

# Recycling and Reusing of $\text{Li}_2\text{CO}_3$ and $\text{Co}(\text{OH})_2$ from Waste Lithium ion Batteries for Energy Storage and Thermal Studies

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**Citation:** Mylarappa M, Venkata Lakshmi V, Kantharaju S (2019) Recycling and Reusing of  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  from Waste Lithium ion Batteries for Energy Storage and Thermal Studies. J Waste Manag Disposal 2: 301

**Article history:** Received: 12 July 2019, Accepted: 09 September 2019, Published: 11 September 2019

## Abstract

The present study is revealed the recycling and reusing of  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  obtained from waste lithium ion batteries using eco-friendly leaching materials (oxalic acid and citric acid) and their energy storage and thermal properties were studied. The oxidation states, composition and chemical formula of elements in the dry powder were analyzed using X-ray photoelectron spectroscopy (XPS). The particle size and surface morphologies were done by using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The Energy Dispersive X-Ray analysis (EDAX) and Fourier Transform Infrared Spectrometer (FTIR) were employed to know the chemical constituents and functional groups identification in the samples. The obtained  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  particles from waste batteries were further used to study their energy storage and thermal properties.

**Keywords:** Waste LIB's;  $\text{Li}_2\text{CO}_3$ ;  $\text{Co}(\text{OH})_2$ ; Energy storage; Thermal Studies

**List of abbreviations:** LIBs: Li-Ion Batteries; EDAX: Energy-Dispersive X-Ray Spectrometer; OA: Oxalic Acid; CA: Citric Acid; SEM: Scanning Electron Microscopy; FTIR: Fourier Transform Infrared Spectroscopy; XRD: X-Ray Diffraction Analysis; XPS: X-Ray Photoelectron Spectroscopy; CV: Cyclic Voltammetry; EIS: Electrochemical Impedance Spectroscopy; Rct: Charge Transfer Resistance; Cdl: Double-Layer Capacitance; NMP: N-Methyl-2-Pyrrolidone; PVDF: Polyvinylidene Fluoride; ICP-OES: Inductive Coupled Plasma-Optical Emission Spectrometry; TGA: Thermal Gravimetric Analysis; DSC: Differential Scanning Calorimeter; DTA: Differential Thermal Analysis; PTFE: Polytetrafluoroethylene; SF: Stacking Fault;  $\epsilon$ : Strain;  $\delta$ : Dislocation Density; FWHM: Full Width At Half Maximum; HF: Hydrogen Fluoride; Tg: Glass Transition Temperature; GCD: Galvanostatic Charge-Discharge;  $\Delta V$ : Potential Window; Ip: Peak Current; D: Diffusion Co-Efficient; W: Warburg Impedance; A: Active Surface Area; EO: Oxidation potential; ER: reduction potential;  $\Delta t$ : Discharge time; Cs: Specific Capacitance; E: Energy Density; P: Power Density

## Introduction

Nowadays, it is necessary to minimize the utilization of batteries such as Li-ion, Ni-Cadmium, lead acid and alkaline type of batteries and these batteries contains hazardous metals (Li, Co, Ni, Cd, and Zn, Mn). The Li-ion batteries (LIB's) are the electronic wastes have developed quickly due to operation of new techniques in electronic devices and energy storage devices [1-3].

The usage of these batteries in day to day life increases at worldwide. The LIBs are used as power sources in mobile telephone, cameras, computers and other modern life purposes due to their light weight, high voltage, small self-discharge rates, good performance and high energy density [4-7]. On the other hand, the waste LIB's are not only containing valuable metal but also produce large amounts of metal-containing hazardous waste to the soil, air and water sources in the environment [8]. Moreover, when comes in contact with the industrial waste and sewage, it percolates into the soil to water bodies [9-10].

Discarded Li-ion batteries are defined as hazardous waste by every county and causes severe damage to the environment and public health [11]. On the other hand waste batteries contain valuable metals like Co, Li, Mn and Ni [12]. In this regard, the recycling and re-use of Li and Co from waste Li-ion batteries can take enormous economic profits, environmental protection and resource conservation. Hence, development of recycling technologies for spent LIB's has attracted great attention, both for environmental protection and resource conservation [13]. The recovery as well as recycling of Li and Co from the waste batteries will not only

preserve the natural resources but will also decrease environmental problems. The recovery steps involve a sequence of separation and purification of Li, Co and other constituents which may yield secondary contamination. Hence, it is essential and needed to change simple, profitable.

Different experimental procedures for recovery of Li and Co from waste LIBs have been described using pyrometallurgical, bio-metallurgical and hydrometallurgical methods [14]. In the recovery of Li and Co from pyrometallurgical, the binder, release of harmful gases and organic electrolyte were burnt off and also Li and Al are vanished in the slag due to high energy consumption. The bio-hydrometallurgical processes have some benefits such as higher productivity, low cost but the handling period is long and the necessary microorganisms are hard to incubate efficiently [15].

Therefore, hydrometallurgical processes exhibit an alternative method to turn waste batteries into pure metals/metal salts with a low energy, cost and less toxic gases. The hydrometallurgical methods are deliberated appropriate because of the benefits such as high yield of metals, pureness and nominal air emission. Acid leaching is a significant method for recovering metals and it brings metals into solution, helped at times by a reducing agent that converts the metal to a more soluble oxidation state. The presence of metal ions in the aqueous phase is definitely separated by precipitation, electrochemical and solvent extraction techniques [16-18].

Many leaching methods were done using inorganic acid as leaching agents like  $H_2SO_4$  [19], HCl and  $HNO_3$  [20-21]. In hydrometallurgical methods, the recovery of metals from battery waste the use of  $H_2SO_4$  was described as matched to other acids and the  $H_2SO_4$  is less harmful to the surroundings [22]. We are selecting low- environmental-impact recovery process using oxalic acid ( $H_2C_2O_4$ ) and citric acid ( $C_6H_8O_7$ ) as leachants to recover Li and Co from waste LIBs. The two acids were selected because of their easy natural degradation and the absence of toxic gases in the leaching process and these two acids were superior leachants to  $H_2SO_4$ .

The main significance of oxalic acid and citric acid in the soil pore water results greater solubility and the formation of compounds of oxalic acid and citric acid with the soil salts result in the improvement of the absorption of nutrients by plants [23]. Due to the complexation action of OA and CA, they have ability to supply protons to the soil solution [24] and from the formation of soluble cation-organic acid complexes, which delivers a straight route for absorption [25-27]. Even though these chelating combinations mobilize the soil heavy metals and also purify a soil via soil washing experiments.

According to literature, several main techniques have already been investigated to recover metals from waste LIBs as indicated in Table 1.

References	Sample	Condition	Method
Y. Shen, <i>et al.</i> [28]	Co, Ni	6M HCl 95 °C,	Hydrometallurgical
Y. Pranolo, <i>et al.</i> [29]	Co,Li,	$H_2SO_4$ 40 °C,	Solvent Extraction
K. Provazi, <i>et al.</i> [30]	Mixed	$H_2SO_4$ ,100 °C,	Precipitation
J.M. Zhao, <i>et al.</i> [31]	LIBs	Cyanex 272	Solvent Extraction
S. Castillo, <i>et al.</i> [32]	LIBs	$HNO_3$ , HCl,80 °C	Precipitation
Contestabile, <i>et al.</i> [33]	LiCoO <sub>2</sub>	4M HCl, 80 °C	Laboratory Process
Jingu Kang, <i>et al.</i> [34]	Co,Li, Ni	2M $H_2SO_4$ ,0 °C,	Solvent Extraction
Wang <i>et al.</i> [35]	Co, Li	4M HCl, 80 °C,	Hydrometallurgical
G. Dorella <i>et al.</i> [36]	Co, Li,	$H_2SO_4$ , 80 °C,	Liq-Liq Extraction
J. Li, <i>et al.</i> [37]	Co,Li, Ni	4M HCl, 80 °C,	Precipitation
L. Chen, <i>et al.</i> [38]	CoC <sub>2</sub> O <sub>4</sub>	4 M $H_2SO_4$ ,85 °C	Hydrometallurgical
C. Lupi, <i>et al.</i> [39]	Ni, Co	pH 3-3.2, 50 °C	Hydrometallurgical
Badawy, <i>et al.</i> [40]	Co	4M HCl, 80 °C	Precipitation
D. Mishra, <i>et al.</i> [41]	Co,Li	ferrooxidans	Bioleaching
P. Zhang, <i>et al.</i> [42]	Co,Li	4M HCl, 80 °C	Hydrometallurgical
Li Li, <i>et al.</i> [43]	Co,Li	Citric acid, 90 °C	Hydrometallurgical
S.M Shin, <i>et al.</i> [44]	Co,Li	$H_2SO_4$ , 75 °C.	Hydrometallurgical
Mantuano, <i>et al.</i> [45]	Co, Li	$H_2SO_4$ , Cyanex	Hydrometallurgical
B. Xin, <i>et al.</i> [46]	Co,Li	ferrooxidans	Bioleaching
K.K. Yoo, <i>et al.</i> [47]	LIBs	ferrooxidans	Bioleaching
M.S. Sonmez, <i>et al.</i> [48]	(Pb-Acid)	Citric acid, 20 °C	Pb citrate synthesis

**Table 1:** Separation and recovery methods studied by several earlier references

The recycling and re-use of  $Li_2CO_3$  and  $Co(OH)_2$  from waste LIBs using environment friendly materials by hydrometallurgical method and their characterizations, cyclic voltammetry (CV), electrochemical impedance spectra (EIS), Galvanostatic charge-discharge and thermal analysis have not yet been reported. The present research work is focus on the recovery of  $Li_2CO_3$  and  $Co(OH)_2$  obtained

from battery leach solution using eco-friendly materials (oxalic acid and citric acid) by hydrometallurgical process. From the battery leached solution, prepared nano sized  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  nano particles. The recovered  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  particles are used to study their cyclic voltammetry (CV), electrochemical impedance spectra (EIS), Galvanostatic charge-discharge and thermal analysis.

## Experimental

### Materials and Methods

The materials used for the entire work with all the specifications, purity, grades, structural and chemical formulas with supplier names are mentioned in Table 2. The black mass of waste Li-ion batteries was obtained from different manufactures in Bengaluru, India. The hydrometallurgical method is adapted for the recovery of the metals like Zn, Mn, Li, Co, Ni and Cd from the waste batteries.

Materials	Specifications	Suppliers
Waste batteries	1/2AA, AAAA,AAA, AA, A C, D types	different manufactures, Bengaluru India
Oxalic acid di-hydrate $\text{HO}_2\text{CCO}_2\text{H} \cdot 2\text{H}_2\text{O}$	Molar mass: 192.16 g/mol	Merck, Bengaluru, India
Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )	Molar mass: 34.01 g/mol	Merck, Bengaluru, India
Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ )	Molar mass: 126 g/mol	Merck, Bengaluru, India
Sulphuric acid ( $\text{H}_2\text{SO}_4$ )	Molar mass: 39.9 g/mol	Merck, Bengaluru, India
Sodium Hydroxide (NaOH)	Molar mass: 40 g/mol	Merck, Bengaluru, India
N-Methyl-2-Pyrrolidone ( $\text{C}_5\text{H}_9\text{NO}$ )	Molar mass: 99.13 g/mol	Sigma Aldrich
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	Molar mass: 105.98 g/mol	Merck, Bengaluru, India

Table 2: Details about the chemicals used in this work

**Metal Composition in Waste Lithium Ion Batteries:** 10 g of active material was poured in to the 250 mL iodine flask and kept on water bath at constant temperature. The inductive coupled plasma optical emission spectroscopy (ICP-OES) was used to study the concentration of Li and Co in the above obtained mixture. After leaching, it was filtrated. The percentage recovery of metals was calculated according to the following formula (1).

$$X_B = \frac{m_1}{m_2} \times 100\% \quad (1)$$

Where  $X_B$  is recovery of metal, %.  $m_1$  is actual quality of metal leaching in gram.  $m_2$  is metal quality of raw material in gram [49,50].



Figure 1: Laboratory process for the recovery of Li and Co from waste Li-ion batteries

**Recovery of Lithium Cobalt Oxide from Battery Waste:** The lithium cobalt oxide material ( $\text{LiCoO}_2$ ) was recovered from waste lithium batteries by crushing, sieving and magnetically separation as shown in Figure 1 [51]. The thermal pre-treatment was required to remove acetylene black and Polyvinylidene fluoride (PVDF) in the active materials. The spent LIB's were dismantled manually to eliminate both the plastic and steel cases that cover the batteries. The plastic cases around the batteries were removed using a small knife and screwdriver. All steps in the experimental procedure were carried out using safety glasses, gloves and gas masks for safe operation. The anode and cathode materials were manually separated and the cathode material was treated with NMP at  $100\text{ }^\circ\text{C}$  for 24 hrs. After drying at  $100\text{ }^\circ\text{C}$ , thermal pre-treatment was necessary to eliminate graphite and PVDF in the cathode active materials. The cathode materials was calcined at  $400\text{ }^\circ\text{C}$  for 3 hours in a muffle and then cooled to room temperature. After roasting and cooling the cathodic material, dried the sample and obtained cathode material ( $\text{LiCoO}_2$ ) was ground for 1hour to enable easy leaching. A measured amount of  $\text{LiCoO}_2$  powder and known amount organic acids like citric acid and oxalic acid were added to the round bottom flask with constant stirring by REMI magnetic stirrer. After the leaching period, the obtained solution was filtered and washed with distilled water yielding a pink colored filtrate and a black residue for analysis.

**Acid Leaching Procedure:** Leaching test was conducted in a 250ml iodine flask with a mechanical stirrer, a temperature sensor and a refluxing condenser fitted to it. For each test the solution mixture was freshly prepared by dissolving the requisite amount of analytical grade oxalic acid (OA) or citric acid (CA) and washed battery powder in 100 ml of 3M  $\text{H}_2\text{SO}_4$  solution, according to the experimental plan. During each test 1ml of leach liquor was withdrawn after 1h, 3h and 5h to measure the concentration of Li and Co by inductive optical emission spectroscopy (ICP-OES). Each sample was diluted 1:10 by an acidic solution of  $\text{HNO}_3$  (pH~2) to avoid precipitation of metals and kept at  $5\text{ }^\circ\text{C}$ . After 5 hours, when reactions were stopped, pH was measured and the mixtures were filtered, washed and put in the oven at  $100\text{ }^\circ\text{C}$ . After 24h solid residues were recovered and weighted to evaluate the weight loss. All leaching experiments were performed at a constant stirring speed of 400 rpm. NaOH was used to precipitate Co from leach Liquor as cobalt hydroxide ( $\text{Co}(\text{OH})_2$ ). After the recovery cobalt the leach liquor was concentrated and treated with  $\text{Na}_2\text{CO}_3$  to precipitate Li as lithium carbonate ( $\text{Li}_2\text{CO}_3$ ). The possible leaching reaction as indicated in equation 1 (Figure 2).

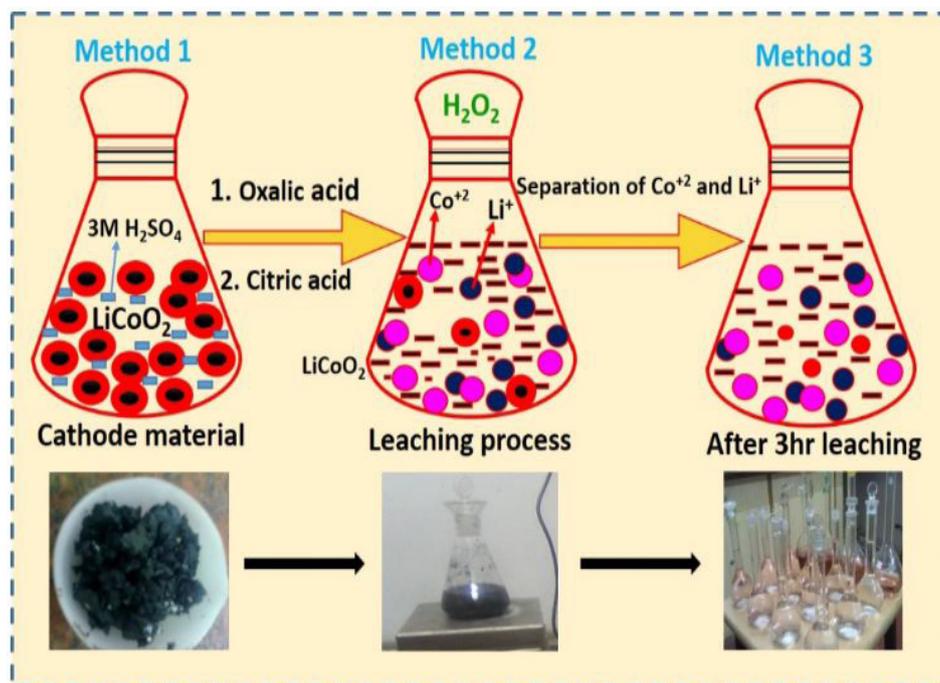


Figure 2: Possible leaching reaction process of cathode material with OA and CA leachants

## Results and Discussions

### X- Ray Photoelectron Spectroscopy (XPS) Studies

The valence states, composition and empirical formula of elements in the dry powder were analyzed using X- ray photoelectron spectroscopy method as shown in the Figure 3a-3f.

Figure 3b) and 3c), the peak at  $\text{Li } 1s = 55.6\text{ eV}$ ,  $\text{Co } 2p_{3/2} = 781.1\text{ eV}$  and  $\text{Co } 2p_{1/2} = 796.4\text{ eV}$  corresponds to lithium and cobalt. In Figure 3d) and 3e), the peaks at the binding energy  $\text{C } 1s = 284.5\text{ eV}$  and  $\text{oxygen } 1s = 533.1\text{ eV}$  are confirming the presence of carbon and oxygen respectively. In Figure 3f), the binding energy  $642.0\text{ eV}$  and  $653.1\text{ eV}$  are attributed to manganese of  $2p_{3/2}$  and  $2p_{1/2}$  core level.

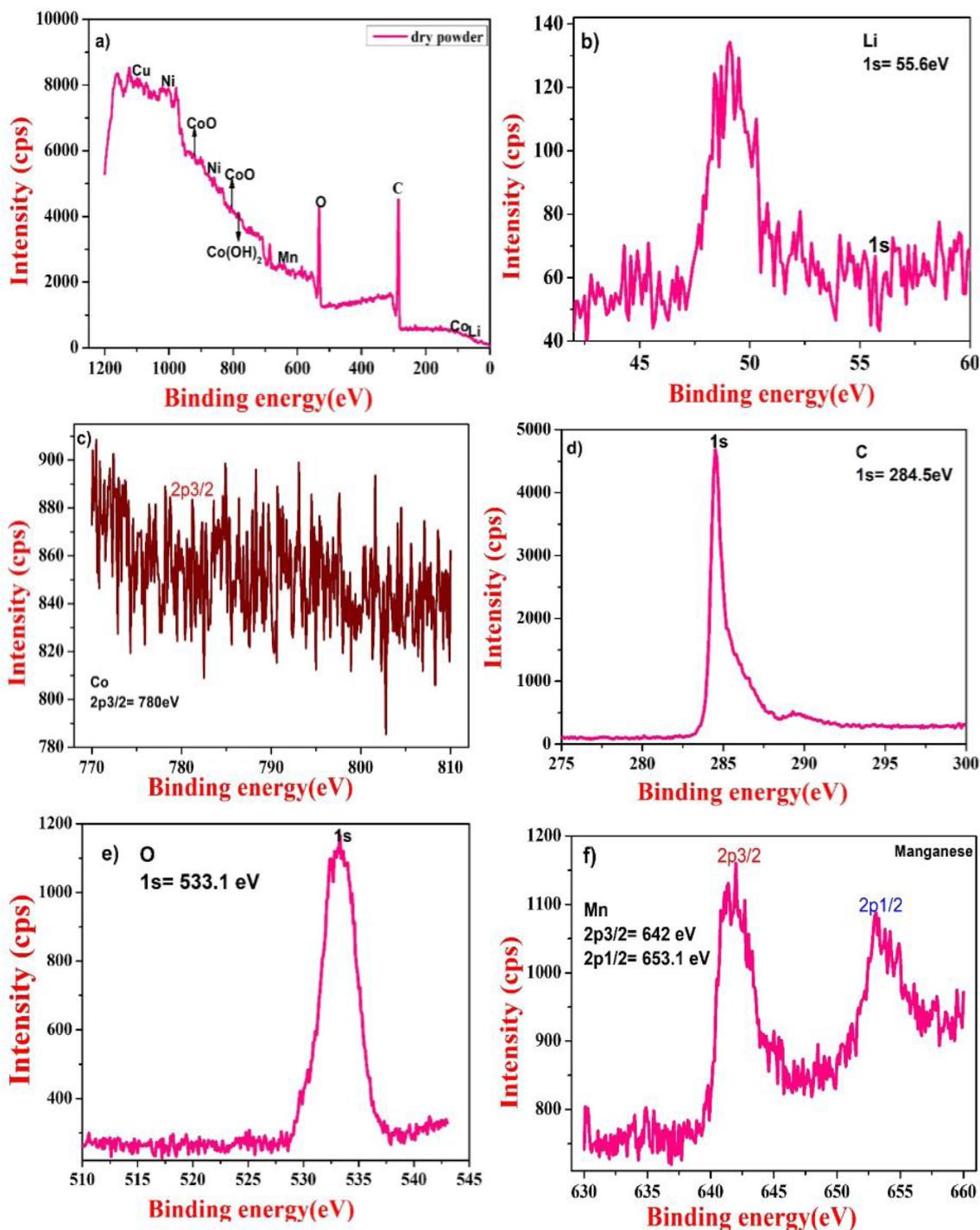


Figure 3: XPS spectra: (a) Wide angle spectrum of dry powder, (b) lithium (Li), (c) cobalt (Co), (d) carbon (C), (e) oxygen (O), (f) Manganese (Mn)

### X-Ray Diffraction (XRD) Studies

The XRD of before and after treating with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  were shown in Figure 4 a) to 4 b). The particle sizes of all the samples were evaluated with Scherrer's equation and also other constraints such as strain ( $\epsilon$ ), stacking fault (SF) and dislocation density ( $\delta$ ) calculated by the following Equations (2 to 6).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

Where  $k$ ; constant depends on the grain shape (about 0.90),  $\lambda$ ; the X- ray wavelength (0.15418 nm),  $\beta$ ; the full width at half maximum (FWHM) of the diffraction line and  $\theta$ ; the diffraction angle.

$$\cos\theta = \epsilon(4 \sin\theta) + \frac{\lambda}{D} \tag{3}$$

The Williamson and Hall (W-H) process were suggested that when the area result and lattice micro strain effect were together simultaneously working, their mutual properties give the final line broadening FWHM which was the summation of crystallite size and lattice alteration. In Equation (2),  $4\sin\theta$  and  $\beta\cos\theta$  gives straight line where  $\epsilon$  is the strain related with obtained samples and intercept ( $0.90\lambda/D$ ) of the line provides average crystallite size ( $D$ ) and slope of line gives the strain ( $\epsilon$ ).

The values found were equivalent with the size measured from Scherrer's Equation. The occurrence of dislocations strongly affects various properties of the materials. The movement of a dislocation is hindered by new dislocations present in the sample. The greater dislocation density indicates a higher hardness of the materials and the structural parameters ( $\delta$ ,  $\epsilon$  and SF) were controlled by the additional connection as indicated in Table 3 [52].

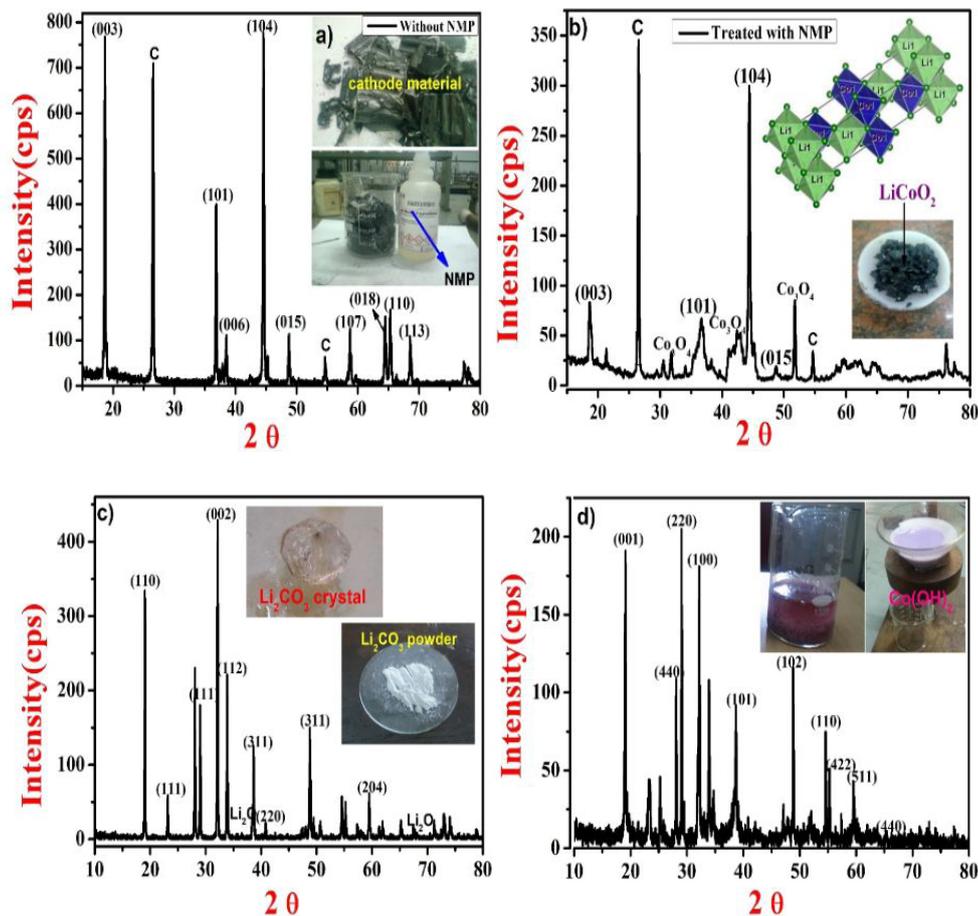
$$\delta = \frac{1}{D^2} \quad (4)$$

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (5)$$

$$SF = \frac{2\pi^2}{45\sqrt{3}\tan\theta} \quad (6)$$

Sample	FWHM (rad)	Average Crystalline Size (nm)	Strain ( $\epsilon$ ) $\times 10^{-3}$	stacking fault SF	dislocation density ( $\delta$ ) ( $10^5 \text{ lin m}^{-2}$ )
Without NMP	0.22	39.15	0.0509	0.396	6.52
With NMP	0.21	36.18	0.0535	0.522	7.67
$\text{Li}_2\text{CO}_3$	0.144	57.03	0.0348	0.497	3.06
$\text{Co}(\text{OH})_2$	0.169	49.14	0.0405	0.471	4.14

**Table 3:** The crystallite size and other structural parameters of powder without treating with NMP, powder with NMP  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$



**Figure 4:** XRD spectrum of (a)  $\text{LiCoO}_2$  without NMP, (b)  $\text{LiCoO}_2$  with NMP, (c)  $\text{Li}_2\text{CO}_3$ , (d)  $\text{Co}(\text{OH})_2$

The calculated average crystalline size of cathode material without treated with NMP as well treated with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  were found to be 39.15, 36.18, 49.14 nm in sizes indicated in Table 3. In the XRD of all the samples were shown in the spectra which were more intense and sharp, demonstrating excellent crystalline nature.

In Figure 4a) and 4b) shows XRD patterns of the cathode material without NMP as well treated with NMP are dismantled from waste LIBs and calcined at 400 °C for 3 hrs. Lithium cobalt oxide ( $\text{LiCoO}_2$ ),  $\text{Co}_3\text{O}_4$  and carbon were main constituents present in the powder (JCPDS: 65-6212) as found in Figure 4a) and 4b).

The crystalline  $\text{LiCoO}_2$  phase was clearly indicated in the XRD. The  $\text{Co}_3\text{O}_4$  present in the active material comes from a transformation of the cathode material ( $\text{LiCoO}_2$ ). The appearance of  $\text{Co}_3\text{O}_4$  is due to PVDF addition because PVDF can give out HF when heating, HF with  $\text{LiCoO}_2$  to produce  $\text{HCoO}_2$  and  $\text{HCoO}_2$  is not steady at high temperature, it will decompose to  $\text{Co}_3\text{O}_4$ . In Figure 4b, the % carbon gets reduced because of its easy to oxidize by  $\text{O}_2$  at higher temperature in air and at 400 °C, carbon should be minimized or removed [51-54].

The XRD pattern of  $\text{Li}_2\text{CO}_3$  (JCPDS: 83-1454) and  $\text{Co}(\text{OH})_2$  (JCPDS: 73-1701) as shown in the Figure 4c and 4d. Figure 4c, the peaks at  $2\theta$  values of 19.02°, 23.17°, 29.08°, 33.97°, 38.5°, 40.88°, 48.8° and 59.6° corresponds to the crystal planes of (110), (111), (002), (112), (220), (311) and (204) of  $\text{Li}_2\text{CO}_3$  nano particles. The strong and fine peak suggests that material has well crystalline nature of particles. Certain peaks of  $\text{Li}_2\text{O}$  (lithium oxide) was also identified, signifying the occurrence of traces of metallic oxide. In Fig.4 d) the peaks at  $2\theta$  values of 19.02°, 28.06°, 29.08°, 32.09°, 38.86°, 48.92°, 54.57°, 55.32°, 59.72° and 65.36° resembles to the crystal planes of (001), (440), (220), (100), (101), (102), (110), (422), (511) and (440) of  $\text{Co}(\text{OH})_2$  nano particles.

### Scanning Electron Microscopy (SEM) Studies

The SEM images of cathode material ( $\text{LiCoO}_2$ ) without treated with NMP and treated with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  were shown in Figure 5a) to 5d). In Figure 5a), the waste cathode materials before treating with NMP contained large secondary particles with irregular morphologies. In Figure 5b), the fine distributed particles can be observed and the size of  $\text{LiCoO}_2$  with homogenous and well-defined shape was observed for  $\text{LiCoO}_2$  calcined at 400 °C for 3 hour as shown in the Figure 5b). These results indicating that most of the PVDF dissolved in NMP and  $\text{LiCoO}_2$  particles separated. The microscopic structure of  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  are shown in Figure 5c) to 5d). In Figure 5c), the particles exhibit straight/rod like structure. The hierarchical structure of  $\text{Li}_2\text{CO}_3$  is about 10 $\mu\text{m}$  in size. In Figure 5d),  $\text{Co}(\text{OH})_2$  reveals an identical morphology of three dimensional (3D) multi-pods nano structures and branches are highly crystalline nature. In Figure 5d), most of the multi pods are present more than ten pods [55-58].

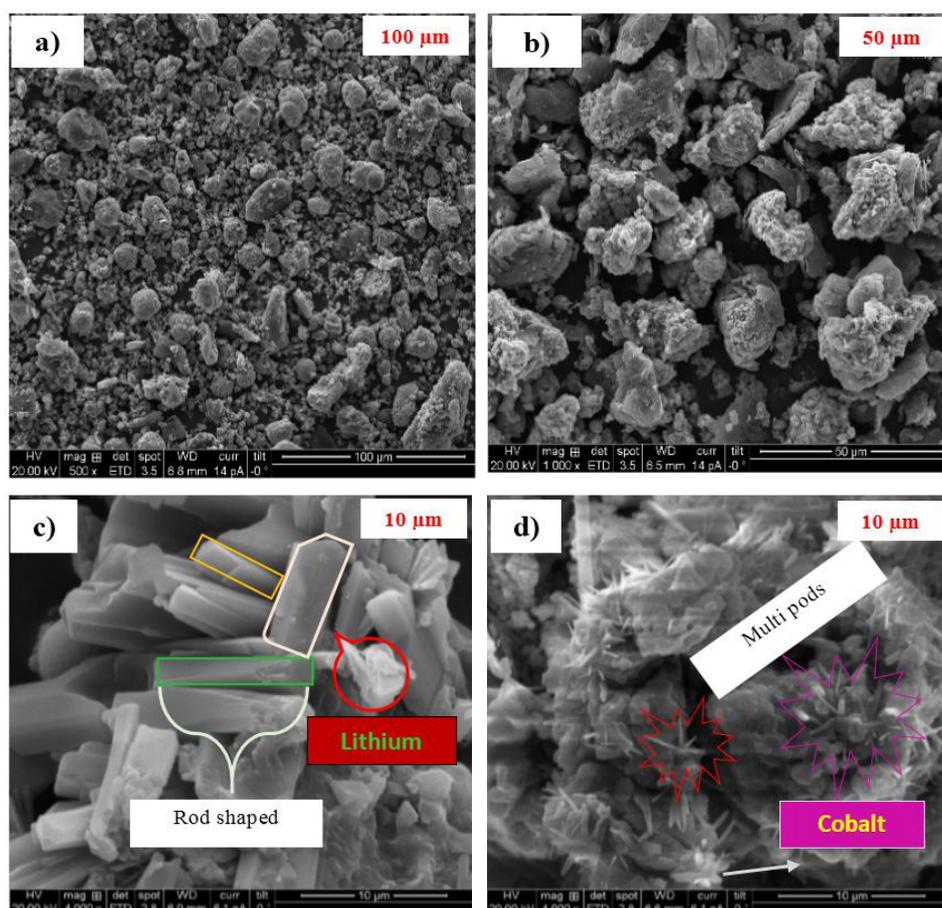


Figure 5: SEM images of (a)  $\text{LiCoO}_2$  without NMP, (b)  $\text{LiCoO}_2$  with NMP, (c)  $\text{Li}_2\text{CO}_3$ , (d)  $\text{Co}(\text{OH})_2$

## Energy Dispersive X-Ray Analysis (EDAX)

EDAX analysis was performed for cathode material ( $\text{LiCoO}_2$ ) without treated with NMP and treated with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  were shown in Figure 6a) to 6d). In Figure 6a, the powder constitutes 40.56 wt. % of C, 18.92 wt. % of Co and 17.07 wt. % of Ni, 15.82 wt. % of Mn with small quantity of Al, Cu, O and P were the main elements present in the powder. In Figure 6b, 93.03 wt. % of Co, 6.23 wt. % of Co with little amount of aluminium. EDAX study was the conventional solid-state analysis techniques and it does not identify lithium because of the too low energy of Li ( $Z = 3$ ) K X-rays. In Figure 6c) and 6d), the  $\text{Li}_2\text{CO}_3$  comprises 64.71 wt. % of Co, 19.32 wt. % of Oxygen, 15.97 wt. % of carbon and for  $\text{Co(OH)}_2$  contains 91.79 wt. % of Co and 8.21 wt. % of oxygen.

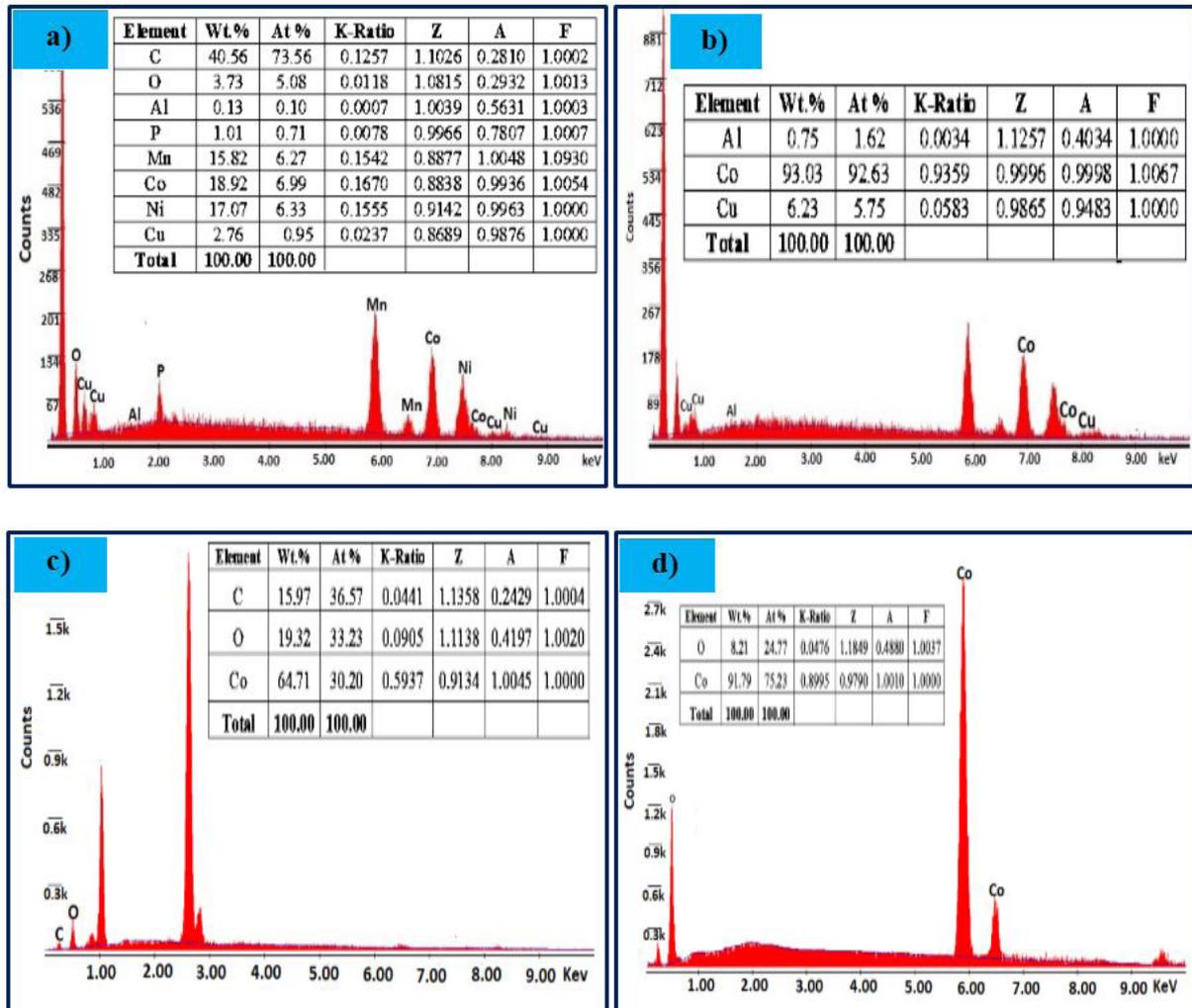


Figure 6: EDAX spectrum of (a)  $\text{LiCoO}_2$  without NMP, (b)  $\text{LiCoO}_2$  with NMP, (c)  $\text{Li}_2\text{CO}_3$ , (d)  $\text{Co(OH)}_2$

## Fourier Transforms Infra-Red Spectroscopy (FTIR) Studies

FTIR was performed for cathode material ( $\text{LiCoO}_2$ ) without treated with NMP and treated with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  which were shown in Figure 7a) to 7d). In Figure 7a, the cathode materials before and after treated with NMP were characterized by using FTIR spectrum as shown in Figure 7a) to 7b).

The cathode material before and after treated with NMP found at the wave numbers of 2317.3, 2097.7, 2006.9, 1407.4, 860.9 and 465.8  $\text{cm}^{-1}$ . But after treating with NMP indicating that, PVDF is decomposed completely after heating at 400  $^{\circ}\text{C}$  for 3hrs. The band 2097 $\text{cm}^{-1}$  can be assigned to the vibration of  $\text{CO}_2$  in the gas phase physically adsorbed on the material surface and band at 1407  $\text{cm}^{-1}$  can be recognized to the bending mode of the  $\text{H}_2\text{O}$  molecule. In Figure 7c, the wave numbers found at 2340.9, 2105.5, 1111.9 and 613.8 $\text{cm}^{-1}$  are the main characteristic bands of  $\text{Li}_2\text{CO}_3$ . The absorption peak at 3600 $\text{cm}^{-1}$  corresponds to O-H stretching vibrations of  $\text{LiOH}$  and the peak at 1600  $\text{cm}^{-1}$  for water molecule in  $\text{LiOH}$ . Other absorptions below 1000 $\text{cm}^{-1}$  are associated with Co-O stretching and Co-OH bending vibrations. The broad peaks at low-frequency absorption 613 $\text{cm}^{-1}$  is attributed to M-O bond (Li-O). The FTIR spectrum of  $\text{Co(OH)}_2$  sample as shown in the Figure 7d). The strong peak at 3600 $\text{cm}^{-1}$  corresponding to the free O-H group and absorption frequency at 1600 $\text{cm}^{-1}$  is due to bending mode of the -OH group of  $\text{H}_2\text{O}$  molecule. The broad peaks at low-frequency absorption 613 $\text{cm}^{-1}$  is associated with Co-O stretching as well as Co-OH bending vibration [59,60].

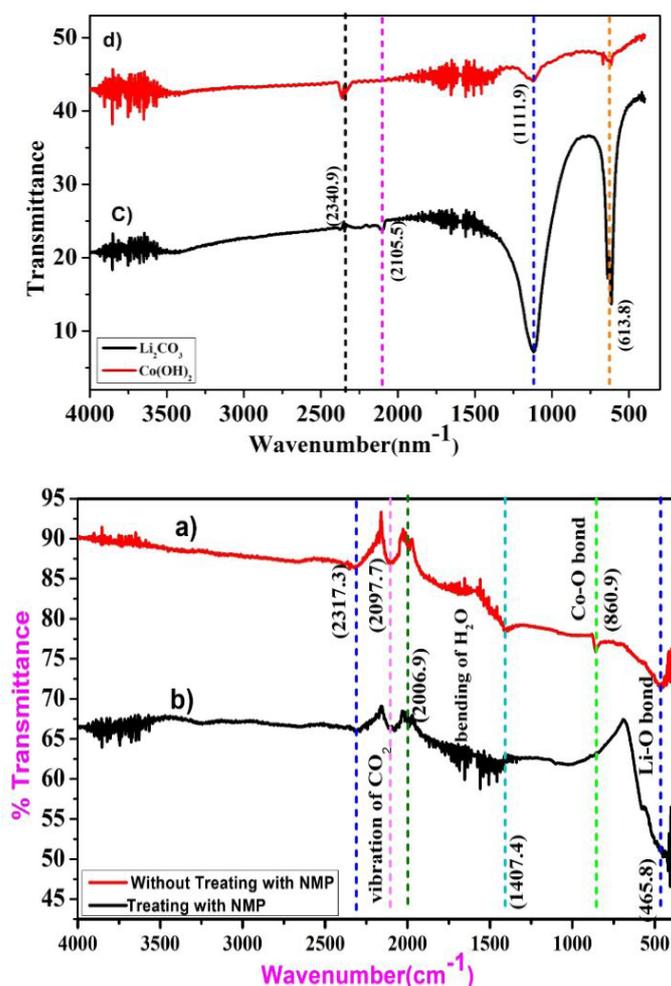


Figure 7: FTIR spectrum of (a)  $\text{LiCoO}_2$  without NMP, (b)  $\text{LiCoO}_2$  with NMP, (c)  $\text{Li}_2\text{CO}_3$ , (d)  $\text{Co(OH)}_2$

### Recovery of $\text{Li}_2\text{CO}_3$ and $\text{Co(OH)}_2$ from Leach Solution

The measured volume of leached solution was taken in a 500ml beaker with a slight excess of 4M NaOH which was added to the beaker with constant magnetic stirring speed (300rpm) and 30 min reaction time. The  $\text{Co}^{2+}$  ions reacts with NaOH present in the leach solution to completely precipitate as  $\text{Co(OH)}_2$  nano particles. The solution was filtered using Whatmann paper 42 and the solid residue was dried at 100 °C for 24 hours. Similarly, for recovery of lithium, saturated solution of sodium carbonate with a high temperature (95 °C) was used to precipitate Li as  $\text{Li}_2\text{CO}_3$  nano particles.

### Differential Scanning Calorimetry (DSC) and TGA analysis

The  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  nano particles were recovered from waste leached battery solution as shown in Figure 8a) to Figure 8b). In Figure 8a demonstrate the  $\text{Li}_2\text{CO}_3$  nano particles reveals three separate thermal decomposition steps. The initial decomposition of the weight loss at about 80 °C can be recognized to the loss  $\text{H}_2\text{O}$  molecules and the first phase weight loss occur at 278.8 °C (95.4 %) which indicating the removal of some gases like  $\text{CO}_2$  because  $\text{CO}_3^{2-}$  based precursor accompanied by exothermic peaks can be appeared in the DSC curve in the sample.

The second decomposition curve starts at 464.18 °C (22.4 %) and the third exo-endothermic phase is around 715 °C (5.44 %) can be attributed to the melting point of  $\text{Li}_2\text{CO}_3$  nano particles [61,62]. The mass loss between 464.18 °C and 715 °C is mainly due to the conversion of reactants into the product. The total mass loss occurs under 715 °C so it can be highlighted that the thermal stability of  $\text{Li}_2\text{CO}_3$  recovered from waste battery is started at 460 °C [63].

In Figure 8b, the  $\text{Co(OH)}_2$  nano particles shows two separate thermal decomposition steps. The initial weight loss at 63 °C can be ascribed to the elimination of water and  $\text{CO}_2$  from the dehydroxylation and fragmentation of carbonate assemblies. The first decomposition mass loss arised at occur at 424.12 °C (95.6 %) which signifying the exclusion of certain gases like  $\text{CO}_2$ . The second exo-endothermic phase is around 632 °C (85.6 %) can be recognised to the melting point of  $\text{Co(OH)}_2$  nano particles. It is noticed that both exothermic (DTA), endothermic peaks (DSC) and glass transition temperature ( $T_g$ ) are recognized about 374 °C for  $\text{Li}_2\text{CO}_3$  and 567 °C for  $\text{Co(OH)}_2$  as shown in the Figure 8a) and 8b). Generally under  $T_g$ , the fragments do not have segmental motion and adjacent  $T_g$ , the fragments can start exciting. It is supposed that the increase in  $T_g$  is related to the increase in thermal

stability of the sample. The above results indicating that the recovered  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  from waste Li-ion batteries are more thermally stable and their excellent use full materials for energy storage applications.

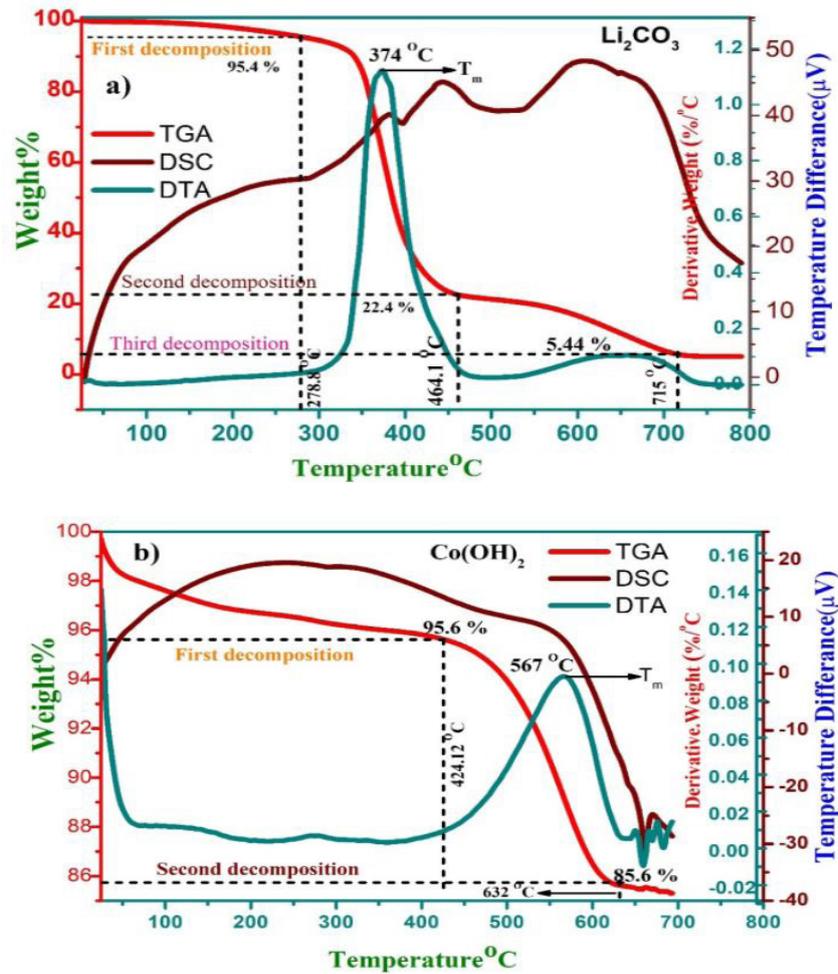


Figure 8: TGA/DSC/DTA of (a)  $\text{Li}_2\text{CO}_3$  and (b)  $\text{Co}(\text{OH})_2$

## Electrochemical Studies of $\text{Li}_2\text{CO}_3$ and $\text{Co}(\text{OH})_2$

**Cyclic Voltammetry (CV) Studies:** CV is one of the Potentiodynamic form used for electrochemical evaluation. In an experiment of CV, the potential of working electrode is ramped versus time in linearly. To present the cyclic voltammogram outline, the obtained working electrode current is plotted against the voltage applied (i.e., potential of working electrode). The reversibility of the redox couple is more, the shape of oxidation and reduction peaks becomes exactly similar. For this reason, the CV data can make available in sequence about potentials of redox couple and rates of electrochemical reaction.

In the CV analysis, the working electrode (5%  $\text{Li}_2\text{CO}_3$  or 5%  $\text{Co}(\text{OH})_2$ ) was prepared by mixing 0.025g of active material +0.475g of graphite + 3-5 drops of polytetrafluoroethylene (PTFE) solution which was added as a binder and blended by hand mixing with a mortar and pestle for about 30 min until a uniform thin sheet achieved. The obtained thin sheet was pressed on nickel mesh (area about  $1 \text{ cm}^2$ ) to create a good conductivity with the Ni mesh and active material. In the same way, 10%, 15%  $\text{Li}_2\text{CO}_3$  and 10%  $\text{Co}(\text{OH})_2$  electrodes were prepared. Finally the obtained electrode was dried at  $50^\circ\text{C}$  for 48 hours and the prepared electrodes were kept for 20 days electrode setting because for stability of the electrode.

An electrochemical measurement comprises three electrode system having active material ( $\text{Li}_2\text{CO}_3/\text{Co}(\text{OH})_2$ ), Ag/AgCl electrode and a platinum as counter electrode. CV measurements were applied in the potential range +0.2 to -0.6V using 3M KOH as shown in the Figure 9a-c and Figure 10a-c. In Figure 9a-c, the electrochemical reversibility was calculated by seeing of the difference between the  $E_0$  and  $E_R$  at 0.01 V/s scan rate. We can report that the electrode reversibility reaction of 15%  $\text{Li}_2\text{CO}_3$  was minimum as compared to that of 5%  $\text{Li}_2\text{CO}_3$  and 10%  $\text{Li}_2\text{CO}_3$  and CV curves displays a quasi-reversible electron transfer process representing that capacitive behavior was predominantly based on the redox mechanism as indicated in Table 4. The electrochemical reversibility of 10%  $\text{Co}(\text{OH})_2$  was decreased as compared to that of 5%  $\text{Co}(\text{OH})_2$  as shown in the Figure 10a-c. According to the Randles-Sevcik equation for reversible process, the height current is denoted by the Equation 7.

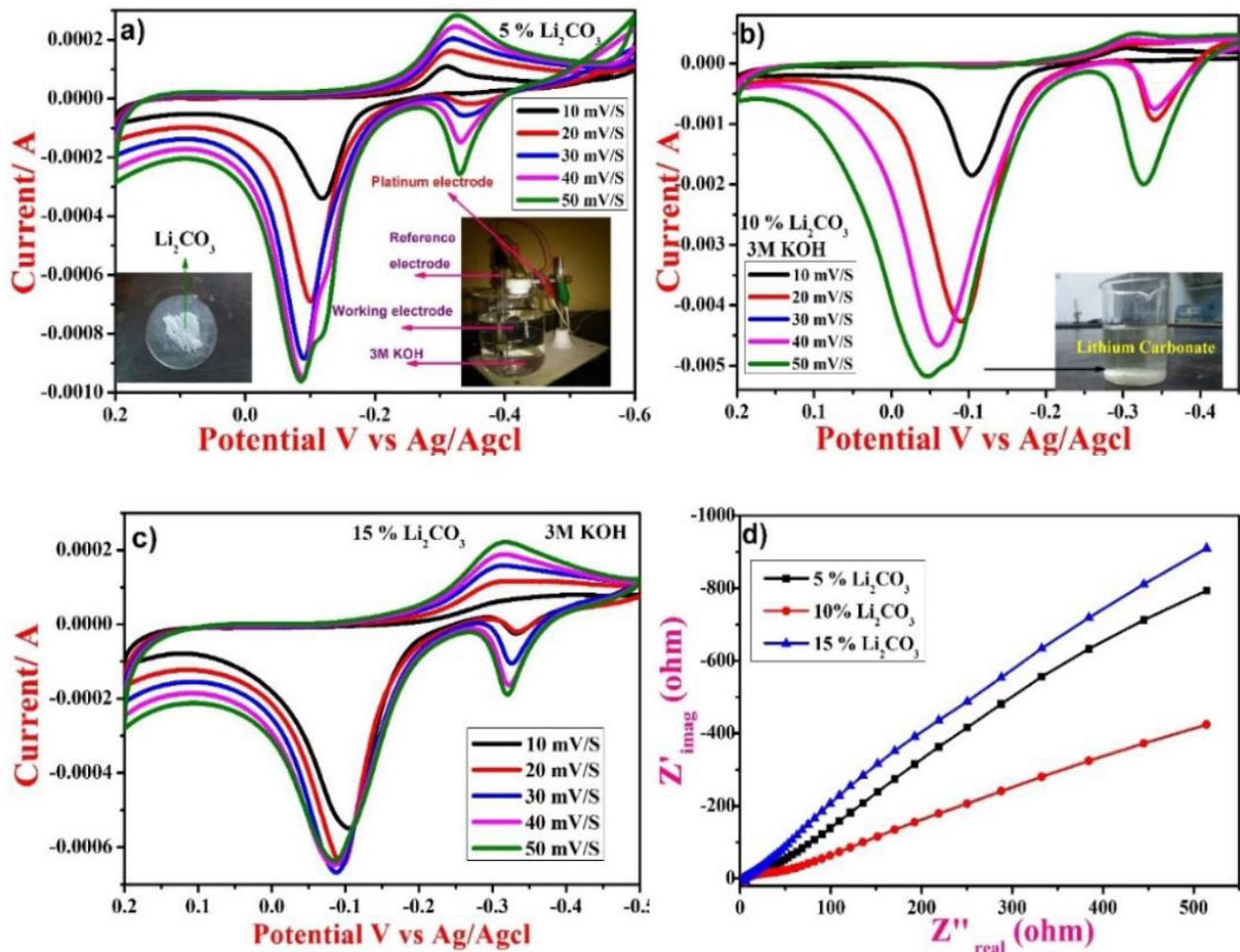
$$I_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C_0 \times v^{1/2} \quad (7)$$

Where  $n$  is the number of electron transferred in the reaction, the active surface area ( $A$ ), diffusion co-efficient ( $D$ ), scanning rate ( $v$ ) and initial concentration of the chemical ( $C_0$ ) respectively. The greater linear association involving in peak current ( $i_p$ ) and number of electron transferred ( $n^{1/2}$ ) confirm that the electrode reaction of  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  were measured by hydrogen diffusion co-efficient ( $D$ ). The increased  $D$  value of 15%  $\text{Li}_2\text{CO}_3$  and 1%  $\text{Co}(\text{OH})_2$  revealed that electrochemical activity was more effective compared to that of 5%  $\text{Li}_2\text{CO}_3$  and 10%  $\text{Li}_2\text{CO}_3$  and 5%  $\text{Co}(\text{OH})_2$ .

Sample	$E_o$ (V) $\times 10^{-3}$	$E_R$ (V) $\times 10^{-3}$	$E_o - E_R$ (V) $\times 10^{-3}$	$D(\text{cm}^2\text{S}^{-1}) \times 10^{-5}$	Rct ( $\Omega$ )	$C \times 10^{-8}$
5 % $\text{Li}_2\text{CO}_3$	0.105	-0.357	0.462	3.537	749.5	1.104
10 % $\text{Li}_2\text{CO}_3$	0.269	-0.189	0.458	9.03	753.1	5.514
15 % $\text{Li}_2\text{CO}_3$	0.059	-0.056	0.115	14.52	958.0	10.02
5 % $\text{Co}(\text{OH})_2$	1.08	-0.128	1.208	0.698	14.3	3.085
10 % $\text{Co}(\text{OH})_2$	0.056	-0.215	0.27	3.417	27.5	4.871

**Table 4:** Oxidation potential ( $E_o$ ), reduction potential( $E_R$ ), the difference between  $E_o$  and  $E_R$  and diffusion co-efficient of different electrodes

**Electrochemical Impedance Spectroscopy (EIS) Studies:** Electrochemical impedance is usually measured by means of making use of an AC capacity to an electrochemical cell after which computing the current throughout the cell. The electrochemical impedance was measured by the use of small excitation signal and it is achieved in order that the pseudo-linear cell response. In a system of linear or pseudo-linear, the current responsible to sinusoidal potential can be a sinusoid on the similar frequency however transferred in phase. The EIS is a powerful tool for studying electron transfer between active surface and electrolyte. AC impedance was carried out for  $\text{Li}_2\text{CO}_3$  and  $\text{Co}(\text{OH})_2$  with an ac bias voltage of 5 mV in the frequency range from 1Hz to 0.1MHz as indicated in Figure 9d and 10d. In these graphs the semi-circle seems at higher frequency region, the charge-transfer resistance (Rct) is parallel connection to double layer capacitance ( $C_{dl}$ ) and Warburg impedance ( $W$ ) is arised to the diffusion of ions [64]. In Figure 9d and Figure 10c-d, the charge transfer resistance (Rct) and capacitance ( $C$ ) value of 15%  $\text{Li}_2\text{CO}_3$  and 10%  $\text{Co}(\text{OH})_2$  electrode is far greater than that of other electrodes, which shows that the electrochemical reaction of electrode precedes more over other electrodes as given in Table 4.



**Figure 9:** CV curves of ( a) 5%  $\text{Li}_2\text{CO}_3$ , (b) 10%  $\text{Li}_2\text{CO}_3$ , (c) 15%  $\text{Li}_2\text{CO}_3$ , (d) Nyquist plots for 5%  $\text{Li}_2\text{CO}_3$ , 10%  $\text{Li}_2\text{CO}_3$  15%  $\text{Li}_2\text{CO}_3$  using 3M KOH solutions

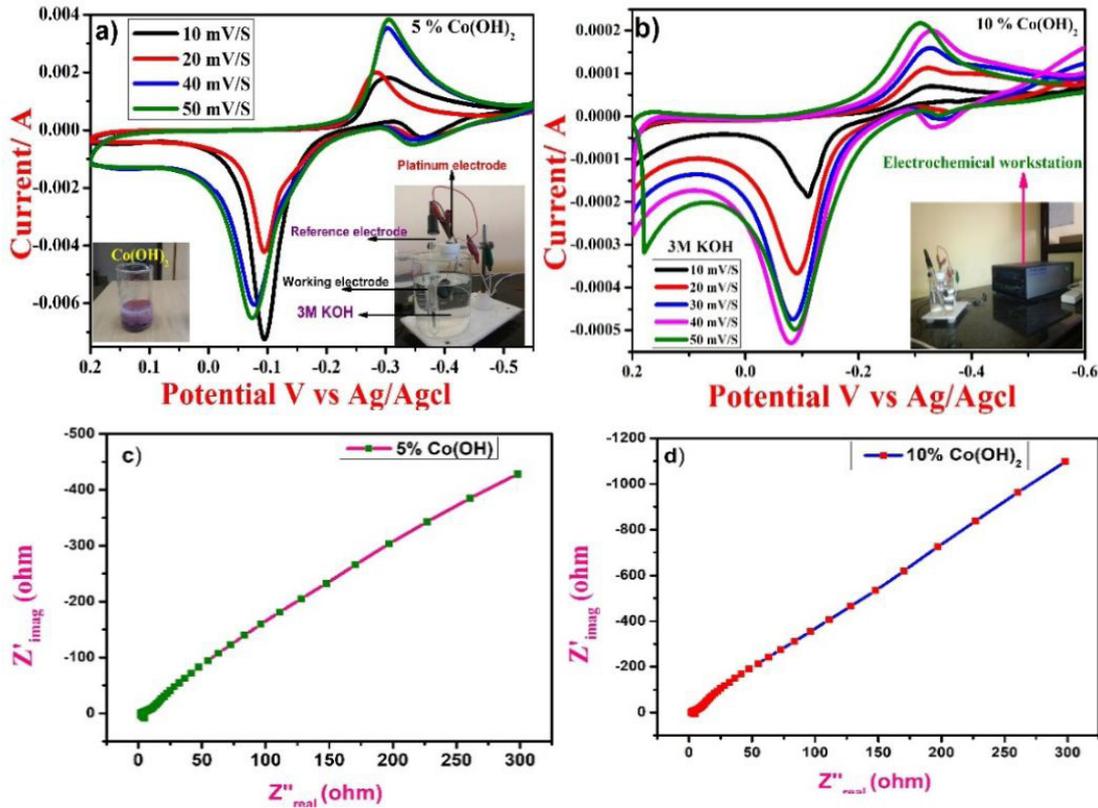


Figure 10: CV curves of (a) % Co(OH)<sub>2</sub>, (b) 10% Co(OH)<sub>2</sub>, (c) Nyquist plots for 5% Co(OH)<sub>2</sub>, d) 10% Co(OH)<sub>2</sub> using 3M KOH solution

**Galvanostatic Charge-Discharge Analysis (GCD):** The recovered Li<sub>2</sub>CO<sub>3</sub> from leach solution was used as working electrode using 3M KOH solution as the electrolyte, Ag/AgCl as the reference electrode and platinum wire used as the counter electrode in a three electrode configuration system. The working electrode (5% Li<sub>2</sub>CO<sub>3</sub>) was prepared by mixing 0.025g of active material +0.475g of graphite +3-5 drops of PTFE and in the same way, 5% Co(OH)<sub>2</sub>, 10% Co(OH)<sub>2</sub> and 15% Co(OH)<sub>2</sub> were prepared. The suspended solution was coated on to nickel mesh with area 1cm<sup>2</sup>. Finally the obtained electrodes were dried at 50 °C for 48hrs. The galvanostatic charge-discharge (GCD) curves for 5% Li<sub>2</sub>CO<sub>3</sub>, 10% Li<sub>2</sub>CO<sub>3</sub>, 15% Li<sub>2</sub>CO<sub>3</sub> and 5% Co(OH)<sub>2</sub>, 10% Co(OH)<sub>2</sub> and 15% Co(OH)<sub>2</sub> were shown in Figure 10a-c and Figure 11a-c. Within the potential window of -0.6 to 0.6 V vs. Ag/AgCl. The specific capacitance (Cs) of Li<sub>2</sub>CO<sub>3</sub> and Co(OH)<sub>2</sub> electrode was calculated by the following Equation (8).

$$C = \frac{I\Delta t}{m\Delta V} \quad (8)$$

Where,  $I$  is the current,  $\Delta V$  is the potential window,  $\Delta t$  is the time of a discharge cycle and  $m$  is the mass of active material. In Figure 11a-c, the specific capacitance values of were calculated and found to be 138.4Fg<sup>-1</sup>, 189.4Fg<sup>-1</sup> and 2631Fg<sup>-1</sup>. Likewise, in Figure 11a-c the specific capacitance values of 5% Co(OH)<sub>2</sub>, 10% Co(OH)<sub>2</sub> and 15% Co(OH)<sub>2</sub> were found to be 147.9Fg<sup>-1</sup>, 150.1v and 2133.8 Fg<sup>-1</sup> respectively. The specific energy density ( $E$ ) and power density ( $P$ ) can be calculated from the GCD curve by Equation (9 and 10).

$$E = \frac{1}{2}C_s V^2 \quad (9)$$

$$P = \frac{E}{\Delta t} \quad (10)$$

Where  $E$  is the energy density,  $C_s$  is the capacitance,  $V$  is the potential window;  $P$  is the power density and  $\Delta t$  is the discharging time.

The specific energy density of the 5% Li<sub>2</sub>CO<sub>3</sub>, 10% Li<sub>2</sub>CO<sub>3</sub> and 15% Li<sub>2</sub>CO<sub>3</sub> were 19.6whkg<sup>-1</sup>, 26.8whkg<sup>-1</sup> and 412.5whkg<sup>-1</sup> and the specific power density were found to be 15.9wkg<sup>-1</sup>, 10.63wkg<sup>-1</sup> and 3.87wkg<sup>-1</sup>. Also, energy density of 5% Co(OH)<sub>2</sub>, 10% Co(OH)<sub>2</sub> and 15% Co(OH)<sub>2</sub> were seemed 0.207 whkg<sup>-1</sup>, 0.186 whkg<sup>-1</sup> and 467.3whkg<sup>-1</sup> and power density were found to be 0.295wkg<sup>-1</sup>, 0.183wkg<sup>-1</sup> and 14.29wkg<sup>-1</sup> respectively as indicated in the Table 5 [65,66]. The above outcomes showed that the charge-discharge curves display well-symmetry and linear deviations with change of the time indicating superior capacitance and cycle performance of Li<sub>2</sub>CO<sub>3</sub> and Co(OH)<sub>2</sub>. This is predominantly because of the electrode reversible reaction and also revealed that as a kind of super capacitor electrode materials. The recovered Li<sub>2</sub>CO<sub>3</sub> and Co(OH)<sub>2</sub> electrode materials from battery waste showing the highest specific capacitance with excellent rate capability and outstanding cycling stability (Figure 12).

Electrode	Specific Capacity (Fg <sup>-1</sup> )	Energy density (whkg <sup>-1</sup> )	Power density (wkg <sup>-1</sup> )
5% Li <sub>2</sub> CO <sub>3</sub>	138.4	19.6	15.93
10% Li <sub>2</sub> CO <sub>3</sub>	189.4	26.8	10.63
15% Li <sub>2</sub> CO <sub>3</sub>	2631	412.5	3.87
5% Co(OH) <sub>2</sub>	147.9	0.207	0.295
10% Co(OH) <sub>2</sub>	150.01	0.186	0.183
15% Co(OH) <sub>2</sub>	2133.8	467.3	14.29

Table 5: The specific capacitance, Energy and power density values of Li<sub>2</sub>CO<sub>3</sub> and Co(OH)<sub>2</sub>

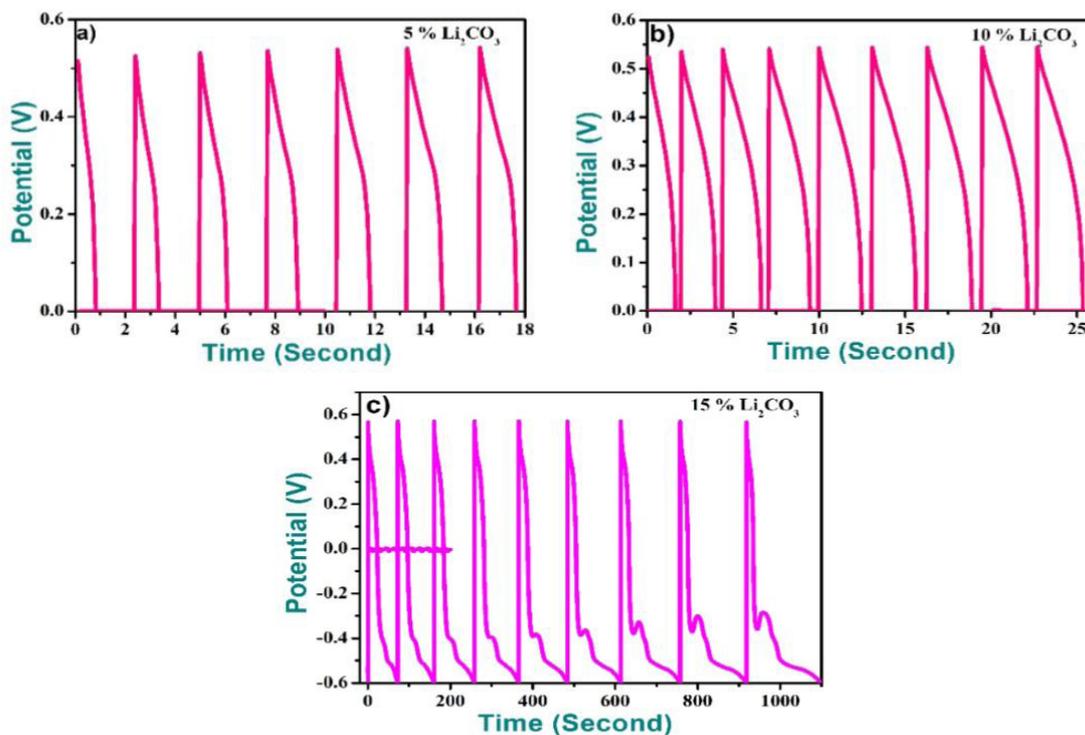


Figure 11: Charge-discharge curve (20 segments) of (a) 5% Li<sub>2</sub>CO<sub>3</sub>, (b) 10% Li<sub>2</sub>CO<sub>3</sub>, (c) 10% Li<sub>2</sub>CO<sub>3</sub>

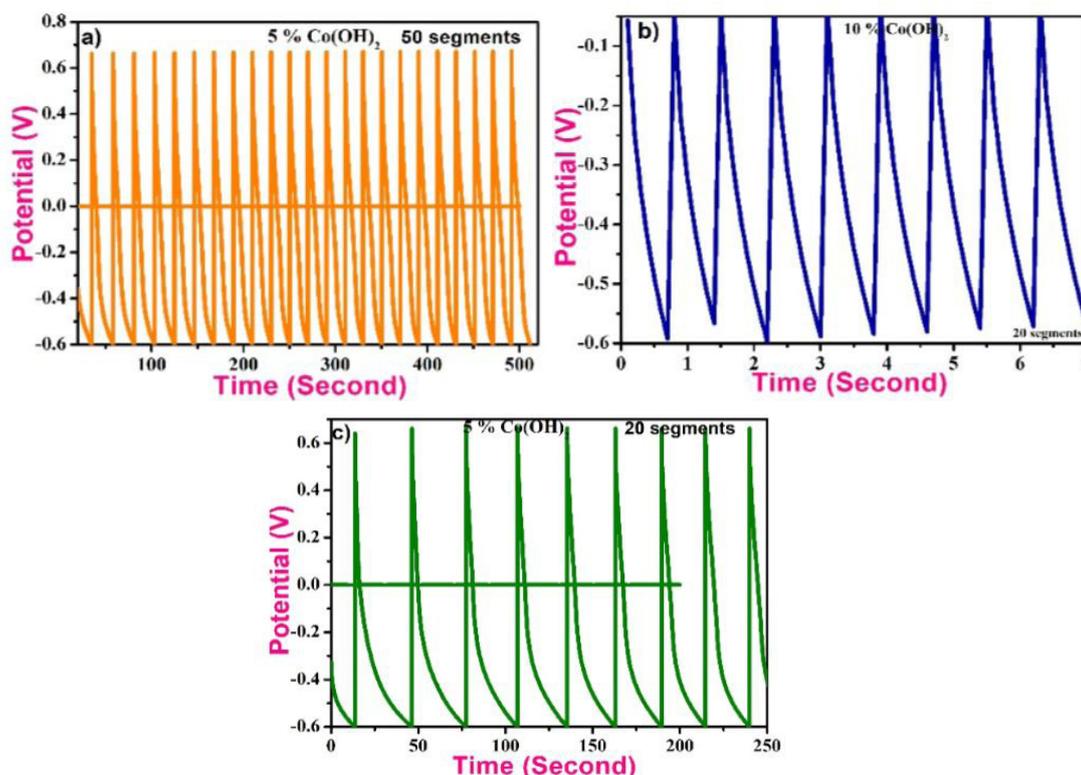


Figure 12: Charge-discharge curve of (a) 5% Co(OH)<sub>2</sub> for, (b) 5% Co(OH)<sub>2</sub> for 50 segments, (c) 10% Co(OH)<sub>2</sub>, (d) 15% Co(OH)<sub>2</sub>

## Conclusion

The average crystalline sizes of  $\text{LiCoO}_2$  without treated NMP, treated with NMP,  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  were found to be 39.15, 36.18, 57.03 and 49.14 nm respectively. From SEM study  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  particles have rod like and multi pod structures and the recovered materials were thermally stable up to 715 °C to 632 °C. From electrochemical properties, the extreme specific capacitance of  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$  was found to be 2631  $\text{Fg}^{-1}$  and 2133.8  $\text{Fg}^{-1}$ . These results confirmed that a high energy density battery can store lots of energy and a high power density battery will charge faster than a low power density battery. The charge-discharge curves display well-symmetry and linear deviations with change of the time indicating superior capacitance and cycle performance of  $\text{Li}_2\text{CO}_3$  and  $\text{Co(OH)}_2$ .

## References

1. Chen X, Chen Y, Zhou T, Liu D, Hu H, et al. (2015) Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. *Waste Manage* 38: 349-56.
2. Nayaka GP, Manjanna J, Pai KV, Vadavi R et al. (2015) Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids. *Hydrometallurgy* 151: 73- 7.
3. Pananelli F, Moscradini E (2014) Acid reducing leaching of cathodic powder from spent lithium ion batteries: Glucose oxidative pathways and particle area evolution. *J Indust Eng chem* 20: 3201-7.
4. Castillo S, Ansart F, Laberty-Robert C, Portal (2002) Advances in the recovering of spent lithium battery compounds. *JJ Power Sources* 112: 247-54.
5. Contestabile M, Panero S, Scrosati B (2001) A laboratory-scale lithium-ion battery recycling process. *J Power Sources* 92: 65-9.
6. Zhang P, Yokoyama T, Itabashi O, Wakui Y, Suzuki TM, et al. (1998) Hydrometallurgical Process for Recovery of Metal Values from Spent Nickel-Metal Hydride Secondary Batteries. *Hydrometallurgy* 50: 61-75.
7. Spencer CM, Houpt TA (2001) Dynamics of c-fos and ICER mRNA expression in rat forebrain following lithium chloride injection. *Molecular Brain Res* 93: 113-26.
8. Mylarappa M, Venkata Lakshmi V (2018) Cyclic Voltammetry, Impedance and Thermal Properties of  $\text{CoFe}_2\text{O}_4$  Obtained from Waste Li-Ion Batteries. *Materials Today: Proceed* 5: 22425-32.
9. Aslan A, Salur E, Gunes A, OS Sahin, HB Karadag, et al. (2019) The mechanical properties of composite materials recycled from waste metallic chips under different pressures. *Int J Environ Sci Technol* 16: 5259-66.
10. Aslan A, Gunes A, Salur E (2018) Mechanical properties and microstructure of composites produced by recycling metal chips. *Int J Miner Metall Mater* 25: 1070-9.
11. Shin SM, Kim NH, Sohn JS, Yang DH, Kim YH (2005) Development of a Metal Recovery Process from Li-Ion Battery Wastes. *Hydrometallurgy* 79: 172-81.
12. Kang J, Sohn G, Chang H, Senanayake G (2010) Preparation of cobalt oxide from concentrated cathode material of spent lithium ion batteries by hydrometallurgical method. *Adv Power Techno* 21: 175-9.
13. Shin SM, Kim NH, Sohn JS, Yang DH, Kim YH (2005) Development of a Metal Recovery Process from Li-Ion Battery Wastes. *Hydrometallurgy* 79: 172-81.
14. Espinosa DCR, Bernardes AMJ (2004) an overview on the current processes for the recycling of batteries. *Power Sources* 135: 311-9.
15. Li L, Ge J, Chen R, Wu F, Chen S (2010) Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manage* 30: 2615-21.
16. Lupi C, Pasquali M, Dell Era A (2005) Nickel and cobalt recycling from lithium-ion batteries by electrochemical processes. *Waste Manage* 25: 215-20.
17. Swain B, Jeong J, Lee JC, Lee GH (2007) Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries. *J Power Sources* 167: 536-44.
18. Lupi C, Pasquali M (2003) Electrolytic nickel recovery from lithium-ion batteries. *Miner Eng* 16: 537-42.
19. Nan J, Han D, Yang M, Cui M (2006) Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. *Hydrometallurgy* 84: 75-80.
20. Lee CK, Rhee K (2003) Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* 68: 5-10.
21. Lee CK, Rhee K (2002) Preparation of  $\text{LiCoO}_2$  from spent lithium-ion batteries. *J Power Sources* 109: 17-21.
22. Jha M K, Kumari A, Jha A K. (2013) Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *waste Manage* 33: 1890-7.
23. Dakora FD, Phillips DA (2002) Root Exudates as Mediators of Mineral Acquisition in Low-Nutrient Environments. *Plant Soil* 245: 35-47.
24. Jones DL, Darrah PR (1994) Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. *Plant Soil* 166: 247-57.
25. Ryan PR, Delhaize E, Jones DL (2001) Function and Mechanism of Organic Anion Exudation from Plant Roots. *Plant Mol Bio* 52: 527-60.
26. Strom L, Owen (2005) Organic Acid Behaviour In A Calcareous Soil Implications for Rhizosphere Nutrient Cycling. *AG Soil Bio Biochem* 37: 2046-54.
27. Mylarappa M, Venkata Lakshmi V, Vishnu Mahesh KR, Kantharaju S Sreenivasa S (2018) Effect of Oxalic Acid and Citric Acid on Recovery of Ni and Cd from Waste Batteries: Electrochemical and Thermal Investigation of  $\text{Ni(OH)}_2$  Obtained from Leach Solution. *Res J Chem Environ* 22: 1-15.
28. Shen Y, Xue W (2008) Recovery of Co(II) and Ni(II) from hydrochloric acid solution of alloy scrap *Trans. Nonferrous Met Soc China* 18: 1262-8.
29. Pranolo Y, Zhang W, Cheng CY (2010) Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system. *Hydrometallurgy* 102: 37-42.
30. Provazi K, Campos BA, Espinosa DCR (2011) Recovery of Metals from Electronic Waste by Physical and Chemical Recycling Processes. *Waste Manage* 2: 3159-64.
31. Zhao JM, Shen XY, Deng FL, Wang FC, Wu Y (2011) Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. *Sep Purif Technol* 78: 345-51.
32. Castillo S, Ansart F, Laberty-Robert CJ (2002) Advances in the recovering of spent lithium battery compounds. *Power Sources* 112: 247-54.

33. Contestabile M, Panero S, Scrosati B (2001) A laboratory-scale lithium-ion battery recycling process. *J Power Sources* 92: 65-9.
34. Kang J, Senanayake G, Sohn J (2010) Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272. *Hydrometallurgy* 100: 168-71.
35. Wang, Lin Y, Wu S (2009) Hydrometallurgical Recovery of Value Metals from Spent Lithium Ion Batteries. *Hydrometallurgy* 99: 194-201.
36. Dorella G, Mansur MB (2007) Leaching study of spent Li-ion batteries. *J Power Sources* 170: 210-5.
37. Li J, Shi P, Wang Z, Chen Y, Chang C (2009) A combined recovery process of metals in spent lithium-ion batteries. *Chemosphere* 77: 1132-6.
38. Chen L, Tang X, Zhang Y, Li L, Zeng Z (2011) Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy* 108: 80-6.
39. Lupi C, Pasquali M, Dell'Era A (2005) Nickel and cobalt recycling from lithium-ion batteries by electrochemical processes. *Waste Manage* 25: 215-20.
40. Sayed M, Badawy AA, Nayl RA, El-Khateeb MA (2014) Cobalt separation from waste mobile phone batteries using selective precipitation and chelating resin. *J Mater Cycles Waste Manage* 2014: 739-46.
41. Mishra D, Kim DJ, Ralph DE, Ahn JG (2008) Bioleaching of metals from spent lithium ion secondary batteries using *Acidithiobacillus ferrooxidans*. *Waste Manage* 28: 333-8.
42. Zhang P, Yokoyama T, Itabashi O, Suzuki TM (1998) Precipitation–stripping processes for heavy metal. *Hydrometallurgy* 47: 259-71.
43. Li L, Ge J, Wu F, Chen R, Chen S, et al. (2010) Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J Hazard Mater* 176: 288-93.
44. Shin SM, Kim NH, Sohn JS, Dong HY, Young HK (2005) Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy* 79: 172-81.
45. Mantuano DP, Dorella G, Renata CAE, Marcelo BM (2006) Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid–liquid extraction with Cyanex 272. *Power Sources* 159: 1510-8.
46. Xin BP, Zhang D, Zhang X, Feng W, Li L (2009) Bioleaching mechanism of Co and Li from spent lithiumion battery by the mixed culture of acidophilic sulfur oxidizing and iron-oxidizing bacteria. *Bioresour Technol* 100: 6163-9.
47. Yoo KK, Shin SM, Yang DH (2010) Biological treatment of wastewater produced during recycling of spent lithium primary battery. *Miner Eng* 23: 219-24.
48. Sonmez MS, Kumar RV (2009) Leaching of waste battery paste components. Part 1: Lead citrate synthesis from PbO and PbO<sub>2</sub>. *Hydrometallurgy* 95: 53-60.
49. Wang J, Chen M, Chen H, Luo T, Xu Z (2012) Leaching study of spent Li-ion batteries. *Procedia Environ Sci* 16: 443-50.
50. Li Li, Jing Ge, Chen R, Wua F, Chen S, et al (2010) Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manage* 30: 2615-21.
51. Li Li, Dunn JB, Zhang XX, Gaines L, Chen RJ, et al (2013) Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. *J Power Sources* 233: 180-9.
52. Mylarappa M, Venkata Lakshmi V, Vishnu Mahesh KR, Nagaswarupa HP, Raghavendra N (2017) Synthesis and characterization of Mn-ZnFe<sub>2</sub>O<sub>4</sub> and Mn-ZnFe<sub>2</sub>O<sub>4</sub>/rGO nanocomposites from waste batteries for photocatalytic, electrochemical and thermal studies. *Mater Res Express* 4: 115603.
53. Liang Chen, Xincun Tang, Yang Zhang, Lianxing Li, Zhiwen Zeng, et al (2011) Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy* 108: 80-6.
54. Li Li, Zhai L, Zhang XX, Jun L, Renjie C, et al. (2014) Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. *J Power Sources* 262: 380-5.
55. Covarrubias C, Duran JP, Maureira M (2018) Facile synthesis of lithium carbonate nanoparticles with potential properties for bone repair applications. *Mater Lett* 219: 205-8.
56. Shao L, Ma R, Wu K, Shui M, Lao M, et al. (2013) Metal carbonates as anode materials for lithium ion batteries. *J Alloys Compd* 581: 602-9.
57. Pen Chen, Li Gub, Xuebo Cao (2010) From single ZnO multipods to heterostructured ZnO/ZnS, ZnO/ZnSe, ZnO/Bi<sub>2</sub>S<sub>3</sub> and ZnO/Cu<sub>2</sub>S multipods: controlled synthesis and tunable optical and photoelectrochemical properties. *Cryt Eng Comm* 12: 3950-8.
58. Nethravathi C, Catherine R, Sanjay S, Rajamathi, Claudia F (2017) High coercivity stellated cobalt metal multipods through solvothermal reduction of cobalt hydroxide nanosheets. *RSC Adv* 7: 1413.
59. Ray LE, Klopogge JT (1999) Infrared emission spectroscopic study of brucite. *Spectrochim Acta Part A: Mol Biomol Spectr* 55: 2195-205.
60. Sang WK, Bob JK, Jeong HP, Hur MG, Yang SD, et al. (2010)  $\gamma$ -ray Radiation Induced Synthesis and Characterization of  $\alpha$ -Cobalt Hydroxide Nanoparticle. *Korean Chem Soc* 31: 910-4.
61. Oberhofer M, Scharmann A (1981) Applied thermoluminescence dosimetry. Published for the Commission of the European Communities 108.
62. Oberhofer M, Scharmann A (1993) Techniques and management of personnel thermoluminescence dosimetry services. Kluwer academic publishers, London.
63. Manteghi F, Kazemi SH, Peyvandipoor M, Ahmad A (2015) Preparation and application of cobalt oxide nanostructures as electrode materials for electrochemical supercapacitors. *RSC Adv* 93: 75838-6665.
64. Mylarappa M, Venkata Lakshmi V, Vishnu Mahesh KR, Kantharaju S (2018) Effect of Oxalic Acid and Citric Acid on Recovery of Ni and Cd from Waste Batteries: Electrochemical and Thermal Investigation of Ni (OH)<sub>2</sub> Obtained from Leach Solution. *RJCE* 22: 1:15.
65. Barbieri EMS, Lima EPC, Cantarino SJ, Lelis MFF, MBJG Freitas (2014) Recycling of spent ion-lithium batteries as cobalt hydroxide, and cobalt oxide films formed under a conductive glass substrate, and their electrochemical properties. *J Power Sources* 269: 158-63.
66. Yanan Xu, Wang X, An C, Wang Y, Jiao L, et al. (2014) Facile synthesis route of porous MnCo<sub>2</sub>O<sub>4</sub> and CoMn<sub>2</sub>O<sub>4</sub> nanowires and their excellent electrochemical properties in supercapacitors. *J Mat Chem A* 2: 16480-8.