

# Elaboration and Characterization of Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub> Intrinsic and Cu Doped

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**Abstract:** In this work we have synthesized Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub> using sulfates metals Ni, Co and Mn and LiCl salt. The used method is easy and led to yield higher than 75%. Identification and lamellar  $\alpha$ -type NaFeO<sub>2</sub> of the composite synthesized were demonstrated by X-ray diffraction and FTIR spectroscopy. We demonstrated that the product is pure and its crystallinity changes according to the parameters of the annealing step. The electronic structure of the compound has been modified by doping with monovalent Copper cation. The results are encouraging and show that the lamellar structure is not altered. We noticed an increase in infill distances that can affect the mobility of lithium cations during the insertion cycles / extraction. Indeed, the charge on the surface of the doped product is -90mV after 60 minutes and that of the undoped compound is -241mV.

**Keywords:** Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) OH<sub>2</sub>, Battery Li-ion, LiCoO<sub>2</sub>,  $\alpha$ -Type Layer NaFeO<sub>2</sub>

## 1. Introduction

In battery technology, researches are persisting continuously to develop new materials that form the electrodes. This continuous effort aims to achieve gains in energy density, capacity, safety, durability and cost while preserving the environment by reducing toxic materials. The lithium-ion batteries, by their properties, are a real achievement for portable apparatus such as computers and phones. The development in this type of battery is summarized in new cathode materials in particular oxides of LiMO<sub>2</sub> structure of transition metals. The LiCoO<sub>2</sub> cobalt oxide is the material that is most currently used but the trend is towards replacing cobalt in order to reduce the cost and toxicity effect of this metal. A series of similar materials whose the composition is Li (Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>) O<sub>2</sub> were synthesized to partially substitute Co with Ni and Mn [1, 2]. The Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub> has attracted much attention with the valence states are Ni<sup>2+</sup>, Co<sup>3+</sup> and Mn<sup>4+</sup>, respectively. The

crystal structure of this material is hexagonal in  $\alpha$ -type layer NaFeO<sub>2</sub> with a group of R-3m space.

Synthesis of Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub> was the subject of several studies. Several methods have been mentioned among those that will be used in industry because of their promising results sol-gel [3-5] method and co-precipitation method [6-8]

In this work, we synthesized the compound Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub> intrinsic and doped with copper by the method of co-precipitation using sulfates of Ni, Co, and Mn. Lithium is added to the precursor (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)(OH)<sub>2</sub> under LiOH form prepared previously. The final material obtained is characterized by the X-ray diffraction and by FTIR spectroscopy. In addition, other electrochemical characterizations were performed to demonstrate the desired properties to a cathode of a lithium battery.

## 2. Results and Discussion

Indexing of XRD diagram peaks of the Figure 1 shows that

this one contains all the peaks that correspond to the composite Li (NiCoMn) O<sub>2</sub> especially two higher peaks (003) and (104) and no additional peak of other products is detected. So it seems that the prepared composite is Li (NiCoMn) O<sub>2</sub>. It seems also that the product is pure and does not contain any other compound particularly LiOH. In addition, it is known that the ratio  $R = I(003) / I(104)$  is used to evaluate the degree of mixing of the Li and Ni cations. Indeed a low ratio ( $R < 1.2$ ) indicates an unordered mixture and ineffective [4, 5]. In addition, the presence of peaks (018), (110) and (006), (012) finely separated, in the XRD diagram, is a character of a well crystallized product in a laminar structure Type  $\alpha$ -NaFeO<sub>2</sub> [11, 12, 13]. In our case, the ratio  $R$  is greater than 1.2 and the two doublets (018), (110) and (006), (012) appear well separated. Figure 4 present XRD powder diffraction of different materials synthesized: the precursor, the composite annealed at 1000°C, the mixture precursor CuCl and the doped composite annealed at different temperatures 700°C, 800°C and 1000°C.

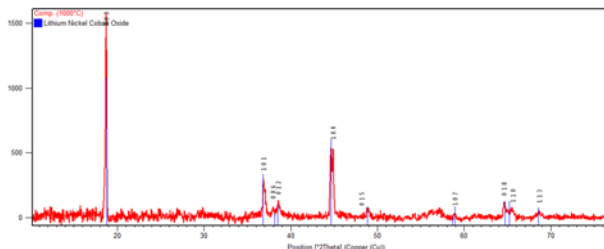


Figure 1. The XRD diffraction of the prepared Li (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) O<sub>2</sub>.

The review of XRD powder diffraction (Fig. 2) shows that the precursor is not fully crystallized and shows the presence of MnO<sub>2</sub> phase. However, the composite annealed at 1000°C has a better crystallinity. On the other hand, the full width at half maximum (FWHM) peaks gives an indication of the change in the crystallite size. After annealing at 700°C and 800°C the composite Li (NiCoMn) O<sub>2</sub> doped gives the same composite and with the same phases but with a slight shift of the peaks. The ratio  $R = I(003) / I(104)$  changes when a doping copper take place, but it is still higher than 1.2. So it seems that Cu doping does not alter the laminar structure of the composite, but the lattice parameters and Li mixing ratio is changed due to the incorporation of copper.

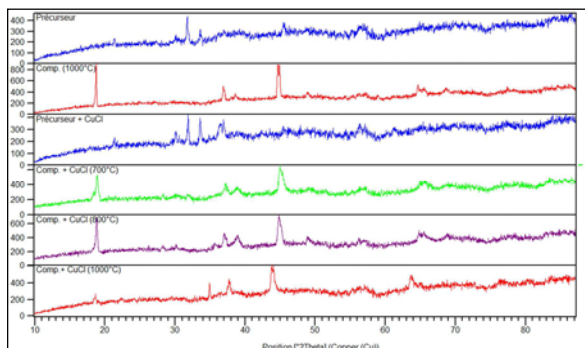
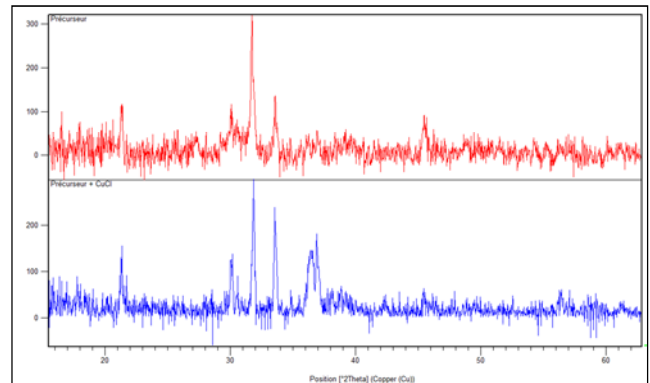


Figure 2. XRD powder diffraction of prepared compounds from top to bottom.

1-Precursor, 2-composite annealed at 1000°C, 3-Precursor+CuCl, 4-Composite+CuCl Annealed at 700°C, 5-Composite+CuCl Annealed at 800°C, 6-Composite+CuCl Annealed at 1000°C

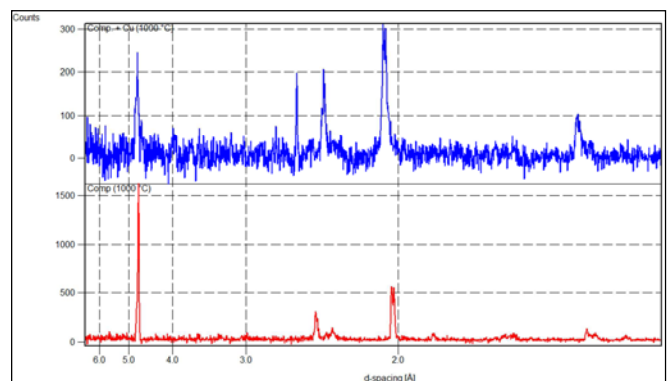
Before annealing the doped precursor, the resulting XRD diffractogram (fig. 2) and (fig. 3) corresponds to LiOH with additional peaks ( $2\theta = 29.68^\circ, 36.68^\circ, 42.6^\circ$ ) which shows the presence of a Cu<sub>2</sub>O phase [14]. With increasing annealing temperature, Cu<sub>2</sub>O oxidizes and becomes progressively CuO justified by the gradual appearance of one peak on the XRD diffractogram at  $2\theta = 39^\circ$  approximately [14].



Top: intrinsic precursor. Bottom: Copper doped precursor

Figure 3. XRD powder diffraction of precursor before annealing ( $2\theta$ ,  $\lambda_{Cu}$ ).

After annealing at 1000°C (fig. 2) and (fig. 4), the peaks corresponding to CuO and Cu<sub>2</sub>O disappear completely and the XRD diffractogram obtained becomes so similar to that of the undoped composite but with a shift of the peaks and lower ratio  $R = I(003) / I(104)$ . Therefore, it is clear that the final product annealed at 1000°C is not a mixture of phases, but a homogeneous product with a single phase where the copper is incorporated into the compound. We can conclude the annealing parameters have a great effect on the final structure of the composite and should be optimized.

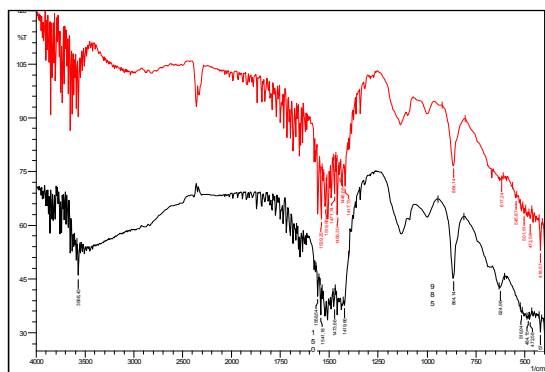


Top: Copper doped Li (NiCoMn) O<sub>2</sub>. Bottom: intrinsic Li (NiCoMn) O<sub>2</sub>

Figure 4. XRD powder diffraction of Li (NiCoMn) O<sub>2</sub> ( $d_{hkl}$ ,  $\lambda_{Cu}$ ).

Figure 5 shows the FTIR spectra of the intrinsic and doped copper compound. A comparative analysis of these spectra with the LiOH shows the presence of weak absorption bands at 1000cm<sup>-1</sup> and 3567cm<sup>-1</sup> indicating that the product probably contains a very small amount of LiOH not react. This low impurity is not detected by the X-ray diffraction, because this one is less sensitive than the analysis by FTIR. The comparison between the spectrum of intrinsic and doped

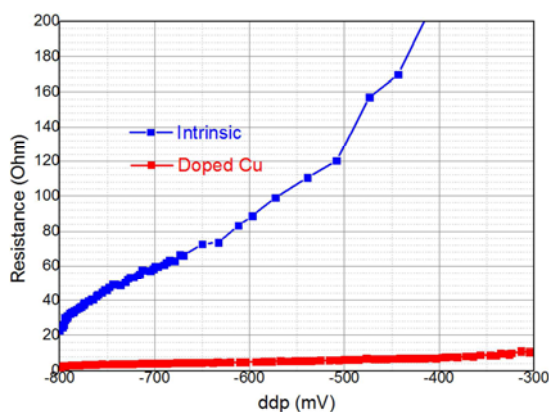
compound shows the presence of a band at  $625\text{ cm}^{-1}$  and a broad band of water to  $3400\text{ cm}^{-1}$  in the spectrum of the doped compound. According to the literature, the band of  $625\text{ cm}^{-1}$  is due to vibration of the Cu bonding (I)-O of  $\text{Cu}_2\text{O}$  [14-16]. In addition, the spectrum of the doped compound showed bands grouped to  $500\text{ cm}^{-1}$  showing the presence of CuO characterized by the presence of three bands at about 588, 534 and  $480\text{ cm}^{-1}$  [16-18]. These results agree well with those obtained by X-ray diffraction.



Top: intrinsic  $\text{Li (NiCoMn) O}_2$ . Bottom: Copper doped  $\text{Li (NiCoMn) O}_2$

Figure 5. FTIR spectrum of prepared  $\text{Li (NiCoMn) O}_2$ .

Measurements of the resistivity of the doped and intrinsic composite gave the results shown on figure 6. Doped compound has a resistivity smaller than the undoped compound. So it seems that copper doping improves the electrical conductivity of material showing that the electronic structure of the compound was changed after doping. This improvement in conductivity is an advantage on the mobility of Li cation during charge / discharge cycles of the battery as this will reduce energy loss by Joule effect.



Top: intrinsic  $\text{Li (NiCoMn) O}_2$ . Bottom: Copper doped  $\text{Li (NiCoMn) O}_2$

Figure 6. Resistance of  $\text{Li (NiCoMn) O}_2$ .

### 3. Materials and Methods

#### 3.1. Synthesis of $\text{Li (Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ Intrinsic and Doped with Copper

Synthesis of  $\text{Li (Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  is made in two stages. First step is the synthesis of  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$  called

precursor and second step is the insertion of lithium in the  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$  compound in order to obtain  $\text{Li(Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$

##### 3.1.1. Synthesis of $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$

We synthesized  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$  compound by co-precipitation method developed by Z. Jianxin [9]. The reagents used were: nickel sulfate  $\text{Ni (SO}_4\text{)}$ ;  $6\text{H}_2\text{O}$  (98.0-102.0 %), cobalt sulphate  $\text{Co (SO}_4\text{)}$ ;  $7\text{H}_2\text{O}$  (99%), manganese sulfate  $\text{Mn (SO}_4\text{)}$ ;  $\text{H}_2\text{O}$  (99.5%) and sodium hydroxide  $\text{NaOH}$  (97.9%).

A stoichiometric mixture of cobalt sulfate, nickel sulfate and manganese sulfate is dissolved in deionized water to obtain a homogeneous solution with a concentration of 10 mM for each sulfate. Precipitation is stabilized at pH 10 by adding 2M of  $\text{NaOH}$  under continuous stirring. The precipitate obtained after centrifugation is then washed three times with distilled water and ethanol and finally dried at  $70^\circ\text{C}$  in oven for 12 hours.

##### 3.1.2. Inserting the Lithium and Formation of $\text{Li(Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$

The  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$  compound called gel precursor is mixed with an excess of 5%  $\text{LiOH}\cdot\text{H}_2\text{O}$  previously prepared from  $\text{LiCl}$ . The "precursor- $\text{LiOH}$ " mixture is finely powdered, homogenized and annealed in air atmosphere and at different temperature from  $600^\circ\text{C}$  to  $1000^\circ\text{C}$  for different duration from 3 hours to 24 hours. The yield of total reaction is 78.9%.

The synthesis of  $\text{LiOH}$  is done in two steps from  $\text{LiCl}$ . In the first step,  $\text{Li}_2\text{CO}_3$  is obtained by mixing an amount of  $\text{LiCl}$  with  $\text{Na}_2\text{CO}_3$  and 20 ml of distilled water heated at  $90^\circ\text{C}$ . The precipitate is washed with hot distilled water then dried at a temperature of  $70^\circ\text{C}$  for 2 hours. This step is summarized by the following reaction (1).



In the second step the  $\text{Li}_2\text{CO}_3$  obtained above is mixed with  $\text{Ca (OH)}_2$  in a volume of 20ml of distilled water heated at  $90^\circ\text{C}$ . After stirring for 30 min, we make a filtration in order to separate the  $\text{LiOH}$  solution and  $\text{CaCO}_3$  precipitated. The  $\text{LiOH}$  solution was then evaporated to get a white powder. This step is summarized by the following reaction (2).



##### 3.1.3. Copper Doping

Copper doping is done by mixing the  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{(OH)}_2$  precursor with 5% of a mixture ( $\text{LiOH}$ ;  $\text{H}_2\text{O}$  +  $\text{CuCl}$ ). After mixing, the mixture is then annealed and then powdered. The yield of this synthesis is 87.7%.

#### 3.2. Synthesis of $\text{CuCl}$

The preparation of  $\text{CuCl}$  is made by mixing one volume of an aqueous solution containing 25% (w/v) of  $\text{CuSO}_4$ ,  $5\text{H}_2\text{O}$  and 15% of  $\text{NaCl}$  with same volume of aqueous solution containing 13% (w/v) of  $\text{Na}_2\text{SO}_3$ . The addition of this second solution to the first is made slowly under continuous stirring.

At the end of this operation we obtain a white suspension. Under stirring, we add to this suspension 10 volumes of dilute solution hydrochloric acid  $2.10^{-2}\text{N}$  containing 0.1% (w/v) of  $\text{Na}_2\text{SO}_3$ . After standing a pale blue powder is

obtained. This one is filtered, and then washed once with the hydrochloric acid solution and again with concentrated acetic acid and ethanol. The following diagram (fig. 7) shows the synthetic routes of the synthesized compounds.

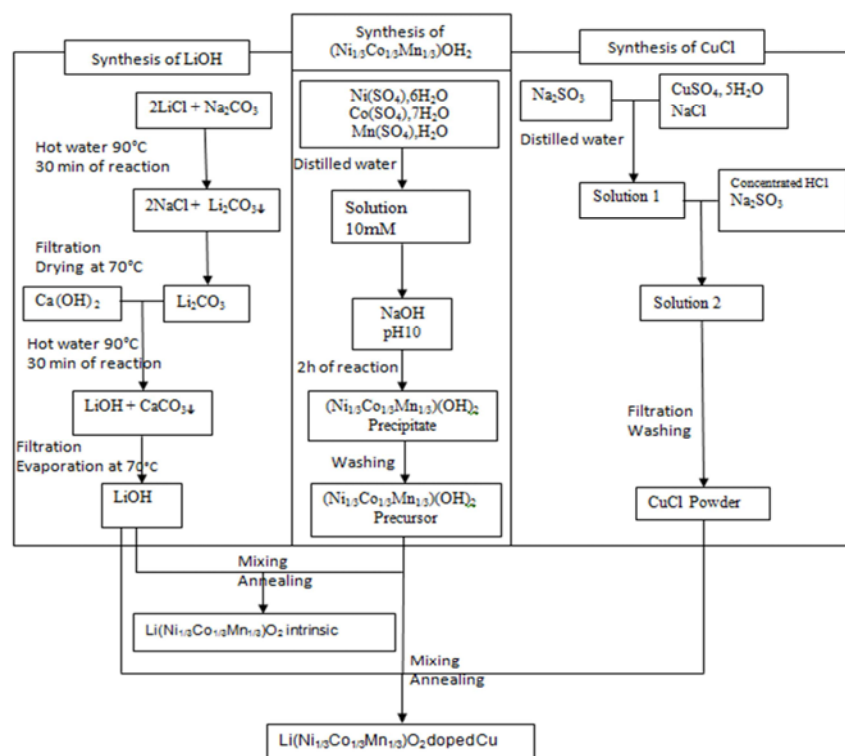


Figure 7. Synthesis of Li ( $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ )  $\text{O}_2$  undoped and Cu doped.

### 3.3. Electrical and Electrochemical Characterization and Testing

#### 3.3.1. X-ray Diffraction and FTIR Spectroscopy Characterization

The compound obtained is characterized by X-ray diffraction and FT-IR spectroscopy. FTIR measurement is done in transmission mode on the pellets prepared by mixing 1% of compound with KBr.

The X-ray powder diffraction have been recorded using a diffractometer with copper  $\text{K}\alpha$  radiation and data were obtained in the  $2\theta$  range of  $10^\circ$ – $80^\circ$ .

#### 3.3.2. Electrochemical Measurement

The electrochemical study was obtained using the potentiostat galvanostat apparatus on a sintered pellet and having circular faces, planes and smooth. The measurement is carried out in beaker containing distilled water at room temperature and three electrodes: a platinum electrode, a reference electrode and the composite compact, have been linked to the potentiostat.

## 4. Conclusions

The synthesis of the compound Li ( $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ )  $\text{O}_2$  intrinsic and doped with copper by the method of co-precipitation was performed using the sulphate of Ni, Co, and

Mn in combination with LiOH. This method is easy and gives a good yield higher than 75%. The analyses performed by FTIR and the RX diffraction shows that the Li compound ( $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ )  $\text{O}_2$  lamellar  $\alpha$ - $\text{NaFeO}_2$  type is obtained with good quality and it contains little or no LiOH. The post synthesis annealing is an important step in determining the crystallinity and size of product particles obtained. We tested the annealing at temperatures between  $500^\circ\text{C}$  and  $1000^\circ\text{C}$  under ambient atmosphere. We noticed the material properties change depending on the parameters of a phase mixture to a homogeneous product doped.

The electronic structure of the compound Li ( $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ )  $\text{O}_2$  has been modified by doping with monovalent Cu + cation. The results obtained show that the lamellar structure was not altered. We noticed an increase in infill distances that can affect the mobility of lithium cations during the insertion cycles / extraction.

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