Preparation of $LiCoO_2$ and $LiNi_xCo_{1-x}O_2$ by Solid State Reaction Technique

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***Abstract*- $LiCoO_2$ is generally used as cathode active material for the lithium based batteries. Due to the extraordinary properties of nanostructure materials, researchers focus on the synthesis of Nano structured cathode, anode and electrolyte materials. In this study, we aimed to have $LiCoO_2$ nanostructures prepared by solid state reaction technique and investigate crystal structure. We examined the effect of calcinated time on the crystallization; therefore samples were prepared in the same conditions and calcinated at 900ºC but in different calcinated times. Obtained results were discussed. Then, nickel doped $LiCoO_2$ was prepared by the same technique and under same conditions. Subsequently, the effect of nickel dopant was evaluated. Thermal stability of the $LiCoO_2$ precursor powders evaluated by TGA/DTA analysis using Netzsch STA 409 and heating rate was adjusted 10°C/min up to 900°C in air atmosphere. Obtained crystal structures were investigated by XRD, surface morphology was investigated by SEM and results were discussed.**

Keywords*- $LiCoO_2$; $LiNi_xCo_{1-x}O_2$; Solid State Reaction Technique

I. INTRODUCTION

Nowadays, fossil fuels are rapidly running out and this is a crucial factor for the environment pollution. For this reason, necessity to develop new systems to reduce combustion technologies has been urged. Rechargeable Li-ion batteries can be given as examples for the future energy technologies [1]. $LiCoO_2$ has been widely used as the cathode material for commercial lithium-ion battery because it's easy to synthesis and stable discharge capacity [2]. Two-dimensional (2D) $LiCoO_2$ and $LiNiO_2$ adapt the α-$NaFeO_2$ type structure, which can be regarded as a distorted rock salt superstructure [3]. According to the other studies, $LiCoO_2$ can be divided into two classes; LT-$LiCoO_2$ (low temperature $LiCoO_2$) and HT- $LiCoO_2$ (high temperature $LiCoO_2$). HT- $LiCoO_2$ has a layered type (rhombohedral) structure with symmetry $R\bar{3}m$. On the other part LT-$LiCoO_2$ is related to a spinel type structure (cubic structure) with symmetry $Fd\bar{3}m$ [4].

Stoichiometric $LiCoO_2$ in its layered structure has a trigonal crystal lattice with $R\bar{3}m$ symmetry, detoned the O_3 structure. The unit cell can be indexed as rhombohedral or hexagonal. In Fig. 1 a schematic of the hexagonal coordinates to illustrate the layered character of the material [5]. Some techniques for preparation of $LiCoO_2$ have been reported in literature. These include sol-gel [6], solid state [7] and pulsed laser deposition [8]. $LiCoO_2$ powder generally is prepared by solid state reactions. This technique has advantages such as simple, cheap, etc. Besides this, solid state technique has disadvantages such as inhomogeneity, irregular morphology and big particle size.

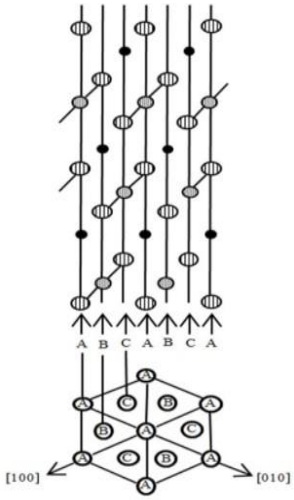


Fig. 1 The layered structure $LiCoO_2$ [5].

:Oxygen :Lithium :Cobalt

In this study, $LiCoO_2$ and $LiNi_xCo_{1-x}O_2$ structure has been synthesized by solid state reaction technique. Thermal stability of the $LiCoO_2$ precursor powders were investigated by TGA/DTA measurements then obtained crystal structure investigated by XRD and surface morphology investigated by SEM.

II. EXPERIMENTAL

$LiCoO_2$ and $LiNi_xCo_{1-x}O_2$ were synthesized by solid state reaction technique. Li_2CO_3, Co_2O_3 and NiO were used as starting materials. According to the other study about synthesizing $LiCoO_2$ and $LiNi_xCo_{1-x}O_2$, starting materials need to be calcinated higher than 800ºC and more than 10 hours [9]. In this study, firstly; Li_2CO_3, Co_2O_3 and NiO were mixed in stoichiometric ratio. Prepared samples were grinded in an agate mortar approximately 30-40 min. then obtained powders were made pellet. The aim of the pellet, by making the reacting atoms closer to eachother , was to increase crystallization. Finally, pellets were calcinated at 900ºC for 10 to 12 hours in an air atmosphere by box

furnace. When the sufficient temperature is reached, Li_2CO_3 and Co_2O_3 react by following equations:

$$Li_2CO_3+Co_2O_3 \rightarrow 2\ LiCoO_2+CO_2$$
$$Li_2CO_3 + (x)\ NiO + (1\text{-}x)\ Co_2O_3 \rightarrow LiNi_xCo_{1-x}O_2 + CO_2$$
$$(x=0.2)$$

The structure obtained from powder samples were characterized by a Rigaku D/Max-IIIC diffractometer range from $2\Theta=10^0$ *to* 90^0 with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA.

III. RESULT AND DISCUSSION

TGA/DTA Analysis

In Figure 2, TGA/DTA curves which belong to stoichiometric mixture of Li_2CO_3 and Co_2O_3 have been shown. According to this data, 18% mass loss in TGA curve may be a result of lithium carbonate decomposing in $Li_2CO_3 \rightarrow Li_2O + CO_2$ equation. Energy at around 400°C-700°C has been lost in order to get the lithium carbonate decomposition and melting, this was shown as occurrence of endothermic peak at around 710°C [13] in DTA curve. Exothermic peak which can be observed in DTA curve at around 790°C means that $LiCoO_2$ was formed as a result of Li_2O and Co_2O_3 reaction.

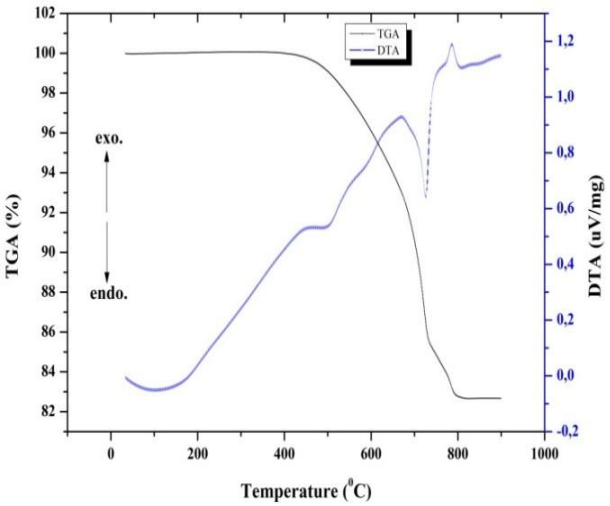


Fig. 2 TGA/DTA curves for $LiCoO_2$ precursor powders

XRD Analysis

According to the XRD result 10 h and 12 h calcinated samples have a $LiCoO_2$ structure but we can say 12 h calcinated $LiCoO_2$ has more crystallization than the other. This result clearly observed from the XRD data. According to XRD result, we can compare with standart and observed interplaner distance (d). Interplaner distance "d" values were calculated by relation "$n\lambda = 2d\sin\Phi$", where "n" is an integer, "λ" is the wavelenght of the x-rays, "d" is the distance between crystal planes and "Φ" is the angel between the incident ray and scattering planes [1]. Standart and calculated interplaner distances values were shown in Table 1. These results show that our results are comply with standart values.

TABLE I STANDARD AND OBSERVED 'd' VALUES

(hkl)	Standard d(Å)	Calculated d(Å)	
		10h calcinated $LiCoO_2$	12h calcinated $LiCoO_2$
003	4.6771	4.8513	4.5578
101	2.4002	2.4499	2.3721
012	2.3020	2.3469	2.2768
104	2.0019	2.0350	1.9812
015	1.8412	1.8502	1.8246
107	1.5491	1.5671	1.5384
018	1.4247	1.4405	1.4165
110	1.4075	1.4199	1.3984
113	1.3480	1.3594	1.3407

XRD results have shown that all of these samples have a hexagonal crsytal structure. Characteristic XRD pattern of $LiCoO_2$ and $LiNi_xCo_{1-x}O_2$ was shown in Fig. 3. The profiles show only slight changes as the dopand nickel in the compounds is varied. According to the other studies since Ni^{+3} replaces with Co^{+3} isomorphically in the solid solutions implying that the lithium ions occupy octohedral sites between $[Ni_x\ Co_{1-x}O_2]$ infinite slabs formed by edge sharing $[Ni_x\ Co_{1-x}O_6]$ octohedral. For this reason all the XRD patterns of $LiCoO_2$ and solid solutions were indexed in hexagonal system assuming the $R\bar{3}m$ symmetry [10-11].

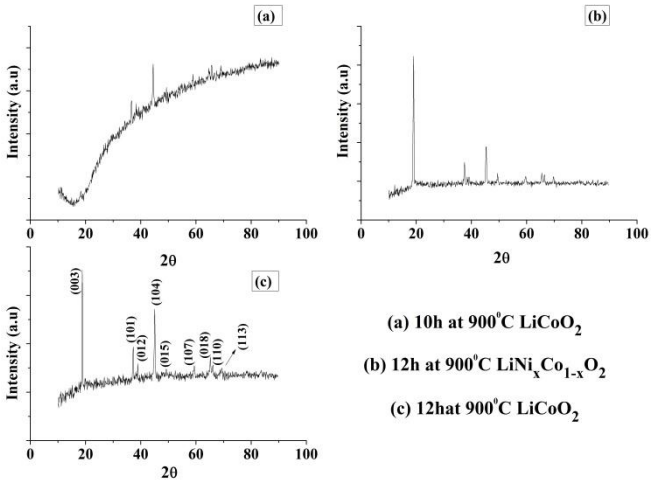


Fig. 3 XRD pattern of samples

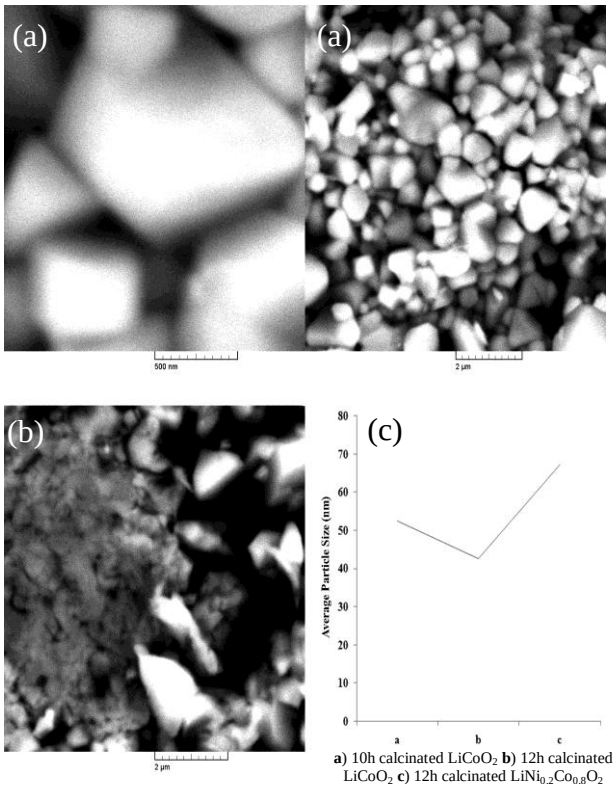
Table 2 shows calculated lattice constant. These results are approximately equal to the standard lattice constants are taken from JCPDS Card No: 50-0653.

TABLE II. STRUCTURAL PARAMETERS OF $LiCoO_2$ AND $LiNi_{0.2}Co_{0.8}O_2$

Sample	Calculated lattice constants (Å)		
	a	c	c/a
10h calcinated $LiCoO_2$	2,219	14,553	6.558
12h calcinated $LiCoO_2$	2,283	13,673	5.989
12 calcinated $LiNi_{0.2}Co_{0.8}O_2$	2.294	13.904	6.061

SEM Analysis

Fig. 4 shows that SEM images of samples and average particle size calculated from scherrer formula. $D = \frac{0.9\lambda}{\beta cos\theta}$ [16] and micro-strain (ε) values calculated by $\varepsilon = \frac{\beta}{4tan\theta}$ [14]. Where D is grain size, λ- X-ray wavelength (1.5418 Å), 0,9 the crystal shape constant, Θ-the reflection angle of the peak, and β is the Corrected full width at half maximum (FWHM) of the highest peak in radians.



a) 10h calcinated $LiCoO_2$ **b**) 12h calcinated $LiCoO_2$ **c**) 12h calcinated $LiNi_{0.2}Co_{0.8}O_2$

Fig. 4 SEM images of a) 12h calcinated $LiCoO_2$ b) 12h calcinated $LiNi_{0.2}Co_{0.8}O_2$ c)Average particle size obtained from scherrer formula

The dislocation density (δ) of the $LiCoO_2$ was estimated using the equation, $\delta=1/D^2$ (lines/m^2) [12]. The calculated D, δ and ε values were showed in Table 3. The grain size 'D' increased by annealing of the $LiCoO_2$ and it was observed that δ decreased by annealing. Micro-strain values are related to average particle size. In previous study, it has been observed that ε values were changed by average particle size [15]. In this study we observed that ε values increased by decreasing particle size. According to those values; defect concentration increase by the increasing ε values. The dislocation density (δ) was described as the length of dislocation lines per unit volume is the measure of the amount of the defects in a crystal. Although the nickel doped lithium cobalt oxide under the same condition with the lithium cobalt oxide, average particle size and ε values greater than the other. As the reason of this result, we can say that defects are created by nickel doping in the crystal structure. According to the SEM images in Figure 4, obtained structure has a uniform morphology about the 500 nm and 2 µm. About the 2 µm $LiCoO_2$ have smoother surface morphology than the $LiNi_{0.2}Co_{0.8}O_2$ therefore we can see independed particle of $LiCoO_2$ and according to this we can talk about the existence of $LiCoO_2$ nanostructures.

TABLE III. CALCULATED "D" ,"δ","ε" VALUES FOR $LiCoO_2$ AND $LiNi_{0.2}Co_{0.8}O_2$

Sample	D(nm)	δx10^{14} (lines/m^2)	εx10^{-3} lines^{-2}m^{-4}
10h calcinated $LiCoO_2$	52,42	3,63	1,7
12h calcinated $LiCoO_2$	42,53	5,52	3,8
12h calcinated $LiNi_{0.2}Co_{0.8}O_2$	67,36	2.20	3,1

IV. CONCLUSION

The aim of this study was to make a $LiCoO_2$ nanostructure by combustion synthesis. For this, we used lithium carbonate, nickel oxide and cobalt oxide starting materials. We observed that when the sufficient temperature was reached, Li_2CO_3, NiO and Co_2O_3 decomposed. According to the TGA/DTA results, the temperature for the formation of $LiCoO_2$ was determined as 800-850°C. Besides, in the study we investigated the effects of calcinated time on the crystallization. For this, prepared samples were calcinated for 10 h to 12 h at 900ºC. According to the results, crystallization increased with calcination time increment. "a" and "c" lattice constant were calculated from the XRD data for each sample, were harmony with the other studies. As a result of this study, $LiCoO_2$ and nickel doped $LiCoO_2$ nanostructures were formed by this technique.

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