## ULTRASONIC SOUND ASSISTED PROCESSING AND CHARACTERIZATION OF Li(Ni-Co-Al) OXIDE AS CATHODE ACTIVE MATERIAL FOR Li-ION BATTERIES

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## CANSU SAVAŞ

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## Approval of the thesis:

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Submitted by **CANSU SAVAŞ** in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical and Material Engineering, Middle East Technical University by,

Prof. Dr. Gülbin Dural Ünver Dean, Graduate School of <b>Natural and Applied Sciences</b>	
Prof. Dr. C. Hakan Gür Head of Department, <b>Metallurgical and Materials</b> Engineering Department	
Prof. Dr. M. Kadri Aydınol Supervisor, <b>Metallurgical and Materials</b> Engineering Department, METU	
Examining Committee Members:	
Prof Dr. Tayfur Öztürk Metallurgical and Materials Engineering Dept., METU	
Prof. Dr. M. Kadri Aydınol Metallurgical and Materials Engineering Dept., METU	
Prof. Dr. M. Timur Aydemir Electrical and Electronics Engineering Dept., Gazi University	
Assist. Prof. Dr. Metin Özgül Materials Science and Engineering Dept., Afyon Kocatepe University	
Assist. Prof. Dr. Mert Efe Metallurgical and Materials Engineering Dept., METU	
	D ( 00 00 00 17

Date: 22.08.2017

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: CANSU, SAVAŞ

Signature:

### ABSTRACT

# ULTRASONIC SOUND ASSISTED PROCESSING AND CHARACTERIZATION OF Li(Ni-Co-Al) OXIDE AS CATHODE ACTIVE MATERIAL FOR Li-ION BATTERIES

Savaş, Cansu

M. Sc., Department of Metallurgical and Materials Engineering Supervisor: Prof. Dr. M. Kadri Aydınol

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Layered LiNiO<sub>2</sub> compared to its commercial counterpart LiCoO<sub>2</sub>, has higher energy density and lower cost. However, it is difficult to synthesize and has stability and safety problems. These properties were improved with alloying, and today LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) electrode material is commercially produced. However, it is still not considered as safe, due to inherent chemistry and morphological particle characteristics. In this study, LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>z</sub>M<sub>v</sub>O<sub>2</sub> compounds (M=Na, Ca, Fe, Cu, Cr, La, Y, V, Zr) will be synthesized. In order to control crystallite and particle sizes, morphology and size distribution, ultrasonic sound assisted (co/sequential)-precipitation method will be utilized. Synthesized NCA cathode active materials will be characterized using PSA, SEM, XRD, EDS, ICP, EIS and galvanostatic charge discharge tests, focusing on the improvement of capacity, cycle life, safety and rate capability.

**Keywords:** Lithium ion battery, co-precipitation, sonochemistry, ultrasound, cathode material

# LİTYUM İYON BATARYALARINDA KATOT MALZEMESİ OLARAK Li(Ni-Co-Al) OKSİTİN ULTRASONİK DALGA YÖNTEMİYLE ÜRETİLMESİ VE KARAKTERİZASYONU

Savaş, Cansu

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü Tez Yöneticisi: Prof. Dr. M. Kadri Aydınol

Ağustos 2017, 84 sayfa

Katmanlı yapıdaki LiNiO<sub>2</sub>, ticari emsali olan LiCoO<sub>2</sub> ile kıyaslandığında daha yüksek enerji yoğunluğuna sahip ve daha düşük maliyetlidir. Bunların yanında sentezlenmesi zor ve kararlılık ile güvenli olmama gibi problemlere sahiptir. Bu özellikler alaşımlandırarak geliştirilmiştir ve günümüzde LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) elektrodu ticari olarak üretilmektedir. Ancak, kimyasal tabiatı ve parçacık morfolojisi nedeniyle hala güvenilir olmadığı düşünülmektedir. Bu çalışmada, LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>z</sub>M<sub>v</sub>O<sub>2</sub> bileşikleri (M=Na, Ca, Fe, Cu, Cr, La, Y, V, Zr) üretilecektir. Parçacık boyutu, morfolojisi ve boyut dağılımını kontrol edebilmek için, ultrasonik dalga destekli-çöktürme yöntemi kullanılacaktır. Sentezlenen NCA katot malzemeleri PSA, SEM, XRD, EDS, ICP, EIS ve galvanostatik yük boşaltımı test yöntemleriyle kapasite, çevrim ömrü ve güvenilirlik açısından karakterize edilecektir.

Anahtar Kelimeler: Lityum iyon batarya, eş-çöktürme, sonokimya, ultrason, katot malzemesi.

Dedicated to

My sister Nilay Tam

and

Beloved Özcan Uygur

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## LIST OF ABBREVIATIONS

CA	Citric Acid
СТ	Charge Transfer
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FWHM	Full Width at Half Maximum
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LMO	Lithium Manganese Oxide
LNO	Lithium Nickel Oxide
LNCO	Lithium Nickel Cobalt Oxide
LNCA	Lithium Nickel Cobalt Aluminum Oxide
NCA	Nickel Cobalt Aluminum
NMC	Nickel Manganese Cobalt
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SF	Surface Film
US	Ultrasonic Wave
XRD	X-Ray Diffraction

## **CHAPTER 1**

## **INTRODUCTION**

## 1.1. Lithium-Ion Battery History and Developments

Battery technology based on the use of lithium metal as an anode material facilitates the design of lightweight storage systems with high energy density because of that lithium is the most electropositive as well as the lightest metal on the periodic table [1]. Research and development of that kind of storage system stems 1970s with the primary Li-ion cell technology. In 1980s, with the development of the portable electronics (walkman, cameras etc.), work on rechargeable lithium-ion batteries accelerated. In 1991, first lithium-ion battery was commercialized by Sony [2]. This commercialization provided gradual increase in the consumption of rechargeable lithium-ion batteries as a power source. Widespread use of cell phones, tablets, laptops and other portable electronic devices created a need for developments and researches in this area to supply demands.

Lithium ion batteries have a higher specific energy and longer cycle life compared to other battery systems, allowing them to find an important place in commercial applications. Nowadays, lithium-ion battery technology has faced the challenge to be used for larger energy demands such as hybrid and electric vehicles and renewable energy storage applications. However, their energy density is not enough to satisfy this large energy demand [3]. The major limiting factors for lithium ion battery usage in hybrid and electric vehicles are their large mass and volume, and frequent charge requirement due to their limited energy density.

In the following years, competition in battery technology has increased rapidly and efforts to improve battery pack cycle life (charge-discharge cycle), specific energies, volumetric energy densities, safety and stability at high temperatures have accelerated [4].

Unlike other battery systems, the active substances in lithium ion battery do not participate into irreversible reactions unless electro-active species degrade. Instead, lithium ions are constantly exchanged between positive and negative electrodes. This ion exchange is explained with oxidation and reduction reactions what makes lithium ion battery rechargeable. The performance of a battery extremely depends on chemical species which participate in oxidation and reduction reactions. These species are mainly anode, cathode and electrolyte.

Studies on the development of Li-ion batteries concentrate on the anode, cathode and electrolyte, as well as work on the entire system [5, 6]. Looking at the historical development of anode materials, it is first seen that lithium metal was used in the 1970s. Although lithium metal has a high energy density, lithium metal is a flammable alkaline metal that suddenly reacts with water. During use of the battery, exothermic reaction results in sudden heat rise which causes important safety problems. After that, carbon started to be used as an anode material [7]. Today, carbon-based materials are still used as anodes in lithium-ion battery technologies, and the majority of them are graphite anodes. Having lower working potential and higher cycle life as compared to lithium anode is the main reason for graphite to be preferred as anode material [8]. But the low capacity of carbon made scientific world research to find alternative anode materials. In this manner, silicon and tin were studied as anode materials due to their higher theoretical capacity as compared to graphite [9].

The parameters considered in the studies are the capacity, the availability of the material on the earth, the reliability during the battery life, the effect of the battery on the environment (toxicity, suitability for recycling process), cell production cost and manufacturability by different methods [10, 11].

The energy density of Li-ion batteries, however, depends on especially the cathode materials. In parallel with the increase in consumption, the studies on cathode material selection and production methods become important to produce lithium ion-batteries, which are improved in terms of cost and performance.

Cathodes in the TiS<sub>2</sub> structure were produced for the first time, in 1970, when the benefits of using lithium metal in energy applications were noticed. It was discovered in 1980 that the sulfur-containing cathode materials in the layered structure do not remain stable over high number of cycles. After that, Goodenough and his colleagues suggested using metal oxides as cathode active materials, alternatively. For the first time, in 1991, Sony Co. developed this vision and produced the first commercial lithium ion battery. In these cells where LiCoO<sub>2</sub> is used as cathode and carbon used as anode, it has been achieved to produce lithium ion batteries with potential over 3.6 V and stable over long cycles. Since this compound has safety problems and high cost, cobalt has been replaced with nickel to eliminate these shortcomings. However, LiNiO<sub>2</sub> cathode material is difficult to produce and a thermally unstable compound. Decomposition of nickel atoms into divalent nickel ions and the migration of these ions to the lithium site results in cation mixing. It was reported that cation mixing causes the capacity loss of a battery [12]. In this manner, Ni-Co mixed oxides were produced to cheapen the LiCoO<sub>2</sub> compound as well as to improve electrochemical features [13]. It was observed that alloying with aluminum improved the stability of this compound [14]. As a result, NCA compound has begun to be used as a cathode active material that is cheaper and has higher capacity, energy density and very high rate performance in commercial applications.

## 1.2 Aim of This Work

In the scope of this study, NCA material will be synthesized using the chemical coprecipitation method as well as the sonochemical approach to have a spherical and very narrow particle size distribution of the powders to be used in large energy required applications. The main purpose of sonochemical approach is to obtain narrow particle size distribution. By this way, density of active material will be homogeneously distributed during coating on the current collector leading comparable as well as better electrochemical performance. Experimental parameters determined by traditional co-precipitation will be used during ultrasound assisted co-precipitation; In addition to that, ultrasonic process parameter optimization will also be carried out.

In the scope of this study, the effects of alloying elements on the electrochemical and structural properties of the cathode active material will also be investigated. Choosing doping elements, priority was given to elements not being tried in literature before. Ca, La, Y, V and Zr elements were tried for the first time as dopants for LNCA in literature by this study. Elements used as dopants in this study and their ionic radius and oxidation states were listed in table 1.1. Ca and Na elements were intended to occupy Li sites to enlarge Li-gap since ionic radius of Li, Ca and Na very close to each other. Li-gap enlargement provides increase in the Liion kinetics. In layered systems, during intercalation of the Li-ion to the active material, entrance of the lithium expands Li-gap while this spacing contract during de-intercalation process. Presence of an element with larger ionic radius in the atomic site of the lithium, may immobilize the Li-gap providing increase in the Liion kinetics. Increased LI-ion kinetics also contributes to rate capability of these materials. Moreover, presence of a cation other than Li in the atomic site of lithium may prevent the occupancy of Ni atom to the Li site (cation disorder) which results in structural instability. If Ni occupancy to Li site can be prevented by this way, capacity retention and cycle of these doped systems will also be increased.

Fe, Cu, Cr, La, Y, V, Zr elements, on the other hand, were intended to be replaced with Ni atom. Ionic radius of Ni, Fe, Cu and Cr are very similar, but La, Y, V and Zr have much larger ionic radius than that of Ni. However, trying these elements as dopants may provide contribution to the literature. In addition to ionic radius of dopant, oxidation state is also important in terms of electrical properties. Inserting an element with oxidation state lower or larger than that of base element may disrupt charge neutrality. In fact, most systems have tendency to keep charge balance which is provided by defect formation in the structure. This charge unbalance and defect formation greatly affect the electrical properties of materials. However, defect formation and mechanism are not the subject of this study and will not be investigated. These cations, on the other hand, may stabilize charge state of Ni-ion by charge compensation providing the improvement in cyclic stability of the LNCA.

Elements	<b>Oxidation State</b>	Ionic radius (nm)
Li	+1	0.076
Ca	+2	0.100
Na	+1	0.102
Ni	+2	0.056
Fe	+3	0.055
Cu	+2	0.054
Cr	+3	0.062
La	+3	0.103
Y	+3	0.090
V	+5	0.064
Zr	+4	0.072

Table 1.1. Oxidation state and ionic radius of elements used in this study.

Finally, particle size and morphology, ionic conductivity, crystal structure and chemical composition, discharge capacity, charge-discharge rate capability and cycle life of the produced materials will be characterized.

### **CHAPTER 2**

### THERORETHICAL BACKGROUND

#### 2.1. Basic Concepts of Battery Systems

Battery is an electrochemical cell which can convert chemical energy -by means of an electrochemical oxidation-reduction reaction- to electrical energy to provide a static potential for power. A battery consists of one or more cells which are connected in series, parallel or both. The connection type and the number of cells are decided with respect to output voltage and capacity requirement.

Chemistry of active species in an electrochemical cell is significant to satisfy the needs for which application battery will be used. The performance of the active species can be designated using specific energy, specific power, life span and cost terms. These terms constitute battery criteria. However, none of batteries can meet all these criteria. Since performance of a battery is determined by cell components, it will be useful to examine these components.

## 2.1.1. Battery Components and Principle of Operation

An electrochemical cell consists of two electrodes (anode and cathode), electrolyte and a separator. During charging and discharging of a battery, oxidation halfreaction takes place in the anode, reduction half-reaction takes place in the cathode and lithium ion transfer occurs from positive electrode to negative electrode. In the case of discharge, negative electrode will be the anode since oxidation by electron loss always occurs in the anode. However, positive electrode will be the cathode where reduction half-reaction takes place by gain of electrons. In the case of charging of a battery, anode will be positive electrode and cathode will be negative electrode. Oxidation and reduction reactions during charging and discharging are summarized in table 2.1.

	DISCHARGE	CHARGE
Negative Electrode	$A \rightarrow A^+ + e^-$	$A^+ + e^- \rightarrow A$
Positive Electrode	$B + e^- \rightarrow B^-$	$B^- \rightarrow B + e^-$
<b>Overall Reaction</b>	$A + B \rightarrow A^+ + B^-$	$A^+ + B^- \rightarrow A + B$

**Table 2.1.** Oxidation and reduction half-reactions of a battery.

Figure 2.1 shows the electrical and ionic flow during charge and discharge operations. During discharge, electrons flow from anode to cathode through external load which makes anode negative electrode. Ionic flow, on the other hand, occurs from cathode to the anode. Electrochemical reactions take place spontaneously during discharge. However, electrons flow from cathode to anode and ions in the electrolyte flows from anode to cathode during charging of a battery. Since electrochemical reactions are non-spontaneous during charging, the counter current is required and it is supplied by the power source in the external circuit. Separator is placed between the two electrodes avoiding the electron transport. Because, electron flow through separator causes electrical shortcut of the battery. But, it allows transport of the ions between two electrodes to complete the circuit while electron flow takes place through the external circuit. In an electrochemical system, electrolyte provides the medium for charge transfer, as ions, between the anode and the cathode [15]. Most electrolytes are in a liquid form, but, there are also solid electrolytes. Choosing the type of an electrolyte mainly depends on the application of a battery.

### **2.1.2.** Classification of Batteries

In terms of chargeability, batteries can be categorized into two which are called as primary and secondary batteries. In the case of primary batteries, electrochemical reactions in the cell is irreversible which means that during discharge, the chemical



Figure 2.1. Electrochemical operation of a cell during discharging and charging.

species in the cell is used up causing that the battery can only be used once. These types of batteries are mainly used in toys, hearing aids, watches, clocks, flashlights, radios, etc. Zinc-carbon batteries, magnesium and aluminum batteries, alkaline-manganese dioxide batteries, mercuric oxide and silver oxide batteries are the major examples of primary batteries. Secondary batteries, on the other hand, can be recharged by applying a current in the opposite direction of discharge current. By this way, batteries can be used more than once through charge/discharge steps. Main applications of secondary batteries are automobiles, lap-top computers, mobile phones, motor drives, etc. Lead-acid batteries, nickel-zinc and nickel-hydrogen batteries, and lithium-ion batteries are in the secondary battery category. Among them, lithium ion batteries have a great importance due to their widespread applicability. Last decades, having started to take place in electric and hybrid vehicle applications in addition to portable electronic devices, studies on lithium ion batteries have been accelerated.

### 2.2. Lithium-Ion Batteries

Lithium ion battery is one of the most important secondary (rechargeable) batteries due to its remarkable progress of electrochemical features in years. Having a high energy density makes lithium ion batteries more advantageous than other battery systems. Figure 2.2. shows the comparison of specific energies of lead acid, nickel cadmium, nickel metal hydride and lithium ion batteries in terms of different cathode materials used in Li-ion battery systems. Almost all lithium ion battery systems have higher specific energy than other types of batteries.



Figure 2.2. Specific energy values of various battery systems. [16]

Unlike other battery systems, it is quite advantageous to use lithium-ion batteries because of the variety of chemical structure especially for the cathode materials. In order to examine the cathode materials used in commercial applications in more detail, they can be separated into three headings considering the structural properties: layered, spinel and olivine.  $LiCoO_2$  (LCO),  $LiNiO_2$  (LNO),  $Li(NiCoAl)O_2$  (NCA) and  $Li(NiMnCo)O_2$  (NMC) are the examples of cathode materials having layered structures.  $LiMn_2O_4$  (LMO) has a spinel structure with pure and alloyed variants, while LiFePO<sub>4</sub> (LFP) has olivine structure likewise with pure and alloyed variants.

These materials are used considering the battery criteria such as energy, power, safety, cost and performance. However, since no cathode materials can meet these criteria precisely until now, it is aimed to provide improvements by alloying and nanotechnology methods, and studies in this area are still ongoing [17-22].

Graphite anode is the most widely used negative electrode in Li-ion batteries. It is more advantageous to use graphite anode instead of lithium metal which is the first material used as an anode in lithium batteries. The reason why lithium metal is not used is that solid electrolyte interface (SEI) forms on the Li metal and grows as dendrites through positive electrode. When these dendrites reach positive electrode, this causes the short circuit of the battery, which is an important safety issue and should be avoided [23]. At this point, it will be beneficial to explain the formation of solid electrolyte interface.

SEI is a kind of passivation layer that forms due to the irreversible decomposition of electrolyte. In Li-ion batteries, this decomposed layer forms on negative electrode because at the operating voltage of this electrode, most electrolytes are not stable during charging of a battery. In most cases, this passivation layer protects the electrode material hindering further degradation in that it does not conduct electrons and does not allow electrolyte molecules to pass through. However, lithium ions are able to pass through SEI layer. As a result, cycling maintenance of the battery is not affected from this passivation layer [24, 25].

In lithium ion batteries, electrical energy is stored by intercalation of lithium ions through delithiated negative electrode. This ion migration through negative electrode is named as charging. Battery becomes discharged when lithium ions migrate from negative electrode. Leaving lithium ions from this electrode is named as deintercalation. Intercalation/deintercalation process of lithium ions, typical anode half-cell, cathode half-cell and the full cell reactions can be seen in the equations 2.1, 2.2, and 2.3 which are given below [26].

Cathodic-half reaction :  $\text{Li}_{x}(\text{TM})\text{O}_{2} \quad \longleftrightarrow \text{Li}_{x-y}(\text{TM})\text{O}_{2} + y\text{Li}^{+} + ye^{-}$  (2.1)

Anodic-half reaction :  $\text{Li}_{x-y}C + y\text{Li}^+ + ye^- \iff \text{Li}_xC$  (2.2)

Overall cell reaction : 
$$\text{Li}_{x}(\text{TM})O_{2} + \text{Li}_{x-y}C \quad \longleftrightarrow \text{Li}_{x-y}(\text{TM})O_{2} + \text{Li}_{x}C$$
 (2.3)

### 2.3. Active Material Synthesis Methods

Electrode powders for lithium ion batteries can be synthesized using various production methods. These methods can be basically separated into two with respect to physical states of the reactants, i.e. in the solid state or in a solution. In the case of solid state reaction route, mixing and grinding can be carried out by hand or by ball milling. Grinding process breaks the particle bonds and provides the creation of chemically reactive new surfaces. This results in the reaction of solid particles with each other and with their surroundings. In addition to grinding, particles can be activated using microwave, as well. However, solid state reaction route should be followed by calcination at high temperatures because of the slow reaction kinetics at the solid state to allow diffusion of the solid particles. Besides, liquid state reaction route can also be separated into two as sol-gel and crystallization methods. If crystallization is carried out at high temperature and pressure, this is named as hydrothermal method. Crystallization occurring at atmospheric pressure is named as co-precipitation methods [27, 28].

Co-precipitation method can be mainly explained as simultaneous precipitation of metal salts as hydroxides, formates, etc. It is advantageous to synthesize powders via this method because it is a simple production method which can be carried out using reusable glassware and does not require expensive equipment. Precipitation occurs when thermodynamic conditions are satisfied, i.e. when solution is supersaturated. Ammonium hydroxide, lithium hydroxide and sodium hydroxide are

commonly used as precipitating agents to form a basic environment for the solution. Precipitation duration mainly depends on the mixing degree, temperature and the purity of the solvent. The pH value of the medium is another parameter which affects most significantly the solubility of the components, chemical composition of the precipitate and kinetics of the reaction. It also affects the surface area, particle size and size distribution of the precipitate, i.e. if pH value increases, particle size gets smaller and distribution becomes narrower [29-32].

In this study, NCA powders were synthesized by co-precipitation method using magnetic stirring and ultrasonic sound wave. Hydroxide precipitates of precursors were obtained by pH control. The pH value of the aqueous solution was chosen using Pourbaix diagrams of metals used in this study and precipitates were obtained in a basic environment.

## 2.4. Ultrasonic Sound Theory and Applications

Sonochemistry is based on bubble formation, growth and collapse, i.e. acoustic cavitation. It is believed that this acoustic cavitation procedure satisfies breaking of chemical bonds at lower frequencies and power in the orders of 20 kHz and 0.3  $W/cm^2$ , respectively [33]. These bubbles are formed as a result of ultrasonic irradiation which is composed of alternating compression and expansion of the waves. Once these bubbles are formed, they grow with the diffusion of vapor solute through these bubbles. Growth of bubbles continue until reaching critical size which is in the range of ten microns to a few hundred microns. When bubbles reach the critical size, they collapse and this leads a 5000 °K local temperature and 1000 bar pressure. As a result of local increase in temperature and pressure, chemical bonds are broken [34]. Ultrasonic wave motion resulting in acoustic cavitation was demonstrated in figure 2.3(a).



**Figure 2.3.** (a) Ultrasonic wave motion and acoustic cavitation, (b) Bubble and its surrounding region.

Figure 2.3. (b) shows the bubble formed in a liquid phase and its surrounding region. After the bubble collapse, surrounding region of the bubble reaches 1900 °K temperature. This region has approximately 200 nm width. The importance of this region comes from that sonochemical reactions take place not only in the bubble (in a vapor phase) but also at the surrounding region (in a liquid phase) of the bubble after collapse.

Another significant virtue of bubble formation via ultrasound is that these bubbles act as nucleation sites for new particles to form in the solution. This process is named as sonocrystallization [35]. However, if the cooling rate of collapsed bubble is high, particles do not have much time to crystallize. As a result, amorphous structure formation takes place. This phenomenon occurs in the case of volatile solutes in a solution.

Although, it is difficult to predict the particle shapes formed by ultrasound, particle size distribution is narrower as compared to other synthesis methods. It was reported that at the beginning, particles form as spheres or almost spheres [36]. It can be seen from the figure 2.4 that size of the spherical particles is homogenously distributed in the structure which results in a narrow particle size distribution. Moreover, size of the particles ranges from 70 nm to100 nm which is one the most important advantages of ultrasonic treatment to obtain particles in nanoscale. It was reported that the size of the particles depends on the solution concentration and

volume, i.e. the more concentrated and larger the volume of the solution, the larger particles are formed [37].

Frequency, intensitiy, power and duration of the ultrasonic waves, tip diameter and amplitude are other important parameters affecting the sonocrystallization behavior of particles in addition to solution volume and concentration. Crystallization rate increases with the increasing tip diameter and intensity while particle size gets smaller with the increasing power. Amplitude of the tip dipped into the solution varies depending on the device. Frequencies in the order of 15-30 kHz has not much effect on morphology, size and the distribution of the particles since these ranges are larger that the nuclei size. However, higher frequencies are used for metallic glass to reach glass transition temperature in order to allow crystallization neart his temperture. Increasing power and duration of the ultrasonic wave reduces the particle size. [38]



**Figure 2.4.** SEM images of NCA powder synthesized via ultrasound as a cathode material for lithium ion battery at a magnification of (a) 15,000x and (b) 120,000x.

Ultrasound has a wide application range. The most known application of ultrasonic waves is in medicine during destroying cancer cells. In biology, it is used to demolish the cell walls. It is also helpful to perforating and cleaning the teeth in dentistry, location designation of minerals, oil deposits, etc. in geology, degassing

in metal casting, drilling, cutting, welding and grinding in engineering [39-41]. In addition to these applications, mesoporous catalyst synthesis, drying vegetables controlling water transport mechanisms, surface deposition of silica spheres, synthesis of electrode materials for lithium ion batteries, etc. are the current study topics in this area.

#### **CHAPTER 3**

#### LITERATURE REVIEW

### 3.1. Evolution of Li-Ion Battery Cathodes Towards Li(NiCoAl)O<sub>2</sub> Compound

The first commercialized cathode material for lithium ion battery is  $LiCoO_2$  compound. In 1981, Mizushima et al. [42] prepared this material mixing  $Li_2CO_3$  and  $CoCO_3$  using a solid state reaction route at 900 °C

for 20 hours. This long calcination period resulted in grain coarsening, but it was necessary due to slow kinetics of precursors. After that, this compound was synthesized via many different methods and these methods were summarized by Antolini [43], i.e. solid state synthesis, spray drying, sol-gel, freeze drying, mechanical activation and microwave synthesis to solve grain coarsening problem. This cathode active material is easy to synthesize, but it is expensive, toxic, thermally unstable and its specific capacity (140 mAh/g) is limited [44]. On the other hand, LiNiO<sub>2</sub> as a cathode material is cheaper, has a higher specific capacity (150 mAh/g) and energy density but, difficult to synthesize and more thermally unstable than LCO [45]. Furthermore, tendency of Ni<sup>2+</sup> ions to move Li<sup>+</sup> sites makes this compound insufficient as a cathode active material.

In many studies, it was stated that intensity ratio of (003) and (104) peaks  $(I_{(003)}/I_{(104)})$  gives an information about cation ordering in the crystal lattice. It was claimed that as this ratio gets higher better cation ordering is obtained. Arof [46] studied structural characteristics of LCO, LNO and LNCO mixed oxides and stated that higher  $I_{(003)}/I_{(104)}$  ratio is an indication of better cation ordering. Similarly, Jeong and Lee [47] synthesized LCO cathode active material via mechanical milling method and they obtained decrease in  $I_{(003)}/I_{(104)}$  ratio after high temperature sintering (at 850 C for 24 hours). They claimed that high temperature sintering caused lithium loss in the structure. Therefore, absence of Li ions in the atomic site

of lithium allowed Co ions to occupy Li sites and this leads lower  $I_{(003)}/I_{(104)}$  ratio. Sathiya et al. [48] studied the LCO cathode and supported this approach. They reported that when  $I_{(003)}/I_{(104)}$  ratio is higher than 1.2, this indicates the absence of cation disorder. Similarly, LNO cathode researchers used same approach in their studies. Larcher et al. [49] stated that intensity ratio of (003) and (104) peaks higher than 1.3 is an indication of well-ordered structure without cation disorder. Chang et al. [50] synthesized LiNi<sub>1/3</sub>Co<sub>1/3</sub>Al<sub>1/3</sub>O<sub>2</sub> cathode active material using eutectic molten salt LiOH-LiNiO<sub>2</sub> and Ni<sub>1/3</sub>Co<sub>1/3</sub>Al<sub>1/3</sub>(OH)<sub>2</sub> precursor by mixing them followed by three-phase temperature sintering. They used  $I_{(003)}/I_{(104)}$  ratio and splitting of (006)/(102) and (018)/(110) peaks as indications of well-ordered layered crystal structure. They investigated the effect of different lithium salts on structural and electrochemical behavior. They obtained  $I_{(003)}/I_{(104)}$  ratio as 1.65, 1.64, 1.70, 1.73 and first discharge capacities as 131.9 mAh/g, 136 mAh/g, 146.2 mAh/g, 151.5 mAh/g for LiOH, LiNO<sub>3</sub>, LiOH:LiNO<sub>3</sub> = 0.5:0.5 and LiOH:LiNO<sub>3</sub> = 0.38:0.62samples, respectively. They reported that the larger the intensity ratio, the lower the cation mixing. They concluded that when LiOH:  $LiNO_3 = 0.38:0.62$  mixed lithium salt was used the better structural as well as electrochemical performance was obtained.

Kalyani and Kalaiselvi [51] reported that partial substitution of nickel with cobalt is required to stabilize Ni<sup>3+</sup> to prevent migration of divalent nickel ions to the lithium sites. Zhechava and Stoyanova [52] stated that cobalt substitution improved layered crystal structure characteristics and rise in the trigonal distortion is the evidence of this improvement. Itou and Ukyo [53] achieved 155 mAh/g first discharge capacity at 0.1 C and 85 % capacity retention after 500 cycles.

After mixed oxide discovery, this idea was developed by many researchers, i.e. Liang et al. [54] synthesized LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cathode active material via coprecipitation method. They obtained 172.1 mAh/g first discharge capacity between 2.8 - 4.3 V at 1 C rate and this compound preserved 94.3 % of its capacity after 100 cycles. Shaju et.al. [55], on the other hand, synthesized Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub> via
mixed hydroxide method and achieved 200 mAh/g capacity at cut-off voltage range between 2.8-4.6 V. Pişkin and Aydinol [56] synthesized four different NMC compounds, i.e.  $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ ,  $Li(Ni_{0.2}Mn_{0.2}Co_{0.6})O_2$ ,  $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ and  $Li(Ni_{0.2}Mn_{0.6}Co_{0.2})O_2$ , via spray pyrolysis method. It was reported that 85.3 % and 90 % of capacities were preserved after 32 cycles for  $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$  and  $Li(Ni_{0.2}Mn_{0.6}Co_{0.2})O_2$  samples, respectively.

Albrecht et al. [57] synthesized aluminum and magnesium doped LNCO powders in order to improve the structural and electrochemical stability of this compound. It was reported that doping either aluminum or magnesium reduces the cation disorder and improves thermal and cycling stability. Kim et al. [58] synthesized aluminum and gallium doped mixed oxides to investigate charge-discharge features of these compounds. They observed 191 and 210 mAh/g first discharge capacities for aluminum and gallium doped samples, respectively.

#### 3.2. Structural Properties of Li(NiCoAl)O<sub>2</sub> Cathode Active Material

Cathode materials for Li-ion batteries are mostly in the lithiated form, which means that they are in discharged state, while anode materials such as graphite in the delithiated form. This configuration of anode and cathode provides them to be paired so that lithium transition is satisfied between these two electrodes. Most common cathode materials used in lithium ion batteries categorized into three with respect to their structures. LiMn<sub>2</sub>O<sub>4</sub> (LMO) and LiFePO<sub>4</sub> (LFP) are the examples of spinel and olivine structures, respectively. LiCoO<sub>2</sub> (LCO), LiNiO<sub>2</sub> (LNO), Li(NiMnCo)O<sub>2</sub> (NMC), Li(NiCoAl)O<sub>2</sub> (NCA) are, on the other hand, examples of layered structures. In this regard, Li(NiCoAl)O<sub>2</sub> cathode active material has a layered atomic structure which provides easy intercalation/de-intercalation behavior due to large number of diffusion paths for lithium ions during charge/discharge process of a battery [59, 60].

Kalyani et al. [61] reported superior features of aluminum as a dopant. In addition to its low cost and weight, it stabilizes Ni preventing the decomposition into Ni<sup>2+</sup>

ion which causes the cation disorder. Moreover, +3 is the only oxidation state of aluminum which limits the amount of lithium inserted. This prevents the overcharging of a battery depending on the amount of aluminum inserted into the structure. They carried out charge-discharge cyclic tests with a 0.1 mA/cm<sup>2</sup> current density between 3-4.5 V range up to 15 cycles and they observed maximum capacity as145 mAh/g for LiNi<sub>0.7</sub>Al<sub>0.3</sub>O<sub>2</sub> sample with 10 % capacity fading. Kikuya et al. [62] studied the LiOH –as a lithium source- insertion should be carried out via either dry or wet process. They stated that LiNiCoAlO<sub>2</sub> synthesized with wet process has higher  $I_{(003)}/I_{(104)}$  ratio than that of dry process, i.e. intensity ratio for wet process is 1.39, while 1.08 for dry process. Doeff [63] reported that NCA cathode material have high specific energy and good power capability. These features make this material a significant candidate for vehicle applications.

## 3.3. Production Methods of Li(NiCoAl)O<sub>2</sub> Cathode-Active Material

Kim et al. [64] synthesized  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  compound via continuous coprecipitation method using chelating agent (acetylacetone). Their aim was synthesizing high density cathode material controlling the average particle size with chelating agent to enhance capacity. In this regard, they produced LNCA powder both mixing aluminum with cobalt and nickel (in the same batch) and inserting aluminum separately. They obtained high density powder when aluminum added separately.

Guilmard et al. [65] synthesized LiNi<sub>0.70</sub>Co<sub>0.15</sub>Al<sub>0.15</sub>O<sub>2</sub> cathode material by coprecipitation method. They reported that distinguishably splitting of (006)/(102) and (018)/(110) peaks and obtaining high  $I_{(003)}/I_{(104)}$  (1.26) ratio is the evidence of wellordered layered structure formation. As a result, LiNi<sub>0.70</sub>Co<sub>0.15</sub>Al<sub>0.15</sub>O<sub>2</sub> compound gave 150 mAh/g first discharge capacity in the 3-4.15 V range and preserved its 83 % of discharge capacity after 50 cycles at C/20 rate. Han et al. [66] synthesized four different compounds (LiNi<sub>0.80</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub> where x = 0, 0.01, 0.03, 0.05) with solgel method to investigate the effect of aluminum amount on electrochemical behaviors. It was observed that although  $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$  has the lowest first discharge capacity, it has the highest capacity retention among four compounds.

Duvigneaud and Segato [67] synthesized  $\text{LiNi}_{1-x-y}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  compounds via nitrate-PVA precursor method and drying process carried out with either traditional evaporation or spray drying. They obtained first discharge capacity as 105mAh/g and reported that water removal via spray drying method favors the Li<sub>2</sub>CO<sub>3</sub> formation as a secondary phase which causes the capacity loss and capacity fading. On the other hand, first discharge capacity was obtained as approximately 160 mAh/g when traditional evaporation was applied.

## **3.4. Doping Element Effect on Li(NiCoAl)O**<sub>2</sub>

Li et al. [68] doped fluorine to the LiNi0<sub>.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode material to investigate the influence on structural features, electrochemical features and surface chemistry. In this regard, LiNi0<sub>.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) and 2 mole % (NCAF-2), 4mole % (NCAF-4), 6 mole % (NCAF-6) NH<sub>4</sub>F dissolved in alcohol, mixed, dried and calcined under air. Of all compositions, NCAF-2 showed better structural order in terms of absence of cation disorder, lithium slab spacing and hexagonal ordering. Although first discharge capacity of this sample was lower than that of pristine sample (NCA), it showed the best capacity retention behavior at all C-rates (0.1C, 0.2C, 0.5C, 1C, 2C, 5C), at room temperature after 100 cycles and at 55 °C after 50 cycles.

Fey et al. [69] synthesized  $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Ti}_{0.5}\text{Al0}_{.05}\text{O}_2$  mixed oxide as cathode material through solid-state reaction route. First discharge capacity and capacity retention after 40 cycles were 152 mAh/g and 92.7 %, respectively. Xie et al. [70] investigated the effect of sodium doping on electrochemical features of  $\text{Li}_{1-x}\text{Na}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (where x=0, 0.01, 0.02, 0.05) compound. They used Na<sub>2</sub>CO<sub>3</sub> as a sodium source and they found that sodium occupied to the lithium sites. Since ionic radius of sodium is much larger than ionic radius of lithium, it enlarges the distance between transition metal layers where lithium intercalates/de-

intercalates. This made easier the motion of lithium ions because ions found a larger spacing to enter. Although sodium doped samples had lower first discharge capacities than the capacity of un-doped sample, their capacity retention values increased, i.e. 90.71 % for Li<sub>0.09</sub>Na<sub>0.01</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> while 80.46 % for LiNi<sub>0.80</sub>Co<sub>x</sub>Al<sub>y</sub>O<sub>2</sub>.

#### 3.5. Ultrasonic Sound Assisted Synthesis of Battery Materials

Song et al. [71] synthesized Li<sub>1.3</sub>Ni<sub>0.21</sub>Mn<sub>0.64</sub>O<sub>2+d</sub> layered cathode material via coprecipitation method using two different routes: traditional route and ultrasound treatment route. Sulfates of nickel and manganese metals were mixed with NH<sub>4</sub>OH and NAOH to set pH to 11. As a result, Ni<sub>0.25</sub>Mn<sub>0.75</sub>(OH)<sub>2</sub> precursor was observed. This precursor mixed with Li<sub>2</sub>CO<sub>3</sub> and calcined to obtain Li<sub>1.3</sub>Ni<sub>0.21</sub>Mn<sub>0.64</sub>O<sub>2+d</sub> powder. Lattice parameter-c was larger in the case of ultrasound treatment indicating the wider lithium layer spacing. Larger first discharge capacity (251 mAh/g for US treatment and 235 mAh/g for traditional route) was also obtained besides structural improvement. These advances were attributed to nano-sized particle formation with sonochemistry.

Ghosh and Barpanda [72] used ultrasound to synthesize Li-Ti-Na-O anode material for secondary batteries. As compared to solid-state synthesis (12-24 h), anodes produced by this method requires short calcination period (1-2 h) providing energy conservation. Electrochemical and structural stability were also improved by sonochemical treatment.

Okawa et al. [73] synthesized FePO<sub>4</sub> electrode (cathode) material via ultrasonic sound method for Li-ion batteries using ammonium hydrogen phosphate and iron sulfate as precursors. Calcination was carried out for 3 hours at 350 °C and 700 °C ended up with amorphous and crystalline structure formation, respectively. Amorphous FePO<sub>4</sub> showed a better cycling performance, i.e. first discharge capacity was as twice as that of crystalline structures sample, due to crystalline FePO<sub>4</sub> being electrochemically inactive. It was stated that coating amorphous FePO<sub>4</sub> with carbon will make this material a promising competitor of present cathodes.

#### 3.6. Composite and Core-Shell Nano Powders Containing Li(NiCoAl)O<sub>2</sub>

Yoon et al. [74] synthesized LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>-graphene composite powders via mechanical ball milling. It was reported that graphene insertion improved the electrochemical properties. Composite electrode provides 180 mAh/g capacity and 97 % capacity retention after 80 cycles while pristine LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode gives 172 mAh/g capacity and 91 % capacity retention value. Moreover, insertion of graphite doubled the high rate capability of the cell, i.e. 112 mAh/g capacity С Kim preserved at 20rate. and Kang [75] synthesized Li<sub>2</sub>MnO<sub>3</sub>·Li(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> composite nano powders via spray pyrolysis method. First discharge capacity of composite powders increased from 163 mAh/g to 235 mAh/g as compared Li(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> powders while capacity retention of composite powder raised to 85 % from 58 % after 50 cycles. Even if exact splitting at (006)/(102) and (108)/(110) doublets, which indicates the layered structure formation, was not observed, considerable improvement in electrochemical features was obtained.

Ju and Ryu [76] synthesized Li(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)<sub>0.8</sub> (Ni<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>0.2</sub>O<sub>2</sub> cathode material using co-precipitation method. The originality of this study was forming a core-shell structure, i.e. using Li(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> as a core and Li(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>0.2</sub>O<sub>2</sub> as an external layer. The outer shell thickness was obtained as 12.5  $\mu$ m using FE-SEM. High rate capability was improved, i.e. capacity retention raised from 21.6% to 65.1 % at 5C rate, when core-shell structure was used as a cathode active material. It was stated that increase in capacity retention was provided by the outer shell which acted as a protective layer being more stable than the core structure (LNCAO) during electrolyte interaction with electrode.

Likewise, Yoo et al. [77] synthesized core shell structure via co-precipitation method using  $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  as a shell and  $Li(Ni_{0.6}Co_{0.1}Mn_{0.3})O_2$  as a core

structure with a stoichiometric ratio of 2:1.  $Li(Ni_{0.6}Co_{0.1}Mn_{0.3})_{0.36}(Ni_{0.8}Co_{0.15}Al_{0.05})_{0.64}]O_2$  cathode material showed better electrochemical performance owing to improved structural stability.  $I_{(003)}/I_{(104)}$  intensity ratios were given as 1.01 and 1.72 for core (NCM) and core shell structures, respectively. This drastic increase satisfied also progress in the capacity retention (increase from 89.94% to 99.27 % after 50 cycles) and first discharge capacity (increase from 133 mAh/g to 192 mAh/g). Having low cobalt content also is an advantage to use this structure as an electrode material.

## **CHAPTER 4**

## **EXPERIMENTAL PROCEDURE**

## 4.1. Introduction

Experimental procedure will be given in two sections. First section-preliminary work- contains experimental studies on precipitation behavior of nickel, cobalt and aluminum. Binary solutions with a fixed composition of these elements were studied using two different pH controllers. In this regard, in addition to ammonium hydroxide, lithium hydroxide and sodium hydroxide were tried to obtain efficient precipitation behavior. After that, these two pH controllers were tried on the nickel, cobalt, aluminum containing solution. Detailed information about compositions, pH controllers and precipitation characteristics were given in section 4.2. The following section continues with the main steps of the experimental procedure. Powder synthesis was carried out using two different methods which are co-precipitation with magnetic stirring and ultrasonic sound assisted co-precipitation. Citric acid was used as a chelating agent with different compositions to investigate the effect of citric acid on precipitation behavior of the solution. Lithium carbonate and lithium hydroxide were tried as a lithium source to determine the effectiveness of these two compounds on the intercalation behavior of lithium. Different amounts of lithium were also studied for the same purpose. In addition to lithium, sodium carbonate and calcium carbonate was added to Li<sub>x</sub>(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compound in an attempt to improve the capacity retention. Variable heat treatment temperatures and times were also investigated. Finally, calcium, sodium, iron, chromium, copper, vanadium, lanthanum, yttrium and zirconium were used as doping elements to improve structural and electrochemical characteristics of Li<sub>x</sub>(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> within this context. All experimental parameters are given in the table 4.1 and chemicals mentioned above which are used in this study are given in the table 4.2.

Table 4.1. All experimental parameters investigated in this study.

pH controllers	LiOH, NaOH
lithium sources	LiOH, Li <sub>2</sub> CO <sub>3</sub>
calcination temperatures	700 °C, 800 °C, 900 °C
lithium amount (Li:NCA)	0.90, 0.95, 1.00, 1.05, 1.10
citric acid amount (Ni:CA-Co:CA)	4:1, 2:1
doping elements replaced with Li	Ca, Na
doping elements replaced with Ni	Fe, Cu, Cr, La, Y, V, Zr

Table 4.2. Chemicals used in this study.

Li <sub>2</sub> CO <sub>3</sub>	$Ni(NO_3)_2 \cdot 6H_2O$	$La(NO_3)_3 \cdot 6H_2O$	$(NH_4)_2CrO_4$
LiOH	$Co(NO_3)_2 \cdot 6H_2O$	$Y(NO_3)_3 \cdot 6H_2O$	$(NH_4)_6W_{12}O_{39}\cdot 9H_2O$
NaOH	$Al(NO_3)_3 \cdot 9H_2O$	NH <sub>4</sub> OH (28% NH <sub>3</sub> )	NH <sub>4</sub> VO <sub>3</sub>
Na <sub>2</sub> CO <sub>3</sub>	$Fe(NO_3)_3 \cdot 9H_2O$	$C_6H_8O_7 \cdot H_2O$	
CaCO <sub>3</sub>	$Cu(NO_3)_2 \cdot 2.5H_2O$	$Zr(SO_4)_2 \cdot 6H_2O$	

#### 4.2. Preliminary Work

In this section, experimental studies were carried out using Ni-Al and Ni-Co binary solutions to determine the precipitation behavior of these elements in each other. In this regard, 95 at. % nickel and 5 at. % aluminum containing 50 ml 0.2 molar solution was prepared by distilled water. This solution was dripped into 200 ml 3 molar NaOH solution. Meanwhile, NaOH solution was exposed to ultrasonic sound by probe dipped into this solution to obtain a homogeneous precipitation. After precipitation is completed, pH value of this solution was recorded. Then, this solution was filtered, washed with distilled water and dried at 80 °C for 18 hours. Dried sample was calcined at 450 °C for 5 hours and furnace cooled until it reached to room temperature. After that, the sample was grinded and reduced to powder form to carry out EDS, SEM and XRD analysis of the sample. To investigate the precipitation characteristics and define the differences, same procedure was carried out by using 200 ml 3 molar LiOH solution as a pH controller. Secondly, 90 at. % nickel and 10 at. % cobalt containing binary solution and finally, 80 at. % nickel, 15

at. % cobalt and 5 at. % aluminum containing NCA solution was prepared and these experiments were carried out by the same way. However, NCA solution was exposed to further calcination at 900 °C for 2 hours. Experimental parameters of these studies were given in table 4.3.

Sample Name	Elements	Molar Ratio	pH Controller	pH Value
NA05-Na	Ni-Al	0.95 : 0.05	NaOH	13.6
NA05-Li	Ni-Al	0.95 : 0.05	LiOH	12.9
NC10-Na	Ni-Co	0.95 : 0.10	NaOH	13.7
NC10-Li	Ni-Co	0.95 : 0.10	LiOH	13.0
NCA-Na	Ni-Co-Al	0.80:0.15:0.05	NaOH	13.7
NCA-Li	Ni-Co-Al	0.80:0.15:0.05	LiOH	12.8

**Table 4.3.** Experimental Parameters of Preliminary Work.

# 4.3. Synthesis of Li(NiCoAl)O<sub>2</sub>

Synthesis of Li(NiCoAl)O<sub>2</sub> compound was carried out using two different production methods. Firstly, NCA compound was synthesized by co-precipitation method using magnetic stirring to determine experimental parameters such as the amount of citric acid and lithium, calcination time and temperature and doping element effect on the performance of the cathode active material (NCA). After that, Li(NiCoAl)O<sub>2</sub> compound was synthesized by ultrasonic sound assisted coprecipitation using the parameters designated from magnetic stirring experiments.

## 4.3.1. Synthesis of Li(NiCoAl)O<sub>2</sub> by Co-Precipitation with Magnetic Stirring

In this regard, firstly, 250 ml 0.05 molar solution was prepared by dissolution of aluminum in distilled water. 10 ml NH<sub>4</sub>OH (28% NH<sub>3</sub>) was added to this aluminum solution to raise the pH value to 10.5. Then, 300 ml 0.125 molar solution was prepared in a different beaker by dissolution of cobalt in distilled water and this solution was dripped into aluminum solution while 35 ml NH<sub>4</sub>OH (28% NH<sub>3</sub>) was also being dripped into the same solution to keep pH value of the total solution at

10.5. After that, 800 ml 0.25 molar solution was prepared in a different beaker by dissolution of nickel in distilled water. This nickel solution and 150 ml NH<sub>4</sub>OH (28% NH<sub>3</sub>) was added to total solution. This final solution was kept on the magnetic stirring at 200 rpm for 20 minutes to obtain complete dissolution of the precursors. Finally, 150 ml 6 molar NaOH solution was added to the total solution to raise pH value of the final solution to 13.5 and kept on the magnetic stirring at 200 rpm for 20 minutes again. Then, it was waited overnight to obtain complete precipitation. The precipitate was separated from the liquid part by filtering and dried overnight at 110 °C. After that, it was pre-calcined at 300 °C for 12 hours to allow nitrate species to be volatilized and obtain a single-phase nickel oxide. This sample was grinded, washed with distilled water using ultrasonic probe dipped into the solution and dried overnight at 110 °C.

Lithium addition was carried out using two different precursors i.e. LiOH and  $Li_2CO_3$  to obtain  $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound where x=1.10. After Li addition at the solid state, these two samples were calcined at 800 °C for 18 hours. After characterization of these samples, it was decided that  $Li_2CO_3$  is more effective as a lithium source such that there is no secondary phase formation in addition to layered  $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound. The following experiments were carried out using  $Li_2CO_3$  as a lithium source with different amounts. In this case,  $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compounds were synthesized where x=1.05, 1.10, 1.15 and 1.20.

After lithium addition, calcination parameters were designated. In this regard, 3 different temperatures and 2 different calcination durations were tried. To allow layered structure formation high calcination temperatures are required. Considering this concept, calcinations were carried out at 700 °C, 800 °C and 900 °C. In addition to calcination temperature, calcination time is an also important concept. It requires long enough time since layered structure formation kinetics is sluggish. Thus, calcination was carried out for 12 hours and 24 hours separately at each of

three temperatures. At the end of this study, it was decided that calcination for complete phase transformation should be carried out at 800 °C for 24 hours.

The amount of citric acid was another parameter determined in this part of the experimental section. Two different amounts of citric acid were studied to designate the effectiveness of this chelating agent. In this regard, citric acid was added to cobalt-distilled water and nickel-distilled water solutions at the very beginning of the experimental setup to retard the precipitation of these chemicals. The aim of the use of this chelating agent is to allow precipitation of nickel, cobalt and aluminum at the same time. To satisfy co-precipitation of these three elements, the weight percent ratio of nickel to citric acid was set to 4:1 and 2:1. Likewise, the weight percent ratio of cobalt to citric acid was also adjusted to 4:1 and 2:1. Other than citric acid addition, all the experimental steps was the same as it was mentioned above. At the end of this study, it was decided that optimum nickel or cobalt to citric acid ratio is 4:1.

Finally, doping element effect on structural and electrochemical properties was investigated. In this regard, iron, copper, chromium, vanadium, lanthanum, yttrium and zirconium were studied as a dopant. The amount of doping elements was set to 2 at. %. These elements were added to the  $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound decreasing the amount of nickel from 80 at. % to 78 at. %. In this case, 200 ml 0.05 molar solution was prepared by dissolution of aluminum in distilled water. 10 ml NH<sub>4</sub>OH (28% NH<sub>4</sub>) was added to this aluminum solution to raise the pH value to 10.5. Then, 50 ml 0.25 molar solution was prepared in a different beaker by dissolution of dopant and citric acid in distilled water and this solution was dripped into aluminum solution while 3 ml NH<sub>4</sub>OH (28% NH<sub>3</sub>) was also being dripped into the same solution to keep pH value of the total solution at 10.5. The following steps were the same as previous experiments.

### 4.3.2. Ultrasonic Sound Assisted Co-Precipitation of Li(NiCoAl)O<sub>2</sub>

In this method, experimental parameters which were decided by magnetic stirring method was mostly repeated. In this case, 600 ml 0.02 molar aluminum, 300 ml 0.125 molar cobalt and 300 ml 0.67 molar nickel solutions was prepared with distilled water. The number of moles, type of pH controllers and their amount, the amount of citric acid and the final pH value of these solutions were kept constant as they were compared to previous experiments. The aim of molarity and volume change of this primary solutions were to raise the volume of the first solution put into the feeding chamber of the device. During circulation of the solution from feeding chamber to the reactor where ultrasonic sound is applied to this solution, the solution in the feeding chamber should be at a certain level to provide complete circulation (Hielscher Ultrasound Technology, UIP2000hdT generator). At this stage, circulation pump was set to 40 % and it was kept constant until the end of the experiment. Cooling unit of the device, on the other hand, was set to 18 °C to prevent the heating of the reactor. When the ultrasonic energy given to the solution reaches to 350.00 Wh which takes approximately 80 minutes, the sonication was stopped. After draining of the final solution from the device, it was dried overnight at 110 °C. The following steps were the same as previous experiments until the addition of lithium to the NCA powder. In this case, Li<sub>x</sub>(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compounds were synthesized where x=0.90, 0.95, 1.00, 1.05 and 1.10. Li<sub>2</sub>CO<sub>3</sub> was added to NCA powder at the solid state and mixed using mixer mill. After that, these five samples were calcined at 800 °C for 24 hours. Schematic representation of continuous sonication system was given in figure 4.1.

Another study was carried out adding  $Na_2CO_3$  and  $CaCO_3$  to the  $Li_{1.05}(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound. The aim of this study is to increase the capacity retention of layered  $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound. In this regard,  $Li_xA_y(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$  compound was synthesized where A=Na or Ca, x=1.03 and y=0.02. After lithium was added to NCA at the solid state, this powder mixture was calcined at 800 °C for 12 hours. After that, calcium and sodium was added in

the same way how lithium added to obtain two different samples to compare. This powder mixture was exposed to further calcination at 800 °C for 12 hours.

Finally, ultrasonic sound assisted processing was carried out using seven different doping elements.  $Li_{1.05}(Ni_{0.78}D_{0.02}Co_{0.15}Al_{0.05})O_2$  compounds were synthesized where D=Fe, Cu, Cr, La, Y, V or Zr. Replacing these doping elements by nickel atoms, improvement of electrochemical and structural properties was aimed. In this regard, 50 ml doping element-distilled water solution was prepared in addition to aqueous solutions of nickel, cobalt and aluminum. The amounts of these three aqueous solutions were the same as previous experiments. Firstly, one of the aqueous solutions of doping elements were added to aqueous aluminum solution, then the following steps were repeated just as previous experiments.



Figure 4.1. Schematic representation of continuous sonication system.

# 4.4. Doping of Li(NiCoAl)O<sub>2</sub>

Doping of Li(NiCoAl)O<sub>2</sub> was carried out using different experimental routes. These routes are summarized in figure 4.2. Experimental details about doping procedure

carried out with classical co-precipitation (by magnetic stirring) was explained in the section 4.3.2. Ultrasonic sound assisted co-precipitation of doped NiO phase and its experimental steps was also expressed in section 4.3.3.

In addition to these two routes, doping elements were included with two different experimental routes to pure NiO phase which was produced via ultrasonic sound assisted co-precipitation. In the first route, doping element addition was carried out before lithium addition to pure NiO phase. In this regard, 2 at. % of doping elements (Fe, Cu, Cr, La, Y, V or Zr) were dissolved in the trace amount of distilled water, then pure NiO powder was added to this mixture and stirred for 10 minutes with a probe. The total mixture was dried in the room temperature and calcined at 700 °C for 8 hours. Finally, lithium was added to this powder and Li<sub>1.05</sub>(Ni<sub>0.78</sub>D<sub>0.02</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compound (D=Fe, Cu, Cr, La, Y, V, Zr) was obtained. In the second route, doping element addition was carried out after lithium addition to pure NiO phase. In this regard, first, Li<sub>1.05</sub>(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compound was synthesized, then doping elements were added to this compound by the same procedure with the first route.



Figure 4.2. Schematic representation of doping element experimental routes.

## 4.5. Electrode Preparation and Cell Assembly

In electrode making process, cathode active material, carbon black and nmp-pvdf binder were mixed by the help of mixer mill. The weight percent ratio of these three constituents, cathode active material to carbon black to nmp-pvdf binder was 90:5:5, respectively. In this regard, 0.039 grams of carbon black and 0.780 grams of nmp-pvdf binder were added to 0.700 grams of cathode active material ( $Li_{1.05}(Ni_{0.80}, xD_xCo_{0.15}Al_{0.05})O_2$ . After that, 0.05 ml nmp was added to this mixture and all these constituents were blended via mixer mill for 15 minutes. Then, this mixture was coated on aluminum foil, which is used as current collector, with the coating thickness of 250 µm by the help of doctor blade. Coated foil was dried at 100 °C for 1 hour and cut into 18 mm diameter discs. These discs were put into drying-oven under vacuum at 120 °C for 12 hours then worked up into electrochemical cell in the glove box. At this stage, lithium foil having 0.3 mm thickness and 18 mm diameter was used as anode material and glass microfiber (GMF) having 18 mm diameter was used as a separator. Finally, 1 M LiPF<sub>6</sub> in a 50:50 EC:DEC solution was added as electrolyte and cell assembly was completed.

#### 4.6. Characterization of Synthesized Powders

#### **4.6.1. Structural Analysis Tests**

XRD analysis was carried out by XRD, Bruker D8 Advance device. In this regard, diffraction data was collected within the 2-theta range of 20-85°, with a scan rate of  $1^{\circ} \cdot \min^{-1}$  for pre-calcined powders and between 15-80°, at  $0.02^{\circ} \cdot \min^{-1}$  for calcined powders. Collected data was used in Rietveld Refinement method, which is carried out by MAUD software [78], to obtain information about crystal structure of the synthesized powders. By this method, oxygen and lattice parameters of the synthesized powders can be obtained. Using these parameters, the distance between  ${}_{80}Co_{0.15}Al_{0.05})O_2$  sample set. All samples other than  $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  sample set were the oxygen atoms where lithium enters can be calculated. Schematic illustration of Li-gap in LNCA structure was given figure 4.3. In this regard, Li-gap

calculation was carried out using equation below where z is oxygen parameter and c is the lattice parameter [79].

$$Li - gap = \left(\frac{2}{3} - (2 x z)\right) x c$$
 (4.1)

The morphology and crystallite size of synthesized powders was investigated using scanning electron microscope (FESEM, Nova NanoSEM 430) at various magnifications (10000x, 15000x, 20000x, 40000x, 60000x). In addition to crystallite size, particle size distribution of the synthesized powders was obtained using Mastersizer 2000 device. These two methods were carried out for both pre-calcined and calcined powders, as well.



Figure 4.3. Schematic illustration of Li-gap in LNCA structure. [79]

#### 4.6.2. Chemical Analysis Tests

Chemical compositions of the synthesized powders were obtained using inductively coupled plasma mass spectroscopy (ICP-MS) method by Perkin Elmer DRC II device. Energy dispersive x-ray spectroscopy (EDS) method was also used to determine chemical composition by FESEM Nova NanoSEM 430 device. This test was carried out from 3-4 different fields of powders and the average of this data was recorded.

### 4.6.3. Electrochemical Tests

The produced batteries were first charged at C/18 C-rate, which can be considered as the formation charge. Then they were discharged at the same rate to determine the nominal capacity. Then electrochemical tests were continued with the cycling at C/12 rate for 22 cycles for the  $\text{Li}_x(\text{Ni}_{0.} \text{ cycled at C/12 (10 cycles) and C/4 (10 cycles) C-rates}$ . Their cyclic discharge capacity plots and voltage profiles were recorded.

After first discharge, electrochemical impedance spectroscopy (EIS) technique was carried out for all samples and EIS plots were recorded. This technique was applied also after cycling and EIS plots after cycling (22 cycles for  $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$  sample set and 20 cycles for sample set containing doping elements) were recorded. The frequency range was set to 3 mHz – 300 kHz with an AC amplitude of ±10 mV.

## **CHAPTER 5**

### **RESULTS AND DISCUSSION**

## 5.1. Characterization of Preliminary Experiments

Table 5.1 shows the chemical analysis of produced powders which are obtained via energy dispersive spectroscopy (EDS) method. It can be seen that atomic and weight percent of the produced powders coincide with the amounts of the chemicals added to the solution at the beginning. In order to investigate whether single or multiple phases were precipitated, x-ray diffraction (XRD) method was used. Figure 5.1. (a) shows 100 % cubic NiO phases for both NA05-Na (95 mol. % Ni, 5 mol. % Al and NaOH as a pH controller) and NA05-Li (95 mol. % Ni, 5 mol. % Al and LiOH as a pH controller) samples. But, when the chemical components in the solution was changed, i.e. when nickel was doped with cobalt instead of aluminum, unwanted phases were seen. In figure 5.1. (b), Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> phases were seen in addition to NiO phase. Presence of these additional phases can be due to the existence of cobalt in the solution. It was seen that Na<sub>2</sub>CO<sub>3</sub> phase forms when NaOH was used likewise the Li<sub>2</sub>CO<sub>3</sub> phase formation when LiOH was used as a pH controller. Since there is no carbonate containing precursors in the solution, carbonate containing Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> phases probably formed using the carbon dioxide in the air bubbles caused by the sonication process. But, this problem can be solved by further washing the precipitated powder.

NC10-Na (90 mol. % Ni, 10 mol. % Co, NaOH as a pH controller) and NC10-Li (90 mol. % Ni, 10 mol. % Co, LiOH as a pH controller) samples mainly consist of cubic NiO phase. However, 23 % Li<sub>2</sub>CO<sub>3</sub> and 16 % Na<sub>2</sub>CO<sub>3</sub> phases were seen in the XRD diagrams. These phases can be removed by further washing. Besides, the alloying element-cobalt does not form a secondary phase. The lattice parameter of nickel oxide phase in these samples were 4.151 and 4.177 Å, respectively. These

lattice parameter values imply 0.82 % and 1.45 % lattice expansion of NiO phase for NC10-Li and NC10-Na samples, respectively. This expansion is again the evidence for the entering of cobalt element into the nickel oxide phase.

Sample	Ni		Со		Al	
	at. %	wt. %	at. %	wt. %	at. %	wt. %
NA05-Na	93.52	96.91	-	-	6.48	3.08
NA05-Li	93.36	96.84	-	-	6.64	3.16
NC10-Na	37.72	58.21	4.35	6.74	-	-
NC10-Li	89.30	89.26	10.70	10.74	-	-
NCA-Na	73.54	78.83	14.08	15.07	11.60	5.68
NCA-Li	78.20	81.16	14.94	15.56	6.86	3.27

**Table 5.1.** Chemical analysis results obtained by EDS.

In the experiments carried out by the contribution of three elements, further calcination was applied at 900 °C for 2 hours. Figure 5.1. (c) shows the XRD diagrams of NCA(Pre)-Na and NCA(Pre)-Li samples which are obtained after calcination at 450 °C for 5 hours in the same way with NA05-Na, NA05-Li, NC10-Na and NC10-Li samples. It was understood that, the NCA(pre)-Na and NCA(pre)-Li samples mainly consist of cubic NiO phase, but 18 % Na<sub>2</sub>CO<sub>3</sub> and 12 % Li<sub>2</sub>CO<sub>3</sub> were found as secondary phases, respectively. After calcination at 900 °C for 2 hours, some parts of the carbonated phases were disintegrated, but 12 % Na<sub>2</sub>CO<sub>3</sub> and 10 % Li<sub>2</sub>CO<sub>3</sub> remained in the structure. Calcination carried out at high temperatures provided the removal of carbonated phases. Although this problem can be solved by proper washing process, extending the period of calcination time can be another recipe. In addition, longer calcination periods allow structural reorientation from cubic nickel oxide to (layered) hexagonal lithium nickel dioxide. Considering all these, calcination period was set to 24 hours in the following experiments and the effect of calcination temperature on the structural characteristics were studied. Detailed information about these studies were given in section 5.3.



**Figure 5.1.** XRD spectrums of (a) NA05-Na and NA05-Li, (b) NC10-Na and NC10-Li, (c) NCA(Pre)-Na and NCA(Pre)-Li, (d) NCA-Na and NCA-Li samples.

# 5.2. Effect of Citric Acid on Structural Behaviors

Simultaneous precipitation of nickel, cobalt and aluminum was satisfied using citric acid (CA) as a chealating agent. In this regard, three different experiments were carried out to investigate the effect of citric acid on the precipitation behavior of these three elements. In addition to comparing two different citric acid content in the solution, one experiment was performed without citric acid addition. Table 5.2 summarizes the citric acid contents of the samples.

Figure 5.2. shows that both NCA 4/1 CA and NCA 2/1 CA samples consist of 100 % NiO phase. However, 1.7 % Al<sub>2</sub>O<sub>3</sub> formation was observed as a secondary phase when the experiment was performed without citric acid. On the other hand, co-precipitation of nickel, cobalt and aluminum was satisfied with the aid of citric acid whether the ratio was 2/1 or 4/1. Since nickel-to-citric acid and cobal-to-citric acid

ratio 4:1 was enough for co-precipitation of three elements, this ratio was set to 4:1 in the following experiments.

	Molar ratio of					
Sample	Nickel : citric acid	Cobalt : citric acid				
NCA w/o CA	without citric acid	without cirtic acid				
NCA 4/1 CA	4:1	4:1				
NCA 2/1 CA	2:1	2:1				

 Table 5.2. Citric acid contents of the samples.



Figure 5.2. XRD spectrums of NCA w/o CA, NCA 4/1 CA and NCA 2/1 CA.

## **5.3. Temperature Effect on Structural Behaviors**

Production of NCA cathode materials from nitrates of the precursors was provided by co-precipitation as hydroxides of these three elements with the aid of pH control. After that, pre-calcination for 12 hours at 300 °C was applied to remove the organic impurities by pyrolysing them. As a result of this step, pure nickel oxide phase was obtained. Since crystallization requires time to allow complete transformation from cubic NiO phase to layered  $Li(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  phase, calcination was carried out for 24 hours. The effect of calcination temperature on the structural behavior was also investigated.

In this regard, calcination was performed at 700 °C, 800 °C, 900 °C and their structural characterization was carried out using SEM, PSA and XRD. Figure 5.3. demonstrates the SEM micrographs taken before calcination and after calcination at 700 °C, 800 °C and 900 °C, respectively. Mainly fine crystallites with the spherical morphology was obtained before calcination which is shown in figure 5.3.(a). At this step, the measured average crystallite size was 230 nm. Moreover, it seemed that these spherical crystallites were homogeneously distributed in the structure. This spherical shape of the crystallites remained same when the calcination was carried out at 700 °C which is shown in figure 5.3.(b). These particles combined with each other and formed irregular shaped and micron sized particles as well as agglomerates in places when calcined at high temperatures which can be seen in figure 5.3.(c) and 5.3.(d).

In addition to shape of the crystallites, particle size distribution also differs with respect to calcination temperature. Figure 5.4. shows the effect of calcination temperature on particle size and distribution. Among three samples, NCA-800 gave the narrowest particle size distribution having a FWHM value of 1.737. As the temperature increased, the size increased gradually due to agglomeration and/or coelescence of the particles.

Figure 5.5. shows the XRD spectrums of  $Li(NCA)O_2$  powders calcined at three different temperatures after lithium addition at the solid state. Lithium carbonate was used as a lithium source where the ratio of lithium to transition metals was 1:1 for all samples. It can be seen that, NCA-700 sample has extra peaks at 21.5° and 30° which belong to  $Li_2CO_3$  phase. Presence of this secondary phase can be derived from the untransformed lithium carbonate remained in the structure. The reason

why untransformed lithium carbonate exist in the structure is that 700 °C calcination temperature may not be sufficient for complete crystallization. Quantitative phase analysis, which was obtained from Rietveld refinement, showed that NCA-700 sample has 6.6 % Li<sub>2</sub>CO<sub>3</sub> as a secondary phase. When the temperature was raised to 800 °C or 900 °C, complete transformation from cubic NiO to layered Li(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> phase has occured. Since all peaks in the XRD NCA-800 and spectrums of NCA-900 samples belong to Li(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> phase, these two samples consist of 100 % layered  $Li(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  phase.



Figure 5.3. SEM images of (a) cubic NiO and layered Li<sub>1.00</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> powders calcined for 24 hours at (b) 700 °C, (c) 800 °C and (d) 900 °C.



**Figure 5.4**. Particle size distribution of NCA powders calcined at 700 °C, 800 °C and 900 °C.

In addition to quantitative phase analaysis, splitting characteristics of the (006)/(012) and (018)/(110) peaks give an information about the structure of layered compounds. The decomposition of these peaks is an indication of successful layered structure formation [80]. If the layered structure is not formed, these peaks overlap and give a single peak apperance. It seems from figure 5.5. that NCA-700 sample does not show splitting of these peaks. This is an indication that layered structure has not been succesfully formed at 700 °C. However, calcination carried out at 800 °C or 900 °C was sufficient for NCA samples to obtain layered structure formation. Even though both of NCA-800 and NCA-900 samples show layered characteristics related to seperation of (006)/(012) and (018)/(110) peaks, splitting of these peaks are more obvious in the XRD pattern of NCA synthesized at 800 °C.

Table 5.3 demonstrates the Rietveld refinement results of the NCA-700, NCA-800 and NCA-900 samples. In addition to quantitative phase analaysis, intensity ratios

of the peaks at (003) and (104) planes, lattice parameters of hexagonal  $Li(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  structure, occupancy of the oxygen atoms, calculated layer separation where the lithium ions intercalate (or deintercalate) through this space (Li-gap) and  $R_w$  % of the refinements are listed in this table.



Figure 5.5. XRD spectrums of layered Li<sub>1.00</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> powders calcined for 24 hours at 700 °C, 800 °C and 900 °C.

Since Ni<sup>2+</sup> and Li<sup>+</sup> have similar ionic radius ( $r_{Li+} = 0.076$  nm and  $r_{Ni2+} = 0.069$  nm), Ni<sup>2+</sup> ions can occupy to the 3b sites of Li<sup>+</sup> ion in the rhombohedral  $\alpha$ -NaFeO<sub>2</sub> (R $\overline{3}$ m space group) structure. This migration of Ni<sup>2+</sup> ions slows down Li<sup>+</sup> diffusivity and causes capacity loss. As suggested in section 3.1, in the case of doped layered systems, if the intensitiy ratio,  $I_{(003)}/I_{(104)}$  is higher than 1.2, this shows the absence of cation disorder [48]. Among three samples, NCA-800 gave the highest intensity ratio. This ratio is also above the critical value for NCA-700. Since  $I_{(003)}/I_{(104)}$  ratio

is lower than 1.2 for sample NCA-900, it can be said that, Li/Ni cation mixing presents in this structure.

**Table 5.3.** Rietveld analysis results of the samples produced at different calcination temperatures.

Sample	% %		I <sub>(003)</sub> /	lattice parameter			Oxygen	Li-gap	%
Sumpro	Li(NiCoAl)O <sub>2</sub>	Li <sub>2</sub> CO <sub>3</sub>	$I_{(104)} = a(A) - c$		c (Å)	c/a	parameter	(A)	<b>R</b> <sub>w</sub>
NCA-700	93.4	6.6	1.28	2.869	14.171	4.939	0.2575	2.1490	6.478
NCA-800	100	-	1.34	2.871	14.208	4.949	0.2596	2.0964	5.521
NCA-900	100	-	1.10	2.885	14.290	4.953	0.2618	2.0461	9.022

It can be seen in table 5.3 that as calcination temperature increases, lattice parameters a, c and c/a ratio increases gradually. This ratio gives an information about the trigonal distortion of layered systems. Julien et al. [81] claimed that c/a ratio higher than 4.899 indicates the high cation ordering. In this manner, this ratio is higher than 4.899 for all samples. However, intensity ratio of the sample NCA-900 contradict with this statement since its intensity ratio is lower than the critical value.

Oxygen atom positions were also indexed in the table 5.3. These oxygen parameters were taken advantage of calculation of the Li-gap together with the lattice parameter, *c*. Calculated Li-gap shows the distance between oxygen atoms where lithium intercalates/de-intercalates in the structure. Among three samples, NCA-700 has the highest Li - gap value which is 2.1490 Å. It is known that as this value gets higher, lithium ion diffusion gets easier.

Considering all structural parameters, there exists high cation ordering but, poor splitting characteristics of (006)/(012) and (018)/(110) peaks for sample NCA-700. Presence of 6.6 % Li<sub>2</sub>CO<sub>3</sub> as a secondary phase is also disadvantageous for this sample. Besides, sample NCA-900 consists of 100 % layered Li(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> phase but, has poor structural characteristics in terms of

cation ordering. Among three samples, sample NCA-800 has the optimum structural properties considering the high cation ordering, narrow particle size distribution and the absence of secondary phases. Hence, calcination temperature was decided as 800 °C for 24 hours for the following experiments.

# **5.4. The Effect of Lithium Amount on Structural and Electrochemical Properties**

Lithium stoichiometry is an important factor for electrochemical performance of a battery in the case of LiNiO<sub>2</sub> systems. Because, deviation from ideal stoichiometry especially the lithium deficiency can cause  $Ni^{2+}$  ions occupy the lithium sites. In this study, considering the cation mixing behavior of LiNiO<sub>2</sub> systems,  $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$  compounds (x= 0.90, 0.95, 1.00, 1.05 and 1.10) were synthesized and the effect of lithium amount on electrochemical and structural behaviors was investigated.

The ICP-MS analysis for  $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$  compounds are listed in table 5.4. The composition of compounds was calculated from the obtained concentrations with the ICP-MS. The results are in agreement with the calculated values within the limits of error except the  $Li_{1.10}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  composition. Lithium amount in this composition is very close to that of  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compound according to calculated formulas listed in the table 5.4. This situation is probably due to the volatility of lithium. For all compositions, lithium amount is lower than the amount added at the beginning which coincides with the previous statement.

The morphology of cubic NiO phase and all layered  $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compounds were obtained by SEM. Figure 5.6 (a) shows the cubic NiO phase which has particles with multidimensional morphology and comprises spherical, very fine crystallites. The mean particle size of this powders were obtained as 7.385  $\mu$ m. After heat treatment at 800 °C for 24 hours, mean particle size of layered  $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compounds rises up to 25  $\mu$ m and spherical particles turn

into multidimensional morphology. In figure 5.7, d(0.1), d(0.5) and d(0.9) implies the 10, 50, 90 volume % of the powders are below the given values in microns, respectively. The width at the half height of the peak point inserted as FWHM column in the figure 5.7. The FWHM gives an information about the measure of the particle size distribution to compare all samples numerically.

**Table 5.4.** Chemical analysis results of layered  $Li_x(NCA)O_2$  samples obtained by ICP-MS analysis.

Commle	Concentration (wt. %)				Coloulated Formula	
Sample	Li	Ni	Со	Al	Calculated Formula	
Li <sub>0.90</sub> (NCA)O <sub>2</sub>	6.91	54	9.32	1.22	$Li_{0.89}(Ni_{0.82}Co_{0.14}Al_{0.04})O_2$	
Li <sub>0.95</sub> (NCA)O <sub>2</sub>	7.29	54	9.28	1.26	$Li_{0.93}(Ni_{0.82}Co_{0.14}Al_{0.04})O_2$	
$Li_{1.00}(NCA)O_2$	7.37	52	8.99	1.23	$Li_{0.98}(Ni_{0.82}Co_{0.14}Al_{0.04})O_2$	
$Li_{1.05}(NCA)O_2$	7.56	51	8.93	1.19	$Li_{1.02}(Ni_{0.82}Co_{0.14}Al_{0.04})O_2$	
$Li_{1.10}(NCA)O_2$	7.63	52	8.90	1.23	$Li_{1.02}(Ni_{0.82}Co_{0.14}Al_{0.04})O_2$	



Figure 5.6. SEM images of (a) cubic NiO and layered (b)  $Li_{0.90}(NCA)O_2$ , (c)  $Li_{0.95}(NCA)O_2$ , (d)  $Li_{1.00}(NCA)O_2$ , e)  $Li_{1.05}(NCA)O_2$ , f)  $Li_{1.10}(NCA)O_2$  compounds.

Figure 5.8. represents the XRD diagram of NiO phase recorded within the 2 $\theta$  range of 25° - 85°, with a scan rate of 1°·min<sup>-1</sup>. As a result of Rietveld refinement, 3.3604 % R<sub>w</sub> value was obtained showing that diffraction peak positions match well with those of NiO phase. The lattice parameter, *a* of pure cubic NiO phase raises from 4.117 Å to 4.181 Å. This 1.56 % increase in lattice parameter, *a* is the evidence that aluminum and cobalt atoms may have occupied to atomic site of nickel and these three atoms share this sites leading the formation of solid solution of Ni-Co-Al elements.



Figure 5.7. Particle size distribution of (a)cubic NiO phase and (b)layered  $Li_x(NCA)O_2$  compounds (x= 0.90, 0.95, 1.00, 1.05 and 1.10).

Figure 5.9. XRD spectrums shows the of single-phase layered Li<sub>x</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> compounds (x= 0.90, 0.95, 1.00, 1.05 and 1.10) recorded within the 20 range of  $15^{\circ}$  -  $85^{\circ}$ , with a scan rate of  $0.02^{\circ} \cdot \text{min}^{-1}$ . This figure shows that all peaks match well with the standard layered structure of a-NaFeO2 (space group  $R\bar{3}m$ ). There is no secondary phase formation. In fact, all compositions consist of 100 % Li(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> for all compositions. Moreover, splitting characteristics of (006)/(102) and (108)/(110) peaks are also an indication of layered structure formation, as mentioned before. It can be seen from the figure 5.9. that all samples show obvious decomposition of (006)/(102) and (108)/(110) peaks.

Lattice parameters, *a* and *c* of layered compounds were obtained by Rietveld refinement and listed in the table 5.5. As lithium amount increases, lattice parameters, *a* and *c* have almost no change which results in almost constant trigonal distortion, *c/a*. No change in *c/a* ratio suggests that layered characteristic does not affected from the increased amount of lithium. However, the intensitiy ratio,  $I_{(003)}/I_{(104)}$  has more dependance on the lithium stoichiometry. Although all layered  $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$  compounds (x= 0.90, 0.95, 1.00, 1.05 and 1.10) have  $I_{(003)}/I_{(104)}$  ratio larger than even 1.30, they show differences with repect to changing lithum amount in the structure. Among  $Li_x(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compounds,  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  have the highest  $I_{(003)}/I_{(104)}$  ratio.



Figure 5.8. Rietveld refinement of cubic NiO phase.

Oxygen parameters also indexed in the table 5.5. were Among Li<sub>x</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compounds, Li<sub>1.05</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> has the highest Li gap value which is 2.1444 Å. As this value gets higher, lithium ion diffusion gets easier. This result coincides with the capacity values such as  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compound has the highest capacity value and the least capacity fading as well. Having the least degree of cation mixing and largest Li gap value,  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  capacity retention has the highest value with 95 % as can be seen from the table 5.6



Figure 5.9. XRD spectrums of layered  $\text{Li}_x$  (Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compounds (x= 0.90, 0.95, 1.00, 1.05 and 1.10).

Figure 5.10. demonstrates the voltage profiles at C/18 and C/12 rates, respectively. Of all compositions,  $Li_{1.05}(NCA)O_2$  gave the highest nominal voltage and capacity which can also be seen in the table 5.6. The reason is that its structural properties are superior as compared to other compositions which can be seen in table 5.5. Moreover, excess lithium probably provides the saturation of lithium ion sites. Therefore, nickel ion migration to lithium ion site is prevented. This saturation was also contributed to the capacity retention providing the better cycling performance. But, Li<sub>1.10</sub>(NCA)O<sub>2</sub> gave the lowest capacity and capacity retention value. The reason might be that all lithium added to this compound may have not occupied to the atomic site of lithium, i.e. some part of the lithium may have occupied to the nickel site for this composition. This can be the reason of lower  $I_{(003)}/I_{(104)}$  ratio and Li-gap values of Li<sub>1.10</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> composition. Even if calculated formula using ICP-MS are chemical analysis results the same for Li<sub>1.05</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> and Li<sub>1.10</sub>(Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> compositions, lower  $I_{(003)}/I_{(104)}$  ratio and Li-gap values of  $Li_{1.10}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  composition may have caused the poorer electrochemical performance of this sample

**Table 5.5.** Structural parameters of  $Li_x(NCA)O_2$  samples obtained by Rietveld Refinement.

Sample	a(Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Oxygen parameter, z	Li-gap (Å)	% R <sub>w</sub>
Li <sub>0.90</sub> (NCA)O <sub>2</sub>	2.8721	14.2157	4.9496	1.3301	0.2589	2.1135	4.7301
Li <sub>0.95</sub> (NCA)O <sub>2</sub>	2.8711	14.2007	4.9461	1.3737	0.2579	2.1402	6.5756
Li <sub>1.00</sub> (NCA)O <sub>2</sub>	2.8710	14.2041	4.9474	1.3591	0.2589	2.1139	4.3762
Li <sub>1.05</sub> (NCA)O <sub>2</sub>	2.8712	14.2096	4.9490	1.3864	0.2578	2.1444	4.8972
Li <sub>1.10</sub> (NCA)O <sub>2</sub>	2.8713	14.2133	4.9501	1.3778	0.2581	2.1336	5.4655

**Table 5.6.** Capacity and Capacity Retention of layered Li<sub>x</sub>(NCA)O<sub>2</sub> samples.

Sample	First Discharge Capacity at C/18 (mAhg <sup>-1</sup> )	Discharge Capacity after 1 cycle at C/12 (mAhg <sup>-1</sup> )	Discharge Capacity after 22 cycles at C/12 (mAhg <sup>-1</sup> )	Capacity Retention after 22 cycles at C/12 (%)
Li <sub>0.90</sub> (NCA)O <sub>2</sub>	122	103	79	76.8
Li <sub>0.95</sub> (NCA)O <sub>2</sub>	132	111	87	77.8
Li <sub>1.00</sub> (NCA)O <sub>2</sub>	132	108	82	76.7
Li <sub>1.05</sub> (NCA)O <sub>2</sub>	138	134	127	94.6
Li <sub>1.10</sub> (NCA)O <sub>2</sub>	106	75	34	45.5

Figure 5.11 shows the cyclic discharge capacity plots of all  $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$  compositions. Until 7<sup>th</sup> cycle,  $\text{Li}_{0.90}(\text{NCA})\text{O}_2$ ,  $\text{Li}_{0.95}(\text{NCA})\text{O}_2$ ,  $\text{Li}_{1.00}(\text{NCA})\text{O}_2$  compositions lost 22.8 %, 16.6 %, 17.6 % of their discharge capacity, respectively. Since capacity loss of these samples after 22 cycles were 23.2 %, 22.2 %, 23.3 % for  $\text{Li}_{0.90}(\text{NCA})\text{O}_2$ ,  $\text{Li}_{0.95}(\text{NCA})\text{O}_2$ ,  $\text{Li}_{1.00}(\text{NCA})\text{O}_2$  samples, respectively, it can be said that these samples lost majority of their capacity until 7<sup>th</sup> cycle. This loss can be associated with the SEI formation due to chemical decomposition of the electrolyte which causes the lithium loss leading the capacity loss. After 6<sup>th</sup> cycle,

discharge capacity of Li<sub>0.90</sub>(NCA)O<sub>2</sub>, Li<sub>0.95</sub>(NCA)O<sub>2</sub>, Li<sub>1.00</sub>(NCA)O<sub>2</sub> compositions stayed almost stationary. Of all compositions, Li<sub>1.05</sub>(NCA)O<sub>2</sub> has the highest first discharge capacity (138 mAh/g) and gave the best cyclic reversibility, i.e. saved its 95 % of capacity after 22 cycles. Li<sub>1.10</sub>(NCA)O<sub>2</sub> composition, on the other hand, has the lowest first discharge capacity (106 mAh/g) and lost 54% of its capacity consistently, i.e. capacity loss started with the first cycle and proceeded during the whole cycling process. This can be associated with the continuing chemical decomposition of electrolyte until the last cycle [82]. It can be said that, this composition is the least enduring one in terms of reversible cycling.



Figure 5.10. Voltage profiles of Li<sub>x</sub>(NCA)O<sub>2</sub> compounds at (a) C/18 and (b) C/12

Figure 5.12 and table 5.7 shows the electrochemical impedance spectroscopy results of  $\text{Li}_x(\text{NCA})O_2$  samples. $R_{el}$  implies the electrolyte resistance,  $R_{SEI}$  is related to the Li-ion migration through the passivation layer (SEI) and  $R_{ct}$  is attributed to the charge transfer resistance. Charge transfer resistance is based on the hindrance of charge transfer at the surface whereas the SEI resistance is based on the migration of lithium ions through the passivation layer. Thus, these resistances are significant while determining the electrochemical performance of the active materials.

Of all compositions,  $Li_{1.05}(NCA)O_2$  showed the best performance in terms of electrochemical impedance spectroscopy measurements. Only  $Li_{1.05}(NCA)O_2$  composition gave that much low charge transfer and solid/electrolyte interface (SEI) resistances.



Figure 5.11. Cyclic discharge capacity plots of layered  $Li_x(NCA)O_2$  compounds at C/12 rate for 22 cycles.

Wang et al. [16] reported that increasing SEI resistance is due to the rise in the thickness of surface film over increasing number of cycles. The thickness of SEI film increases as a consequence of irreversible decomposition of the elctrolyte (as well as lithium consumption). In the case of this study,  $R_{SEI}$  values of all samples increased except that of Li<sub>1.05</sub>(NCA)O<sub>2</sub> sample. There is almost no change  $R_{SEI}$  value of this sample which can be explained by the stability of the surface film over cycling. Since  $R_{SEI}$  value of Li<sub>1.05</sub>(NCA)O<sub>2</sub> sample is almost constant, it can be said that the amount of lithium consumed does not change much over cyling. The obtained highest capacity retention for this sample supports the previous statement. Small increases in the resistance values after 22 cycles can also be explained by the

aging of the battery. Among five compositions, however,  $Li_{1.00}(NCA)O_2$  and  $Li_{1.10}(NCA)O_2$  samples showed the worst EIS profiles even only after 1 cycle as can be seen in figure 5.12. Having narrower Li-gap may obstruct Li-ion intercalation/de-intercalation resulting in larger resistance values.



**Figure 5.12.** Electrochemical impedance spectroscopy graphs of  $Li_x(NCA)O_2$  samples at 0 % SOC (a) after first discharge and (b) after 22 cycles.
Samnle		after	1 cycle		after 22 cycles				
Sample	$\mathbf{R}_{\mathrm{el}}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{SEI}}(\Omega)$	$R_{ct}(\Omega)$	χ2	$\mathbf{R}_{\mathrm{el}}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{SEI}}(\Omega)$	$\mathbf{R}_{\mathrm{ct}}(\Omega)$	χ2	
Li <sub>0.90</sub> (NCA)O <sub>2</sub>	6.7	112.6	1182	2.35E-03	6.6	269.3	790.3	2.49E-03	
Li <sub>0.95</sub> (NCA)O <sub>2</sub>	5.9	121.8	1188	1.66E-03	5.4	215.3	1140	1.19E-03	
Li <sub>1.00</sub> (NCA)O <sub>2</sub>	5.4	385.7	3208	2.21E-03	4.9	691.3	1579	6.01E-03	
Li <sub>1.05</sub> (NCA)O <sub>2</sub>	4.8	130.1	386.5	3.67E-03	4.6	125.7	494.8	4.51E-03	
Li <sub>1.10</sub> (NCA)O <sub>2</sub>	5.7	230.3	1481	4.95E-03	5.4	610.6	1867	2.00E-03	

**Table 5.7.** EIS results of Li<sub>x</sub>(NCA)O<sub>2</sub> samples after first discharge and 22 cycles.

## **5.5. The Effect of Sodium and Calcium on Structural and Electrochemical Properties**

In this study,  $Li_{1.03}Na_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  and  $Li_{1.03}Ca_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  compounds were synthesized. In this regard, 2 % sodium or calcium was inserted to  $Li(NCA)O_2$  structure so that these atoms occupy the lithium ion sites. Kang et. Al. [83] reported that capacity retention increases with the increasing lithium ion spacing. Since ionic radii of  $Ca^{2+}(r_{Ca}^{2+} = 0.100 \text{ nm})$  and  $Na^+(r_{Na}^+ = 0.102 \text{ nm})$  are larger than that of  $Li^+$  ion  $(r_{Li}^+ = 0.076 \text{ nm})$ , insertion of these atoms may increase the Li-gap.

Figure 5.13. demonstrates the XRD spectrums of layered  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ ,  $Li_{1.03}Ca_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  and  $Li_{1.03}Na_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  samples. It can be seen from this figure that 100 % layered  $Li(NiCoAl)O_2$  phase was formed for all samples without any secondary phase formation. Splitting of (006)/(102) and (018)/(110) doublets is also the evidence of successful layered structure formation.

Structural parameters of the samples were investigated by Rietveld refinement and given in the table 5.8.  $I_{(003)}/I_{(104)}$  ratio is larger than 1.20 for all samples which shows the absence of cation disorder. Insertion of calcium or sodium to the structure increased both lattice parameters and lithium layer spacing compared to the pristine structure. This result is predictable since ionic radii of Ca<sup>2+</sup> and Na<sup>+</sup> are larger than

that of  $Li^+$  ion. Occupancy of either Ca or Na to the Li site enlarges the lithium layer spacing which can be seen in the table 5.8. Moreover, c/a ratios of all samples are larger than 4.899 which is the measure of trigonal distortion showing the layered structure formation. It can be said that layered structure formation is successfully achieved for all samples.

**Table 5.8.** Structural parameters of Li(NCA), LiCa(NCA) and LiNa(NCA) samples obtained by Rietveld Refinement.

Sample	a(Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Oxygen parameter, z	Li-gap (Å)	% R <sub>w</sub>
Li(NCA)	2.8672	14.1668	4.9409	1.3229	0.2579	2.1373	8.4229
LiCa(NCA)	2.8675	14.1879	4.9478	1.3117	0.2568	2.1717	4.0381
LiNa(NCA)	2.8683	14.1942	4.9486	1.3521	0.2576	2.1499	3.7635



Figure 5.13. XRD spectrums of  $Li_{1.05}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ ,  $Li_{1.03}Ca_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  and  $Li_{1.03}Na_{0.02}(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$  samples.

Particle size distributions of three samples are given in figure 5.14. It can be said from the figure that there is almost no change in the particle size distribution when calcium or sodium are added to the structure. The broadest particle size distribution belongs to Li(NCA) sample whereas it is narrower for LiCa(NCA) and LiNa(NCA) samples. This little difference can be due to the primary particle size of the samples. Figure 5.15 shows the SEM images of Li<sub>1.05</sub>(NCA)O<sub>2</sub>, Li<sub>1.03</sub>Ca<sub>0.02</sub>(NCA)O<sub>2</sub>, Li<sub>1.03</sub>Na<sub>0.02</sub>(NCA)O<sub>2</sub>. The measured average crystallite sizes are 0.85  $\mu$ m, 0.95  $\mu$ m, 1.7  $\mu$ m for the pristine, Ca and Na doped LNCA. It is known that as the particle size gets smaller, samples become more prone to agglomeration due to enhanced surface to volume ratio of nanoparticles. Since particle size analysis cannot detect that the measured particles are whether primary particles or agglomerates, samples with smaller crystallite size may have broader particle size distribution due to their agglomeration tendency.



Figure 5.14. Particle size distribution of  $Li_{1.05}(NCA)O_2$ ,  $Li_{1.03}Ca_{0.02}(NCA)O_2$ and  $Li_{1.03}Na_{0.02}(NCA)O_2$  samples.

First discharge capacity at C/18 and discharge capacities at two different C-rates, i.e. C/12 and C/4, are listed in addition to capacity retention values in table 5.9. It can be seen in this table that doped systems gave larger first discharge capacity than that of Li(NCA) sample. After 10 cycles at C/12, Li(NCA), LiCa(NCA), LiNa(NCA) samples sustained 96.6 %, 97.1 %, 99.1 % of their capacity, respectively. At slower C-rate, calcium doped LNCA gave the highest capacity while sodium doped LNCA was giving the highest capacity retention. At faster Crate, i.e. C/4, however; calcium doped LNCA gave both the highest capacity and capacity retention value. Despite this performance of calcium doped LNCA, sodium doped LNCA gave the highest overall capacity retention value, i.e. 81.7 %. Nevertheless, this value is not much higher than that of calcium doped LNCA. Discharge capacity change with respect to increasing number of cycles is given in the figure 5.16 which summarizes the capacity fading behavior of three samples. In brief, both calcium doped and sodium doped samples showed better electrochemical performance as compared to un-doped LNCA. These results coincide with the c/a (trigonal distortion) and Li-gap (lithium layer spacing) values of these samples. In fact, as the Li-gap value and c/a ratio increases, layered structure features get better which leads enhancement in capacity retention and discharge capacity.



Figure 5.15. SEM images of (a) $Li_{1.05}(NCA)O_2$ , (b) $Li_{1.03}Ca_{0.02}(NCA)O_2$  and (c) $Li_{1.03}Na_{0.02}(NCA)O_2$  compounds.

Figure 5.17. shows the first discharge voltage profiles of Li(NCA), LiCa(NCA) and LiNa(NCA) cathodes between 2.8-4.2 V cut-off voltages. Doped cathode materials gave almost same nominal voltage while un-doped Li(NCA) sample had lower nominal voltage value than that of doped samples.

Table	5.9.	Capacity	and	Capacity	Retention	of	Li(NCA),	LiCa(NCA)	and
LiNa(N	NCA)	samples.							

Samples	Li(NCA)	LiCa(NCA)	LiNa(NCA)
First discharge capacity at C/18 (mAhg <sup>-1</sup> )	132	150	142
Discharge capacity after 1 cycle at C/12 (mAhg <sup>-1</sup> )	129	141	137
Discharge capacity after 10 cycles at C/12 (mAhg <sup>-1</sup> )	125	137	136
Capacity retention after 10 cycles at C/12 (%)	96.6	97.1	99.1
Discharge capacity after 1 cycle at C/4 (mAhg <sup>-1</sup> )	104	121	118
Discharge rapacity after 10 cycles at C/4 (mAhg <sup>-1</sup> )	100	120	116
Capacity retention after 10 cycles at C/4 (%)	96.2	99.5	98.4
Capacity retention after 20 cycles (%)	75.8	80.2	81.7



**Figure 5.16.** Cyclic discharge capacity plots of Li(NCA), LiCa(NCA), LiNa(NCA) compounds.



Figure 5.17. Voltage profiles of Li(NCA), LiCa(NCA), LiNa(NCA) at 0.06C.

Figure 5.18 (a), (b), (c) show EIS profiles of Li(NCA), LiCa(NCA), LiNa(NCA) samples at 0 % SOC after first discharge, at 0 % SOC after 20 cycles and at 100 % SOC after 20 cycles, respectively. Although all EIS data were collected between the same frequency range, when cathode material is charged to 100 % SOC, Warburg element representing the diffusion of lithium ion at small frequncies showed up as can be seen in figure 5.18 (c). Equivalent circuit models used in fitting EIS data were also illustrated in figure 5.18. Equivalent circuit models were particular for each sample set. However, in the 0 % SOC after 20 cycles sample set, while Li(NCA) and LiNa(NCA) samples were explained with the same model, LiCa(NCA) sample was modelled with different equivalent circuit due to presence of Warburg element in the EIS plot.

In addition to surface film (SEI) and charge transfer resistances, Warburg and diffusion coefficients were also listed in table 5.10. As can be seen that the smallest surface film and charge transfer resistances belongs to LiNa(NCA) sample at 100 %

SOC. At the beginning, LiNa(NCA) sample had the lowest  $R_{SEI}$  value while other two samples had similar SEI resistances.

After 20 cycles, SEI resistances of all samples became almost same, but this time  $R_{ct}$  value of LiCa(NCA) sample was visibly smaller than that of other two samples. Increase in SEI resistance at 0% SOC can be associated with the increase in the thickness of surface film over cycling. However, 20<sup>th</sup> discharging followed by charging of the cell to 100 % SOC resulted in the decrease in SEI resistances for all three samples. This decrease indicates that during charging and discharging, SEI thickness changes reversibly but, this does not mean that SEI film completely dissappers during charging (deintercalation) and then it suddenly builts up the same thickness over discharging of the cell (intercalation) [84].

It can be seen in the table 5.10 that charge transfer resistances of all samples decrease at 0 % SOC over cycling. This can be associated with the capacitive behaviour of the electrode. At lower discharge rates, charge stored in the electrode can be larger than charge stored at higher discharge rates. This means that at higher discharge rates, number of already occupied Li sites is smaller than that of at slower discharge rates. This leads faster deintercalation rate with the increased exhange current density parellel with the decreased charge transfer resistance at higher C-rates.

Sa	mple	R <sub>el</sub> (Ω)	R <sub>SEI</sub> (Ω)	R <sub>ct</sub> (Ω)	σ (S·sec <sup>0.5</sup> )	$D \ge 10^{-9}$ (cm <sup>2</sup> ·sec <sup>-1</sup> )	χ2	Equivalent circuit model
Li(NCA)	after first	5.5	90.0	420.9	-	-	2.0E-03	R(QR)(QR)
LiCa(NCA)	discharge at	5.4	76.5	393.3	-	-	1.7E-03	R(QR)(QR)
LiNa(NCA)	0 % SOC	4.1	41.5	264.5	-	-	4.3E-03	R(QR)(QR)
Li(NCA)	after 20	6.2	93.3	192.1	-	-	1.0E-03	R(QR)(QR)
LiCa(NCA)	cycles at 0 %	6.0	109.4	97.1	0.2344	0.84	2.2E-03	R(QR)(Q(RW))
LiNa(NCA)	SOC	5.8	100.7	189.2	-	-	1.0E-03	R(QR)(QR)
Li(NCA)	after 20	6.4	66.7	91.3	0.0365	0.02	7.1E-04	R(QR)(Q(RW))
LiCa(NCA)	cycles at 100	4.5	53.3	48.7	0.6063	5.62	1.8E-03	R(QR)(Q(RW))
LiNa(NCA)	% SOC	5.5	46.0	25.9	0.4193	2.71	3.7E-04	R(QR)(Q(RW))

Table 5.10. EIS results of Li(NCA), LiCa(NCA), LiNa(NCA) samples.



Figure 5.18. EIS plots of Li(NCA), LiCa(NCA), LiNa(NCA) samples (a) after first discharge at 0 % SOC, (b) after 20 cycles at 0 % SOC and (c) after 20 cycles at 100 % SOC.

The lowest charge transfer resistances were obtained at 100 % SOC (fully charged state) for all samples as expected. Moreover, presence of Warburg element obtained at lower frequencies provided to investigate diffusive behavior of lithium and calculated diffusion coefficients were alse listed in table 5.10.

Diffusion coefficient was calculated using the equation below where *R* is the gas constant (J·K<sup>-1</sup>·mol<sup>-1</sup>), *T* is the absolute temperature (K), *A* is the electrode surface area (cm<sup>2</sup>), *n* is the number of electrons transferred per mole (for Li intercalacion/deintercalation process n=1), *F* is the Faraday's constant, *C* is the concentration of Li-ion (mol/cm<sup>3</sup>) and  $\sigma$  is the Warburg coefficient (S·sec<sup>0.5</sup>) [85]. Among three samples, LiCa(NCA) has the highest diffusivity. Having the highest Li-gap where lithium intercalates/deintercalates provides this sample to have high diffusivity.

$$D_{Li}^{+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^4 \sigma^2}$$
(5.1)

# 5.6. The Effect of Doping Elements on Structural and Electrochemical Properties

 $Li_{1.05}(Ni_{0.78}D_{0.02}Co_{0.15}Al_{0.05})O_2$  compounds (D=Fe, Cu, Cr, La, Y, V, Zr) were synthesized using three reaction routes. Detailed information about these routes can be found in section 4.4. In brief, 2 at. % of doping elements were replaced by nickel atoms to improve structural and electrochemical performance of layered LNCA in the scope of this study.

Figure 5.19 shows the XRD spectrums of doped samples having cubic NiO phase (before lithium addition and calcination). It can be seen from the figure that no secondary phase formation was observed which means the 100 % cubic NiO phase formation was obtained for all doped samples.



Figure 5.19. XRD spectrums of doped-NiO phases.

Choosing the doping elements, priority was given to elements not being tried in literature before. In the case of doped systems, the ionic radius of doping element is significant to be able to occupy the atomic site of the element to be replaced with. In fact, the ionic radius of the dopant should be similar to that of base element, i.e. in this case nickel atom  $(r_{Ni}^{3+} = 0.056 \text{ nm})$ . If the ionic radius of dopants used in this study is considered, ionic radius of Fe, Cu, Cr and V are similar to that of Ni<sup>3+</sup>, however, ionic radius of La, Y and Zr are similar to ionic radius of Li<sup>+</sup>  $(r_{Li}^{+} = 0.076 \text{ nm})$ .

Table 5.11 demonstrates the lattice parameters and the lattice parameter changes (with respect to pure NiO phase) of samples synthesized directly ultrasonic wave treatment. Since lattice parameter of pure NiO phase was obtained as 4.181 Å, it can be seen in the table 5.1 that lattice parameter of all samples increased. This lattice parameter change can be the evidence that dopants were able to enter into the structure.

Doping Element	Fe	Cu	Cr	La	Y	V	Zr
a (Å)	4.1909	4.1879	4.1889	4.1866	4.1937	4.1888	4.1919
a change (%)	0.2370	0.1655	0.1884	0.1351	0.3030	0.1873	0.2599
$\mathbf{R}_{\mathbf{w}}(\mathbf{\%})$	3.2544	3.9222	4.0480	3.9923	3.5094	3.7402	3.5509
Ionic radius (nm)	0.0550	0.0540	0.0615	0.1032	0.0900	0.0640	0.0720

 Table 5.11. Structural parameters of doped-NiO phase obtained by Rietveld

 Refinement.

XRD spectrums of doped systems in layered structure form were given in figure 5.20. In the case of doped systems, in contrast to sodium and calcium doped systems, secondary, even tertiary phase formations were observed. Figure 5.20 (a) represents the doped system in NCA-Li-M route. In this regard, all samples in this route consists of 100 % layered Li(NiCoAl)O<sub>2</sub> phase except NCA-Li-La sample. In this sample,  $3.48 \ \ La_2 Li_{0.5} Ni_{0.5} O_4$  phase formation was observed. In fact, the same phase was seen in all lanthanum doped samples and the amount of this phase was 3.48, 1.31 and 1.17 weight percent for NCA-Li-La, NCA-La-Li and US-La-Li samples, respectively.

In the case of NCA-M-Li synthesis route, all samples contain monoclinic Li<sub>4</sub>CoO<sub>4</sub> phase which can be seen in figure 5.20 (b). The amount of this impurity was obtained as 2.17 %, 2.70 %, 2.92 %, 3.11%, 3.25 %, 0.63 % and 2.73 % for NCA-Fe-Li, NCA-Cu-Li, NCA-Cr-Li, NCA-La-Li, NCA-Y-Li, NCA-V-Li, NCA-Zr-Li samples, respectively. Moreover, 0.82 % and 0.61 % Li<sub>2</sub>CO<sub>3</sub> phase formed in the structure of NCA-Y-Li and US-Cr-Li samples, respectively which can be seen from figure 5.20 (a) and 5.20 (b). If splitting behavior of (006)/(102) and (018)/(110) peaks is investigated, it can easily be seen that layered structure was successfully formed for all sample sets.

Structural parameters of all doped samples are listed in tables 5.12, 5.13, and 5.14.  $I_{(003)}/I_{(104)}$  ratios (showing the absence of cation disorder when larger than 1.2) of all samples are larger than 1.2 except the samples synthesized by NCA-M-Li route.

Presence of cation disorder caused poor electrochemical performance for this set, i.e. much lower first discharge capacity and capacity retention values as compared to other two doping routes. Lithium layer spacing values of the samples will be discussed with electrochemical results.

Figure 5.21. shows the SEM images of all doped samples. Similar morphology, which is irregular primary particles forming agglomerates, was observed for all powders. Although small morphology differences were seen for some samples, this discrepancy stems from the difference in dopants, synthesize route and experimental incoherence.

First discharge capacities (at C/18 rate) and discharge capacities at two different Crates, i.e. C/12 and C/4, are listed in addition to capacity retention values in tables 5.15, 5.16 and 5.17. Cyclic discharge capacity plots summarizing the capacity fading behavior of all doped samples which were given in figure 5.22. Figure 5.23 shows the first discharge voltage profiles of doped LNCA cathodes together with the un-doped cathode material between 2.8-4.2 V cut-off voltages. In this manner, US-doped cathode materials gave almost same nominal voltage values with small differences in first discharge capacities except Cu-doped sample. However, solidstate-doped samples (NCA-Li-M and NCA-M-Li) had lower nominal voltages varying with synthesize route and doping element. In the case of NCA-M-Li route, poor electrochemical performance can be related to that Li<sub>4</sub>CoO<sub>4</sub> phase was obtained as a secondary phase for all samples. Presence of this phase causes the lithium and cobalt loss in the Li<sub>1.05</sub>(Ni<sub>0.78</sub>D<sub>0.02</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> phase (where D=Fe, Cu, Cr, La, Y, V, Zr). This deficiency leads to capacity loss as well as the poor cyclic stability since presence of cobalt stabilizes the Ni<sup>3+</sup> ions to prevent migration of divalent nickel atoms to the lithium site. Furthermore, lithium deficiency in the structure may allow easier migration of divalent nickel atoms to the lithium sites. Lower  $I_{(003)}/I_{(104)}$  ratios in the NCA-M-Li sample set, which is an indication of cation disorder, support the previous statements.

It can be seen in these tables and figures that the largest capacity retention values were obtained in lanthanum doped samples even if the first discharge capacity was not the largest. Lithium layer spacing values of La-doped samples are 2.1735 Å, 2.1716 Å, 2.1068 Å for NCA-Li-La, NCA-La-Li and US-La-Li, respectively. It can be seen that the smallest value belongs to US-La-Li sample among the three synthesis routes. The reason is that ionic radius of lanthanum is much larger than that of nickel to occupy its atomic site. Ultrasonic wave treatment may satisfy homogenous distribution and small particle size to allow easier diffusion of lanthanum atoms through nickel sites. However, in the solid state doping routes, lanthanum may occupy Li sites where lithium intercalates/de-intercalates. This occupancy behavior resembles that of calcium and sodium doped samples which was discussed in section 5.5. Larger Li-gap values leading the high capacity retention values may be explained by this way for La-doped samples

Highest first discharge capacities are 152 mAh/g, 88 mAh/g, 132 mAh/g which belong to NCA-Li-La, NCA-Cr-Li, US-Zr-Li samples, respectively. Having the largest capacity value, NCA-Li-La is the most promising sample of all compositions. Cu-doped samples of all three routes gave the highest capacity fading especially at higher C-rates. The poor rate capability of these samples can be due to having large charge transfer resistances which can be seen in figure 5.24 and tables 5.18 and 5.19. After 20 cycles, this resistance increases due to decomposition of active materials through cycling. Figure 5.24 shows the EIS profiles of doped systems between the frequency range of 3 mHz and 300 kHz. All samples fitted to R(QR)(QR) equivalent circuit model and electrolyte, surface film and charge transfer resistances were fitted according to this model. If electrochemical stabilities in terms of EIS measurements are considered, NCA-Y-Li and NCA-V-Li samples become prominent since there is almost no change in both R<sub>SEI</sub> and R<sub>ct</sub> values over cycling.



Figure 5.20. XRD spectrums of (a) NCA-Li-M, (b) NCA-M-Li, and (c) US-M-Li doped systems (M=Fe, Cu, Cr, La, Y, V, Zr).

Sample	a(Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Oxygen parameter, z	Li-gap (Å)	% R <sub>w</sub>
NCA-Li-Fe	2.8629	14.1180	4.9313	1.29	0.2546	2.2236	9.15
NCA-Li-Cu	2.8628	14.0759	4.9168	1.26	0.2587	2.0997	7.70
NCA-Li-Cr	2.8633	14.1221	4.9322	1.19	0.2511	2.3229	6.50
NCA-Li-La	2.8638	14.1300	4.9341	1.38	0.2564	2.1735	10.97
NCA-Li-Y	2.8721	14.2100	4.9476	1.39	0.2572	2.1639	11.47
NCA-Li-V	2.8718	14.2097	4.9480	1.35	0.2587	2.1219	11.09
NCA-Li-Zr	2.8715	14.2119	4.9492	1.22	0.2568	2.1763	8.26

 Table 5.12. Structural parameters of NCA-Li-M samples obtained by Rietveld

 Refinement.

**Table 5.13.** Structural parameters of NCA-M-Li samples obtained by RietveldRefinement.

Sample	a(Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Oxygen parameter, z	Li-gap (Å)	% R <sub>w</sub>
NCA-Fe-Li	2.8805	14.2211	4.9371	1.15	0.2574	2.1611	6.59
NCA-Cu-Li	2.8791	14.2050	4.9339	1.15	0.2572	2.1621	6.20
NCA-Cr-Li	2.8747	14.1506	4.9225	0.90	0.2521	2.2986	8.04
NCA-La-Li	2.8778	14.1990	4.9337	1.17	0.2569	2.1716	6.13
NCA-Y-Li	2.8765	14.1765	4.9284	1.14	0.2573	2.1559	8.23
NCA-V-Li	2.8797	14.2079	4.9339	1.11	0.2568	2.1745	6.55
NCA-Zr-Li	2.8833	14.2255	4.9310	1.07	0.2558	2.2045	7.12

**Table 5.14.** Structural parameters of US-M-Li samples obtained by RietveldRefinement.

Sample	a(Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Oxygen parameter, z	Li-gap (Å)	% R <sub>w</sub>
US-Fe-Li	2.8701	14.2069	4.9499	1.38	0.2590	2.1107	3.95
US-Cu-Li	2.8701	14.1927	4.9465	1.26	0.2577	2.1479	5.02
US-Cr-Li	2.8685	14.1796	4.9433	1.42	0.2587	2.1177	5.67
US-La-Li	2.8684	14.1838	4.9448	1.44	0.2591	2.1068	4.19
US-Y-Li	2.8690	14.1921	4.9466	1.42	0.2595	2.0958	5.34
US-V-Li	2.8699	14.1945	4.9459	1.36	0.2589	2.1134	4.65
US-Zr-Li	2.8711	14.1953	4.9442	1.44	0.2591	2.1087	4.71





Figure 5.21. SEM images of NCA, LNCA and doped LNCA samples.

 Table 5.15. Capacity and Capacity Retention Values of NCA-Li-M Samples.

Samples	First discharge capacity at C/18 (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/12 after 10 cycles (%)	Discharge capacity at C/4 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/4 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/4 after 10 cycles (%)	Capacity retention after 20 cycles (%)
NCA-Li	132	129	125	96.6	104	100	96.2	75.8
NCA-Li-Cu	63	43	39	90.7	-	-	-	-
NCA-Li-Cr	143	131	116	88.6	81	78	97.1	54.9
NCA-Li-La	152	139	137	98.5	123	122	99.2	80.1
NCA-Li-Y	148	139	138	98.8	122	122	99.5	82.6
NCA-Li-V	142	133	125	94.1	84	82	97.5	57.9
NCA-Li-Zr	133	127	120	95.1	95	92	97	69.2

 Table 5.16. Capacity and Capacity Retention Values of NCA-M-Li Samples.

Samples	First discharge capacity at C/18 (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/12 after 10 cycles (%)	Discharge capacity at C/4 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/4 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/4 after 10 cycles (%)	Capacity retention after 20 cycles (%)
NCA-Li	81	68	56	82.3	30	24	81.9	30.1
NCA-Fe-Li	79	64	57	88.8	28	19	69.5	24.5
NCA-Cu-Li	75	52	31	59.8	13	10	74.5	13
NCA-Cr-Li	88	79	66	84.1	40	37	94.2	42.2
NCA-La-Li	87	78	73	93.3	40	40	99.3	45.4
NCA-Y-Li	73	60	40	67.3	19	16	82.4	21.8
NCA-V-Li	53	48	30	63.2	10	10	96.3	18.2
NCA-Zr-Li	64	51	42	82.4	8	-	-	-

**Table 5.17.** Capacity and Capacity Retention Values of (US)-Doped Samples.

Samples	First discharge capacity at C/18 (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/12 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/12 after 10 cycles (%)	Discharge capacity at C/4 after 1 cycle (mAhg <sup>-1</sup> )	Discharge capacity at C/4 after 10 cycles (mAhg <sup>-1</sup> )	Capacity retention at C/4 after 10 cycles (%)	Capacity retention after 20 cycles (%)
US-Li	132	129	125	96.6	104	100	96.2	75.8
US-Fe-Li	124	121	118	97.6	100	99	99	79.8
US-Cu-Li	114	95	84	89.1	64	63	97.5	55.1
US-Cr-Li	131	126	124	98.2	109	108	98.6	82.2
US-La-Li	125	125	123	98.9	109	107	98.4	85.5
US-Y-Li	128	123	116	94.3	89	83	93.5	64.9
US-V-Li	131	126	118	93.9	92	86	93.9	66.1
US-Zr-Li	132	127	121	95.1	108	107	99	81.3



**Figure 5.22.** Cyclic discharge capacity plots of a) NCA-Li-M, (b) NCA-M-Li, and (c) US-M-Li doped systems (M=Fe, Cu, Cr, La, Y, V, Zr).



Figure 5.23. Voltage profiles of a) NCA-Li-M, (b) NCA-M-Li, and (c) US-M-Li doped systems (M=Fe, Cu, Cr, La, Y, V, Zr) at 0.06C.



**Figure 5.24.** Electrochemical impedance spectroscopy graphs of doped samples at 0 % SOC (a),(c),(f) after first discharge and (b), (d), (e) after 20 cycles

Method	Impedance	Dopant						
		Fe	Cu	Cr	La	Y	V	Zr
NCA-Li-M	$R_{el}(\Omega)$	-	1.6	4.6	4.8	5.5	5.2	5.1
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	-	430.5	314.1	27.5	35.8	334	166.7
	$\mathbf{R}_{\mathrm{ct}}(\mathbf{\Omega})$	-	1150.4	666.4	529.2	656.4	636.2	471.5
	χ2	-	2.30E-03	2.48E-03	1.42E-03	1.54E-03	2.45E-03	3.11E-03
NCA-M-Li	$R_{el}(\Omega)$	4	4.9	5.9	5.9	5.6	4.5	4.8
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	171.4	16.4	56.5	104.5	59	30.3	306.8
	$\mathbf{R}_{\mathrm{ct}}(\mathbf{\Omega})$	222	2409	658.1	273.7	265.5	307.9	968.4
	χ2	1.92E-03	2.68E-03	1.51E-03	1.37E-03	2.44E-03	3.14E-03	4.83E-03
US	$R_{el}(\Omega)$	5.8	2.5	2.9	4.8	2.7	2.4	3.6
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	67.1	103	45.8	51.9	774.7	282	499.4
	$\mathbf{R}_{\mathrm{ct}}(\mathbf{\Omega})$	645.8	873.1	664	640.2	237	183.1	44.7
	χ2	2.09E-03	4.71E-03	5.10E-03	7.45E-04	8.16E-03	8.13E-03	1.07E-03

 Table 5.18. EIS results of doped samples after first discharge at 0 % SOC.

 Table 5.19. EIS results of doped samples after 20 cycles at 0 % SOC.

Method	Impedance	Dopant							
		Fe	Cu	Cr	La	Y	V	Zr	
NCA-Li-M	$R_{el}(\Omega)$	-	6.2	5.3	5.8	5.6	5.9	6.7	
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	-	750	547.9	64.3	74.2	364.7	273.6	
	$\mathbf{R}_{\mathrm{ct}}(\mathbf{\Omega})$	-	1214	305.5	142.8	135.3	274.4	181.3	
	χ2	-	2.43E-03	2.34E-03	2.67E-03	1.96E-03	2.73E-03	6.16E-04	
NCA-M-Li	$R_{el}(\Omega)$	4.7	4.9	6.1	5.5	5.7	4.7	5.6	
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	167.4	21.2	80.5	82.4	59.7	20	85.4	
	$\mathbf{R}_{\mathrm{ct}}(\mathbf{\Omega})$	320.6	499.6	138.5	239.7	229.6	315.1	214.9	
	χ2	3.31E-03	1.79E-03	1.29E-03	1.26E-03	1.75E-03	4.49E-03	3.80E-04	
US	$R_{el}(\Omega)$	7.5	3.2	3.5	6.2	3.6	2.8	3.8	
	$\mathbf{R}_{\mathrm{SEI}}(\mathbf{\Omega})$	183	146.1	142.3	162.2	268.9	114.4	97.1	
	$R_{ct}(\Omega)$	258	183.7	318.9	308.6	271.7	256.5	183.9	
	χ2	1.61E-03	3.96E-03	4.20E-03	8.53E-04	2.92E-03	4.15E-03	2.96E-03	

#### **CHAPTER 6**

#### CONCLUSION

One of the aims of this study was to use ultrasonic sound assisted synthesis route for NCA cathode active material to obtain a narrow particle size distribution leading a better structural stability and electrochemical performance. Other aims were to investigate the effect of pH controller, citric acid amount, calcination time and temperature, lithium amount and doping elements on structural and electrochemical properties.

Considering experimental variables, it was determined that it was better to use NaOH as compared to LiOH as pH controller. 4:1 Ni to citric acid, and Co to citric acid ratio is enough to satisfy simultaneous precipitation of nickel, cobalt and aluminum. Long calcination periods were required to satisfy solid state diffusion and reorganization of atoms from cubic to hexagonal structure. Calcination was carried out at 700 °C, 800°C and 900°C. The temperature was determined as 800 °C since 700 °C was not enough to form layered hexagonal structure and 900 °C caused the coarsening of particles. Therefore, the optimum calcination parameters were determined as 800°C and 24 hours.

Five different lithium compositions were studied to determine the structural features and electrochemical performance of LNCA cathode materials. Of all compositions,  $Li_{1.05}(NCA)O_2$  showed the best structural stability  $(I_{(003)}/I_{(104)}=1.3864$ , Ligap=2.1444 Å), first discharge capacity (138 mAh/g with 94.6 % capacity retention) and the lowest SEI (130.1  $\Omega$ , 125.7  $\Omega$ ) and charge transfer resistances (386.5  $\Omega$ , 494.8  $\Omega$ ) during cycling. Thus, this composition was used in terms of lithium content for the following investigations. Another important aim was to see the effect of alloying elements. Calcium and sodium were used as dopants so that these atoms occupy the lithium sites. In this study, the purpose was to increase Li-gap inserting these two dopants having larger ionic radii than that of lithium. Rietveld refinement showed that these atoms were successfully enlarged the lithium spacing, i.e. 2.1373 Å for pristine, 2.1717 Å for LiCa(NCA) and 2.1499 Å for LiNa(NCA). This increase in the Li-gap provided higher diffusivity to the Li ion, higher first discharge capacity (132 mAh/g for Li(NCA), 150 mAh/g for LiCa(NCA) and 142 mAh/g for LiNa(NCA)) and higher capacity retention. Capacity retention after 20 cycles increased from 75.8 % to 80.2 % and 81.7 % for LiCa(NCA) and LiNa(NCA) samples, respectively. When diffusion coefficients of these three samples are considered, the highest value (5.62x10<sup>-9</sup> cm<sup>2</sup>·sec<sup>-1</sup>) belongs to LiCa(NCA) sample. This can be associated with the having the highest Li-gap value of this sample since the Li-gap value increases, capacity fading decreases and diffusivity becomes easier.

Using three different doping routes with seven different dopants (Fe, Cu, Cr, La, Y, V, Zr) 27 samples were also synthesized in the scope of this study. Among 27 doped samples, NCA-Li-La and NCA-Li-Y showed similar good performances in terms of first discharge capacity (152 mAh/g and 148 mAh/g), high rate capability (99.2 % and 99.5 % capacity retention at C/4 rate), overall capacity retention (80.1 % and 82.6 %) and SEI resistance (27.5  $\Omega$ , 35.8  $\Omega$  after first discharge capacity of LNCA from 138 mAh/g to 148 mAh/g and 152 mAh/g for NCA-Li-Y and NCA-Li-La samples, respectively and these two samples preserved approximately 80 % of their capacity after 20 cycles. Therefore, lanthanum and yttrium can be promising elements as dopants to improve the performance of LNCA cathode active material during cycling for lithium ion batteries.

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