

Direct Synthesis of Li-Mn-Rich Cathode Precursor from End-of-Life Li-Ion Batteries

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An innovative hydrometallurgical process is analysed, enabling the direct synthesis of graphene oxide and lithium-manganese rich cathode materials from the electrodic powder ("black mass") of spent lithium-ion batteries. The black mass leaching is performed by the Hummers' method, an established solution to produce graphene oxide from graphite. The proposed strategy is based on the observation that the reagents H_2SO_4 and H_2O_2 , which are conventionally used to perform the leaching of the black mass, are also used, along with KMnO_4 and NaNO_3 , in the implementation of the Hummers' method. Accordingly, the Hummers' method is here carried out to extract the cathode metals from the black mass (Li, Mn, Co, Ni). To valorise the manganese excess generated by the addition of KMnO_4 , co-precipitation from the residual solution obtained after graphene oxide recovery is carried out to synthesize the precursor of the lithium-manganese rich cathode materials, which is then used to produce the cathode material by solid-state reaction with LiOH . In this contribution, an experimental analysis of this resynthesis process is presented, allowing to evaluate the impact of the main process parameters on the precursor material synthesis. The proposed process includes the removal of impurities such as copper, iron, and aluminium, followed by the coprecipitation of a precursor with the composition $\text{Ni}_{0.375}\text{Mn}_{1.375}\text{Co}_{0.25}(\text{OH})_2$.

1. Introduction

Many daily activities, such as driving electric vehicles, using smartphones, or converting renewable energy, rely on batteries, with Li-ion batteries (LIBs) being the most common (van de Ven et al., 2024). These batteries are expected to play a key role in transitioning from fossil fuels to renewable energy and reducing greenhouse gas emissions (Pacala & Socolow, 2004). The European Union has set a goal for all new cars to be zero-emission by 2035 to help achieve net-zero emissions in the transportation sector by 2050 (European Parliament, 2023). This shift will drive increasing demand for batteries, leading to higher volumes of spent LIBs and the need for efficient recycling. LIBs consist of an anode for Li intercalation and a cathode made of transition metal oxides (e.g., LiCoO_2 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, $x+y+z=1$), along with an electrolyte, separator, and current collectors (Dobó et al., 2023). These materials, including Co, Li, Mn, and Ni, are classified as Critical Raw Materials (CRMs) by the EU due to their limited availability and importance for the economy (European Union, 2023). Recycling LIBs is crucial for securing the supply of these materials and reducing reliance on imports. LIB recycling processes are generally categorized into pyrometallurgy and hydrometallurgy (Bhattacharyya et al., 2024). Pyrometallurgy uses high temperatures to extract metals from spent Li-ion batteries, but it loses Li (Schiavi et al., 2024) and graphite during the process. While it has been economically justified by cobalt recovery, which is the most expensive metal in the cathode, its attractiveness has diminished as new batteries contain less cobalt (T. Yang et al., 2023). Hydrometallurgy, on the other hand, relies on leaching the electrodic powder (black mass) from LIBs using mineral acids and reducing agents, producing a liquid phase rich in metals and a solid phase mainly composed of graphite (J. Zhang & Azimi, 2022). This process recovers all battery materials with a lower environmental impact than pyrometallurgy, though it requires a complex and costly sequence of refining stages to separate the metals. These stages often involve organic solvents and, for lithium recovery, concentration by

evaporation, increasing energy consumption. Additionally, graphite recovered from the leaching process undergoes purification to be reused as an anode material in new Li-ion batteries (Schiavi, Altamari, et al., 2021). To overcome these limitations, the solution obtained by leaching can be directly used to synthesize the precursor of new Li-ion batteries, excluding the complex and costly separation of the different metals. This strategy, referred to as “resynthesis” of electrode materials, has been previously implemented to synthesize NMC cathode materials. The main limitation is the addition of high-purity salts that are needed to correct the stoichiometry at the precursor synthesis stage. In this article, to enhance the economic competitiveness of the recycling process, an innovative “resynthesis” strategy is analysed allowing the conversion of the graphite to graphene oxide (GO) and directly synthesizing lithium-manganese rich cathode materials. The process is described by the block-scheme reported in Figure 1. The main idea is the leaching of the black mass by the application of the Hummers’ method, which is extensively used to convert graphite to graphene oxide (GO). The Hummers method includes the application of H_2SO_4 and H_2O_2 which are the mineral acid and the reducing agent, respectively, commonly used to perform the leaching of the black mass. Therefore, by applying the Hummers method, electrodic metals are extracted from the black mass and dissolved into the liquid phase, achieving simultaneously conversion of the graphite fraction to GO. In addition to H_2SO_4 and H_2O_2 , KMnO_4 are used to implement the Hummers method, which increases the Mn concentration in the residual solution. To valorise this excess, co-precipitation of the metals (Ni, Co and Mn) from the residual solution is then carried out to directly synthesize the precursor Li-Mn-rich cathode materials. In this way Mn excess, added via KMnO_4 , required for GO synthesis, is not wasted. By solid-state reaction of the precursor with LiOH , the cathode material is then obtained.

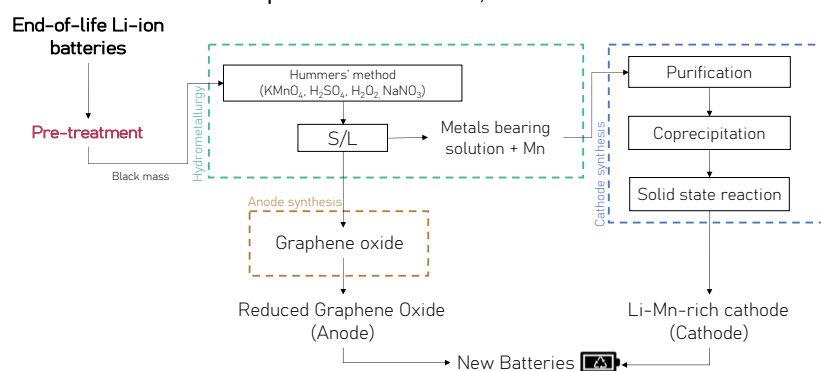


Figure 1. Block diagram of the proposed process for the treatment of end-of-life Li-ion batteries.

In this contribution, an experimental analysis of the above-described resynthesis strategy is presented. In particular, the analysis will be mainly focused on evaluating the impact of Hummers’ solution purification and co-precipitation parameters. Preliminary results of the precursor synthesis, obtained using this process, will be presented, analysing the stoichiometry, the obtained particles size and the effectiveness of the integrated process with the Hummers method.

2. Materials and methods

The black mass used in the current study was recovered by physical pre-treatment of end-of-life lithium-ion batteries conducted by TES Recupyl SAS (FR). As benchmark for the precursor synthesis, the co-precipitation process was also carried out from a synthetic solution prepared by employing commercial salts with the same stoichiometry as that of the end-of-life batteries.

2.1 Black mass chemical characterization

The black mass, subjected to mechanical pretreatment, was chemically characterized through a mineralization process in a microwave mineralizer (Milestone Ethos 900 Microwave Labstation). Mineralization involves the use of an acid solution capable of dissolving the metals contained in the black mass. Six powder samples (0.25 g each) were prepared, to which 4 mL nitric acid (HNO_3 , Carlo Erba 65%), 4 mL hydrochloric acid (HCl , VWR 35%) and 2 mL hydrogen peroxide (H_2O_2 , Sigma-Aldrich 30%) were added. The solution was prepared in polytetrafluoroethylene (PTFE) vessels, which were sealed and placed in the mineralizer. The samples were then heated to and maintained at 200°C for 30 minutes. After mineralization, the samples were brought to a final volume in a 50 mL flask. Following filtration, the solution was analyzed using ICP-OES (Avio 220 Max Perkin Elmer) to determine the concentrations of the metals of interest. The solid residue from filtration was dried and weighed to calculate the percentage of graphite in the black mass.

2.2 Hummers Method

The black mass was first characterized, and the Hummers' method was carried out using 8.3 g of black mass powder, ensuring it contained 3 g of graphite: using the % of solid residue in the powder (Equation 3). The procedure was performed in a 1 L jacketed reactor, initially set to 0°C and under constant stirring. To this reactor, 69 mL of sulfuric acid, 1.5 g of sodium nitrate (NaNO₃), and 9 g of potassium permanganate (KMnO₄) were added. The temperature was kept below 20°C during the addition of KMnO₄ to prevent excessive heat. Once the reactor reached 35°C, it was stirred for 30 minutes. Next, 138 mL of distilled water was added, followed by heating the reactor to 98°C and stirring for 15 minutes. Then, 420 mL of distilled water and 5 mL of hydrogen peroxide (H₂O₂) were added. The mixture was stirred, and the contents were decanted into 50 mL Falcon tubes, centrifuged at 4000 rpm for 30 minutes. The supernatant, rich in metals, was transferred to a 1 L flask. The solid residue (graphite oxide) was washed by adding 15 mL of hydrochloric acid (HCl 1.12 M) to each tube, followed by another centrifugation, and washing with water. This washing and centrifuging process was repeated two times. The supernatants from the centrifuge tubes were combined, brought to volume, and filtered by vacuum filtration. The filter was weighed before and after filtration, and then freeze-dried for further quantification of graphene oxide (GO). The post-centrifugation solid residue (graphite oxide) was placed in a beaker for magnetic stirring overnight to initiate exfoliation. The mixture was then sonicated for 30 minutes, followed by centrifugation at 3000 rpm for 40 minutes. The supernatant containing graphene oxide was transferred to pre-weighed Falcon tubes, separating it from the sediment (oxidized graphite and charcoal).

Both the supernatant and the solid residue were freeze-dried and weighed to determine the productivity of GO, based on the equation (Eq 1) provided below:

$$GO \text{ productivity} = \frac{GO [g]}{GO [g] + \text{graphite oxide} [g]} \quad (1)$$

As mentioned before this process was used, at the same time, to extract the metals. The metals extraction yield is calculated basing on Equation 2.

$$\text{Metals extraction yield (\%)} = \left(\frac{M \text{ in Hummers solution } \left[\frac{mg}{g} \right]}{M \text{ in initial powder characterization } \left[\frac{mg}{g} \right]} \right) * 100 \quad (2)$$

Where M= Metal.

2.3 Purification process

As mentioned earlier, the Hummers method also produced a liquid phase that is rich in the metals of interest. To remove impurities (such as Al, Cu, and Fe), which can negatively affect the electrochemical performance of the cathode material, a precipitation process was carried out. This process involved adding NaOH (5 M) to the solution until a pH of 6.5 was reached. This pH value was chosen to achieve a balance between maximizing the precipitation of impurities and minimizing the loss of the metals of interest. Once the suspension was filtered, the resulting solution contained only Ni, Mn, and Co.

2.4 Co-precipitation process

A stoichiometric adjustment was required to obtain the target stoichiometry of the Li-Mn rich cathode. This adjustment was done using CoSO₄*7H₂O, NiSO₄*6H₂O and MnSO₄*H₂O to achieve target mixed metal hydroxide Ni_{0.375}Mn_{1.375}Co_{0.25}(OH)₂. Then the solution underwent co-precipitation process. For comparison, the same co-precipitation process was also replicated on a synthetic solution in which the concentration of Co, Mn and Ni was the same of the solution resulting after the Hummers method. These last concentrations were achieved dissolving CoSO₄*7H₂O, NiSO₄*6H₂O and MnSO₄*H₂O in water. In the latter solution no metal impurities were added. The co-precipitation process was carried out using 250 ml of the metal solution. Precipitation was achieved by increasing the pH up to 11 using NaOH 5 M while NH₄OH 2 M with a 10% stoichiometric excess, was used as a complexing agent. First the solution and all the necessary reagents are degassed by stripping with Ar for 1 h. Then the chelating agent is added and using a peristaltic pump NaOH is added until pH 11 is reached. Once the pH is reached, the co-precipitation process will last 24 h with a temperature of 60°C and a stirring speed of 500 rpm. During the whole precipitation time temperature, pH, and agitation speed will be controlled and the reactor was maintained at 200 mbar overpressure using Ar. At the end of 24 hours, the filtration process takes place maintaining the inert atmosphere. Solid precursor was washed with water (previously degassed) until a neutral pH of the resulting washing water was obtained. The precursor was dried under vacuum maintaining the inert atmosphere by flowing Ar. The precursor material, which is to be analyzed by ICP-OES, undergoes a mineralization process. Three samples of the precursor are weighed, and then 4 mL of nitric acid (HNO₃, Carlo Erba 65%), 4 mL of hydrochloric acid (HCl, VWR 35%), and 2 mL of

hydrogen peroxide (H₂O₂, Sigma-Aldrich 30%) are added to a 50 mL flask. The mixture is then placed on a hot plate until all the solid has dissolved; the resulting solution is subsequently analyzed.

3. Results and discussion

3.1 Black mass chemical characterization

The concentration of the metals in the black mass determined by mineralization and ICP-OES analysis is reported in Table 1:

Table 1. Chemical characterization of the black mass (Rhino 3) obtained from end-of-life Li-ion batteries.

Black mass	Average [mg/g]	St.dev.
Co	93.0	2
Ni	100.6	3
Mn	78.9	2
Li	36.2	1
Cu	7.8	1
Fe	31.7	3
Al	0.5	0

According to the stoichiometric ratios between Ni, Mn, Co, and Li, this electrode powder is similar to that expected for NMC111 (LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂) batteries. As mentioned in section 2.1, the chemical characterization also allowed the calculation of the percentage of solid residue corresponding to the graphite and carbon content in the black mass. The method used for this estimation involved filtering the mineralized solution, weighing the filter before filtration, drying the filter, and then weighing it again after drying. This way, the solid residue percentage could be quantified as follows:

$$\%solid\ residue = \left(\frac{g\ solid\ residue\ dried}{g\ black\ mass} \right) * 100 \quad (3)$$

For the Black Mass, the solid residue is 36.13 %. Here, it should be mentioned that this solid residue is composed of graphite (the anode material from the spent batteries) and carbon black (Super P). The latter material is found in both the cathodic and anodic slurries where it is introduced to increase the electrical conductivity of the electrodes.

3.2 Metals bearing solution purification

As previous mentioned, the Hummers' method is also used to extract the metals, as two of its reagents are the same as those used in the leaching process. As reported in Schiavi et al., 2021 this process allows for a quantitative recovery of the metals of interest. This solution, rich in metals, needs to be purified due to the presence of Al, Cu and Fe, which originate from the imperfect separation of the black mass from the current collectors and the battery case during physical pretreatment. This purification is necessary because these impurities can negatively affect the electrochemical performances of the final cathode material (Sa et al., 2015; R. Zhang et al., 2020, 2021). The purification was achieved by precipitation of the metal impurities by adding NaOH to the solution obtained from the Hummers method (see Section 2.3). NaOH was added until a pH of 6.5 was reached.

Table 2. Metals precipitation during purification process

Metal	Precipitation (%)
Ni	0
Mn	0
Co	2
Al	99
Fe	86
Cu	80

Table 2 shows the precipitation yields (%) of the metals. More than 80% of any metal impurity was precipitated at the selected pH in the form of hydroxide whereas for each of the metals of interest the precipitated fraction was lower than 10%.

3.3 Precursor co-precipitation

The purified solution will undergo a stoichiometric adjustment (as described in Section 1.4) to achieve a stoichiometry of $\text{Ni}_{0.375}\text{Mn}_{1.375}\text{Co}_{0.25}(\text{OH})_2$. This stoichiometry allows to produce a manganese-rich precursor. This choice is because, as a reminder, Mn was also added as a reagent (KMnO_4) during the Hummers process. Therefore, this decision was made to Mn excess and to prevent the need to add too many commercial salts to achieve different stoichiometries. After that the solution will undergo the Co-precipitation process.

The precipitation percentages are reported below, calculated from the solution after the filtration process.

Table 3. Precipitation % of the metals of interest after o-precipitation process.

Metal	Precipitation (%)
Ni	100
Mn	99.6
Co	100

The obtained precursor was characterized by ICP-OES to evaluate the composition and the stoichiometric ratios between Ni, Co and Mn. The metal concentrations were used to confirm that the desired stoichiometry was achieved. SEM images of the precursor particles are reported in Figure 2.

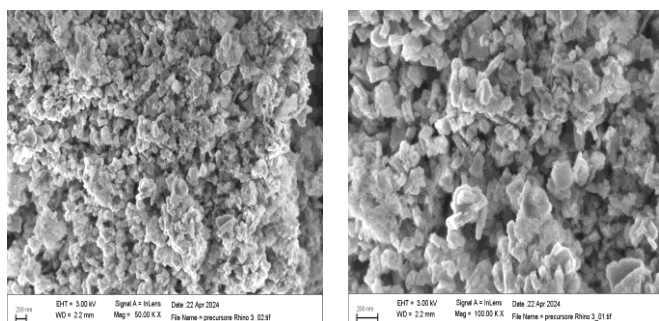


Figure 2. SEM images for the precursor obtained from spent Li-ion batteries after co-precipitation process.

SEM images (Figure 2) show typical hydroxide particles with a flaky structure, and their size is smaller than the typical range (1–10 μm) required for final cathode materials (Purwanto et al., 2024). The precipitation process is driven by the equilibrium between ammonia complex formation and metal precipitation. The crystalline structure analysis reveals metal ions at the center of an octahedral cell, surrounded by OH^- anions. These crystallites then undergo agglomeration and growth. The chelating agent (NH_4OH) plays a key role in controlling particle growth, promoting a homogeneous crystalline structure (De Conti et al., 2023; Y. Yang et al., 2015). The smaller particles observed may be due to an incorrect chelating agent concentration, as different concentrations are reported in literature, but not specifically for metal leaching in recycling. The lower metal molarity in the leaching solution compared to synthetic materials may affect the chelating agent's effectiveness, requiring further investigation (Wang et al., 2018).

4. Conclusions

Hydrometallurgical processes offer an alternative method to recover materials from Li-ion batteries by extracting key metals with less environmental impact than pyrometallurgy. However, they require complex and costly refining stages. To address this, an innovative "resynthesis" approach was implemented using the leachate to directly synthesize new Li-ion battery cathode precursors, bypassing metal separation. In the proposed process, graphite is converted to graphene oxide (GO) using the Hummers' method, while metals (Ni, Co, Mn) are simultaneously extracted. The black mass from spent batteries was first characterized and then subjected to the Hummers' method. The resulting solution was purified to remove Cu, Fe, and Al, which can negatively affect the final electrochemical performance. The purification yields 99% for Al, 86% for Fe, and 80% for Cu. Stoichiometric adjustments were then introduced by adding salts (e.g., CoSO_4 , NiSO_4 , MnSO_4) to the resulting solution and achieve the correct precursor composition in the co-precipitation process. The obtained precursor material has the desired metals stoichiometry while SEM characterization has shown particles with a smaller size to respect the common precursors particles size (1–10 μm). The smaller particles size may be attributed both to the concentration of metals in the solution used for the co-precipitation and of the chelating agent, though further studies are needed to confirm this.

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