

RESEARCH ARTICLE | MAY 03 2023

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AIP Conference Proceedings 2517, 020009 (2023)

<https://doi.org/10.1063/5.0121103>



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# Synthesis and Characterization of NMC111 Cathode by Co-precipitation Method

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**Abstract.** Lithium-Nickel-Manganese-Cobalt-Oxide ( $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ,  $x+y+z = 1$ ) — Li-NMC, currently become a dominant focus for cathode material development. NMC cathode is an important material and is widely used for the development of lithium ion batteries which require specific energy and high energy density also reducing environmental impact. In this work,  $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precursor has been synthesized by co-precipitating oxalate method with different reaction time of 40 and 120 minutes. Those precursors were mixed with appropriate amount Lithium carbonate then calcined at  $900^\circ\text{C}$  for 12 hours to obtain  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  (NMC111) cathode active materials. The crystal structure of  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  was characterized by an X-ray diffraction (XRD) in order to investigate crystallite size and crystallite phase. The results show that the crystal phase hexagonal  $\alpha$ - $\text{NaFeO}_2$  structure that belongs to NMC111 (R-3m) space group. The structure did not change with the reaction time. However, the crystallite size increased with increasing of reaction time, namely 820.30 Å and 986.50 Å, for 40 and 120 minutes, respectively. **Keywords:** *NMC111, Synthesis NMC Cathode, Co-Precipitation Method.*

## INTRODUCTION

The use of electricity continues to grow considering that electricity-based technological innovations are growing rapidly and are used in almost all sectors. The main component that cannot be separated from the increase in electricity demand is energy storage. Technological developments, especially in the field of electrical energy storage in the form of batteries. Electronic devices require batteries as a source of propulsion, so batteries have the prospect of becoming a strategic and economical source of energy. The most dominant and widely used battery is lithium ion (Li-ion) rechargeable battery. A battery is an electronic device that can produce an electric current, involving the transfer of electrons through the negative electrode (anode) to the positive electrode (cathode) [1]. From a battery, each battery cell can store electrical energy in the form of chemical energy in two electrodes. There are two electrodes that act as a reducing agent (anode) and as an oxidant (cathode), in the battery structure the two electrodes are separated by an electrolyte that transmits ionic components from chemical processes inside the cell and makes the movement of electronic components outside the battery. The output produced during discharge is an external electric current  $I$  at a voltage  $V$  for the duration  $\Delta t$  [2].

Li-ion batteries have started to enter the transportation market and are under development in drivetrains of hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs). The potential market for Li-ion batteries in the automotive sector especially for electric vehicles (EV) has created a strong interest in understanding the costs of production and future use of Li-ion batteries and other chemical batteries [3]. Current

developments in the electric vehicle battery market largely depend on the resulting range of electric vehicles. A battery cell for an EV must produce a specific energy of about 300–400 Wh/kg for a range of 300 miles, which is 2.5 times more energy than most Li-ion batteries can store today. In order to achieve and meet these targets, modifications are made to the cathode material by increasing the material used, such as lithium nickel manganese cobalt oxide ( $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  with  $x + y + z = 1$ , NMC) are being developed [4]. By using Lithium Nickel-Manganese-Cobalt Oxides (Li-NMC) cathode material in Li-ion batteries, it can produce a battery with the characteristics of high thermal stability, high power and high energy density. The NMC cathode material can be modified to achieve a wide range of charges so that it can be used in various types of batteries. In batteries with NMC cathode materials there are variations in the composition of nickel, manganese, and cobalt which are used to influence the characteristics of the battery and each composition is tailored for a particular application. Increasing the proportion of nickel in the cathode affects the aspect of increasing the specific energy, while increasing the proportion of manganese can increase the specific power [5]. NMC batteries were commercialized for the first time in late 2004, but these batteries already dominate in EV and PHEV applications, especially in small electric vehicles such as electric bicycles and electric motorcycles because NMC batteries can produce batteries with a compact size and has good durability. Currently, most electric car manufacturers use NMC Li-ion batteries as their energy source where NMC batteries can produce a specific energy of about 200 Wh/kg. While also used in power tools, medical devices, and portable electronics. In the future, there will also be projections of NMC batteries for the use of grid-connect. [6].

One of the most widely used methods to synthesize layered Li-ion battery cathode materials such as NCA and NMC is Co-precipitation. The Co-precipitation method requires one to understand well how the mechanism and system work and understand several parameters that affect the synthesis results such as reagent molarity, pH, reaction temperature, feed rate, and mixing conditions such as speed and duration of mixing. The Co-precipitation method is admittedly more complicated than other methods, but this method can produce the best NMC cathode material in terms of electrochemical performance characteristics and produce a spherical single-crystal morphology of NMC [7]. Co-precipitation itself has several advantages and disadvantages of the method. The advantages of this method itself are possible to control the composition and particle size, possible to change the surface state of the particles, the resulting products are homogeneous, low temperature, and low energy consumption. Meanwhile, the disadvantages of this method are does not apply to neutrally charged species, the reactants must have the same precipitation characteristics, spend a lot of time, and the problem is with reproducibility [6].

In this work,  $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{-C}_2\text{O}_4$  precursors were synthesized from oxalate Co-precipitation method and characterization of  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  or Li-NMC111 cathode material for secondary lithium batteries by X-ray diffraction (XRD). In this experiment, the value that is varied is the precipitation reaction time (40 and 120 minutes). The preparation of oxalate Co-precipitation and several parameters that affect the synthesis results such as reagent molarity, pH, reaction temperature, feed rate, and mixing conditions such as speed and duration of mixing [8].

## METHODOLOGY

In this research, the materials used for the synthesis of the active material NMC111 were  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , NaOH,  $\text{NH}_4\text{OH}$ ,  $\text{Li}_2\text{CO}_3$  and demineralized water. In this research, the equipment used were glass beaker, glass stirrer, spatula, measuring pipette, glass measuring cup, watch glass, thermometer, pH-meter, universal pH, analytical balance, magnetic stirrer, filter paper, glass funnel, oven, porcelain crucible, furnace, mortar, and characterization instruments such as XRD.

In this research, laboratory standard materials such as  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , NaOH,  $\text{NH}_4\text{OH}$ ,  $\text{Li}_2\text{CO}_3$ , and deionized water (DI) were used for the synthesis of the co-precipitation method. The first process carried out is to weigh each material used, from transition metals to precipitates. In the precursor manufacturing process, the transition metal sulphate and oxalate reagents are dissolved separately in deionized water (DI), for transition metal solutions are dissolved using 0.20 L of deionized water (DI) and the oxalate solution is dissolved using 0.10 L of deionized water (DI). The transition metal solution is then poured all at once into the oxalate solution to initiate the co-precipitation reaction. Then, the solution mixture was heated to 60 °C on a hot plate using a magnetic stirrer and the temperature was maintained during the reaction at 60 °C. The total volume of the mixed solution was about 0.35 L (in a 0.50 L beaker) for all synthesis, and the reagent mass was adjusted according to each desired solution concentration and transition metal composition ratio. The co-precipitation solution was stirred constantly at 370 rpm with a magnetic stirrer to keep the solution homogeneous during the formation of precipitates and to prevent particles from settling in the suspension, and the pH and temperature values

of the reacted solutions were observed. After 5 minutes the pH of the solution was measured, then 8 ml of  $\text{NH}_4\text{OH}$  was added using a measuring pipette until it reached around pH 7. The stirring time was carried out with two variations, namely 40 and 120 minutes. After the reaction, the precursor in the form of a slurry was filtered using filter paper, and then rinsed with  $\sim 1.2$  L deionized water (DI) until it reached pH 7. After the precursor was washed and then dried in an oven at  $120^\circ\text{C}$  for 2 hours.

The NMC oxalate precursor is mixed with  $\text{Li}_2\text{CO}_3$  with an excess of 2% and the ratio of Li:TM is 1:5. The precursors were mixed manually by shaking by hand for 30 minutes. After that, the mixed precursor was put into the alumina crucible according to each variation. This mixture is then calcined in a furnace (Muffle furnace 1200) in an air atmosphere at a temperature of  $550^\circ\text{C}$  for 5 hours and at a temperature of  $900^\circ\text{C}$  for 12 hours to obtain a cathode active material with a cathode composition of  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  (NMC111). The rate of increase of the furnace temperature was set at a maximum of  $5.25^\circ\text{C}/\text{min}$ , and during the calcination process the temperature of the furnace was programmed for the time of rising and falling of temperature to avoid damage to the material structure and decomposition of oxalate, respectively. Then, the active cathode material produced was characterized using X-Ray Diffraction (XRD) to determine the crystal structure and composition formed.

### Materials characterization



FIGURE 1. Final results of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  cathode active material powder

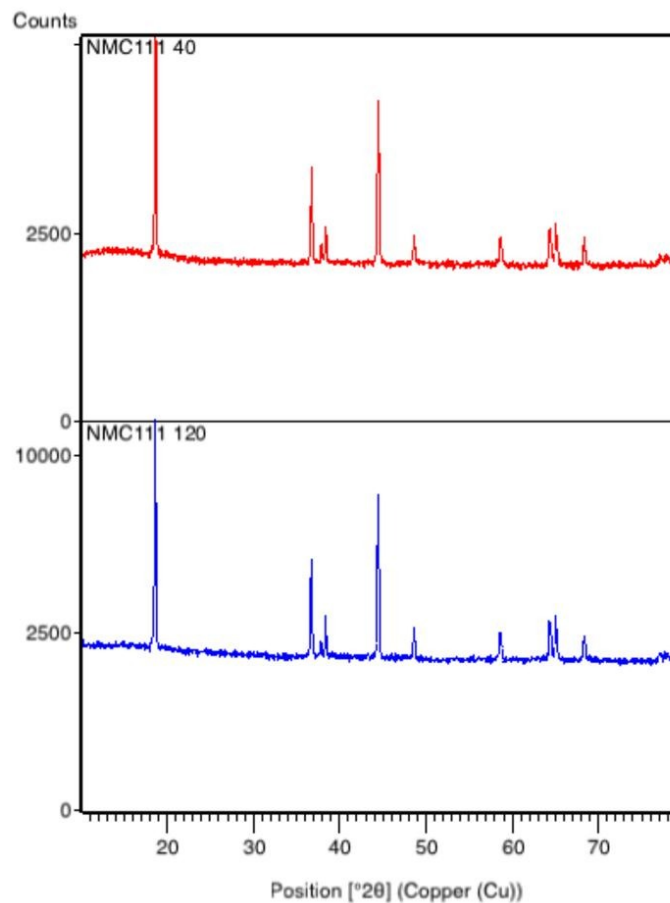
### RESULTS AND DISCUSSION

X-ray diffraction (XRD) is a non-destructive analysis technique using monochromatic X-ray diffraction intensity, where as a function of incident and angle of exit. XRD can also be used to calculate precise lattice parameters, crystal sizes, and preferential orientations. XRD information can be used to study the crystallographic structure, chemical composition, and physical properties of materials and thin films. In addition, XRD can also be used to calculate precise lattice parameters, crystal size, preferred orientation, and lattice parameters [9]. In this research, XRD was used to study the synthesis of NMC active cathode powder which was synthesized using the Co-precipitation oxalate method. The process of the Co-precipitation method is superior to other methods in terms of ease of control [10]. So in the process, one must understand each parameter such as the pH level of the solution, the amount of chelating agent, the conditions during the mixing reaction, such as temperature, speed, and reaction time in synthesizing homogeneous the spherical  $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{-C}_2\text{O}_4$  particles. All these things are done to get good and

appropriate final product precursors [7]. The three transition metals (TM) materials are important to be able to be deposited simultaneously. In addition, Mn materials are usually easily oxidized even at low temperature conditions during the Co-precipitation process. This method is said to be quite simple because there is no need for complicated pH adjustments. Materials that are also important in the Co-precipitation process for cathode materials are chelating agents. Chelating agents perform the formation of complex materials so as to slow down the precipitation reaction, this is what makes this method more controllable. The formation of nucleation was dominated by the growth of crystals that had been formed along with the increase in the amount of  $\text{NH}_4\text{OH}$ . As a result, the particle size increases which can be observed from the results of the XRD characterization that has been carried out [8].

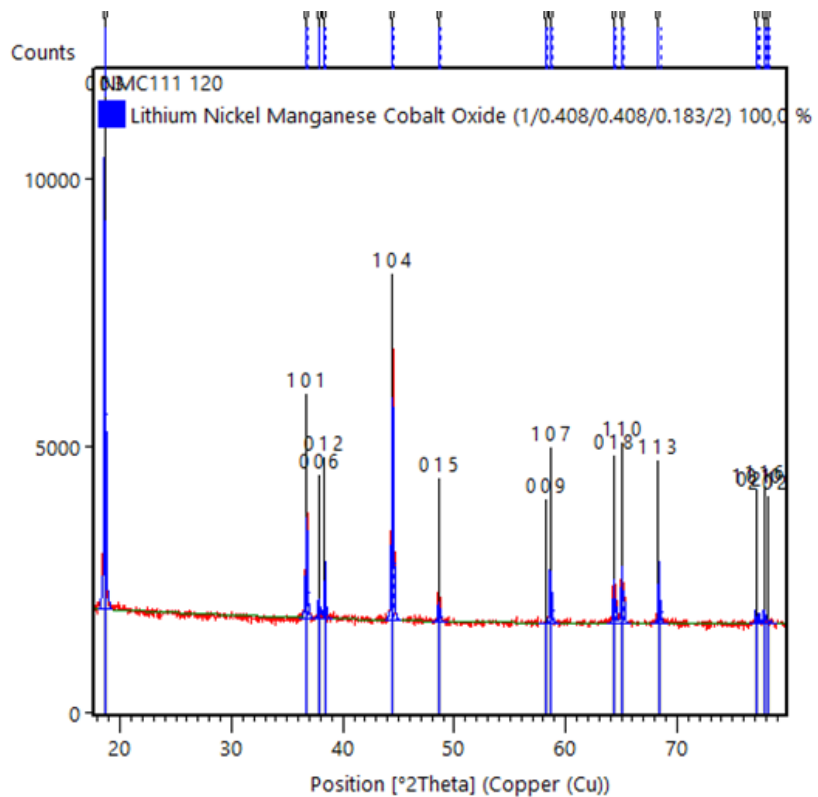
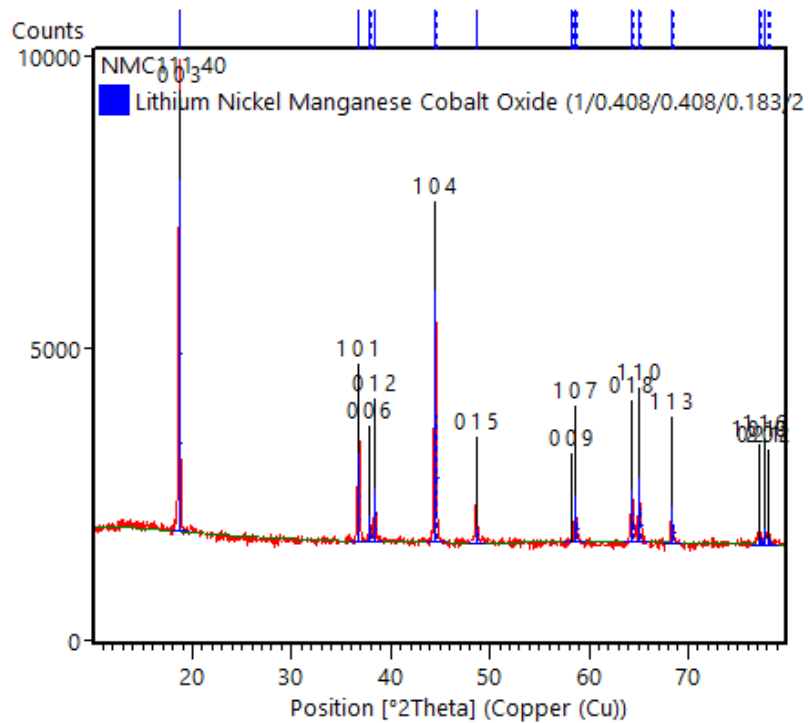
In this work, the temperature used to mix the TM and the precipitate is  $60^\circ\text{C}$  so that each component of the Co-precipitation process material can have a good and homogeneous reaction, and the value that observed and varied were the length of reaction times (40 and 120 minutes) to determine its effect on the final product of the active material produced. when observed using XRD. The reaction time is one of the important parameters in the Co-precipitation process which affects the morphology and, as a result, the electrochemical and physicochemical properties of the resulting cathode active material [10]. Several previous studies have shown that the stirring reaction time affects the particle properties of the active material produced. The report states that the longer the stirring reaction time, the larger and spherical of the resulting particles [11]. Primary NMC particles that may form during agglomeration grow larger and fill any porosity in it. Thus, it can increase the particle density so that the resulting active material is better. In this experiment, the precursor is filtered, washed, and dried so that there are no impurities contained in it which will affect the performance of the final cathode active material.

The results of previous studies and XRD characterization showed that the most stable surfaces for NMC111 were polar (012) and (001), nonpolar surfaces (104), and polar surfaces (110) reconstructed. The intermediate spin  $\text{Co}^{3+}$  ion can lower the surface energy level (104). To remove oxygen from the surface (104) is more difficult than the surface (012), so it depends on the formation of oxygen vacancies on the surface [12]. These results provide an overview of the rational control of parameters in the synthesis and become material for future mechanistic studies regarding the surface instability of NMCs that can be developed such as the results of XRD characterization that are in accordance with theoretical values. At the peak of XRD when the reaction time increases, a sharper peak will be formed. In addition, the mixing of cations involving Ni decreased while the hexagonal ordering increased with increasing stirring reaction time in the Co-precipitation process [12]. Several components and characteristics of the XRD results mentioned earlier will be the basis for determining the success of a Li-NMC synthesis process. It will also give an idea about the composition of the active cathode material formed, whether it is in accordance with the desired composition. In carrying out data processing and analysis of XRD data obtained, in this study the High Score Plus software was used. High Score Plus is used to compare the XRD results obtained with the database owned by the application, so that it can determine the quality of the active cathode material.



**FIGURE 2.** Powder XRD patterns of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  with 40 and 120 minutes reaction time

The NMC powder was analyzed by XRD using High Score Plus software and produced XRD peak patterns as can be seen in Figure 2. The figure shows that the shift of the distinct peaks indicating the layers return to their initial position, and recreation of the pure unit cell parameters. As is well known, the retaliation process can produce anti-site mixing as a side effect which adds impedance to the interfacial ion transfer. From XRD analysis, peak intensity ratios 003 and 104 could qualitatively evaluate  $\text{Li}^+/\text{Ni}^{2+}$  anti-site mixing (cation mixing), with higher I003/I104 ratios indicating less site mixing. An important decrease was observed especially for delithiated NMCs after annealing, in accordance with the hypothesis that in the absence of lithium in the layer, nickel cations may migrate under the influence of temperature. Samples with a lithium coating that charge showed minimal change in ratio. From the XRD results, it can be seen that the pattern of each peak is in accordance with the standard XRD pattern.



**FIGURE 3.** Rietveld refinement XRD pattern of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  with (a) 40 minutes reaction time, (b) 120 minutes reaction time.

**TABLE 1.** Powder XRD intensity ratio of NMC111

Mixing Time (Minutes)	Intensity Ratio ( $\geq 1.2$ better)
40	1.558
120	1.619

From the XRD data obtained and displayed using HighScore Plus software, the Rietveld method was used to improve the crystal structure of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  and obtain the crystalline characteristic parameters formed from samples made at temperatures of 550 °C and 900 °C. After the sample was refined, it was found that there was a very good match between the observed patterns and the calculated patterns, and it could be seen that there was no appearance of the superstructure in the compounds formed. Rietveld refinement measures the crystal lattice parameters as a hexagonal arrangement, and the results obtained from all XRD data samples are identical and close to each other for each parameter. The results of the crystal lattice parameters obtained from XRD data for each reaction time variation are as follows, at a time variation of 40 minutes, the value  $a = 2.86522 \text{ \AA}$  and  $c = 14.24857 \text{ \AA}$  are obtained. As well as the lattice parameter values for the time variation of 120 minutes, the values of  $a = 2.86332 \text{ \AA}$  and  $c = 14.23894 \text{ \AA}$  are obtained. Another parameter that is observed is the comparison value of R expected and R profile, in the XRD Li-NMC111 sample, the R expected and R profile values are obtained which are close to each other for all variations in reaction time. From the results of Rietveld refinement also obtained the value of the crystallite size of each data. In this study, the crystal size was obtained for each time variation, namely 820.30 Å and 986.50 Å, for each time of 40 minutes and 120 minutes. The values measured in this study are consistent with other values reported in the literature of previous studies [8].

From the results of XRD characterization, it can be seen that active cathode material formed has no impurities such as iron or sodium. To see the quality of the active material made, it can be seen from the intensity ratio. In this experiment the distance of the intensity ratio of peak value should obtained a value of more than 1.2 and its close to the value of standard products as shown in Table 1. For best results is in time of 120 minutes with higher intensity ratio. From the data obtained a directly proportional relationship, namely the XRD peak will become sharper when the reaction time increases. However, the crystallite size increased with increasing of reaction time. This research can be said to have succeeded in making the active material for the Li-NMC111 cathode using the oxalate co-precipitation synthesis method if considering the data obtained, from the experiment it can be concluded that the oxalate co-precipitation method is an efficient and easy method because it can produce good precursors without complicated pH treatment conditions.

## CONCLUSION

We can conclude that Co-precipitation is one of the best methods for synthesizing layered cathode materials such as Li-NMC. As seen in the results of this experiment where the intensity ratio of  $I_{(003)}/I_{(104)}$  Bragg peaks shows a value of more than 1.20 which is the key factor of the active cathode material, namely 1.558 and 1.619, for 40 and 120 minutes, respectively. In this experiment, it was shown that variations in the length of stirring time affect the size of the crystallites where the longer the stirring time, the larger the crystallite size, namely 820.30 Å and 986.50 Å, for 40 and 120 minutes, respectively. For the best results obtained at a variation of the stirring time of 120 minutes.

## ACKNOWLEDGMENTS

This work is financially supported by the LPDP number 84/E1/PRN/2020 through the National Research Priority (PRN) Mandatory on Energy Storage 2020 under the Ministry Research and Technology.



## REFERENCES

1. S. S. Zhang, "Unveiling Capacity Degradation Mechanism of Li-ion Battery in Fast-charging Process," *ChemElectroChem*, vol. 7, no. 2, pp. 555–560, 2020, doi: 10.1002/celec.201902050.
2. J. B. Goodenough and K. S. Park, "The Li-ion rechargeable battery: A perspective," *J. Am. Chem. Soc.*, vol. 135, no. 4, pp. 1167–1176, 2013, doi: 10.1021/ja3091438.
3. G. Pistoia, *Lithium-Ion Batteries* 1st Edition. 2014.
4. R. Jung, M. Metzger, F. Maglia, C. Stinner, and H. A. Gasteiger, "Chemical versus electrochemical electrolyte oxidation on NMC111, NMC622, NMC811, LNMO, and conductive carbon," *J. Phys. Chem. Lett.*, vol. 8, no. 19, pp. 4820–4825, 2017, doi: 10.1021/acs.jpcclett.7b01927.
5. G. W. Yoo, B. C. Jang, and J. T. Son, "Novel design of core shell structure by NCA modification on NCM cathode material to enhance capacity and cycle life for lithium secondary battery," *Ceram. Int.*, vol. 41, no. 1, pp. 1913–1916, 2015, doi: 10.1016/j.ceramint.2014.09.077.
6. G. Zubi, R. Dufo-López, M. Carvalho, and G. Pasaoglu, "The lithium-ion battery: State of the art and future perspectives," *Renew. Sustain. Energy Rev.*, vol. 89, no. April 2017, pp. 292–308, 2018, doi: 10.1016/j.rser.2018.03.002.
7. B. Cem, "Reactor Design, Characterization and Production of Cathode Active Material via Co-Precipitation Method for Lithium Ion Batteries," *Orphanet J. Rare Dis.*, vol. 21, no. 1, pp. 1–9, 2020.
8. M. H. Lee, Y. J. Kang, S. T. Myung, and Y. K. Sun, "Synthetic optimization of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  via co-precipitation," *Electrochim. Acta*, vol. 50, no. 4, pp. 939–948, 2004, doi: 10.1016/j.electacta.2004.07.038.
9. B. Leó and J. A. Jansen, *Thin calcium phosphate coatings for medical implants*. 2009.
10. Y. Jiang, F. Zhou, C. Wang, J. Kong, and L. Xu, "Influence of co-precipitation temperature on microstructure and electrochemical properties of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  cathode materials for lithium ion batteries," *Ionics (Kiel)*, vol. 23, no. 3, pp. 585–596, 2017, doi: 10.1007/s11581-016-1863-2.
11. A. Van Bomme and J. R. Dahn, "Analysis of the growth mechanism of coprecipitated spherical and dense nickel, manganese, and cobalt-containing hydroxides in the presence of aqueous ammonia," *Chem. Mater.*, vol. 21, no. 8, pp. 1500–1503, 2009, doi: 10.1021/cm803144d.
12. J. C. Garcia *et al.*, "Surface Structure, Morphology and Stability of  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  Cathode Material," pp. 1–29.