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Synthesis and characterization of $LiCoO_2$ fine particles prepared by soft chemical routes

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Abstract:Lithium ion batteries have revolutionized the portable electronics market now-a-days. Rechargeable lithium batteries based on layered cathode phases viz., $LiCoO_2$ have received a great deal of attention in recent years. We report the preparation of $LiCoO_2$ fine particles synthesized by simple soft chemistry routes such as combustion technique and solvothermal precipitation process in this research article. The prepared $LiCoO_2$ particles were characterized by XRD, SEM and Particle size analysis. The powder XRD data obtained on $LiCoO_2$ powder was in good agreement with the standard reported XRD data. The presence of larger particles in the powder may be due to the agglomeration of particles at high temperature treatment.

Keywords: $LiCoO_2$ fine particles, soft chemical routes, characterization.

1. Introduction

Portable power technology plays a vital role in the advancement of electronic devices such as Lap-top computers, cellular phones and most portable electronic memory devices etc as required by the modern civilization [1]. Also find in the biomedical devices, including pacemakers and implantable defibrillators. Thus, research focused on the development of rechargeable, high-energy density power sources. Although various types of battery chemistries exist-such as nickel-metal hydride (Ni-MH) and nickel-cadmium (Ni-Cd)-lithium (Li) ion batteries are dominant as they have significant advantages in energy density. A major technological barrier to improve energy densities and reliability of the Li-ion battery systems is related to the stability of the anode and cathode materials. From this, we understood that there exists a large thermodynamic driving force which enables the transport of Li ions from the negative to the positive electrode on discharge, and relatively large voltages must me applied to fully recharge the battery. One of the reasons that Li-ion chemistries exhibit high energy densities is because of the relatively high cell voltage. The thermodynamic instability of the Li-ion battery chemistries results in materials reliability issues that continue to be addressed by multiple investigators. The large volumetric and gravimetric energy densities exhibited by Li-ion batteries allow their volume and mass to be reduced by 20% and 50%, respectively. In-fact, a Li battery can provide three times the voltage of a

Ni-Cd or Ni-MH battery. The self-discharge rate of Li batteries is very small over a long period of time, while their operating voltage allows a reduction in the number of batteries required to operate a device.

Finally, it should be mentioned that – unlike other battery base materials (Cd,Ni) – Li is non-toxic and as opposed to them Li-batteries have no memory effect. The reliability issues of electrode materials used in Li-ion systems appear to be related to both mechanical and chemical instabilities. The charging capacity i.e., total time integrated battery current per mass is not reduced by repeatedly charging and discharging to insufficient levels, and therefore partial charging is possible, i.e., discharging process takes place during the operation of the respective electronic device. The goals of this type of research are to improve the storage life and cycle life of Li-ion batteries, while reducing cost and maintaining or improving the energy density.

Different processes are reported in the literature for the preparation of $LiCoO_2$ particles [2]. In this research work, we report the preparation of $LiCoO_2$ particles prepared by simple soft chemistry routes such as combustion technique and solvothermal precipitation process. The prepared $LiCoO_2$ particles were characterized with XRD, particle size analyzer and SEM. The obtained data was discussed and reported in this research article.

2. Experimental Method

Synthesis of $LiCoO_2$ particles by combustion technique

The $LiCoO_2$ particles werre prepared by the combustion synthesis process using urea / glycine / glucose as fuels. The chemicals used in the preparative method are: $LiNO_3$, $Co(NO_3)_2$, NH_2-CO-NH_2 (urea) / NH_2-CH_2COOH (glycine) / $C_6H_{12}O_6$ (glucose). The combustion synthesis involves the combustion of saturated aqueous solution containing stoichiometric quantities of the corresponding nitrates (oxidizers) and urea (NH_2-CO-NH_2) / glycine (NH_2-CH_2COOH) / glucose ($C_6H_{12}O_6$) fuel. The stoichiometric ratios of the precursor salts were weighed accurately, taken in silica crucible and dissolved in triple distilled water. Calculated amount of fuel (urea / glycine / glucose) was added to the above solution with continuous stirring and homogenized well. The oxidizer: fuel ratio was calculated based on oxidizing (O) and fuel (F) valencies of the reactants keeping O/F =1 as reported [3,4]. The aqueous redox solution containing metal nitrates and glycine when introduced into a muffle furnace preheated to 823 K, boils, froths, ignites and catches fire (temperature 1373 ± 100 K). At this higher temperature the metal nitrates decompose to metal oxides and oxides of nitrogen and hence act as oxidizer for further combustion, which leads to a voluminous, foamy combustion residue in less than 5 minutes. The flame persisted for about 1 minute. The foam was then lightly ground in a silica basin with porcelain pestle to obtain fine powders. The procedure is explained in the schematic (Fig. 1). The stoichiometric proportion of precursor materials used for the synthesis of $LiCoO_2$ particles is indicated in Table 1. The stoichiometric redox reactions between metal nitrates and urea or glycine or glucose to produce $LiCoO_2$ particles can be represented by the following theoretical equations:

To prepare $LiCoO_2$ by combustion technique with urea as a fuel:

$LiNO_3 + Co(NO_3)_2 + 2.49\ NH_2CONH_2 + 0.235\ O_2 \rightarrow LiCoO_2 + 2.49\ CO_2 + 3.99\ N_2 + 4.98H_2O$

To prepare $LiCoO_2$ by combustion technique with glycine as a fuel:

$LiNO_3 + Co(NO_3)_2 + 1.66\ NH_2CH_2\ COOH + 0.235\ O_2 \rightarrow LiCoO_2 + 3.32\ CO_2 + 2.33\ N_2 + 4.15\ H_2O$

To prepare $LiCoO_2$ by combustion technique with glucose as a fuel:

$LiNO_3 + Co(NO_3)_2 + 0.6249\ C_6H_{12}O_6 \rightarrow LiCoO_2 + 1.8747\ CO_2 + 1.5\ N_2 + 3.7494\ H_2O + 1.6253\ O_2$

The as-synthesized powder was carried out in clean alumina crucibles and calcined in air at 1073 K for 3 hours to remove the deposited carbon and the unreacted organic residues and to get phase pure compound [5].

Synthesis of $LiCoO_2$ particles by solvothermal precipitation process

$LiCoO_2$ particles were prepared by the solvothermal precipitation [6] process as per the details indicated below. The chemicals used in the preparative method are: $LiNO_3$, $Co(NO_3)_2$, Ethanol and NaOH. All the reagents were analytical grade and were used without any further purification. In this process, 100 ml of 0.5 M $LiNO_3$ (3.44 g dissolved in 100 ml ethanol) was added slowly to 100 ml 0.5 M of $Co(NO_3)_2$ (14.55 g dissolved in 100 ml ethanol). The resulting solutions were stirred thoroughly in a 500 ml round bottom flask at 323 – 343 K for about 24 hours. During the stirring, the colour of the solution was changed from light orange colour to crimson red colour. Then, the round bottom flask was cooled. 100 ml 0.5 M NaOH (6.0 g dissolved in 100 ml water) was slowly added dropwise with a burette to the above resulting solution under continuous stirring in a magnetic stirrer. The resulting precipitate was filtered and air-dried at room temperature. The final product was calcined at 1073 for 3 hours. The flow chart to prepare $LiCoO_2$ particles by solvothermal precipitation process is indicated in Fig. 2

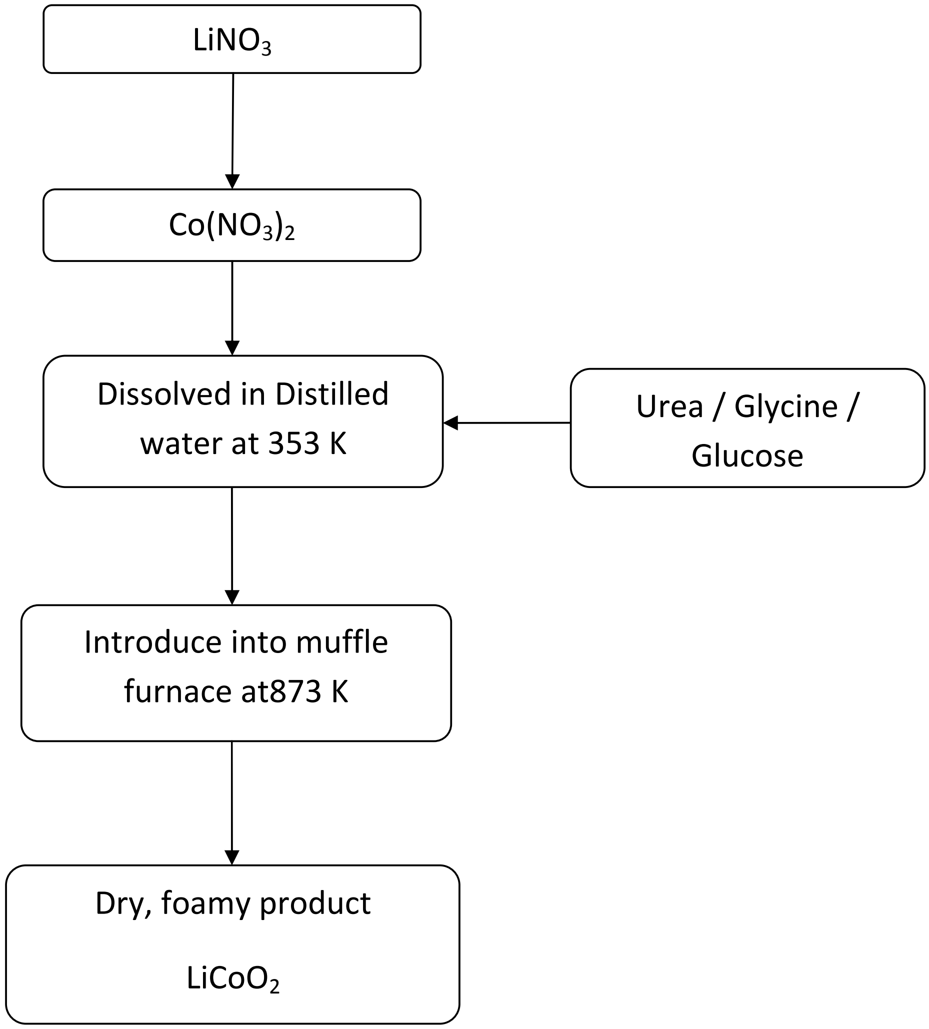


Figure 1 Flow chart to prepare $LiCoO_2$ particles by combustion technique using urea / glycine / glucose as fuels

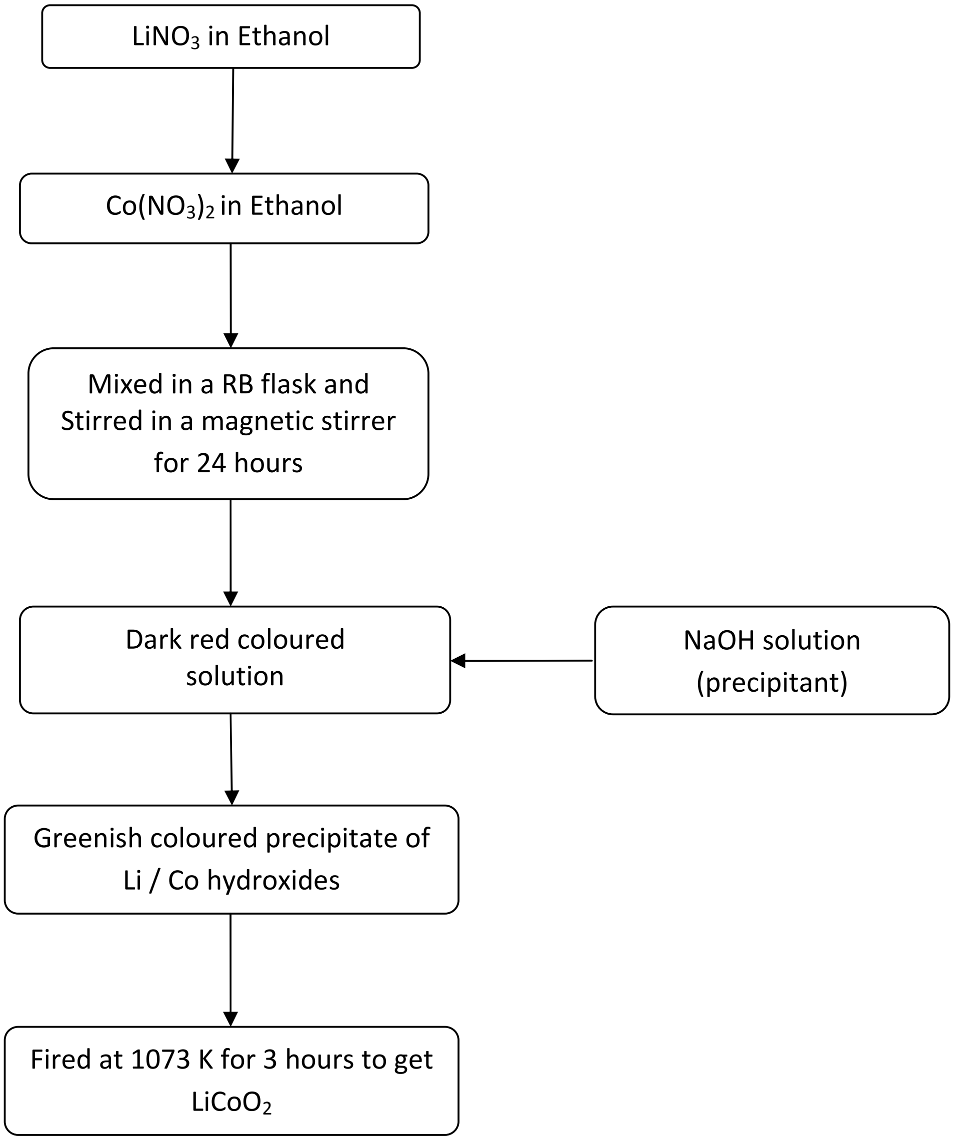


Figure 2 Flow chart to prepare $LiCoO_2$ particles by solvothermal precipitation process

Table 1 Stoichiometric proportion of the precursor materials used for the synthesis of $LiCoO_2$ particles by combustion technique

Weight of $LiNO_3$ (g)	Weight of $Co(NO_3)_2$ (g)	Weight of urea (g)	Weight of glycine (g)	Weight of glucose (g)	Weight of as synthesized $LiCoO_2$ powder (g)
0.68	2.91	1.49	--	--	0.49
0.68	2.91	--	3.0	--	2.61
0.68	2.91	--	--	1.1258	0.97

Characterization of $LiCoO_2$ particles

The powder XRD study was carried out using a Shimadzu XRD6000 X-ray diffractometer using CuKα radiation. The crystallite sizes of the $LiCoO_2$ were calculated by Scherrer's formula. The particle size of the powder was measured using a Malvern Particle Size Analyzer using triple distilled water as medium. The morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope.

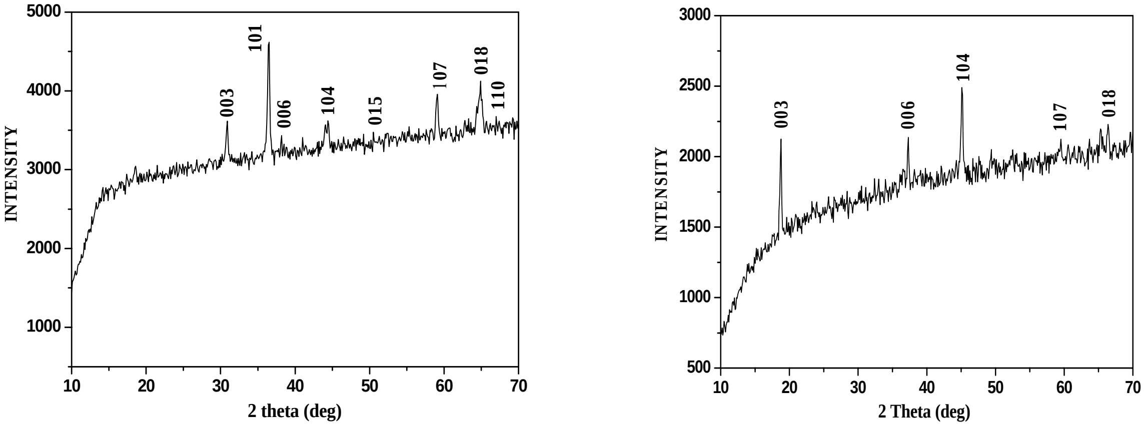
3. Results and Discussion

X-ray diffraction studies

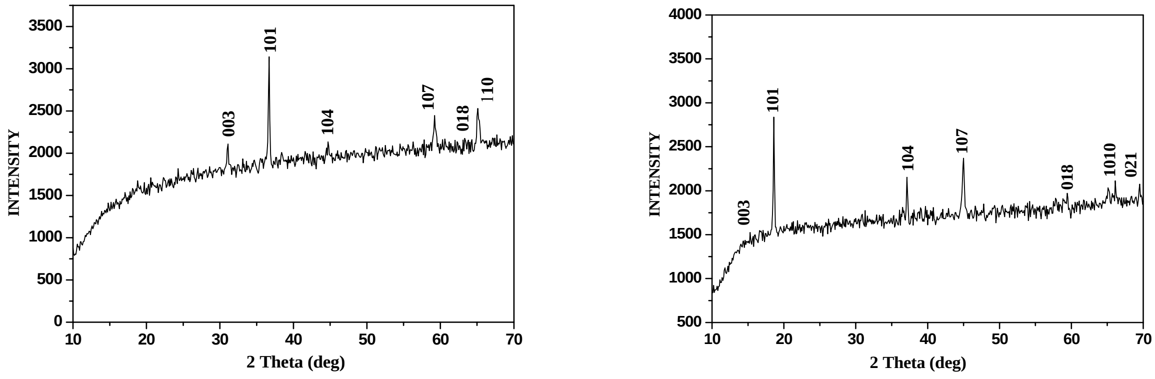
Figs. 3 (a), (b), (c) and (d) illustrate the X-ray diffraction patterns of the combustion-derived and calcined $LiCoO_2$ particles prepared with urea, glycine and glucose as fuels and $LiCoO_2$ prepared by solvothermal process. The $LiCoO_2$ powder prepared by both combustion technique (with all fuels) and solvothermal process is indexed to the rhombohedral cell geometry. The XRD pattern of $LiCoO_2$ is compared with standard JCPDS data (card No. 50-0653). Tsuruhama et. al have prepared epitaxial thin films of layered rhombohedral $LiCoO_2$ grown on Al2O3(0001) substrates using pulsed laser deposition. They reported that the secondary phases like Co_2O_3, Co_3O_4, and $LiCo_2O_4$ were also appeared in that powder [6]. Sathia et.al has synthesized HT-$LiCoO_2$ material by nitrate – melt route and they reported the crystalline structure as rhombohedral cell geometry with space group: R 3m with a small impurity Co_3O_4. However, Chung-Hsin Lu et.al has prepared $LiCoO_2$ by micro emulsion method and they reported the structure as hexagonal [7]. The 2θ values of the combustion derived $LiCoO_2$ sample were compared with the above standard JCPDS data. From this, it was found that all the peaks except three peaks appeared at $2\theta = 31.04^0$, 38.36^0 and 69.20^0 in $LiCoO_2$ prepared with urea as fuel, four peaks appeared at $2\theta = 37.25^0$, 39.00^0, 49.80^0 and 68.900 in $LiCoO_2$ prepared with glycine as fuel, three peaks appeared at $2\theta = 38.60^o$, 49.14^o and 68.57^o prepared with glucose as fuel and four peaks appeared at $2\theta = 37.30^0$, 48.79^0, 68.19^0 and 80.49^0 prepared by solvothermal process are similar to those of reported pattern of $LiCoO_2$ existing in JCPDS card No. 50-0653. The impurity phases may be due to presence of oxide of cobalt as reported [6]. The crystallite sizes for the samples were found to be in the range of 15 to 20 nm.

Particle characteristics studies

The prepared $LiCoO_2$ particles (after calcination at 1073 K for 3 h) were subjected to particle size measurements using Malvern particle size analyzer with triple distilled water as medium. For all the measurements, 0.30 g of sample is sonicated in 30 ml triple distilled water for about 10 minutes and after that the sample is subjected for particle size analysis. The particle size distribution curves of $LiCoO_2$ are shown in Figs. 4 (a) – (h). From the particle characteristics data, it was found that the $LiCoO_2$ prepared by combustion technique using glucose as a fuel has greater average particle size than the sample prepared with combustion technique using urea as a fuel and lesser particle size than the sample prepared with combustion technique using glycine as a fuel. The particle characteristics data revealed that the $LiCoO_2$ particles are present in micron size range. The particles prepared with solvothermal precipitation method exhibited very low particle size. The particle characteristics data obtained on $LiCoO_2$ particles is indicated in Table 2.



(a) (b)



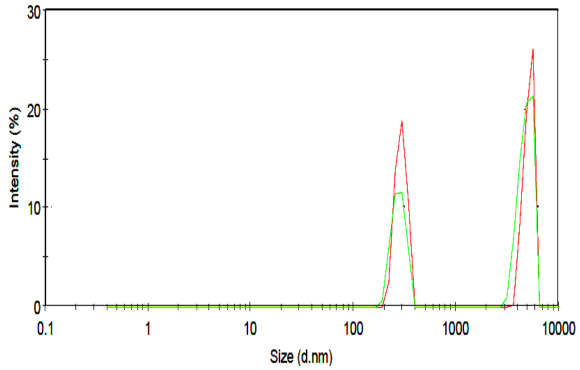
(c)

(d)

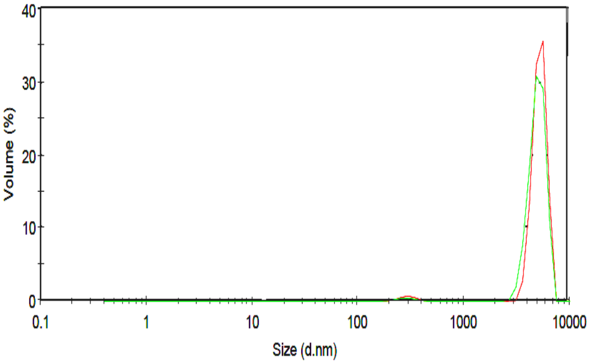
Figure 3: Powder XRD patterns obtained on $LiCoO_2$ prepared (a) by combustion synthesis using urea as a fuel (b) by combustion synthesis using glycine as a fuel (c) by combustion synthesis using glucose as a fuel (d) by solvothermal precipitation process

Table 2 Particle characteristics data obtained on $LiCoO_2$ particles

Process	Intensity/ Volume	Peak 1		Peak 2		Average particle size(d.nm)
		% of particles	Diameter (µm)	% of particles	Diameter (µm)	
Combustion with urea as fuel	Intensity	64.5%	4.747	35.5 %	0.275	784.2
	Volume	98.6%	4.948	1.4%	0.282	
Combustion with glycine as fuel	Intensity	75.7 %	4.806	24.3 %	0.315	1633
	Volume	99.1 %	4.984	0.9 %	0.322	
Combustion with glucose as fuel	Intensity	54.2 %	5.060	45.8 %	0.289	807.0
	Volume	98 %	5.184	2.0 %	0.296	
Solvothermal precipitation process	Intensity	53.5 %	0.165	46.5 %	2.365	253.3
	Volume	9.8 %	0.152	90.2 %	2.741	


Intensity (%)
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

(a)


Volume (%)
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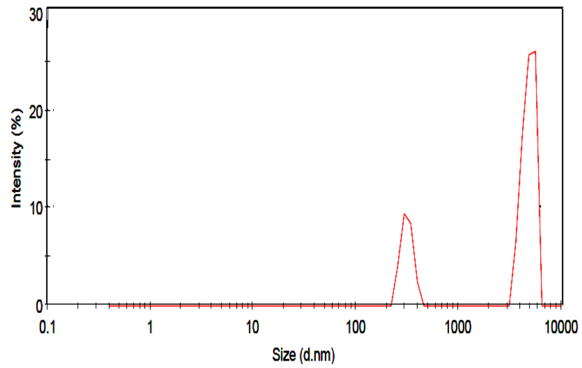
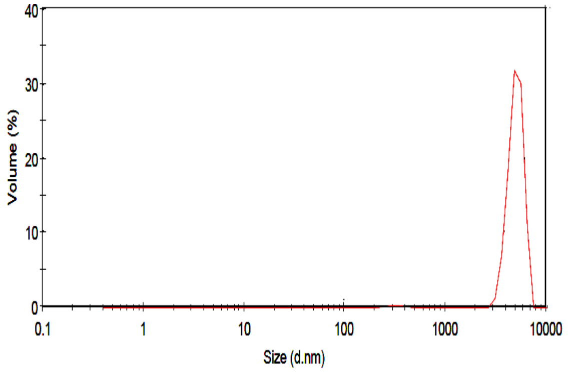
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

(b)


Intensity (%)
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

(c)


Volume (%)
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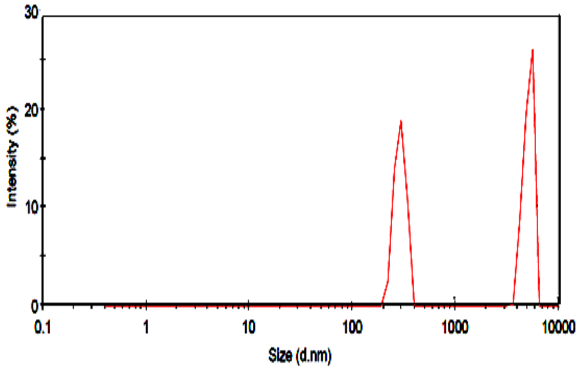
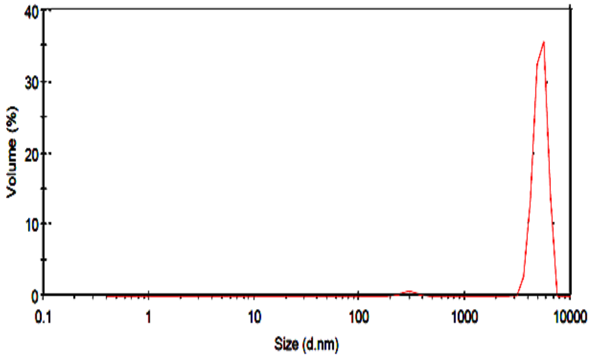
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

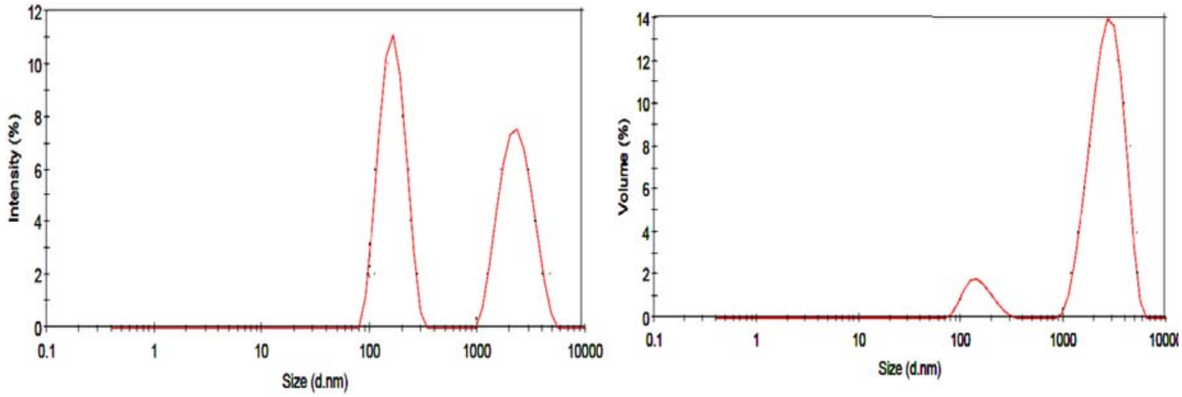
(d)


Intensity (%)
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

(e)


Volume (%)
40
30
20
10
0
0.1
1
10
100
1000
10000
Size (d.nm)

(f)



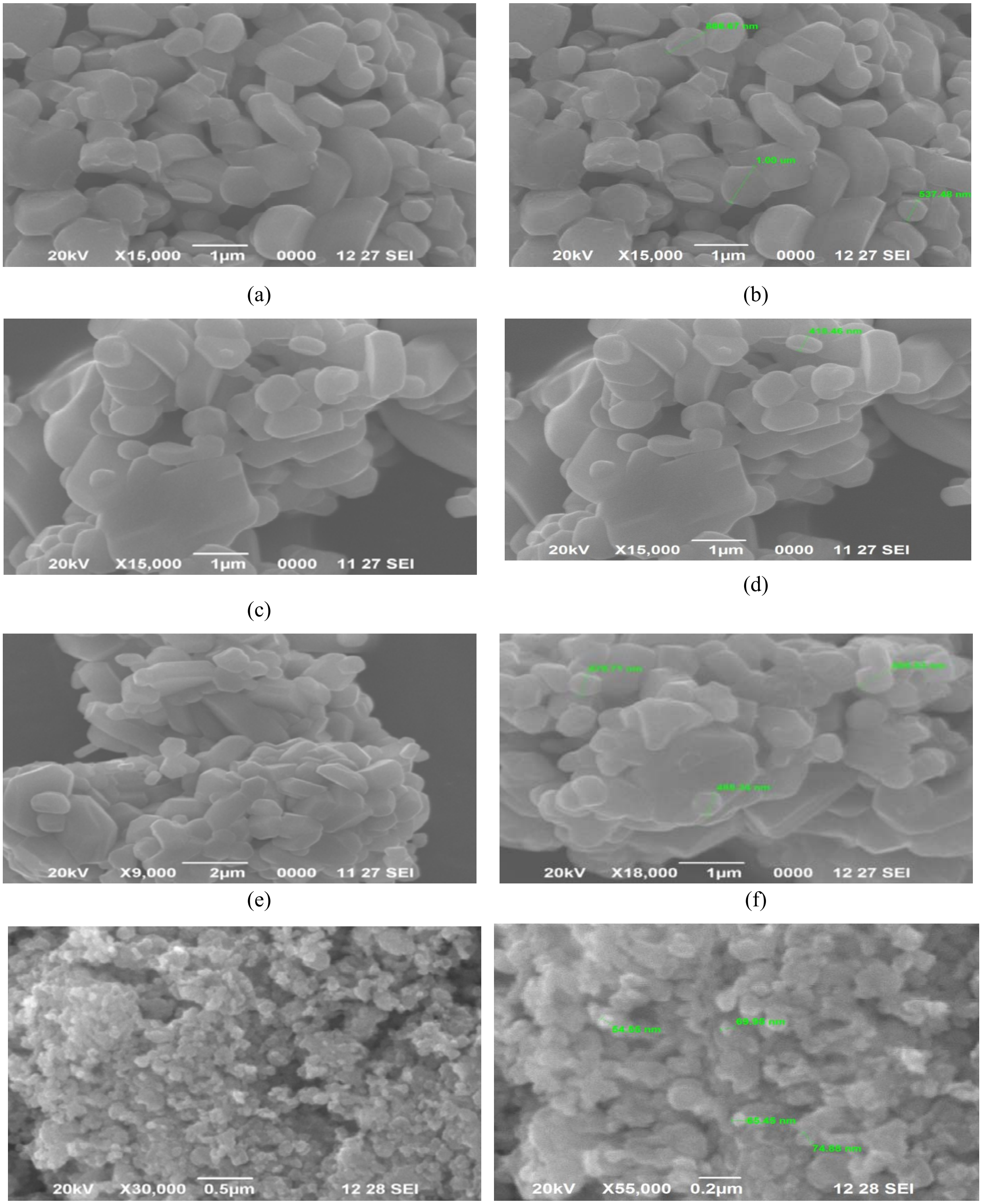
(g)

(h)

Figure 4 Particle distribution pattern obtained on $LiCoO_2$ prepared (a) & (b) by combustion synthesis using urea as a fuel based on % intensity and % volume respectively; (c) & (d) by combustion synthesis using glycine as a fuel based on % intensity and % volume respectively; (e) & (f) by combustion synthesis using glucose as a fuel based on % intensity and % volume respectively; (g) & (h) by solvothermal precipitation process based on % intensity and % volume respectively

Scanning Electron Microscopic (SEM) studies

The surface microstructure of $LiCoO_2$ particles was studied with SEM. The arrangement of grains, size of grains, etc. were differed for the samples based on the preparative conditions. Scanning electron micrographs of combustion derived samples reflect agglomerated, porous, flaky morphologies for the samples [8]. The SEM photographs of $LiCoO_2$ particles are shown in Figs. 5 (a) – (h). The sample prepared with combustion synthesis using urea (Figs. 5 (a) and (b)) as a fuel has grains with average size of 0.50 to 1 μm. However, the grain size is less (< 0.50 μm) for the sample prepared with combustion synthesis using glycine as a fuel. The presence of agglomeration in the sample (Figs. 5 (c) and (d)) may due to the high temperature heat treatment. Also, the photographs revealed the fluffy / foamy nature of the powder. The sample prepared with combustion synthesis using glucose as a fuel (Figs. 5 (e) and (f)) consists of grains with average size of 0.50-0.60μm and the presence of interconnecting of grains found in the powder. The sample prepared with solvothermal precipitation process (Figs. 5 (g) and (h)) exhibited the particle size between 50 to 70 nm.



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 5 SEM photographs obtained on LiCoO$_2$ prepared (a) & (b) by combustion synthesis using urea as a fuel; (c) & (d) by combustion synthesis using glycine as a fuel; (e) & (f) by combustion synthesis using glucose as a fuel; (g) & (h) by solvothermal precipitation process

4. Conclusion

Synthesis of $LiCoO_2$ fine particles by combustion technique and solvothermal precipitation process for the application as cathode materials in Li-ion batteries is dealt with. The powder XRD data obtained on $LiCoO_2$ powder is in good agreement with the standard reported XRD data except with few impurity phases. The particle characteristics data revealed the presence of nano / micron sized particles in the $LiCoO_2$ powder. The particulate properties suggest that the as-formed powders are porous. The Scanning Electron Microscope (SEM) studies also confirmed the presence of nano / micron sized particles in the powder which is in agreement with the particulate properties data.

5. Acknowledgments

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