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PREPARATION AND CHARACTERIZATION OF $LiNi_{1-X}Co_XO_2$ ($0.2 \le X \le 0.5$) NANOCRYSTALLINE POWDER

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Abstract

The main aim of the research work is to study the preparation and characterization of $LiNi_{1-x}Co_xO_2$ ($0.2 \le x \le 0.5$) nanocrystalline powder. $LiNi_{1-x}Co_xO_2$ ($0.2 \le x \le 0.5$) nanocrystalline powders for lithium ion batteries were prepared by a modified sol–gel method using lithium nitrate ($LiNO_3$), cobalt (II) nitrate ($Co(NO_3)_2.6H_2O$), nickel(II) nitrate ($Ni(NO_3)_2.6H_2O$) as starting materials, de-ionized water as solvent, citric acid ($C_6H_8O_7.H_2O$) as chelating agents and carboxy methyl cellulose as dispersant agent. The prepared $LiNi_{1-x}Co_xO_2$ ($0.2\le x \le 0.5$) nanocrystalline powder was characterized by TG- DTA, XRD, FT IR and SEM analyses.TG-DTA analysis of the synthesized $LiNi_{1-x}Co_xO_2$ ($0.2 \le x \le 0.5$) nanocrystalline powder was carried out to determine the appropriate calcination temperatures. The prepared $LiNi_{0.8}Co_{0.2}O_2$ powders were calcined at 600, 700, 800, 900 and 1000 °C. The resulting calcined powders were characterized by XRD technique. The lattice parameters and the average crystalline size of the samples calcined at different temperatures were calculated using Debye Scherrer equation. It was observed that the crystallite size increases with increasing calcination temperature which may be due to the growth of particle size but the sample calcined at 800 °C was selected as optimum temperature because the sample ($LiNi_{0.8}Co_{0.2}O_2$) has high crystallinity and small crystallite size at this temperature. From XRD spectrum, the observed value of average crystallite size of $LiNi_{0.8}Co_{0.2}O_2$ are 29.58 nm, 32.24 nm, 17.22 nm, 29.25nm and 47.62 nm at different temperatures. Therefore, the other three compounds such as $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ were also prepared by using the same methods. The prepared ($LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$) nanopowders calcined at 800°C were characterized by XRD. From XRD spectrum, the average crystalline size of prepared three compounds are 69.94 nm, 41.76 nm, and 43.43 nm at 800 °C. From FT IR analysis, it was only found stretching vibration of metal- oxygen chemical bonds. Surface feature study of the prepared nanocrystalline powders were observed from SEM. It was observed that agglomeration increase with high porosity and increasing Co doping levels.

Keywords: $LiNi_{1-x}Co_xO_2$nanopowders, sol-gel, calcination temperatures, crystallite size

Introduction

The lithium nickel–cobalt oxide (Li Ni_{1-x} Co_xO_2) used as cathode material was grown at appropriate temperature using sol-gel method. Lithium nickel cobalt oxide ($LiNiCoO_2$) has been widely studied as a cathode material for lithium ion secondary batteries since it has good capacity, high specific energy, good power rates, low self-discharge, and excellent cycle life (Lu *et al.*, 2014).

Layered lithium transition-metal oxides (LTMOs) such as lithium cobalt and lithium nickel are the most advanced studied electrode materials. Many lithium intercalated transition metal oxides have been studied as the positive electrode material used in high energy density rechargeable batteries (Sathiy *et al.*, 2011).

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The sol–gel method has been used to prepare $LiNi_{1-x}Co_xO_2$ at lower temperature and shorter time, and mostly, compound powders with uniform morphology, narrow particle size distribution, and high homogeneity.

In the present work, $LiNi_{1-x}Co_xO_{2,}$ nanopowders for lithium ion batteries were prepared by a modified sol–gel method. The prepared $LiNi_{1-x}Co_xO_2$powders were calcined at different temperature. The characterization of the $LiNi_{1-x}Co_xO_2$powders ($0.2 \leq x \leq 0.5$) nanocrystalline powders were prepared at optimum temperature by sol-gel method. The prepared nanocrystalline powders were also characterized by XRD, SEM, FT IR and TG-DTA techniques.

Materials and Methods

Sample Collection

Lithium nitrate, cobalt nitrate, nickel nitrate, citric acid, carboxy methyl cellulosewas purchased from BDH Chemicals Ltd. Poole Englandandcitric acid used as achelating agent and carboxy methyl cellulose used as a dispersant agent. Distilled water was used as the solvent in all analyses.

Modern instruments techniques were used SEM (Scanning Electron Microscope), XRD (X- ray Diffractometer), TG-DTA (Thermogravimetry /Differential Thermal Analysis) and FT IR (Fourier Transform Infrared Spectroscopy).

Preparation of $LiNi_{1-x}Co_xO_2$ ($0.2 \leq x \leq 0.5$) Nanocrystalline Powder

$LiNi_{1-x}Co_xO_2$nanocrystallinepowder was prepared by sol-gel method using lithium nitrate, cobalt nitrate, nickel nitrate, citric acid, carboxy methyl cellulose and deionized water.

Firstly, (6.9 g) oflithium, (23.2g), (20.35 g), (17.44 g), (14.54 g) of nickel (II) and (5.8 g), (8.73 g), (11.64 g), (14.55 g) of cobalt (II) nitrate salts (1:0.8:0.2M), (1:0.7:0.3 M), (1:0.6:0.4 M), (1:0.5:0.5 M) was added 100 ml of deionized water. Next, 42 g of citric acid (the molar ratio of citric acid/ total metal ions = 1) was added 100 ml of deionized water. The individual solutions were mixed and after that with a small amount of carboxy methyl cellulose (the molar ratio of cellulose to total cations was 5×10^{-6}) was added into this solution. The mixture solution was heated at 65°C for 12 h under constant stirring to form the sol. The sol was then evaporated at 120°C in dry oven until the gel was formed. The gel solution was calcined at various temperatures (300°C, 600°C, 700°C, 800 °C, 900°C and 1000°C for 4 h). Finally, the samples were ground smoothly in an agitate motor. The resulting powders were characterized by SEM, XRD, FT IR and TG-DTA.

Characterization of the Prepared Samples

The chemical composition of$LiNi_{1-x}Co_xO_2$in mass percentage was determined by Flame spectroscopy and Wet analysis. The structural characterization of $LiNi_{1-x}Co_xO_2$ nanocrystalline powder was analysed using FT IR. The interaction of $LiNi_{1-x}Co_xO_2$ nanocrystalline powder was investigated by XRD analysis. Thermal properties of these powders were evaluated by TG-DTA. The morphological structure of the prepared these powder was characterized by SEM.X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat. No 9240 J 101, Japan. Copper tube with nickel filter was used. FT IR spectrum was recorded in the range of 4000-400 $cm^{-1}$by using 8400 SHIMADZU, Japan FT IR spectrophotometer. The scanning electron microscopy (SEM) images were obtained using JSM-

5610 Model SEM, JEOL-Ltd., Japan. Thermogravimetric analyses of samples were performed using TG-DTA apparatus, (Hi-TGA 2950 model).The temperature ranged between 0°C and 600 °C under nitrogen gas (at a rate of 50mL/min).

Results and Discussion

XRD Analysis

The XRD pattern of the prepared $LiNi_{0.8}Co_{0.2}O_2$ nanocrystalline powders calcined at different temperatures are shown in Figures 1- 4 and the average crystalline size, crystal system and lattice parameter are listed in Table 1. XRD pattern of the prepared $LiNi_{1-x}Co_xO_2$ ($0.2 \leq x \leq 0.5$) nanocrystalline powders calcined at 800 °C are shown in Figure 5 and summarized in Table 2. The prepared sample calcined at 800 ºC was selected as optimum temperature because it has high crystallinity and small crystallite size at that temperature. By XRD analysis to the four Co doped $LiNiO_2$ samples, it was found that the layer structure is not very clear in $LiNi_{0.8}Co_{0.2}O_2$ sample. But increasing Co doping level the layer structure formation are distinct. Among the different doping level of $LiNiO_2$ compounds it was found that $LiNi_{0.6}Co_{0.2}O_2$ has perfect layer structure and small crystallite size than other two compounds ($LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$). The crystalline size of $LiNi_{1-x}Co_xO_2$nanocrystalline powder was calculated by using Scherrer's equation (Ahmed *et al*., 2012).

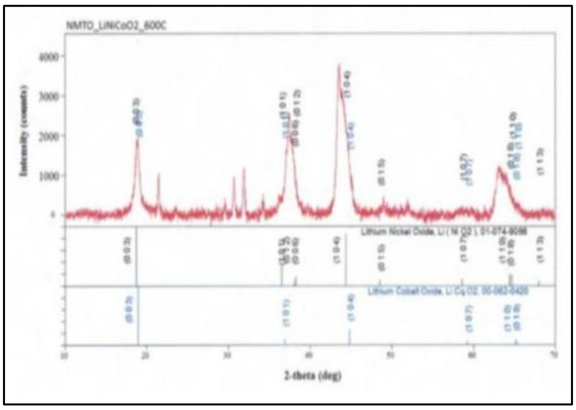


Figure 1 XRD diffractogram of prepared $LiNi_{0.8}Co_{0.2}O_2$ powder at 600 °C

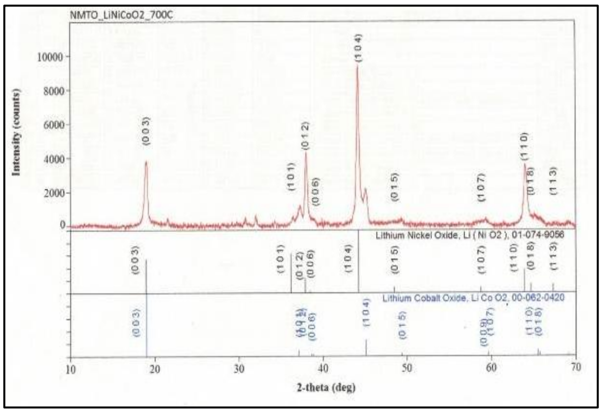


Figure 2 XRD diffractogram of prepared $LiNi_{0.8}Co_{0.2}O_2$ powder at 700 °C

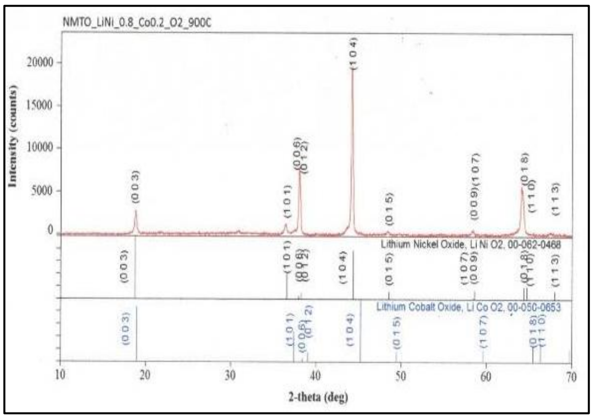


Figure 3 XRD diffractogram of prepared $LiNi_{0.8}Co_{0.2}O_2$ powder at 900 °C

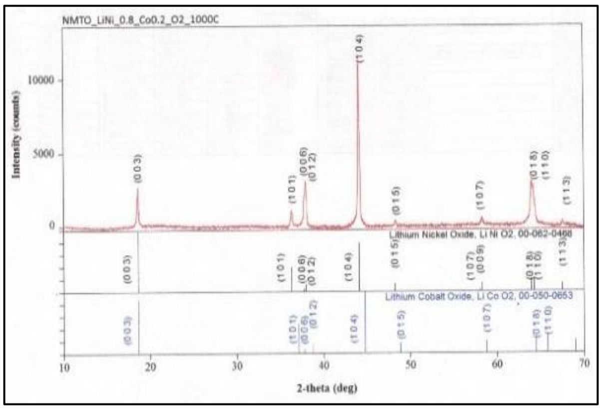
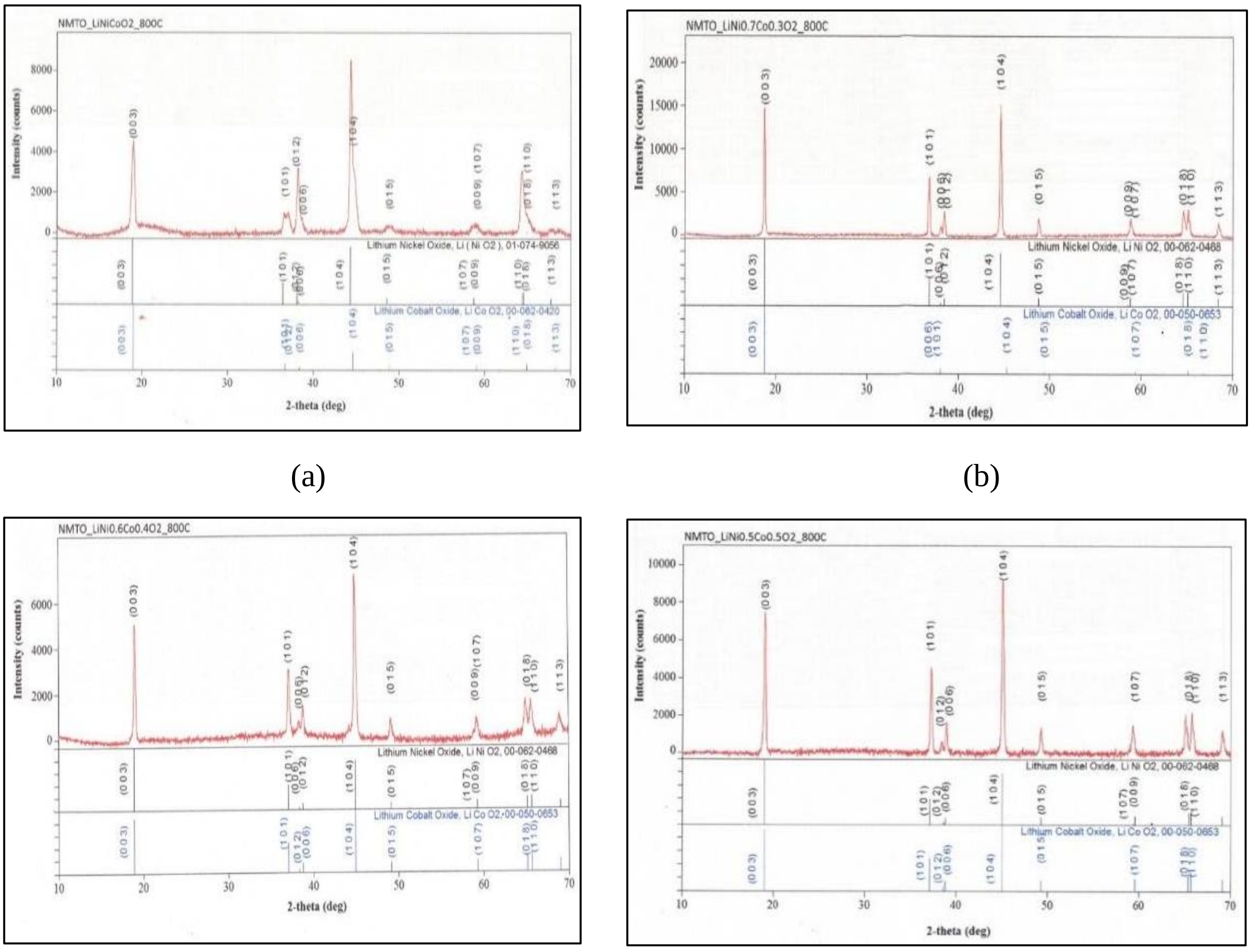


Figure 4 XRD diffractogram of prepared $LiNi_{0.8}Co_{0.2}O_2$ powder at 1000 °C

Table 1 Average Crystalline Size of the Prepared $LiNi_{1-x}Co_xO_2$ Powder at 800 °C for 4 h from XRD analysis

Temperature (°C)	Average crystalline size from		Lattice Parameters		Crystal System
	XRD data (nm)	by using Debye Scherrer equation (nm)	a /A°	c /A°	
600	21.5	29.58	2.8804	14.1890	Hexagonal
700	28.98	32.24	2.9101	14.0365	Hexagonal
900	33.74	29.25	2.8150	14.0493	Hexagonal
1000	54.73	47.62	2.8362	14.2793	Hexagonal



(a) (b)

(c) (d)

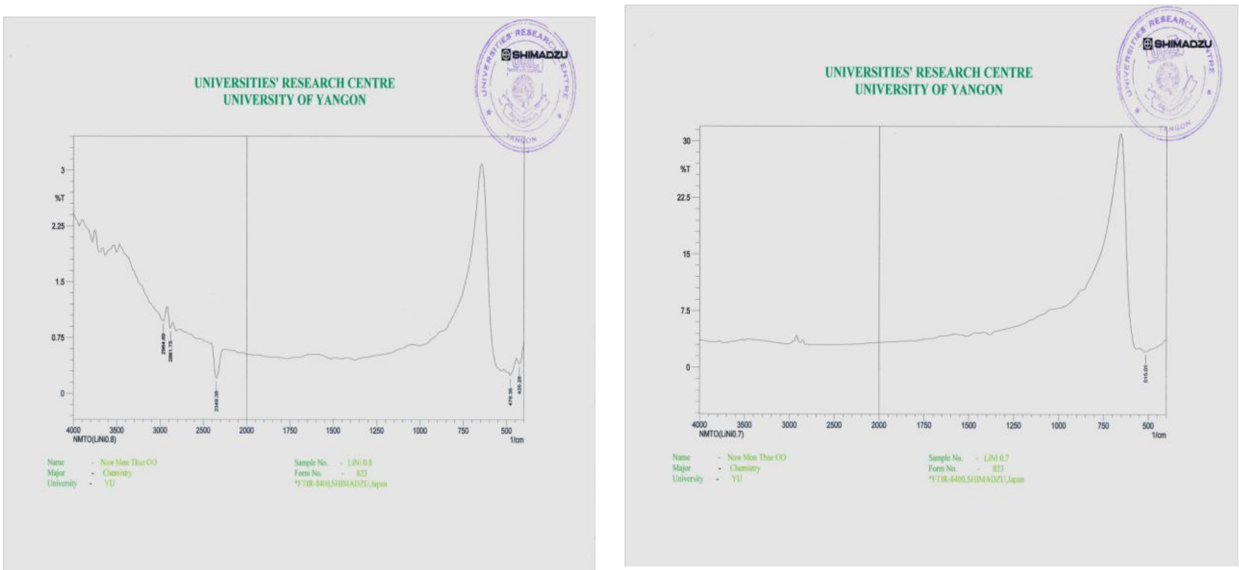
Figure 5 XRD diffraction patterns of (a) $LiNi_{0.8}Co_{0.2}O_2$ (b) $LiNi_{0.7}Co_{0.3}O_2$ (c) $LiNi_{0.6}Co_{0.4}O_2$ (d) $LiNi_{0.5}Co_{0.5}O_2$powder by sol-gel method calcined at 800 °C for 4 h

Table 2 Average Crystalline Size of Prepared $LiNi_{1-x}Co_xO_2$ Powder at 800 °C for 4 h from XRD analysis

Samples	Average crystalline size (nm)		Lattice Parameters		Crystal System
	XRD data	by using Debye Scherrer equation	a / A°	c /A°	
$LiNi_{0.8}Co_{0.2}O_2$	19.49	17.22	2.8925	14.1185	Hexagonal
$LiNi_{0.7}Co_{0.3}O_2$	75.5	69.94	2.7979	14.1885	Hexagonal
$LiNi_{0.6}Co_{0.4}O_2$	39.91	41.76	2.8412	14.0712	Hexagonal
$LiNi_{0.5}Co_{0.5}O_2$	42.58	43.43	2.8386	13.9974	Hexagonal

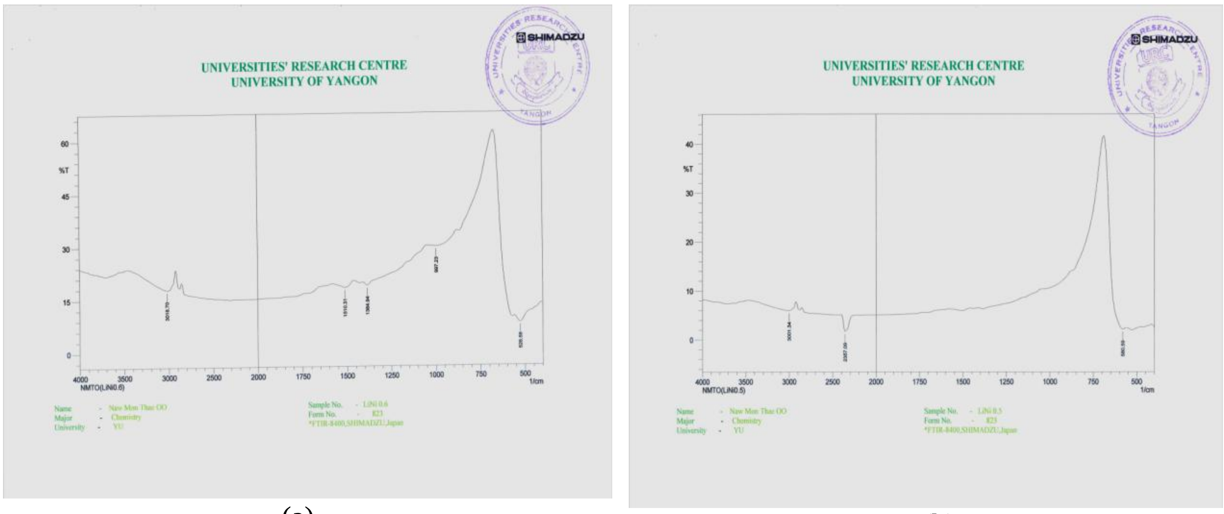
FT IR Analysis

FT IR data indicated the presence of functional groups in the $LiNi_{1-x}Co_xO_2$ powder. The FT IR spectra of the prepared $LiNi_{1-x}Co_xO_2$ powder calcined at 800 °C are shown in Figures 6 and 7, the spectral assignments shown in Table 3. In the spectrum of $LiNi_{1-x}Co_xO_2$ ($0.2 \leq x \leq 0.5$) nanocrystalline powder, the peak observed stretching vibration of metal oxygen bond (Silverstein *et al*., 2013).



(a) (b)

Figure 6 FT IR spectra of (a) $LiNi_{0.8}Co_{0.2}O_2$ (b) $LiNi_{0.7}Co_{0.3}O_2$ nanocrystalline powder prepared by sol-gel method calcined at 800°C for 4 h



(a)

(b)

Figure 7 FT IR spectra of (a) $LiNi_{0.6}Co_{0.4}O_2$ (b)$LiNi_{0.5}Co_{0.5}O_2$ nanocrystalline powder prepared by sol-gel method calcined at 800 °C for 4 h

Table 3 Band Assignments of FT IR Spectra of the Prepared $LiNi_{1-x}Co_xO_2$ Powder by Sol-gel Method Calcined at 800°C for 4 h

Observed wave number (cm^{-1})				***Literature Wave Number (cm^{-1})**	**Band Assignments**
$LiNi_{0.8}Co_{0.2}O_2$	$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.6}Co_{0.4}O_2$	$LiNi_{0.5}Co_{0.5}O_2$		
478	515	526	580	650-400	Stretching vibration of M-O bond

Silverstein *et al*., 2003

SEM Analysis

Particle morphology was studied by obtaining micrographs using JOEL-JSM-5610, Japan, Ion sputter-JEC-1600 (Sahoo *et al.*, 2010). The morphology of prepared $LiNi_{1-x}Co_xO_2$ Powder were investigated by SEM in Figure 8-9. SEM microphotograph of $LiNi_{1-x}Co_xO_2$ Powder calcined at 600 and 800 °C show the spherical agglomeration of porous nature and irregular shaped morphology. When the temperature was increased to 800°C well defined form of particles was observed. It was observed that agglomeration increase with increasing Co doping levels. The $LiNi_{0.5}Co_{0.5}O_2$ has higher porosity than other three compounds.

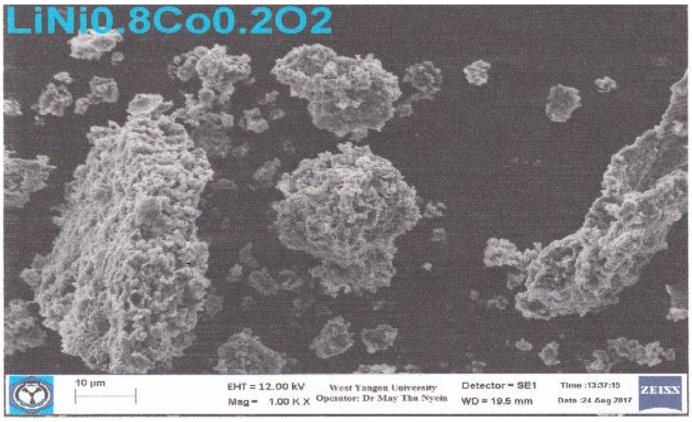
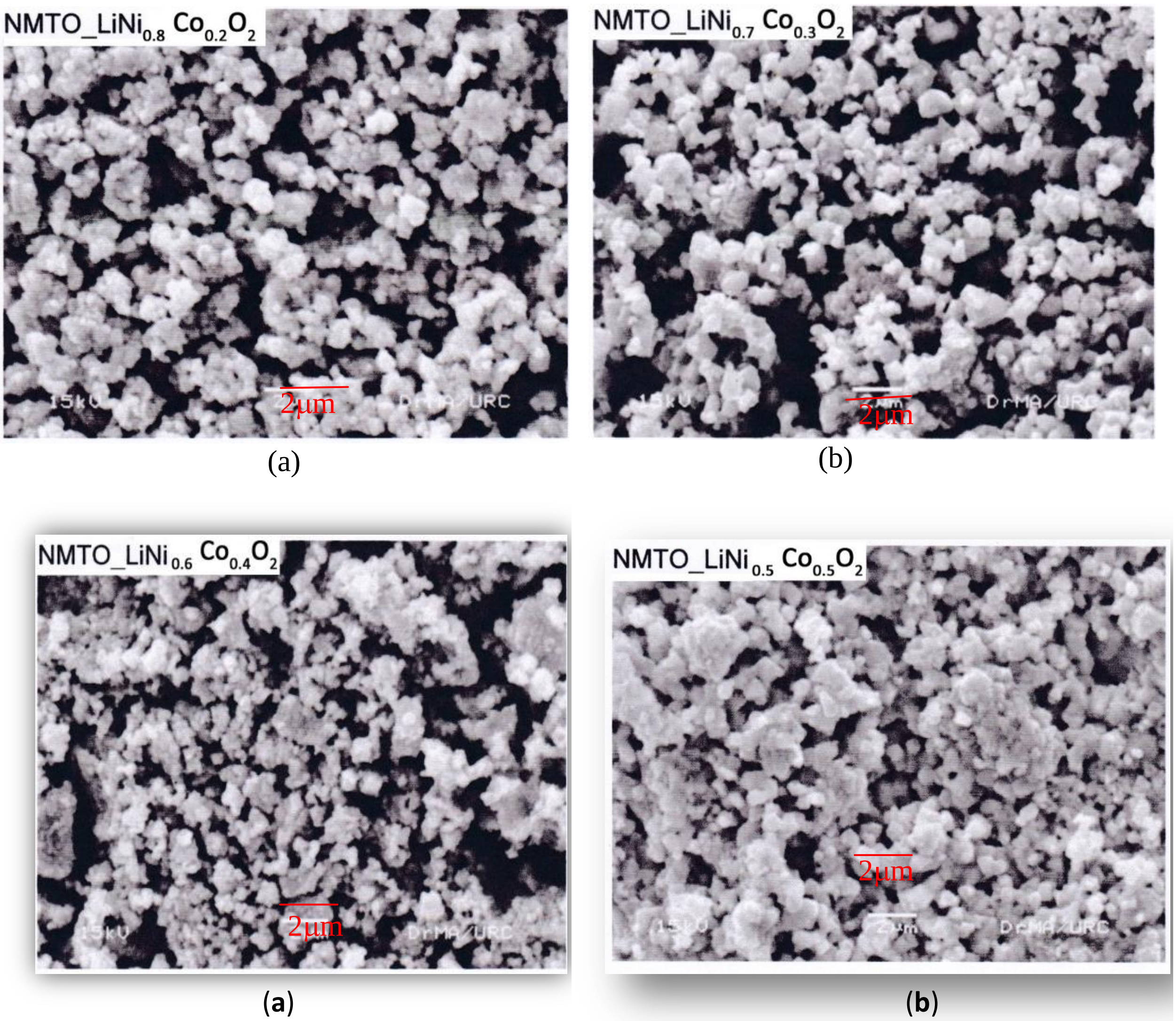


Figure 8 SEM microphotograph of the prepared $LiNi_{0.8}Co_{0.2}O_2$ powders at 600 °C



(a) (b)

(a) (b)

Figure 9 SEM microphotographs of the prepared (a) $LiNi_{0.8}Co_{0.2}O_2$ (b) $LiNi_{0.7}Co_{0.3}O_2$ (c) $LiNi_{0.6}Co_{0.4}O_2$(d) $LiNi_{0.5}Co_{0.5}O_2$ powder by sol-gel method calcined at 800 ˚C for 4h

Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) themogram of prepared $LiNi_{1-x}Co_xO_2$ powders heated at 300 °C, are shown in Figure 10. Total weight loss $LiNi_{1-x}Co_xO_2$are listed in Table 4. It was found the prepared sample calcined at 300 °C, the temperature range between38-110 °C, endothermic peak was observed. And The first weight loss is due to the removal of absorbed water and moisture. The temperature range between 110-410 °C, exothermic peak was observed. The second weight loss is due to the decomposition of nitrate and the burn out of organic species in the powder 410-600°C, endothermic and exothermic peak was observed. The final weight loss is due to the burning of carbon-residue in the temperature range between 410-600°C, endothermic peak was observed. Prepared $LiNi_{1-x}CoO_2$ nanocrystalline powder calcined at 800 °C are shown in Figure 11 and there are no prominent weight losses observed in TG curves and there are also no prominent heat absorbing or evolving processes found in DTA curves at this temperature are summarized in Table 5.

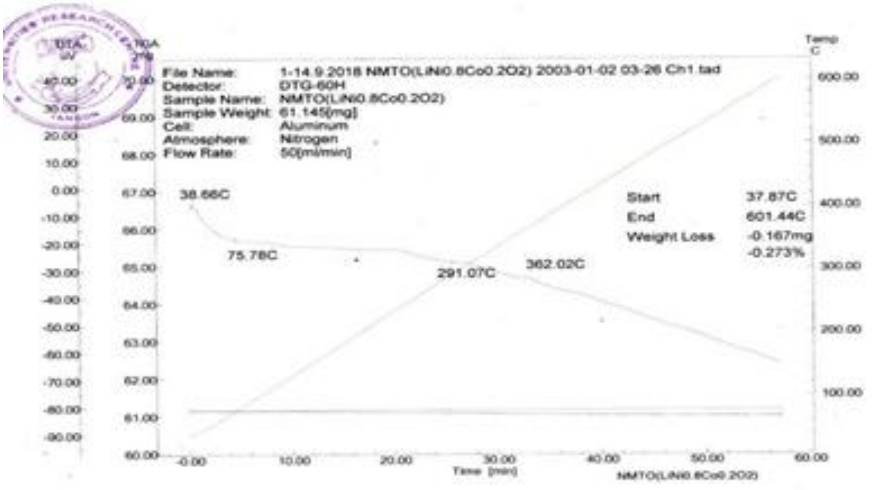
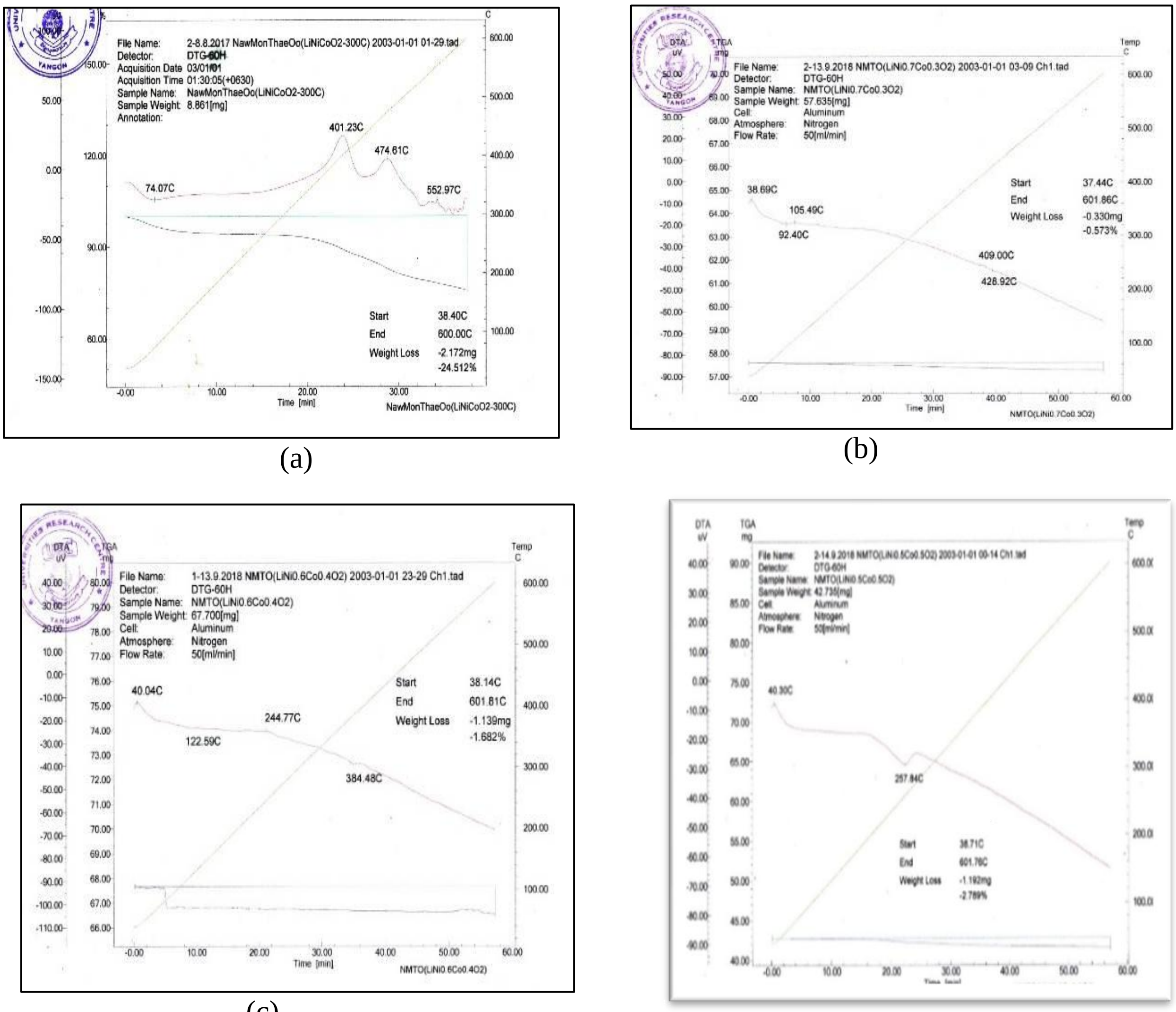


Figure 10 TG -DTA thermogram of the prepared $LiNi_{0.8}Co_{0.2}O_2$powderat 300 °C

Table 4 Thermal Analysis of $LiNi_{0.8}Co_{0.2}O_2$ Powders at 300 °C from TG-DTA Data

Temperature range (°C)	Weight loss (%)	Peak's Temperatures (°C)	Nature of peak	TG remark
38-110	5.06	74	Endothermic	The first weight loss Is due to the removal of absorbed water and moisture
110-410	6.49	401	Exothermic	The second weight loss is due to the decomposition of nitrate and the burn out of organic species in the powder
410-600	12.97	474 552	Exothermic Exothermic	The third weight loss is due to the burning of carbon-residue
Total weight loss 24.52				



(a) (b)

(c) (d)

Figure 11 TG -DTA thermogram of the prepared (a) $LiNi_{0.8}Co_{0.2}O_2$ (b) $LiNi_{0.7}Co_{0.3}O_2$ (c) $LiNi_{0.6}Co_{0.4}O_2$ (d) $LiNi_{0.5}Co_{0.5}O_2$ powder by sol-gel method calcined at 800 °C for h

Table 5 Total Weight Loss Percent of $LiNi_{1-x}Co_xO_2$nanocrystalline powder from TG-DTA Analyses

Samples	Weight loss (%)	TG remark
$LiNi_{0.8}Co_{0.2}O_2$	0.273	Thermally stable within the temperature range between 38 and 600 °C
$LiNi_{0.7}Co_{0.3}O_2$	0.573	
$LiNi_{0.6}Co_{0.4}O_2$	1.682	
$LiNi_{0.5}Co_{0.5}O_2$	2.789	

Conclusion

$LiNi_{1-x}Co_xO_2$ nanocrystalline powder was prepared by using sol-gel method at different calcination temperatures. By using Scherrer's equation, the crystalline size of $LiNi_{1-x}Co_xO_2$ nanocrystalline powder was calculated to be 29.58 nm (600°C), 32.24 nm (700°C), 17.22 nm (800°C), 29.25 nm (900°C) and 47.62 nm (1000°C). The sample calcined at 800 ºC was selected as optimum temperature because it has high crystallinity and small crystallite size at that temperature. By XRD analysis, Co doped $LiNiO_2$ samples, it was found that layer structure is not very clear in $LiNi_{0.8}Co_{0.2}O_2$ sample. But increasing Co doping level the layer structure formation are distinct. Diffraction patterns of other three sample clearly show (0 0 6)/ (0 1 2) peaks and (0 1 8)/ (1 1 0) peaks splitting and it is the characteristic of a perfect layer structure. Average crystalline size of three prepared $LiNi_{0.7}Co_{0.3}O_2$, $LiNi_{0.6}Co_{0.4}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ samples are 69.94, 41.76 and 43.43 nm. According to TG-DTA performance on $LiNi_{0.8}Co_{0.2}O_2$ sample calcined at 300 °C, it was found that crystallization temperature is about 500 °C. Total weight loss percent is 24.52% observed in TG curves. Prepared $LiNi_{1-x}Co_xO_2$ sample calcined at 800°C, there are no prominent weight losses observed in TG curves and there are also no prominent heat absorbing or evolving processes found in DTA curves. From FT IR analysis, it was only found the stretching vibration of metal- oxygen chemical bonds and so it may conclude that the prepared four $LiNi_{1-x}Co_xO_2$ samples calcined at 800 °C have no impurity. Agglomeration of $LiNi_{0.5}Co_{0.5}O_2$is more than other three compounds. It was observed that agglomeration increase with increasing the Co doping levels. The $LiNi_{0.5}Co_{0.5}O_2$ has higher porosity than other three compounds and it may be concluded that the porosity decrease with increasing the Co doping levels.

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