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# The Effect of Lithium Excess on Synthesizing NMC 811 Cathode Material

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**Abstract.** Battery becomes the main challenge for hastening the Electric Vehicles (EV) market penetration. Currently, lithium-ion battery (LIB) technology is broadly used for EV industry due to its high energy density. However, scientific discovery is still needed to compete on energy density, power capability, driving range, and also charging time aspect. Since its utilized for mobility, the LIB technology preference belongs to high-rich nickel cathode active materials. Besides, in terms of LIB supply chain, Indonesia is benefited with 23% of global nickel reserves. According to market projection trends, $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811) grasps the huge attention on the LIB technology for EV industry. Nevertheless, there are some technical challenges that need to be solved for mass production. For instance, Li/Ni cation mixing that affect significant volume of Li ions intercalation/deintercalation process on microscopic level, which leads to poor electrochemical performance. One of the promising solutions is by adding amount of additional lithium element. This work investigated the effect of lithium content excess on the synthesis of NMC 811 cathode active material. The synthesis route was co-precipitation with amount of lithium excess on 1%, 3%, 5%, and 7%. For attaining crystal structure data, it followed by X-Ray Diffraction (XRD) analysis. The result depicted that lithium excess on NMC 811 cathode active material influenced cation mixing. More excess lithium affected cation mixing reduction of cathode product.

## INTRODUCTION

Climate change becomes a main issue that threatened human life. The latest report of Intergovernmental Panel on Climate Change (IPCC) on Working Group III mentioned that the rise of earth temperature after pre-industrial level is inevitable[1]. The surge of greenhouse gases (GHG) emission in the atmosphere for last decade brings us to the $1.5^oC$ tipping point under Paris Agreement. Almost 60% of carbon emission is contributed by fossil fuel industry and transportation with 4% of increment every year[2]. Succeeding the Internal Combustion Engine (ICE) into Electric Vehicles (EV) becomes a prominent solution. Besides it will be benefited the economic sector due to the emerging clean market[3], EV also will guarantee less emission production compared to the ICE. This momentum will avoid the 10 Gigaton $CO_2$ equivalent from transportation sector released to atmosphere by 2050[4].

The main problem for hastening the EV market penetration is battery technology. Currently, it still stands on lithium-ion battery (LIB) that comprehensively used because of its high energy density[5], long cycle life[6], high-operating voltages[7], and lack of memory effect[8]. Yet, the breakthrough is still needed to compete on energy density & power capability and also driving range & charging time. For escalating the competitive advantages of LIB, it precisely depends on the cathode materials that affecting the discharge capacity. Among various types of LIB, cathodes with high-rich nickel $LiNi_{1-x-y}Mn_xCo_yO_2$ (1-x-y > 0.5) or so-called NMC has a promising aspect to be

developed. Besides, Indonesia will gain multidimensional benefit through its status as the biggest global nickel reserve with 4.9 billion metric tons[9].

Larger nickel content will provide higher capacity, cobalt will increase electronic conductivity that affect on higher rate performance, and manganese will maintain the safety and lower the cost[10]. On the market perspective, $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811) grasps the huge attention on the LIB technology for EV development. However, serious problem on capacity fading and also structural decomposition need to be addressed. In detail, there are some technical challenges that hinder large-scale application for nickel rich NMC cathode materials. Such as $Li^+/Ni^{2+}$ cation mixing, micro-strain and crack formation caused by significant volume during $Li^+$ deintercalation or intercalation process, and also safety concern due to the aggressive thermal reactions[11].

Related to cation mixing phenomenon happens due to the difficulty on maintaining all the nickel in the 3+ valence state, in certain layer structure materials, buttressed by similar ionic radii on 0.76 Å and 0.69 Å for $Li^+$ and $Ni^{2+}$ ions, respectively[12]. The existence of $Ni^{2+}$ ions in the Li layer hinders the diffusion process of $Li^+$ ions. At the same time, it also reduces the reversible capacity of $Li^+$ ions. The main consequence from above condition is poor electrochemical performance. When Li+ ions occupy the layer of transition metal (TM), the crystal lattice will be difficult to deintercalate[11]–[14].

This work focuses on the cation mixing phenomenon in the NMC 811 cathode material. In terms of terminology, cation mixing is a phenomenon of $Li^+$ and $Ni^{2+}$ disordering that is frequently observed in cathode materials with layered structures due to the similar Bohr radius of $Li^+$ and $Ni^{2+}$ ions[15]. Since that event happens in the scale of cathode materials, synthetic condition becomes the principal factor for attaining more optimum result[16]–[18]. Such as pH value on co-precipitation[14], lithium content[19], particle size[11], calcination temperature[20], calcination atmosphere[5], and also heating/ cooling rates[19]. Therefore, this research aims to investigate the effect of lithium content excess on the synthesis of NMC 811 cathode active material. The characterization on crystal structure of NMC 811 was analyzed by an X-Ray Diffraction (XRD).

## METHODOLOGY

The whole process of the work involved various industrial grade materials, such as $NiSO_4.6H_2O$, $MnSO_4.H_2O$, $CoSO_4.7H_2O$, NaOH, $NH_4OH$, $LiOH.H_2O$ and demineralized water. The synthesis reaction was co-precipitation method. It is well-known method along with evaporation and sol-gel route. The co-precipitation referred to basic precipitating and complexing agent that involves mixing stoichiometric transition metal[14]. It produces mixed-transition metal precursor to the lithiated oxide at the end product. The main benefit of co-precipitation route is multiple condition reaction control, such as pH, temperature to reaction time. It affects morphology, tap density, and particle forms that suitable for gaining the optimum precursor[7].

In this co-precipitation synthesis, basic precipitating agent so-called transition metals such as $NiSO_4.6H_2O$, $MnSO_4.H_2O$, and $CoSO_4.7H_2O$ were dissolved separately in 2 Molar demineralized water solution. The complexing agent such as NaOH and $NH_4OH$ were poured into 4 Molar solution of demineralized water. Both precipitating and complexing agent were reacted in the 20 Litre of Continuous Stirred Tank Reactor (CSTR) for 24 hours. The reactor temperature was kept constantly at 60ºC, followed by Nitrogen gas flow and pH 11.5 control.

The wet precursor was obtained and maintained the pH through filtration process until neutral. Then, the precursor was dried at 120ºC along 5 hours in the oven. The parched precursor was blended with $LiOH.H_2O$ through solid-state reaction for 30 minutes. Since this experiment would state the effect of lithium excess, it has four sample of mol variations: 1%, 3%, 5%, and 7%. This Li excess was used to compensate the loss of lithium element during high-temperatures calcination. In addition, for nickel-rich cathode, $LiOH.H_2O$ is broadly used as lithium source due to its lower thermal decomposition temperature[14], [19], [21]. Figure 1 is a solid-state reaction between precursor and lithium. For obtaining the NMC 811 cathode active material, the samples were heated-up in the oxygen-rich furnace in two steps of temperature process. The first one is at 550ºC for 5 hours and the final step is at 900ºC for 15 hours[16]–[18]. The characterization data of crystal structure and phase composition were obtained from the cathode product through X-Ray Diffraction (XRD) with Cu Kα radiation (PANalytical Empyrean).

**FIGURE 1.** Solid-State Reaction of precursor and lithium.

## RESULTS AND DISCUSSION

Since precursor has a prominent factor for gaining the optimum cathode active material, it has been characterized and obtained the precursor crystal structure. Figure 2 (a) depicts the XRD pattern of crystal precursor from $10°$ to $80°$ for all four samples. The diffraction peaks appear at $19.3°$, $33.2°$, $38.9°$, and $52.2°$ in which identified as $Ni_xMn_yCo_z(OH)_2$ on the alfa/beta phase. This single crystalline phase of powder exhibited a hexagonal structure on R-3m space group without any impurities. Additional information, in Figure 2 (b) shows the colour of precursor powder is brown, little bit different with the common colour which is dark green. It caused by $Mn_3O_4$ oxidation on the surface during continuous co-precipitation[14].
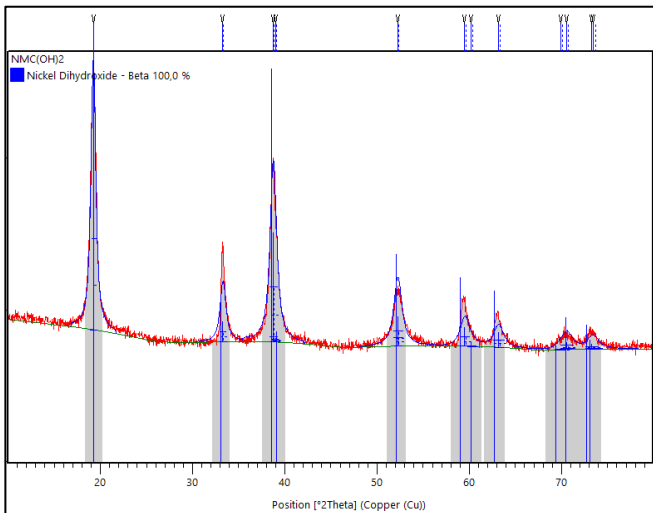


(a)



(b)

**FIGURE 2.** (a) XRD pattern of precursor and (b) brown precursor.

In terms of sintering process, this work used two steps. Pre-heating at $550°C$ for 5 hours and crystal formation at $900°C$ for 15 hours. Another scholar's work discovered that different sintering condition affect the crystal quality[5]. Specific on NMC cathode, two steps heating process significantly increase the performance potential and also affect the inhibiting structure change on cycle aspect of charge discharge[8], [20], [22]. However, for the nickel-rich cathode, lithium loss always happens during sintering process and declines cell performance[10], [11]. There are two alternative solutions, that used in this work, for maintaining the lithium element on ideal composition during

sintering process. Adding amount of lithium excess during solid-state reaction[5] and adopting oxygen atmosphere during calcination process[19].

Firstly, adopting oxygen atmosphere. This initiative comes up caused by the existence of surface residual Li on nickel-rich layer cathode that inhibits cell performance[23]. Thus, oxygen atmosphere protects the calcinated sample from other substrate, because this work did not use the vacuum furnace. It reduces the side reaction and suppress residual Li to attain smooth surface of the secondary particles[8], [24]. Secondly, adding amount of lithium excess that used to compensate lithium loss through high-temperature calcination. During the quenching process, the surficial $Li^+$ ions mostly extracted from layered oxides to form LiOH. It facilitates continuous Li migration from the precursor bulk to the surface due to $Li^+$ concentration gradient[10], [15], [25]. Hence, Li-deficient layer is formed and the amount of lithium excess will fulfill its deficiency. Figure 3 shows the calcination product of NMC 811 cathode active material.



**FIGURE 3.** NMC 811 cathode active material product.

Figure 4 depicts the existence of diffraction peaks from the NMC 811 cathode active materials for 1%, 3%, 5%, and 7% of lithium excess sample variations. The XRD patterns cover the crystal cathode from 10° to 80° with the NMC 811 cathode active material diffraction peaks appear at 18.8°, 36.5°, 38.2°, and 44.3°. It indicates well-indexed pattern on R-3m space group with hexagonal α-$NaFeO_2$ structure. However, formed crystalline ordering in the layered structure was not too excellent. From qualitative analysis, it indicates unclear splitting of (006)/(012) and (108)/(110) planes. On the other hand, the obtained intensity ratio or $I_{(003)}/I_{(004)}$ for all samples are less than 1.2 which mean undesirable of cation mixing. The intensity ratio of each sample are as follows: 0.7 (1%), 0.68 (3%), 0.69 (5%), and 0.69 (7%). According to self-analysis and compared to other scholars, the intensity ratio occurs below the standard mainly caused by the forming crystallinity on sintering process. In this work, based on previous precursor crystal analysis, problem comes from the furnace that should be vacuum for high-rich nickel sample[7], [20], [23].
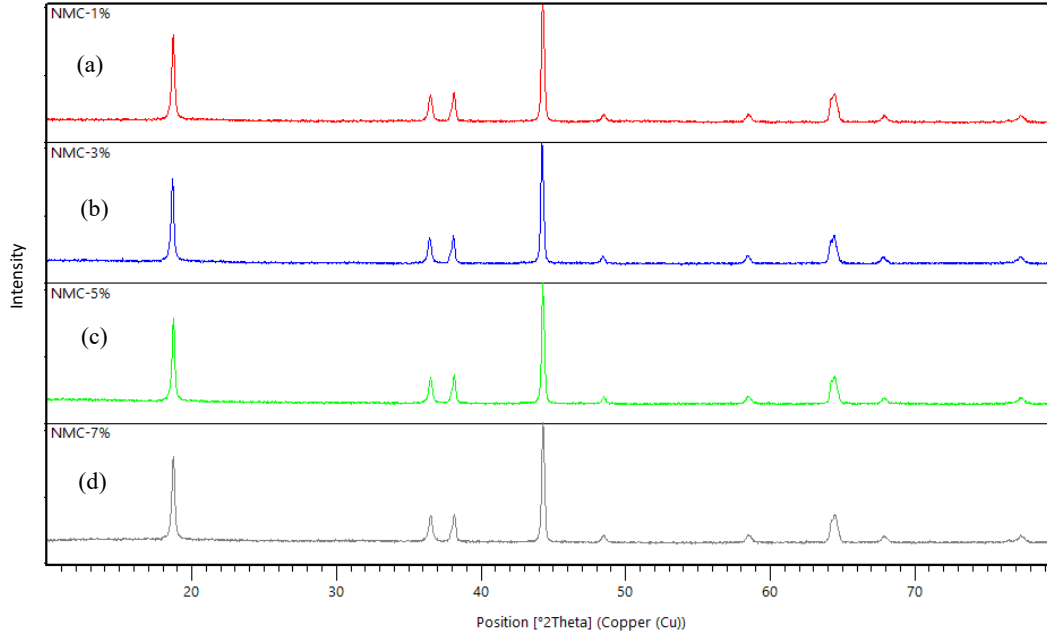
**FIGURE 4.** The XRD patterns of NMC 811 cathode active materials on (a) 1%, (b) 3%, (c) 5%, and (d) 7% of lithium excess sample variations.

Analyzing on Li/Ni cation mixing, it frequently happens on cathode structure in particular. It is caused by the similar ionic radii of the $Ni^{2+}$ (0.69 Å) and $Li^+$ (0.76 Å). Although the order difference is on decimal, but the effect is countable. It provides the site ions exchanging between $Ni^{2+}$ and $Li^+$. Referring to NMC 811 cathode active material crystal analysis above, through R-3m hexagonal structure, lithium layer is on 3b sites while transitional metal (including nickel) fulfills 3a sites. When substitution occurs between $Li^+$ and $Ni^{2+}$ on 3b sites, partial oxidation of $Ni^{2+}$ to $Ni^{3+}$ happens for preserving the lattice electroneutrality. Consequently, it decreases the lattice parameters [5], [10], [19]. Table 1 contains Rietveld refinement from this work.

**TABLE 1.** Rietveld refinement of NMC 811 cathode active material

| Lithium Excess Samples | Ni in 3b site | c/a |
|---|---|---|
| 1% | 0.1803 | 4.9293 |
| 3% | 0.1768 | 4.9287 |
| 5% | 0.1819 | 4.9284 |
| 7% | 0.1684 | 4.9298 |

On the macroscopic level, the Ni in 3b site data seems do not affect the material system since it is still on the same order. However, it will be important if it compared with Bragg diffraction data. Using space group R-3m model, it has been discovered $Li^+$ ions and some $Ni^{2+}$ ions exist at the 3b sites (0, 0, ½), transitional metal ions and some $Li^+$ ions occupy 3a sites (0, 0, 0), and oxygen ions appear at the 6c sites (0, 0, $Z_{ox}$)[5]. This aspect will useful for delving the intercalation/deintercalation process analysis[13], [15].

Although this work obtained undesirable cation mixing due to its unexpected intensity ratio, the rest of manuscript still do the evaluation on the effect of lithium excess with the cation mixing. Because referring to Rietveld refinement, the c/a data (on table 1) are more than 4.899 for all samples. It means, the samples have an ideal partial cation mixing. Back to the calcination process, lithium excess inhibits Li/Ni cation mixing to enhance the layered Li storage structure. Ideally, it also affects the XRD pattern in the microscopic order, since a and c axis enlarge with increasing Li. This indicates the filling of the available sites of lithium through the excess[5], [13], [22]. Means, the lithium excess affects the cation mixing. This evidence also amplified by other scholar's result[25]. More excess Li results in a reduction of cation mixing.

# CONCLUSION

NMC 811 cathode active material synthesis was successfully conducted through co-precipitation route with amounts of lithium excess that separated into four samples. This work involved intercalation/deintercalation process of Li/Ni as one of the parameters. The result pointed that lithium excess on NMC 811 cathode influenced cation mixing. More excess lithium during solid state reaction with precursor affected cation mixing reduction of cathode product. However, it still needs further improvement and analysis on the intercalation/deintercalation modelling and through cell performance. The calcination process needs to be concerned for gaining better intensity ratio with clear splitting planes. Also, more instrument analysis should be considered to attain more qualitative and quantitative data for supporting the work.

# ACKNOWLEDGMENTS

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