



Article Removal of SO₄²⁻ from Li₂CO₃ by Recrystallization in Na₂CO₃ Solution

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Abstract: Li₂CO₃ with high purity is an important raw material for the fabrication of lithium rechargeable batteries. This paper reports a facile recrystallization way to produce Li₂CO₃ with high purity from commercial Li₂CO₃ containing 0.8 wt % of SO₄²⁻ by the treatment of the commercial Li₂CO₃ in Na₂CO₃ solution. The increase of temperature from 30 °C to 90 °C favored the recrystallization of Li₂CO₃ in Na₂CO₃ solution and promoted the removal of SO₄²⁻ adsorbed or doped on/in the commercial Li₂CO₃. The content of SO₄²⁻ in Li₂CO₃ decreased to 0.08 wt % after the treatment of the commercial Li₂CO₃ in 1.0 mol·L⁻¹ Na₂CO₃ solution at 90 °C for 10.0 h.

Keywords: Lithium carbonate; sulfate; recrystallization; sodium carbonate

1. Introduction

Li₂CO₃ with high purity is widely used for the fabrication of lithium rechargeable batteries, and is usually produced from lithium-bearing minerals such as spodumene (Li₂O·Al₂O₃·4SiO₂), containing 5.8%–8.1 wt % Li₂O, and lepidolite (K(Li,Al)₃(Si,Al)₄O(F,OH)₂), containing 3.2%–6.45 wt % Li₂O, or from the Li-bearing brines in salt lakes containing 0.005%–0.2 wt % Li⁺. Sulfation roasting (roasting of the mixture of lepidolite, Na₂SO₄ and CaCl₂) and alkaline roasting (roasting of spodumene or lepidolite with limestone) are usually adapted to convert the lithium-bearing minerals to soluble Li-bearing salts. The soluble Li-bearing salts are then leached with acid or water, and the purified solutions are then reacted with soluble carbonates to form Li₂CO₃ [1–5]. The Li-bearing brines usually contain impurities like SO₄²⁻, K⁺, Na⁺, Mg²⁺, Ca²⁺ and Cl⁻, etc. and the formation of Li₂CO₃ from the Li-bearing brines is often carried out by evaporation and crystallization: the Li-bearing brines are concentrated by multi-step evaporations and then reacted with soluble carbonates. The commercial Li₂CO₃ produced either from the minerals or the Li-bearing brines usually contains impurities such as SO₄²⁻, Mg²⁺, Ca²⁺, Fe³⁺, K⁺, Na⁺, Cl⁻, etc., and further purification is often needed before its application in lithium batteries.

The soluble cations like K⁺, Na⁺ and soluble anions such as Cl⁻ and partial SO₄²⁻ can be removed by washing with purified water. There are two main ways to remove Mg²⁺ and Ca²⁺, which often exists as insoluble MgCO₃ and CaCO₃ in Li₂CO₃. One way is causticization-carbonation: Li₂CO₃ slurry is reacted with Ca(OH)₂ at elevated temperature: (Li₂CO₃ + Ca(OH)₂ \rightarrow 2LiOH + CaCO₃) [6], the impurities such as Mg²⁺ and Fe³⁺ are precipitated as Mg(OH)₂ and Fe(OH)₃ residues, and the obtained LiOH solution is purified by ion exchange to remove minor soluble ions such as Ca²⁺ and Mg²⁺ and then reacted with CO₂ to form purified Li₂CO₃. Another way is hydrogenation-decomposition [7–9]: Li₂CO₃ is converted to soluble LiHCO₃ by carburizing reaction (Li₂CO₃ + CO₂ + H₂O \rightarrow 2LiHCO₃), the soluble impurities in LiHCO₃ solution are separated by ion exchange and purified Li₂CO₃ is formed by subsequent decomposition of LiHCO₃ at elevated temperature (2LiHCO₃ \rightarrow Li₂CO₃ + H₂O + CO₂). Up to now, most former work has been focused

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mainly on the removal of Mg^{2+} and Ca^{2+} , and little work has been concerned with the removal of SO_4^{2-} , which is also one of the common impurities in commercial Li_2CO_3 .

This paper reports a facile way to remove SO_4^{2-} from commercial Li₂CO₃ containing SO_4^{2-} by recrystallization in Na₂CO₃ solution. The behaviors of the adsorbed and doped SO_4^{2-} on/in Li₂CO₃ in recrystallization process are discussed and an optimized method is suggested to fabricate Li₂CO₃ with high purity and high conversion ratio.

2. Materials and Methods

Commercial Li₂CO₃ containing 99.2 wt % of Li₂CO₃ and 0.8 wt % of SO₄²⁻ was used in the experiments. 100.0 g of commercial Li₂CO₃ was mixed with 400.0 g of 1.0 mol·L⁻¹ Na₂CO₃ solution at room temperature, keeping the stirring speed at 300 min⁻¹. The mixture was then heated to 30–90 °C and kept in an isothermal state for 10.0 h. The purified Li₂CO₃ was then filtered, washed with distilled water three times, and dried at 150 °C for 10.0 h.

The contents of Li⁺ and SO₄²⁻ in samples were detected by ion chromatograph (IC-300, Shenghan Chromatography Technology Co., Ltd., Qingdao, China) equipped with a SH-CC-3 column. The contents of CO_3^{2-} in samples were determined by the HCl titration method. The crystallinities of the samples were analyzed by X-ray diffractometer (XRD, D8 advanced, Bruker, Karlsruhe, Germany) using Cu-K α radiation (λ = 1.54178 Å). The surfaces of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Model PHI-5300, PHI, Minneapolis, MN, USA) with a Mg-K α photon energy of 1253.6 eV. The functional groups of the samples were examined by a Fourier transform infrared spectrometer (FT-IR, Nicolet 670, Thermo Fisher, Waltham, MA, USA), using KBr (AR) as the background.

3. Results and Discussion

3.1. Characterization of Commercial Li₂CO₃

Figure 1a shows the XRD patterns of commercial Li₂CO₃. Most of the XRD peaks of the commercial Li₂CO₃ were quite identical with the standard peaks of the pure Li₂CO₃ (JCPDS 36-0787), and the peak located at $2\theta = 21.76^{\circ}$ indicated the existence of Li₂SO₄ (JCPDS 87-0729). The left shift of the XRD peaks of the commercial Li₂CO₃ compared with those of standard Li₂CO₃ (the dotted lines in Figure 1a) indicated the increase of the corresponding interplanar spacings, which should be connected with the doping of SO₄²⁻ in Li₂CO₃ since the radius of SO₄²⁻ (2.44 Å) was bigger than that of CO₃²⁻ (1.64 Å) [10].

Figure 1b shows the S2p XPS patterns of the commercial Li_2CO_3 in the banding energy range of 164–174 eV. The original data can be divided into two peaks located at 169.5 eV and 168.5 eV, corresponding to the 2p1/2 and 2p3/2 peaks of S, respectively [11], which should be connected with the adsorption of SO_4^{2-} on Li_2CO_3 surface.

Figure 1c shows the morphology of the mommercial Li_2CO_3 . Un-regular particles with a diameter of 1–10 μ m were aggregated with each other, forming agglomerates with a diameter of about 35 μ m.

Chemical analysis showed that the commercial Li_2CO_3 was composed of 99.15 wt % of Li_2CO_3 , 0.8 wt % of SO_4^{2+} , 0.0045 wt % of Ca^{2+} and 0.0187 wt % of Na⁺.

3.2. Recrystallization of Commercial Li₂CO₃

Figure 2a,b show the variations of the soluble [Li⁺] and $[CO_3^{2-}]$ with reaction time at 30–90 °C. The initial quick increase of the soluble [Li⁺] and $[CO_3^{2-}]$ indicated that the dissolution of Li₂CO₃ was much faster than its precipitation at the initial stage, and the subsequent slight decrease of the soluble [Li⁺] and $[CO_3^{2-}]$ indicated that the precipitation of Li₂CO₃ was a little faster than its dissolution at the later time. The data in Figure 2a,b confirmed the recrystallization of Li₂CO₃ in Na₂CO₃ solution:

$$\text{Li}_2\text{CO}_3 \to \text{Li}^+ + \text{CO}_3^{2-} \xrightarrow{\text{Na}_2\text{CO}_3} \text{Li}_2\text{CO}_3 \downarrow . \tag{1}$$

Meanwhile, the comparatively low $[Li^+]$ and $[CO_3^{2-}]$ at high temperature could be attributed to the low solubility of Li_2CO_3 at high temperature (the solubility of Li_2CO_3 were 1.26 g·100 mL⁻¹, 1.01 g·100 mL⁻¹ and 0.72 g·100 mL⁻¹ at 30 °C, 60 °C and 90 °C, respectively).



(c)

Figure 1. (a) XRD; (b) XPS and (c) SEM patterns of commercial Li₂CO₃.



Figure 2. Variation of (a) soluble $[Li^+]$; (b) $[CO_3^{2-}]$ and (c) supersaturation with reaction time.

Figure 2c shows the variation of the supersaturation (the ratio of $[\text{Li}^+]^2[\text{CO}_3^{2-}]$ to K_{sp} of Li_2CO_3) with reaction time based on the data shown in Figure 2a,b. K_{sp} of Li_2CO_3 at 30 °C, 60 °C and 90 °C were 4.278×10^{-4} , 2.031×10^{-4} and 8.864×10^{-5} , respectively [12]. The comparatively high supersaturation at high temperature favored the quick precipitation of Li_2CO_3 .

3.3. Removal of SO_4^{2-} from Li_2CO_3

Figure 3a shows the XRD patterns of Li_2CO_3 before and after recrystallization. The disappearance of the Li_2SO_4 peak (located at $2\theta = 21.76^\circ$) in the Li_2CO_3 samples after recrystallization at 30–90 °C indicated the removal of Li_2SO_4 from Li_2CO_3 .

Figure 3b shows the variation of SO_4^{2-} in Li_2CO_3 with reaction time at 30–90 °C. With the increase of reaction time, more and more SO_4^{2-} was removed from Li_2CO_3 , leading to the gradual decrease of SO_4^{2-} in Li_2CO_3 . The increase of temperature from 30 °C to 90 °C favored the removal of SO_4^{2-} from Li_2CO_3 . Chemical analysis showed that the purity Li_2CO_3 increase up to 99.8 wt %, the conversion ratio of the commercial Li_2CO_3 to Li_2CO_3 with high purity was 97.2 wt %, and the content of SO_4^{2-} in Li_2CO_3 decreased to 0.08 wt % after treating the commercial Li_2CO_3 in 1.0 mol·L⁻¹ Na₂CO₃ solution at 90 °C for 10.0 h.



Figure 3. (a) XRD patterns of of Li_2CO_3 samples before and after recrystallization in Na_2CO_3 solution; (b) Variation of SO_4^{2-} in Li_2CO_3 sample after recrystallization with reaction time.

3.3.1. Behavior of Adsorbed SO_4^{2-}

Figure 4 shows the FT-IR spectra of Li₂CO₃ before and after recrystallization in 1.0 mol·L⁻¹ Na₂CO₃ solution at 30–90°C for 3.0 h. The peaks located at 1090 cm⁻¹, 1430 cm⁻¹ and 1482 cm⁻¹ were attributed to the vibration of the symmetric (1090 cm⁻¹) and antisymmetric (1430 cm⁻¹ and 1482 cm⁻¹) stretching vibrations of C-O bond in Li₂CO₃, respectively, while the peaks located at 1118 cm⁻¹ and 1650 cm⁻¹ were attributed to the symmetric (1118 cm⁻¹) and antisymmetric (1650 cm⁻¹) stretching vibrations of S-O bond of Li₂SO₄, respectively. The increase of temperature from 30 °C to 90 °C led to the enlargement of the peaks for Li₂CO₃ and the shrinkage of the peaks for SO₄^{2–}, indicating the enhanced desorption of SO₄^{2–} from Li₂CO₃ surface at elevated temperature. Comparing the data in Figure 1b with those in Figure 4, it was known that the peaks for the stretching vibration of C-O shifted from 1439 cm⁻¹ and 1495 cm⁻¹ for commercial Li₂CO₃ to 1430 cm⁻¹ and 1482 cm⁻¹ for purified Li₂CO₃, which should be attributed to the desorption of SO₄^{2–} from Li₂CO₃ [13,14], the desorption of SO₄^{2–} thus enhanced the polarity of Li⁺ and led to the red shift of the C-O peaks in Li₂CO₃.



Figure 4. FT-IR spectra of Li₂CO₃ samples before and after recrystallization in Na₂CO₃ solution.

Figure 5 shows the XPS spectra of S2p in Li₂CO₃ samples before and after recrystallization in 1.0 mol·L⁻¹ Na₂CO₃ solution at 30–90 °C for 3.0 h. As shown in Figure 5a, the S2p peaks located at 168.75 eV became much smaller after recrystallization at elevated temperatures, indicating the enhanced removal of SO₄^{2–} at elevated temperatures. Table 1 shows the composition of Li₂CO₃ on surface and in bulk detected by XPS and ion chromatograph, respectively. The surface concentration of SO₄^{2–} on surface was calculated by the equation (2). The atomic ratios of S to C on Li₂CO₃ surface decreased from 1:17.2 (for commercial Li₂CO₃) to 1:49.2, 1:61.3 and 1:88.2 (for the samples after crystallization at 30 °C, 60 °C and 90 °C, respectively). The data in Table 1 proved the concentrations of SO₄^{2–} on surface were larger than those in the bulk, and the increase of temperature favored the desorption of SO₄^{2–} from Li₂CO₃ surface.

Surface concentration of
$$\text{Li}_2\text{SO}_4 = \frac{M(\text{SO}_4^{2-})}{N(\text{C:S}) \times M(\text{Li}_2\text{CO}_3) + M(\text{Li}_2\text{SO}_4)}$$
 (2)



Figure 5. XPS spectra of S2p in Li₂CO₃

Table 1. Composition of Li₂CO₃ on surface and in bulk.

SO_4^{2-} in Bulk	
(wt %)	
)	

3.3.2. Behavior of Doped SO_4^{2-}

Figure 6 shows the XRD patterns of ($\overline{110}$), ($\overline{202}$) and (002) planes of Li₂CO₃ samples after crystallization in 1.0 mol·L⁻¹ Na₂CO₃ solution at 30–90 °C for 3.0 h. The 20 values of ($\overline{110}$) peaks were 21.267° at 30 °C, 21.298° at 60 °C and 21.309° at 90 °C, corresponding to the interplanar spacings of 4.1744 Å, 4.1684 Å and 4.1663 Å, respectively, according to the Bragg equation ($2dsin\theta = \lambda$). The removal of the doped SO₄^{2–} from Li₂CO₃ led to the decrease of the lattice distance of ($\overline{110}$) plane since the radius of SO₄^{2–} (2.44 Å) was bigger than that of CO₃^{2–} (1.64 Å). Similar phenomena occurred for ($\overline{202}$) and (002) planes: the 20 values of ($\overline{202}$) peaks were 30.563° at 30 °C, 30.586° at 60 °C and 30.602° at 90 °C, corresponding to the interplanar spacings of 2.9225 Å, 2.9204 Å and 2.9189 Å, respectively, while the 20 values of the (002) peaks were 31.755° at 30 °C, 31.73° at 60 °C and 31.788° at 90 °C, corresponding to the interplanar spacings of 2.8155 Å, 2.8137 Å and 2.8130 Å, respectively.

The crystallinities of Li₂CO₃ samples could be calculated out based on the half-widths (β) of the peaks of ($\overline{1}10$), ($\overline{2}02$) and (002) planes shown in Figure 5 and the Scherrer equation $D = K\lambda/\beta cos\theta$, where K = 0.86. The half-widths of ($\overline{1}10$) peaks were 0.144° at 30 °C, 0.128° at 60 °C and 0.113° at 90 °C, corresponding to the crystal sizes of 55.5 nm, 62.5 nm and 70.8 nm, respectively. The increase of temperature favored the recrystallization of Li₂CO₃ and the formation of Li₂CO₃ with bigger sizes. Similar phenomena occurred for ($\overline{2}02$) and (002): the half-widths of ($\overline{2}02$) peaks were 0.222° at 30 °C, 0.208° at 60 °C and 0.187° at 90 °C, corresponding to crystal sizes of 36.7 nm, 39.2 nm and 43.61 nm, respectively, while the half-widths of (002) peaks were 0.261° at 30 °C, 0.229° at 60 °C and 0.195° at 90 °C, corresponding to crystal sizes of 31.33 nm, 35.71 nm and 41.94 nm, respectively.

The above work showed that the enhanced recrystallization of Li_2CO_3 at elevated temperature promoted the formation of Li_2CO_3 crystals with bigger sizes, which favored the desorption of the adsorbed SO_4^{2-} and the removal of the doped SO_4^{2-} from Li_2CO_3 . The schematic diagram for the recrystallization of Li_2CO_3 is shown in Figure 6.



Figure 6. XRD spectra of $(\overline{1}10)$, $(\overline{2}02)$ and (002) planes of Li₂CO₃ samples after recrystallization in Na₂CO₃ solution.

4. Conclusions

A facile method shown in Figure 7 was developed to purify commercial Li₂CO₃ containing 0.8 wt % of SO₄²⁻ by recrystallization of the commercial Li₂CO₃ in Na₂CO₃ solution at 30–90 °C: Li₂CO₃ \rightarrow Li⁺ + CO₃²⁻ $\xrightarrow{Na_2CO_3}$ Li₂CO₃ \downarrow . The increase of temperature from 30 °C to 90 °C promoted the recrystallization of Li₂CO₃ and the formation of Li₂CO₃ crystals with bigger sizes, which favored the removal of SO₄²⁻ adsorbed or doped on/in the commercial Li₂CO₃ in 1 mol·L⁻¹ Na₂CO₃ at 90 °C for 3.0 h.



Figure 7. Schematic drawing for recrystallization of Li₂CO_{3.}

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