-loop flowsheet based on the green solvent ethanol is proposed for purification of LiCl, a precursor for battery-grade LiOH·H₂O. High-purity LiCl solution (> 99.5% Li) could be obtained in a single-process step comprising the simultaneous selective dissolution of LiCl and the precipitation of Mg(OH)₂ and Ca(OH)₂ using LiOH·H₂O in 95 vol% ethanol. However, the analogous process in aqueous solution resulted in impure LiCl (typically less than about 75%).

Graphical Abstract



Keywords Battery · Extractive metallurgy · Hydrometallurgy · Lithium · Solution chemistry · Solvometallurgy

Introduction

Lithium is a crucial raw material for lithium-ion batteries, where it is used as a constituent of the electrolyte and electrode materials [1–3]. The main lithium sources are brines from salt lakes (*salars*) and hard-rock lithium ores (mainly

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spodumene) [4–6]. Lithium is extracted through a series of processing steps (including heating, precipitation, carbonation) as lithium carbonate (Li₂CO₃), which presently is the most important lithium compound for lithium-ion battery applications [7–10]. However, the importance of lithium hydroxide, in the form of its monohydrate LiOH·H₂O, is increasing sharply, mainly because it can be used as a starting compound for nickel-rich NMC cathode materials, which are desirable for their high reversible capacity, high energy density, good rate capability, and relatively low cost [11–13]. LiOH allows for fast and complete synthesis of the cathode materials at lower temperatures than when using

Li_2CO_3 [14, 15]. The production of LiOH typically includes the reaction between Li_2CO_3 and $\text{Ca}(\text{OH})_2$, with formation of CaCO_3 as a residue [14, 16]. This process is characterized by poor production yields and losses of Li_2CO_3 with CaCO_3 , due to the reduced solubility of Li_2CO_3 in the presence of LiOH , and inefficiencies during washing and settling operations of the CaCO_3 precipitate [14]. Alternatively, a process for direct conversion of lithium chloride (LiCl) into $\text{LiOH}\cdot\text{H}_2\text{O}$, bypassing the Li_2CO_3 intermediate, would be advantageous to reduce the number of processing steps, including lower consumption of chemicals and generation of less waste. However, such process implies the purification of technical-grade LiCl from common impurities such as sodium, potassium, calcium, and magnesium, into a battery-grade LiCl , with a purity of at least 99.5% trace metal basis.

The use of organic solvents instead of aqueous solvents in extractive metallurgy is referred to as “*solvometallurgy*” [17]. The organic solvents can significantly increase the selectivity of dissolution processes. Several organic solvent-based processes for LiCl purification have been reported, including processes based on differences in solubilities of metal chloride salts in alcohols [18–20]. However, these methods are not suitable for removal of high concentrations of calcium and magnesium impurities by a simple dissolution process, because magnesium chloride (MgCl_2) and calcium chloride (CaCl_2) are quite soluble in more polar alcoholic solvents.

In this paper, we present a simple and efficient solvo-metallurgical process for the purification of technical-grade LiCl to a high-purity final solution product (> 99.5% of Li) that is suitable for further conversion into a battery-grade $\text{LiOH}\cdot\text{H}_2\text{O}$, for instance by an electrodialysis process [16, 21].

Experimental

Chemicals

Nitric acid (65%), hydrochloric acid (37%), standard solutions ($1000\ \mu\text{g mL}^{-1}$) of sodium, potassium, magnesium, calcium, lithium, scandium and yttrium, and potassium chloride (99.5%) were purchased from Chem-Lab NV (Zedelgem, Belgium). Ethanol (99.8%), sodium hydroxide pearls ($\geq 98\%$), and sodium chloride ($\geq 99.5\%$) were purchased from Fisher Chemicals (Geel, Belgium). Anhydrous calcium chloride (96%) was purchased from Acros Organics (Geel, Belgium). Lithium chloride ($\geq 99.5\%$) was obtained from Carl ROTH (Karlsruhe, Germany). Lithium hydroxide monohydrate ($\geq 98\%$) and anhydrous magnesium chloride (99%) were purchased from Alfa Aesar (Steinheim and Kandel, Germany). The ultrapure water with a resistivity of $> 18.2\ \text{M}\Omega\cdot\text{cm}$ at $25\ ^\circ\text{C}$, and $\text{TOC} \leq 5\ \mu\text{g L}^{-1}$ was obtained from a

Milli-Q™ Reference Ultrapure Water Purification System (Millipore).

Instrumentation

The dissolution and precipitation experiments were performed using a Thermo Fisher shaker (Type 462–0355). The simultaneous dissolution/precipitation process on a large scale was studied using a customized 1-L jacketed laboratory reactor (HiTec Zang GmbH, Herzogenrath, Germany) with an overhead stirrer and an automatic filtration unit (LabKit 36167) (Figure S1 in the electronic supplementary material). The anchor stirrer of the reactor was made of stainless steel covered with PTFE. The length of the stirrer was 450 mm, and the diameter was 80 mm. The ratio between the diameter of the stirrer and the diameter of the reactor vessel was 0.8. The concentrations of elements in solutions were measured by an inductively coupled plasma–optical emission spectrometer (ICP–OES) (Perkin Elmer Avio 500) equipped with an axial/radial dual plasma view, a GemCone High Solids nebulizer, a baffled cyclonic spray chamber, and a demountable quartz torch with a 2.0 mm internal diameter alumina injector. The lines at 279.077, 317.900, 589.592, 610.362, and 766.490 nm are typically used for the determination of magnesium, calcium, sodium, lithium, and potassium, respectively. Yttrium ($5\ \text{mg L}^{-1}$) measured at 324.227 nm and 371.029 nm was used as an internal standard. The concentrations of sodium (Na-23) and potassium (K-39) in ethanolic solutions were also measured by inductively coupled plasma–mass spectrometer (ICP–MS) (Perkin Elmer Nexion 5000) equipped with four quadrupoles. The elements were quantified with matrix-matched calibration standards containing LiCl , and scandium (Sc-45) was added as an internal standard ($50\ \mu\text{g L}^{-1}$). The calibration standards, blanks, and all samples were prepared with 2 wt% HNO_3 . The samples were diluted at least 500 times for ICP–OES analysis and 1000 times for ICP–MS analysis. The high dilution factors reduced the impact of matrix effects on measurement with these techniques, originating either from high salt concentrations or from ethanol.

Methodology

The dissolution tests were performed by adding 10 mL of 95 vol% ethanol or ultrapure water to various solid mixtures of MgCl_2 , CaCl_2 , NaCl , KCl , and LiCl , as shown in the Table S1. The mixtures were shaken for 30 min at room temperature and 300 rpm and then filtered through a syringe filter with $0.45\ \mu\text{m}$ pore size. In an analogous way, the one-step dissolution/precipitation tests were performed by adding 10 mL of $0.105\ \text{mol L}^{-1}\ \text{LiOH}\cdot\text{H}_2\text{O}$ in 95 vol% ethanol or in ultrapure water.

The continuous, upscaled one-step dissolution/precipitation process in the 1-L glass reactor (HiTec Zang) was performed with the solid salt mixture: 3.5 g MgCl₂, 3.5 g CaCl₂, 10 g KCl, 13 g NaCl, and 186 g LiCl (i.e., 2.08% Mg, 2.94% Ca, 12.2% K, 11.9% Na, and 70.9% Li, calculated based on masses of metal ions without the chloride content for easier comparison of Li metal purity before and after the purification process). A 1 L solution of 0.128 mol L⁻¹ LiOH·H₂O in 95 vol% ethanol was added, and the solid mixture was stirred at the speed of 400 rpm, at room temperature for 30 min. The mixture was filtered through a glass filter (pore size of 160–250 μm) which was covered with Manchery-Nagel MN 615 cellulose filter paper, with 4–12 μm retention capacity.

The one-step dissolution/precipitation of mixtures mimicking brine compositions was performed with NaOH and LiOH solutions. A sample of 10 mL of 0.282 mol L⁻¹ NaOH in 95 vol% ethanol or in water was added to a mixture of MgCl₂, CaCl₂, NaCl, KCl, and LiCl. After shaking the mixture at 300 rpm and room temperature for 30 min, 3 mL of 0.210 mol L⁻¹ LiOH·H₂O in 95 vol% ethanol was added to the ethanolic mixture, and 0.210 mol L⁻¹ LiOH·H₂O in water was added to the aqueous mixture. The mixtures were shaken for additional 5 min, and filtered through a syringe filter with 0.45 μm pore size. Samples without the addition of LiOH·H₂O were prepared in the same way. The conceptual flowsheet proposed in the manuscript is based on the experimental conditions for the one-step dissolution/precipitation either by NaOH or LiOH·H₂O in 95 vol% ethanol.

The experiments with a solution volume of 10 mL were performed in triplicate. The purity of lithium-rich solution was calculated based on the average concentrations of the elements in the filtrates, by applying the following equation:

$$\text{Li purity(\%)} = \frac{m_{\text{Li}} \cdot 100}{m} \quad (1)$$

where m_{Li} is the mass of lithium and m is the total mass of all metal ions (calcium, magnesium, sodium, potassium and lithium) in the filtrate. The masses were calculated based on the concentrations of elements in the filtrate, measured by ICP-OES and/or ICP-MS. Therefore, it should be noted that the calculated purity of lithium refers only to the trace metal purity of the solution, without considering the concentrations of anions (chlorides or hydroxides).

Solvents of 25 vol% to 95 vol% of ethanol, prepared by adding a certain amount of water, were used to investigate the influence of the water content on the precipitation of magnesium and calcium from the mixtures of MgCl₂, CaCl₂, and LiCl. A volume of 0.250 mL of 4 mol L⁻¹ LiOH·H₂O in water was added to a 5 mL sample of the salt mixture in ethanol of different concentrations. The mixture was shaken at a speed of 300 rpm for 15 min at

room temperature and then filtered through the syringe filter with 0.45 μm pore size.

The precipitation efficiency of magnesium and calcium ions was calculated as follows:

$$\text{Precipitation(\%)} = \frac{(c_1 - c_2) \cdot 100}{c_1} \quad (2)$$

where c_1 (mmol L⁻¹) is the initial metal ion concentration and c_2 (mmol L⁻¹) is the final concentration of metal ions in the solution corrected by the dilution factor due to the addition of 4 mol L⁻¹ LiOH·H₂O in water.

Results and Discussion

Dissolution of Salts in Ethanol

Dissolution tests were performed in 95 vol% ethanol with different solid mixtures of LiCl and other alkali and alkaline-earth chloride salts, which are similar to lithium hard-rock concentrates (Table 1 and S1, Feed 1–3) [22]. Besides, solid mixtures containing a similar composition of various lithium brines with low concentrations of LiCl and high concentrations of the other chloride salts were also investigated (Table 1 and S1, Brine 1–2) [23].

NaCl and KCl have a limited solubility of 0.064 g and 0.07 g in 100 g of ethanol, respectively, at 25 °C (Table S2) [24]. This property allows them to be separated from LiCl, which has a high solubility of 24.28 g in 100 g of ethanol, at 20 °C [24]. Therefore, only trace amounts of sodium and potassium ions could be detected in the ethanolic solutions after removal of the solid residue by filtration (Table 2). The solubility of NaCl and KCl was slightly influenced by the initial composition of the salts (Tables 1, 2). The findings render ethanol a potential solvent for the recovery of highly pure LiCl from a wide variety of sources with different compositions, i.e., from lithium-containing hard rocks to brines. Note that the concentration of sodium and potassium in solution increased as a function of increasing water content in ethanol (Tables 2, 3). Therefore, ethanol with less than 5

Table 1 Theoretical elemental composition of the tested chloride salt mixtures in 10 mL solution (g L⁻¹), calculated based on the masses of the salts given in the Table S1

Feeds	Mg	Ca	K	Na	Li
Feed 1			5.24	5.12	30.8
Feed 2	0.18	0.29	5.24	5.12	30.8
Feed 3	0.92	1.41	5.24	5.12	30.8
Brine 1	30.9	39.0	25.0	103	1.57
Brine 2	2.99	3.00	2.99	70.0	1.57

Table 2 Concentration of elements (g L⁻¹) after dissolution of chloride salts in 95 vol% ethanol

	Mg	Ca	K	Na	Li
Feed 1	–	–	0.071	0.024	27.9
Feed 2	0.135	0.231	0.058	0.024	26.4
Feed 3	0.683	1.028	0.096	0.031	26.7
Brine 1	16.5	29.1	0.032	0.006	1.19
Brine 2	2.43	2.19	0.053	0.105	1.25

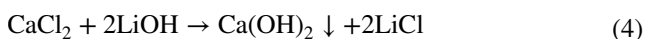
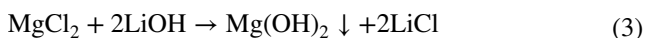
Table 3 Concentration of elements (g L⁻¹) after dissolution of chloride salts in 90 vol% ethanol

	Mg	Ca	K	Na	Li
Feed 1	–	–	0.167	0.045	27.1
Feed 2	0.137	0.221	0.130	0.042	27.0
Feed 3	0.672	1.053	0.175	0.044	27.3

vol% of water is the most suitable solvent to keep the solubility of NaCl and KCl low. On the other hand, there is no need to work with absolute ethanol, which largely improves the economics of the process.

One-Step Dissolution/Precipitation Process for Purification from Minerals

MgCl₂ and CaCl₂ co-dissolved along with LiCl, unlike NaCl and KCl (Table 2). Therefore, the removal of these ions by a combined dissolution/precipitation process was investigated in order to obtain a Li-rich solution in one step. When dissolving the solid mixtures of chloride salts (Table 1 and S1, Feed 2–3) in 10 mL of a 0.105 mol L⁻¹ solution of LiOH·H₂O in 95 vol% ethanol or in ultrapure water, the following reactions can occur:



Unlike their corresponding chloride salts, the hydroxides of Mg and Ca have very low solubility in ethanol (Table S2). Therefore, simultaneous dissolution of LiCl, MgCl₂, and CaCl₂ and precipitation of magnesium and calcium as Mg(OH)₂ and Ca(OH)₂ were performed by LiOH·H₂O in 95 vol% ethanol. NaCl and KCl remained undissolved (Fig. 1, Table S3), thus, could not further react to form their hydroxides which are soluble in ethanol. LiCl solutions with >99.5% of Li were obtained after a single-processing step (Fig. 1; Table S3). Similar results were obtained from a low-grade LiCl feed, which was prepared with 50% less amount of LiCl than typically used in this study (Table S4).

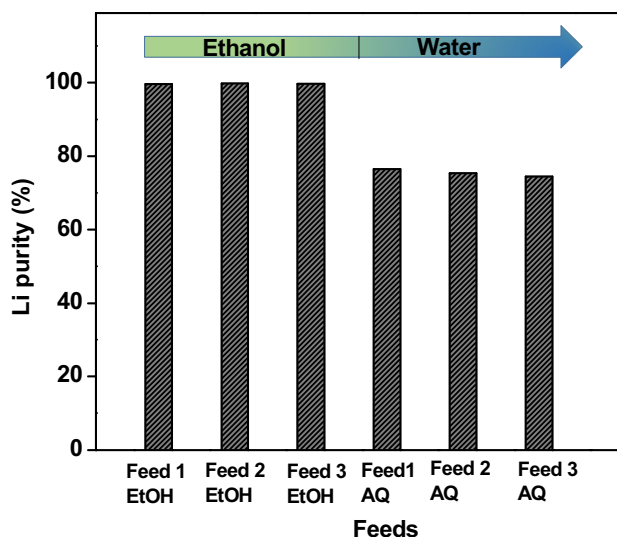


Fig. 1 Purity of lithium chloride solution after one-step processing of the chloride salt mixtures given in the Table 1 (Feeds 1–3) by 0.105 mol L⁻¹ LiOH·H₂O in 95 vol% ethanol

In the same one-step dissolution/precipitation process, but with an aqueous solution of LiOH·H₂O rather than an ethanolic solution, the vast majority of magnesium ions were also removed from the feed by precipitation (Fig. 1, Table S3). However, the precipitation of calcium was not efficient under these experimental conditions, due to a relatively high solubility of Ca(OH)₂ in water: 0.129 g of CaO per 100 g of solution saturated with fine Ca(OH)₂ at 25 °C (Table S2) [24]. Moreover, large amounts of NaCl and KCl co-dissolved along with LiCl, resulting in a LiCl solution with a purity of only 76.5% of Li (Fig. 1; Table S3).

The one-step dissolution/precipitation process was also performed in an upscaled glass reactor with 1 L of LiOH·H₂O in 95 vol% ethanol (Fig. S1). A slight excess of LiOH·H₂O (0.128 mol L⁻¹) compared to the small-scale batch experiments (0.105 mol L⁻¹) was used to ensure a complete precipitation of calcium and magnesium in the upscaled experiment. The temperature of the reaction mixture sharply increased up to 60 °C upon the addition of the ethanolic solution to the solid mixture due the exothermic character of the reactions, but it gradually decreased when mixing was complete. The concentration of lithium in the filtrate was 27.2 ± 1.3 g L⁻¹, and that of potassium was 0.10 ± 0.01 g L⁻¹. The concentrations of the magnesium, calcium, or sodium impurities were below the detection limit of ICP-OES. The upscaling of the process also resulted in a LiCl solution with >99.5% trace metal purity.

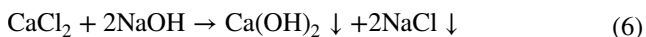
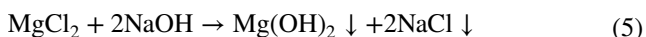
Table 4 Concentration of elements (g L^{-1}) in solutions after dissolution of their chloride salts in 0.282 mol L^{-1} NaOH and 0.210 mol L^{-1} LiOH·H₂O solutions

Solution	Mg	Ca	K	Na	Li
NaOH in 95 vol% ethanol	ND	1.21	0.060	0.154	1.45
NaOH and LiOH in 95 vol% ethanol	ND	ND	0.065	0.160	1.27
NaOH in water	ND	2.42	3.11	72.9	1.47
NaOH and LiOH in water	ND	1.55	2.47	56.3	1.49

ND not detected by ICP–OES

One-Step Dissolution/Precipitation Process for Purification from Brines

The one-step dissolution/precipitation process with LiOH·H₂O in 95 vol% ethanol for obtaining a high-purity LiCl solution can be considered suitable for the removal of various amounts of NaCl and KCl, and relatively low concentrations of MgCl₂ and CaCl₂ (e.g., Table 1, Feed 2–3). LiOH·H₂O is not very soluble in ethanol: 2.18 g of this compound dissolves in 100 g of ethanol at 20 °C, after 48 h of mixing (Table S2) [25], and using LiOH·H₂O to precipitate large amounts of magnesium or calcium would be neither practical nor economical. Therefore, the precipitation of magnesium and calcium from their concentrated feed was investigated by step-wise dissolution and precipitation, first in a NaOH solution, and then in a LiOH·H₂O solution. The chloride salts (Table 1 and S1, Brine 1) were added in a 0.282 mol L^{-1} solution of NaOH in 95 vol% ethanol or in water. Magnesium and the vast majority of calcium ions were precipitated by NaOH in the ethanolic feed (Table 4). In this step, NaCl was formed according to the reactions:



The formed NaCl does not dissolve well in ethanol (Table S2), so that the solution was simultaneously purified from magnesium, sodium, and the majority of calcium ions (Table 4). Less than the stoichiometric amount of NaOH required for precipitation of magnesium and calcium was added to avoid contamination of the LiCl ethanolic solution with sodium ions due to unreacted NaOH. The traces of calcium ions that remained in the ethanolic solution were then precipitated by addition of a solution of LiOH·H₂O in ethanol. LiOH·H₂O was added in a slight excess to ensure complete precipitation of the remaining calcium. It should be noted that the final purity of LiCl solution in this experiment was < 99.5%, due to the low concentration of lithium in the tested solid mixtures. However, when compared to the initial composition of the solid mixture (Table 1, Brine

1), it is evident that only traces of sodium and potassium ions were left along with lithium ions in the ethanolic feed (Table 4). The ethanolic solution of NaOH can, therefore, be used to simultaneously precipitate large amounts of magnesium and calcium, while still allowing dissolution of LiCl. Once again, the precipitation of calcium from the aqueous feed was not efficient, neither with NaOH or LiOH solutions (Table 4). Moreover, large amounts of sodium and potassium salts were dissolved in the aqueous solution.

Influence of the Water Content on the Precipitation Efficiency

Obviously, the water content in the organic solvents can greatly affect the precipitation efficiency of calcium (Tables 2, 3, 4). To get more insight into the role of water, the removal of magnesium and calcium from LiCl solution (27.7 mg L^{-1} of lithium) in ethanol–water mixtures (from 95 to 25 vol% of ethanol) was studied by the addition of 4 mol L^{-1} LiOH·H₂O in water. Dilute solutions with an average of 0.739 mg L^{-1} of magnesium and 1.14 mg L^{-1} of calcium were studied (Table S5). High precipitation efficiencies of impurity metals and LiCl solutions with > 99.5% metal purity were obtained from feed solutions with up to 50 vol% of water (Fig. 2; Table S5). The precipitation efficiency of calcium decreased with increasing water content in the organic solutions (Fig. 2; Table S5), due to the higher solubility of Ca(OH)₂ in water (Table S2).

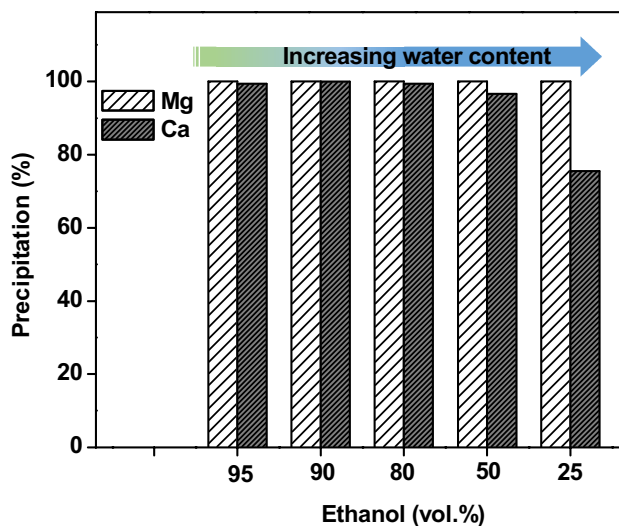


Fig. 2 Precipitation efficiency (%) of magnesium and calcium by 0.250 mL of 4 mol L^{-1} LiOH·H₂O in water from 5 mL of LiCl solution (27.7 g L^{-1} of Li) in ethanol–water mixtures, comprising 0.739 g L^{-1} of Mg and 1.14 g L^{-1} of Ca

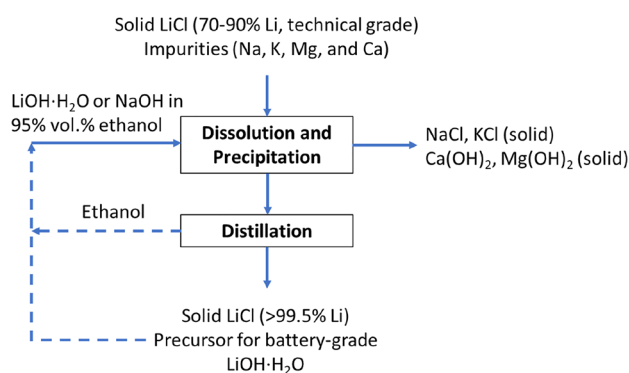


Fig. 3 Conceptual flowsheet for solvometallurgical purification of LiCl solution, as a precursor for battery-grade LiOH·H₂O

Conceptual Flowsheet

Based on the observations on the difference in the solubility of lithium and of other alkali and alkaline-earth metal salts and hydroxides in ethanol, a conceptual flowsheet for obtaining battery-grade LiCl in one-step solvometallurgical process is proposed (Fig. 3). The single-step process combines the dissolution of technical LiCl by LiOH·H₂O solution in ethanol at room temperature for 30 min and simultaneous precipitation of magnesium and calcium as their insoluble hydroxides. NaCl and KCl are virtually insoluble in such a solution. After the selective dissolution/precipitation step, the ethanol solvent can be recovered by distillation and reused in the process, and the remaining solid LiCl can be further processed to obtain battery-grade LiOH·H₂O. For this, an aqueous LiCl solution can be transformed first into a LiOH solution, for instance by membrane electro dialysis, followed by crystallization of LiOH·H₂O [14, 26]. A demonstration of this conversion of LiCl into LiOH·H₂O was outside the scope of the present study. A small part of the end-product, LiOH·H₂O, can be used to prepare the LiOH solution for the selective dissolution/precipitation process, thus, rendering this a closed-loop process. The solution of NaOH in ethanol can be used for the removal of larger amounts of magnesium and calcium ions, as found in lithium brines. It is obvious that consumption of too much LiOH solution must be avoided.

The fundamentals of the proposed solvometallurgical process are based on the intrinsically lower solubility of alkali and alkaline-earth compounds in less polar solvent such as ethanol than in water [27, 28]. Small ions of high charge density, like lithium ions, bind tightly polar molecules, such as water or ethanol molecules, whereas large monovalent ions of low charge density, like sodium or potassium ions, bind polar molecules weakly when compared to the strength of solvent–solvent interactions in bulk solution [29]. Small ions are strongly solvated because their point charge is close

to the point charge of opposite sign on the solvent molecule, whereas large ions are weakly solvated because their point charge is distant from the point charge of opposite sign on the solvent molecule. Small-large ion pairs (LiCl) tend not to form inner sphere ions, they remain apart in solution, thus, are soluble in ethanol, whereas small-sized, medium-sized, large-sized ions of opposite charge (comparable-sized or comparable charge density) will tend to pair and result in low solubility in ethanol (NaCl, KCl, Mg(OH)₂, Ca(OH)₂).

Conclusions

A solvometallurgical process that produces a battery-grade (trace metal basis) LiCl precursor for LiOH·H₂O by using a green solvent such as ethanol was developed. To the best of our knowledge, this is the first example of a process that produces a battery-grade LiCl precursor in a single-processing step. The inherent difference in solubility of LiCl and other alkali and alkaline-earth chlorides and hydroxides in a solution of LiOH·H₂O in 95 vol% ethanol enabled the production of the high-purity LiCl feed (>99.5% of Li) at room temperature. The developed process is feasible with feeds that contain less than 50 vol% of water. The presented process is versatile and suitable for purification of a wide range of solid mixtures of LiCl and other alkali and alkaline-earth metals, especially for lithium hard-rock ores (e.g., spodumene). The samples with large concentrations of magnesium and calcium can also be pre-purified with NaOH in ethanol, instead of LiOH·H₂O in ethanol, to remove the vast majority of these ions.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s40831-022-00540-w>.

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Declarations

Conflict of interest There are no conflicts to declare.

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