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Ce-Doped NMC 811 Synthesis as Cathode Material

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Abstract. One of the promising solutions for broadening the energy access to the rural area is portable energy storage. Government created an initiative so called *Talis (tabung listrik)*. It is a portable energy storage that stores the electricity from renewable energy microgrid for rural area. Yet the minimum weight of *Talis* is almost 5 kg and not too suitable for high-mobility. Lithium ion battery with the cathode materials $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC 811) becomes a promising solution for tackling those heaviness issue. In addition, it also has a high energy density, but limited capacity degradation at higher rate and longer cycles. The performance improvement is needed to overcome such problem. Doping becomes a well-known method for modifying the crystal structure and increasing the cell performance. The cathode material can potentially be doped by rare earth elements (REE). Cerium is the most favorable material among REE due to its widely used for catalyst and addition in various fields. In fact, Indonesia has an abundance REE resource. In this research, NMC 811 has been doped by cerium (IV) sulfate ($\text{Ce}(\text{SO}_4)_2$) using a co-precipitation method followed by calcination for 5 hours. There are three variations of Ce-doped; no doped or pristine (Ce_0), 0.01 mol composition ($\text{Ce}_{0.01}$), and 0.005 mol composition ($\text{Ce}_{0.005}$). For understanding the crystal structure, the product was analyzed by X-Ray Diffraction (XRD). The result shows doping intervention did not alter the layered oxide structure of NMC 811, but only increasing the crystallite size, which is linear with the doping composition.

INTRODUCTION

The electricity shortage has an enormous impact for human life. Not only about low-economic and poverty, lack of electricity also means lack of competitiveness. It also has a causal effect of electrification ratio on certain economic indicator, for instance expenditure and employment [1]. Hence, energy access becomes the seventh Sustainable Development Goals (SDGs) agenda. It declared about universal energy access in which every people in the planet has an access to affordable, reliable, and sustainable electricity [2]. This noble goal is quite challenging to be achieved in Indonesia, since the vary of electrification rates significantly across more than 17,000 islands.

Although in Indonesia the electricity ratio claimed to almost 99.4% by the Ministry of Energy and Mineral Resources (MEMR) [3], the NASA night satellite image showed many areas without light in the east of Indonesia [4]. On the other side, the State Electricity Company has set the target for renewable energy portion by 51.6% on electricity supply business plan (RUPTL) 2021-2030. It provides more rural area with microgrid solar photovoltaic based [5]. For tackling the intermittency issue, the State Electricity Company supplies *Talis (tabung listrik)* as portable energy storage. However, the minimum weight of *Talis* is almost 5 kg and not suitable for high-mobility.

Some scholars believe that lithium ion battery with nickel-rich cathode becomes a promising solution for tackling those heaviness issue. Even many scientists targeted nickel-rich cathode, in which more than 60% nickel composition, to be the top research priority on battery development. Since it obtains a novelty on high energy density with the lightest component and also the quality of cathode materials affects the lithium ion battery performance [6-10]. In Indonesia, the cathode materials $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC 811) has a great challenge to develop, since Indonesia has an abundances global nickel reserve [11, 12]. However, the main problem on NMC 811 cathode is performance drop

at high potential cycle. It caused a low rate capability and obvious capacity degradation. It can be solved by doping with structures modification for improving the electrochemical performances.

The cathode material can potentially be doped by rare earth elements (REE). Because of its high charge and large ionic radius [13]. In addition, Indonesia becomes the biggest deposits for REE [14]. Doping with REE materials have been testified for escalating electrochemical properties. Cerium is the most favorable material among REE due to its widely used for catalyst and addition in various fields. Besides its resource is about 0.0046% in the earth's crust, the highest abundance [14], cerium offers various manifold properties. Such as high thermal stability [15], diffusivity and electrical conductivity [16], and optical properties [17]. Furthermore, cerium also has a fast and direct transformation of Ce (III) and Ce (IV) that represents a lithium battery electrode material [17].

Moreover, Ce³⁺ doped demonstrates a better cycling property, because of its smaller resistance of charge transfer and more layered crystal lattice [18]. Another scholar observed the superiority of Ce-doped on NMC cathode on electrochemical performance compared to non-doped sample [19]. However, the REE doped for cathode nickel rich is still infrequent. Therefore, this research aims to doped the NMC 811 through cerium as one of promising REE and explore the impact for increasing the battery performance. One of the methods that widely used to synthesize NMC cathode is co-precipitation [20]. Because it attains good electrochemical performance. This research aims to synthesize NMC 811 cathode and doped by cerium (IV) sulfate (Ce (SO₄)₂) using co-precipitation method. Then, it is followed by a calcination at 550°C for 5 hours and 900°C for 12 hours.

METHODOLOGY

In this work, the materials used for the synthesis were NiSO₄·6H₂O, MnSO₄·H₂O, CoSO₄·7H₂O, H₂C₂O₄, NaOH, Li₂CO₃ from industrial grade and demineralized water. Analytical grade Ce (SO₄)₂·4H₂O (Merck) was used as the source of Cerium.

In the co-precipitation synthesis, transition metals such as NiSO₄·6H₂O, MnSO₄·H₂O, CoSO₄·7H₂O and doping material Ce (SO₄)₂·4H₂O were dissolved separately in demineralized water. The variation of cerium addition were 0.0, 0.01 and 0.05 mol, denoted by (Ce-₀) or pristine, (Ce-_{0.01}), and (Ce-_{0.05}), respectively. The precipitant solution from NaOH and H₂C₂O₄ was added to the transition metal solution when the temperature raised to 50°C. 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. In addition, cerium also widely observed in the oxalate precursor during the high temperature calcination process [21].

Practically, there are some well-known methods to dope the precursor on synthesis process. From co-precipitation, sol-gel, to evaporation method. However, this research has used the co-precipitation synthesis process due to its better control parameter. The properties of final product precursor 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 [18]. In terms of transition metal, chelating agent will keep the stability of molecule form after reactions. For instance, the increasing amount of NH₄OH as chelating agent secured the growth of formed crystals on nucleation formation. In this work, oxalates stands to be a chelating agent.

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 120°C in 3 hours. Before calcination, the precursor was mixed with Li₂CO₃ for 30 minutes. The samples were fired in the furnace with oxygen-rich at 550°C for 5 hours and 900°C for 12 hours to obtain the cathode active material.

The sample products were characterized by X-ray diffraction (XRD) was used to analyze the crystal structure and phase composition using Cu K_α radiation (PANalytical Empyrean).

RESULTS AND DISCUSSION

Figure 1 (a, b, c) showed the X-RD patterns the samples (Ce-₀) or pristine, (Ce-_{0.01}), and (Ce-_{0.05}), respectively. The x-ray data of Ce-₀ has a single crystalline phase belongs to the hexagonal structure of Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂. All of the powders exhibited a well-defined layer structure based on a hexagonal a-NaFeO₂ structure with a R3m space group and no impurity phases. The x-ray data of Ce-0.01 and Ce-0.05 showed two phases, a hexagonal structure NMC811 and another phase of cerium dioxide 0.5% and 10%, respectively. It seems the filtration process becomes the main factor [17]. It was also observed 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 referred to the (003), (101), (104), and (110) lines of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, respectively. At glance, the diffraction peak is sharp and observed as a fine crystal structure.

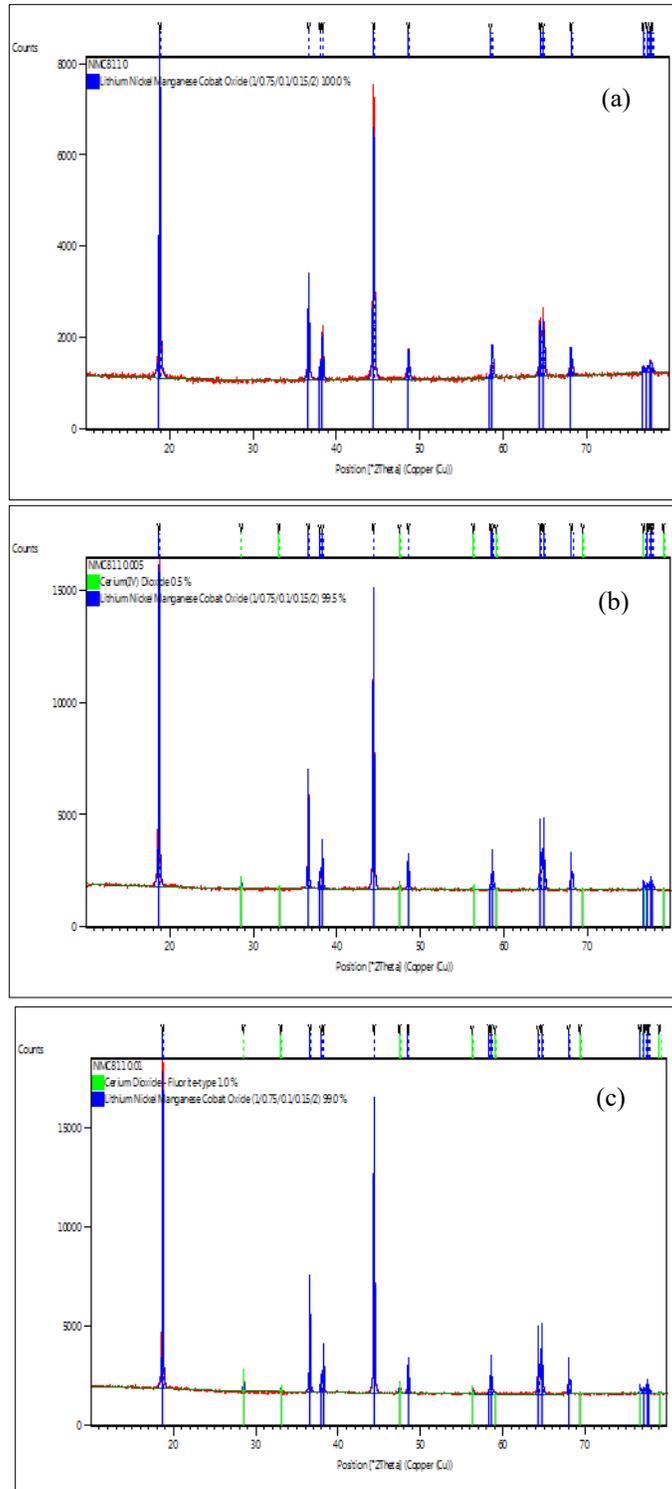


FIGURE 1. The XRD patterns of (a) Ce-0, (b) Ce-0.01 and (c) Ce-0.005

Furthermore, figure 2. presents the existence of diffraction peaks from the doped Ce on NMC811, which marked by an Asterix (*). Those peaks are as follows; 28.5°, 33.1°, 47.5°, 56.3°. The Ce_{-0.01} and Ce_{-0.005} potentially attributed to CeO₂, compared to plain Ce₋₀. It was validated with a previous investigation conducted by Wu *et al.*[8, 19] and Li *et al.* [18].

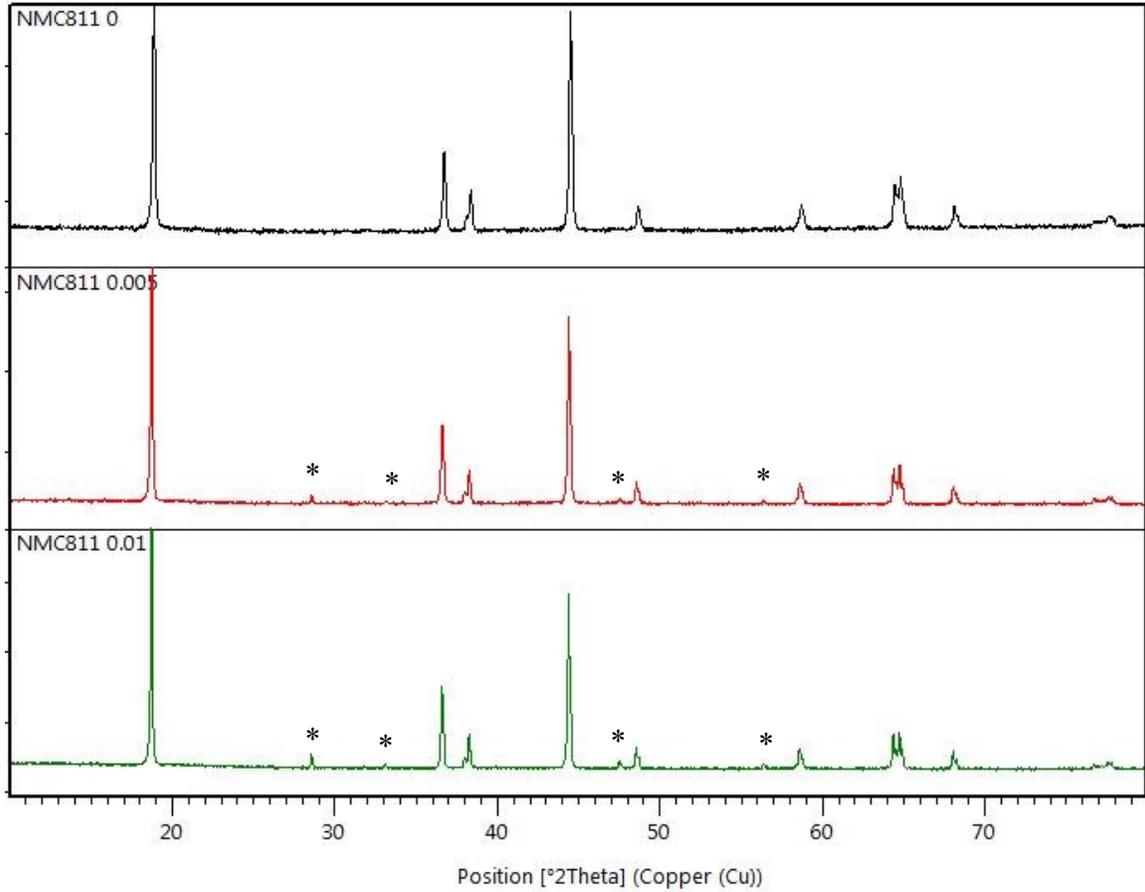


FIGURE 2. The existence of diffraction peaks on Ce-doped NMC-811 cathode.

XRD pattern also showed a well indexed pattern as structure of hexagonal α -NaFeO₂ from R-3m space group. The sharp peaks indicated stable structure and complete lattices. The distinct split 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 comparison between Ce_{-0.01} and Ce_{-0.005} showed a shifting pattern with low angle after doping. It interprets Ce has been successfully doped into the cathode and expands the c axis. It improves the rate capability and worthwhile to the Li⁺ ions migration [22]. In fact, the XRD pattern showed no additional high angle peaks. It means cerium doping did not affect the layered oxide structure of NMC-811.

In order to acquire more details result, Rietveld refinement was operated to expose the lattice parameters. Table 1 shows the crystallite size calculation and Rietveld refinement results of Ce-doped NMC 811.

TABLE 1. Refinement result of Ce-Doped NMC 811

Parameters	Ce-0	Ce-0.01	Ce-0.005
R_{exp}	2.882	2.339	2.352
R_{wp}	3.924	3.181	3.939
a (Å)	2.880	2.877	2.878
c (Å)	14.222	14.209	14.212
Crystallite size (Å)	654.2	1088.0	1987.7

It was observed the value of *a*-lattice almost constant between three samples, while the *c*-lattice of ce-doped decreased in small scale. Meanwhile crystallite size is being larger following the doping composition. 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.* [8, 19] in his research within two reasons. First, the increasing of lattice parameters caused by the ionic radius of Ce³⁺ (1.14 Å) is larger than Ni³⁺ (0.69 Å) and Mn⁴⁺ (0.54 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 has a main role if the cerium composition reached more than 0.01 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 Co³⁺ as replaced atom has 2.00 Å ionic radius, larger than Ce³⁺ as dopant. Besides, the Ce_{-0.01} and Ce_{-0.005} crystallite size is being bigger than Ce₋₀. Xu *et al.* [16] observed that cerium doping has decreased Li⁺ and Ni³⁺ mixing degree, augmenting the Li⁺ amount that is de-intercalated. In addition, the enlargement of lithium layer can potentially obtain by *c* axis enhancement. Such condition will give the benefit to the intercalation/deintercalation of Li⁺ ions during charge and discharge cycle and presides to excellent electrochemical performance [17].

CONCLUSION

Cerium doped NMC 811 cathode active material was successfully conducted by using co-precipitation method. The results show that the Ce-doped on NMC811 did not alter the layer structure of pristine, but exhibits extra phase of Ce-oxide and also increased crystalline size with mol% Ce doping. This affected the enlargement of lithium layer, thus improve cell performance and capacity retention. However, it still needs further improvement to attain an excellent doping performance. The length of calcination process need to be extended to gain a better result. Also, the homogeneity of sample processing is strongly needed.

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