



## Short communication

# Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries



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## H I G H L I G H T S

- A leaching process for the recovery of Li, Ni, Co, Al from NCA cathode is developed.
- Hydrochloric acid leads to a higher leaching efficiency than sulfuric or nitric acid.
- Ni and Co separation is carried out by precipitation of  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  using  $\text{NaClO}$ .
- Nickel is recovered by nickel hydroxide precipitation.
- A high rate of nickel and cobalt recovery is reached.

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## A B S T R A C T

A hydrometallurgical process is developed to recover valuable metals of the lithium nickel cobalt aluminum oxide (NCA) cathodes from spent lithium-ion batteries (LIBs). Effect of parameters such as type of acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ), acid concentration ( $1\text{--}4 \text{ mol L}^{-1}$ ), leaching time (3–18 h) and leaching temperature ( $25\text{--}90 \text{ }^\circ\text{C}$ ) with a solid to liquid ratio fixed at 5% (w/v) are investigated to determine the most efficient conditions of dissolution. The preliminary results indicate that  $\text{HCl}$  provides higher leaching efficiency. In optimum conditions, a complete dissolution is performed for Li, Ni, Co and Al. In the nickel and cobalt recovery process, at first the  $\text{Co(II)}$  in the leaching liquor is selectively oxidized in  $\text{Co(III)}$  with  $\text{NaClO}$  reagent to recover  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  by a selective precipitation at  $\text{pH} = 3$ . Then, the nickel hydroxide is precipitated by a base addition at  $\text{pH} = 11$ . The recovery efficiency of cobalt and nickel are respectively 100% and 99.99%.

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## 1. Introduction

Nowadays, the depletion of resources in fossil fuels and the necessity to reduce environmental impact urges people to develop sustainable energy including renewable energy sources such as: advanced batteries, fuel cells, solar cells or wind energy. Batteries and specifically the LIBs are undoubtedly an alternative to reduce the current dependence to fossil fuel resources. The worldwide consumption of batteries is significant and LIBs are already present on the market of nomadic technologies, such as mobile phones and laptops, but also in hybrid and electric vehicles. However, green

energies involve to consider the life cycle of a product from “cradle to grave”, requiring to pay attention to recycling routes for a safe disposal. Efficient recycling of battery materials is essential for a sustainable battery industry. Moreover, the requirements of the European directive on batteries recycling (2006/66/CE Directive) drives industrials to increase the recycling efficiency of LIBs. Finally, economic, strategic, environmental and safety aspects require to consider batteries recycling.

Li-ion batteries represent an active research field which includes a plurality of systems and components. Currently, most of research works are focused on the development of alternative cathode materials to  $\text{LiCoO}_2$ , mainly due to cost and safety issues and containing other transition metals such as nickel or manganese, to substitute partially or totally the cobalt:  $\text{LiFePO}_4$  (LFP),  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC),  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) and  $\text{LiMnO}_2$  (LMO) [1].

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In one hand, pyrometallurgical processes are commonly used in industry for recovering valuable metals in spent batteries with a high efficiency and high productivity [2,3]. However, this type of processes involves a loss of materials, emission of hazardous gases, dust and is high energy consumer. Moreover, the residual alloy requires a hydrometallurgical process to refine it into pure forms (salts, hydroxides, metals). In the other hand, basic hydrometallurgical processes represent an alternative and an opportunity to turn spent batteries into pure metals or metal salts with a low energy requirement but produce salts as by-products.

Despite the large number of studies on hydrometallurgical processes for battery electrodes, very scarce information is available on the NCA material, while it is considered as a promising material [4]. Indeed, its high specific energy and power density, as well as its long life span get the attention of the automotive industry [5]. On a recycling point of view, the possibility to use it in industry scale involves to consider the recycling from the early stages of research.

Therefore, this work is focused on a hydrometallurgical route in order to recover and separate valuable metals (Ni, Co) from NCA powder. Indeed, cobalt oxide is six time more expensive than nickel oxide [6]. The mechanical treatments required in the first step of LIBs recycling such as sorting, dismantling and grinding are not considered in this study.

The first step considered is the acid leaching of a chemically stable material. Usually, hydrometallurgical processes use strong acids to leach materials such as  $\text{H}_2\text{SO}_4$  [7–13],  $\text{HCl}$  [14–17] or  $\text{HNO}_3$  [18]. These acids are investigated for different concentrations (between  $2 \text{ mol L}^{-1}$  and  $9 \text{ mol L}^{-1}$ ) and different temperatures (between  $40$  and  $100$  °C). Additionally, operational variables like the solid to liquid ratio (around 2–20% (w/v)) and the leaching time are studied in order to size the recovery process.

The second step deals with the selective recovery of nickel and cobalt from the acid solution. According to literature, several main techniques have already been investigated to recover metals from acid solution, such as:

- the solvent extraction [8,10,15,19–23]
- the resin ion exchange [22]
- the electrochemical techniques [24]
- the selective precipitation [16,18,22,25].

Among them, the precipitation technique is selected, which is the easiest to set up at industry scale. However, the main challenge is to separate efficiently elements which have close electronical structures and therefore similar properties but different values.

In the literature, the separative precipitation of transition metal ions has also been intensively studied by usual methods. Generally, the balance can be shifted toward a precipitation reaction by pH variations or/and the presence of reactive compounds. Thus, it is shown that aluminum, cobalt and nickel can be recovered from spent batteries by neutralization [10,16]. It is also well known that nickel can be precipitated by dimethylglyoxime [16,18] and the cobalt by ammonium oxalate [11]. Nickel and cobalt can also be separated using sodium sulfide [20], cobalt sulfide [11], ozone, Caro's acid or chlorine [22]. But these reagents are expensive and often hazardous. This work is focused on the selective recovery of nickel and cobalt from a cathode material by a selective precipitation. According to the literature, such a recycling process has not been addressed yet from a NCA material. Moreover, the previous works dealing with the separation between nickel and cobalt are based either on a liquid/liquid extraction process [10,15,19,22] for the metal purification or on the use of an organic extracting molecule for a selective precipitation of nickel from solutions presenting a very different Ni/Co ratio that studied in the present work [16,18].

## 2. Experimental procedure

### 2.1. Material and reagents

In the present study, NCA material,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , supplied by Toda Kogyo is investigated. At first, a chemical analysis of the material is performed by an Induced Coupled Plasma Optical Emission Spectrometer (Agilent Technologies 700 Series ICP-OES) with a complete dissolution in acid (70 (vol.%) of  $\text{HNO}_3$  and 30 (vol.%) of  $\text{HCl}$ ) by a microwave digestion system (Multiwave 3000, Perkin Elmer, Anton Paar).

The particles mean size of NCA powder is  $7 \mu\text{m}$  and the specific surface area measured by BET method is  $0.41 \text{ m}^2 \text{ g}^{-1}$ .

Chemical reactants used for experiments are reagent grade reactants supplied by Sigma Aldrich.

### 2.2. Material leaching and metals separation by precipitation

At first, experiments are conducted to determine the most efficient leaching conditions by studying the acid nature (hydrochloric, sulfuric and nitric acid), the leaching time (3 and 18 h), the concentration (1, 2, 3 and  $4 \text{ mol L}^{-1}$ ) and the temperature (25 and 90 °C), with the solid to liquid (S/L) ratio fixed at 5% (w/v). The cathode material is leached in a 100 mL one neck glass reactor placed into an oil bath to control the reaction temperature. The solution is stirred at 350 rpm and a vapor condenser is used to reduce the water and acid evaporation.

After leaching, the unleached material is filtered with paper filter (VWR Folded qualitative filter paper, 313, particle retention 5–8  $\mu\text{m}$ ), and washed with 50 mL of distilled water. The concentrations of Li, Ni, Co and Al in the leaching liquor are measured to compute the leaching efficiency by chemical analysis performed with ICP-OES (Agilent Technologies 700 Series ICP-OES). The standard deviation of chemical analysis is measured for all considered elements at  $0.02 \text{ g L}^{-1}$ .

A pH-meter (PHM220 Lab pH Meter MeterLab) is used to control pH during metals extraction process. The filtration and washing of precipitates and the chemical analysis of solutions are performed as described in the leaching process. The quantities of precipitated metals are deduced from the analysis of ions concentrations remaining in solution.

### 2.3. Purity analysis of recovered materials

A purity analysis of recovered materials is conducted by Inductively Coupled Plasma – Optical Emission Spectrometer, after dissolving all precipitates in  $4 \text{ mol L}^{-1}$  hydrochloric acid at room temperature and diluting them in an appropriate concentration with distilled water.

## 3. Results and discussion

### 3.1. Leaching process

The process of corrosion has both thermodynamic as well as kinetic implication. In the case of NCA material, the thermodynamic data from the literature allow to predict the dissolution of nickel, cobalt and aluminum in acidic media [26]. However, on a kinetic point of view, the leaching efficiency results from the energy barrier arising in a rate-determining step that controls the mechanism of corrosion. Thus, in order to evaluate the highest efficient conditions for material leaching, experiments have to be conducted by studying the effect of parameters such as acid nature, concentration, temperature and leaching time with a constant solid to liquid ratio (set at 5% (w/v)).

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