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Mechanochemistry synthesis of high purity lithium carbonate

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Abstract−A technique for preparing high purity Li_2CO_3 powders has been developed through mechanochemical process coupled with the dissolution-filtration process. The first step as mechanochemical reaction of both Na_2CO_3 and LiCl mixtures was designed to obtain the primary Li_2CO_3 powders using a ball mill. The second step as the dissolution-filtration process was performed to obtain high purity Li_2CO_3 powders. Experimental results indicate that the three parameters of milling time, rotation speed, and ball-to-sample mass ratio can closely relate with purity of primary Li_2CO_3 powders. The XRD patterns of primary Li_2CO_3 powders indicate that mechanochemical reaction of both Na_2CO_3 and LiCl can be completed in 15 min under optimal conditions at rotation speed as 600 rpm, ball-to-sample mass ratio as 5/1, and molar ratio of Na_2CO_3 to LiCl as 1/2. The target products of Li_2CO_3 powders contain impurity of Na^+ less than 0.1 mass% with the minimum values as 0.073 mass%. Two shapes of massive particles and smaller grains less than 1 μm in nano scale can be observed in the target products of Li_2CO_3 powders.

Keywords: Synthesis, Mechanochemical Reaction, High Purity Lithium Carbonate, Lithium Chloride (LiCl), Sodium Carbonate (Na_2CO_3)

INTRODUCTION

Lithium and the lithium-containing compounds are usually extracted in large-scale from salt lake brines [1-3] due to production expense and purity compared with from lithium mines. Lithium carbonate (Li_2CO_3) in white, hygroscopic powders [4] is one of the main products from salt lake brines. The purity of Li_2CO_3 powders can largely affect the application fields. Low purity Li_2CO_3 powders ($Li_2CO_3 \leq 99.0$ mass%) can be used in many different industries such as ceramics and porcelain glazes, varnishes, dyes, pharmaceuticals and so on [5]. High purity Li_2CO_3 powders ($Li_2CO_3 > 99.0$ mass%) are the key material for production of photoelectric crystals such as $LiNbO_3$ and $LiTaO_3$, high purity lithium metal, battery industries and so on [6-8]. With the rapid development of battery industries, the short supply of high purity Li_2CO_3 powders [6,9] as the starting material has seriously affected the large-scale production of lithium batteries. The statistic results [10] showed the annual expansion rate of lithium battery industries was about 20% in the last few years. Meanwhile, the wide application of lithium batteries in the upcoming electric and hybrid vehicles will also greatly increase the demand for lithium-containing compounds. Therefore, producing high purity Li_2CO_3 powders has become one of the inevitable challenges from the viewpoint of market supplement.

The key reaction for producing low purity Li_2CO_3 powders takes place in solution containing lithium species and carbonate reagents including sodium carbonate (Na_2CO_3) or ammonium carbonate ($(NH_4)_2CO_3$) or carbon dioxide (CO_2), regardless of the raw materials from lithium mine or salt lake brines. The widely applied process by solution reaction with lithium-rich brine as LiCl(aq.) and Na_2CO_3 can be described as

$$2LiCl(aq.)+Na_2CO_3(aq.)=Li_2CO_3(\downarrow)+2NaCl(aq.) \qquad (1)$$

However, tremendous industrial experience and laboratory scale experiments indicate that the synthesis reaction of Li_2CO_3 powders in Eq. (1) should be operated at a temperature of about 90 °C. In addition, the yield of Li_2CO_3 powders in Eq. (1) is lower than about 70%; meanwhile the impurity content mainly as sodium ion (Na^+) is also higher than the criterion of high purity requirements after repeated washing. Thus, there are three disadvantages as the higher reaction temperature, lower yield and greater impurity content of Na^+ in the solution reaction processes.

Actually, high purity Li_2CO_3 powders are always extracted from the crude ones with low purity at the aim of decreasing the production expense. Brown et al. [11,12] proposed a primary purification process for preparing high purity Li_2CO_3 powders in the 1970s. Up to now, the carbonation-decomposition process [6] has been considered as the most promising process for preparing high purity Li_2CO_3 powders due to its low cost, high efficiency, and small pollution emissions. However, mechanochemistry [13-17] as a branch of chemistry has attracted much attention on chemical and physico-chemical transformations of substances including ceramic, alloy, organic and inorganic synthesis [18]. Compared with the wet chemical process in Eq. (1), the mechanochemical process with high energy input is an environment-friendly and efficient technology because of the absence of solution. To the knowledge of the present authors,

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no relevant reports are available on the mechanochemical milling synthesis of high purity Li_2CO_3 powders.

According to the basic principles of mechanochemistry, high purity Li_2CO_3 powders are synthesized by a mechanochemical milling method using Na_2CO_3 and LiCl mixtures as raw materials. To further improve the purity of primary Li_2CO_3 powders from mechanochemical process, the dissolution-filtration process was applied according to the solubility difference of Li_2CO_3 and sodium chloride (NaCl). The influences of the main operation parameters of mechanochemical milling on the purity of Li_2CO_3 powders were experimentally investigated. Furthermore, the basic morphological properties of target product as Li_2CO_3 powders were also characterized. The results indicate that mechanochemical milling process coupled with the dissolution-filtration process can be applied to prepare high purity Li_2CO_3 powders.

EXPERIMENTAL

1. Raw Materials

The reagent grade reagents of both LiCl (95.0 mass%) and Na_2CO_3 (99.8 mass%) were used as raw materials for preparing Li_2CO_3 powders through mechanochemical dry milling. The intended products of Li_2CO_3 powders were obtained by distillation using deionized water. Note that reagent grade LiCl powders should be heated at 105 °C for at least 3 hr to remove moisture due to their high moisture absorptivity.

2. Synthetic Procedures

The proposed flow chart of the synthetic procedure is illustrated in Fig. 1. There are two steps as mechanochemical reaction of Na_2CO_3 and LiCl powders by dry milling as well as the removal of soluble products from primary purity Li_2CO_3 powders by deionized water. The reaction was carried out in a planetary type ball mill (Fritsch, Pulverisette 7 plus model, Germany) with an 80 ml ZrO_2 milling chamber. Meanwhile, ceramic balls of ZrO_2 in 5 mm diameter were applied as the grinding balls in this study for milling. During the process of mechanochemical dry milling, the rotation program was set to have a pause of 5 min for preventing temperature rise in the mill.

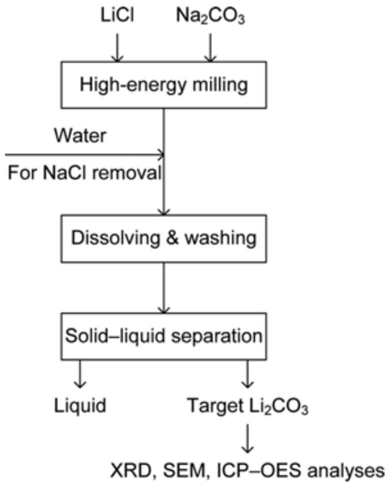

Fig. 1. Flow sheet of mechanochemical reaction between Na_2CO_3 and LiCl.

The dissolution-filtration operation is the other step for separating primary purity Li_2CO_3 powders owing to large discrepancy of solubility in aqueous solution of reactants and products. The reactants of both Na_2CO_3 and LiCl and one of the products as NaCl can be easily dissolved in water while the intended products as Li_2CO_3 have a small dissolution in water. Therefore, the filtering operation was adopted to separate primary products from mechanochemical reaction for obtaining high purity Li_2CO_3 powders. The experimental results indicate that one-time washing is enough to obtain high purity Li_2CO_3 powders.

Four series of experiments were conducted to clarify the effects of milling time, rotation speed, ball-to-sample mass ratio, and molar ratio of the two reactants.

3. Characterization of Primary and Target Products of Li_2CO_3 Powders

XRD analyses (X'Pert PRO MPD, PANalytical B. V., Netherlands) were performed of products using Cu Kα radiation over a range of 10-90° as 2θ, using a step interval of 0.01708° and 3 s count time per step. The XRD patterns of products were identified by comparing with the measured patterns of the samples to the JCPDS data cards. The X-ray powder diffraction patterns of products were used to determine the reaction extent. When the X-ray powder diffraction patterns of both reactants in primary products disappear, the reaction is thought finished completely.

The ICP-OES (Perkin Elmer, Optima 8000, USA) was used to determine the content of Na^+ impurity in target products as Li_2CO_3 powders after one-time water washing. The target products of Li_2CO_3 powders were dissolved by sulfuric acid (H_2SO_4) and then the solutions were detected.

Field emission scanning electron microscopy (FE-SEM, 30 kV-137 eV, JSM-7001F+INCA, X-MAX, Japan, UK) was used to examine the morphology of both primary and target products. The primary or target products were adhered to a side of carbon tape to observe the surface morphology. The transmission electron microscope (TEM, 200 kV, JEM-2100F, Japan) was used to observe the microstructures or morphology of the one-time water washing products. And the laser particle size analyzer (Beckman, LS13320, USA) was used to determine the size distribution of both primary and target products.

RESULTS AND DISCUSSION

The developed technique of preparing high purity Li_2CO_3 powders contains two steps as mechanochemical process as well as the dissolution-filtration process. The effects of related four parameters including milling time, rotation speed, ball-to-sample mass ratio, and molar ratio of the reactants on purity of primary Li_2CO_3 powders were experimentally investigated. After that, the characterizations of primary Li_2CO_3 powders as well as the aimed product as high purity Li_2CO_3 powders through the dissolution-filtration process were also experimentally detected through aforementioned various analysis techniques.

1. Mechanochemical Dry Milling Process

1-1. Effect of Dry Milling Time

Comparison of the XRD patterns from the primary products

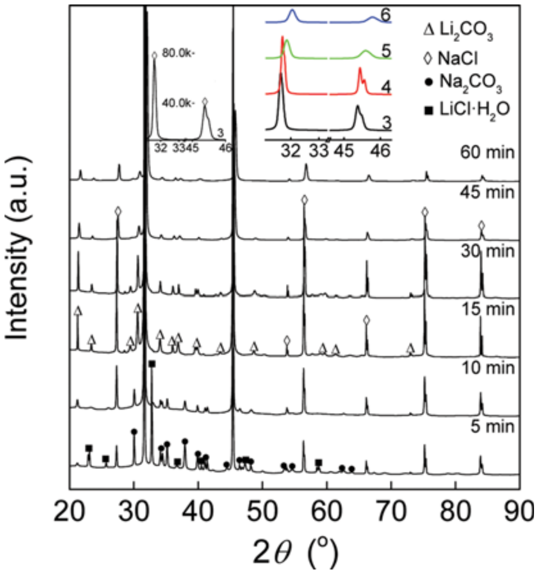

Fig. 2. Comparison of XRD patterns for mechanochemical reaction products from Na_2CO_3 and LiCl as reactants at six reaction times as 5 min, 10 min, 15 min, 30 min, 45 min, and 60 min.

obtained after 5, 10, 15, 30, 45 and 60 min of mechanochemical dry milling is shown in Fig. 2. The other parameters of milling were controlled at rotation speed as 600 rpm, ball-to-sample mass ratio, *i.e.*, m_{ball}/m_{sample}, as 5/1, and molar ratio of Na_2CO_3 to LiCl, *i.e.*, $n_{Na_2CO_3}/n_{LiCl}$, as 1/2.

The XRD patterns in Fig. 2 and in other figures in the following text, four peaks of Na_2CO_3 (JCPDS No. 72-0628), $LiCl{\cdot}H_2O$ (JCPDS No. 73-1273), Li_2CO_3 (JCPDS No. 72-1216), and NaCl (JCPDS No. 77-2064) are observed. The peak of $LiCl{\cdot}H_2O$ can be detected because of high moisture absorptivity of LiCl which induces LiCl quickly converts into $LiCl{\cdot}H_2O$ during testing.

It can be deduced from Fig. 2 that 1) the mechanochemical reaction between Na_2CO_3 and LiCl starts in 5 min in the mill, which is confirmed by the peaks of Li_2CO_3 and NaCl as mechanochemical reaction products after 5 min milling; 2) the peaks of both Li_2CO_3 and NaCl as products are strengthened after 10 min milling accompanied with weak of the peaks of both Na_2CO_3 and LiCl as reactants; and 3) the XRD patterns of primary products after 15 min milling cannot be sought any peaks of both Na_2CO_3 and LiCl. This implies that the reactants of both Na_2CO_3 and LiCl have been completely converted into Li_2CO_3 and NaCl in 15 min.

Further increasing the milling time beyond 15 min had few effects on conversion of mechanochemical reaction. However, all peaks of both Li_2CO_3 and NaCl became broader but weaker in intensity. This can be attributed to the amorphous transformation of both Li_2CO_3 and NaCl as products and their lattice distortion with prolonging milling time. In addition, the peaks of both Li_2CO_3 and NaCl show slightly shifted as shown in the enlarged sub-figures in Fig. 2. The lowest intensity of peaks of both Li_2CO_3 and NaCl was observed after milling 60 min as illustrated in Fig. 2. Thus, it can be deduced that 15 min dry milling is enough to complete the mechanochemical reaction. So, the optimal dry milling time was set as 15 min in the next two series of experiments.

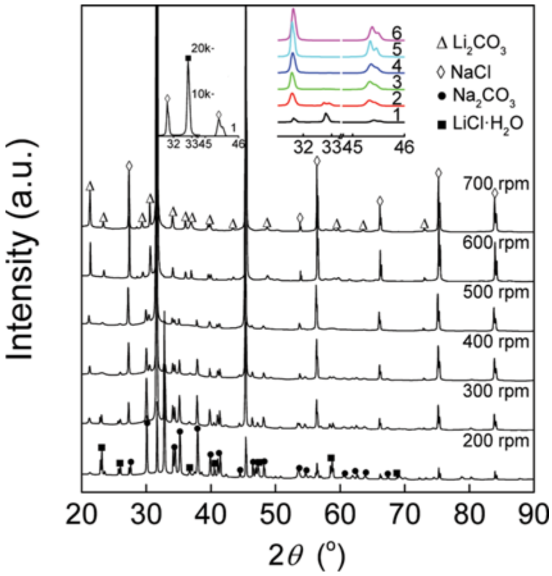

Fig. 3. Comparison of XRD patterns for mechanochemical reaction products from Na_2CO_3 and LiCl as reactants at six rotation speeds as 200 rpm, 300 rpm, 400 rpm, 500 rpm, 600 rpm, and 700 rpm.

1-2. Effect of Rotation Speed

The rotation speed is an important parameter for the mechanochemical dry milling process. A group of experiments over a range from 200 rpm to 700 rpm were carried out to determine the reasonable rotation speed. As shown in Fig. 3, the peaks of both reactants of Na_2CO_3 and LiCl cannot be detected at the rotation speed greater than 600 rpm. Increasing the rotation speed from 200 rpm to 600 rpm can result in weaker intensity of peaks of both reactants, corresponding to stronger intensity of peaks of both products of Li_2CO_3 and NaCl. This finding is to some degree consistent with the conclusion by Pourghahramani and Forsberg [19] that stress energy in the grinding process directly related to the rotation speed can promote the mechanochemical reaction within the specific limits. However, too much higher rotation speed cannot effectively promote the conversion of mechanochemical reaction in this study.

1-3. Effect of Ball-to-sample Mass Ratio

The effect of ball-to-sample mass ratio, *i.e.*, m_{ball}/m_{sample}, on the XRD patterns for mechanochemical reaction between Na_2CO_3 and LiCl is displayed in Fig. 4. The intensity of peaks of both reactants of Na_2CO_3 and LiCl decreases gradually until vanishing under the condition of the ball-to-sample mass ratio greater than 5/1, corresponding to the intensity of peaks of both products of Li_2CO_3 and NaCl improved in all cases. The grinding balls have significant effects on the mechanochemical reaction as summarized in two aspects: 1) grinding balls as the medium to transfer energy for crossing over the reaction energy barrier; 2) the surfaces of grinding balls are considered as main positions for mechanochemical reaction. Sufficient balls can make the reaction proceed further. However, a ball-to-sample mass ratio greater than 5/1 cannot show obvious promotion effect. Hence, the optimal value of the ball-to-sample mass ratio is recommended as 5/1 in this study.

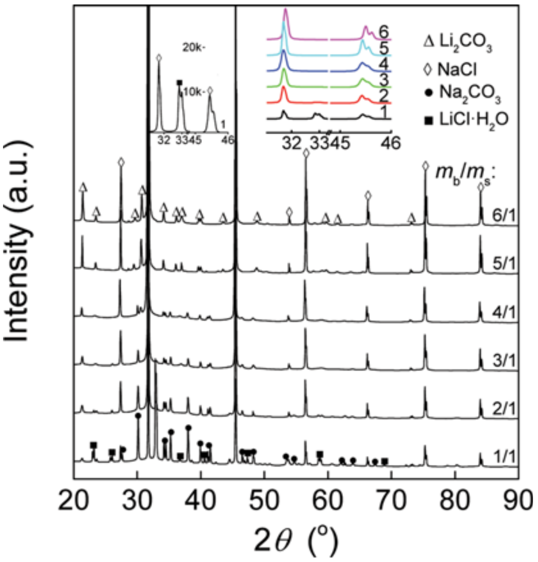

Fig. 4. Comparison of XRD patterns for mechanochemical reaction products from Na_2CO_3 and LiCl as reactants at six ball-to-sample mass ratios as 1/1, 2/1, 3/1, 4/1, 5/1, and 6/1.

1-4. Effect of Molar Ratio of Na_2CO_3 to LiCl

To clarify the effect of the molar ratio of Na_2CO_3 to LiCl, *i.e.*, $n_{Na_2CO_3}/n_{LiCl}$, from 1/2 to 2/2 on the mechanochemical reaction between Na_2CO_3 and LiCl, the operation parameters were set at milling time as 5 min, rotation speed as 600 rpm, and the ball-to-sample mass ratio as 5/1. It can be observed in Fig. 5 that increasing the molar ratio of Na_2CO_3 to LiCl from 1/2 to 1.4/2 can lead to a decreasing tendency of the peaks of $LiCl·H_2O$. It is confirmed that greater stoichiometric mass of Na_2CO_3 is slightly beneficial to the mechanochemical reaction via increasing the probability of collision between Na_2CO_3 and LiCl.

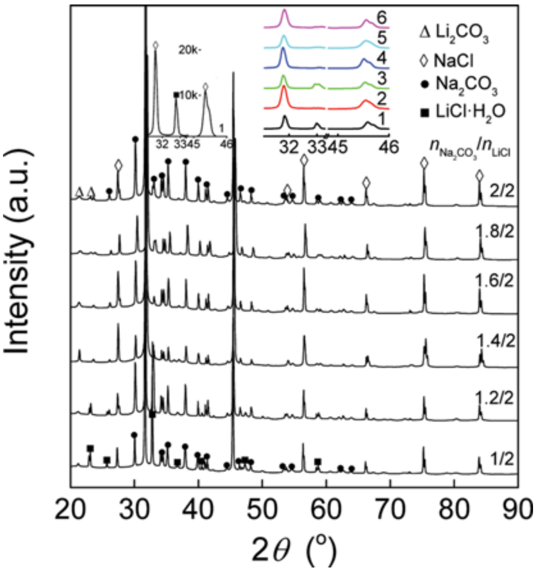

Fig. 5. Comparison of XRD patterns for mechanochemical reaction products at six mole ratios of Na_2CO_3 to LiCl as 1/2, 1.2/2, 1.4/2, 1.6/2, 1.8/2, and 2/2.

Further increasing the molar ratio of Na_2CO_3 to LiCl cannot cause a promotion trend of the mechanochemical reaction. In this study, the optimal molar ratio of Na_2CO_3 to LiCl was chosen at 1/2, which can effectively avoid bringing in unnecessary impurity from Na_2CO_3.

1-5. Morphology and Particle Size Distribution of Primary Products

Scanning electron microscopy (SEM) was employed to study the morphology of primary products from mechanochemical process at different milling times as shown in Fig. 6. The mechanochemical reaction between Na_2CO_3 and LiCl can form a mixture of large agglomerates much larger than 1 μm encapsulating plenty of finer grains in nanoscale at 5 min as shown in Fig. 6(a). Clearly, the fine grains in nanoscale are embedded in the pulpy mixture which is continuous without distinct boundaries. High moisture absorptivity of LiCl as one of reactants is the main reason for formation of pulpy mixture.

Many ordered grains in smaller size can be formed at 10 min as displayed in Fig. 6(b). This result can be explained as that prolonging milling time can effectively decrease the amount of reactant as LiCl. Prolonging the milling time to 15 min can result in the formation of larger and better defined crystals in two shapes as fine granular and rod-shaped as shown in Fig. 6(c). The length of most rod-like particles is around 600 nm and the width is less than 200 nm. In addition, the SEM image in Fig. 6(d) at 30 min has not large difference with that in Fig. 6(c) at 15 min. This means that no obvious changes happened on morphology of primary products at milling time longer than 30 min.

Further prolonging the milling time to 45 min, the formed particles become irregular in shape in Fig. 6(e). The rod-shaped particles in Fig. 6(d) turn into irregular massive shape shorter in length and longer in width. In addition, prolonging milling time from 45 min to 60 min, the SEM image in Fig. 6(f) has no clearly changes compared with that in Fig. 6(e) at 45 min.

The particle size distribution curves of primary products from mechanochemical process with six milling times varying from 5 min to 60 min are shown in Fig. 7. It can be deduced that the results in Fig. 7 are particle sizes of the aggregates in primary products because the particle size of real Li_2CO_3 powders is in several hundreds of nanometers as shown in Fig. 6 for the SEM images. A cursory look in Fig. 7 shows that increasing the milling time from 5 min to 60 min cannot significantly affect particle size of the aggregates in primary products. However, it can be obtained by keeping a close watch in Fig. 7 that increasing milling time from 5 min to 15 min can slightly promote the particle size of the aggregates; further increasing milling time from 15 min to 60 min cannot lead to significant influence on particle size of the aggregates with 8.3 μm as average diameter. The particle size distribution curves of the aggregates in primary products in Fig. 7 are related to the reaction procedure shown by the SEM images in Fig. 6.

2. Characterization of Target Li_2CO_3 Powders

It has been mentioned in Section 1 that the target product of Li_2CO_3 powders should only be obtained through dissolution-filtration treatment from primary products. To identify the purity of target Li_2CO_3 powders, it is necessary to clarify the formation of primary Li_2CO_3 powders in milling period, rather than in dissolution-filtration period. Only the primary products from the mecha-

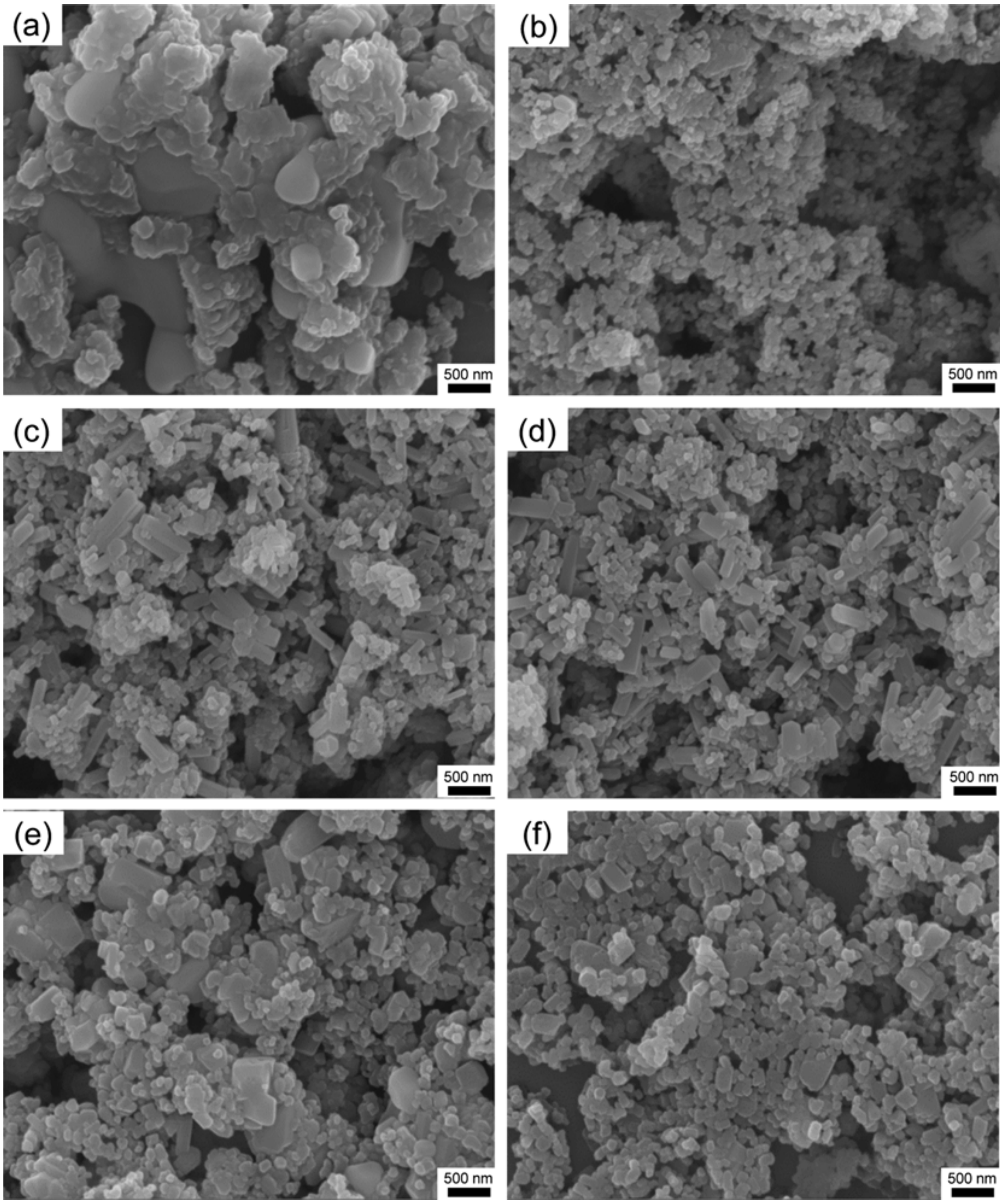

Fig. 6. SEM images of primary products from mechanochemical reaction between Na_2CO_3 and LiCl at six milling times (a) 5 min, (b) 10 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min, respectively.

nochemical process without any peaks matched both reactants of Na_2CO_3 and LiCl were used for the dissolution-filtration treatment.

2-1. XRD Analysis of Target Li_2CO_3 Powders

The XRD patterns of target products after dissolution-filtration treatment with different milling times longer than 15 min are shown in Fig. 8. It can be obtained through comparing with the reference patterns of standard Li_2CO_3 (PDF card 72-1216) that the purity of t target Li_2CO_3 powders with NaCl as major impurity is ideal enough.

2-2. Content of Na^+ Ion in Target Li_2CO_3 Powders

Na^+ content in target products, detected by the XRD analysis, was determined by ICP-OES. The determined results of Na^+ contents in target products from different milling times are listed in Table 1. Na^+ content in four samples through one-time water washing with different milling times was smaller than 0.1 mass% with the minimum values as 0.073 mass%. No obvious effect of milling time on Na^+ content could be found. This means that one-time water washing can largely remove Na^+ from target Li_2CO_3 powders.

2-3. Morphology of Target Li_2CO_3 Powders

The influence of milling time on the morphology of target Li_2CO_3 is shown in Fig. 9. The SEM images in Fig. 9 show that the target Li_2CO_3 powders are in two shapes as massive particles and small grains. The small grains adhere on the surface of massive particles and accumulate on each other spontaneously. The aver-

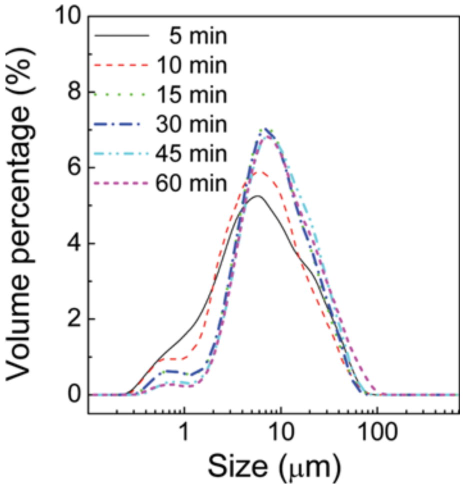

Fig. 7. Size distribution of primary products from mechanochemical reaction between Na_2CO_3 and LiCl at six milling times of 5 min, 10 min, 15 min, 30 min, 45 min, and 60 min, respectively.

age size of the fine grains reaches over a range from 100 to 200 nm, while the size of massive particles is larger than 500 nm in length. The morphology of target Li_2CO_3 powders slightly changes at different milling times. Strictly, longer milling time can lead to target Li_2CO_3 powders more uniform and smaller in size.

To clearly define two shapes of target Li_2CO_3 powders, a trans-

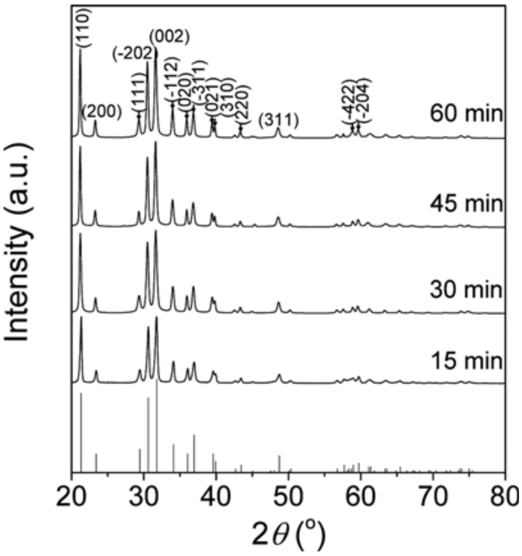

Fig. 8. Comparison of XRD patterns for target products of Li_2CO_3 powders at four milling times as 15 min, 30 min, 45 min, and 60 min.

Table 1. Contents of Na^+ as impurity in target products of Li_2CO_3 powders at four milling times

Milling time (min)	15	30	45	60
Content of Na^+ (mass%)	0.070	0.097	0.096	0.094

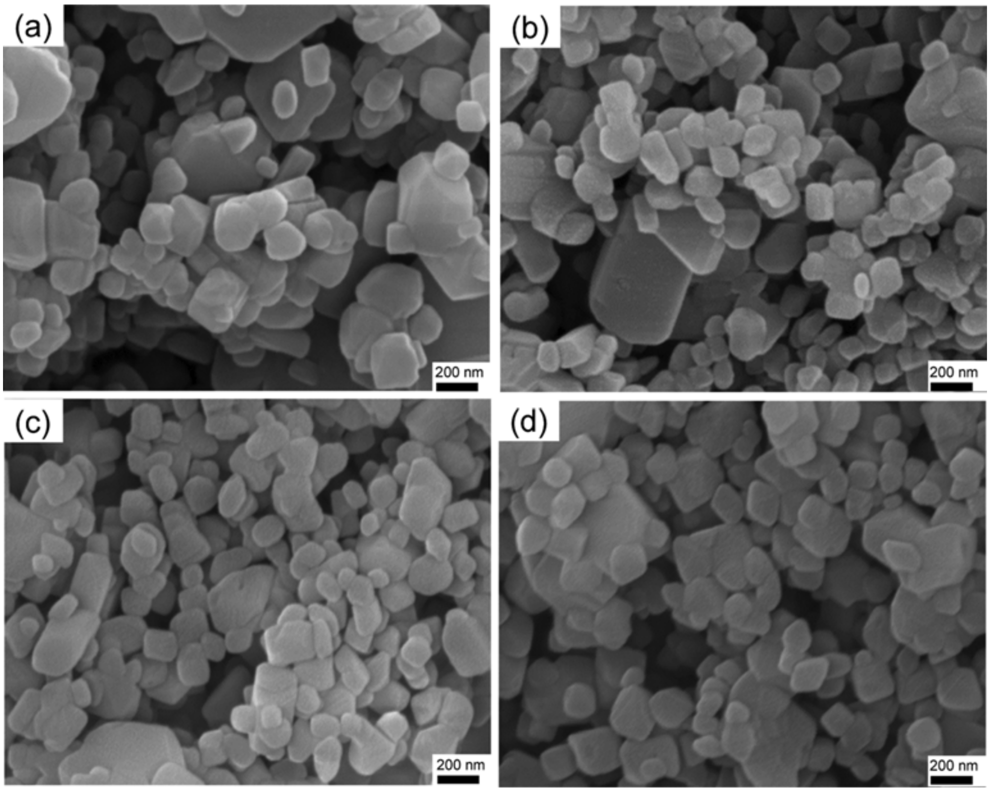

Fig. 9. SEM images of one-time washing products of Li_2CO_3 powders at four milling times (a) 15 min, (b) 30 min, (c) 45 min, and (d) 60 min, respectively.

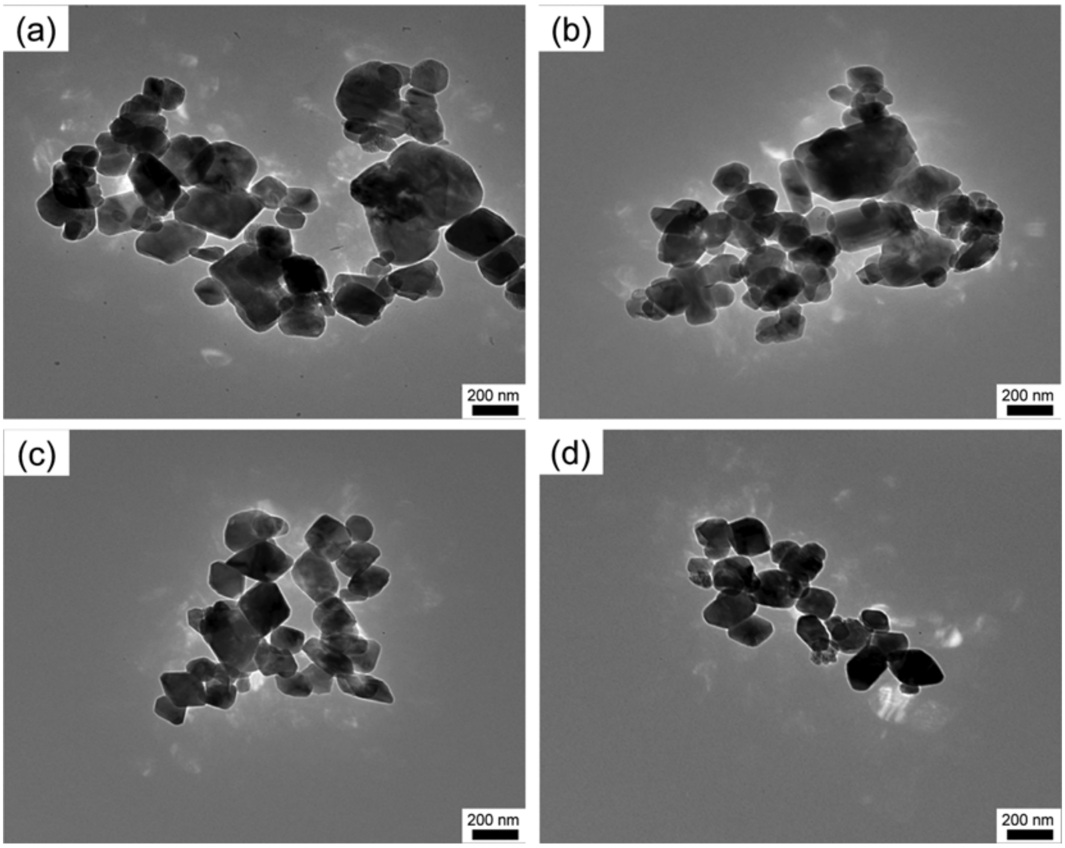

Fig. 10. TEM images of one-time washing products of Li_2CO_3 powders at four milling times (a) 15 min, (b) 30 min, (c) 45 min, and (d) 60 min, respectively.

mission electron microscope (TEM) characterization was also performed on the samples after the SEM analysis. It is clearly shown in Fig. 10 that the target Li_2CO_3 powders at four different milling times present different properties in sharp.

The massive particles in target products at 15 min milling in Fig. 10(a) are more than those at 30 min milling in Fig. 10(b). Prolonging the milling time can lead to the formation of small grains in target products as shown in Fig. 10(c) at 45 min milling and Fig. 10(d) at 60 min milling. In addition, the properties of each subfigure in Fig. 10 at different milling times are consistent with the SEM images in Fig. 9 at the same milling time.

2-4. Particle Size Distribution of Aggregates in Target Li_2CO_3 Powders

The particle size distribution curves of target products at four milling times from 15 min to 60 min are illustrated in Fig. 11. From a comparison of the particle size distribution curves in Fig. 11 with the SEM images in Fig. 9 and the TEM images in Fig. 10, it can be deduced that the results in Fig. 11 are the aggregates of Li_2CO_3 powders, rather than real Li_2CO_3 powders. Evidently, prolonging milling time from 15 min to 60 min cannot largely affect particle size of the aggregates in target products as shown in Fig. 11 as well as that in primary products as displayed in Fig. 7. The average diameter as 7-8 μm for the aggregates in target products in Fig. 11 is in good agreement with that in primary products in Fig. 7. Increasing milling time from 15 min to 45 min can only result in a small decrease of average diameter of the aggregates from 8.1 to 6.9 μm in target products.

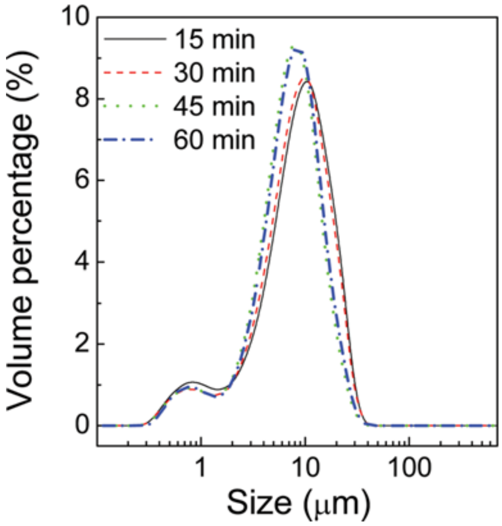

Fig. 11. Size distribution of one-time washing products of Li_2CO_3 powders at four milling times of 15 min, 30 min, 45 min, and 60 min, respectively.

CONCLUSIONS

High purity Li_2CO_3 powders can be successfully prepared through mechanochemical process coupled with the dissolution-filtration process. The primary Li_2CO_3 products from mechanochemical process using dry co-milling of both Na_2CO_3 and LiCl powders are heavily affected by three parameters: milling time, rotation speed, and ball-to-sample mass ratio at a fixed molar ratio of reactants. The XRD patterns of primary products from mechanochemical process indicate that the mechanochemical reaction of both Na_2CO_3 and LiCl can be completed in 15 min with the optimal conditions at rotation speed as 600 rpm, ball-to-sample mass ratio as 5/1, and molar ratio of Na_2CO_3 to LiCl as 1/2. This result confirms that structures of Na_2CO_3 and LiCl can be easily broken to induce the reaction happened through dry milling. The dissolution-filtration process is indispensable for further improving the purity of Li_2CO_3 powders through one-time water washing. Two shapes as massive particles and smaller grains less than 1 μm in nano scale can be observed in the target products of Li_2CO_3 powders. The developed technique combining mechanochemistry synthesis with dissolution-filtration process can be applied to prepare high purity Li_2CO_3 with impurity of Na^+ less than 0.1 mass% and has a bright application potential in insufficient water areas such as northwestern China, especially in Qinghai-Tibet plateau.

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