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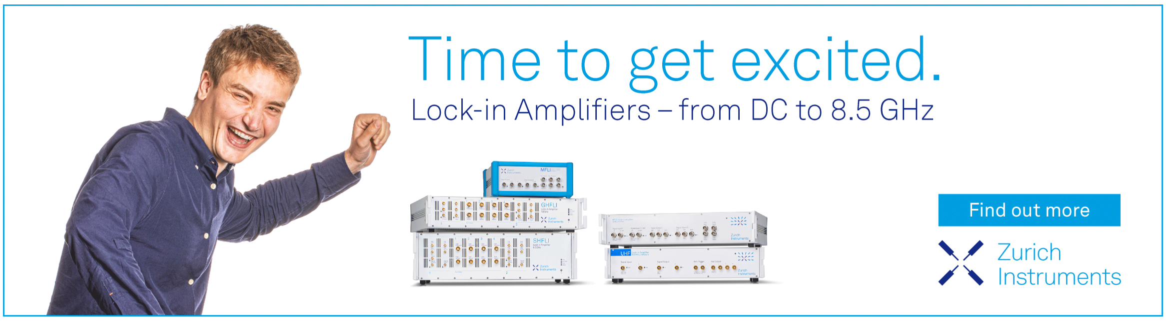

Synthesis and Structural Study of Ce-Doped NMC 811 as the Cathode Material

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Abstract. Lithium ion battery is essential for electric vehicles development. One of the most promising cathode materials for Li-ion battery is $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811) due to its high energy density. However, it caused a low rate capability and obvious capacity degradation at high potential cycle. These limits its practical application. One of the potential solutions to overcome that problem is by doping. In order to modify the crystal structure for performance improvement, the cathode material can be doped by rare earth elements (REE). Besides, Indonesia has one of the biggest deposits for REE. The most promising REE is cerium, because it has been much widely used for catalyst and addition in many fields. In this research, NMC 811 is doped by Cerium Nitrate ($Ce(NO_3)_3$) using co-precipitation method for 5 hours followed by heat treatment. The product was characterized by XRD (X-Ray Diffraction), in order to understand its structural behavior. The cerium has reduced the cobalt composition by 0.02, 0.03, and 0.04 mol. The result shows that the doping did not affect the layered oxide structure of NMC 811, except the increasing of Ce-doped crystallite size to 1275.6 Å rather than pristine. **Keywords:** *Cerium Doped, Cathode Synthesis, NMC811, Structural Study, Rare Earth Elements, XRD.*

INTRODUCTION

Nowadays, the internal combustion engine vehicle becomes the greatest supplier for the world carbon emission. Conventional car produces more than 60% greenhouse gasses pollution that aggravate the climate crisis effect [1]. One of the promising solution is electric vehicles (EVs) without any carbon combustion residue. Globally, today's EVs market is rapidly increasing. For instance, the first quarter of 2020, Europe expandend its EVs market share to 26%, growing by 44% after 2019 slowing down [2]. This condition will lead human to the age of EVs. Furthermore, the biggest challenge of EVs technology stand on the energy storage system. Recent solution makes lithium-ion battery (LIB) are being comprehensively used in diverse applications such as EVs. Because of their high energy density [3], long cycle life [4], high operating voltage [5], and lack of memory effect [6].

The lithium ion battery performance depends on the cathode materials. Today, scholars tend to explore the nickel-rich cathode with more than 60% nickel composition due to its high energy density [7-10]. One of the most promising cathode material for Lithium ion battery is $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$. The cathode of NMC 811 has a great potential to develop in Indonesia due to high amount of nickel resource [11, 12]. In addition, Indonesia has the biggest global nickel reserves [13]. However, NMC 811 cathode caused a low rate capability and obvious capacity degradation at high potential cycle. These limits its practical application. One of the potential solutions to overcome that problem is by doping. It modifies the cathode materials structures and improve electrochemical performances.

The impressive material candidate for doping is rare earth elements (REE). Because of its high charge and large ionic radius [16]. The resource of cerium in the earth's crust is about 0.0046%. It becomes the highest abundance among REE. Indeed, Indonesia becomes the biggest deposits for REE [14]. Doping with REE ions has been

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demonstrated to be a promising method to increase the properties of electrochemical [15-17]. As one of the most potential REE, cerium is an important element which offers manifold properties. Such as high termal stability [18], oxygen storage capacity [19], optical properties [20], diffusivity and electrical conductivity [21]. Cerium also represents as lithium battery electrode materials. Because of the fast and direct transformation of Ce (III) and Ce (IV).

Furthermore, Yao *et al.* [22] has observed Ce^{3+} doped $Li_3V_2(PO_4)_3/C$ demonstrates better cycling properties, because of its smaller resistance of charge transfer and more layered crystal lattice. In addition, Xia *et al.* [23] showed the superiority of Ce-doped NMC-532 electrochemical performance compared to non-doped pristine samples. This work, aim to synthesized NMC 811 and doped by Cerium Nitrate (Ce $(NO_3)_3$) using co-precipitation method for 5 hours followed by heat treatment. One of the methods that widely used to synthesize NMC cathode is co-precipitation. Because it yields good electrochemical performance for NMC cathode. The crystal structure will be evaluated with the XRD.

METHODOLOGY

In this research, the materials used for the synthesis were $NiSO_4.6H_2O$, $MnSO_4.H_2O$, $CoSO_4.7H_2O$, $H_2C_2O_4$, NaOH, Li_2CO_3 from industrial grade and demineralized water. Analytical grade $Ce(NO_3)_3.6H_2O$ (Merck) was used as the source of Cerium.

In the co-precipitation synthesis, transition metals such as $NiSO_4.6H_2O$, $MnSO_4.H_2O$, $CoSO_4.7H_2O$ and doping material $Ce(NO_3)_3.6H_2O$ were dissolved separately in demineralized water. The variation of cerium addition were 0.02 ($Ce\text{-}_{0.02}$), 0.03 ($Ce\text{-}_{0.03}$), and 0.04 ($Ce\text{-}_{0.04}$) mol in order to reduce the cobalt composition. The precipitant solution from NaOH and $H_2C_2O_4$ was added to the transition metal solution when the temperature raised to 50ºC. The ratio of transition metal and doping solution was 2M and precipitant solution was 4M. The reason why oxalates is used because of its affordable cost and easily obtained. Besides, oxalates also have an impressive structure stability and low decomposition temperature in air, relatively. Szenknect *et al.* [24] often observed the cerium in the oxalate precursor during the high temperature calcination process.

The co-precipitation synthesis was stirred continuously at 500 rpm for 5 hours using magnetic stirrer to maintain the homogeneous factor and avoid particles from settling with the suspension. The precursor was gathered by filtration method and washed by demineralized water until reach the neutral ph. Then, the precursor is dried in the oven at 120ºC in 3 hours. Before calcination, the precursor was mixed with Li_2CO_3 (excessed 3% each sample) for 30 minutes. The samples were fired in the furnace with oxygen-rich at 550ºC for 5 hours and 900ºC for 12 hours to obtain the cathode active material (with the target composition being $LiNi_{0.8}Mn_{0.1}Co_{0.1-x}Ce_xO_2$).

For sample characterization, X-ray diffraction (XRD) was used to analyze the crystal structure and phase composition using Cu K_α radiation (PANalytical Empyrean).

RESULTS AND DISCUSSION

Precursor Synthesis

There are three methods to dope the precursor on synthesis process using additional material. Such as co-precipitation, sol-gel, and evaporation method. However, this research has used the co-precipitation synthesis process due to its better control parameter among the rest of methods. The precursor final product properties was controlled by some variables as follows; pH level, stirring consistency, temperature, mixing time, and the chelating agent. Theoretically, the role of chelating agent will slow down the reaction during the synthesis and keep it more controlled process [23]. In terms of transition metal, chelating agent will keep the molecule form stability after reacting with metal ions. For instance, the increasing amount of NH_4OH as chelating agent secured the growth of formed crystals on nucleation formation. In this work, oxalates stands to be a chelating agent.

The XRD pattern of cerium doped-precursor NMC 811 product was shown in Fig.1. Ideally, it has only one formed phase due to its homogenity, which is $MC_2O_4.2H_2O$ with M belongs to Ni, Mn, Co, and Ce elements. However, as shown in Fig.1, another phase formed. It has indicated by the existence of small peak in the left side of XRD pattern. For further, the database could not identified the new phase. It seems $Ce_2(C_2O_4)_3$) was formed because the difference of valency factor (the doping atom was Ce^{3+} and the rest atom was M^{2+}). Fortunately, those circumstance did not affect the cerium distribution and still possible to be homogenized during the calcination process.

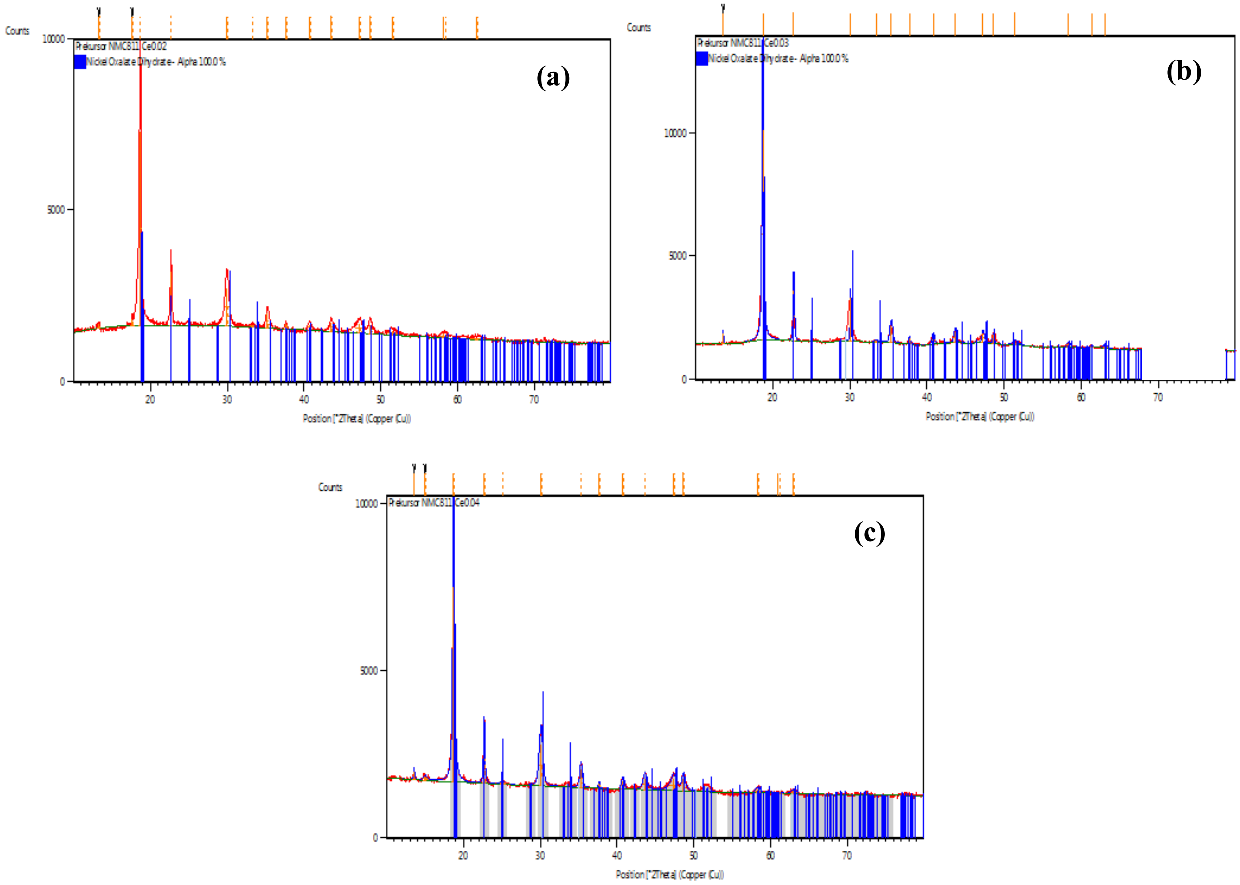

FIGURE 1. XRD patterns precursor of (a) $Ce_{0.02}$-doped NMC 811 (b) $Ce_{0.03}$-doped NMC 811 and (c) $Ce_{0.04}$-doped NMC 811.

Ce-Doped NMC-811 Cathode Structural Study

Fig 2. shows the patterns of XRD from the $LiNi_{0.8}Mn_{0.1}Co_{0.1-x}Ce_xO_2$ (x = 0.02, 0.03, and 0.04). It has discovered that all samples belong to the disordered spinel structure of the Fd3m space group. The diffraction peaks appeared at 18.6°, 36.1°, 44°, and 64.12°. It can be attributed to the (003), (101), (104), and (110) lines of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, respectively. At glance, the diffraction peak is sharp and signifies a fine crystal structure. Furthermore, the existence of diffraction peaks at position $2\theta = 28.5°$, 33.1°, 47.5°,56.3° may be attributed to CeO_2. It was consistent with a previous investigation conducted by Wu *et al.* [25] and Li *et al.* [26].

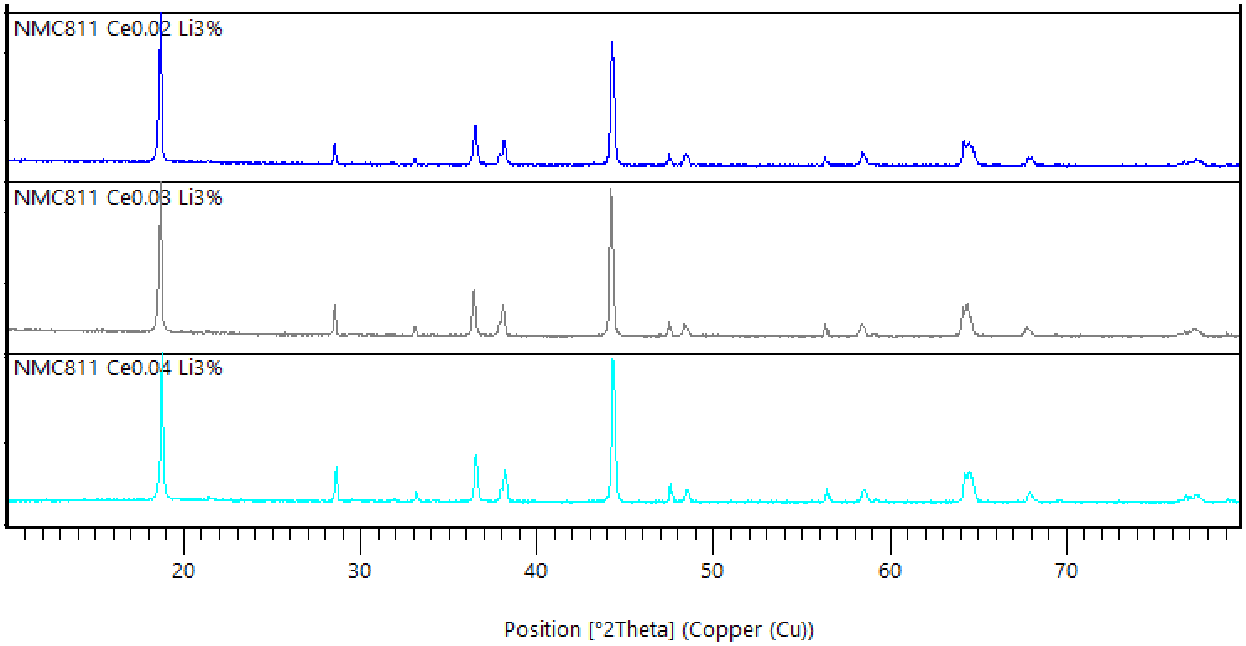

FIGURE 2. XRD patterns of Ce-doped NMC-811 cathode.

XRD pattern after analysis was shown in Fig. 3, which the patterns were well indexed as structure of hexagonal α-$NaFeO_2$ from R-3m space group. The sharp peaks indicated stable structure and complete lattices. The distinct splitting of (108)/(110) and (006)/(012) planes indicated more ordered layered hexagonal structure and a favorable stratified structure. The high ratio of $I_{(003)}/I_{(104)}$=1.34 or more than 1.2 denote desirable cation mixing. The R factor yielded 0.408 and c/a = 4.946 belongs to partial cation mixing, with ideal c/a more than 4.899. In fact, the XRD pattern showed no additional peaks. It means cerium doping did not affect the crystal structure of NMC-811.

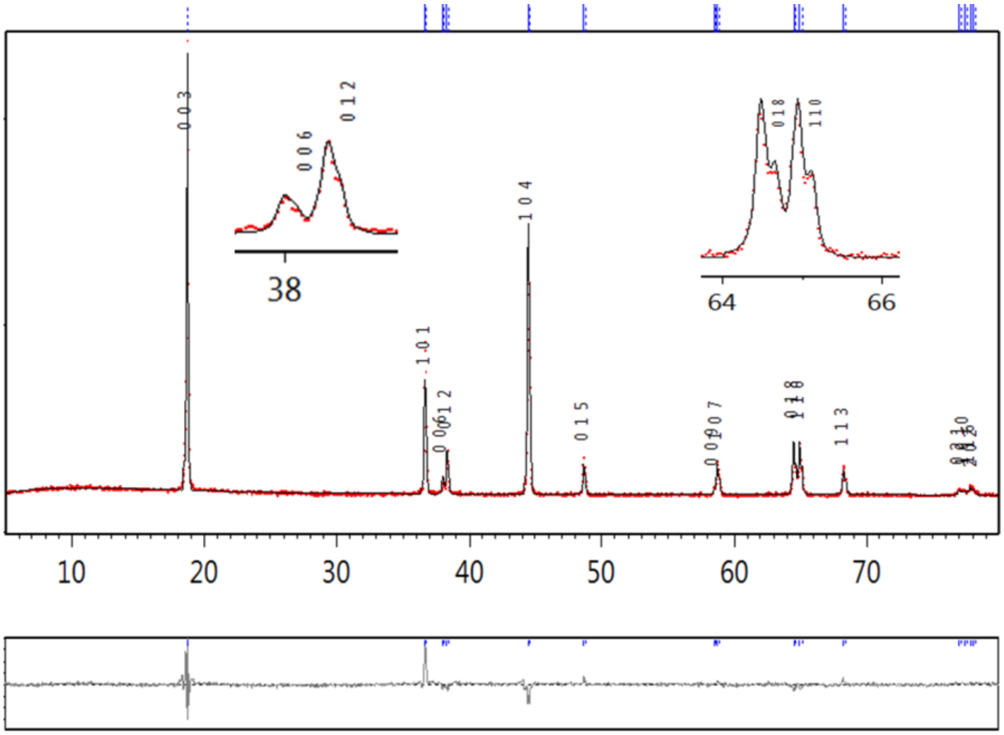

FIGURE 3. XRD pattern of $Ce_{0.04}$-doped NMC 811 after analysis.

After calcination, the CeO_2 phase could be found in XRD pattern. It leads to two possibilities; Cerium doped partially and the rest formed to CeO_2 or all cerium fully transformed to CeO_2. In order to obtain more detailed result, Rietveld refinement was performed to expose the lattice parameters. Table 1 shows the crystallite size calculation and Rietveld refinement results of Ce-doped NMC 811 compared by pristine.

TABLE 1. Refinement result of pristine and Ce-Doped NMC 811

Parameters	**Pristine**	**Ce-$_{002}$**	**Ce-$_{003}$**	**Ce-$_{004}$**
R_{exp}	1.351	2.2	2.2	2.2
R_{wp}	4.796	3.91	3.92	3.92
a (Å)	2.868	2.865	2.866	2.868
c (Å)	14.185	14.185	14.187	14.187
Crystallite size (Å)	834.0	1274.9	1275.3	1275.6

It was observed the value of a-lattice constant between pristine and ce-doped constant, while the c-lattice of ce-doped increased in small scale compared to pristine. Meanwhile ce-doped crystallite size larger than pristine. It means that there is no doping effect happened to layered oxide structure, except the increasing of ce-doped crystallite size. This phenomenon explained by Wu *et al.* [25] in his research within two reasons. First, the increasing of lattice parameters caused by the ionic radius of Ce^{3+} (1.14 Å) is larger than Mn^{4+} (0.54 Å) and Ni^{3+} (0.69 Å). Second, the shrinkage of the cell volume may happen. Its because of the Ce-O bonding energy being stronger than Mn-O and Ni-O. In fact, the first factor is more dominant, but the second factor will has a main role if the cerium composition reached more than 0.03 mol.

In addition, there are two basic characteristic identified excellent doping; the change of lattice parameters (the dopant ionic radius larger than replaced atom radius) and the crystallite size is being smaller. Unfortunately, in this work, the excellent doping is still unable to reach. Because the Co^{3+} as replaced atom has 2.00 Å ionic radius, larger than Ce^{3+} as dopant. Besides, the ce-doped crystallite size is being bigger than pristine. Xu *et al.* [27] observed that cerium doping has decreased Li^+ and Ni^{3+} mixing degree, augmenting the Li^+ amount that is de-intercalated. At glance, the doping in this work is still not optimum because of the calcination process. So, the next repairing step will extend the time of calcination process to obtain the excellent ce-doped NMC 811.

CONCLUSION

Cerium doped NMC 811 cathode active material was successfully conducted by using co-precipitation method. However, it still needs further improvement to obtain excellent doping performance. The time of calcination process need to be extended to gain a better result.

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