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Cite as: AIP Conference Proceedings **2257**, 020007 (2020); <https://doi.org/10.1063/5.0023663>  
Published Online: 03 September 2020

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# Production of Nanostructured Electrodes from Spent Lithium Ion Batteries and Their Application in New Energy Storage Devices

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**Abstract.** The present work is aimed at demonstrating the potentiality of lithium ion batteries recycling through the production of high added value nanostructured material. Nanostructured electrodic materials were synthesized starting from waste lithium ion batteries (LIBs). Firstly, the metals contained in the electrodic powder of exhausted LIBs were extracted by acid-reducing leaching. After filtration, metals rich solution was separated from graphite. Nanoparticles-based electrodes were produced by controlled precipitation and subsequent calcination of metals in order to obtain nanoparticles of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , one of the most employed LIBs cathodic material. Cathodic materials synthesized starting from waste LIBs and from high grade synthetic reagents were compared after their characterization by SEM, EDX and XRD. The electrochemical performance of the electrodes was evaluated by galvanostatic cycling the electrodes in a lithium half-cell. Remarkably, the electrochemical performances obtained with the electrodes produced by the recovery of metals are close to those recorded using electrodes produced by synthetic reagents.

## INTRODUCTION

The increasing market of mobile electronic devices and electric vehicles, together with the gradual replacement of fossil fuels with renewable sources, requires highly performing energy storage systems. Li-ion batteries (LIBs) are currently the system of choice for these latter applications due to their fast charge-discharge rate, high power and energy density [1]. On the other hand, LIBs have a limited life thus huge amounts of spent LIBs are and will be produced. The recycling of spent LIBs becomes fundamental to prevent the dispersion into the environment of hazardous elements and, more importantly, to sustain the demand of materials needed to produce new energy storage devices [2]. Batteries electrode materials include strategic or critical raw materials such as graphite, cobalt, nickel and manganese and need to be recovered and recycled into the batteries manufacturing chain [3].

The major obstacles encountered with the extensive LIBs recycling are the high cost and negative environmental impact of the employed processes. Currently pyrometallurgical processes are used for the recovery of nickel and cobalt from LIBs, but some of the products like lithium, aluminum and graphite are involved in secondary reactions or lost in the smelting slag. In this perspective, LIBs recycling exploiting hydrometallurgical processes seems to be a promising alternative [4]. This latter approach is characterized by lower investment costs, emissions and potentially all the materials composing LIBs can be recovered. On the other hand, the complex and variable chemistry of the LIBs cathodes requires several separation stages for the obtainment of metal salts with the purity grade required by the market and generally involve solvent extractions for the separation of Ni and Co. All the purification and separation stages produce large amount of liquid and solid wastes that must be disposed and, in addition, require energy and reactants that generally hinder the economic feasibility of the hydrometallurgical processes [5]. In this

work, a different approach for the recovery of metals contained in waste LIBs was followed. Metals extraction was reached by a consolidated acid-reducing leaching of the electrodic powder [6]. The obtained leach liquor composed mainly by cobalt, nickel and manganese, was directly employed for the synthesis of new cathodic material avoiding all the separation/purification steps usually employed for the recovery of cobalt, nickel and manganese as high-grade salts. The stoichiometry of cobalt, nickel and manganese in the leach liquor was adjusted in order to obtain, after precipitation, the mixed metals hydroxide ( $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ ) precursor. Finally, the cathodic material  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) was obtained by a solid-state reaction between the mixed hydroxide and lithium carbonate at high temperature.

## MATERIALS AND METHODS

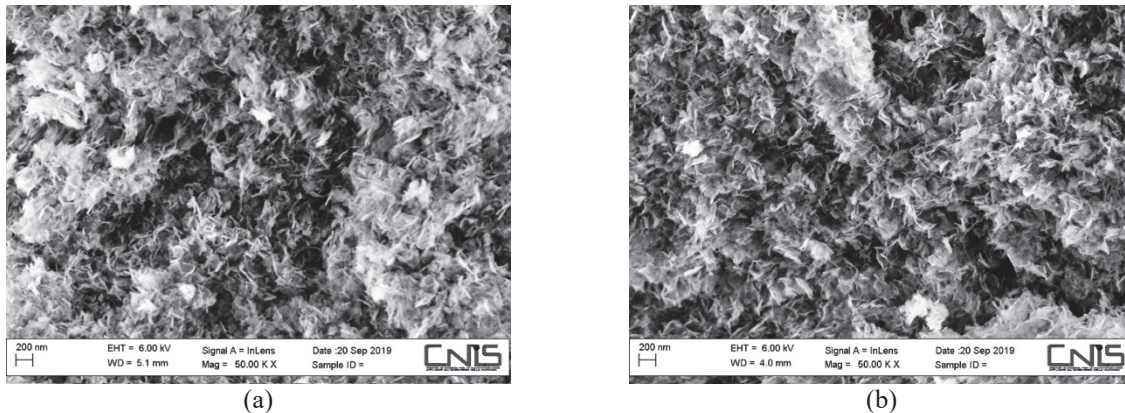
### Synthesis of NMC from waste LIB

Exhausted LIBs were collected and crushed by an Italian waste disposal company (SEVal s.r.l.). The resulting crushed material was sieved allowing the separation of the electrodic powder, composed by graphite and cathodic materials, from current collector (Al, Cu), plastics, papers and steel. The extraction of metals contained in the electrodic powder was performed by acid-reducing leaching using sulfuric acid and hydrogen peroxide as oxidant and reducing agent, respectively. Electrodic powder was leached with  $\text{H}_2\text{SO}_4$  1.5 M in a jacketed glass reactor at controlled temperature of 85 °C. A solid to liquid ratio of 1:10 was employed and the leaching was carried out under stirring for 3 h. These leaching conditions allow to obtain a metals extraction yield up to 96% [6, 7]. Following leaching, a filtration was performed to separate the liquid solution from the residual carbon fraction. The extracted metals were then recovered by two sequential precipitations. The first precipitation involves the increase of leach liquor pH to 6.5 in order to selectively precipitate copper, iron and aluminium impurity. After filtration, the residual cobalt, nickel, manganese rich solution was analyzed by atomic absorption spectroscopy. The molar concentration of the metals was adjusted with commercial Ni, Co and Mn salts in order to obtain a molar ratio of 1:1:1 among the metals.  $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$  precursor was precipitated increasing the pH of solution from 6.5 to 11 by the controlled addition of NaOH and  $\text{NH}_4\text{O}$ . Finally,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  was obtained by calcination of hydroxide precursor at 900°C with  $\text{Li}_2\text{CO}_3$ . The above reported synthesis procedure was repeated starting from a synthetic solution prepared dissolving commercial Ni, Co and Mn salts. The electrochemical performances of the as obtained synthetic NMC were compared with those of the recovered NMC.

### Chemical and electrochemical characterizations

Field emission scanning electron microscopy (SEM, Zeiss Auriga) was employed to characterize the morphology of synthesized  $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . The chemical composition of the cathodic materials was determined by energy dispersive X-ray spectroscopy (EDX, Bruker QUANTAX 123 eV). Powder X-ray diffraction (XRD, Rigaku, D-Max Ultima) employing Cu  $K\alpha$  radiation was used to identify the crystalline phase of the prepared materials.

Electrochemical characterizations were carried out using electrodes prepared by casting a dispersion of the cathodic materials on aluminium foil current collector. The dispersion was composed by 10% of carbon conducting agent (Super P, Timcal), 10% binder (PVDF Sigma-Aldrich) and 80% of synthesized cathodic materials in N-methyl pyrrolidone (NMP, Sigma-Aldrich). The resulting film was cut into disks of 10 mm diameter and dried. The prepared cathodes were assembled in a two electrode R2032 coin-type cells where lithium metal disk was used as negative electrode. The employed electrolyte was  $\text{LiPF}_6$  1 M in an Ethylene Carbonate - Dimethyl Carbonate, 1:1 v:v solution (LP30). Each cell was assembled in an argon-filled glove box with a content of  $\text{O}_2$  and  $\text{H}_2\text{O}$  less than 1 ppm. Galvanostatic cycling tests at a current rate of C/10 ( $1\text{C}=160\text{mAhg}^{-1}$ ) were carried out with a battery tester (Maccor series 4000) using a voltage range between 4.8–2.3 V.



**FIGURE 1.** SEM images of the mixed hydroxide  $\text{Co}_{0.1/3}\text{Ni}_{0.1/3}\text{Mn}_{0.1/3}(\text{OH})_2$  obtained after precipitation of a leaching solution (a) and a synthetic solution (b)

## RESULTS AND DISCUSSION

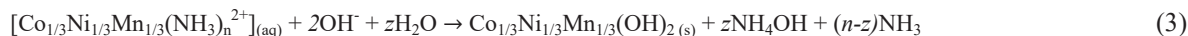
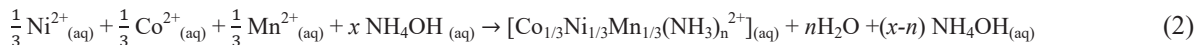
The extraction of metals from electrodic powder needs acid-reducing conditions in order to reduce the targeted metals from higher oxidation states ( $\text{Co}^{3+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Mn}^{3+}$ ) to water soluble species. Hydrogen peroxide is largely employed as reducing agent for the extraction of metals from LIBs electrodic powder due to the high extraction rate that can be attained. The extraction of metals involves the following reaction[6]:



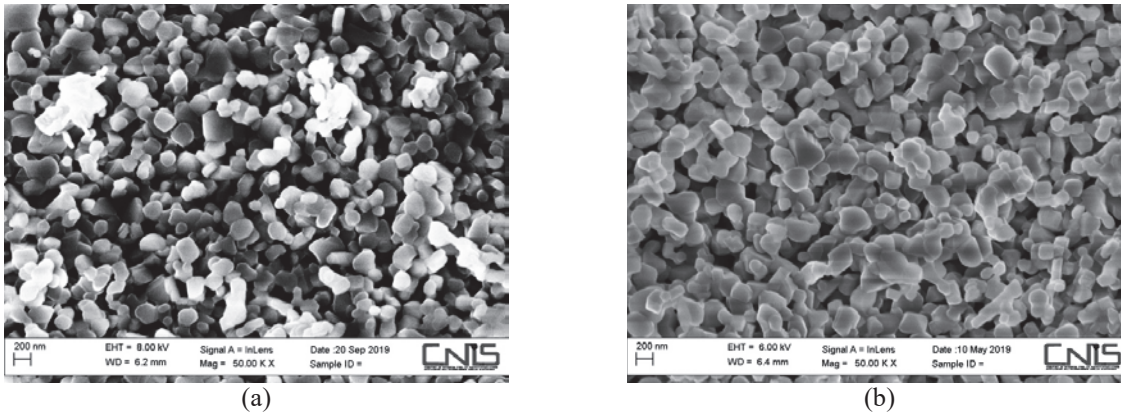
The above reported reaction considers  $\text{LiCoO}_2$  as reagent due to its major contents on the currently collected exhausted LIBs. In facts,  $\text{LiCoO}_2$  is characterized by excellent electrochemical performances and was the most employed cathodic materials for the manufacturing of LIBs in the last years. Nowadays, in order to reduce the cobalt consumption, other cathodic materials were developed introducing different amount of nickel and manganese on the cathode structure ( $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ) [8]. Currently, collected end of life batteries including these cathodic materials still represent a small fraction of the total disposed LIBs. This leads to a minor presence of nickel and manganese on the electrodic powder that is recovered from waste LIBs.

The resulting leachate undergone a first precipitation step at pH 6.5 where Cu, Fe and Al impurities are selectively removed from the solution. Since cobalt is the more concentrated metal in the purified leachate, nickel and manganese sulfate were added in order to obtain an equal molar concentration of all the metals.

The increase of pH from 6.5 to 11 of the purified solution allowed the precipitation of the mixed metals hydroxide  $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ . Precipitation of hydroxide was carried out adding  $\text{NH}_4\text{OH}$  as a chelating agent to control particle size and tap density. It is well known that  $\text{NH}_4^+$  ions can play a role to promote the formation of precipitated solid with a controlled and homogeneous dimension according to the following reactions[9]:



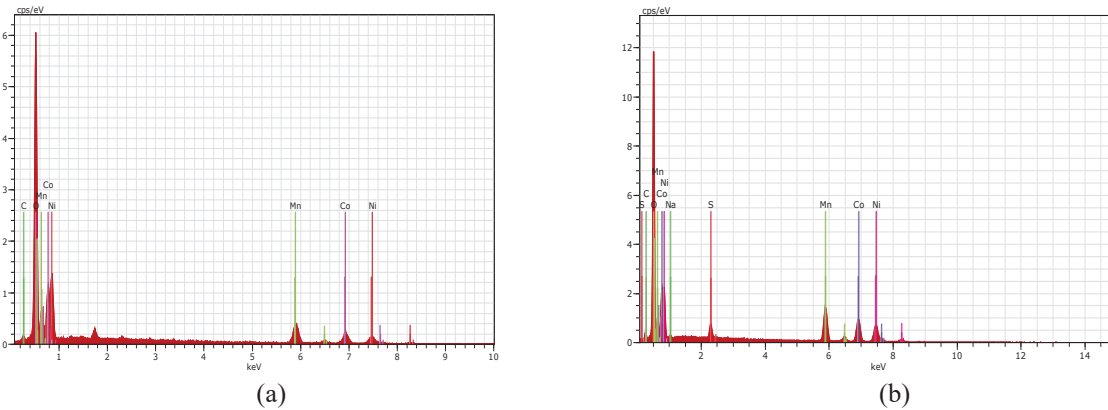
Further, the addition of  $\text{NH}_4\text{OH}$  solution ensures the formation of the mixed hydroxide respect the single metal hydroxide  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Mn}(\text{OH})_2$  that can be formed as impurity phase when the chelating agent is not employed [9, 10].



**FIGURE 2.** SEM images of the  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  obtained after calcination of the hydroxide relative to the leaching solution (a) and the synthetic solution (b)

For comparison, a synthetic solution prepared from commercial Co, Ni, Mn salts was employed for the precipitation of a synthetic mixed hydroxide following the same experimental procedure. Figure 1 shows the SEM images of the mixed hydroxide produced by the leaching and synthetic solution. Homogeneous nanoflakes were found on both the samples and no significant difference can be seen between the synthetic and the recovered hydroxide. The as prepared hydroxides were calcined in air at  $900^\circ\text{C}$  with the appropriate amount of  $\text{Li}_2\text{CO}_3$  for the production of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ .

A little excess of lithium ( $\text{Li}/[\text{Ni} + \text{Co} + \text{Mn}] = 1.10$ ) was added in order to compensate its evaporation during the high temperature calcinations[11]. In Figure 2 SEM images of the resulting  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) were displayed.

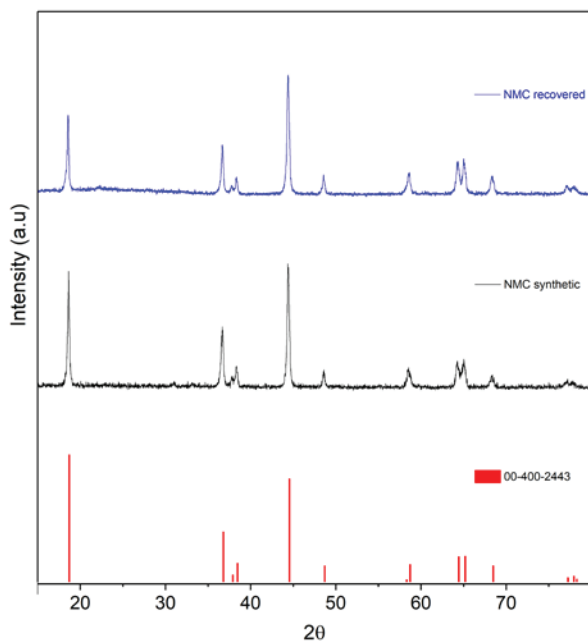


Element	recovered NMC [at.%]	dev.std [at.%]	synthetic NMC [at.%]	dev.std [at.%]
O	66	4	76	5
Ni	10	1	8	1
Mn	12	1	8	0.5
Co	11	1	9	1

(c)

**FIGURE 3.** EDX spectra of the  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  obtained after calcination of the hydroxide relative to the leaching solution (a) and the synthetic solution (b)





**FIGURE 4.** XRD pattern of the recovered and synthetic  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NMC).

As well as for the hydroxides, also the final NMC cathodes obtained recovering the metals from the exhausted LIBs and from the synthetic solution are similar. Nanoparticles with a dimension of about 250 nm were found on both the samples. In order to evaluate the stoichiometry of the produced NMC materials, EDX measurements of the recovered and synthetic NMC were performed. Figure 3-a,b display the recorded EDX spectra for the two samples. A part of carbon coming from the sample support, oxygen, cobalt, nickel and manganese are the main components of the samples. To identify the crystalline phase of the prepared NMC, XRD measurements were performed. The synthesized NMC powders showed the typical layered structure of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  phase (Fig.4)[9]. Remarkably, no other crystalline phases can be found in the synthetic and recovered sample. As can be seen from Fig.4, all the peaks on the experimental spectra match the reference pattern for  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ .

The electrochemical performance of the NMC synthesized from the recovered metals was benchmarked against the NMC produced from the synthetic solution. In Figure 5 were reported the specific capacity values recorded during the galvanostatically cycling of the electrodes. No significative differences were found in the specific capacity values obtained for the synthetic and the recovered NMC. A stable capacity value of  $115 \text{ mAhg}^{-1}$  was attained until the 60<sup>th</sup> cycle. After the 60<sup>th</sup> cycle the capacity of the recovered NMC starts to decrease and following the 80<sup>th</sup> cycle the capacity value drops to about  $90 \text{ mAhg}^{-1}$ . On the other hand, the battery performances of both the synthesized electrodes are lower if the recorded specific capacities are compared with the commercial NMC values ( $150 \text{ mAhg}^{-1}$ ).

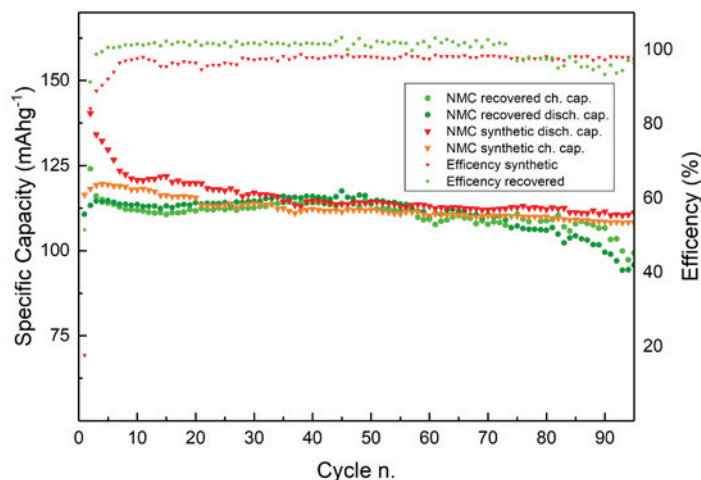


FIGURE 5. Galvanostatic cycling of the NMC electrodes performed at C/10.

## CONCLUSIONS

A simple co-precipitation synthesis route was proposed allowing the simultaneous recovery of Co, Ni and Mn from waste LIBs and the production of new nanostructured cathodic materials. The NMC synthesized from the solution obtained by leaching the waste LIBs was compared with a NMC obtained from a synthetic solution of Co, Ni and Mn. Comparing the synthetic and the recovered NMC, no relevant difference was found in their morphology, composition and crystalline phase. On the other hand, when the electrodes were tested as positive electrode in a half-lithium cell, a difference on the final specific capacities values was found. Particularly, the recovered NMC has shown a drop on the capacity after the 80<sup>th</sup> cycle. Even though, both the NMC electrode were characterized by a specific capacity values ( $115\text{mAhg}^{-1}$ ) lower than expected for this kind of cathodic material ( $150\text{mAhg}^{-1}$ ), the showed results could provide a preliminary idea for the development of an innovative LIBs recycling process.

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