

Coupled Reaction and Solvent Extraction Process to Form Li_2CO_3 : Mechanism and Product Characterization

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*A coupled reaction and solvent extraction process to produce Li_2CO_3 from LiCl and CO_2 is proposed. The aqueous reaction occurs with difficulty and is not spontaneous at 298 K. To ensure the continuous reaction between LiCl and CO_2 to produce Li_2CO_3 , it is necessary to remove HCl . Experiments conducted in an open reactor at room-temperature showed that the product sample was pure Li_2CO_3 with a particle-size distribution in two regions and a larger number of small crystals. The large and small crystals were obtained by radial growth in the free aqueous phase and in water-in-oil structures with growth space constraints, respectively. Factors influencing the particle-size distribution and Li_2CO_3 morphology were investigated. A short reaction time, large phase ratio (O/A), low-temperature, and surfactant addition (TritonX-100) can increase the number of small particle crystals and reduce the number and volume of large particle crystals. © 2013 American Institute of Chemical Engineers *AIChE J.*, 60: 282–288, 2014*

Keywords: coupled process, extraction, equilibrium constant, crystal growth, particle size distribution

Introduction

Lithium is used routinely in developing technologies, mostly because of its crucial role in energy production and storage. Lithium and its compounds are used extensively in various industrial fields,^{1–4} especially in Li ion batteries.^{5–8} Therefore, the recovery of lithium from salt lake brine reserves has recently attracted increased attention.^{9–15} A possible process for the recovery of lithium from salt lake brines in China, including extraction, washing, and stripping, has been described in our previous work¹⁶ where LiCl was the main product. Li_2CO_3 is an important chemical compound used in various industrial fields, such as application for CO_2 absorbent,¹⁷ pharmaceutical applications,¹⁸ production of electronic grade crystals,¹⁹ especially as an important material for Li ion batteries.²⁰ With the development of Li ion batteries and single crystal industries in the world, the synthesis of Li_2CO_3 has attracted increased attention recently. Thus, preparation of Li_2CO_3 , especially high-purity Li_2CO_3 , has become extremely necessary nowadays.

In the industrial process for producing Li_2CO_3 using LiCl and Na_2CO_3 , the NaCl byproduct is difficult to deal with and can cause environment pollution. In this work, a new process for producing Li_2CO_3 from LiCl and CO_2 is proposed. The factory exhaust, CO_2 , was selected as one of the reactants and carbon source, thereby reducing greenhouse gas emissions. The byproduct is HCl , which can be used to produce polyvinyl chloride. The reaction of LiCl and CO_2 may not be spontaneous at room-temperature. To allow the reaction to proceed continuously, HCl removal by solvent extraction to another phase was considered. Tri-*n*-octyl amine (N235) was selected

as the extractant, and isooctanol as the diluent. N235 is a typical industrial mixed reagent for trioctyl amine (TOA). Both TOA and N235 are typical extractants for HCl recovery from waste water.^{21–24} Isooctanol is a typical polar organic reagent, which is always used as diluent. The isooctanol used for diluent for N235 cannot only reduce the viscosity of the extractant, but also avoid the formation of the third phase during extraction. This new promising way for producing Li_2CO_3 is a typical coupled reaction and solvent extraction process with process intensification. It uses the greenhouse gas (CO_2) instead of Na_2CO_3 as the carbon source, which can avoid introducing other metal cations and causing environment pollution.

In this work, the mechanism of the coupled reaction and solvent extraction process was studied. Factors influencing the equilibrium of the coupled reaction and solvent extraction process, and the particle-size distribution and morphology of Li_2CO_3 were also studied.

Experimental

Materials

Analytical reagents used were as follows: LiCl (>97% pure, Beijing Yili Fine Chemical Co., Beijing, China), absolute ethyl alcohol (>97% pure, Beijing Chemical Plant, Beijing, China), and isooctanol and TritonX-100 (>99.7 and 97% pure, respectively, Sinopharm Chemical Reagent Beijing Co., Beijing, China). CO_2 gas (>95% pure, Tsinghua University, Beijing, China) and N235 industrial reagent (Sinopec, Beijing, China) were used.

Methods

All coupled reaction and solvent extraction processes were performed in an open 500-mL reactor at room-temperature and an open temperature-controlled 1000-mL reactor. The

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temperature in the 1000-mL volume reactor was controlled by circulating water through a jacket. To the open reactor were added 150 mL of 50% N235 and 50% isooctanol along with 50 mL of an aqueous solution containing 6-mol/L LiCl. To the controlled temperature reactor, were added 300 mL of 50% N235 and 50% isooctanol along with 100 mL of an aqueous solution containing 6-mol/L LiCl. Both reactors were stirred at 700 rpm for approximately 20 min and CO₂ washed by distilled water was dispersed into the reactor through a 1-μm sand core. The process is shown in Figure 1. The reactor contents were left to settle for 10 min, during which time the two phases separated. A sample of micron-sized white solids for analyzing particle-size distribution and observing morphology was obtained after centrifuging.

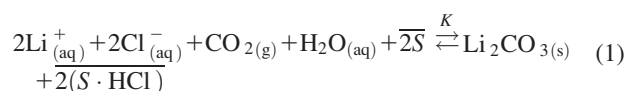
Analysis

The coupled process samples were washed repeatedly using ethanol and their composition analyzed using X-ray diffraction (XRD; D8-Advance, Bruker, Germany). Particle-size distribution was determined using a Malvern particle size analyzer (Mastersizer2000, Malvern, England) and morphology by a scanning electron microscope (SEM; JSM7401, Jeol, Japan). The Li concentration was analyzed using inductively coupled plasma spectrometry (Vista-MPX, Varin, USA).

Results and Discussion

Mechanism of coupled reaction and solvent extraction process

The coupled reaction and solvent extraction process is a new process for producing Li₂CO₃ from LiCl and CO₂. The equation for the overall reaction is as follows



Equations for the aqueous reaction and solvent extraction are given by Eqs. 2 and 3, respectively

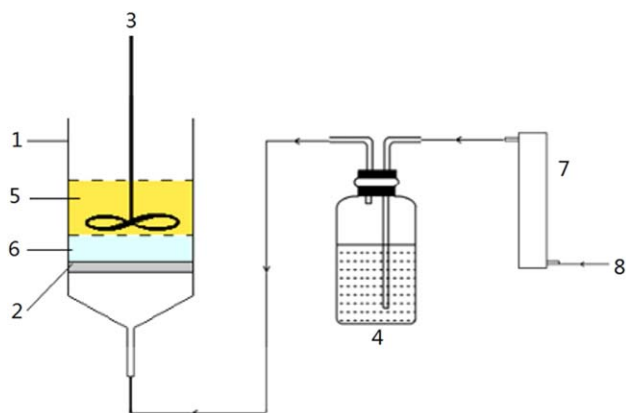
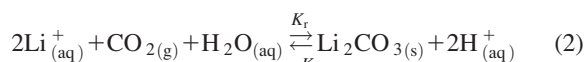
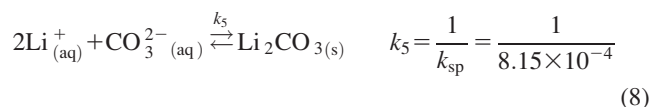
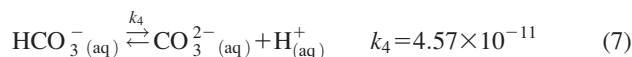
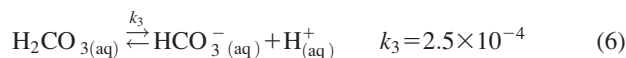
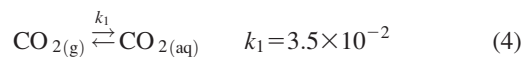


Figure 1. Experimental setup for preparation of Li₂CO₃ in an open reactor. 1, reactor; 2, 1-μm sand core; 3, mixer; 4, gas bottle; 5, organic phase; 6, aqueous phase; 7, rotameter; and 8, CO₂.

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where the gaseous, aqueous, and solid phases are denoted by the subscripts g, aq, and s, and the organic phase is denoted by the overline, respectively. *S* represents the extractant. *K* is the reaction equilibrium constant. The equilibrium constants for the aqueous reaction and solvent extraction are denoted by the subscripts r and e, respectively.

Eq. 2 can be derived from the following equations^{25,26}



where *k_n* (*n* = 1–5) is the reaction equilibrium constant for each step reaction. *k_{sp}* is the solubility product constant for Li₂CO₃. The equilibrium constant (*K_r*) for the aqueous reaction can be obtained as follows

$$K_r = k_1 k_2 k_3 k_4 k_5 = \frac{k_1 k_2 k_3 k_4}{k_{\text{sp}}} = 1.28 \times 10^{-15} \quad (9)$$

The thermodynamic parameters for all reactants are listed in Table 1.²⁵ Using the following equations, the equilibrium constant (*K_r*) calculated from thermodynamic parameters is 1.126×10^{-15} at 298 K, which confirms the equilibrium constant (*K_r*) calculated from the equilibrium constants of a five-step reaction

$$\Delta_r G_m^0 = \Delta_r H_m^0 - T \cdot \Delta_r S_m^0 \quad (10)$$

$$K_r' = \exp \left(-\frac{\Delta_r G_m^0}{RT} \right) \quad (11)$$

where $\Delta_r G_m^0$, $\Delta_r H_m^0$, and $\Delta_r S_m^0$ represent the Gibbs free energy change, enthalpy change, and entropy change, respectively.

The calculated values of *K_r* indicate that the aqueous reaction occurs with difficulty. $\Delta_r G_m^0 = 85.32 \text{ kJ mol}^{-1} > 0$, which indicates that this aqueous reaction is not spontaneous at 298 K. The Gibbs free energy for the overall reaction, $\Delta_r G_m^0 = \Delta_r G_m^0 + 2\Delta_e G_m^0$, should be negative to ensure the overall reaction is spontaneous. It is necessary to remove HCl to another phase by solvent extraction to allow the aqueous reaction to proceed continuously and a typical extractant for HCl, trioctylamine (N235), was selected to do so.

Table 1. Thermodynamic Parameters of Reactants²⁵

Formula	$\Delta_f H_m^0$ (kJ/mol)	S_m^0 (J/mol · K)
Li ⁺ _(aq)	−278.47	12.24
CO _{2(g)}	−393.51	213.785
H ₂ O _(aq)	−285.83	69.95
Li ₂ CO _{3(s)}	−1215.9	90.4
H ⁺ _(aq)	0	0

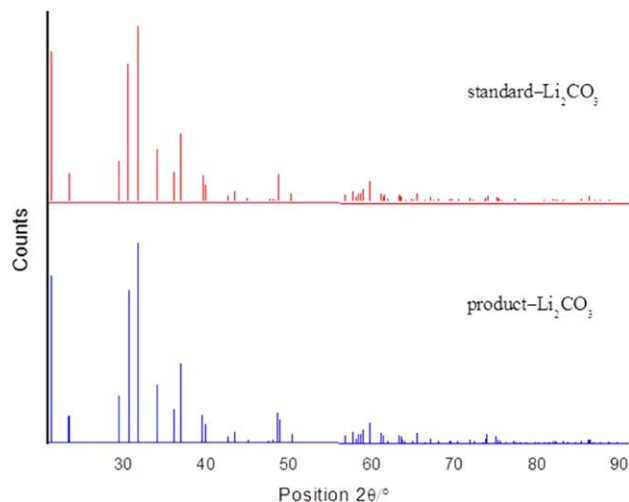


Figure 2. Comparison of XRD spectra for standard-Li₂CO₃ and prepared sample.

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Preparation of Li₂CO₃ in an open reactor at room-temperature (298 K)

Experiments to prepare Li₂CO₃ were conducted in an open 500-mL reactor at 298 K. A comparison of the XRD spectra for the sample of micron sized white solids obtained after centrifuging and that for standard Li₂CO₃ (Figure 2) indicates that these spectra are almost the same. Therefore, the product sample obtained from the coupled reaction and solvent extraction process is Li₂CO₃. There are two particle-size distributions of the prepared Li₂CO₃ (Figure 3) in the 0.1–1 μm and 10–100 μm ranges, and there are more particles in the smaller size range. Figure 4 shows the morphology of the prepared Li₂CO₃ particles obtained by SEM. There are two obvious size distributions, which confirms the particle-size distribution analysis.

The large particles are few in number and form flake or bulk crystals with sharp edges and corners. Li₂CO₃ growth is of the typical radial form, which means that growth occurs by diffusion around a nucleus as starting point.^{27,28} Radial

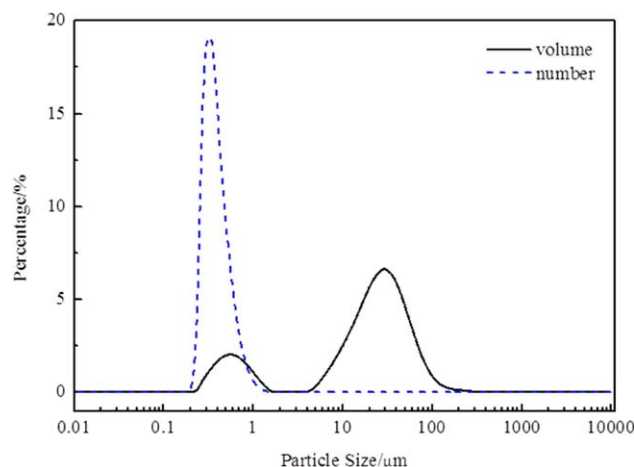
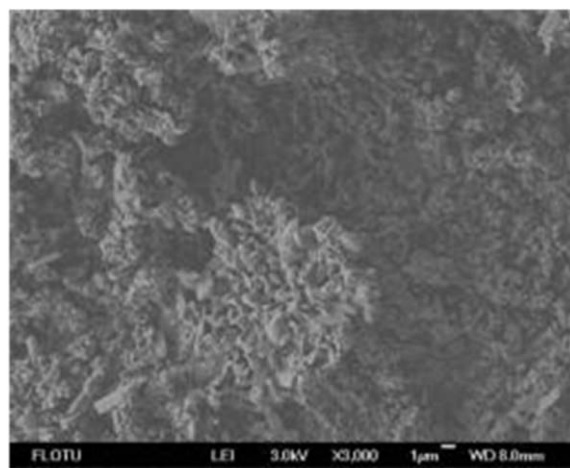
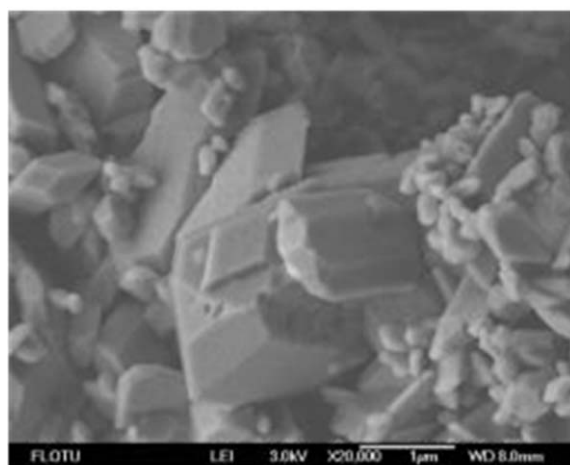


Figure 3. Particle-size distribution of crystals prepared in an open reactor.

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(a)



(b)

Figure 4. SEM images of crystals prepared in an open reactor.

growth can occur again with a new grown raised point. Thus, large particles that cannot easily be broken can be obtained by this type of growth. Typical radial growth is shown in the red circle in Figure 5. In contrast, many small particles exist as ellipsoidal crystals. The crystallization

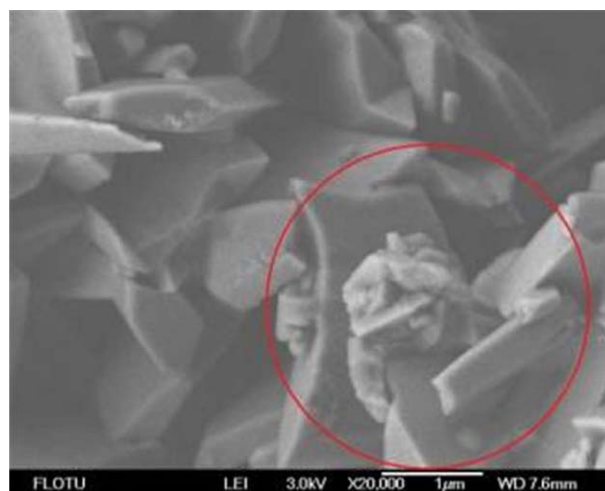


Figure 5. Radial growth for prepared Li₂CO₃.

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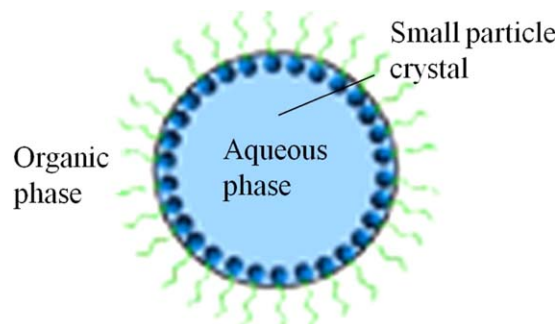


Figure 6. Water-in-oil structure.

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environment for large and small particles is completely different. As the phase ratio (O/A, where O and A stands for the organic and aqueous phases, respectively) is 3 in this work and a large volume of organic solvent exists in the reactor. The two phases are well-mixed by high stirring speed, which can easily result in a water-in-oil structure, as shown in Figure 6. Because the size of the water-in-oil structure is usually less than 1- μm , small particles are formed with significant growth space constraints. This can prevent continuous radial crystal growth, resulting in particles of morphology similar to the water-in-oil structure. Although the water-in-oil structure exists in the mixed solutions, part of the water is free from the organic phase. When the coupled reaction and solvent extraction process occurs in the two phase interface, large particles can be obtained by radial growth of crystals into the aqueous phase with no growth space constraints.

Experimental verification of growth mechanism of crystal particles

As noted above, there exist two kinds of crystal particle-size regions in the prepared Li_2CO_3 . Large particles were obtained by radial growth in the free aqueous phase, and the small ones resulted from the water-in-oil structure. Three groups of experiments were designed for verification of this growth mechanism.

Effect of Experimental Conditions. Three experiments for preparing Li_2CO_3 under different conditions were designed for analyzing particle-size distribution, as shown in Table 2. Figure 7 shows the particle-size distribution under three different experimental conditions. The particle size ranges for the large particles fluctuate considerably, whereas the small particles are mostly in the 0.1–1 μm size range. This occurs because the water-in-oil structure is almost unaffected by different experimental conditions. From a comparison between Experiments 2 and 3, it can be seen that a longer reaction time favors destruction of water-in-oil structure and radial growth of large particles. From a comparison of Experiments 1 and 2, it can be seen that the change in

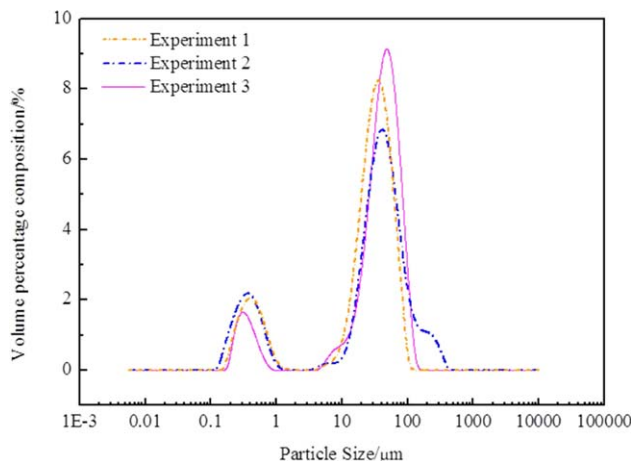


Figure 7. Particle-size distribution of crystals prepared in an open reactor under different experimental conditions (Table 2).

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volume concentration of N235 has almost no effect on small particle growth and little effect on large particle size.

Effect of Phase Ratio (O/A). Three experiments with different phase ratios, while maintaining all other conditions the same, were conducted in an open reactor at 298 K. Figure 8 shows that increasing the phase ratio increases the number of small particle crystals. A larger phase ratio means a larger volume of organic phase, which can raise the number of water-in-oil structures. More water-in-oil structures result in an increased number of small particle crystals. Meanwhile, increasing the phase ratio reduces the relative volume of the free aqueous phase, which limits large particle crystal growth.

Effect of Surfactant Volume (TritonX-100). The surfactant reagent can increase the number of water-in-oil structures in mixed solutions significantly. Three experiments with different surfactant volumes were conducted in an open reactor at 298 K. Solutions with high salinity and vigorous stirring can maintain emulsions. Thus, lower LiCl molar concentrations and stirring speed benefit the formation of water-in-oil structures. As shown in Figure 9, the addition and increase in volume of surfactant increases the number of small particle crystals significantly and reduces the number and volume of large particle crystals.

Results from these three groups of experiments confirm the growth mechanism of crystal particles concluded above. Although an increase of water-in-oil structures can increase the number of small particle crystals, the growth of large flake or bulk crystals cannot be restrained completely. Because the water-in-oil structure is unstable, small particle crystal aggregation can occur during the breaking process. Increasing the number and controlling the stability of the

Table 2. Effect of Different Experimental Conditions

Number	Phase Ratio: O/A	Volume Concentration of N235	Molar Concentration of LiCl (mol/L)	Gas Flow Rate of CO_2 (mL/min)	Stirring Rate (r/min)	Reaction Time (min)
1	3:1	70%	6	60	700	20
2	3:1	50%	6	60	700	20
3	3:1	50%	6	60	700	90

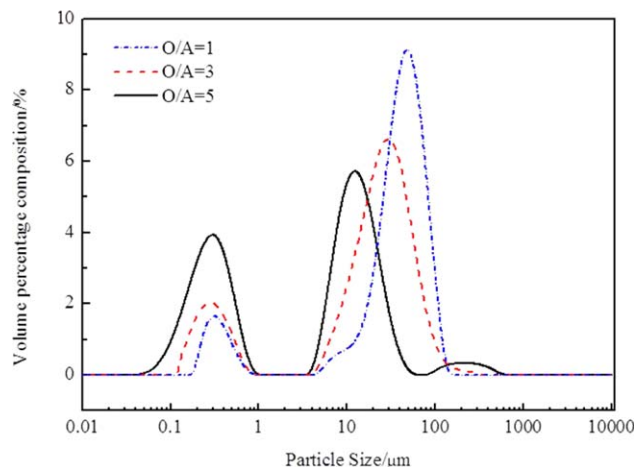


Figure 8. Particle-size distribution of crystals prepared in an open reactor for different phase ratio (organic/aqueous).

(Volume concentration of N235: 50%; Molar concentration of LiCl: 6 mol/L; Gas flow rate of CO₂: 60 mL/min; Stirring rate: 700 r/min; Reaction time: 20 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water-in-oil structures can be used to obtain the largest number of small particle crystals.

Preparation of Li₂CO₃ in an open temperature-controlled reactor

Temperature is another key factor that influences crystal growth significantly. Based on the above open reactor, an open temperature-controlled 1000-mL reactor was designed to study the influence of temperature on crystal growth. This reactor is an amplifying device with two times the volume of the reactor used in an open reactor at room-temperature. The temperature of this reactor is controlled by circulating water through a jacket. Temperatures of 278, 298, and

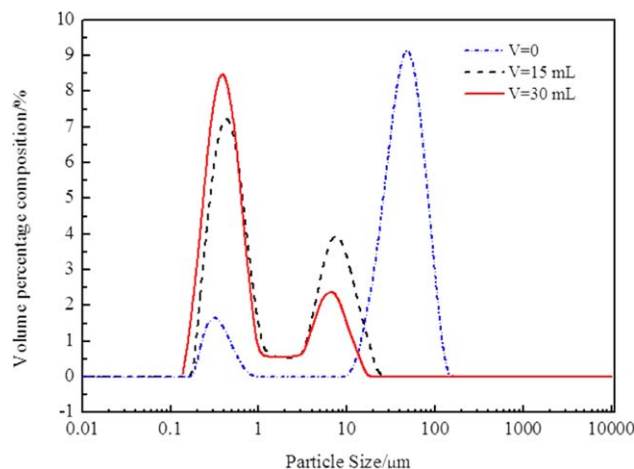


Figure 9. Particle-size distribution of crystals prepared in an open reactor for different volume of Triton-100.

[Phase ratio (O/A): 10:1; Molar concentration of LiCl: 4 mol/L; Gas flow rate of CO₂: 60 mL/min; Stirring rate: 60 r/min; Reaction time: 20 min]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

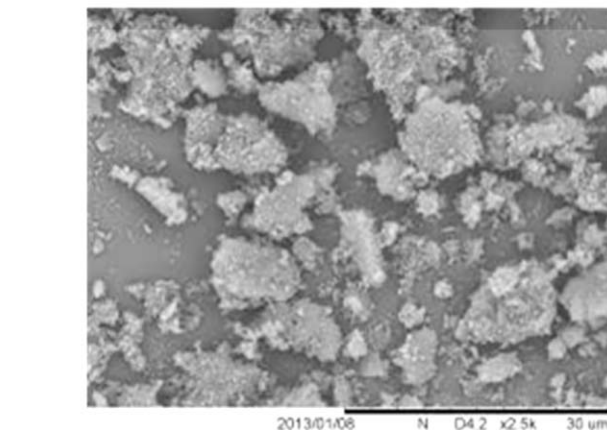
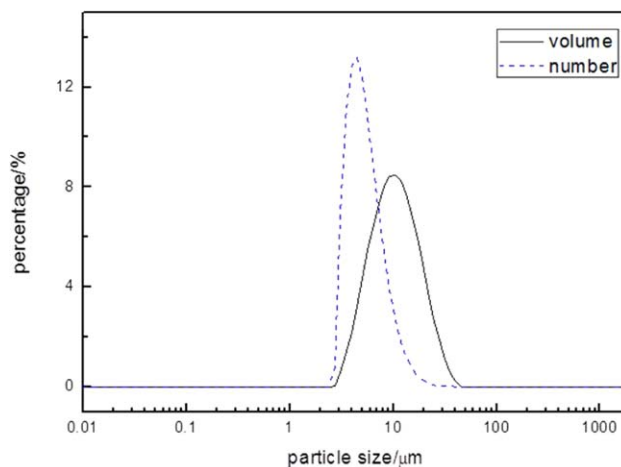


Figure 10. Particle-size distribution and SEM image of crystals prepared in an open temperature-controlled reactor at 278 K.

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318 K were selected for preparing the Li₂CO₃ particles. The particle-size distribution of the crystals at 278 K (Figure 10) show that particles are distributed in only one size region, 1–100 μm, for both volume and number. The SEM image (Figure 10) shows that low temperature does not benefit radial growth of large flake or bulk crystals. On the contrary, many more small crystals were obtained in the water-in-oil structure. Low temperature favors the formation of large particles from these small crystals, which are different from the large flake or bulk crystals obtained directly in the aqueous phase. These large crystals were formed from the physical bonding of small ones.

The particle-size distribution and SEM images of crystals at 298 K are shown in Figure 11. From a comparison of the particle-size distribution of crystals in an open reactor at room-temperature and an open temperature-controlled reactor at 298 K, it can be seen that the particle size of the small crystals in the temperature-controlled reactor is distributed in the 0.01–0.1 μm size range, which is smaller than that in the open reactor. The temperature-controlled reactor can control the temperature of the mixing solutions as 298 K accurately when the two phases react. However, the mixing solution temperature may be higher than room-temperature when the two phases react. The particle-size distribution and SEM images of crystals at 318 K are shown in Figure 12. The particle sizes of both large and small crystals at 318 K are larger than that at 298 K. A comparison of the SEM images

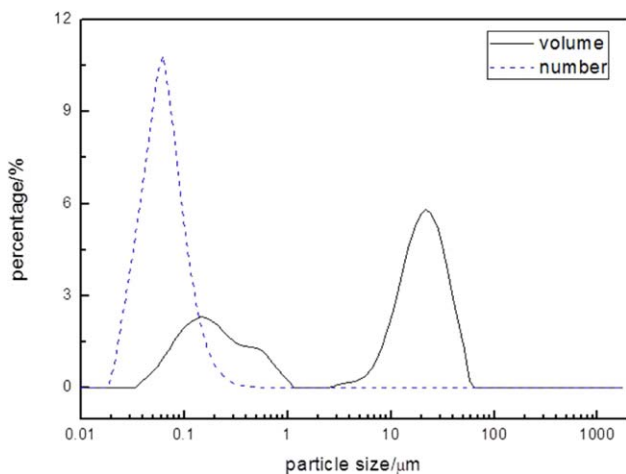


Figure 11. Particle-size distribution and SEM image of crystals prepared in an open temperature-controlled reactor at 298 K.

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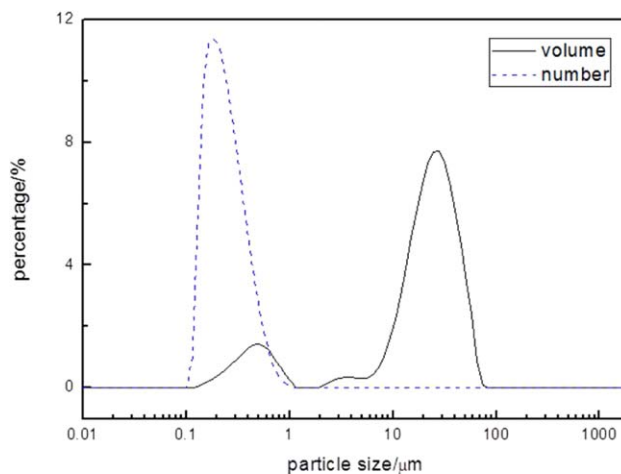


Figure 12. Particle-size distribution and SEM image of crystals prepared in an open temperature-controlled reactor at 318 K.

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in Figures 11 and 12 shows that the number of large flake or bulk crystals with sharp edges and corners at 318 K is larger than that at 298 K, which confirms the results at 278 K. High temperature favors the radial growth of large flake or bulk crystals.

Conclusions

In this work, the mechanism of a coupled reaction and solvent extraction process to form Li_2CO_3 from LiCl and CO_2 , and the particle-size distribution and morphology of the prepared Li_2CO_3 were investigated. The equilibrium constants (K_r) for the aqueous reaction obtained from the reaction equilibrium constant for each step reaction and thermodynamic parameters were 1.28×10^{-15} and 1.126×10^{-15} at 298 K, respectively. This indicates that the aqueous reaction occurs with difficulty. The aqueous reaction is not spontaneous at 298 K, which indicated that it is necessary to remove HCl to another phase by solvent extraction to allow the aqueous reaction to proceed continuously. The product sample obtained by the coupled reaction and solvent extraction process is Li_2CO_3 . The particle sizes of the prepared Li_2CO_3 obtained from the open reactor at room-temperature were distributed in two ranges, 0.1–1 μm and 10–100 μm , and the number of particles in the former range was higher than that in the latter. Large flake or bulk crystals with sharp edges and corners were

obtained by radial growth in the free aqueous phase with no growth space constraints. Small ellipsoidal crystals were obtained in water-in-oil structures with growth space constraints. A long reaction time favors destruction of water-in-oil structure and the radial growth of large particles. A large phase ratio and the addition and increased volume of surfactant can increase the formation of small particle crystals and reduce the number and volume of large particle crystals. High temperature favors the radial growth of large flake or bulk crystals.

Acknowledgments

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