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La-Incorporated NMC811 as a New Li-ion Battery Cathode Material

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Abstract. The application of high energy density $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) is often limited by its discharge capacity retention due to its rich nickel content. Some improvements such as doping and coating by rare earth materials have been used to increase the electrochemical stability. In this work, Lanthanum was used to modify NMC811 via a simple solvent evaporation method. The XRD results showed the presence of an additional phase in the form of $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$, though that there was no change in the lattice parameters. SEM-EDS results with La mapping showed that La was evenly distributed forming a layer of $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ on the surface of the NMC811 particles, without any La atoms entering the layered oxide structure. The formation of new layer on the surface will improve stability and electrochemical performance of NMC811.

INTRODUCTION

As one of the most promising cathode, NMC811 ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$) is expected to be the most widely applied cathode type in EVs due to its high energy density [1-2]. The high capacity is due to the high nickel content, which is a major contributor on increasing NMC cathode capacity. However, the high Ni content was also accompanied by a decrease in the stability of the cathode surface which resulted in a significant decrease of discharge capacity in longer cycles [3]. Various efforts have been made to improve the performance of NMC811, such as doping or coating with rare earth materials. Lanthanum (La) is one them, that often used to enhance the cycle ability of cathode materials. Lanthanum can be used as a dopant to modify the crystal lattice or as a coating layer on the surface of the cathode particles. This coating layer can be a unary, binary, or ternary oxide [4].

In this study, La will be used to modify NMC811 by solvent evaporation method. The effect of La will be investigated in terms of the phase composition, the crystal structure and the particle morphology.

METHODOLOGY

Materials

Technical grade $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were used as the source of transition metals of the cathode materials. For precipitating solution, a mixture of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), NaOH and ammonia was utilized. Li and La source for of NMC cathode was LiOH and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively. All chemicals used in this study was technical grade except for analytical grade 25-% ammonia solution, LiOH and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Merck). Distilled water was used for the whole processes, that need water.

Sample Preparation

NMC precursor was prepared by oxalate co-precipitation. Metal sulphates with a composition of Ni:Mn:Co=8:1:1 were dissolved in distilled water to get 2M solution. A 0.5 M Oxalate solution as precipitating agent was obtained by dissolving equimolar Oxalic Acid and NaOH. A proper amount of 25%-ammonia solution was added to the solution as chelating agent. Co-precipitation reaction was conducted in 25 L batch reactor. Firstly, precipitating solution was poured to the reactor and heated to 60°C followed by continuous agitation. Then, an equimolar metal sulphates solution was added. Reaction was maintained at 60°C for 5 hours with continuous stirring. Precipitate was collected filtered and washed thoroughly to remove various water-soluble impurity. The precursor was dried in an oven at 110°C, and then heated at 700°C for 2 hours to obtain metal oxide precursor. The metal oxide powder was dispersed in distilled water for an hour with 1:4 wt./vol. solid to liquid ratio. A proper amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and LiOH were dissolved into the suspension to get a resulting mixture of 1%-mol La and 5%-stoichiometric excess of Li. The mixture was then heated at 80°C to evaporate the water solvent. The dried solid mixture was calcined at 800°C for 12 hours at 5°C/min heat rate and the product was referred as La-NMC811. As comparison, bare NMC cathode was also prepared by mixing metal oxide precursor with 5%-excess LiOH. The calcination procedure was the same as La-incorporated sample and the product was referred as bare-NMC811.

Sample Characterization

X-Ray Diffraction (XRD, PANalytical Empyrean) was utilized to investigate the phase compositions and crystal structures. Morphology and mapping of atomic composition of the particle were characterized by using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS, JEOL JSM6510LA).

RESULTS AND DISCUSSION

Sample Characterization

Figure 1 shows XRD patterns of bare-NMC811 and La-NMC811. Both patterns were well indexed as $\alpha\text{-NaFeO}_2$ hexagonal structure layered oxide. For the La-NMC811, there were some additional peaks corresponding to $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ phase. The Rietveld refinement results and crystallite size analysis were listed in Table 1. It is shown that the lattice parameters were not much different, showing that the addition of La caused the formation of La compound, not the penetration of La atoms to the structure of layered oxide that could enlarge the lattice parameters [5–8].

Inset picture in Fig. 1 shows the magnification of two pairs of adjacent peaks at 2θ of 37.5–38.5° and 64–65°. The separation of the peaks (006)/(012), and also (018)/(110) is an indicator of the ordering of the layered hexagonal structure [9–12]. Both samples showed clearly separate peaks of the two pairs peaks. However, La-NMC811 had more distinct peaks, meaning that La-NMC811 had higher order crystalline structure.

A c/a ratio of more than 4.96 indicates the occurrence of cation mixing, where a few Ni^{2+} ions that should be at the 3a site swap places with Li^+ ions at the 3b sites because of their similar ionic radii. The ideal value of the ratio despite the cation mixing is more than 4.899 [9–10]. Both samples show values that are still in the range of 4.899–4.96 which indicates the occurrence of cation mixing but is still within ideal limits.

There are also three more parameters that can be used to evaluate the quality of the hexagonal layered oxide crystal structure (1) $I_{(003)}/I_{(104)}$ ratio, (2) R value, and (3) lattice ordering factor, y . The formula of R and y are given in Table 1. The higher $I_{(003)}/I_{(104)}$ ratio, the lower the degree of cation mixing that occurs. Desired cation mixing is obtained when the value of $I_{(003)}/I_{(104)} \geq 1.2$ [9–10]. In Table 1, the ratio of $I_{(003)}/I_{(104)}$ of La-NMC811 was 1.203 indicating a desired cation mixing, whereas the bare-NMC811 has the value lower than 1.2 showing excessive cation mixing. The lower the R value and the higher the y value, the higher the lattice ordering of the NMC crystal structure [9]. The addition of La had increased a lattice ordering and decreased a $\text{Li}^+/\text{Ni}^{2+}$ cation mixing. Those values exhibited better qualities of the coated La-NMC811, that can improve electrochemical performance of the battery.

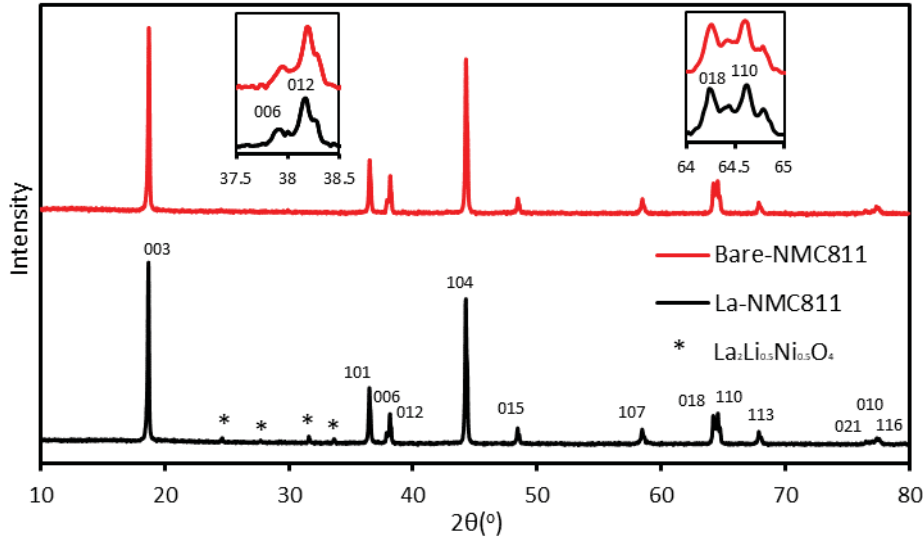


FIGURE 1. XRD patterns of bare-NMC811 and La-NMC811.

TABLE 1. Rietveld refinement and size analysis results of XRD patterns

Parameters	Bare-NMC811	La-NMC811
R_{exp}	2.335	2.429
R_{wp}	3.725	3.475
a (Å)	2.884	2.881
c (Å)	14.229	14.222
c/a	4.934	4.936
$I_{(003)}/I_{(104)}$	1.203	1.161
$R=[I_{(012)}+I_{(006)}]/I_{(101)}$	0.951	0.740
$y=1.073-0.228R+0.039R^2$		
Crystallite size (Å)	1026.8	1113.1

The SEM images of both samples are shown in Fig. 2. Both bare-NMC811 and La-NMC811 had single crystal-like irregular shapes and formed aggregates. This may be due to the nature of oxalate precursor, $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which is decomposed below 350°C . The heating process to obtain the oxide compound at 700°C caused agglomeration of the precursor, and further agglomeration of the solid phase reaction with LiOH. This is also consistent with previous studies using oxalate precursors, which the calcined NMC particles tend to agglomerate [11-16]. Particle sizes of La-NMC811 were bigger than the bare-NMC811, which is in agreement with the calculation of the crystallite size in Table 1.

The EDS mapping of La, Ni, Mn, Co, and O on La-NMC811 was shown in Fig. 3. All the atoms were distributed evenly, including La atoms. From this experiment, it can be concluded that the addition of La by evaporation of the solvent from a system consisting of La, Li and NMC precursor gave the result of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ -coated NMC product. The addition of La was initially expected to be as a doping of La atoms or La_2O_3 coating. However, it turned out that Lanthanum reacted with a small amount of Ni on the surface of the precursor and Li of LiOH to form $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$. Previous studies using similar method at the NCA cathode also resulted in the formation of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ instead of La_2O_3 . In a study in which La was added to NMC532, $\text{LaNi}_{0.5}\text{Co}_{0.5}\text{O}_3$ phase was formed together with $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$. This may be due to the higher amount of Co and lower Ni compared to NMC811. This indicates that the $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ phase is preferably to form, instead of La_2O_3 , when there is sufficient Ni on the surface of the precursor particles or cathode.

The usage of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ as a coating layer has been proved to be beneficial in increasing the performance of the Ni-rich layered oxide cathode. $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ coating layer can increase the electronic and ionic conductivity significantly [17-18]. This coating layer can also result in increasing stability at higher working voltage and temperature [19-20].

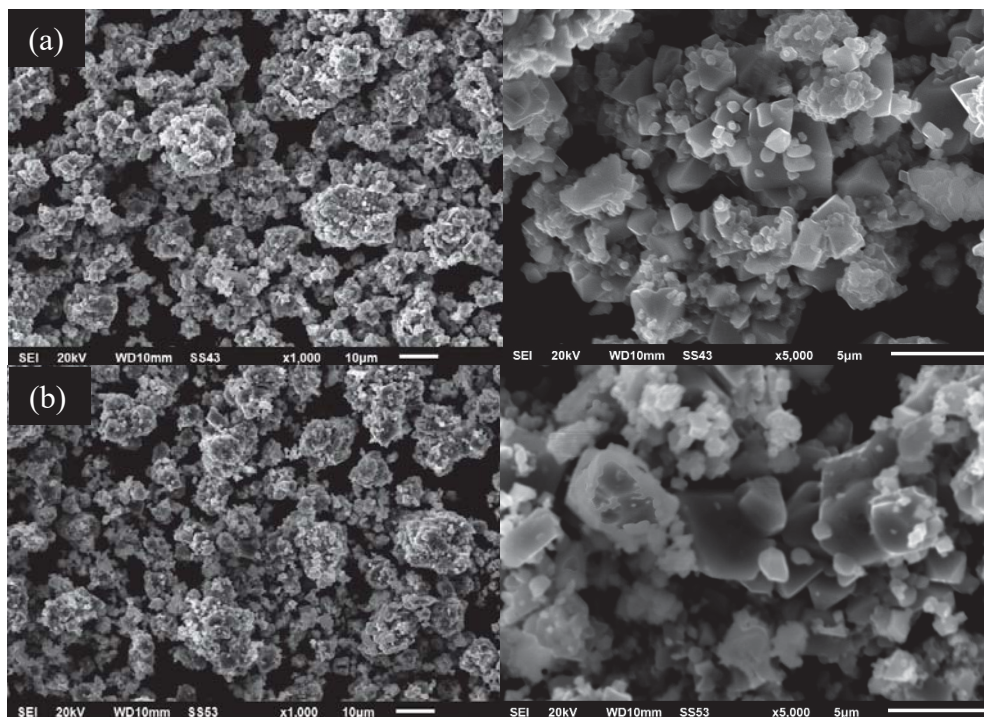


FIGURE 2. SEM image of (a) Bare-NMC811, and (b) La-NMC811.

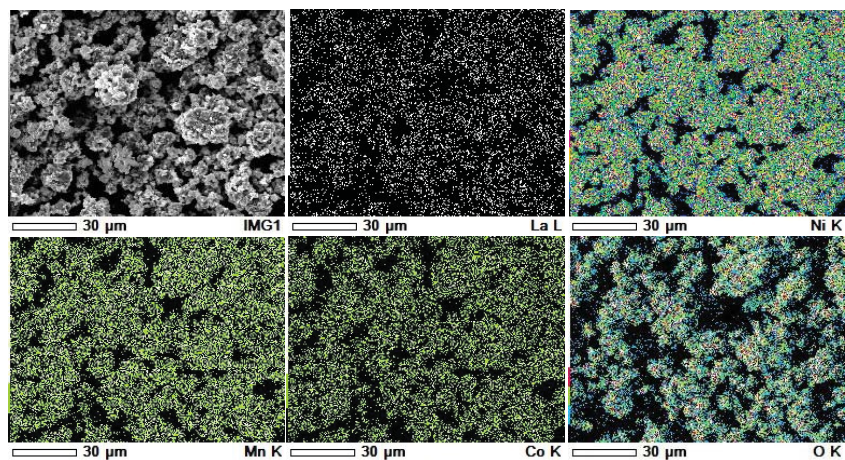


FIGURE 3. EDS mapping of La-NMC811

CONCLUSION

La-NMC811 was successfully synthesized by adding La together with lithium into the precursor NMC811. Analysis of XRD and SEM indicated that La was coated on the surface of NMC811 particles in the form of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ instead of predicted La_2O_3 coating or La doping. Thus, direct addition of proper amount of La compound to the mixture of Li source and Ni-rich NMC precursor can successfully produce NMC cathode coated by beneficial $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ layer. From previous studies, $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ has been known to be beneficial in significantly increasing thermal and high voltage stability of NMC cathode.

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