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A novel liquid precipitation route to synthesize high-quality cobalt carbonate with low chloride ions concentration

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Abstract. Herein, high-quality cobalt carbonate is synthesized by employing a novel liquid phase precipitation route, where CoCl_2 and ammonium bicarbonate solutions are used as the raw material and precipitator, respectively. The morphology of primary and secondary particles and agglomeration due to their nucleation and growth are influenced by the stirring speed, reaction temperature and pH value. Furthermore, the influence of process parameters on physiochemical properties has been systematically studied by measuring apparent density, FSSS particle size, specific surface area and chloride ions concentration. Under optimal processing conditions, i.e., stirring speed of 100 rpm, pH value of 7.0-7.1 and a reaction temperature of 55°C , the as-synthesized cobalt carbonate rendered an apparent density of 0.74 g/cm^3 and chloride ions concentration of 19 ppm. The results reveal that the washing efficiency of chloride ions is affected by the morphology of primary particles and stacking mode of the secondary particle in cobalt carbonate. In general, the higher BET specific surface area of cobalt carbonate results in lower chloride ions concentration.

1. Introduction

The cobalt carbonate (CoCO_3) precursor is prepared by the precipitation method from cobalt chloride and is being widely applied in the industrial production of cobalt powder which is used as a raw material for cemented carbide, and cobalt oxide which is electrode materials for lithium-ion batteries [1-5]. Owing to the widespread industrial utilization of cobalt and cobalt oxide powders, the downstream customers demand high-quality and impurity-free cobalt carbonate precursor with desirable physical indices and morphology. For instance, the density of cobalt carbonate and the particle size of FSSS reflect the macroscopic and microscopic structure of the CoCO_3 particles, which determines the physical properties and performance of the downstream products of cobalt carbonate.

In addition, CoCO_3 might contain a variety of impurity cations and anions, which influence the product quality and may harm the industrial equipment. For instance, the commonly found chloride ions cause the corrosion reaction because of their high polarity and strong penetration. Moreover, the chloride ions easily penetrate in all kinds of passivation films, which leads to the cracking of stainless steel and harms the equipment. Furthermore, the presence of chloride ions in CoCO_3 precursor influences the quality of the end product and damages cemented carbide and Li-ion batteries [6-8]. Hence, the concentration of chloride ions in the cobalt carbonate precursor should be lower to achieve high-quality cobalt carbonate product.



It has been reported that the chloride ions are formed through two different mechanisms in cobalt carbonate. First, the chloride ions get adsorbed on cobalt carbonate crystal nucleus during the co-precipitation process. Then, the chloride ions are partially removed by water during the washing process, but a part of them is retained in CoCO_3 due to the retained chloride ions cannot contract with the washing water or the washing process reach the equilibrium state. Second, chloride ions are introduced due to the alkaline conditions in the co-precipitation process, which are caused by non-uniform local concentration. The alkaline conditions form chlorinated carbonate alkali salts precipitation of the chloride ions, which cannot be eliminated by the usual washing procedure [9]. Based on HG/T 4520-2013 industrial standard, the concentration of chloride ions in cobalt carbonate should be less than 300 ppm. However, the general enterprise standards requires that chloride ions concentration should be in the range of 100 to 200 ppm in CoCO_3 , whereas the chloride ions concentration in high-density and high FSSS cobalt carbonate should be above 300 ppm. One should note that the secondary particles of cobalt carbonate are more densely packed in high-density and high FSSS cobalt carbonate. Moreover, the adsorbed chloride ions cannot be removed by the usual washing process due to the adsorption or precipitation of chloride ions in the inner layer during the CoCO_3 precipitation. Therefore, lowering the content of chloride ions below 50 ppm in CoCO_3 is an extremely challenging task.

In general, the industrial processes of removing chloride ions include increasing the washing water amount, extending the washing time and enhancing the washing temperature. However, the washing treatment reaches the equilibrium state after removing a certain amount of chloride ions due to the adsorption and desorption of chloride ions reaches the equilibrium state. Therefore, electro dialysis and direct reduction of cobalt/chloride concentration of reactants are being widely investigated to reduce the content of chloride ions [9-11]. However, the complexity of the electro dialysis method hinders its large-scale utilization in industry. Meanwhile, the direct reduction of cobalt/chloride concentration requires an additional configuration system for cobalt chloride with low chloride ion content, which leads to poor production inefficiency and considerably increases the wastewater.

Herein, we demonstrate a liquid phase precipitation process to synthesize high-density cobalt carbonate, with low chloride ion concentration, by using high concentration cobalt chloride as a raw material. Moreover, the proposed liquid phase precipitation process exhibits promise for large-scale industrialization. Briefly, a semi-arc secondary particle agglomerate, where primary particles are spherical and agglomerate at a certain radius, is developed by controlling the primary particle nucleation and secondary particle agglomeration. The as-synthesized cobalt carbonate exhibits large specific surface area and adsorbed chloride ions on primary and secondary particles, which can be efficiently washed out and a chloride ions concentration of less than 50 ppm is obtained. In addition, the as-synthesized cobalt carbonate precursor can be reduced to upmarket cobalt powder with a spherical shape, low chloride ion concentration and low iron content due to reduce corrosion of equipment by chloride ions, which is highly desirable in high-grade cemented carbide industry.

2. Experimental procedure

2.1. Raw materials and synthesis protocol

The CoCl_2 solution was obtained from Jingmen GEM New Material Co., Ltd. China. Ammonium bicarbonate solution was prepared by using solid industrial ammonium bicarbonate, which was purchased from Sichuan Yuzhong Chemical Co., Ltd. China.

CoCO_3 was prepared by using carbonate liquid precipitation method in a 200 L reactor. A certain amount of pure water was used as the base liquid. Then 220 g/L of NH_4HCO_3 solution and 130 g/L of cobalt chloride solution were pumped into the reactor under vigorous stirring of 100 rpm. The CoCl_2 solution was added at a flow rate of 15 L/h and the pH value was controlled by altering the flow rate of NH_4HCO_3 . After 4 h, the stirring speed was reduced to 50 rpm and the reaction temperature was

raised from 55 °C to 65 °C and maintained for 4 h. Then, the reaction slurry was transferred into the centrifugal machine for solid-liquid separation. Solid cobalt carbonate was washed five times in the centrifuge by using pure waters with a liquid-to-solid ratio of 10:1 and dried at 105 °C for 10 hours to obtain cobalt carbonate powder.

2.2. Material characterization

The morphology was observed by scanning electron microscope (SEM, Quanta FEG 250). The apparent density (AD) was calculated by using FZ4-1 apparent density detector. FSSS was measured by using JS0069 Fischer particle size meter. The particle size distribution was acquired by using Mastersizer 2000E laser particle analyzer and the specific surface area was measured by using the specific surface area and porosity analyzer (Nova 4000e). The nitrogen adsorption/desorption isotherms were used to calculate the Brunauer-Emmett-Teller (BET) surface area. The chloride ion concentration was measured by turbidimetry according to HGT4519-2013 industrial standard.

3. Results and discussion

3.1. Influence of stirring speed on the physical parameters of cobalt carbonate and chloride ion

The stirring energy input in the reactor is an important parameter during the preparation of powder materials by liquid phase precipitation, which significantly influences the product quality. One should note that the the mixture in the reactor and the size of the primary particles nucleating in the solution will be uneven under the condition of low stirring rate, which lead to low collision probability of the primary particles, causing un-dense agglomeration of the secondary particles. On the other hand, if the stirring speed is too high, the particles violently collide with each other and the collision probability of the secondary particles increases, resulting in densely agglomerated secondary particles. Hence, the high-density product can be achieved by using a high stirring rate. However, the concentration of chloride ions in cobalt carbonate might increase due to the adsorbed chloride ions cannot be removed by the usual washing process because the adsorption or precipitation of chloride ions in the inner layer during the CoCO_3 precipitation. **Figure 1** and **Table 1** present the morphology and physicochemical parameters of secondary particles, prepared under stirring rates of 100 rpm and 150 rpm. At low stirring rate (100 rpm), the primary particles exhibited a spherical-like smooth surface and agglomerated in the form of a semicircle with a larger radius. On the other hand, the primary particles exhibited a sphere-like morphology and densely agglomerated into the secondary particles at a high stirring rate (150 rpm), forming a solid sphere-like aggregate. The corresponding particles exhibited an apparent density of 0.74 g/cm³ and 0.83 g/cm³ and FSSS of 2.55 μm and 2.99 μm at a stirring rate of 100 rpm and 150 rpm, respectively. The resulting solid aggregate was washed with pure water for 5 times with a liquid-to-solid ratio of 10:1. The chloride ions concentration in cobalt carbonate was found to be 19 ppm and 356 ppm at the stirring speed of 100 rpm and 150 rpm, respectively.

Because of low pH reaction condition, it is impossible for the chloride ion to precipitate into chlorinated carbonate alkali salts precipitation and the chloride ion will be adsorbed in the cobalt carbonate crystal. **Figure 1** shows that under the condition of low stirring rate (100 rpm), the outside surface of the spherical particles is exposed and makes direct contact with the pure water during the washing process. Hence, the adsorbed chloride ions can be easily removed from the as-synthesized powder. On the other hand, under the condition of high stirring rate (150 rpm), a lot of primary particles are wrapped inside the large secondary particles and the chloride ions are not removed by the usual washing process. Moreover, the as-synthesized powders, prepared under the stirring speed 100 r/min and 150 r/min, have exhibited a BET specific surface area of 100.69 m²/g and 56.21 m²/g, respectively. One should note that the higher specific surface area of cobalt carbonate, prepared under the stirring speed of 100 rpm, provides excessive contact with washing water and results in lower chloride ions concentration in cobalt carbonate.

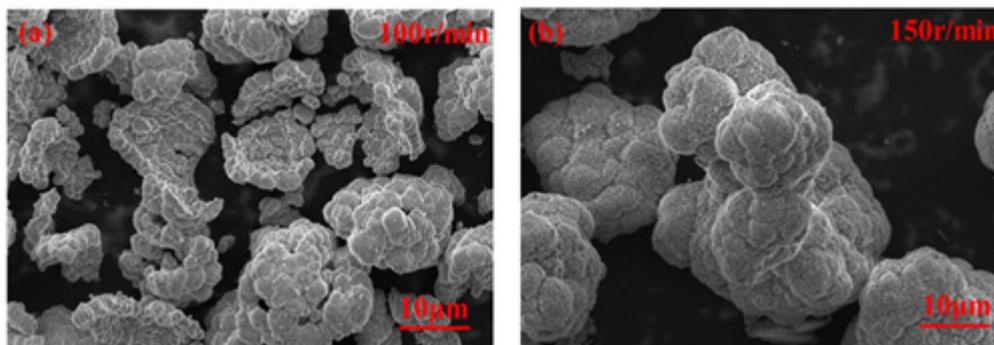


Fig. 1. SEM images of cobalt carbonate, prepared under different stirring speeds: (a) 100 rpm and (b) 150 rpm.

Table 1 Physicochemical parameters of cobalt carbonate, prepared under different stirring speeds

Serial number	Reaction temperature / °C	Stirring speed / r/min	Reaction time / h	Apparent Density / g/cm ³	FSSS / μm	BET Specific Surface Area / m ² /g	Chloride ions concentration / ppm
190103	55	100	4	0.74	2.55	100.69	19
190104	55	150	4	0.83	2.99	56.21	356

3.2. Influence of pH on physicochemical parameters of cobalt carbonate and chloride ions concentration

Furthermore, the pH value of the reaction directly influences the concentration of carbonate ions in the reaction system, and then influences nucleation and growth of the crystalline precipitation during the synthesis process [12]. Moreover, the pH value indirectly determines the physicochemical parameters of cobalt carbonate and the concentration of chloride ions. Fig. 2 shows the influence of four pH segments on the morphology. It can be readily observed that the morphologies of as-synthesized cobalt carbonate, prepared under the pH conditions of 6.9-7.0 and 7.0-7.1, are quite similar. At pH value of 6.9-7.0, the semi-arc secondary particles are formed due to the agglomeration of spherical primary particles. However, the primary particles are agglomerated in the form of closed secondary particles at a pH value of 7.1-7.2. Furthermore, pH value increased from 7.1-7.2 to 7.35-7.5 at the aging temperature of 65 °C and rod-like cobalt carbonate has been formed under the conditions of high temperature and high pH.

Moreover, the morphological changes remarkably affect the physicochemical properties of the as-synthesized cobalt carbonate. Fig. 3 reveals that the morphology of cobalt carbonate significantly influenced the apparent density, FSSS particle size, chloride ions concentration and BET specific surface area of cobalt carbonate. At pH value of 7.0-7.1, the as-synthesized cobalt carbonate exhibited maximum apparent density, highest BET specific surface area and lowest chloride ions concentration. At pH value of 6.9-7.0, the reunion of primary and secondary particles is similar to the behavior of primary and secondary particles at pH value of 7.0-7.1, where semi-arc of cobalt carbonate secondary particles is small. Some of the particles exhibited a complete particle-like morphology, which avoids the water contact and leads to a higher chloride ions concentration after the washing process. The chloride ions concentrations at pH values of 6.9-7.0 and 7.0-7.1 were 55 ppm and 19 ppm, respectively, which are far lower than other pH conditions (7.1-7.2 and 7.2-7.3). At pH value of 7.1-7.2, the serious agglomeration of secondary particles significantly decreased the BET specific surface area and washing channels for chloride ions, resulting in a higher content of chloride ions. At pH value of 7.2-7.3, the cobalt carbonate has exhibited rod-like and aggregated morphologies, hindering the

washing of chloride ions. Moreover, the chlorinated carbonate alkali salts are present under high pH conditions, which led to an extremely high chloride ions concentration of 678 ppm.

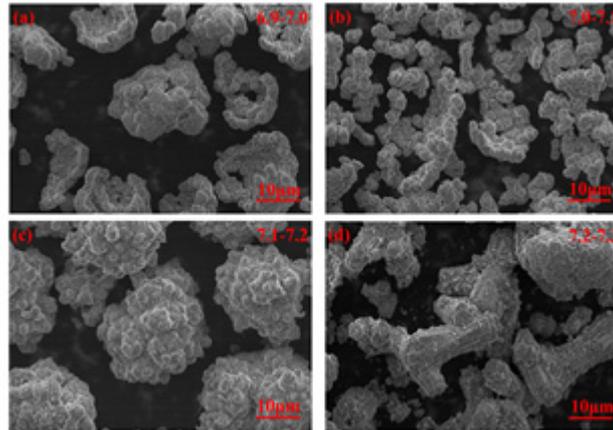


Fig. 2. SEM images of as-synthesized cobalt carbonate, prepared under different pH conditions: (a) pH = 7.0- 7.1, (b) pH = 7.0- 7.1, (c) pH = 7.1- 7.2 and (d) pH = 7.2 -7.3.

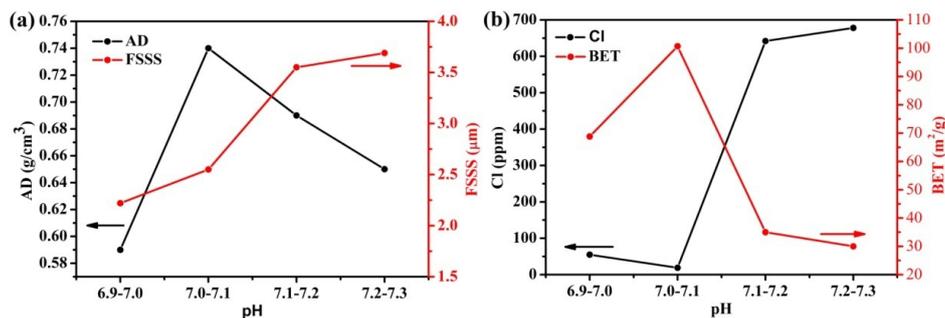


Fig. 3. Influence of pH conditions on physiochemical properties of as-synthesized cobalt carbonate: (a) apparent density and FSSS particle size and (a) chloride ion concentration and BET specific surface area.

3.3. Influence of reaction temperature on physical parameters of cobalt carbonate and chloride ions concentration

The solubility of cobalt carbonate precipitates is different under different temperature conditions. It has been reported that the temperature influences the over-saturation of the reaction system, nucleation and growth during synthesis [13]. Moreover, the morphology of primary particles and the accumulation of secondary particles of cobalt carbonate are affected by the reaction temperature, which subsequently influence the concentration of chloride ions[13]. Fig. 4 presents the SEM images of cobalt carbonated, synthesized at four different reaction temperatures (50 °C, 55 °C, 60 °C and 65 °C). The SEM observations reveal the morphological changes in primary and secondary particles due to the reaction temperature. At low temperatures (50 °C and 55 °C), the primary particles exhibit a spherical morphology and formed secondary particle of semi-arc agglomeration with a large radius. On the other hand, at high temperatures (60 °C and 65 °C), the primary particles exhibit block-like and smooth ball-like microstructure and the secondary particles have shown a hollow agglomeration. One should note that primary and secondary particles exhibited different morphologies due to the supersaturation change at different reaction temperatures. The higher temperature results in a higher degree of saturation and lower supersaturation and cause a higher degree of freedom of the cobalt

carbonate crystal growth. Therefore, the morphology of primary particles is more biased toward the structure of cobalt carbonate hexagonal cell in the horizontal or vertical direction, which led to the formation of a cube-like structure. On the contrary, the lower temperature results in higher supersaturation and accelerates growth rate of each direction. The spherical or quasi-spherical microstructure can be formed at the uniform growth rate in each direction. Moreover, the radius of agglomerated secondary particles can be related to the adsorption force between different primary particles, as well as the morphology and size of primary particles.

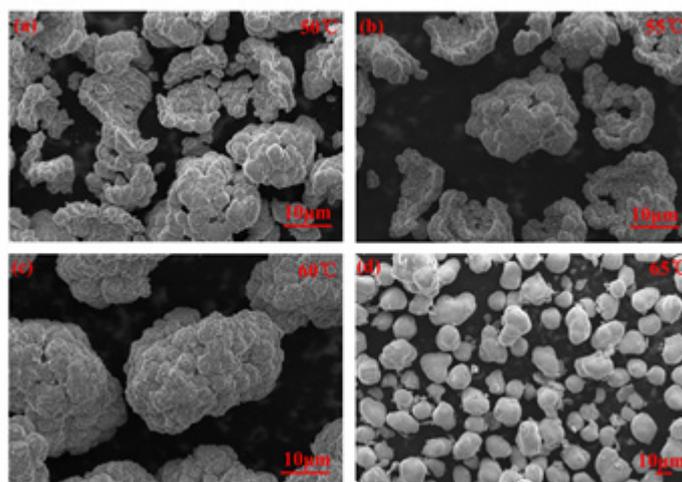


Fig. 4. SEM images of cobalt carbonate, prepared at different reaction temperatures: (a) 50 °C, (b) 55 °C, (c) 60 °C and (d) 65 °C

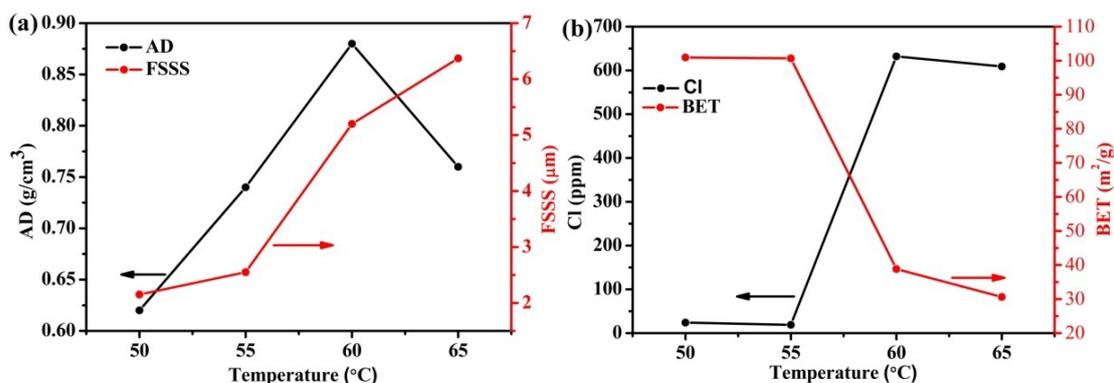


Fig. 5. Influence of reaction temperature on physiochemical properties of as-synthesized cobalt carbonate: (a) apparent density and FSSS particle size and (a) chloride ion concentration and BET specific surface area.

Fig. 5 shows that the apparent density of as-synthesized cobalt carbonate increased with increasing temperature from 50 °C to 60 °C and, then, decreased at 65 °C. Moreover, the FSSS particle size of cobalt carbonate particles increased with increasing reaction temperature due to the increase of the Secondary particle size or the smooth degree. Meanwhile, the BET specific surface area of as-synthesized cobalt carbonate decreased with increasing temperature due to the different aggregation modes of the secondary particle. However, the chloride ions concentration increased with increasing temperature due to the decrease of the BET specific surface area. One should note that the AD remained similar at the reaction temperature of 50 °C and 55 °C. However, at 60 °C, the higher radius of semi-arc secondary particles enhanced the reunion and FSSS granularity of the CoCO₃ particles. Therefore, the apparent density and FSSS particle size increased when the reaction temperature was

increased from 55 °C to 60 °C. Furthermore, at 65 °C, the hollow sphere-like secondary particles led to a decrease in AD due to the formation of a dense structure. However, FSSS continued to increase due to the increase the smooth degree of the secondary particle. On the other hand, at 50 °C and 55 °C, the primary particles of cobalt carbonate consist of globular aggregates and the secondary particles possess a semi-arc morphology. Hence, the BET specific surface area of the cobalt carbonate, prepared at 50 °C and 55 °C, was found to be 100.96 m²/g and 110.6 m²/g, respectively, which is higher than the BET specific surface area of cobalt carbonate, prepared at 60 °C and 65 °C. Furthermore, the surface adsorbed chloride ions can be easily washed due to the higher specific surface area of the cobalt carbonate, prepared at the reaction temperature of 50 °C and 55 °C, exhibited a chloride ions concentration of only 24 ppm and 19 ppm, respectively. However, at 60 °C and 65 °C, the primary particles agglomerated and formed closed spherical secondary particles, which significantly decreased the BET specific surface area to 38.83 m²/g and 12.43 m²/g, respectively, and correspondingly increased the chloride ions concentration to 632 ppm and 609 ppm.

4. Conclusions

In summary, we have demonstrated a novel liquid precipitation route to synthesize cobalt carbonate with high apparent density, large FSSS particle size and low chloride ion concentration by using a high concentration of cobalt situation. Moreover, the influence of stirring speed, pH value and reaction temperature on the morphology of the primary and secondary particles, agglomeration models and physiochemical properties has been systematically investigated. The results revealed that the chloride ions concentration in cobalt carbonate is directly influenced by the morphology of the primary particles and the agglomeration models. Conclusively, the as-synthesized cobalt carbonate exhibited the highest specific surface area (100.69m²/g) and lowest chloride ion concentration (19ppm) when the primary particles have the average diameter of 1-2 μm and the secondary agglomerated particles exhibited a semi-arc shape with a large radius.

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