

Study of High Purity Cobalt Carbonate Nanocrystals Production by Microemulsion as Batteries Precursors

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Abstract

The precipitation of cobalt carbonate nanocrystals was achieved through the reaction of a pure and rich solution of cobalt sulphate (Co^{2+} : 16.80 g/l) with a solution of carbonate solution (200 g/l). A surfactant was added to the reacting mixture in order to control the shape and size of generated crystallites. Two parameters were then varied *i.e.*, the weight of surfactant agent and the precipitation time in accordance with Taguchi's L4 full experimental procedure (2^2). Chemical and structural characterizations tests of the obtained precipitates were done through X-Rays Fluorescence (XRF), Scanning Electron Microscopy (SEM) and X-Rays Diffractometer (XRD); whereas the size of crystallites was assessed according to the Laue-Scherrer formula. The results obtained from the variance analysis (ANOVA) indicated an optimal size of cobalt carbonate's crystallites of 13 nm with a cobalt content of 44.35% (equivalent to 89.45% of CoCO_3) at ambient temperature under the following conditions: pH = 7; Mixing speed: 800 tr/min; Surfactant weight: 8 g; and a mixing time: 10 minutes. SEM images revealed an agglomeration of the obtained nanocrystals due to suspected drying conditions *i.e.*, drying temperature and drying atmosphere. It is suggested that the experiment should be conducted under neutral conditions at a temperature below that of cobalt carbonate's decomposition (181.41 °C).

Keywords

Nanocrystals, Cobalt Carbonate, Microemulsion, Batteries

1. Introduction

The synthesis of inorganic materials with nanoscale morphology has aroused

considerable interests around the globe, making nanoscience an important field in modern research. Popular opinion has projected it to be at the core of the 5th global revolution [1] [2]. Metal salts constitute an important category in nanoscience owing it to their large surface area and their stable chemical and thermal properties [1] [3] [4] [5].

Cobalt carbonate nanocrystals, precursor to cobaltous oxide (CoO), are of evolving interest due to their exceptional properties. They are widely used in rechargeable batteries for electric vehicles (49% in 2018), in catalysis and in the production of magnetic materials owing it to their physical, electrical and chemical properties [4]-[9].

There are several nanocrystals synthesis methods, including [10]-[15]:

- Physical methods such as the vapor condensation, the thermal evaporation, the laser method, the jet pyrolysis method, the mechanosynthesis and the thermochemical decomposition.
- Chemical methods: such as the sol-gel, the precipitation and the microemulsion methods.

In this research, the microemulsion method was used as it is to be one of the most promising technics for the synthesis of nanomaterials [10] [16]-[21].

2. Experimental Procedure

2.1. Reagents Used

A pure sulphate solution and rich in cobalt (Co²⁺: 16.80 g/l), a sodium carbonate solution (200 g/l) prepared from sodium carbonate with 99.5% in purity and a surfactant as nucleation agent and emulsifying agent for the dispersion of the crystallites precipitate were used as reagents.

2.2. Experimental Equipments

A 600 ml beaker, a 50 ml graduated burette, a 250 ml volumetric flask, a watch glass, an OHAUS branded precision weighing scale, a magnetic stirrer, a pH meter HANNA Instruments branded and a filtration device (vacuum pump + filter paper + Buchner) were mainly used to carry out all the precipitation tests.

2.3. Analysis Techniques

The cobalt carbonate precipitate analysis was performed by X-Rays Fluorescence technique.

Crystallization and particle size

The crystallization of generated precipitates was observed using D2 Phaser BRUKER X-Rays Diffractometer equipment; whereas the size of the crystallites was assessed according to the Laue-Scherrer Formula (1):

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

With:

- K : coefficient [$K = 0.9$]

- λ : wavelength of $K\alpha$ Cu X-ray [1542 Å]
- β : Full width at half maximum: FWHM [rad]
- θ : half of the diffraction angle of the wave [rad]

Scanning Electron Microscopy (SEM) was also used to observe the structure of the obtained precipitates.

2.4. Precipitation Tests

A preliminary precipitation test was conducted without surfactant and four additional tests were performed by varying two parameters (weight of surfactant agent and precipitation time) at two levels in accordance with Taguchi's L4 full experimental procedure (2²) given in **Table 1** below.

Both parameters were chosen to control and limit the growth of generated cobalt carbonate crystallites.

3. Results and Discussion

3.1. Preliminary Test without Surfactant

A preliminary test was carried out without the use of surfactant in order to demonstrate the importance of surfactant agent in cobalt carbonate nanocrystals production.

Analysis of the obtained cobalt carbonate precipitates had yielded results on crystallization, purity and size as follows:

1) Crystallization

The sample of cobalt carbonate precipitated without surfactant gave the DRX spectrum shown on **Figure 1** below.

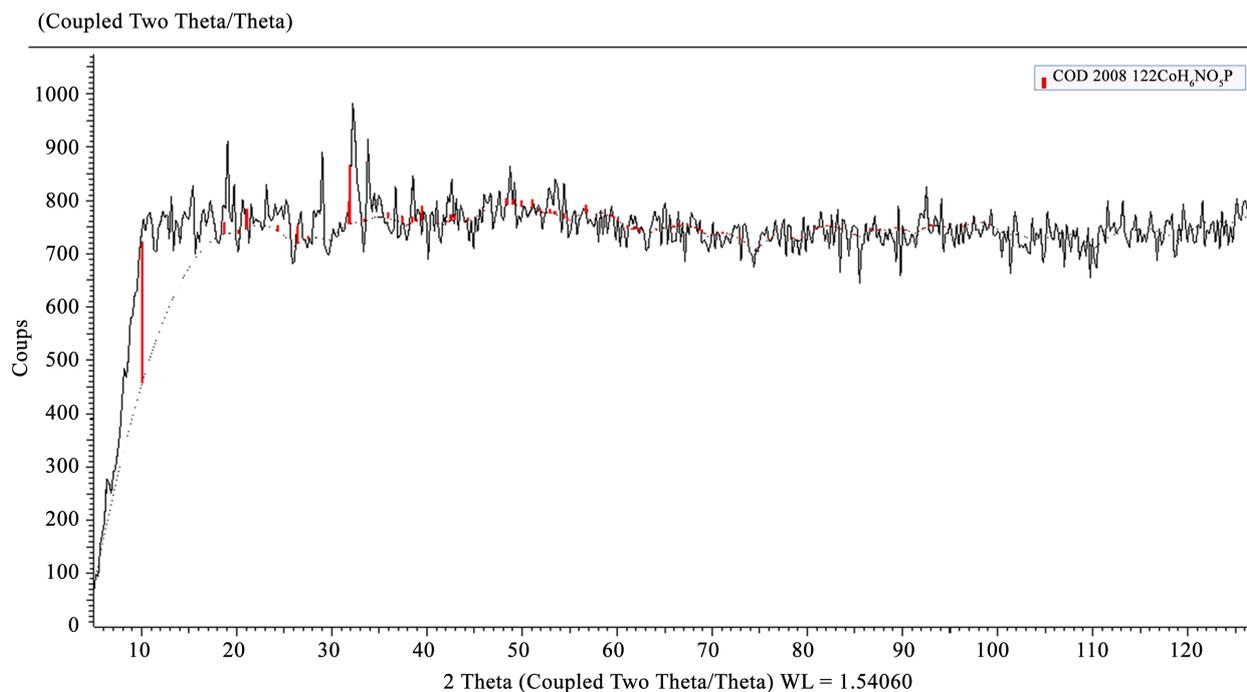


Figure 1. XRD spectrum of cobalt carbonate without surfactant.

Table 1. Full L4 Taguchi's experiment plan.

Surfactant weight [g]	Time [min]
4	10
4	20
8	10
8	20

This spectrum shows, through the absence of characteristic peaks, a low crystallization or even an absence of crystallization of the obtained cobalt carbonate; which could be assimilated to an irregular or amorphous form of cobalt carbonate. This result sufficiently proves the importance of using additives in order to control the shape of the precipitate.

2) Purity

Chemical analysis by XRF of the obtained precipitate without surfactant had yielded a cobalt content of 36.80%; which corresponds to a purity of 74.27% in cobalt carbonate.

3) Size

Due to the irregular shape of the obtained cobalt carbonate, it was almost impossible to calculate the size of the crystallites using the Laue-Scherrer formula. SEM analysis gave a cobalt carbonate crystallite size greater than 100 nm as shown by the micrograph in **Figure 2** below.

3.2. Orientation Test Using a Surfactant

An orientation test was performed with a surfactant agent in order to assess its effects on the size and the structure of the crystals.

1) Crystallization

Analysis of the obtained cobalt carbonate with surfactant gave the XRD spectrum shown above in **Figure 3** and **Figure 4**.

These figures indicate the presence of cobalt carbonate peaks. Therefore, the obtained precipitate has a crystalline structure with the specifications given by XRD's interface showing a rhombohedral crystalline system of 5.67 Å as mesh dimension.

2) Purity

Chemical analysis of the obtained cobalt carbonate in presence of a surfactant through XRF yielded a cobalt content of 44.35% (equivalent to 89.45% of CoCO_3).

From **Figure 3** and **Figure 4**, it appears that there is still 36.9% of amorphous phase and the rest being crystalline; and in the crystalline phase, there are 57.97% of CoCO_3 , 36.63% of Co_3O_4 and 5.40% of CoO . The presence of two oxides before calcination could be explained by uncontrolled conditions during drying which could have led to the start of calcination. However, the drying should imperatively be carried out in a neutral and controlled atmosphere [14].

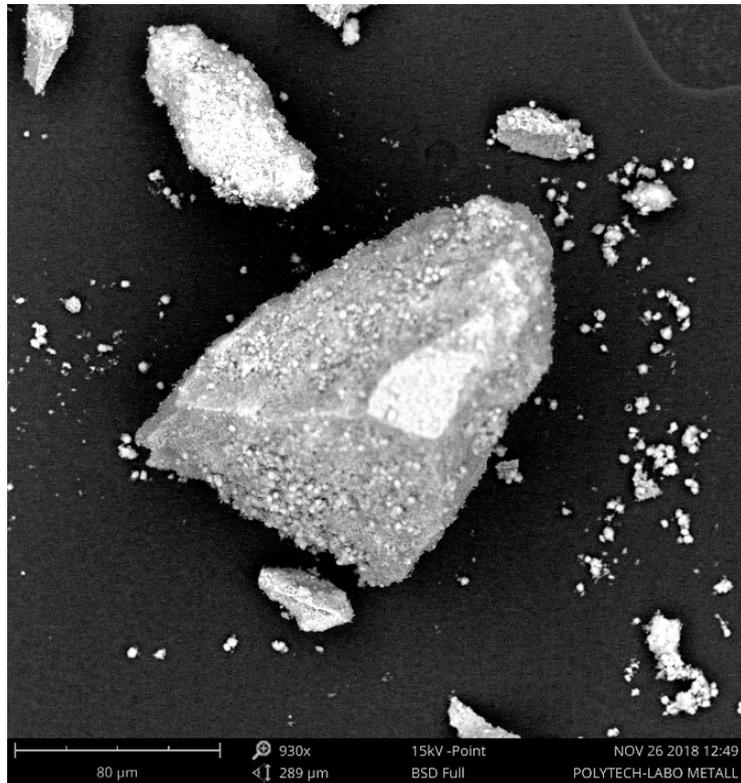


Figure 2. SEM image of cobalt carbonate without surfactant.

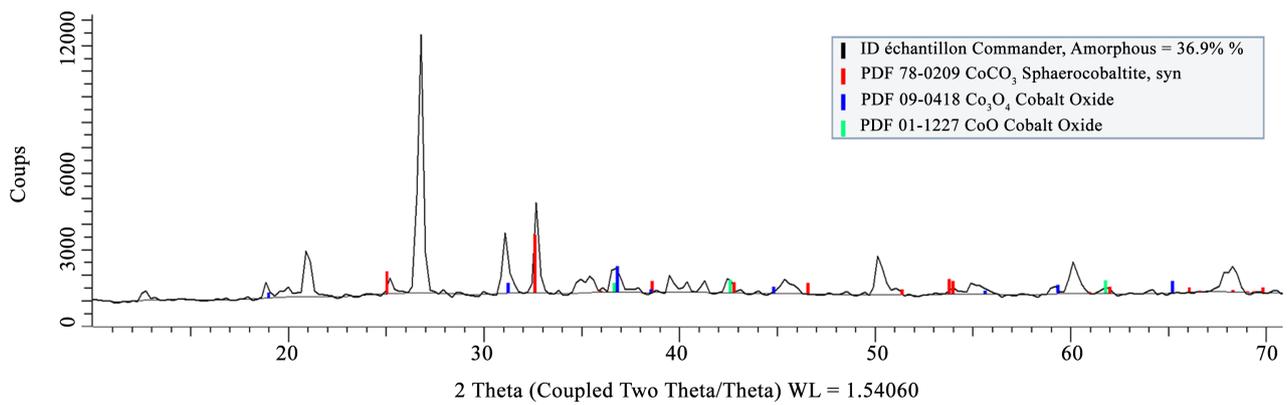


Figure 3. Cobalt carbonate Spectrum with surfactant agent using EVA.

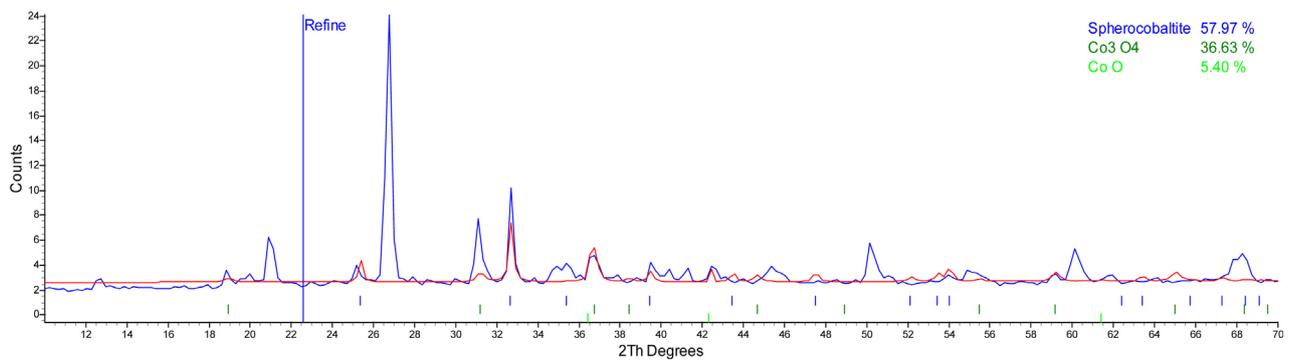


Figure 4. Cobalt carbonate Spectrum with surfactant agent by rietveld refining using Topas.

The presence of the amorphous part in the nanocrystals could be explained by the insufficient quantity of germination sites in the reaction medium. The precipitation of cobalt carbonate under normal conditions in aqueous media leads primarily to an amorphous cobalt carbonate [16] [22]-[29]; thus the surfactant added in the medium played on control of shape and structure.

3) Size

Size of the obtained cobalt carbonate crystallites by considering all characteristic peaks of cobalt carbonate is given in **Table 2** below which indicates a crystallite size of about 27.104 nm. This is a clear indication of beneficial effects of using a surfactant agent to improve crystallite size as compared to results without surfactant [30].

3.3. Influence of Surfactant's Weight and Precipitation Time on Nanocrystals

Cobalt carbonate's crystallites size and purity results obtained by varying the weight of surfactant in the solution and the precipitation time according to **Table 1**, are given in **Table 3** below.

The effects of varying these key parameters are shown on **Figure 5** below.

Under these conditions, optimal value of the crystallite size, could be predicted following the model below [11] [31]:

$$Y_{opt} = \frac{T}{N} + \left(A_i - \frac{T}{N} \right) + \left(B_j - \frac{T}{N} \right) \quad (2)$$

With:

Table 2. Carbonate cobalt nanocrystals size with surfactant.

Conditions					
-	Tube: Cu tube with 1.54184 Å	-	$10^\circ \leq 2\theta \leq 127^\circ$		
-	Detector: SSD160 (1D mode)	-	Duration per point: 3 s		
-	Voltage: 30 kV	-	Total duration: 1617 s		
-	Intensity: 10 mA	-	Rotation: 10 rpm		
Pics	Left angle [°]	Right angle [°]	2θ [°]	FWHM [°]	Size [nm]
1	27.741	25.648	25.205	0.305	29.62
2	31.998	33.359	32.684	0.267	34.43
3	41.976	42.884	42.538	0.435	21.80
4	53.542	54.222	54.003	0.301	32.97
5	61.252	62.386	61.803	0.616	16.70
		Average			27.104

Table 3. Crystallite size and purity of CoCO_3 using a surfactant.

Test	Size (nm)	Co [%]
1	15.29	45.30
2	20.21	44.35
3	1057	43.20
4	16.19	43.32

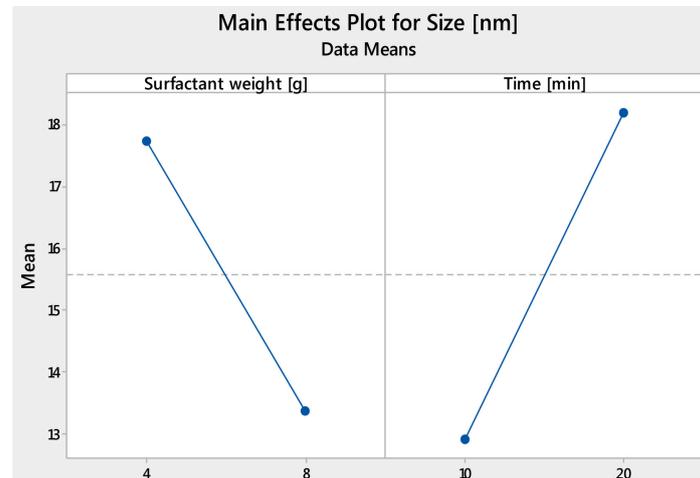


Figure 5. Influence of surfactant weight and precipitation time on crystallite size.

- Y_{opt} : the size of the crystallites at the optimal values of the parameters
- T : the sum of all the tests response
- N : the number of tests performed
- A_p , B_p : the average of tests response at the optimal value of each of the two parameters

The substitution of the aforementioned parameters in Equation (2), resulted in crystallites size estimation of about 13 nm which corresponds to a cobalt carbonate grain size reduction of 72.90% as compared to results without surfactant.

3.4. Observations

From **Figure 5**, some interpretations of the results could be given:

- The two parameters investigated through this work *i.e.*, the weight of surfactant in the medium and the reaction time are both directly proportional to the weight of the obtained precipitate. Thus, the more surfactant is added to the solution, the more cobalt carbonate precipitate will be formed; the longer the reaction time is, the more cobalt carbonate precipitate will be formed. These results could be explained by the number of germination sites present in the medium as well as by the allowed crystals' growth time. It is important to note that the presence of a large quantity of surfactant in the solution, whose role is to create heterogeneous germination sites, could facilitate a high germination rate and subsequently lead to the obtention of many nuclei whose growth in a given lapse of time influences their final weight.
- The greater the surfactant weight in the precipitation solution, the smaller the obtained crystallite size. This could be explained by one of the ideal conditions for obtaining nanoscale crystals. Indeed, Wiswanatha, R. and Sarma, D. have shown that the obtention of nanocrystals is facilitated by a very high germination rate during a very short dispersing time of period these particles; therefore the presence of an optimal amount of surfactant fulfilling both roles *i.e.*, high germination rate and short dispersing time, could be favourable to the reduction of cobalt carbonate crystals size [12] [13] [32]-[41].

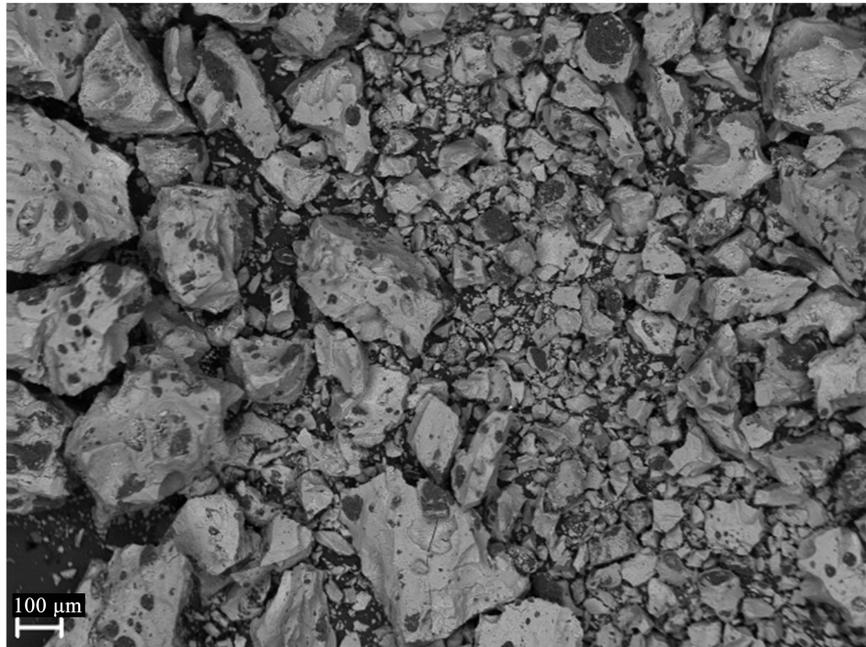


Figure 6. SEM image of the obtained cobalt carbonate nanocrystals.

- The longer the precipitation time, the larger the particles size become. This observation could be attributed to crystallite growth that occurs continuously as function of precipitation time.

Although the determination of crystallites sizes according to Equation (1) indicated nanometric dimensions of particles; SEM images showed an agglomeration of these particles (**Figure 6**) which could be associated with drying conditions. Better drying conditions can be achieved under neutral atmosphere and at a temperature below that of cobalt carbonate decomposition (181.41 °C).

4. Conclusions

Through this study, the importance of adding a microemulsion agent in order to control the structure and size of cobalt carbonate nanocrystals obtained from the reaction of a pure and rich sulphate cobalt solution (Co^{2+} : 16.80 g/l) with sodium carbonate solution (200 g/l) was demonstrated.

A systematic study was conducted by varying the weight of surfactant agent and the precipitation time in accordance with Taguchi's L4 full experimental procedure (2²). The obtained results under optimal conditions have indicated 13 nm as optimal size of cobalt carbonate nanocrystals with a cobalt content of 44.35% cobalt. However, further experiments are yet to be performed in order to eliminate the agglomeration of nanocrystals particles by optimizing drying conditions.

Conflicts of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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