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Article

Innovative Integration of Citric Acid Leaching and Electrodialysis for Selective Lithium Recovery from NMC Cathode Material

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Abstract: With the growing demand for metals driven by technological advancements and population growth, recycling lithium-ion batteries has become vital for protecting the environment and recovering valuable materials. Developing sustainable recycling technologies is now more essential than ever. This paper focuses on using electrodialysis to process a leach solution of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC 111) cathode materials leached with citric acid. This study demonstrates that the complexing properties of citrate anions contribute to the efficient separation of Li from Ni, Co, and Mn by electrodialysis. This is achieved by promoting the formation of anionic species for Ni, Co, and Mn while maintaining Li in its cationic form. The leach solution was produced under the following optimal experimental conditions to reach a final pH of 5 and high leaching efficiency: a citric acid concentration of 1 mol L^{-1} , a leaching temperature of $45 \text{ }^\circ\text{C}$, a leaching time of 5 h, a liquid/solid ratio of 100 g/L , and $8 \text{ vol.}\% \text{ H}_2\text{O}_2$. These conditions resulted in leaching efficiencies of 89.3% for Ni, 95.1% for Co, 77.1% for Mn, and 92.9% for Li. This solution led to the formation of a lithium-rich supernatant and a precipitate. The supernatant was then used as the feed solution for electrodialysis. Pure lithium was successfully separated with a faradic efficiency of 71.4% with a commercial cation-exchange membrane. This strategy enables selective lithium recovery while minimizing membrane fouling during the process.



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Keywords: citric acid; electrodialysis; hydrometallurgy; leaching lithium-ion battery; NMC111; recycling

1. Introduction

Currently, the recycling of lithium-ion batteries (LIBs) primarily involves pyrometallurgical and hydrometallurgical processes [1]. While pyrometallurgy was initially the most common approach, it struggles to effectively separate metals, leading to metal losses, particularly lithium [2]. Hydrometallurgy, which relies on chemical solubilization in aqueous media, is often employed downstream to enable selective metal recovery through leaching, purification, and separation steps. Leaching consists of metal dissolution using acids, bases, or complexing agents, followed by the selective recovery and purification of leached metals through techniques like solvent extraction, ion exchange, precipitation, or crystallization [3]. At the end of the process, metals can be recovered as hydroxide, sulfate, chloride, or carbonate salts, which can be reused in the manufacturing chain (Figure 1a). However, lithium extraction typically occurs as the final step in the LIB recycling process, following the recovery of the other metals (Co, Ni, Fe, Mn, Al, and Cu). This is because leaching solutions

usually have a pH between 0 and 2, while lithium precipitates at higher pH levels, i.e., $\text{pH} > 13$ for lithium hydroxide precipitation and starting at $\text{pH} \sim 4$ with maximum efficiency above $\text{pH} 8$ for lithium carbonate precipitation [4]. Consequently, each extraction step can lead to lithium losses of up to 30% through adsorption or co-precipitation [4]. Nevertheless, combining solvent extraction steps can reduce these losses to around 15%.

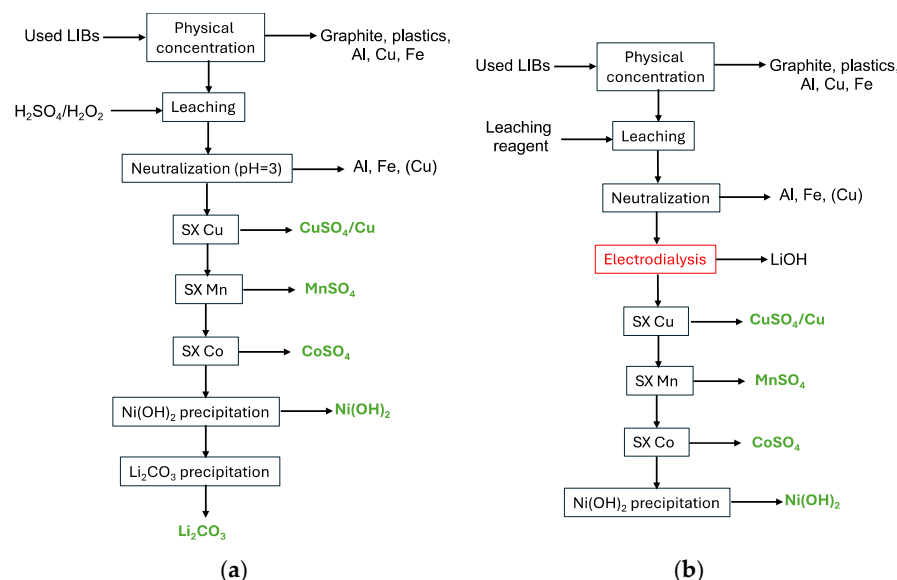


Figure 1. (a) Typical hydrometallurgical flowsheet and (b) implementation of electro dialysis in battery recycling flowsheet (SX: solvent extraction).

Therefore, it is essential to develop an eco-friendly and sustainable technology for extracting metals from used lithium-ion batteries that allows obtaining lithium right from the beginning of the leachate treatment process, as illustrated in Figure 1b. Electrodialysis presents a promising solution for this initial step, offering high selectivity and purity in lithium recovery regardless of the presence of other metal ions. Its integration into hydrometallurgical processes is gaining attention, particularly in the lithium sector, whether for lithium production from spodumene or for metal recovery from used LIBs [5]. Two general approaches have been reported in the literature to separate lithium from cations in leach solutions produced by digesting cathode materials from spent LIBs. The first method, known as selective electro dialysis (SED), relies on the use of monovalent ion-exchange membranes to separate lithium from divalent cations such as Co, Ni, and Mn. Table 1 summarizes recent works focused on this technique for the selective separation of lithium from other metals present in LIB leachates. Gmar et al. [6] demonstrated that SED effectively separates and concentrates lithium from leach solutions of NMC111 cathode materials. Using sulfuric acid at $\text{pH} 2.8$, the process achieved a faradic efficiency of 67% for lithium(I) transfer at a current density of 10 mA cm^{-2} . Yet, prolonged operation led to membrane clogging. These phenomena were caused by cobalt(II), nickel(II) and/or manganese(II) precipitation inside the membranes due to the local increase in pH near the vicinity of the membrane under certain conditions. Similarly, Afifah et al. [7] employed SED to separate lithium from cobalt. They observed precipitation into the membrane at high voltage (15 V) and a decrease in current efficiency from 25% to 8% caused by a local increase in pH due to water dissociation. Membrane clogging was responsible for performance loss of the electro dialyzer and premature aging of the membranes.

Table 1. Lithium separation efficiency from cations in spent LIBs using electro dialysis (U: voltage; j: current density; j_{Li^+} = Lithium flux; P(Li/M) = permselectivity; SEC(Li) = Specific Energy Consumption for lithium index).

Methods	Cathode Materials + Complexing Agent	Membrane Type	U and/or j	Flowrate	Complementary Information	Ref.
Conventional electro dialysis and selective electro dialysis	Leach solution of NMC111 cathodic materials: $0.07 \text{ g L}^{-1} \text{ Li}^+$, $0.2 \text{ g L}^{-1} \text{ Co}^{2+}$, $0.2 \text{ g L}^{-1} \text{ Ni}^{2+}$, $0.18 \text{ g L}^{-1} \text{ Mn}^{2+}$, and SO_4^{2-} + EDTA	Neosepta [®] CMS membrane, Neosepta [®] AMX, and Neosepta [®] CMX	18 V (Stage 1) 18 V (Stage 2) 3 V (Stage 3)	0.75 L min^{-1}	$j_{Li^+} = 0.165 \text{ mol}/(\text{m}^2/\text{h})$ $S_{Li^+}/Mn^+ = 92\%$	[5]
Conventional electro dialysis	Leached solution produced from spent LiCoO_2 [Li^+] = [Co^{2+}] = 0.02 mol L^{-1} + EDTA	1 AEM (Selemion AMV), 1 CEM (Selemion CMV), and two bipolar membranes (Neosepta [®] BP-1E)	20 V	0.375 L min^{-1}	R (Li^+) = R (Co^{2+}) = 99%	[8]
Selective electro dialysis	Typical mixing solution for used NMC [Li] = 2.6 g L^{-1} ; [Co] = 7.88 g L^{-1} [Mn] = 8.01 g L^{-1} ; [Ni] = 4.4 g L^{-1} + Sulfuric acid H_2SO_4	2 MEA 1 MEC monovalent (Neosepta [®])	12.5 mA cm^{-2}	100 mL min^{-1}	$R_f(\text{Li}) = 67.1\%$ $P(\text{Li}/\text{Co}) = 5.6$ $P(\text{Li}/\text{Ni}) = 6.1$ $P(\text{Li}/\text{Mn}) = 5.4$	[6]
Selective electro dialysis	Soluble nitrate salts (LiNO_3 + $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) [Li] = 0.1 g L^{-1} ; [Co] = 0.3 g L^{-1}	5 MEC (PC-MVK) 5 MEA (PC-MVA)	15 V 15 A/m^2	15 L h^{-1}	S (%) = 99.4% Lithium purity = 95.73%	[7]
Selective electro dialysis	[Li] = 0.027 g L^{-1} ; [Co] = 0.108 g L^{-1} ; [Ni] = 0.049 g L^{-1}	PAN-5C8Q membrane	5 V	2.2 L.h^{-1}	$j_{Li^+} = 0.047 \text{ mol}/(\text{m}^2/\text{h})$	[9]
Selective electro dialysis	Leached solution produced from spent lithium ion [Li] = 1.616 g L^{-1} ; [Co] = 0.059 g L^{-1} ; [Mn] = 1.149 g L^{-1} + Sulfuric acid H_2SO_4	1 MEC monovalent (Selemion CSO membrane)	5 V	$17 \text{ cm}^3/\text{min}$	Li_2CO_3 purity = 99.6% SEC(Li) = 0.5 kWh/g $R_f(\text{Li}) = 48.4\%$	[10]
Conventional electro dialysis	Typical mixing solution for used NMC [Li] = 3.27 g L^{-1} ; [Co] = 0.25 g L^{-1} ; [Mn] = 0.28 g L^{-1} ; [Ni] = 0.25 g L^{-1} + Sodium phosphate Na_3PO_4	1 MEC (Nafion 117)	3.5 V	-	SC(P/Li) = 3; Li_2CO_3 purity = 99.3%; SEC(Li) = 0.027 kWh/g ; Current efficiency $\eta(\text{Li}) = 50\%$	[11]

The second method is conventional electro dialysis, which involves the use of standard ion exchange membranes for ion separation. However, its effectiveness in separating is limited by the lack of ion selectivity of standard membranes. In theory, lithium ions and other divalent cations cannot be separated by electro dialysis due to their similar charge densities.

Studies reported in the literature have focused on the use of electro dialysis in inorganic acids to separate lithium from divalent metals contained in aqueous solutions representative of leachates of LIB black masses (BMs). More and more works have aimed at investigating the use of inorganic acids to leach BMs or cathode materials from LIBs [12], whereas only a few papers have addressed the use of electro dialysis to process leaching solutions of BMs or cathode materials or representative solutions of leachates by organic acids. For instance, Chan et al. (2022) [5] studied the use of electro dialysis (ED) to separate lithium(I), cobalt(II), nickel(II), and manganese(II) contained in an aqueous solution resulting from the leaching of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode material by EDTA in the presence of H_2O_2 . Nickel was recovered at approximately 99% at pH 2. In a second step, cobalt was separated with a yield of 87.3% at pH 3. Finally, the separation of lithium(I) and manganese(II) was performed using a monovalent-selective cation exchange membrane (Neosepta[®] CMS), with a separation yield of 99%. Likewise, Iizuka et al. [8] used bipolar membrane electro dialysis to separate lithium and cobalt contained in an aqueous solution produced by leaching LiCoO_2 electrodes with EDTA to form the complex $\text{Co}(\text{EDTA})^{2-}$ at pH = 4. A faradic efficiency of 99% for both metals was achieved.

Among the organic acids, citric acid appears as a good reagent since it is considered an eco-friendly leaching agent due to its natural biodegradability, the absence of harmful gas emissions during the process, and its low cost, unlike conventional inorganic acids [13]. Citric acid was employed for its ability to effectively dissolve NMC electrodes and to

form anionic complexes of cobalt(II), nickel(II), and manganese(II) without complexing lithium(I) within the pH range suitable for electrodialysis. Existing studies have consistently confirmed the effectiveness of citric acid as a lixiviant for the recovery of metals from LIB cathodes (LCO, LMO, and NCM). Table 2 presents a comparison of the leaching conditions of various types of cathodes by citric acid.

Table 2. Experimental conditions reported in the literature for cathode material leaching by citric acid.

Cathode Materials	Citric Acid Concentration (mol L ⁻¹)	Temperature (°C)	Leach Duration (min)	H ₂ O ₂ Content (% in vol.)	S/L (g/L)	Leaching Yields (%)	pH of Leachate Solution	Ref.
LiNi _{0.45} Mn _{0.4} Co _{0.15} O ₂ + LiCoO ₂	1.5	95	30	2%	20	Li = 95.3%, Co = 89.8%, Ni = 93.6%, Mn = 94.4%	2.5	[14]
LiCoO ₂	1 M	80 °C	60	4%	20	Li = 99%, Co = 99.21%	1.29	[15]
LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂ (NMC111)	1.5 M	50 °C	120	0%	20	Li = 82%, Co = 63%, Ni = 74%, Mn = 95%	2	[16]
LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂ (NMC111)	2 M	80 °C	90	2%	30	Ni = 97%, Co = 95%, Mn = 94% Li = 99%	2.31	[17]
LiCoO ₂ (LCO)	0.5 M	60 °C	300	6%	25	Li = 100%, Co = 96%	2.5	[18]

Most of these works focused on parametric studies to find the optimal experimental conditions to leach LIB cathode materials or on comparisons with other organic acids, as investigated by Musariri B [19]. For the sake of illustration, Chen et al. [17] reported that the use of 1.5 mol L⁻¹ citric acid in the presence of 2% (vol.) H₂O₂ at 80 °C with a solid-to-liquid ratio of 30 g/L led to the dissolution of 99%, 97%, 95%, and 94% of Li, Ni, Co, and Mn, respectively, from an NMC111 cathode material.

Given the interesting properties of citric acid—not only its ability to leach NMC cathode materials but also its low toxicity and strong complexing capacity towards cobalt (II), nickel (II), and manganese (II)—it is expected to promote the efficient separation of lithium(I) from these divalent metals. Moreover, by increasing the solubility of cobalt (II), nickel (II), and manganese (II) through complexation, citric acid may help to prevent membrane fouling during downstream processing. Therefore, this study aims to investigate the combined use of citric acid leaching, electrodialysis, and crystallization to produce high-purity lithium salts for LIB production.

2. Materials and Methods

2.1. Materials

The NMC111 used in this study is a black powder primarily composed of Ni (19.175 wt%), Co (19.152 wt%), Mn (17.964 wt%), and Li (7.187 wt%), with trace amounts of Cu and Al (<0.003 wt%) and Fe (0.002 wt%). It was supplied by Xiamen Tob New Energy Technology Co., Ltd. (Xiamen, Fujian, China). Citric acid monohydrate (C₆H₈O₇·H₂O, 99.9%, CAS: 5949-29-1) was obtained from Fisher Scientific (Paris, France) in its crystalline form, and hydrogen peroxide (H₂O₂, 30 wt% in water, CAS: 7722-84-1, 7732-18-5) was provided by Fisher Bioreagents (Paris, France). Lithium hydroxide (LiOH, 98%, CAS: 1310-65-2) was supplied by Sigma Aldrich (Paris, France). Monoelement standard solutions containing 1000 mg/L of Li, Ni, Co, or Mn in 2–5 wt% HNO₃ were used for the calibration of inductively coupled plasma-optical emission spectrometry (ICP-OES, ICAP 6000 series, Thermo Fisher Scientific, Waltham, MA, USA). Deionized water (>18.2 MΩ·cm) was used in all experiments. The filters used for solid–liquid separation after leaching experiments were Teflon membrane filters with a pore size of 0.45 μm and a capacity of 50 mL (SCP Science supplier, Paris, France). Standard buffer solutions at pH 2, 4.7, and 10 supplied by

VWR were used to calibrate the pH meter (VWR® pH 1100 L, Ref: 662-1657, Paris, France). The membranes employed for electro dialysis experiments were Neosepta® CMX-fg as cation-exchange membranes and Neosepta® AMX-fg as anion-exchange membranes. Both types of membranes from Astom Company (Tokyo, Japan) were supplied by Eurodia Industrie (Pertuis, France). The suffix “Fg” designates a commercial product type within the Neosepta membrane series. They are functionally equivalent to the classical CMX and AMX membranes commonly used in electro dialysis. The only difference lies in the reinforcing mesh. The classical CMX/AMX membranes use a PVC mesh, whereas CMX-Fg and AMX-Fg use a PE/PP (polyethylene/polypropylene) mesh.

2.2. Methods

2.2.1. Analyses

Metal concentrations during leaching experiments were determined by microwave plasma-coupled atomic emission spectroscopy (4210 MP-AES, Agilent, Paris, France), whereas metal concentrations for electro dialysis experiments were determined using induced plasma-optical emission spectroscopy (ICP-OES, ICAP 6000 series, Thermo Fisher Scientific, Paris, France).

Total Organic Carbon (TOC) determination was performed with a Shimadzu TOC analyzer by measuring Non-Purgeable Organic Carbon (NPOC) in order to determine the citric acid concentration after leaching. A calibration curve was established using citric acid standard solutions with known carbon concentrations of 0.36 g/L, 0.50 g/L, 0.72 g/L, and 1.00 g/L (the citric acid standard solutions were prepared by dissolving appropriate amounts of citric acid monohydrate in deionized water). The resulting calibration equation was $y = 1723.8x$ with a correlation coefficient $R^2 = 0.9998$, where x represents the carbon concentration in g/L and y denotes for the signal area. The analyzed samples were subjected to a 100-fold dilution.

X-ray diffraction spectroscopy (XRD, Malvern Instruments, Malvern, UK) was performed to determine the crystallographic phases in the precipitates, and data were processed with Match! 4 software by using the Crystallography Open Database (COD: 4504918).

2.2.2. Speciation Calculations

The speciation diagrams of lithium(I), nickel(II), manganese(II), and cobalt(II) in citric acid at different pH values were calculated using the HYDRA-MEDUSA software v1 (Make Equilibrium Diagrams Using Sophisticated Algorithms) [20], as the performance of metal separation by electro dialysis is highly dependent on complexation reactions and pH.

2.2.3. Leaching

Leaching experiments were carried out at different solid-to-liquid (S/L) ratios. Pre-weighed cathode material samples were dissolved in a citric acid solution prepared by dissolving the required amount of citric acid in water. The experiments were conducted in 100 mL glass flasks. To avoid solid agglomeration at the bottom and ensure uniform mixing, the citric acid solution was added first, followed by the cathode material. Once mixed, hydrogen peroxide (H_2O_2) was added to start the leaching reaction. The flasks were placed in a thermostated mechanical shaker (shaker, Gerhardt France) set to 200 oscillations per minute and maintained at the desired temperature. At scheduled intervals, the flasks were removed from the shaker, and the mixtures were immediately filtered using Teflon membrane filters (pore size = 0.45 μm) to separate the liquid leachate from the undissolved solid residue. The pH of the liquid leachate was measured at room temperature using a

calibrated pH meter. The resulting leachate was then analyzed to evaluate the leaching efficiency (%R(*i*)):

$$\%R(i) = \frac{C_{measured}}{C_{total,calc}} \times 100\% \quad (1)$$

where $C_{measured}$ corresponds to the measured concentration and $C_{total,calc}$ represents the concentration that would be obtained after full leaching.

This methodology was applied to all samples, systematically varying the parameters to achieve the desired pH (citric acid concentration = 1 mol L⁻¹, S/L = 20–100 g/L, H₂O₂ content = 2–8% (vol.), and temperature = 30 or 45 °C). These ranges allowed for the evaluation of the influence of each parameter on leaching efficiency while optimizing the process to reach the target pH for electrodialysis separation.

For electrodialysis experiments, a 1 L leachate solution of NMC111 with citric acid was prepared in a thermostated double-jacketed leaching reactor (Heating Circulators, VWR[®] manufacturer, Paris, France) (Supplementary Materials, Figure S1). The diluted acid was added into the reactor under stirring at 600 rpm using an electronic rod stirrer (VOS 40 digital and VOS 60 control, VWR[®] manufacturer, Paris, France) followed by introducing the cathode material. The leaching solution was immediately filtered using vacuum filtration. The experimental conditions were selected based on the results of leaching studies.

2.2.4. Electrodialysis

A four-compartment electrodialyzer was employed for the selective extraction of lithium(I) and divalent metals from an NMC111 leach solution. The compartments were separated by two cation-exchange membranes (CEMs) and an anion-exchange membrane (AEM) alternately positioned between platinized titanium electrodes (Figure 2). The area of each membrane was 40 cm². The system was operated in batch mode. For each compartment, an initial volume of 0.5 L of solution was introduced into a stirred beaker and pumped to ensure recirculation. This volume was selected to ensure complete filling of the compartment and tubes, to promote effective circulation, and to enable sampling throughout the 2 h experiment. The feed compartment was initially fed by the leach solution. The cathodic compartment (lithium recovery compartment) was initially fed with a 0.05 mol L⁻¹ LiOH solution. Lithium ions migrated into this compartment through a CEM. The metal recovery compartment, separated by an AEM, was filled with 0.5 mol L⁻¹ citric acid (C₆H₈O₇) for the recovery of metal–citric acid complexes. The electrolyte compartment, adjacent to the anode, contained initially 0.1 mol L⁻¹ H₂SO₄. This prevented the migration and possible oxidation of the metal complexes. The electrodialysis cell included four compartments.

A constant current of 4 A was applied to the electrodialyzer using DC power (DCS150-7E Sorensen, MB Electronique company, Buc France) for a duration of 2 h. Gases formed at the electrodes were extracted to ensure the safety of the installation. The flowrate of the peristaltic pumps (Masterflex[™] L/S[™] model 77250-62, Parmer instrument company, Vernon Hills, IL, USA) was set at 100 mL min⁻¹. Exactly 20 mL samples were collected every 30 min from the cathodic compartment (lithium recovery compartment) as well as the leachate and the metal recovery compartment for elemental analyses, pH measurements, and ionic conductivity measurements. These analyses enabled real-time monitoring of the separation efficiency between lithium and the transition metals present in the system.

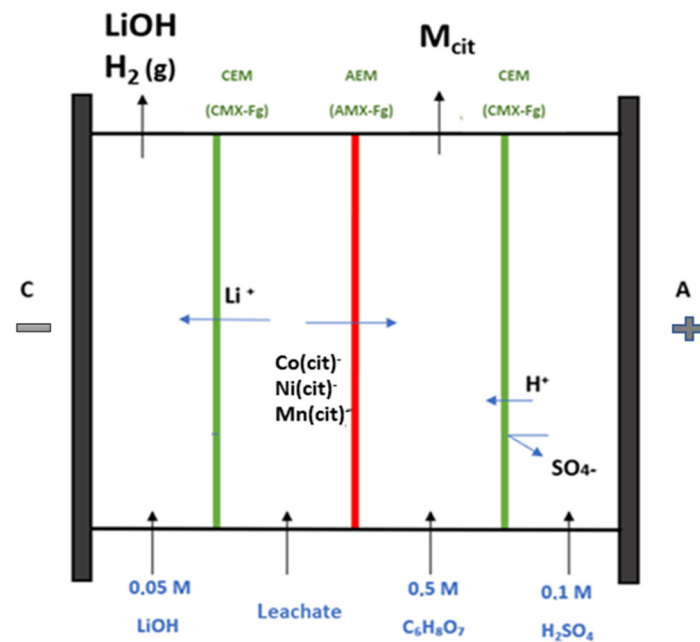


Figure 2. Scheme of the electrodesialysis setup (CEM: cationic exchange membrane CMX-Fg; AEM: anionic exchange membrane AMX-Fg; M_{cit} : metal citrate species; A: anode; C: cathode; $Ni(cit)^-$, $Co(cit)^-$, and $Mn(cit)^-$: metal–citrate complexes of nickel, cobalt, and manganese, respectively).

The performance of the electrodesialysis process was evaluated by calculating the faradic efficiency (R_f):

$$R_f(\%) = 100 \times \frac{zF \Delta n}{I \Delta t} \quad (2)$$

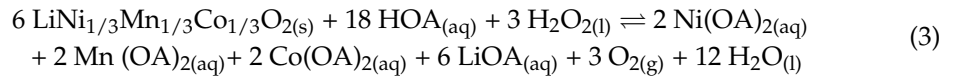
where Δn (mol) is the number of moles of cations transported through the membrane, F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), z is the valence of the ion (for lithium, $z = 1$), I (A) is the applied current, and Δt (s) is the electrodesialysis operating time.

3. Results and Discussion

3.1. Speciation Calculations

Citric acid is a tricarboxylic acid with three carboxyl groups ($-\text{COOH}$) and one hydroxyl group ($-\text{OH}$) on a six-carbon chain (C_6) [21]. Its structure gives its acidic and complexing properties, with three dissociation constants at 25°C ($\text{pK}_{a1} = 3.13$, $\text{pK}_{a2} = 4.76$, and $\text{pK}_{a3} = 6.39$) [22]. In solution, it releases protons (H^+), facilitating the dissolution of metal oxides from the used cathodes (LiCoO_2 , LiNiO_2 , and LiMnO_2) by breaking the metal–oxygen bonds. The released metal ions (Li^+ , Co^{2+} , Ni^{2+} , and Mn^{2+}) can then form bi- or tridentate complexes, as well as binuclear or multidentate structures with citric acid [23]. In the absence of an external reducing agent such as hydrogen peroxide (H_2O_2), citric acid itself can act as a mild reducing agent and undergo oxidation during the leaching process of the cathodes. For this, H_2O_2 is often added to promote the complete reduction of cobalt and manganese to their +II oxidation states, thus improving the leaching efficiency [24]. Although no specific data are available in literature regarding the leaching reaction of NMC111 by citric acid, an analogy can be made with those described for metal oxides of similar composition in the presence of H_2O_2 . The overall reaction is represented by Equation (2), where HOA denotes citric acid and OA^- its carboxylate anion, and citric acid is treated as a monoprotic acid (HOA) for simplification purposes [25]. However, in practice, citric acid is a triprotic acid and can form several partially deprotonated species (H_2cit^- , Hcit^{2-} , and cit^{3-}), which can lead to various metal–citrate complexes depending on the pH. Species such as M(cit)^- and M(Hcit) may dominate the equilibrium, as dis-

cussed in the following section. Consequently, the actual speciation during the leaching mechanism is more complex than that depicted in the simplified Equation (3):



According to the speciation diagram in Figure 3, Ni, Co, and Mn fully form anionic species with citric acid at a pH near to 5, while Li keeps its cationic form (Li^+) at this pH value.

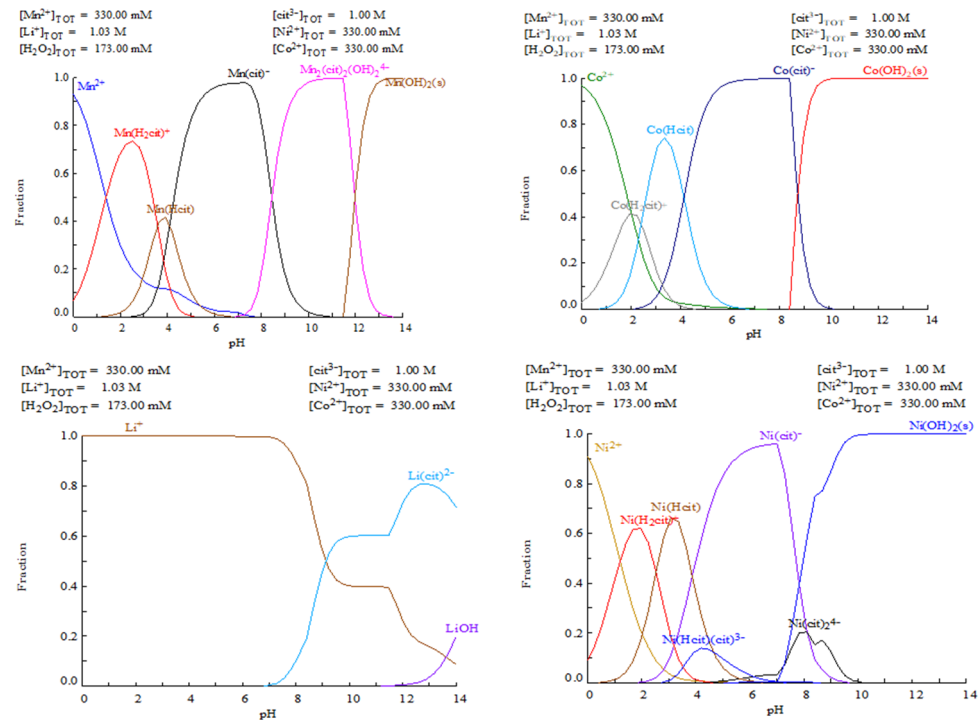


Figure 3. Speciation diagrams of manganese(II), cobalt(II), lithium(I), and nickel(II) in citric acid at 25 °C calculated for an aqueous solution, for which the composition is as follows: $[\text{Mn}^{2+}] = 330 \text{ mmol L}^{-1}$; $[\text{Co}^{2+}] = 330 \text{ mmol L}^{-1}$; $[\text{Ni}^{2+}] = 330 \text{ mmol L}^{-1}$; $[\text{Li}^+] = 1.03 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}_2] = 173 \text{ mmol L}^{-1}$; and $[\text{Cit}^{3-}] = 1 \text{ mol L}^{-1}$ (calculation performed by using the Medusa software v1 with its database).

Therefore, $\text{pH}=5$ may be the optimal value for performing the efficient separation of Li(I) towards C(II), Ni(II), and Mn(II) by taking advantage of the difference in speciation. Furthermore, the complexation of the divalent metals may avoid their precipitation into the membranes and membrane clogging. This pH value can be reached by adjusting the pH after leaching with a base like sodium hydroxide (NaOH) or by choosing the appropriate value of the solid/liquid (S/L) ratio during leaching. This last option appears to be the best one since the use of NaOH for pH adjustment is responsible for the addition of sodium impurity in the leachate.

Therefore, the influence of the S/L ratio on pH and metal leaching efficiency was investigated using 1 mol L^{-1} citric acid with 2% H_2O_2 at 30 °C (Figure 4a). Increasing the S/L ratio from 20 g/L to 100 g/L led to a pH rise from 2.4 to 3.6 after 24 h. Since electro dialysis should operate optimally at pH 4–5 according to speciation calculations (Figure 3), a further increase in the S/L ratio may be beneficial. However, excessive S/L ratios could lower the leaching efficiency due to acid depletion. After 24 h, leaching efficiencies for Mn, Ni, Co, and Li were 62.5%, 74.2%, 70.6%, and 81.6% (Figure 5a),

respectively. From an industrial perspective, a higher S/L ratio improves scalability by enabling larger slurry processing.

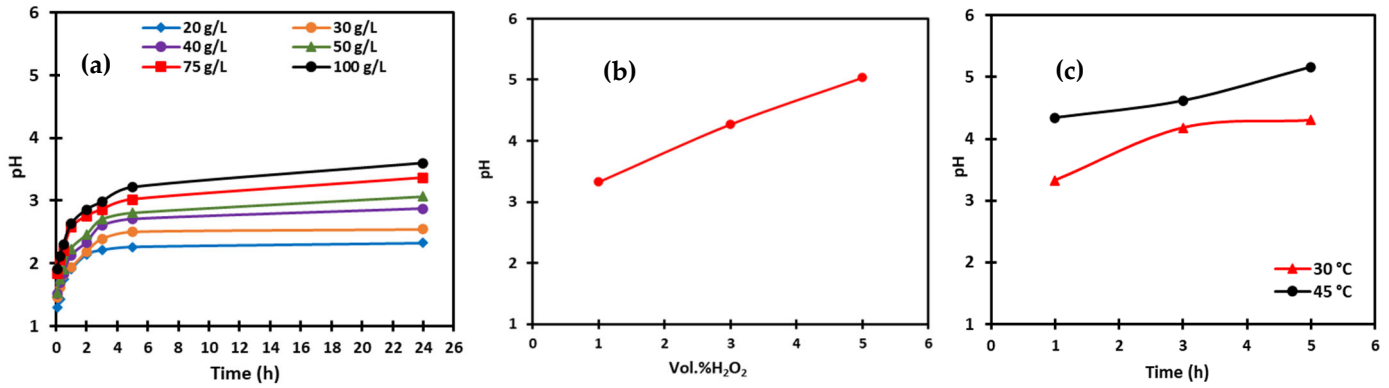


Figure 4. Effect of (a) solid-to-liquid ratio (S/L) (30 °C, %H₂O₂ (vol.) = 2%), (b) H₂O₂ (%vol.) (S/L = 100 g/L, 30 °C, 24 h), and (c) temperature (S/L = 100 g/L, 8% H₂O₂) on the final pH value after leaching.

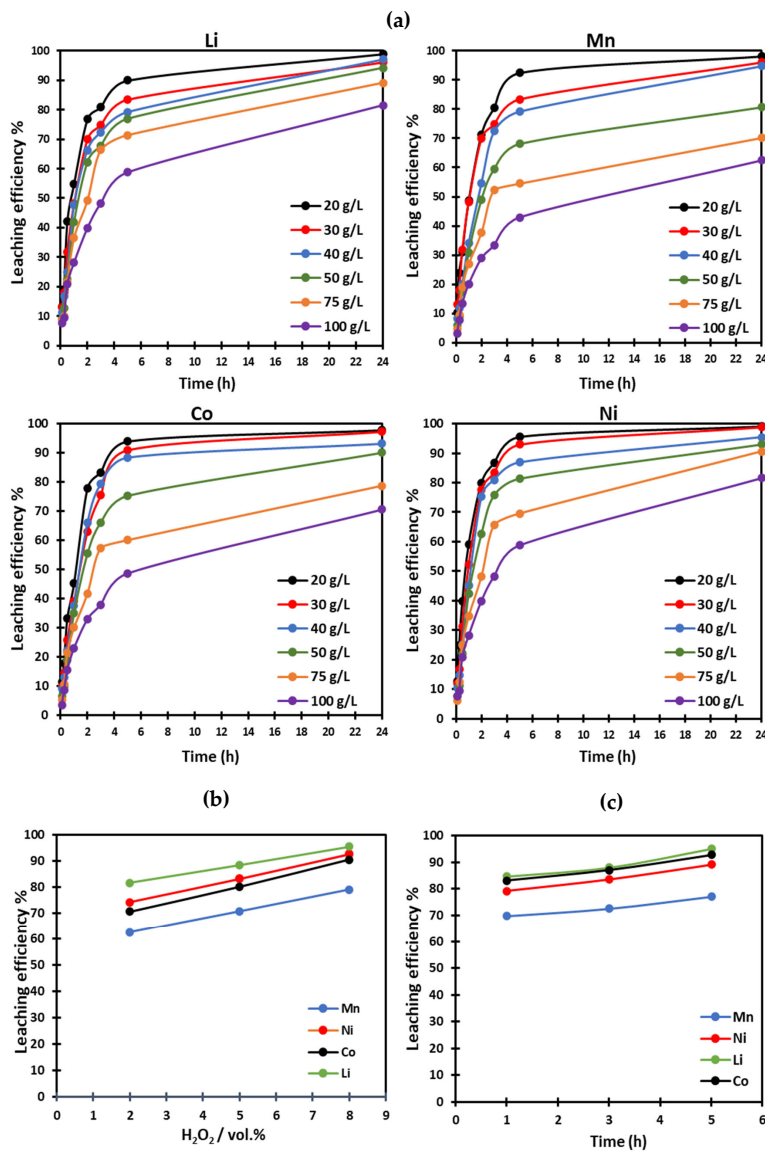


Figure 5. Effect on leaching efficiencies of (a) solid-to-liquid ratio (S/L) (30 °C, %H₂O₂(vol.) = 2%), (b) H₂O₂ (%vol.) (100 g/L, 30 °C, 24 h), and (c) time (100 g/L, 8% H₂O₂, and 45 °C).

The presence of hydrogen peroxide (H_2O_2) significantly affects pH values during the leaching process. Without H_2O_2 , citric acid is consumed by oxidation, leading to a reduction of Co(III) to Co(II). In contrast, H_2O_2 prevents this redox reaction, preserving citric acid in the medium. However, the observed increase in pH with higher H_2O_2 concentrations suggests that citric acid may still be consumed through other pathways, such as complexation reactions.

As shown in Figure 4b, increasing the H_2O_2 concentration from 2% to 8% (vol.) at 30 °C and S/L=100 g/L raised the pH from 3.5 to 5 after 24 h. Leaching efficiencies for Mn, Ni, Co, and Li were 70.7%, 83.2%, 80.1%, and 88.35%, respectively (Figure 5b).

Temperature also has a significant impact on pH evolution during the leaching process. Increasing the temperature from 30 °C to 45 °C accelerated the pH rise from 4.3 to 5.1 over 5 h, indicating an acceleration of chemical reactions, as shown in Figure 4c. Leaching efficiencies of 77.1%, 89.3%, 95.1%, and 92.9% were reached for Mn, Ni, Co, and Li respectively (Figure 5c). This observation aligns with Yao et al. [26], who reported that leaching efficiency and pH follow similar trends over time, indicating that higher temperatures enhance both metal dissolution and pH increase as a result of acid consumption during leaching. Consequently, NMC111 leaching with 1 mol L⁻¹ citric acid in the presence of 8 vol. % H_2O_2 at 45 °C and S/L = 100 g/L for 5 h enables the production of a leach solution at pH 5, and it dissolves 89.3%, 95.1%, 77.1%, and 92.9% of Ni, Co, Mn, and Li, respectively.

3.2. Crystallization After Leaching

A pink precipitate was formed after storing the leachate at room temperature for four days, as shown in Figure S2 (Supplementary Materials). Around 81.5% manganese, 62.5% nickel, and 66.7% Co precipitated, while Li remained predominantly in the liquid phase since 83.8% of Li was found in the supernatant, reflecting its high solubility. This precipitation is advantageous for electro dialysis since it significantly reduces the presence of divalent metals in the leachate, and the solid formed may be used as a precursor for the synthesis of new cathode materials [25,27]. This precipitation step that precedes electro dialysis will be investigated to produce a lithium-rich supernatant and a precipitate that could be used as a potential PCAM material.

On the other hand, the citric acid concentration in the supernatant was determined using Total Organic Carbon (TOC) analysis. The carbon concentration in the leachate was determined to be $m(\text{C}) = 43.6$ g/L. Based on the molecular composition of citric acid and its molar weight, the final concentration was determined to be 0.605 mol L⁻¹. This indicates a loss of citric acid from the solution, since 1 mol L⁻¹ was initially used, most likely due to precipitation during the process. Nevertheless, this change in concentration does not significantly affect metal speciation (see Figure S3, Supplementary Materials). At pH 5, citric acid still forms stable anionic complexes with divalent metal ions, Co^{2+} , Mn^{2+} , and Ni^{2+} , while lithium remains in its cationic form.

The XRD pattern of the sample indicates a crystalline structure (black line in Figure 6) closely matching the reference pattern of tricobalt (II) citrate dihydrate, $\text{C}_{12}\text{H}_{38}\text{Co}_3\text{O}_{28}$ (COD 4504918, red line). This suggests that this compound is one of the major phases present in the precipitate. Mn and Ni are present in the precipitate but not detectable in the XRD pattern, likely due to the formation of amorphous citrate complexes or crystalline structures similar to cobalt citrate, resulting in overlapping diffraction peaks. Or the chemical similarity between Co^{2+} , Mn^{2+} , and Ni^{2+} explains the possibility that the partial substitution of Co^{2+} by Mn^{2+} and Ni^{2+} occurs within the same crystal lattice, without significantly altering the structure. Similar observations were reported in a previous study of Xuan et al. [25], where XRD analysis identified manganese citrate monohydrate ($\text{Mn}(\text{HC}_6\text{H}_5\text{O}_7)\cdot\text{H}_2\text{O}$) in the precipitate after citric acid leaching despite different experi-

mental conditions. This supports the hypothesis that various divalent metal citrates may co-precipitate, possibly forming mixed or structurally similar phases.

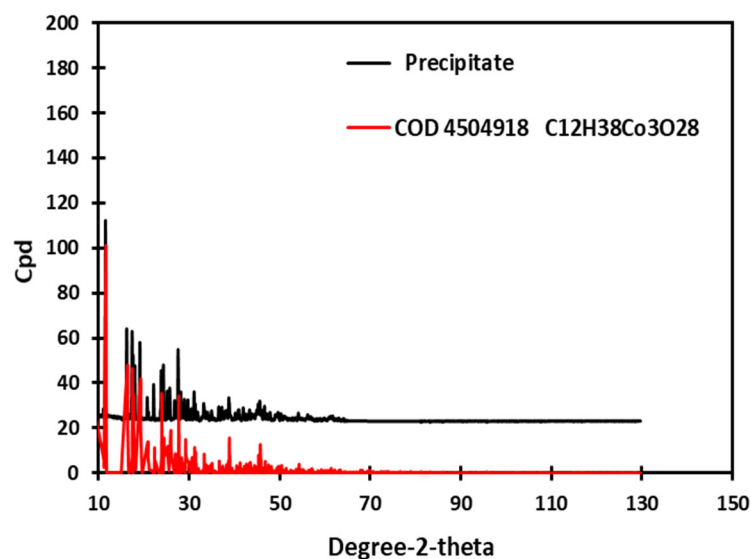


Figure 6. XRD pattern of the precipitate (black) and comparison with the XRD spectrum of tricobalt(II) citrate dihydrate ($C_{12}H_{38}Co_3O_{28}$).

3.3. Electrodialysis

Figure 6 shows the evolution of the lithium concentrations in the different compartments (lithium recovery, leachate, and metal recovery) during electrodialysis. A continuous and regular increase in the lithium concentration in the lithium recovery compartment was observed, from 0.05 mol L^{-1} to approximately 0.49 mol L^{-1} after 2 h, accompanied by a simultaneous decrease in the leachate compartment from 1 mol L^{-1} to 0.69 mol L^{-1} . This evolution reflects an efficient and oriented transfer of lithium ions through the CEM. Simultaneously, the lithium concentration in the metal recovery compartment remains zero throughout the experiment, confirming the total absence of migration to this compartment. This behavior highlights the non-complexation of lithium by citric acid, thus facilitating its exclusive transport through the CEM. Conversely, transition metals (Ni, Co, and Mn), strongly complexed by citric acid, do not cross the CEM but migrate through the AEM into the metal recovery compartment. This is evidenced by the gradual color change observed in the solution, reflecting the progressive migration of these metal–ligand complexes. All of these results underline the selectivity of the process and its effectiveness for the targeted recovery of lithium in a highly pure form from multi-component leachates, with no clogging observed during operation (Supplementary Materials, Figure S4).

In order to calculate the number of moles of Li transferred to the recovery compartment over time, the mass balance must take into account changes in the volume of the various compartments due to sampling, water transfer by osmosis and electroosmosis, and slight evaporation. A notable decrease in leachate volume is observed in the corresponding compartment, leading to an asymmetry in the concentration curves of the two compartments (leachate and cathodic), as shown in Figure 7.

The calculation of the cumulative number of moles of Li transferred as a function of time revealed a linear increase over the first 90 min, with a transfer rate of $3.3 \times 10^{-5} \text{ mol s}^{-1}$. For a current of 4 A, this corresponds to a faradic efficiency of 78.7%. The transfer rate then slowed down between 90 and 120 min due to the decreasing concentration in the leachate compartment, which caused the imposed current to approach the limiting current. After 90 min, the value of the imposed current should have been reduced. The overall faradic efficiency for lithium recovery of the experiment was thus

penalized, dropping to 71.4%. By reducing the current, much higher faradic efficiencies could be expected. To further recover lithium, the current should be reduced as the lithium concentration in the leachate compartment decreases.

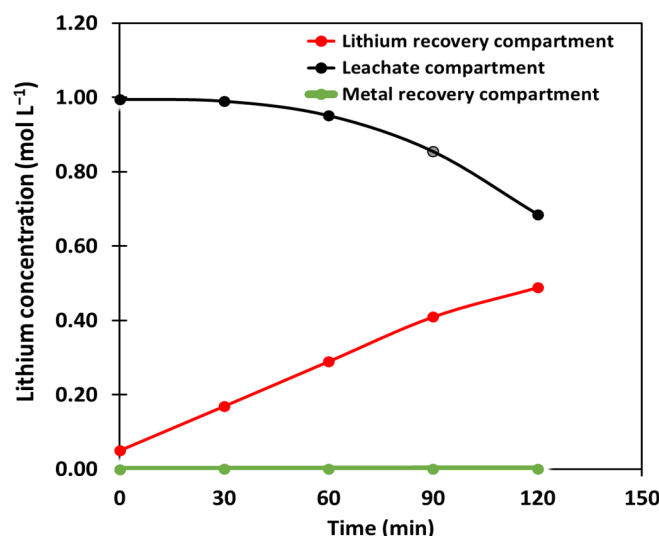


Figure 7. Lithium concentration in the different compartments during electro dialysis ($I = 4\text{ A}$, flowrate = 100 mL min^{-1} , $t = 2\text{ h}$).

Table 3 shows the variation in pH and ionic conductivity as a function of time during electro dialysis in the leachate compartment, the lithium recovery compartment, and the metals recovery compartment.

Table 3. pH and ionic conductivity values recorded in each compartment as a function of time during electro dialysis (κ : ionic conductivity).

Time (min)	ED Compartments					
	Li ⁺ Recovery Compartment		Leachate Compartment		Metal Recovery Compartment	
	pH	κ (mS cm ⁻¹)	pH	κ (mS cm ⁻¹)	pH	κ (mS cm ⁻¹)
0	12.75	9.26	4.8	23.88	1.60	5.42
30	13.47	31.64	4.85	23.53	1.66	5.48
60	13.55	51.60	4.85	23.74	1.98	5.55
90	13.59	70.70	4.75	21.62	2.04	5.62
120	13.67	91.00	4.56	18.90	2.08	5.88

Examination of this table shows an increase in pH from 12.75 to 13.67 in the lithium recovery compartment due to the formation of OH^- ions by water reduction at the cathode, as well as an increase in ionic conductivity from 9.26 mS cm^{-1} to 91 mS cm^{-1} due to Li^+ migration and OH^- formation.

In the leachate compartment, the pH remained relatively stable, changing slightly from 4.80 to 4.56. This pH stability can be attributed to the buffering effect of the medium, whose pH is close to that of pK_{a2} of citric acid ($\text{pK}_{a2} = 4.76$). It enables the limitation of pH fluctuations. This situation preserves the predominance of the $\text{M}(\text{Cit})^-$ species, contributing to the stability of the targeted speciation throughout the process.

4. Conclusions

This study demonstrated the viability of conventional electro dialysis as an effective method for the highly selective separation of lithium from a citric acid-based leachate of

NMC111. The leaching process was found to promote the formation of anionic complexes of Ni(II), Co(II), and Mn(II) in the form of metal citrates, while lithium remained in its cationic form (Li^+). This speciation contrast led to the precipitation of transition-metal-rich solids and a lithium-enriched supernatant. This difference in speciation enabled the full potential of ion-exchange membranes to be exploited: anionic metal complexes migrate through anionic membranes, while lithium cations migrate through cationic membranes. The electro dialysis experiment resulted in the recovery of high-purity lithium with a faradic yield of up to 71.4%.

This study paves the way for an alternative approach combining leaching in organic media, electro dialysis, and crystallization, as depicted in Figure 8. After leaching the black mass in citric acid under the optimized conditions established in this study, a crystallization step precedes electro dialysis to maximize the removal of divalent cations—mainly manganese, cobalt, and nickel citrates—and produces a lithium-enriched solution compatible with electro dialysis. The stoichiometry can be adjusted with additional metal citrates before calcination to produce a pCAM suitable for the synthesis of new cathode materials for LIBS (CAM). A final electro dialysis step is then performed to obtain high-purity lithium hydroxide (LiOH). Recycling of the depleted leachate to the leaching step is proposed to improve process sustainability. Its impact on leaching efficiency remains to be explored in future work.

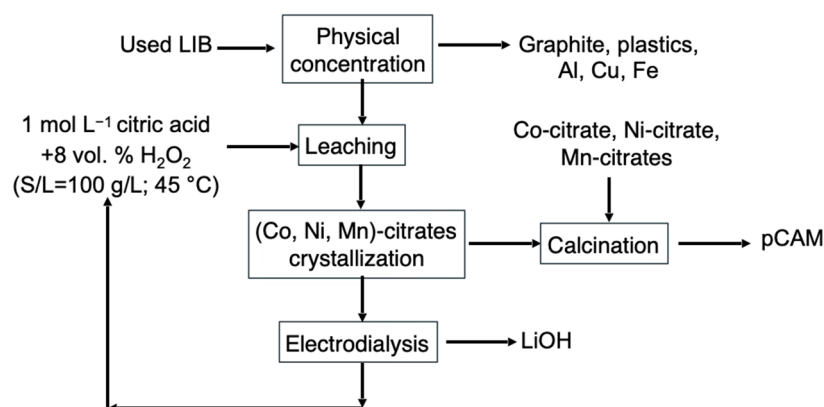


Figure 8. Alternative route for BM treatment by combining leaching, electro dialysis, and crystallization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met15060598/s1>, Figure S1: Setup for leaching experiments using a thermostatic glass reactor. Figure S2: Precipitation observed in the leachate after 4 days of storage and Precipitate after filtration, washing and drying at 40 °C. Figure S3: Speciation diagrams of Mn(II), Co(II), Li(I) and Ni(II) in citric acid at 25° calculated for an aqueous solution which the composition is: $[\text{Mn}^{2+}] = 70 \text{ mmol L}^{-1}$; $[\text{Co}^{2+}] = 150 \text{ mmol L}^{-1}$; $[\text{Ni}^{2+}] = 170 \text{ mmol L}^{-1}$; $[\text{Li}^+] = 850 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}_2] = 173 \text{ mmol L}^{-1}$; $[\text{Cit}^{3-}] = 0.6 \text{ mol L}^{-1}$ (calculation performed by using the Medusa software with its database). Figure S4: Electro dialysis experiments.

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