

# Mechanochemical recovery of Co and Li from LCO cathode of lithium-ion battery

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## Abstract

Increasing demand for lithium-ion batteries (LIBs) that serve as power source for diverse electronic devices, electrical propulsion systems and other applications, calls for economical and environmentally benign recycling of spent LIBs and recovery of critical elements such as Co and Li from rapidly growing volumes of battery wastes. The presented study explores mechanochemical extraction of Co and Li from lithium cobaltate ( $\text{LiCoO}_2$ ), which serves as cathode material in commercial LIBs. Our investigation reveals that solvent-free mechanochemical processing can successfully convert pure, reagent grade  $\text{LiCoO}_2$  into metallic Co and Li-derivatives that are suitable for the further recovery of Li. We also show that the proposed approach can be successfully applied to reclaiming these critical elements from commercial LIBs. Due to its magnetic nature, metallic Co is easy to separate from non-magnetic components of mechanochemically generated powder mixtures using an appropriate magnetic separation technique Li can be reclaimed as  $\text{Li}_2\text{CO}_3$  after an additional liquid-phase processing. The recovery rates achieved during our experiments with pure  $\text{LiCoO}_2$  are ~ 90 % for Co and ~ 70 % for Li.

## 1. Introduction

Exponentially growing use of Li-ion batteries (LIBs) in portable electronics, vehicle propulsion and other energy storage and distribution applications boosts the demand for Li and Co that recently became subject to supply risks, i.e. critical elements [1]. Several different LIB designs are present in the market today. In the majority of cases, graphite is used as working element of battery anodes [2-4], while LIB cathodes utilize  $\text{LiCoO}_2$  (Lithium Cobalt Oxide, LCO) [5, 6],  $\text{Li}(\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y})\text{O}_2$  (Lithium Nickel Cobalt Aluminum Oxide, NCA) [7],  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$  (Lithium Nickel Manganese Cobalt Oxide, NMC), [8] and several other complex oxides and phosphates [9, 10] as active ingredients. Raising volumes of the LIBs production bring about considerable ecological risks and health hazards, which are associated with disposal of used batteries in landfills that is accompanied by spontaneous leaching of Co into the environment [11-13]. At the same time, environmentally benign and economical recycling of LIBs remains technologically challenging and requires further improvements [14].

Several different approaches to recycle LIBs, including pyrometallurgical, hydrometallurgical and biohydrometallurgical methods are known. They usually comprise of several common steps that include,

- (1) initial physical processing, i.e. battery discharge, disassembly and electrode separation;
- (2) mechanical processing by shredding, crushing, grinding and screening;
- (3) chemical conversion;
- (4) separation, and
- (5) purification of the desired elements using appropriate chemical procedures.

In some cases, pyrometallurgical protocols bypass the first two processing steps, and spent LIBs are directly subjected to high-temperature smelting and oxidation that produce polymetallic slags suitable for further reworking. While relatively simple in execution, pyrometallurgical methods cannot avoid inadvertent losses of the valuable elements, produce hazardous gaseous and liquid wastes, and have high energy consumption rates as another disadvantage [15-17].

Hydrometallurgical processes are based on chemical dismantling of spent LIB electrodes using strong acids or bases [18-23]. They are often energy efficient and generate limited amounts of hazardous gases, offer high metal recovery rates and reasonable purity of the reclaimed products. However, hydrometallurgy requires corrosive reagents and produces highly acidic liquid wastes. This, coupled with high cost of battery disassembly and initial processing, limits economic value of hydrometallurgical techniques.

While less hazardous than pyro- or hydrometallurgical approaches, bio-hydrometallurgical recycling suffers from very extensive processing times and faces challenges associated with culture incubation that requires strict pH and temperature control [24-26].

Recent *in-situ* studies of fatigue in commercial 18650-type cells revealed that loss of the active Li in both cathode and anode as well as microstructural changes in the electrodes are responsible for the battery degradation [27]. They also showed that the active component of the battery cathode,  $\text{LiCoO}_2$ , retains its chemical nature also in the spent LIB cathodes. Therefore, pure  $\text{LiCoO}_2$  can serve as representative model for LIB recycling development.

Here we present the results of our investigation into mechanochemical recovery of Co and Li from  $\text{LiCoO}_2$ , which is used as cathode material in commercial LIBs. The developed method integrates the first three steps of the conventional recycling workflow, i.e. disassembly, initial processing and chemical conversion, into a single mechanochemical step which increases efficiency, fosters excellent environmental sustainability and holds potential for reducing overall costs of LIB recycling.

## **2. Experimental**

### *2.1 Materials*

$\text{LiCoO}_2$  (97 wt. %), Al - 325 mesh powder (99.5 wt. %) and Ca metal (99.5 wt. %) were purchased from Alfa Aesar. Li (metal granules, 99 wt. %) was acquired from Sigma-Aldrich and  $\text{Na}_2\text{CO}_3$  (99.9 wt. %) was obtained from Fisher Chemical. Aluminum foil (Reynolds Wrap brand) served as a source of Al in selected

experiments. All materials were used as received. The battery cathode used in our studies was extracted from a commercial Li-ion battery cell of a18650-type.

## 2.2 Experimental procedure

*a) Mechanochemical experiments:* About 2g of a mixture of starting materials are combined in an appropriate molar ratio and ball milled for 1-3 hours in a 65 ml hardened-steel vial with 20 g of steel balls using SPEX 8000 shaker mill. While loading of Al and  $\text{LiCoO}_2$  can be performed in air,  $\text{LiCoO}_2/\text{Li}$  and  $\text{LiCoO}_2/\text{Ca}$  mixtures should be prepared and processed under inert gas atmosphere such as high-purity argon that was used in this study. Handling of the processed samples is also carried out in air or under argon as appropriate.

*b) Cobalt extraction:* As milled samples are combined with deionized (DI) water and stirred for a few minutes in air. Due to air-sensitivity of some milled materials, they should be quenched with small amount of methanol in a glove box prior to the water treatment. The magnetic phase is removed from the aqueous slurries using a strong permanent magnet. Non-magnetic components and the liquid fractions of the slurries are set aside for the further processing. Next, the magnetic materials are dispersed in DI water and the magnetic separation step is repeated. Subsequently, the magnetic products are quickly rinsed with a 3 % hydrochloric acid (HCl) and washed with DI water to remove traces of HCl. For the characterization purposes, obtained magnetic materials can be annealed at 900°C for 36 hours in a quartz tube sealed in vacuum.

In the experiments involving commercial LIB cathodes, traces of the polymer binder and other organic contaminants were removed from the magnetic powder by sonication in acetone using a Buehler Ultramet sonic cleaner.

*c) Lithium extraction:* All liquid materials produced during the magnetic separation step are combined and filtered through a paper filter. The solution obtained is further concentrated by water evaporation, and

combined with an aqueous 1M solution of  $\text{Na}_2\text{CO}_3$ , then stirred for 1h at room temperature and filtered to produce  $\text{Li}_2\text{CO}_3$  that is dried at  $90^\circ\text{C}$  in air.

Alternatively, water from the filtrate can be completely evaporated and the residue formed exposed to  $\text{CO}_2$  in ambient air, which produces  $\text{Li}_2\text{CO}_3$  that after washing with DI water is dried at  $90^\circ\text{C}$  in air.

### *2.3. Materials characterization*

*2.3.1. X-ray powder diffraction (XRD):* Phase analysis of the reaction products was carried out using a PANalytical X'Pert Pro powder diffractometer at room temperature. The XRD measurements were performed using Cu K $\alpha$ 1 radiation with a  $0.02^\circ$   $2\theta$  step between 10 and  $80^\circ$   $2\theta$  degrees. As needed, XRD samples were prepared in a glove box, and the sample holder was covered by a polyimide (Kapton) film that protected the studied material from ambient atmosphere.

*Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) measurements:*

SEM investigations were performed in a FEI Teneo field emission scanning electron microscope and EDS spectra are collected using an Aztec EDS module produced by Oxford Instruments.

## **3. Results and discussion**

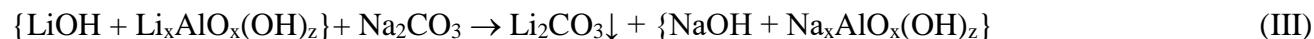
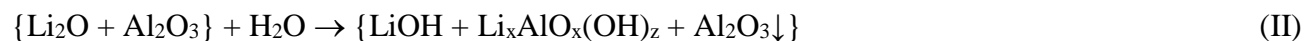
### *3.1. Recovery of Co and Li from $\text{LiCoO}_2$ .*

Mechanochemical reduction of pure  $\text{LiCoO}_2$  using Al, Li and Ca metals as reducing agents produces poorly crystalline powders comprising of a magnetic Co-containing phase and Li-derivatives that can be further dissolved in water and converted into  $\text{Li}_2\text{CO}_3$  by reacting them with an aqueous  $\text{Na}_2\text{CO}_3$  solution or  $\text{CO}_2$  from ambient air. The reducing agents transform into nonmagnetic oxide/hydroxide compounds. Additional heat treatment improves overall crystallinity of the magnetic product, which enables its unambiguous identification using XRD.

#### *3.1.1. Recovery of Co and Li using Al as reducing agent.*

Ball milling of an equimolar mixture of pure LiCoO<sub>2</sub> and Al powder produces a largely XRD amorphous material, in which metallic Co can be vaguely distinguished by the presence of broad reflections at 44.5 and ~47.4 degrees of 2θ (Fig. 1a, b). Heat treatment of the magnetic material that is obtained after the dissolution of *as-milled* sample in water and the subsequent magnetic separation step, improves sample's crystallinity, so that the metallic Co with a cubic (fcc) structure can be clearly identified (Fig. 1c) as reaction product that is recovered with 90% yield. The presence of additional reflections on XRD pattern (at around 23° on Fig. 1b) is attributed to LiAl<sub>2</sub>(OH)<sub>7</sub>·xH<sub>2</sub>O that forms during the washing process and adsorbs on the product's surface.

Combining *as-milled* powder with water transfers Li-containing compounds into the aqueous phase. Once the magnetic material is removed and the slurry left behind is filtered, the resulting solution is treated with the aqueous 1M solution of Na<sub>2</sub>CO<sub>3</sub> to precipitate out a white solid. After filtering and drying at 90°C in air, the solid produces the XRD pattern characteristic for Li<sub>2</sub>CO<sub>3</sub> (Fig. 1d) [28]. The obtained material accounts for 76 % of the entire Li content in the starting LiCoO<sub>2</sub>. The mechanochemical conversion of LiCoO<sub>2</sub> into metallic Co and Li<sub>2</sub>CO<sub>3</sub> using Al as reducing agent can be described by Eq. I – III, where feasible reaction intermediates are given in parentheses.



### 3.1.2. Recovery of Co and Li using the Li and Ca as reducing agent.

Recovery of Co or Li from the pure LiCoO<sub>2</sub> using metallic Li and Ca as reducing agents follows the same workflow as described for the reduction of LiCoO<sub>2</sub> with Al. In a typical process, LiCoO<sub>2</sub> and Li or Ca metals are combined in 1:3 or 1:1.5 molar ratios respectively, and are ball milled in a silicon nitride vial using Spex

8000M shaker mill. All experiments involving Li and Ca are performed under argon as protective atmosphere.

The XRD analysis of the *as-milled* LiCoO<sub>2</sub> / Li mixture indicates its poor crystallinity. However, Bragg reflections from Li<sub>2</sub>O [29] and hexagonal (hcp) Co (Fig. 2a) is clearly distinguished. The reaction can be described as:



After treating ball milled powders with water and the subsequent magnetic separation steps, poorly crystalline Co is isolated (Fig. 2b) [30]. The solution formed after the separation of Co is filtered using filter paper, and Li<sub>2</sub>CO<sub>3</sub> is precipitated using 1M aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. As in the previous case, XRD confirms the chemical identity of Li<sub>2</sub>CO<sub>3</sub> (Fig. 2c). The recovery rate of Li, calculated based on its content in LiCoO<sub>2</sub> and assuming the full recovery of Li used as the reducing agent, is estimated at ~72 %, while Co is recovered with 88 % efficiency.

When Ca is used as the reducing agent, the XRD pattern of the *as-milled* reaction mixture shows only broad Bragg reflections that correspond to CaO. The metallic Co and Li-containing phases are hardly distinguishable in the pattern (Fig. 3a). However, the magnetic materials obtained after the magnetic separation produces Bragg reflections that can be identified as hcp Co. (Fig. 3b). The recovery rate of Co is estimated to be ~ 84 %.

The reduction LiCoO<sub>2</sub> with Ca can be generally described as:



### 3.2. Recovery of Co and Li from commercial Li-ion battery cell using Al as reducing element.

A 4 g fragment of a commercial LIB cathode consisting of an Al current collector covered with LiCoO<sub>2</sub> using polyvinylidene fluoride (PVDF) as binder has been cut in smaller pieces and ball milled with

additional 0.5 g of an Al foil for 3h. Since Al is already present in the cathode, it also participates in the mechanochemical reduction reaction and the amount of Al-foil that has to be added to the reaction mixture is greatly reduced. The presence of PVDF reduces contacts between  $\text{LiCoO}_2$  and Al. Therefore, a prolonged milling may be required in this case. Although the formation of metallic Co is already detectable after 2 h of processing (Fig. 4a), the materials have been milled for an additional two hours to ensure the completion of the mechanochemical reaction. After dispersing in water and magnetic separation, the magnetic material (fcc Co, Fig. 4b) has been additionally sonicated in water for 5 minutes to remove traces of PVDF.

SEM-EDS analysis of the powder ball milled for 2h confirms the presence of metallic Co in the magnetic sample (Fig. 5), which also agrees with the XRD analysis (Fig. 4b). The Co-rich particles, which are visible on SEM image as bright spots, are homogeneously distributed throughout the milled product. One of such particles (shown in Fig. 5b (top)) consists primarily from cobalt. Small amounts of Mn and Ni in the material detected are also present in the original commercial cathode and transfer from there. Minor amounts of Al, O and C that perhaps originate from the reducing agent and the binder are detected as well. Unfortunately, it is not possible to accurately estimate the Co- and Li recovery rates from the commercial LIB cathode since its exact makeup is not provided by the manufacturer. In absolute values, the recycling of 4 g of the cathode material produces 0.6 g of metallic Co and 0.3 g of  $\text{Li}_2\text{CO}_3$  (Figs. 4b and 4c). The weight ratio of the recovered Co to  $\text{Li}_2\text{CO}_3$  is about 2:1, which agrees well with that observed for re-processing of pure  $\text{LiCoO}_2$  (2:1.2).

Reclaiming of Co and Li from the commercial LIB cathode is schematically summarized in Figure 6.

The mechanochemical process is simple for execution, provides excellent recovery rates and appears to be scalable using conventional industrial equipment. Therefore, after an additional optimization this method can provide an excellent alternative to other Li and Co recycling techniques that are present in the market.

## Conclusions



Mechanochemical recovery of Li and Co from pure  $\text{LiCoO}_2$  and commercial LIB cathode using Al, Li and Ca as reducing agents has been successfully demonstrated. The developed process is simple, fast, energy efficient, and does not involve or produce highly corrosive liquid wastes or toxic gases, thus, offering clear advantages over other known LIB recycling techniques.

### **Acknowledgement.**

The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.

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## Figure captions

**Figure 1.** XRD patterns of the mechanochemically processed equimolar (1:1) mixture of  $\text{LiCoO}_2$  and Al: a) *as-milled* material; b) the sample obtained after the magnetic separation step; c) the magnetic phase heat-treated at  $900^\circ\text{C}$  for 36 hours; d)  $\text{Li}_2\text{CO}_3$  recovered from the aqueous solution. XRD patterns of starting materials  $\text{LiCoO}_2$  and Al are included for comparison.

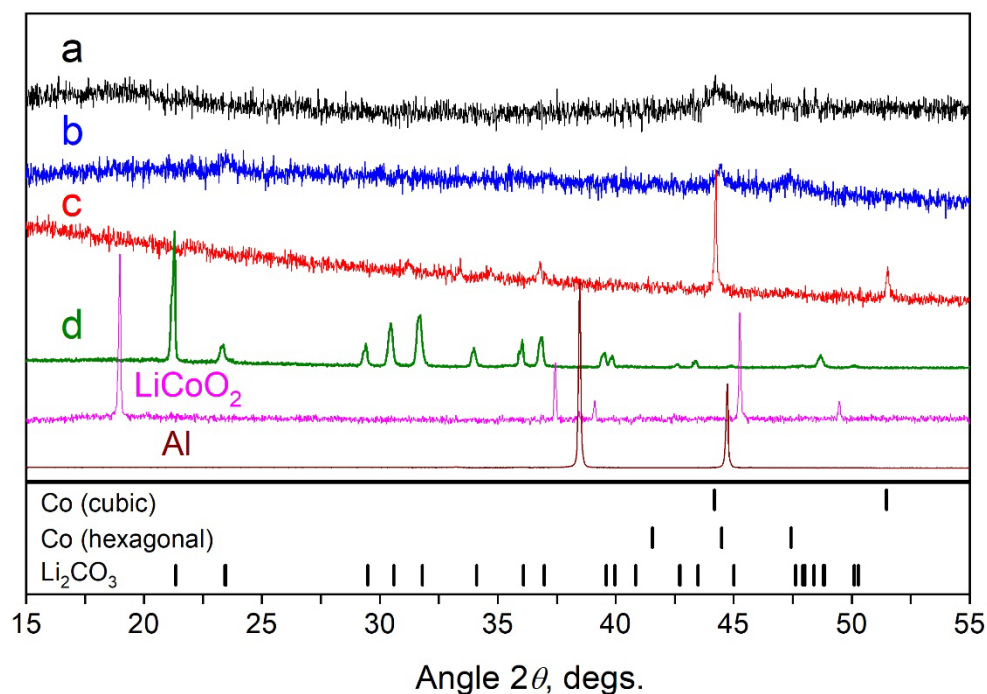
**Figure 2.** XRD patterns of the 1:3 molar mixture of  $\text{LiCoO}_2$  and Li: a) - *as-milled* material; b) – the solid after magnetic separation step; c) –  $\text{Li}_2\text{CO}_3$  recovered.

**Figure 3.** XRD patterns of the 1:1.5 molar mixture of  $\text{LiCoO}_2$  and Ca: a) *as-milled* material; b) the material obtained after the magnetic separation step.

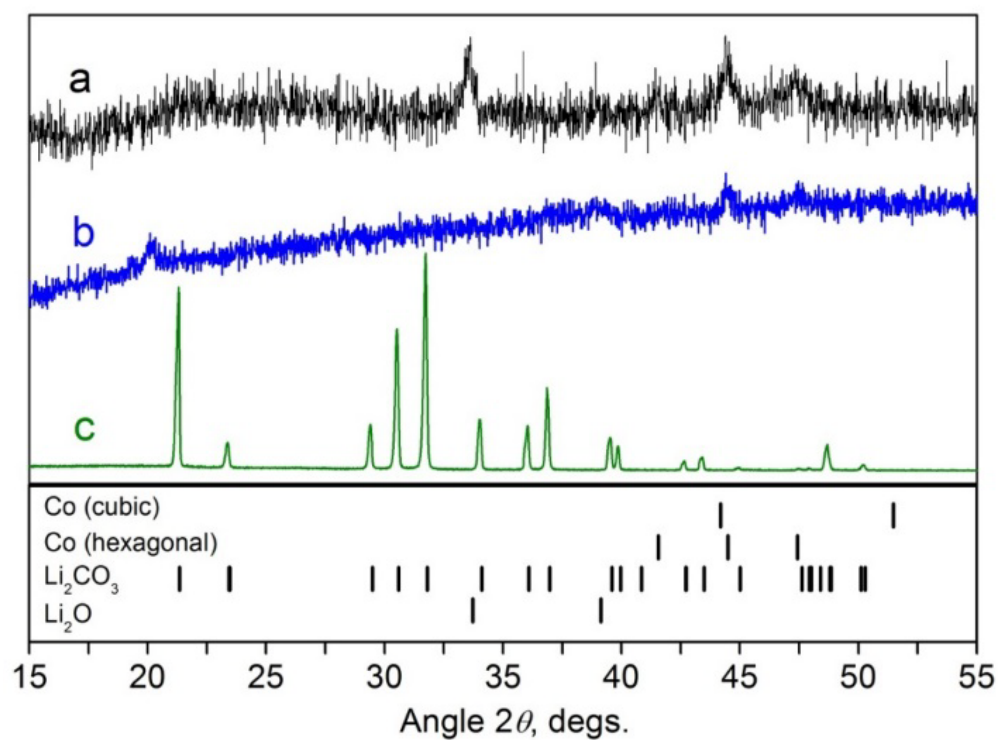
**Figure 4.** XRD patterns of a commercial 18650-type LIB cell: a) cell cathode, ball milled with Al for 2 hours; b) material after magnetic separation; c)  $\text{Li}_2\text{CO}_3$  recovered.

**Figure 5.** a) SEM image of a LIB cathode ball milled with Al for 2 hours. The area marked by the rectangle represents zooming part; b) Zoomed area (top) and EDS spectra (bottom) collected from the area of the particle selected by rectangle. Concentrations of obtained elements presented in atomic %.

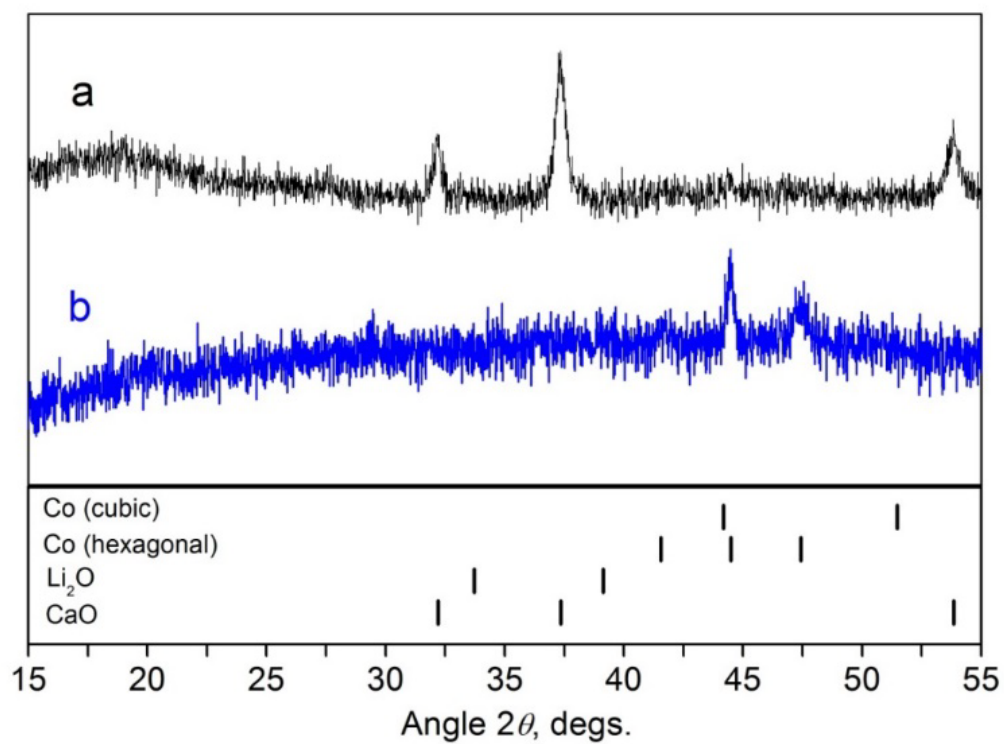
**Figure 6.** The process of mechanochemical/chemical recovery of Li and Co from the Li-ion cell cathode.



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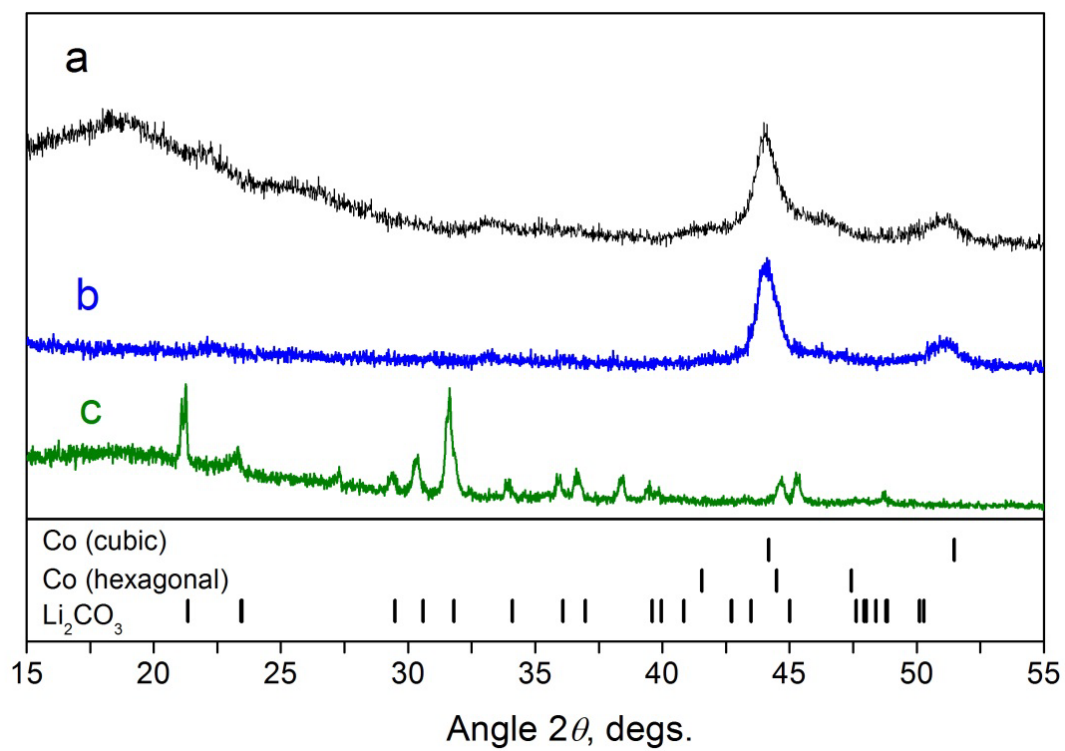


**Figure 2.** XRD patterns of the 1:3 molar mixture of  $\text{LiCoO}_2$  and Li: a) - *as-milled* material; b) – the solid after magnetic separation step; c) –  $\text{Li}_2\text{CO}_3$  recovered.

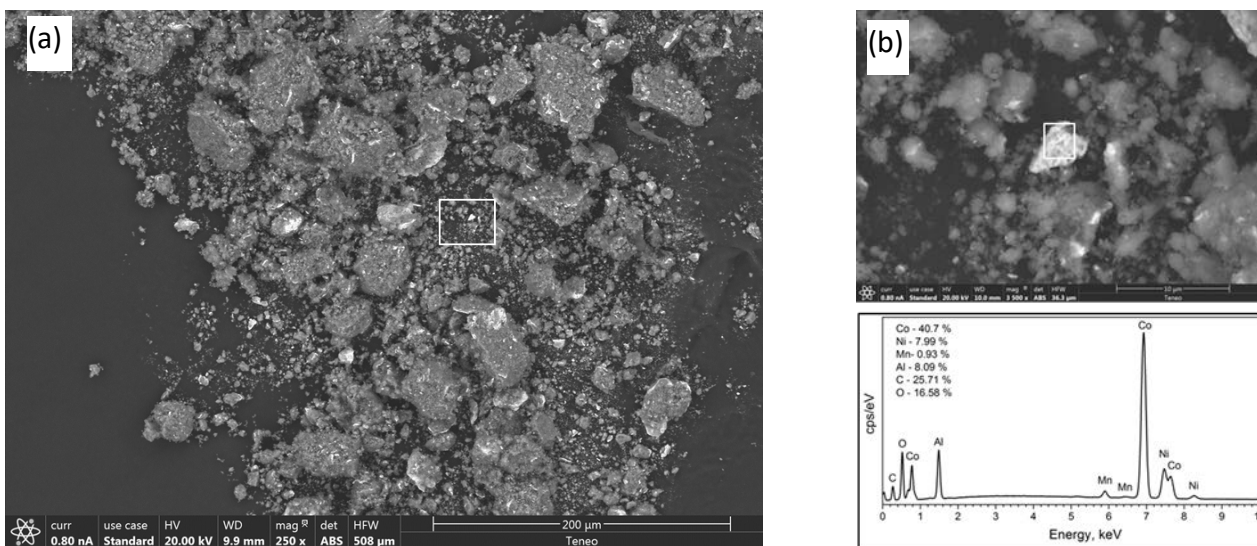


**Figure 3.** XRD patterns of the 1:1.5 molar mixture of  $\text{LiCoO}_2$  and Ca: a) *as-milled* material; b) the material obtained after the magnetic separation step.





**Figure 4.** XRD patterns of a commercial 18650-type LIB cell: a) cell cathode, ball milled with Al for 2 hours; b) material after magnetic separation; c)  $\text{Li}_2\text{CO}_3$  recovered.



**Figure 5.** a) SEM image of a LIB cathode ball milled with Al for 2 hours. The area marked by the rectangle represents zooming part; b) Zoomed area (top) and EDS spectra (bottom) collected from the area of the particle selected by rectangle. Concentrations of obtained elements presented in atomic %.



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