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Preparation of lithium carbonate hollow spheres by spray pyrolysis

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Lithium carbonate (Li_2CO_3) hollow spheres were prepared by spray pyrolysis of lithium bicarbonate ($LiHCO_3$) in this research. The products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), crystal size distribution (CSD) analysis and BET surface area measurement. The XRD figure of the product is nearly the same as the standard pattern, indicating the product achieved by spray pyrolysis has pure Li_2CO_3 crystalline phase. The SEM images show the self-assembly hollow spheres are composed of about 200 nm primary particles. While the CSD analysis shows the macro-volume mean crystal size ranges 4-9 μm depending on the experimental conditions. The BET surface area of the product reaches 7.24 m^2/g, which is much higher than the best value reported in the literature. The product prepared in this work has great potential application prospect in the lithium-battery industry.

1 Introduction

The demand of lithium carbonate (Li_2CO_3) in batteries expanded significantly in recent years, because rechargeable lithium batteries were being used increasingly in cordless tools, portable computers, mobile phones, video cameras, electric vehicles and so on. As a result, the preparation of battery grade Li_2CO_3 has drawn great attention these years. The battery grade Li_2CO_3 has two prominent features: a high purity (≥99.9%) and a small particle size ($D_{0.5}$ < 6 μm) [1].

In the past, several technologies have been put forward to prepare high purity Li_2CO_3, such as recrystallization, precipitation, electrolysis, bicarbonation-decomposition method and so on [2]. Among the above technologies, bicarbonation-decomposition method presents a promising future owing to its low cost and high yield. The process of bicarbonation-decomposition method is described briefly below. The first step is the bicarbonation of crude Li_2CO_3 (see eq. 1), which converts the sparingly soluble Li_2CO_3 into water soluble lithium bicarbonate ($LiHCO_3$) at the room temperature. Next the bicarbonated solution is filtered to remove the insoluble solids such as aluminum silicate, iron and magnesium salts, while the dissolved impurities will be separated by ion exchange. Finally the purified $LiHCO_3$ solution is then heated to liberate carbon dioxide and precipitate Li_2CO_3 (see eq. 2).

$$Li_2CO_3 + CO_2 + H_2O \rightarrow 2LiHCO_3 \quad (1)$$

$$2LiHCO_3 \xrightarrow{\Delta} Li_2CO_3\downarrow + CO_2\uparrow + H_2O \quad (2)$$

It is clear that the decomposition of $LiHCO_3$ in solution is a coupled process of thermal decomposition of $LiHCO_3$ and reactive crystallization of Li_2CO_3. Conventionally, the above decomposition process is conducted in a stirred tank, which has been studied systematically by Sun [3]. It was found that Li_2CO_3 crystals have a serious tendency to cling together and form aggregates in the suspension, so the product prepared in a stirred tank features a wide distribution (ranging from several to hundreds of micrometers) and a large mean crystal size (about 250 μm). Thus, in order to obtain ultrafine Li_2CO_3 powders, a series of further operations are needed, including filtration, drying and crush. Though the big particles prepared in the stirred tank can be crushed by ultrasound or milling, it is difficult to minimize the volume mean crystal size less than 10 μm.

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Spray pyrolysis is a versatile technique regarding the synthesis of various materials in a wide range of composition, size and morphology [4-9]. However, it has not been applied in the decomposition process of $LiHCO_3$ yet. Therefore, the objective of this study is to explore the feasibility of spray pyrolysis in the preparation of battery-grade Li_2CO_3 crystals using the purified $LiHCO_3$ solution as the precursor, which integrates the decomposition, crystallization, drying and crystal shape control into just one step. Additionally, another intention of this paper is to preliminarily investigate the impacts of operational conditions on the crystal shape and crystal size, so as to provide basic data for the further optimization and industrial scale up.

2 Experimental

Set up As should be noted that $LiHCO_3$ only exist in the form of solution. The $LiHCO_3$ solution used in this study was bicarbonated from Li_2CO_3 crystals (99.99%, Shanghai Zhongli Co., Ltd.), high purity CO_2 gas (99.95%, Shanghai Central Industrial Gas Co., Ltd.) and deionized water.

Two laboratory scale spray driers were used in this research. The first one is SY-6000 (Shanghai SY-Bio equipment Co., Ltd., China), and its droplet generation is carried out by a two-fluid nozzle. While the second one is Nano Spray Dryer B-90 (Buchi, Co., Ltd., Swiss), its droplet generation is based on a piezoelectric driven actuator.

Figure 1a shows the schematic diagram of SY-6000. Introduced by a peristaltic pump, the $LiHCO_3$ solution contacted with the compressed air in the 0.7 mm two-fluid nozzle to generate numerous droplets, and then the droplets were rapidly heated in the drying chamber. With the increase of temperature and the evaporation of water, $LiHCO_3$ decomposed and formed Li_2CO_3 crystals. Li_2CO_3 crystals were collected from the carrier gas using a cyclone separator, while the carrier gas (exhaust) was expelled from the system.

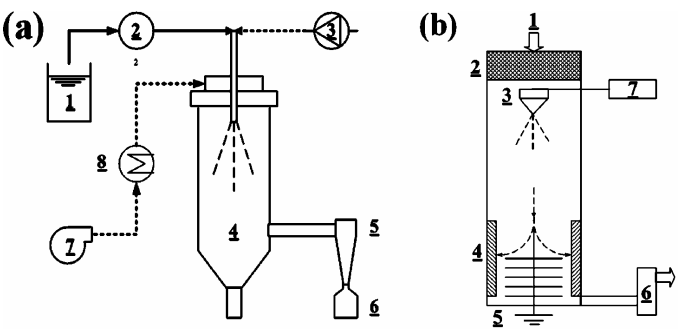

Fig 1 Experimental set up. (a) Micro spray drier SY-6000: 1-sample solution; 2-peristaltic pump;3-compressed air; 4-drying chamber; 5- cyclone separator ; 6-product collector; 7-blower; 8-heater. (b) Nano Spray Dryer B-90: 1-drying gas; 2- heater; 3-spray head; 4-collecting electrode; 5-grounded electrode; 6-filter; 7- sample solution.

Figure 1b shows the schematic diagram of Nano Spray Dryer B-90, which is a newly developed equipment by Buchi, Co., Ltd.. Compared with SY-6000, Nano Spray Dryer B-90 has two main distinctions, namely the piezoelectric atomizing technology and the electrostatic particle collector. To illustrate it, the droplet generation mechanism of Nano Spray Dryer B-90 is based on a piezoelectric driven actuator, vibrating a thin, perforated, stainless steel membrane in a small spray cap. The membrane (spray mesh) features an array of precise micron-sized holes (4 μm). The actuator is driven at an ultrasonic frequency, causing the membrane to vibrate, ejecting millions of precisely sized droplets every second with very narrow droplet size distribution. The novel electrostatic particle collector helps to achieve a high yield of fine particles. The Nano Spray Dryer B-90 is particularly suited to the preparation of ultrafine powders.

The Li_2CO_3 particles were characterized by X-ray diffraction (D/MAX 2550 VB/PC, Rigaku, Japan), scanning electron microscope (JSM-6701, JEOL, Japan), crystal size distribution analysis (Mastersizer 2000, Malvren, UK) and BET surface area measurement (TriStar 3000, Micromeritics, US).

3 Results and discussion

XRD identification The crystalline phase of Li_2CO_3 products were identified using powder X-ray diffraction. An example of the XRD patterns is shown in figure 2, which was produced by SY-6000 (the operational conditions are follows: C_0=0.65 mol/L, u=800 ml/h, P= 4 bar, T_{in}=160 °C, Q=30 m^3/h). It was found that all the XRD figures of the samples, no matter prepared by SY-6000 or by Nano Spray Dryer B-90,

present very good agreement with the standard XRD pattern of Li_2CO_3 (JCPDS 22-1141). No impurity peak was observed, indicating the spray decomposition method can achieve pure Li_2CO_3 crystalline.

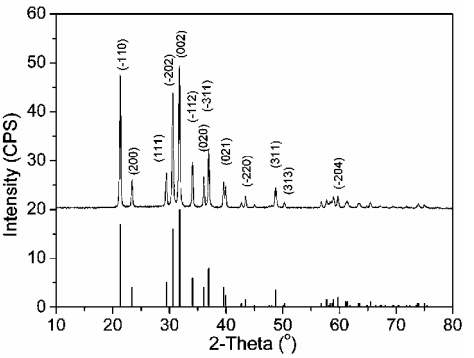

Fig 2 XRD identification.

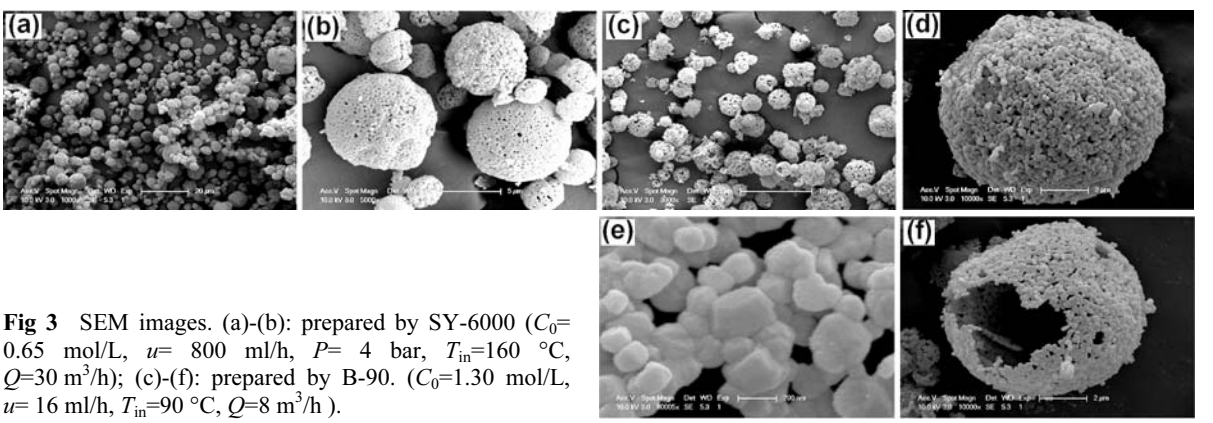

Fig 3 SEM images. (a)-(b): prepared by SY-6000 (C_0= 0.65 mol/L, u= 800 ml/h, P= 4 bar, T_{in}=160 °C, Q=30 m^3/h); (c)-(f): prepared by B-90. (C_0=1.30 mol/L, u= 16 ml/h, T_{in}=90 °C, Q=8 m^3/h).

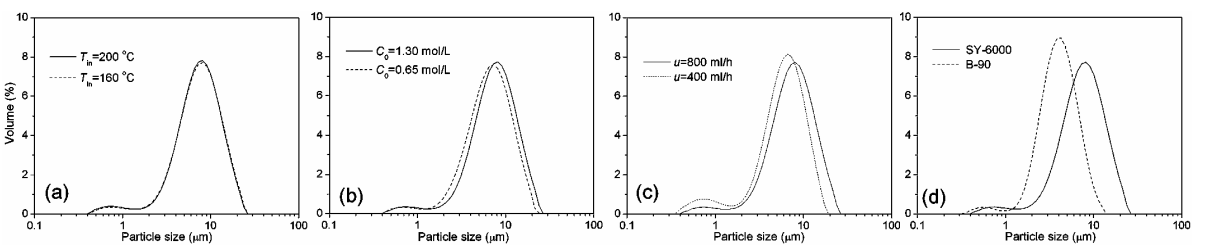

Fig 4 Crystal size distribution. (a): prepared by SY-6000, (C_0=1.30 mol/L, u= 800 ml/h, P=4 bar, Q=30 m^3/h); (b): prepared by SY-6000, (T_{in}=160 °C, u= 800 ml/h, P=4 bar, Q=30 m^3/h); (c): prepared by SY-6000, (T_{in}=160 °C, C_0=1.30 mol/L, P=4 bar, Q=30 m^3/h); (d) CSD comparison between products prepared by SY-6000 (C_0=1.30 mol/L, T_{in}=160 °C, u=800 ml/h, P=4 bar, Q=30 m^3/h) and B-90 (C_0=1.30 mol/L, u= 16 ml/h, T_{in}=90 °C, Q=8 m^3/h).

Morphology observation Figure 3 gives the typical SEM images. It is obvious that the micron Li_2CO_3 particles are porous hollow spheres (see figure 3a-e), which consist of many sub-structure crystals. From the local enlarged image figure 3e, we can see the mean particle diameter of the sub-structure crystals is approximately 200 nm. The formation mechanism of the porous hollow spheres can be explained briefly below. After the $LiHCO_3$ droplets are ejaculated into the drying chamber, they would be heated rapidly. When the droplets temperature reaches the decomposition degree of $LiHCO_3$, the $LiHCO_3$ decomposes and Li_2CO_3 crystals precipitate. Due to the continuous pyrolysis of $LiHCO_3$ and the evaporation of water, the CO_2 gas and the water evaporation act as the blowing agents to create the hollow solid shell, because the gas bubbles within the droplets have a relatively high inner pressure [10]. The pores dotted in the solid shell are the gas flow channels. If the inner bubbles drastically expand, the solid shell would be destroyed by the fast emission of the inner pressure (see figure 3f).

Crystal size distribution analysis The CSD figures are shown in figure 4, which clearly show that all the products feature a very small volume mean crystal size and a very narrow distribution. All the size distributions

are bimodal, the right one corresponds to the mass hollow spheres, and the left one corresponds to the very small agglomerates as well as few individual particles.

Figure 4a shows that as the temperature goes up from 160 to 200 °C with other operating parameters kept as constants, the CSD has nearly no change, suggesting the crystal size has little relation with the drying temperature. This result implies that if the heat flow is already enough to pyrolyze the $LiHCO_3$ and dry the Li_2CO_3 crystals, it is no use to improve the CSD by further enhancing the drying temperature.

As can be seen in figure 4b, with the $LiHCO_3$ concentration drops from 1.3 to 0.65 mol/L, the volume mean crystal size decreases from 8.36 to 7.38 μm, indicating a lower $LiHCO_3$ concentration leads to a smaller crystal size. Two reasons may account for this result. Firstly, during the drying stage, the expansion of a droplet with a lower $LiHCO_3$ concentration is weak than that with a higher $LiHCO_3$ concentration. Secondly, the droplet with a lower $LiHCO_3$ concentration always precipitate less Li_2CO_3 crystals and then form a relatively small solid shell.

Figure 4c shows that the decrease of the feeding rate also reduces the particle's size. This is because with the lower liquid feeding rate, the nozzle can atomize smaller droplets. As is known, the particle size of spray drying product is directly decided by the droplet size, so a smaller droplet must form a smaller particle.

As is known, the droplets size is the decisive factor influencing the product size. Generally, the droplets atomized by the two-fluid nozzle are larger than 5 μm, while most of the droplets generated by the piezoelectric atomizer that equipped in the Nano Spray Dryer B-90 can be less than 8 μm (the 4.0 μm hole size spray cap was used in this work). It is clearly shown in figure 4d that the volume mean crystal size of powders prepared by Nano Spray Dryer B-90 is 4.00 μm, which is about a half of that prepared by SY-6000.

BET surface area measurement Owing to the numerous submicron crystals and the stable hollow spheres, the Li_2CO_3 product prepared by spray decomposition boasts a very high surface area. For example, the BET surface area of powders prepared by SY-6000 (C_0=0.65mol/L, u=800 ml/h, P=4 bar, T_{in}=160 °C, Q=30 m^3/h) reaches 7.24 m^2/g. However, to the best of the authors' knowledge, the best value has been reported of ultrafine Li_2CO_3 powders is 2.79 m^2/g [11], which was produced by reactive crystallization of LiOH and CO_2.

4 Conclusion

Two laboratory scale spray driers, a two-fluid nozzle one and an ultrasonic one, were used in this work to prepare ultrafine powders of Li_2CO_3. The results show spray pyrolisis is a simple and effective method for synthesizing battery-grade Li_2CO_3 crystals. The XRD figure of the product is almost the same as the standard XRD pattern, indicating the spray decomposition method can achieve authentic Li_2CO_3 crystals. The SEM images show the self-assembly hollow spheres are composed of about 200 nm primary particles. The CSD analysis shows the macro-volume mean crystal size of the hollow spheres ranges 4-9 μm. The resulting size of agglomerates depends both on size of individual droplet diameters and agglomeration efficiency in the defined hydrodynamic process conditions. The BET surface area of the product reaches 7.24 m^2/g, which is much higher than the best value reported in the literature. The product prepared in this work has great potential application prospect in the lithium-battery industry.

Nomenclature

C concentration, $mol \cdot L^{-1}$
P compressed air pressure, bar
Q flow rate of drying gas, $L \cdot h^{-1}$
T_{in} temperature of drying gas in the inlet, °C
u feeding rate of $LiHCO_3$, $ml \cdot h^{-1}$

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References

[1] Chinese national standard: battery grade lithium carbonate, YS/T 582-2006.
[2] Z. F. Dai, X. L.Xiao, F. Q. Li, and P. H. Ma, J. Salt Lake Res. **13**, 53 (2005).

[3] Y. Z. Sun, PhD Thesis (East China University of Science and Technology, Shanghai, China, 2010).
[4] S. Che, O. Sakurai, K. Shinnozaki, and N.Mizutani, J. Aerosol Sci. **3**, 271 (1998).
[5] T. Ogiharal, H. Aikiyol, N. Ogatal, K. Katayama, Y. Azuma, H. Okabe, and T. Okawa, Advanced Powder Technol. **13**, 437 (2003).
[6] S. Y. Yang and S. G. Kim, Powder Technol. **146**, 185 (2004).
[7] I. Taniguchi, Ind. Eng. Chem. Res. **44**, 6560 (2005).
[8] M. Eslamian and N. Ashgriz, Powder Technol. **167**, 149 (2006).
[9] S. Gurmen, S. Stopic, and B. Friedrich, Mat. Res. Bull. **41**, 1882 (2006).
[10] J. Phillips, C. C. Luhrs, and P. Fanson, Langmuir **23**, 7055 (2007).
[11] N. Du and G. S. Zhou, Chinese Patent: CN 101209846A.