# Effect of Lanthanum Substitution on the Structure and Conductivity of LNMC Samples as Battery Cathodes

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**Abstract**: Lithium-Nickel-Manganese-Cobalt (LNMC) is one of the most successful types of lithium-ion batteries in the market. This battery is a combination of three main metals, nickel, manganese, and cobalt, with relatively the same composition. Measurements was performed on three LMNC materials combined with La composites to reduce the toxicity level of the Cobalt. The purpose of this research is to synthesize and characterize LMNC materials with certain La combinations, thus it is expected to be able to be used as battery cathode. Characterization of materials was carried out using XRD, SEM, and LCR-meter. In this study, we succeed in synthesizing and characterizing LMNC materials with a size of about 150-750 nm. The LCR-meter characterization found conductivity values of approximately $1.06\times10^{-3}$, $7.07\times10^{-4}$, and $4.05\times10^{-3}$ S/cm at 100 Hz, $2.29\times10^{-3}$, $2.56\times10^{-3}$, and $1.34\times10^{-2}$ S/cm at 2.5 MHz, $2.74\times10^{-3}$, $3.04\times10^{-3}$, and $1.51\times10^{-2}$ S/cm at 5 MHz for La dopping with $x$ = 0.01, 0.03, and 0.05, respectively. The La substitution increases the conductivity value and reduces the particle size to nanoscale.

Keywords: LMNC; La dopping; Cathode; Battery

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## I. INTRODUCTION

Up till now, lithium (Li) ion is the main material for the cathode in the battery, while the material for the anode depends on the type of battery. The rechargeable ones use carbon, and the non-rechargeable ones use Li metal. For rechargeable Li ion-based batteries, the anode (carbon) acts as the negative pole and lithium ions serve as the cathode as well as the Li source. The reaction in it is not a redox reaction, it is the movement of Li ions through the electrolyte used. In this case, the materials usually used as cathodes are $LiCoO_2$, Li-Mn-O, $LiFePO_4$, and layered Li metal oxide [1].

Research on battery cathode materials made from Lithium-Nickel-Manganese-Cobalt (LNMC) has been intensively carried out by several researchers in recent years [2–19]. This is because the LNMC cathode material has high performance, a high-power density, a long life and meets safety standards [2–19]. LNCM-based materials, namely $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM 111), are currently widely used as cathodes in electric vehicles and hybrid electric vehicles because of their high energy density, long lifetime, and safety [2–19]. Increasing the energy density or ability can be done by adjusting the structure and morphology [2, 3, 7, 8, 10, 11, 15]. Several studies have been carried out by substituting La in battery materials, including $LiFePO_4$ and $CoFe_2O_4$ anode materials, showing an increase in battery conductivity and performance [20, 21].

To overcome the problems faced today, we conduct a study on Lithium-Nickel-Manganese-Cobalt (LNMC) materials with La combinations to reduce the toxicity level of the cobalt. The purpose of this research is to synthesize and characterize LNMC materials with certain La combinations which are expected to be able to become battery cathode materials.

## II. METHOD

Samples of $LiNi_{0.8}Mn_{0.1}Co_{0.1-x}A_xO_2$, with $A$ = La, and $x$ = 0.01; 0.03; and 0.05 as battery cathode materials, were made from $Li(OH)_2$, $Ni(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$, and $A(OH)_3$ ($A$ = La), each with purity more than 99%. The mixture of these materials was put in a stainless-steel vial and then processed through a solid-state reaction method using high energy milling (750 rpm) for 10 hours. After that, it was heated at a temperature of 800 $^o$C for 5 hours in the open air in the form of pellets pressed with a pressure of 5000 kg. X-ray diffractometer (XRD) Philips PW1710 type with Cu-K$\alpha$ radiation and a wavelength of 1.5406 Å at a diffraction angle of $2\theta$ = 20- 80$^o$ was used to characterize the phase formation and crystal structure formed. SEM JEOL-type, JED 2300, was used to see the shape and morphology of the granules. The electrical conductivity of the material was characterized by LCR-meter HIOKI-5020 type.

## III. RESULTS AND DISCUSSION

Figure 1 shows the diffraction patterns of $LiNi_{0.8}Mn_{0.1}Co_{0.1-x}La_xO_2$ samples with $x$ = 0.01, 0.03, and 0.05. The results of the refinement using the GSAS program showed that all samples were not in a single phase. Some

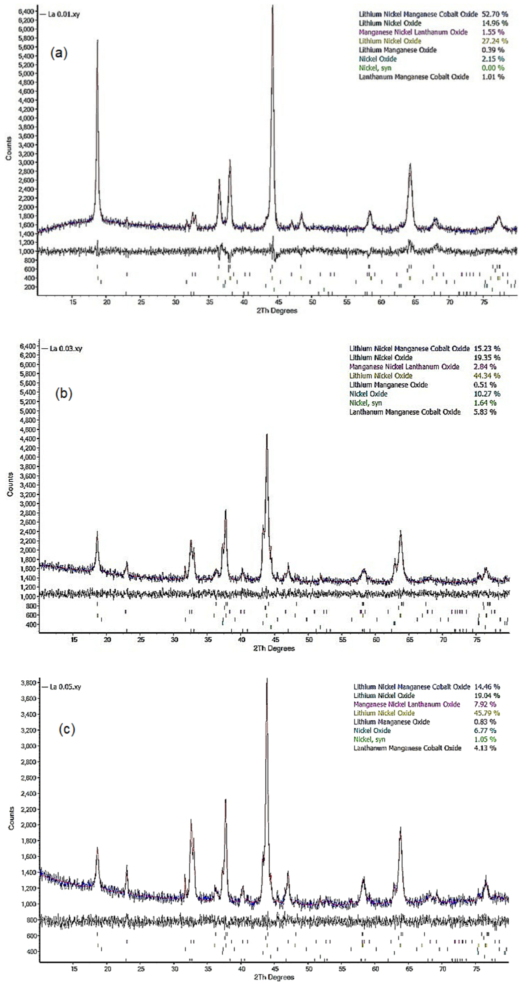


FIG. 1: Rietveld refined results of XRD patterns of $LiNi_{0.8}Mn_{0.1}Co_{0.1-x}La_xO_2$ with (a) $x$ = 0.01, (b) $x$ = 0.03, and (c) $x$ = 0.05.

TABLE I: Relative percentage of each phase obtained by Rietveld refinement of XRD pattern.

| Phase | La-concentration ($x$) | | |
|---|---|---|---|
| | $x$ = 0.01 | $x$ = 0.03 | $x$ = 0.05 |
| LMNC | 52.70% | 15.23% | 14.46% |
| $Li_{0.524}Ni_{1.476}O_2$ | 27.24% | 44.34% | 45.79% |
| $LaMn_{0.25}Ni_{0.75}O_3$ | 1.55% | 2.84% | 7.92% |
| $Li_{0.524}Ni_{1.476}O_2$ | 27.24% | 44.34% | 45.79% |
| $Li_{0.91}Mn_{1.92}O_4$ | 0.39% | 0.51% | 0.83% |
| NiO | 2.15% | 10.27% | 6.77% |
| $La_{0.00064}Ni_{0.99946}$ | 0.00% | 1.64% | 1.05% |
| $LaMn_{0.4}Co_{0.6}O_3$ | 1.01% | 5.83% | 4.13% |

secondary phases were found. By using one pot synthesis, it turned out that the LMNC phase was formed even though the percentage was still low, hence the secondary phases to appear. The relative percentages of the formed phases are summarized in Table I. Moreover, the crystal structure, space group, and lattice parameters of the obtained LNMC can be seen in Table II.

TABLE II: Rietveld refined result of $LiNi_{0.8}Mn_{0.1}Co_{(0.1-x)}La_xO_2$ with $x$ = 0.01, 0.03, and 0.05.

| | $x$ = 0.01 | $x$ = 0.03 | $x$ = 0.05 |
|---|---|---|---|
| Space Group | R-3mH | R-3mH | R-3mH |
| Cell Mass | 277.34(8) | 277.35(1) | 277.35(1) |
| Cell Volume (Å$^3$) | 102.70(2) | 103.84(2) | 104.18(1) |
| Crystal Density (g/cm$^3$) | 4.484(1) | 4.435(1) | 4.421(1) |
| Lattice parameter: $a$ (Å) | 2.8865(2) | 2.8982(2) | 2.9025(3) |
| Lattice parameter: $c$ (Å) | 14.2339(1) | 14.2750(0) | 14.2792(0) |
| Rexp | 2.45 | 2.58 | 2.93 |
| Rwp | 3.09 | 2.87 | 3.16 |
| GoF | 1.26 | 1.11 | 1.08 |

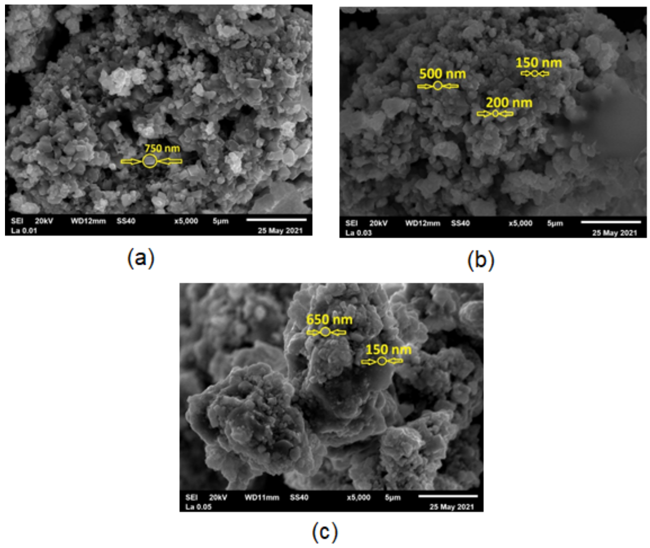


FIG. 2: Result of SEM-EDS analysis of La dopping with (a) $x$ = 0.01, (b) $x$ = 0.03, and (c) $x$ = 0.05.

The results obtained have not met expectations. It is possibly because the milling time (10 hours) or the sintering temperature (800°C) are not sufficient enough. The temperature and duration of sintering influence phase formation. In several studies, it was found that the sintering temperature of 1000 - 1400°C for 2 hours gave optimum results to make promising compounds for scientific and technology applications [17–19].

The results of the refinement are also supported by observations of particle surface morphology for the two composites using SEM as shown in Fig. 2. Although the composites appear to agglomerate and are still heterogeneous in shape, the particle size ranges from 150 - 750 nm. The cause of agglomeration can be in the form of inherited characteristics of the sample, the solvent evaporation process, or by thermal effects, for example sintering or glass transition [23]. Agglomeration causes the sample particle size to be non-uniform. The effect of La substitution can be observed in the particle size $i.e.$, the cell volume increases with the increase in $x$ (see Table II). This is consistent to the fact that the radius of the La ion is larger than the Co ion. Thus, La substitution increases the crystalline size.

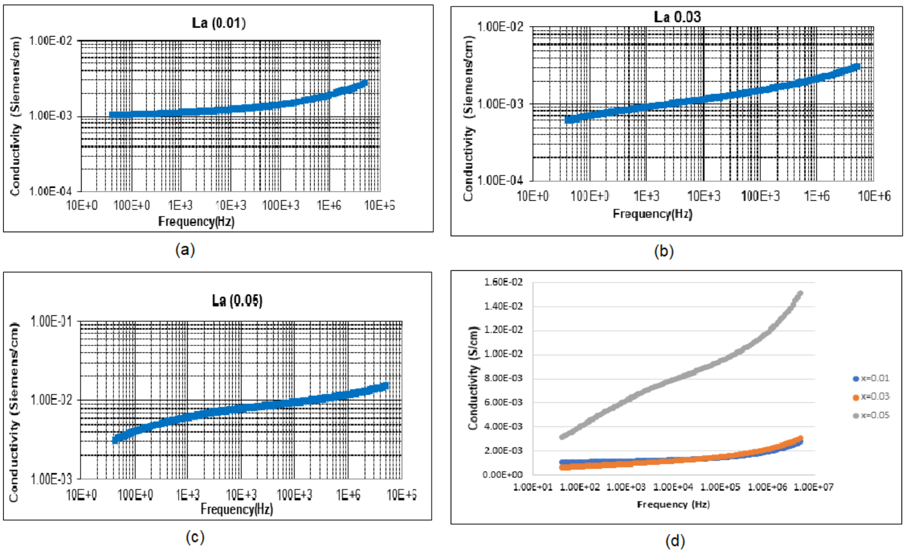


FIG. 3: LCR measurement results for La dopping samples with (a) $x$ = 0.01, (b) $x$ = 0.03, and (c) $x$ = 0.05. (d) Overlaid graph of all samples.

TABLE III: The conductivity of samples with variation of La doping.

| $x$ | Frequency (Hz) | Conductivity (S/cm) |
|---|---|---|
| 0.01 | 100 | $1.06\times10^{-3}$ |
| | $2.5\times10^{6}$ | $2.29\times10^{-3}$ |
| | $5\times10^{6}$ | $2.74\times10^{-3}$ |
| 0.03 | 100 | $7.07\times10^{-4}$ |
| | $2.5\times10^{6}$ | $2.56\times10^{-3}$ |
| | $5\times10^{6}$ | $3.04\times10^{-3}$ |
| 0.05 | 100 | $4.05\times10^{-3}$ |
| | $2.5\times10^{6}$ | $1.34\times10^{-2}$ |
| | $5\times10^{6}$ | $1.51\times10^{-2}$ |

Figure 3 shows the results of LCR measurements using LCR-meter. The complete results of LCR characterization can be seen in Table III. The presence of nickel metal and other phases that appeared causes the conductivity to increase even though the LMNC presentation decreased. On the combined graph of all values of $x$ (Fig. 3d), at low frequencies, the conductivity at $x = 0.01$ is higher than $x = 0.03$. This is because at low frequencies the ions are dominant, while at high frequencies the electrons are moving.

Synthesis and characterization of battery cathode material with Lithium-Nickel-Mangan-Cobalt (LNMC) material have been successfully made with a particle size is about 150 - 750 nm. This is in line with the results obtained by Yuan $et al.$ and Vijayan $et al.$ that the effect of La substitution is to increase the conductivity value and reduce the particle size to nanoscale [16, 20]. It is indeed an effective way to improve the conductivity of LNMC material [21, 22].

## IV. SUMMARY

The battery cathode material of Lithium-Nickel-Mangan-Cobalt (LNMC) with La substitution was successfully synthesized and characterized. The obtained compound has the particle size of 150-750 nm. The surface morphology shows that particles tend to agglomerate, but it is still heterogeneous in shape. The conductivity values of LNMC samples with $x$ = 0.01, 0.03, and 0.05 are $1.06\times10^{-3}$, $7.07\times10^{-4}$, and $4.05\times10^{-3}$ S/cm at 100 Hz, $2.29\times10^{-3}$, $2.56\times10^{-3}$, and $1.34\times10^{-2}$ S/cm at 2.5 MHz, $2.74\times10^{-3}$, $3.04\times10^{-3}$, and $1.51\times10^{-2}$ S/cm at 5 MHz, respectively. The La substitution affects in an increase of the conductivity value and reduces the particle sizes to nano-scale. Our suggestions for further research are to increase the sample milling time of at least 50 hours for each sample, to enhance the heat temperature of at least 1000°C, and to prepare samples with different La compositions.

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