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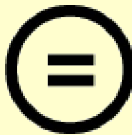
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공학석사 학위논문

Observation of Synergistic Effects of  
Blended Cathode in Lithium Ion Battery

리튬이온배터리 혼합양극의 시너지 효과 연구

2020년 8월

서울대학교 대학원

공과대학 재료공학부

박 순 찬

# Observation of Synergistic Effects of Blended Cathode in Lithium Ion Battery

리튬이온배터리 혼합양극의 시너지효과에 대한 연구

지도교수 김 미 영

이 논문을 공학석사 학위논문으로 제출함

2020 년 7 월

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## **Abstract**

# **Observation of Synergistic Effects of Blended Cathode in Lithium Ion Battery**

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From the past, lithium ion batteries have been widely used in the form of small batteries such as mobile phones, notebooks, and power tools. However, beyond the demand for small batteries, research and development are currently underway to use in the form of medium and large batteries such as electric vehicles and energy storage system. In particular, as the electric vehicle industry develops based on the eco-friendly policies, interests and expectations for lithium ion batteries will increase in the future.

As the shape of lithium ion batteries changes from small to medium and large, the safety is considered to be the most important factor. In addition, high capacity and long life characteristics are required as important factors as

safety. In order to develop a battery that satisfies these various performances, many researches and studies are being conducted on materials.

Since commercialized in 1991,  $\text{LiCoO}_2$ , a cathode material, has been used widely in lithium ion batteries, but it has several problems. The first problem is that due to the irreversible structural transition, only half of the theoretical capacity can be used. The second problem is that the price fluctuation of cobalt caused by unstable supply. Therefore, a high capacity and low cost NCM and NCA based cathode materials compared to  $\text{LiCoO}_2$  have been developed and they are considered as a promising material. This kind of materials exert different properties depending on the composition ratio of the elements. Generally, as the ratio of nickel increases, the capacity is getting higher and lifespan is getting shorter.

In this study, an electrode was fabricated by blending  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) material with long lifespan and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) material with high capacity. Three types of cathodes which are individual NCM, NCA and blended were used to manufacturing 2032 coin half cell. And we evaluated various electrochemical performance of coin cells and performed structural analysis such as XRD and TEM.

Previous studies on blended cathodes were conducted by blending two materials with different structures such as layered-spinel or layered-olivine.

However, this study differs in that we used the same layered structure materials. This study on NCM and NCA blended cathode with long life characteristics is expected to contribute to the development of lithium ion batteries with excellent performances.

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**Keywords :** Lithium ion battery, blended cathode, layered structure materials

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# **Chapter 1. Introduction**

Environmental pollution is accelerating due to the excessive use of fossil fuels. Therefore, environmental regulations are being strengthened worldwide, and this is changing the automobile market from internal combustion engines to electric vehicles. The battery of electric vehicles replaces a role of an engine in internal combustion engine vehicles. This means that the battery determines the performance of electric vehicles. Thus, interest and expectation in batteries is increasing.

Lithium ion batteries are used in electric vehicles<sup>1</sup>. Lithium ion battery is a secondary battery that can be used semi-permanently by charging and discharging process<sup>2</sup>. Because of high capacity per unit weight and volume, high operation voltage, long lifespan and eco-friendly, lithium ion batteries are energy source that has been used a lot since the past<sup>3-4</sup>. Lithium ion battery is composed of four elements which are cathode, anode, electrolyte and separator. Among these components, a cathode is the most important part because it determines the performance of cell and occupies the highest ratio of materials cost. Therefore, we have to research and development cathode materials.

The cathode materials can be divided into three types according to the structure, such as olivine, layered and spinel<sup>5</sup>. The olivine structure materials have one-dimension path of lithium ions. They are cheap and have a long lifespan due to the stable structure. The layered structure materials have two-dimensions path of lithium ions and have the characteristics of high capacity. The spinel structure materials are cheap and have an advantage of power performance because of three-dimensions path of lithium ions. Since each material has its own characteristics, we have to use appropriate materials for the purpose of use. In the case of batteries for electric vehicles, they require a high energy density because the vehicles have to drive a lot distance by one charge<sup>6-7</sup>. Therefore, the layered structure materials are considered as promising materials.

Since commercialized in 1991,  $\text{LiCoO}_2$ , a cathode material that is still widely used, has several problems<sup>3,8,9</sup>. The first problem is that due to the irreversible structural transition, only half of the theoretical capacity can be used<sup>11</sup>. The second problem is that the price fluctuation of cobalt caused by unstable supply. To solve these problems, many researchers developed the NCM and NCA materials which have same structure with  $\text{LiCoO}_2$ . The only difference between  $\text{LiCoO}_2$  and NCM, NCA is a replacement of transition metal ions. These NCM and NCA materials have the advantages in the

perspective of performance and cost<sup>12</sup>. Generally, NCM and NCA materials tend to as the ratio of nickel increases, the capacity is getting higher and lifespan is getting shorter<sup>13-14</sup>. Thus, various methods, such as doping, coating, core-shell structure materials and gradient materials are used to develop cathode materials with high capacity, long lifespan and safety.

One method of developing cathode materials is to manufacture electrodes by physically blending two or more different materials. In the past, many studies of blending layered materials and spinel materials has been conducted<sup>15-17</sup>. The main goal was to fabricate an electrode that exerts all of their advantages by blending layered materials with high capacity and spinel structures with high power, thermal safety and low cost. And now, layered and spinel blended materials are used in electric vehicles.

In this study, we fabricate a blended cathode by blending NCM and NCA materials. They have a same layered structure, but different nickel ratio. And we evaluate the performance of blended cathode coin cell. The goal is to manufacture a cathode having an excellent performance by blending low nickel NCM and high nickel NCA. Low nickel NCM has a long lifespan and high nickel NCA has a high capacity. This study on NCM and NCA blended cathode with long life characteristics is expected to contribute to the development of lithium ion batteries with excellent performances.

## **Chapter 2. Literature Studies**

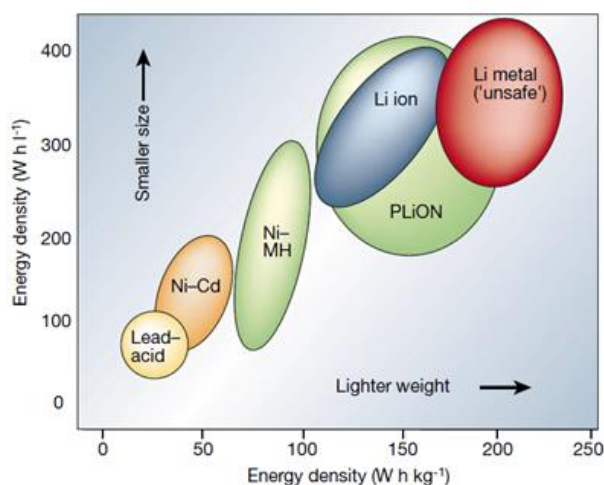
### **2.1. Lithium Ion Battery**

Lithium ion battery is an energy storage device that converts chemical energy generated by a chemical reaction between a positive electrode and negative electrode into an electrical energy. Lithium ion battery, one type of secondary battery that can be charged and discharged, has the advantage of high capacity per unit volume and weight compared to other energy storage devices. In addition, it has a lot of advantages, such as high operation voltage, long lifespan and eco-friendly. Because of these various advantages, lithium ion batteries are currently used in small products such as mobile phones, notebooks and power tools. And now, beyond the demand for small devices, for the purpose of use in medium and large devices such as electric vehicles and energy storage system, various research and development are underway, recently.

Lithium ion battery is composed of four elements which are positive electrode, negative electrode, electrolyte and separator. Positive and negative electrodes are the place where lithium ions are stored. Therefore, the structure of electrode materials must be stable and easy to move lithium ions. The

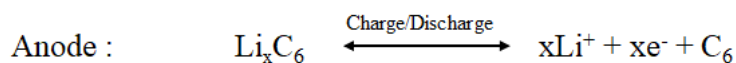
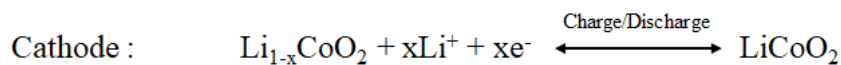


electrode of lithium ion battery is composed of an active material, a conductive agent and a binder. An active material is the place where lithium is stored and a conductive agent facilitates the movement of electrons in the electrode. And a polymer binder keep adhesion all kinds of these electrode materials. An electrolyte consists of a lithium salt dissolved in an organic solvent. Lithium ions can move through electrolytes between positive and negative electrode. The requirements of electrolytes are a high lithium ions conductivity and large electrochemical window not to react in operation voltage. A separator is in the form of less than 20  $\mu\text{m}$  thick porous polymer membrane. It hinders a direct contact between positive and negative electrodes. And also, lithium ions must be easy to pass through the separator. Lastly, aluminum and copper are used as a positive and negative current collector. They are used to provide conduction of electrons from the electrodes to external circuit.

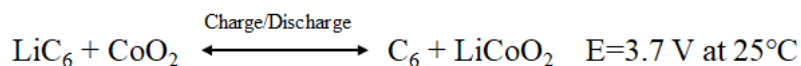


**Figure 1.** Comparison of the different battery technologies in terms of volumetric and gravimetric energy density<sup>3</sup>

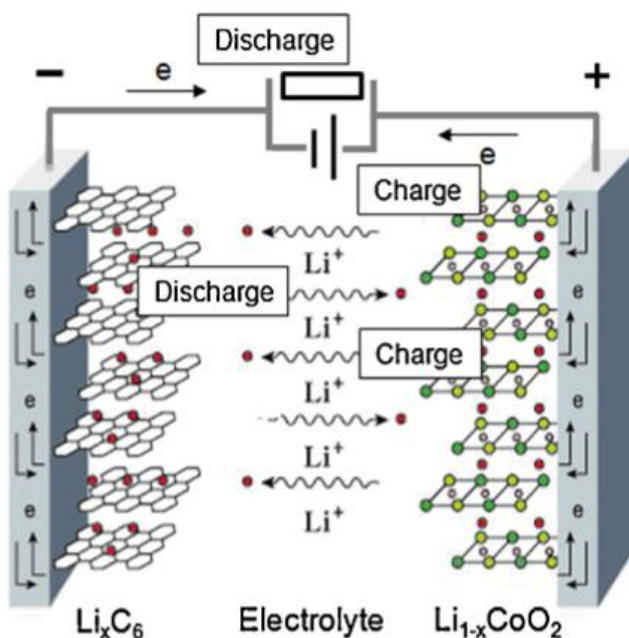
The electrochemical reaction between positive and negative electrodes of lithium ion batteries is described below. It shows an electrochemical reaction of the cell that the positive electrode is  $\text{LiCoO}_2$  and the negative electrode is graphite.



Full Cell Reaction :



In the process of charge, lithium ions are extracted out from the  $\text{LiCoO}_2$  cathode. And then, they go inside of graphite anode through electrolytes and stored. At the same time, electrons move from the  $\text{LiCoO}_2$  cathode to graphite anode through external circuit. During discharge, this mechanism occurs in reverse, lithium ions and electrons move from the graphite anode to the  $\text{LiCoO}_2$  cathode. And in this process, an electrical energy is generated.



**Figure 2.** Schematic figure of a lithium ion battery composed of graphite anode and  $\text{LiCoO}_2$  cathode<sup>10</sup>

The energy that can be stored and extracted in the lithium ion battery through charge and discharge process can be expressed as the product of capacity and operation voltage.

$$\text{Energy density (Wh)} = \text{Capacity (Ah)} \times \text{Voltage (V)}$$

A capacity is determined by the amount of lithium that can be stored in the cathode and anode. And operation voltage of lithium ion battery cell is determined by the difference between a chemical potential of cathode and anode. Therefore, in order to exert a high operation voltage, we have to select a material having a low lithium chemical potential for the cathode and a high lithium chemical potential for the anode.

There are several factors to consider when evaluating cell performance such as specific capacity, power density, lifespan and safety etc. The specific capacity refers to the capacity that can be exerted per weight of the active material and it is proportional to the amount of lithium that can be stored in electrodes. The power density is similar with rate capability and can be calculated by multiplying the current and voltage of operating cell. This factor is related to the impedance generated inside the cell, and the lower internal impedance, the better power characteristics. The lifespan means that the cycle

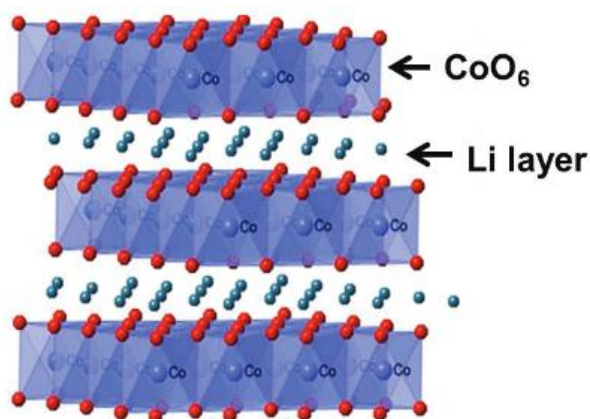
numbers until the specific capacity becomes below a certain level. This is because irreversible structure transition occurred by continuous charge and discharge process. Therefore, the lifespan of cell is influenced by the crystal structure stability of the electrode materials. The safety is affected by the release of oxygen due to the side reaction of electrolytes or exothermic reaction occurring inside the cell. These all properties have a trade-off relationship. Therefore, we need to develop a battery with excellent in all of these characteristics.

## **2.2. Layered Structure Materials**

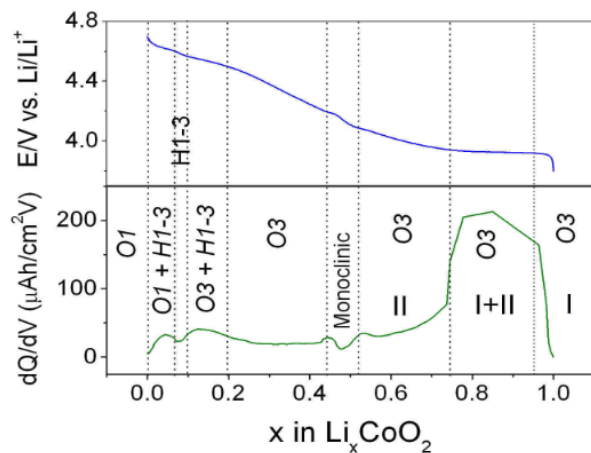
The layered structure materials have the advantage of high specific capacity. The most popular material is  $\text{LiCoO}_2$ , which was commercialized by Sony in 1991<sup>3,8,9</sup>. And this material is still used a lot and widely these days. The crystal structure of  $\text{LiCoO}_2$  is a layered rhombohedral  $\alpha\text{-NaFeO}_2$  structure (R-3m space group). This is O3 type structure and the oxygen layer is stacked in a sequence of ABCABC... . Between oxygen layers, there are cobalt ions in one layer and lithium ions in next layer. Therefore, the structure of  $\text{LiCoO}_2$  is in the form of O-Co-O-Li-O layer by layer. Consequently, the lithium ions are

located between  $\text{CoO}_6$  octahedral layers.

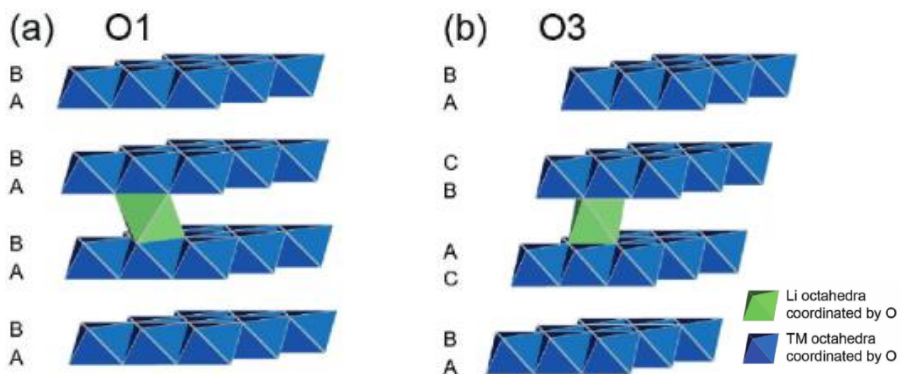
A theoretical capacity of  $\text{LiCoO}_2$  is  $274 \text{ mAh g}^{-1}$ . However, a practical reversible capacity is  $130 \sim 140 \text{ mAh g}^{-1}$  which is only half of the theoretical capacity. This is due to the unstable structure change of  $\text{LiCoO}_2$ . The structure change from rhombohedral to monoclinic structure occurs when more than a half of lithium ions are extracted out from  $\text{LiCoO}_2$ <sup>18,19</sup>. This mechanism causes a rapid decrease in lifespan of cell. In  $\text{CoO}_2$  structure, where all lithium ions are extracted from  $\text{LiCoO}_2$ , one more irreversible structure change takes place from O3 to O1 type structure that the oxygen layer is stacked in a sequence of ABABAB...



**Figure 3.** Crystal structure of  $\text{LiCoO}_2$



**Figure 4.** Voltage profile and the differential capacity,  $dQ/dV$  curve as a function of Li concentration<sup>19</sup>



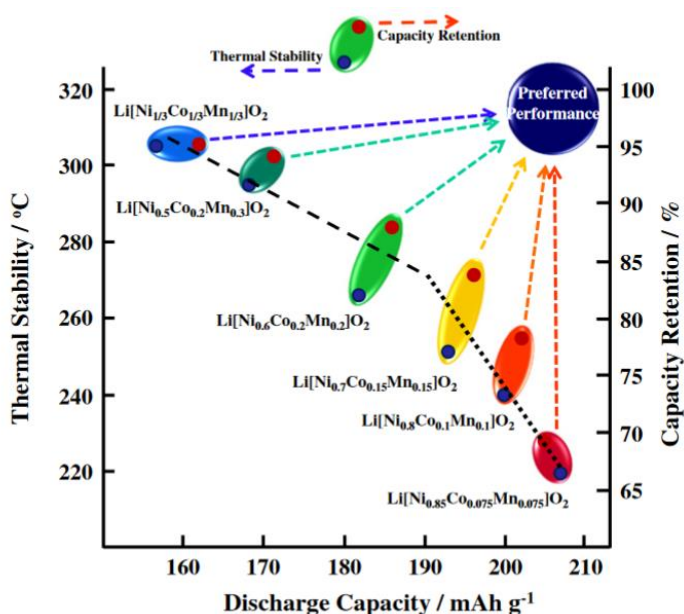
**Figure 5.** Crystal structures of O1 and O3 type materials<sup>20</sup>

Another representative layered structure material is  $\text{LiNiO}_2$ . The crystal structure of  $\text{LiNiO}_2$  is the same as  $\text{LiCoO}_2$ .  $\text{LiNiO}_2$  has been studied as an active material of positive electrode because its capacity is 20% larger than  $\text{LiCoO}_2$ <sup>21</sup>. However, since  $\text{Ni}^{2+}$  ions are more stable than  $\text{Ni}^{3+}$  ions,  $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$  is synthesized easily.  $\text{Ni}^{2+}$  ions replace the octahedral site of  $\text{Ni}^{3+}$  ions and further replace the site of  $\text{Li}^+$  ions, due to the similar ionic radius of  $\text{Ni}^{2+}$  (0.69Å) ions and  $\text{Li}^+$  (0.76Å) ions.  $\text{Ni}^{2+}$  ions present in the lithium layers hinder the path of lithium ions. This is one of the main reason why electrochemical performance of  $\text{LiNiO}_2$  cell become decrease. Also,  $\text{LiNiO}_2$  has characteristics that the lifespan decrease rapidly due to the irreversible phase transition during charge and discharge process.

In order to improve a capacity problem of  $\text{LiCoO}_2$  and a lifespan problem of  $\text{LiNiO}_2$ , many studies have been conducted and finally NCM, NCA based materials are developed. In the case of NCM, various composition such as 1:1:1, 5:2:3, 6:2:2 and 8:1:1 can be synthesized by controlling the ratio of transition metals (Ni, Co, Mn). However, in the case of NCA, high nickel NCA is synthesized and normally the ratio of Ni : Co : Mn is 80 : 15 : 5. These types of Ni based ternary layered structure materials show a property of as the ratio of nickel increases, the capacity increases but lifespan and safety decreases. The rate capability improves as the ratio of cobalt increases and the



structure stability increases as the ratio of manganese and aluminum<sup>22</sup> increases. In the range of low potential versus Li/Li<sup>+</sup> about 3.7 V, nickel ions mainly participate in the redox reaction. And in the range of high potential upper than 3.7 V versus Li/Li<sup>+</sup>, cobalt ions mainly participate in the redox reaction. Manganese and aluminum ions are inactive in the electrochemical reaction<sup>23</sup>.



**Figure 6.** A map of relationship between discharge capacity and thermal stability and capacity retention of Li/LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>x</sub>O<sub>2</sub> (x=1/3, 0.5, 0.6, 0.7, 0.8 and 0.85)<sup>24</sup>

## Chapter 3. Experimental Details

### 3.1. Manufacturing of Lithium Ion Battery

The NCM ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ) and NCA ( $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ ) electrodes were prepared by mixing active material, conductive agent (Super P carbon black), Kureha 7208 binder (8wt% of polyvinylidene fluoride (PVDF) in n-methyl-2-pyrrolidone (NMP) solvent) and additional n-methyl-2-pyrrolidone (NMP). A slurry composition was active material : conductive agent : binder = 85 : 10 : 5 in weight percent. Mixing was conducted by ball mill homogenizer at 2,000 rpm for 15 minutes. After using ball mill homogenizer, the slurry was introduced onto at 12um thick carbon coated aluminum foil to fabricate the NCM and NCA electrodes with a doctor blade. The thickness of electrodes was ca. 24 um. These coated films were dried on a hot plate at 80 °C for 24 hours to evaporate n-methyl-2-pyrrolidone (NMP) solvent. To fabricate a blended cathode, NCM and NCA powder were mixed in 8:2 wt%. Next steps were same as manufacturing process of individual electrodes.

After drying, three electrodes were punched into disks with  $\Phi = 10$  mm. A typical loading level of the cathode electrode was about 3.9-4.1 mg  $\text{cm}^{-2}$ . A 2032 coin-type half cells were assembled in an argon filled glove box. NCM,

NCA, blended cathodes were used as a working electrode and a lithium metal anode was used as a counter electrode. A 1M lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in ethyl carbonate and dimethyl carbonate (1:1 in volume) was used as an electrolyte and GF/F (Glass microfiber filter) was used as a separator. All electrochemical property analyzes were performed after 12 hours of aging process.

### **3.2. Electrochemical Property Analysis**

To remove the effect of initial irreversible reaction, two formation cycles were carried out at room temperature, in the range of 2.8 - 4.3 V at 0.2 C (1 C = 160mA g<sup>-1</sup> for NCM, 1 C = 190mA g<sup>-1</sup> for NCA). After activation of coin cell, reversible charge and discharge profile was measured. The CC-CV (Constant Current - Constant Voltage) charge and CC (Constant Current) discharge were performed with a battery testing system (WBCS3000, Wonatech, Korea). A charge and discharge process was performed in the range of 3.0 - 4.3 V at 1 C and cutoff current was 0.05 C for charge step. Cyclic voltammetry steps were performed after each 50 cycles. A scan rate for cyclic voltammetry was 0.1mV/s. Electrochemical impedance spectroscopy

(EIS) analysis was performed at a fully charged state in the frequency range of 1 MHz to 10 mHz with an AC amplitude of 10 mV using an impedance analyzer (Zive, SP1).

### **3.3. Crystal Structure Analysis**

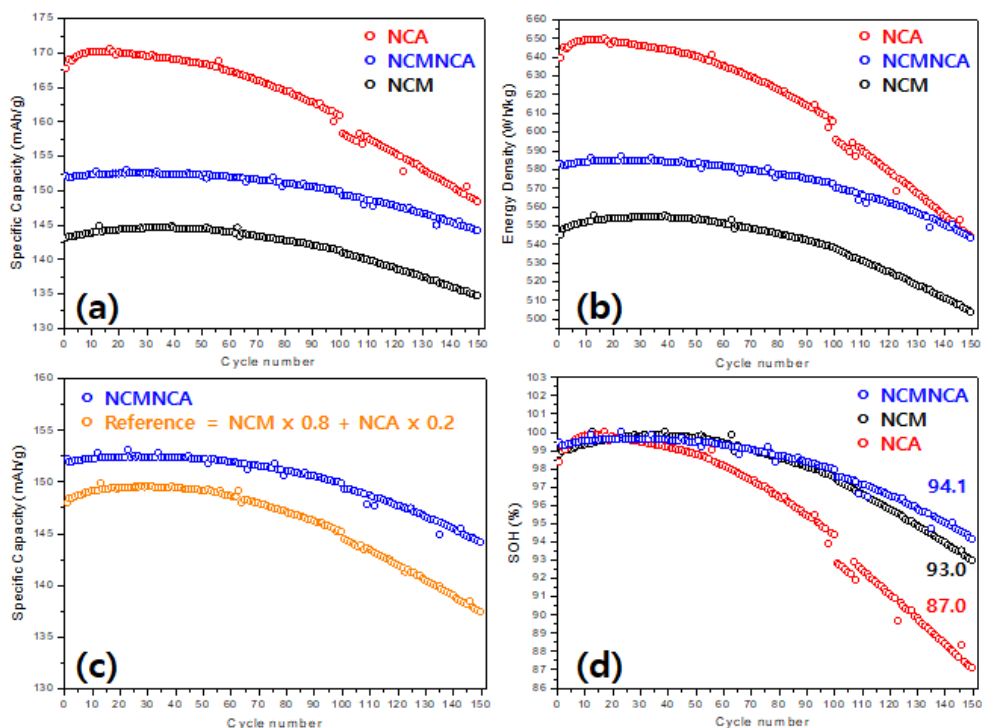
After 150 charge and discharge cycles, the charged electrodes were disassembled from coin-cells and rinsed with DMC solution 2 - 3 times. In order to block the external air, this procedure was performed in the argon filled glove box. Ex-situ XRD (X-Ray Diffraction, Bruker, D8-Advance) analysis was performed to analyze the crystal structure of the bulk state of NCM and NCA electrodes. The morphology of electrodes was analyzed using FE-SEM (Field Emission-Scanning Electron Microscopy, Hitachi, SU70). And cross section analysis of electrodes was performed in a BSE mode. The ion milling technique using a CP (Cross section Polisher, JEOL, IB-19510CP) was conducted to manufacture the cross section samples. For 200kV FE-TEM (Field Emission - Transmission Electron Microscopy, JEOL, JEM-2100F) analysis, samples were prepared by using a FIB (Focused Ion Beam, FEI, Quanta 3D FEG) technique.

## Chapter 4. Results and Discussion

### 4.1. Electrochemical Analysis

Charge and discharge process was conducted to investigate the discharge capacity and lifespan of three kinds of cells. The formation cycles were performed twice at 0.2 C in the range of 2.8 - 4.3 V (vs. Li/Li<sup>+</sup>). A formation cycle is a step of forming and stabilizing the SEI layer at the electrode-electrolyte interface. Thus, it is an essential step to activate the cell before galvanostatic charge and discharge process. And reversible charge and discharge cycles were performed at 1 C in the range of 3.0 - 4.3 V (vs. Li/ Li<sup>+</sup>). The expected specific capacity was 160 mAh g<sup>-1</sup> for NCM and 190mAh g<sup>-1</sup> for NCA. But, the practical specific capacity was less than expected specific capacity in both of electrodes. Due to the electrodes were kept in the air for a long time, the performance of electrodes was decreased. Figure 7a and 7b show the specific capacity and energy density of NCM, NCA and blended cathodes. A maximum specific capacity was 144.78 mAh g<sup>-1</sup> for NCM, 170.45 mAh g<sup>-1</sup> for NCA and 153.01 mAh g<sup>-1</sup> for blended cathode. NCA cathode shows higher specific capacity than NCM cathode. This is because the ratio of nickel is higher in NCA powder than NCM powder. And also

NCA cathode shows the highest value of energy density. To compare the specific capacity of blended cathode, we assumed that there was no interaction between NCM and NCA powder in the blended cathode. And we calculated the specific capacity of reference cathode using linear superposition method from individual discharge capacity values of NCM and NCA cathode. Figure 7c shows specific capacity of blended and calculated reference cathode. Blended cathode exerted more specific capacity than calculated reference cathode about 3 mAh g<sup>-1</sup>. However, this 3 mAh g<sup>-1</sup> capacity increase is not that incredible improvement because it's only 2.07 % for NCM and 1.76 % for NCA cathode. In addition, it is possible that this difference of specific capacity came from computational error. Figure 7d shows life characteristics of NCM, NCA and blended cathodes. After 150 times of charge and discharge cycles, the specific capacities of NCM, NCA and blended cathodes were 134.58 mAh g<sup>-1</sup>, 148.38 mAh g<sup>-1</sup> and 144.05 mAh g<sup>-1</sup>, respectively. When comparing the last specific capacity with the maximum specific capacity of each cathode, a specific capacity retention was 93.0 %, 87.0 % and 94.1 % for NCM, NCA and blended cathode. The capacity retention is same as state of health and lifespan characteristics of cells. The capacity retention was best maintained in a blended cathode. It means that by blending NCM and NCA powder, life characteristics of blended

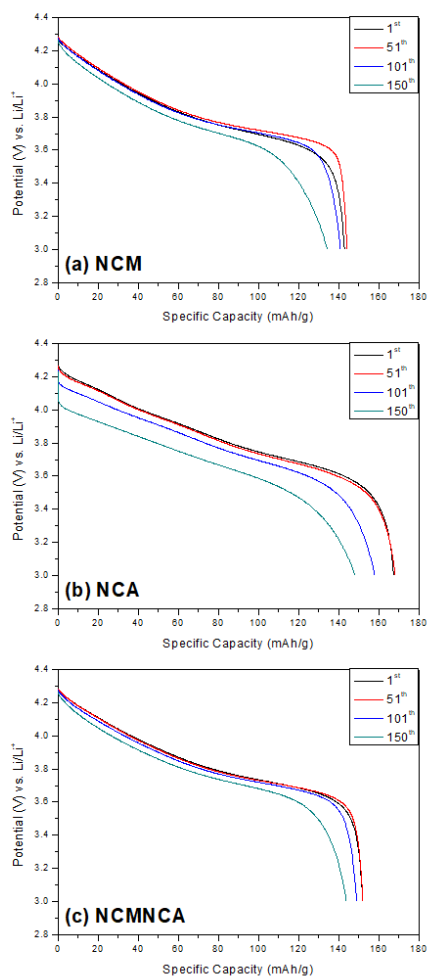


**Figure 7.** (a) Specific capacity and (b) energy density and (d) capacity retention of NCM, NCA and blended cathode (c) Specific capacity of blended and reference cathode

cathode was improved. A slope of NCA cathode decreases faster than NCM cathode and it means that NCA cathode has the shortest lifespan. Figure 8 shows galvanostatic discharge profile of 1<sup>st</sup>, 51<sup>st</sup>, 101<sup>st</sup> and 150<sup>th</sup> for NCM, NCA and blended cathode. NCM cathode shows one plateau at 3.7 V (vs. Li/Li<sup>+</sup>) which represents a steady state as shown in figure 8a. From 1<sup>st</sup> cycle to 101<sup>st</sup> cycle, there was a little capacity decrease, but from 101<sup>st</sup> cycle to 150<sup>th</sup> cycle, a lot of capacity decrease occurred. It can be inferred that more

degradation mechanism occurred after 100 times of charge and discharge cycles. On the other hand, NCA cathode shows three plateau at 3.7 V, 4.0 V and 4.2 V (vs. Li/Li<sup>+</sup>). And the capacity decrease occurred similar from 51<sup>st</sup> cycle to 101<sup>st</sup> cycle and from 101<sup>st</sup> cycle to 150<sup>th</sup> cycle. It means that degradation of NCA cathode occurred steadily from initial to final cycle. Other differences between discharge profile of NCM and NCA cathode were ir drop and polarization. NCM cathode shows a little ir drop and polarization, however, NCA cathode shows noticeable ir drop and large polarization during the charge and discharge progresses. It is consistent with the previous results that NCA cathode showed poor life characteristics than NCM cathode. Figure 8c shows a discharge profile of blended cathode. Because the weight ratio of NCM powder in blended cathode was 80 %, overall profile follows NCM cathode's discharge profile. However, the difference between profile of NCM and blended cathode occurred in 150<sup>th</sup> cycle. A retention of operation voltage and discharge specific capacity were better in blended cathode. It means that small impedance and polarization occurred inside of blended cathode compared to NCM and NCA individual cathode. In other words, a life characteristics of blended cathode was better than NCM and NCA cathode. Blending of NCM and NCA materials in one electrode improves the performance of cell, particularly in life characteristics.



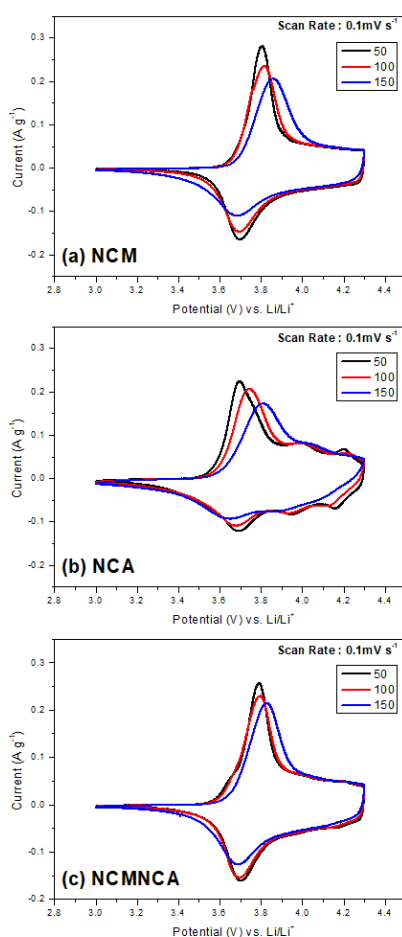


**Figure 8.** Galvanostatic discharge profile of (a) NCM, (b) NCA and (c) blended cathode

To accurately analyze the charge and discharge mechanism occurring inside of cells, the cyclic voltammetry was performed after each 50<sup>th</sup> cycles. Figure 9 shows cyclic voltammetry profile of NCM, NCA and blended cathode after

50<sup>th</sup>, 100<sup>th</sup>, 150<sup>th</sup> cycles. Because a lithium metal was used as a counter electrode in three cells, it can be concluded that the degradation mechanism only occurred at the positive electrodes which were NCM, NCA and blended cathode. And a charge process was intensively analyzed to investigate the unstable state of cathodes which was delithiation process. Three oxidation peaks of NCM cathode were occurred at 3.80 V, 3.81 V and 3.85 V after each 50<sup>th</sup> cycles. And main oxidation peaks of NCA cathodes were occurred at 3.69 V, 3.74 V and 3.80 V after each 50<sup>th</sup> cycles. Oxidation peaks of blended cathode were occurred at 3.79 V, 3.79 V and 3.82 V after each 50<sup>th</sup> cycles. The oxidation peak position after 50 cycles was the lowest in NCA cathode and the highest in NCM cathode. And an oxidation peak of blended cathode occurred in the middle of NCM and NCA cathodes. However, as the charge and discharge cycles progress, the fastest peak shift was occurred in NCA cathode and the slowest peak shift was occurred in blended cathode. A peak shift in cyclic voltammetry is caused by the impedance and polarization generated inside of cells. Therefore, a lifespan of blended cathode is longer than other cathodes. To reveal a reason of improved lifespan in blended cathode, we noticed the oxidation peaks occurred at 4.2 V of NCA and blended cathode. This peak is from H2 to H3 phase transition occurring in high nickel ternary cathode materials<sup>25,26</sup>. Due to a large volume change in

this process, it is one of the main causes of decreasing lifespan of cells. However, this peak was hardly distinguishable in blended cathode as shown in figure 9c. Therefore, we assumed that the H2 to H3 phase transition in blended cathode was suppressed by some reasons and caused a small volume change of NCM and NCA powder in blended cathode.



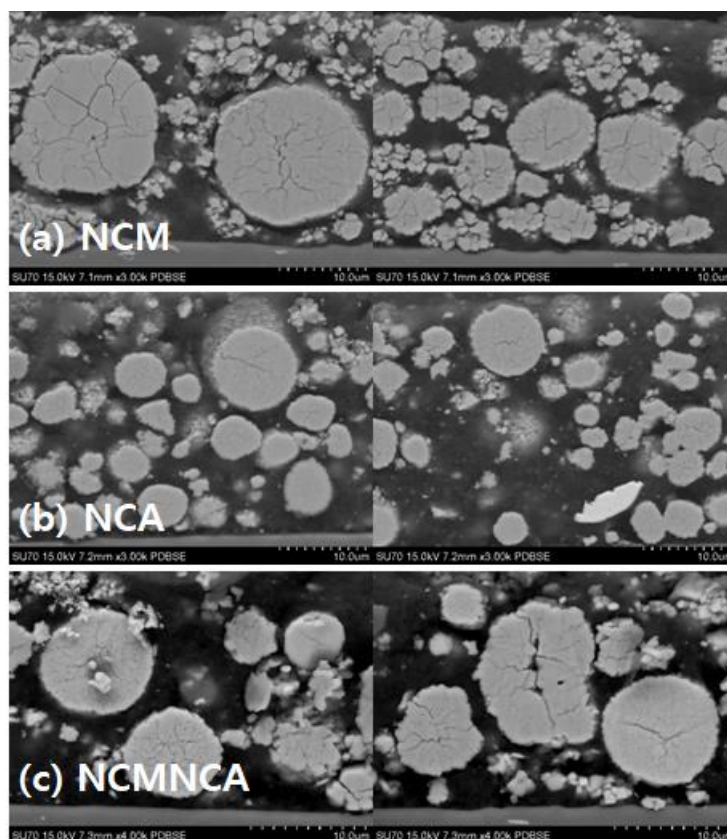
**Figure 9.** Cyclic voltammetry profile of (a) NCM, (b) NCA and (c) blended cathode

	After 50 cycles		After 100 cycles		After 150 cycles	
	Oxidation	Reduction	Oxidation	Reduction	Oxidation	Reduction
NCM	3.8	3.69	3.81	3.69	3.85	3.68
NCA	3.69	3.69	3.74	3.67	3.80	3.64
NCMNCA	3.79	3.70	3.79	3.69	3.82	3.68

**Table 1.** The oxidation and reduction peak positions of NCM, NCA and blended cathode after each 50, 100, 150 times of charge and discharge cycles

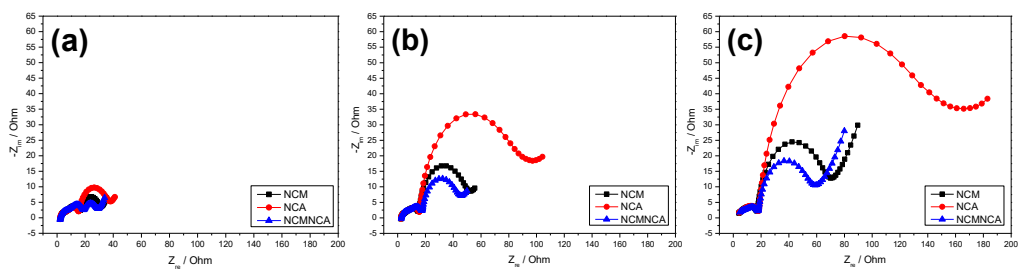
To confirm a cross section SEM image of each electrode, samples were prepared by cross section polisher using argon ion. This is because a crack is generated from the volume change of active materials, especially in H2, H3 transition. To minimize exposure to the air, vacuum packaging and vacuum storage were performed all the time. NCM and NCA particles are 5 ~ 15  $\mu\text{m}$  size of secondary particles composed of primary particles. Differences between NCM and NCA particles are the shape and size of primary particles. NCM particle has a circular shape, however, NCA particle has an angular shape. And the size of NCM primary particle is bigger than NCA primary particle. Figure 10 shows the cross section SEM images of NCM, NCA and blended electrode. After 150 times of charge and discharge cycles, the severe deformation was observed in NCM electrode. Although a more amount of

lithium ions moving in and out from NCA than NCM particle, because of the NCA secondary particles are more compactly constructed, it is thought to withstand the strain caused by volume change. When compared NCM and NCA particles in individual electrodes to particles in blended electrode, there was no obvious differences. The reason of improved life characteristics of blended electrode can't be investigated by observation of cross section SEM image of three electrodes.



**Figure 10.** Cross section SEM images of (a) NCM, (b) NCA and (c) blended electrodes

Electrochemical impedance spectroscopy was conducted to measure the impedance in the coin cell. After each 50 cycles of charge and discharge process, EIS measurement was performed at fully charged state and a result is plotted in Figure 11. The first semi-circles are attributed to surface film resistance and the second semi-circles are attributed to charge transfer resistance. Values of each resistance are listed in Table 2. After each 50<sup>th</sup>, 100<sup>th</sup>, 150<sup>th</sup> times of charge and discharge cycles, a resistance value of blended electrode coin cell was the smallest, and a resistance value of NCA electrode coin cell was the largest. As continuous charge and discharge progress, charge transfer resistances are getting larger in all of NCM, NCA and blended electrode coin cells. However, increasing of NCA coin cell's resistance value is the fastest, especially in the charge transfer resistance. And increasing of blended coin cell's resistance value is the slowest. This result matched well with previous data and we can conclude that lithium ions are easy to move in the blended electrode than other electrodes. Charge transfer resistance is caused by structural change of active materials in electrodes. Thus, we decided to conduct crystal structure analysis of active materials.



**Figure 11.** EIS profile of NCM, NCA and blended electrodes in the coin-cell after (a) 50, (b) 100, (c) 150 cycles

	After 50 cycles		After 100 cycles		After 150 cycles	
	$R_f$	$R_{ct}$	$R_f$	$R_{ct}$	$R_f$	$R_{ct}$
NCM	18.6	17.6	16.2	38.3	18.5	54.6
NCA	17.3	23.6	17.1	78.6	18.7	143.5
NCMNCA	21.3	12.4	19.7	28.9	20.5	42.5

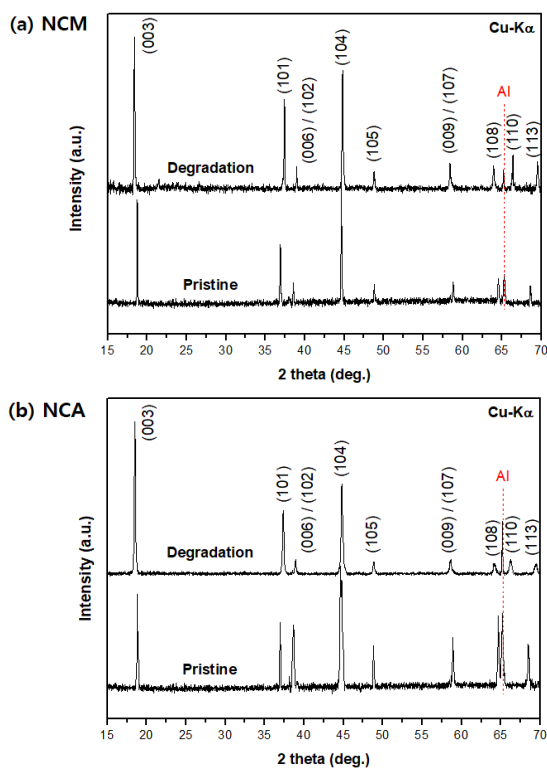
**Table 2.** Resistance values of NCM, NCA and blended cells after each 50 times of charge and discharge cycles

## 4.2. Crystal Structure Analysis

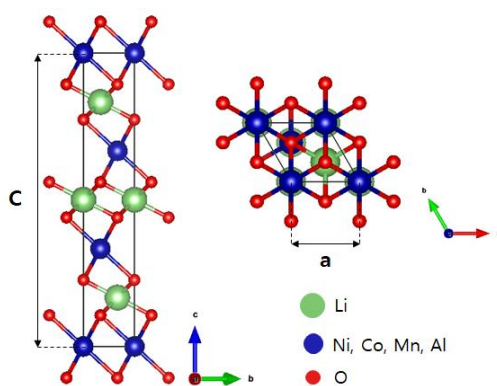
To investigate the crystal structure of electrodes, we conducted XRD analysis. All electrodes were fully charged state. After 150 times of charge and discharge cycles, we collected positive electrodes from 2032 type coin cell, and rinsed with DMC solution. All processes were performed in an argon filled glove box. Because the structure of NCM and NCA active materials were very similar, XRD patterns were almost same each other. In the XRD patterns of blended electrode, NCM and NCA peaks can't be distinguished. Thus, we only plotted individual NCM and NCA electrodes in figure 12. We acquired four XRD patterns from pristine NCM, NCA and cycled NCM, NCA. The “cycled” means after 150 times of charge and discharge cycles. However, cycled NCM and NCA still retained a good layered structure. And there was no other new phases or degradation phases. The only difference between XRD patterns of pristine and cycled electrodes was shift of diffraction peaks. This was because of the change of unit cell parameters caused by extracted lithium ions at 4.3 V cutoff. Figure 14 shows the lattice parameters and unit cell volumes calculated from each XRD patterns. The c-axis lattice constants were obtained from 003 peaks and a-axis lattice constants were obtained from 110 peak. And we confirmed that these a and c lattice constants were well matched



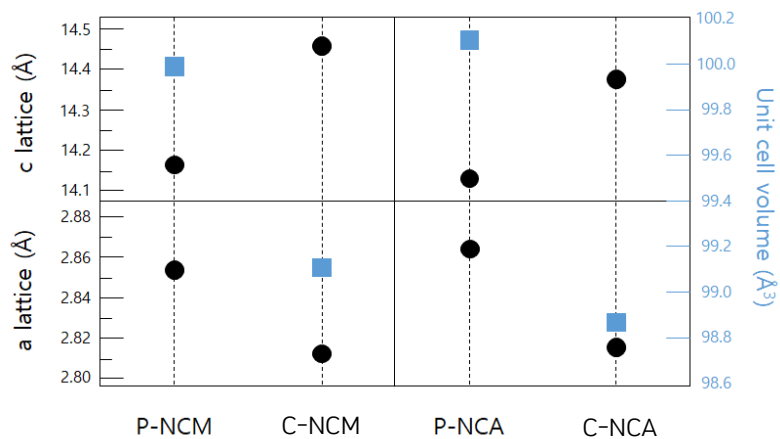
with other diffraction peaks. NCM and NCA active materials undergo a-axis contraction and c-axis expansion during charge process where lithium ions are extracted. In particular, a large change of lattice constant in c-axis direction occurs and this is the result of a strong repulsion between oxygen layers<sup>27,28</sup>. Also, a volume change occurs larger in the NCA active materials than NCM active materials. This is the result of the phase transition from H2 to H3 which occurs around 4.2 V vs Li/Li<sup>+</sup> when charge proceeds in the high nickel layered materials<sup>25,26</sup>. As lithium ions extracted from active materials, the c-axis expansion occurs due to the repulsion between oxygen layers and further extraction of lithium ions make active materials fail to sustain its structure and collapses causing rapid contraction in the c-axis direction. And the large volume change that occurs at this moment has a negative effect on the coin cell and is one of the factors that drastically decrease the lifespan of cell. This volume change occurring in NCA electrode can be the cause of shorter lifespan than NCM electrode.



**Figure 12.** X-ray diffraction (XRD) patterns of (a) pristine and cycled NCM electrodes, (b) pristine and cycled NCA electrodes



**Figure 13.** Schematic of unit cell of  $\text{LiTMO}_2$  (TM = Ni, Co, Mn, Al)



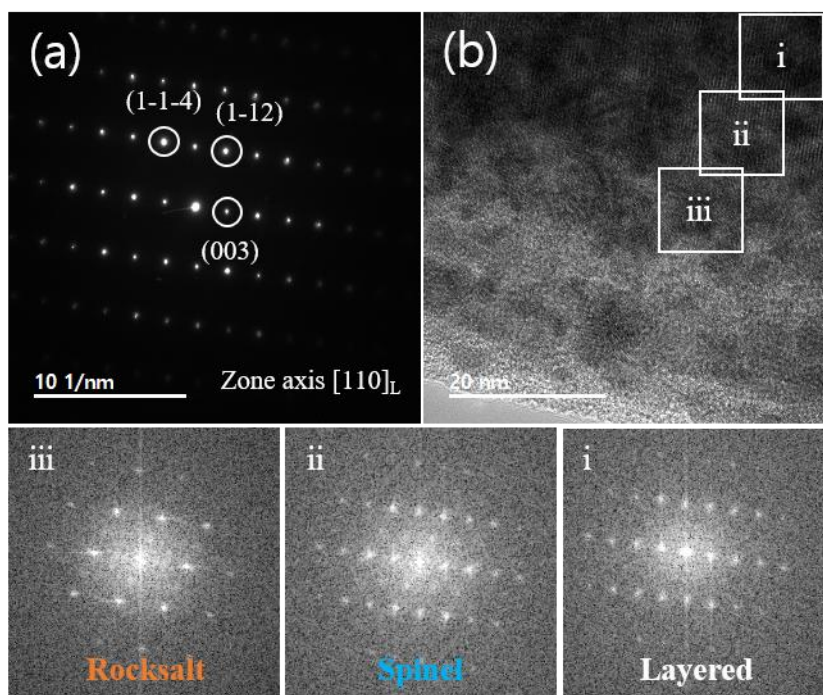
**Figure 14.** Lattice parameter and unit cell volume of P-NCM, C-NCM, P-NCA, C-NCA (P ; pristine electrode, C ; cycled electrode)

	a lattice (Å)	c lattice (Å)
P-NCM	2.855	14.176
C-NCM	2.814	14.459
P-NCA	2.861	14.123
C-NCA	2.818	14.374

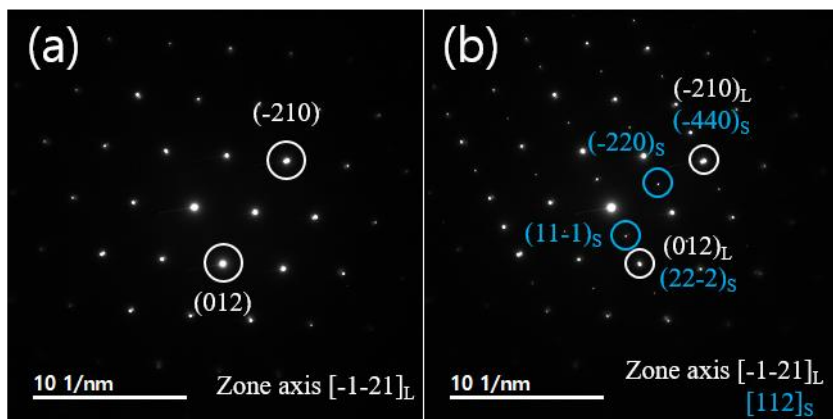
**Table 3.** Lattice parameters of P-NCM, C-NCM, P-NCA, C-NCA (P ; pristine electrode, C ; cycled electrode)

To investigate the micro structure of active materials, TEM analysis was conducted. The samples were prepared by focused ion beam technique using gallium ion sources. The crystal structures of active materials were observed by SAED (Selected Area Electron Diffraction) in a microscale and HR (High Resolution) image in a nanoscale region. Figure 15 shows the SAED pattern, HR image and FFT (Fast Fourier Transform) images of NCM particle. In figure 15a, a diffraction pattern of layered structure was clearly detected and any other additional spots were not found. If there exist other structures such as spinel or rocksalt, there will be additional spots or a clear intensity difference in [110] zone axis of layered structure like figure 15 ii and iii. Figure 15b shows a high resolution image of surface region in the same particle with figure 15a. And FFT image of each marked region in figure 15b are shown in figure 15 i, ii, iii. At the bulk side of this particle, there was only layered structure. However, as we move to the surface region of this particle, there existed a small region of spinel and rocksalt structure. This phase transition occurred because  $\text{Ni}^{2+}$  ions moved to octahedral site of lithium ions in lithium layer. The SAED patterns of another NCM particle are shown in figure 16. In figure 16b, we can find additional spots which are absent in

figure 16a. It means that a large region of spinel structure existed in this particle. Only one diffraction pattern of spinel structure was detected, although we observed 22 primary particles in one NCM secondary particle. This means that NCM particle is robust to phase transition from layered to spinel or rocksalt structure.



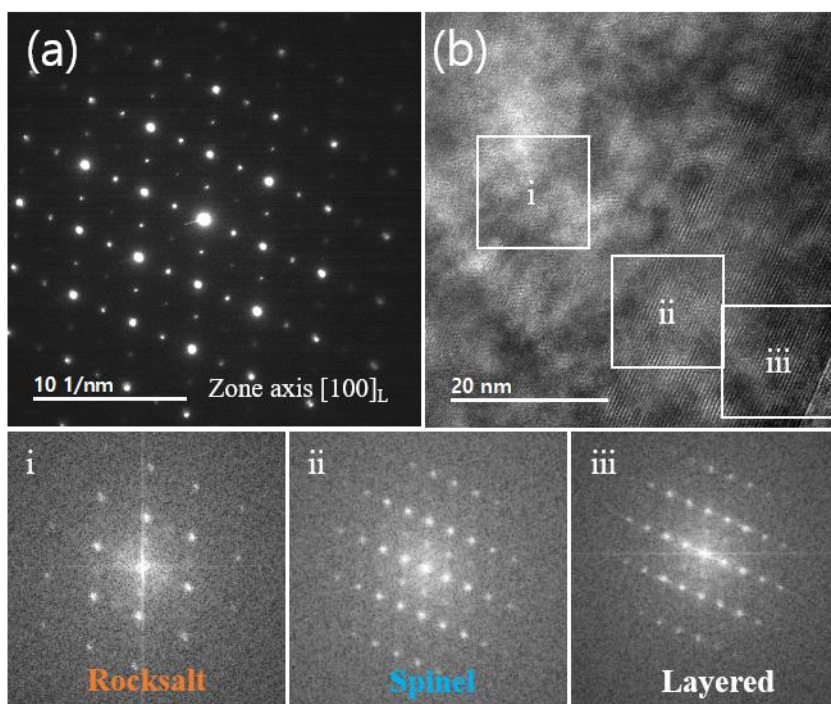
**Figure 15.** (a) Selected Area Electron Diffraction pattern at the zone axis  $[110]$  of NCM primary particle and (b) High Resolution image at the surface region of the same particle, i, ii, iii are Fast Fourier Transform images of each marked region in (b)



**Figure 16.** (a) Selected Area Electron Diffraction pattern at the zone axis  $[-1-21]$  of NCM primary particle and (b) other Selected Area Electron Diffraction pattern right next region of (a) in the same primary particle

Figure 17 shows the SAED pattern, HR image and FFT images of NCA particle. In figure 17a, SAED patterns of layered, spinel and rocksalt structure were detected. The  $[100]$  direction of layered structure and  $[101]$  direction of spinel and rocksalt structure are parallel. Because rocksalt phase has a high symmetry structure, the number of diffraction spots from rocksalt structure is lower than layered and spinel structure. It can be seen in the FFT images, which are figure 17 i, ii, iii. As shown in figure 17b, a layered structure occupies small region of this particle. And, we can see that rocksalt structure is dominant in this particle. The surface region is on the left side and the bulk region is on the right side of this image. Thus, a short distance region from

particle surface is composed of rocksalt structure and inside of particle maintains good layered structure, even if charged state after 150 times of charge and discharge cycles. We can infer that inside region of primary particle is hard to react with electrolyte and keeps good layered structure. However, near from the surface of primary particle reacts vigorously with electrolyte and this cause phase transition. At NCA particle, it tends to be a little bit different from the results of NCM. We observed 20 primary particles. And we can detect diffraction spots from spinel or rocksalt structure in the most of these particles. This means that phase transition from layered to spinel and rocksalt structure in NCA particle occurred at a huge region. In other words, high nickel NCA is easy to experience structure change and this can be cause of short lifespan in NCA electrode.

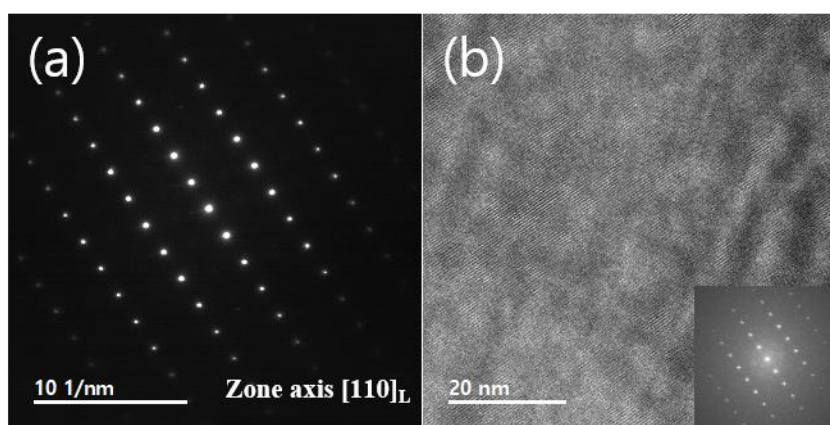


**Figure 17.** (a) SAED pattern at the zone axis [2-21] of NCA primary particle and (b) HR image at the surface region of the same particle, i, ii, iii are FFT images of each marked region in (b)

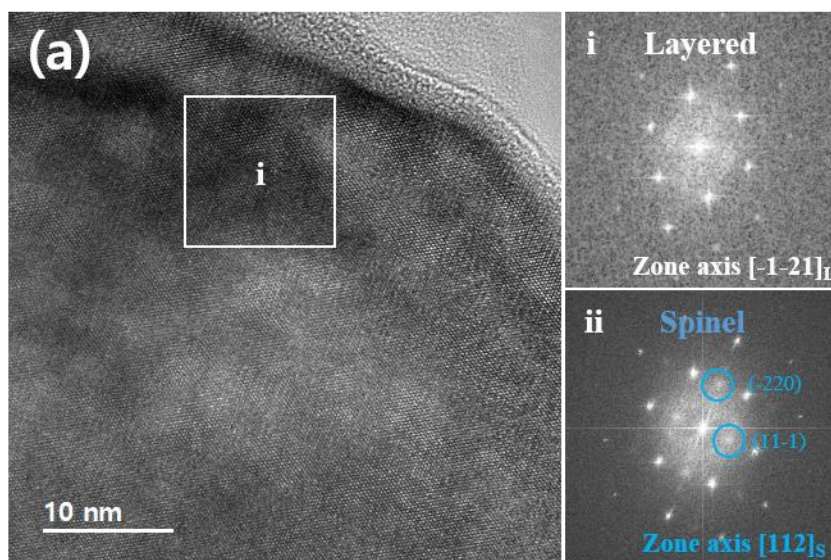
Figure 18 shows the SAED pattern, HR image and FFT image of NCM particle in blended electrode. Figure 18a is a diffraction pattern of layered structure in [110] zone axis. If there were other structure, additional spots will be detected. We further investigated in the nanoscale structure of this particle by HR image. However, there were no additional spots or intensity difference in spots. Figure 19 shows a HR image and FFT images of another NCM



particle from blended electrode. In this NCM primary particle, we can find additional peaks from spinel structure, however, these peaks were faint. This means that very small region of this particle was composed of spinel structure. Compared NCM particle from individual electrode and blended electrode, it was hard to reveal the difference of structures. Although, more than 20 primary particles were investigated, but their tendency was very similar, in other words, there was no difference between NCM particles from individual and blended electrodes.



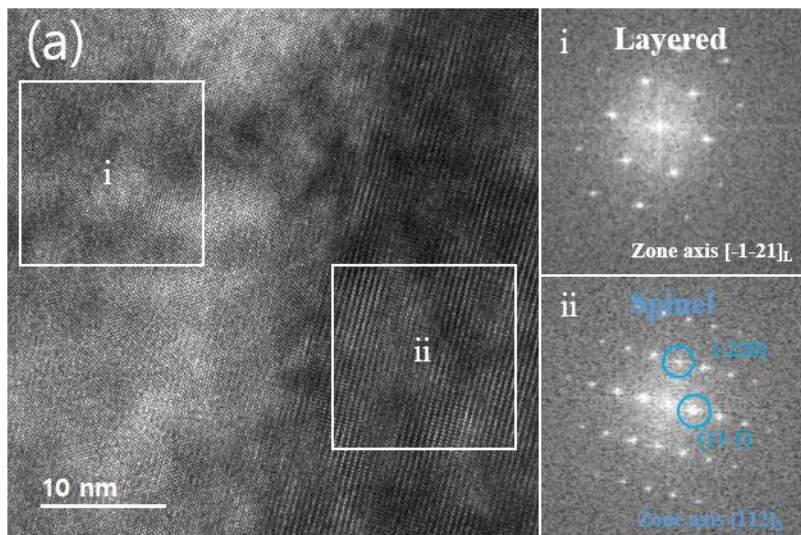
**Figure 18.** (a) SAED pattern at the zone axis  $[110]$  of NCM primary particle from blended electrode and (b) HR image at the same particle, inset image is FFT image of (b)



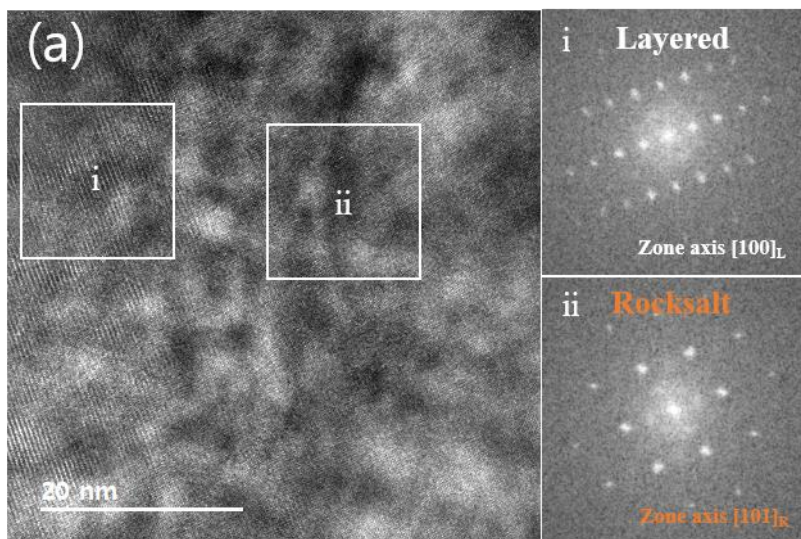
**Figure 19.** (a) HR image of NCM primary particle from blended electrode and i FFT image of marked region in (a), ii FFT image of whole area of (a)

Figure 20 shows HR image and FFT images of NCA particle from blended electrode. In HR image, we can see that there are two clearly distinguished regions. The right side of image looks like a layered structure, however, it is spinel structure in  $[112]$  zone axis. And the left side of image is layered structure in  $[-1-21]$  zone axis. We can see additional spots in FFT image of region ii. Figure 21 also shows HR image and FFT images in another NCA particle from blended electrode. As shown in HR images, there were two structures which are layered and rocksalt. This image was acquired in  $[100]$  zone axis of layered structure which is same as  $[101]$  zone axis of rocksalt

structure. Interestingly, there was hardly no spinel structure between layered and rocksalt structure. The difference between first and second NCA primary particles is that the first particle was in the bulk side of secondary particle and the second particle was also in the bulk side but right next to a crack in the secondary particle. The phase transition of active material occurred differently depending on the region. We observed more than 10 primary particles in one secondary particle. The phase transition from layered to spinel was detected in the inner side of secondary particle and the phase transition from layered to rocksalt was detected in the next side of crack and outer side of secondary particle. We tried to find the difference between NCA particles from individual electrode and blended electrode, however, the tendency was so similar, like NCM particle. Thus, we can't reveal the reason of improved performance in blended electrode by TEM analysis.



**Figure 20.** (a) HR image of NCA primary particle from blended electrode and i, ii FFT images of marked region in (a)



**Figure 21.** (a) HR image of NCA primary particle from blended electrode and i, ii FFT images of marked region in (a)

## Conclusion

We studied about blended electrode made up of NCM and NCA cathode materials. And we evaluated the performance of the blended electrode. As a result,  $3 \text{ mAh g}^{-1}$  was increased in blended cathode compared to reference cathode, however, this capacity increasing was very small, which is only 2.07% and 1.76% of each NCM and NCA discharge capacity. In the case of lifespan characteristics, after 150 times of charge and discharge cycles, state of health values of NCM, NCA and blended cathode were 93.0%, 87.0% and 94.1%, respectively. It was obvious improvement in cycle characteristics. To understand the mechanism of blended cathode and reveal the origin of improved performance, we conducted electrochemical property analysis such as cyclic voltammetry and electrochemical impedance spectroscopy. In the result of EIS experiment, we confirmed the lowest impedance was measured in blended cathode cell. And, XRD and TEM analysis were conducted to observe the crystal structure of cathode materials. There were no other new phases in XRD results. In TEM results, we observed a phase transition from layered to spinel and rocksalt structure in NCM and NCA particles. The phase transition was occurred more in high nickel NCA than low nickel NCM. However, a difference between individual and blended electrodes was hard to observe. More statistical or new approach will be needed to reveal and

perfectly understand the mechanism in blended cathode with same layered structure.

We can do further work related to this study such as the performance of different ratio of NCM and NCA materials or the performance in different temperature, not in room temperature. We expect that these studies will contribute to the development of lithium ion batteries with excellent performances.

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## Abstract in Korean

### 국문초록

## 리튬이온배터리 혼합양극의 시너지 효과 연구

서울대학교 대학원

공과대학 재료공학부

박순찬

과거부터 리튬이온배터리는 휴대폰, 노트북, 전동공구 등 소형전지의 형태로 널리 사용되어 왔다. 하지만 그 수요를 뛰어넘어 현재는 전기자동차, 에너지저장장치 등 중, 대형의 형태로 사용하기 위해 다양한 연구와 개발이 진행되고 있다. 특히, 친환경 정책을 바탕으로 전기자동차 산업이 발전하면서 리튬이온배터리에 대한 관심과 기대가 더욱 커지고 있는 상황이다.

리튬이온배터리의 형태가 변화하면서 안전성이 가장 중요한 요인으로 여겨진다. 안전성에 못지않은 중요한 요인으로는 고용량, 장수명이 있다. 이러한 다양한 조건들을 동시에 만족하는 배터리를 제작하기 위하여 셀의 성능에 영향을 끼치는 양극, 음극, 전해질, 분리막 등의 소재에 대한 연구도 활발히 진행 중이다. 그중, 양극은 셀의 열화와 재료비 측면에서 가장 높은 비율을 차지하고 있기 때문에 연구 필요성은 더욱 크다고 할 수 있겠다.

1991년에 상용화된 이후, 현재까지 사용되고 있는 양극 소재인

LiCoO<sub>2</sub>에서 몇 가지의 문제점들이 발견되었다. 비가역적인 구조 변화로 인해 이론 용량의 절반 수준의 용량만 사용 가능했으며, 코발트의 불안정한 수급으로 인해 가격의 등락이 컸다는 것이다. 따라서, LiCoO<sub>2</sub>에 비해 고용량, 저비용의 특성을 가진 NCM, NCA 계열의 양극 소재가 개발되었고, 현재 큰 주목을 받고 있다. 이러한 니켈 기반의 층상 구조 소재들은 구성하고 있는 전이금속의 비율에 따라 다른 특성을 가진다. 일반적으로 니켈의 비율이 증가함에 따라 고용량 특성을 나타내지만 짧은 수명 특성을 보인다.

본 연구에서는 장수명 특성을 가진 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM) 소재와 고용량 특성을 가진 LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) 소재를 혼합하여 전극을 제조하였다. NCM, NCA 개별 전극과 혼합 전극 등 세 종류의 양극으로 2032 하프 코인 셀을 제작하여 정전류 충, 방전, 순환전압전류법, 전기화학 임피던스 분광법 등의 전기화학적 성능을 측정 및 평가하였고, XRD, TEM을 사용하여 구조분석을 진행하였다.

기존에 진행되었던 혼합 양극에 관한 연구는 층상-스피넬 혹은 층상-올리빈 등 구조가 다른 두 물질을 혼합하였다. 하지만 본 연구에서는 동일한 층상 구조 물질을 사용했다는 것에 차별성이 있다고 할 수 있다. 장수명 특성을 갖는 NCM, NCA 혼합 양극에 관한 이번 연구는 우수한 특성을 갖는 리튬이온배터리 개발에 기여할 수 있을 것으로 예상된다.

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**주요어 :** 리튬이온배터리, 혼합 양극, 층상 구조 물질

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