Removal of $SO_4^{2-}$ from $Li_2CO_3$ by Recrystallization in $Na_2CO_3$ Solution

Wei Cai 1, Ruosong Chen 2, Yurong Yang 1,*, Meigui Yi 1,*, and Lan Xiang 2,*

1 College of Chemical Engineering, Sichuan University, Chengdu 610065, China; 18810530503@163.com (W.C.); yangyr928163.com (Y.Y.)
2 Department of Chemical Engineering, Tsinghua University, Beijing 100084, China; chenruosongxz@163.com
* Correspondence: meiguiyi@scu.edu.cn (M.Y.); xianglan@mail.tsinghua.edu.cn (L.X.)

Received: 4 December 2017; Accepted: 3 January 2018; Published: 5 January 2018

Abstract: $Li_2CO_3$ with high purity is an important raw material for the fabrication of lithium rechargeable batteries. This paper reports a facile recrystallization way to produce $Li_2CO_3$ with high purity from commercial $Li_2CO_3$ containing 0.8 wt% of $SO_4^{2-}$ by the treatment of the commercial $Li_2CO_3$ in $Na_2CO_3$ solution. The increase of temperature from 30 °C to 90 °C favored the recrystallization of $Li_2CO_3$ in $Na_2CO_3$ solution and promoted the removal of $SO_4^{2-}$ adsorbed or doped on/in the commercial $Li_2CO_3$. The content of $SO_4^{2-}$ in $Li_2CO_3$ decreased to 0.08 wt% after the treatment of the commercial $Li_2CO_3$ in 1.0 mol·L$^{-1}$ $Na_2CO_3$ solution at 90 °C for 10.0 h.

Keywords: Lithium carbonate; sulfate; recrystallization; sodium carbonate

1. Introduction

$Li_2CO_3$ with high purity is widely used for the fabrication of lithium rechargeable batteries, and is usually produced from lithium-bearing minerals such as spodumene ($Li_2O$-$Al_2O_3$·4$SiO_2$), containing 5.8%–8.1 wt% $Li_2O$, and lepidolite ($K$($Li$,Al)$_3$($Si$,Al)$_4$($F$,OH)$_2$), containing 3.2%–6.45 wt% $Li_2O$, or from the Li-bearing brines in salt lakes containing 0.005%–0.2 wt% $Li^+$. Sulfation roasting (roasting of the mixture of lepidolite, $Na_2SO_4$ and $CaCl_2$) 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 $Li_2CO_3$ [1–5]. The Li-bearing brines usually contain impurities like $SO_4^{2-}$, $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $Cl^-$, etc., and the formation of $Li_2CO_3$ 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 $Li_2CO_3$ produced either from the minerals or the Li-bearing brines usually contains impurities such as $SO_4^{2-}$, $Mg^{2+}$, $Ca^{2+}$, $Fe^{3+}$, $K^+$, $Na^+$, $Cl^-$, 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 $SO_4^{2-}$ can be removed by washing with purified water. There are two main ways to remove $Mg^{2+}$ and $Ca^{2+}$, which often exists as insoluble $MgCO_3$ and $CaCO_3$ in $Li_2CO_3$. One way is causticization-carbonation: $Li_2CO_3$ slurry is reacted with $Ca(OH)_2$ at elevated temperature: ($Li_2CO_3$ + $Ca(OH)_2$ → 2$LiOH$ + $CaCO_3$) [6], the impurities such as $Mg^{2+}$ and $Fe^{3+}$ 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 $Ca^{2+}$ and $Mg^{2+}$ and then reacted with $CO_2$ to form purified $Li_2CO_3$. Another way is hydrogenation-decomposition [7–9]: $Li_2CO_3$ is converted to soluble $LiHCO_3$ by carburizing reaction ($Li_2CO_3$ + $CO_2$ + $H_2O$ → 2$LiHCO_3$), the soluble impurities in $LiHCO_3$ solution are separated by ion exchange and purified $Li_2CO_3$ is formed by subsequent decomposition of $LiHCO_3$ at elevated temperature ($2LiHCO_3$ → $Li_2CO_3$ + $H_2O$ + $CO_2$). Up to now, most former work has been focused.
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$_2$CO$_3$.

This paper reports a facile way to remove SO$_4^{2−}$ from commercial Li$_2$CO$_3$ containing SO$_4^{2−}$ by recrystallization in Na$_2$CO$_3$ solution. The behaviors of the adsorbed and doped SO$_4^{2−}$ on/in Li$_2$CO$_3$ in recrystallization process are discussed and an optimized method is suggested to fabricate Li$_2$CO$_3$ with high purity and high conversion ratio.

2. Materials and Methods

Commercial Li$_2$CO$_3$ containing 99.2 wt % of Li$_2$CO$_3$ and 0.8 wt % of SO$_4^{2−}$ was used in the experiments. 100.0 g of commercial Li$_2$CO$_3$ was mixed with 400.0 g of 1.0 mol·L$^{−1}$ Na$_2$CO$_3$ 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 Li$_2$CO$_3$ was then filtered, washed with distilled water three times, and dried at 150 °C for 10.0 h.

The contents of Li$^+$ and SO$_4^{2−}$ 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-Kα 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-Kα 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 Li$_2$CO$_3$

Figure 1a shows the XRD patterns of commercial Li$_2$CO$_3$. Most of the XRD peaks of the commercial Li$_2$CO$_3$ were quite identical with the standard peaks of the pure Li$_2$CO$_3$ (JCPDS 36-0787), and the peak located at $2θ = 21.76^°$ indicated the existence of Li$_2$SO$_4$ (JCPDS 87-0729). The left shift of the XRD peaks of the commercial Li$_2$CO$_3$ compared with those of standard Li$_2$CO$_3$ (the dotted lines in Figure 1a) indicated the increase of the corresponding interplanar spacings, which should be connected with the doping of SO$_4^{2−}$ in Li$_2$CO$_3$ since the radius of SO$_4^{2−}$ (2.44 Å) was bigger than that of CO$_3^{2−}$ (1.64 Å) [10].

Figure 1b shows the S2p XPS patterns of the commercial Li$_2$CO$_3$ 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$_2$CO$_3$ surface.

Figure 1c shows the morphology of the commercial Li$_2$CO$_3$. Un-regular particles with a diameter of 1–10 μm were aggregated with each other, forming agglomerates with a diameter of about 35 μm.

Chemical analysis showed that the commercial Li$_2$CO$_3$ was composed of 99.15 wt % of Li$_2$CO$_3$, 0.8 wt % of SO$_4^{2−}$, 0.0045 wt % of Ca$^{2+}$ and 0.0187 wt % of Na$^+$.  

3.2. Recrystallization of Commercial Li$_2$CO$_3$

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 Li$_2$CO$_3$ 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 Li$_2$CO$_3$ was a little faster than its dissolution at the later time. The data in Figure 2a,b confirmed the recrystallization of Li$_2$CO$_3$ in Na$_2$CO$_3$ solution:

\[
\text{Li}_2\text{CO}_3 \rightarrow \text{Li}^+ + \text{CO}_3^{2−} \xrightarrow{\text{Na}_2\text{CO}_3} \text{Li}_2\text{CO}_3 \downarrow. 
\]  

(1)
Meanwhile, the comparatively low [Li⁺] and [CO₂⁻] at high temperature could be attributed to the low solubility of Li₂CO₃ at high temperature (the solubility of Li₂CO₃ 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).

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

**Figure 2.** Variation of (a) soluble [Li⁺], (b) [CO₃²⁻] and (c) supersaturation with reaction time.
Figure 2c shows the variation of the supersaturation (the ratio of [Li+]^2[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 2θ = 21.76°) 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} Na_2CO_3 solution at 90 °C for 10.0 h.

![Figure 3](image_url)

**Figure 3.** (a) XRD patterns 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 Li_2CO_3 before and after recrystallization in 1.0 mol·L^{−1} Na_2CO_3 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 Li_2CO_3, 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 Li_2SO_4, respectively. The increase of temperature from 30 °C to 90 °C led to the enlargement of the peaks for Li_2CO_3 and the shrinkage of the peaks for SO_4^{2−}, indicating the enhanced desorption of SO_4^{2−} from Li_2CO_3 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 Li_2CO_3 to 1430 cm^{−1} and 1482 cm^{−1} for purified Li_2CO_3, which should be attributed to the desorption of SO_4^{2−} from Li_2CO_3 surface since the negative charges provided by SO_4^{2−} weakened the polarity of Li^+ in Li_2CO_3 [13,14], the desorption of SO_4^{2−} thus enhanced the polarity of Li^+ and led to the red shift of the C-O peaks in Li_2CO_3.
Figure 4. FT-IR spectra of Li$_2$CO$_3$ samples before and after recrystallization in Na$_2$CO$_3$ solution.

Figure 5 shows the XPS spectra of S2p in Li$_2$CO$_3$ samples before and after recrystallization in 1.0 mol·L$^{-1}$ Na$_2$CO$_3$ 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 SO$_4^{2-}$ at elevated temperatures. Table 1 shows the composition of Li$_2$CO$_3$ on surface and in bulk detected by XPS and ion chromatograph, respectively. The surface concentration of SO$_4^{2-}$ on surface was calculated by the equation (2). The atomic ratios of S to C on Li$_2$CO$_3$ surface decreased from 1:17.2 (for commercial Li$_2$CO$_3$) 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 SO$_4^{2-}$ on surface were larger than those in the bulk, and the increase of temperature favored the desorption of SO$_4^{2-}$ from Li$_2$CO$_3$ surface.

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

(2)

![Figure 5. XPS spectra of S2p in Li$_2$CO$_3$](image)

Table 1. Composition of Li$_2$CO$_3$ on surface and in bulk.

<table>
<thead>
<tr>
<th>Li$_2$CO$_3$ Samples</th>
<th>Surface Composition</th>
<th>Surface Composition</th>
<th>SO$_4^{2-}$ on Surface (wt %)</th>
<th>SO$_4^{2-}$ in Bulk (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>Li (%) 34.13 S (%) 0.94 C (%) 16.13 O (%) 48.80 C:S 17.16</td>
<td></td>
<td>7.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Recrystallized at 30 °C</td>
<td>Li (%) 34.09 S (%) 0.34 C (%) 16.71 O (%) 48.86 C:S 17.16</td>
<td></td>
<td>2.62</td>
<td>0.17</td>
</tr>
<tr>
<td>Recrystallized at 60 °C</td>
<td>Li (%) 34.87 S (%) 0.28 C (%) 17.16 O (%) 47.69 C:S 61.29</td>
<td></td>
<td>2.11</td>
<td>0.12</td>
</tr>
<tr>
<td>Recrystallized at 90 °C</td>
<td>Li (%) 33.90 S (%) 0.19 C (%) 16.76 O (%) 49.15 C:S 88.21</td>
<td></td>
<td>1.49</td>
<td>0.08</td>
</tr>
</tbody>
</table>
3.3.2. Behavior of Doped SO$_4^{2-}$

Figure 6 shows the XRD patterns of (110), (202) and (002) planes of Li$_2$CO$_3$ samples after crystallization in 1.0 mol·L$^{-1}$ Na$_2$CO$_3$ solution at 30–90 °C for 3.0 h. The 2θ values of (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 ($2\theta = \frac{2\lambda}{d\cos\theta}$). The removal of the doped SO$_4^{2-}$ from Li$_2$CO$_3$ led to the decrease of the lattice distance of (110) plane since the radius of SO$_4^{2-}$ (2.4 Å) was bigger than that of CO$_3^{2-}$ (1.64 Å). Similar phenomena occurred for (202) and (002) planes: the 2θ values of (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 2.8125 Å, 2.8104 Å and 2.8098 Å, respectively, while the 2θ 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 Li$_2$CO$_3$ samples could be calculated out based on the half-widths (β) of the peaks of (110), (202) and (002) planes shown in Figure 5 and the Scherrer equation $D = \frac{K\lambda}{\beta\cos\theta}$, where $K = 0.86$. The half-widths of (110) 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 Li$_2$CO$_3$ and the formation of Li$_2$CO$_3$ with bigger sizes. Similar phenomena occurred for (202) and (002): the half-widths of (202) 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$_2$CO$_3$ at elevated temperature promoted the formation of Li$_2$CO$_3$ 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$_2$CO$_3$. The schematic diagram for the recrystallization of Li$_2$CO$_3$ is shown in Figure 6.

**Figure 6.** XRD spectra of (110), (202) and (002) planes of Li$_2$CO$_3$ samples after recrystallization in Na$_2$CO$_3$ solution.
4. Conclusions

A facile method shown in Figure 7 was developed to purify commercial Li$_2$CO$_3$ containing 0.8 wt % of SO$_4^{2-}$ by recrystallization of the commercial Li$_2$CO$_3$ in Na$_2$CO$_3$ solution at 30–90 °C: Li$_2$CO$_3$ → Li$^+$ + CO$_3^{2-}$ Na$_2$CO$_3$ → Li$_2$CO$_3$↓. The increase of temperature from 30 °C to 90 °C promoted the recrystallization of Li$_2$CO$_3$ and the formation of Li$_2$CO$_3$ crystals with bigger sizes, which favored the removal of SO$_4^{2-}$ adsorbed or doped on/in the commercial Li$_2$CO$_3$. The content of SO$_4^{2-}$ decreased to 0.08 wt % after treatment with the commercial Li$_2$CO$_3$ in 1 mol·L$^{-1}$ Na$_2$CO$_3$ at 90 °C for 3.0 h.

![Schematic drawing for recrystallization of Li$_2$CO$_3$.](image)

**Figure 7.** Schematic drawing for recrystallization of Li$_2$CO$_3$.

Acknowledgments: The authors gratefully acknowledge the financial support from the National Science Foundation of China (No. 51774191, 51234003 and 51374138).

Author Contributions: Wei Cai and Ruosong Chen conceived the research idea; Wei Cai designed the experiments; Wei Cai and Yurong Yang performed the experiments and analyzed the data; Meigui Yi and Lan Xiang advised the experiments; all authors wrote the paper.

Conflicts of Interest: The authors declare no competing financial interests.

References

2. Meshram, P.; Pandey, B.D. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy* 2014, 150, 192–208. [CrossRef]
3. Luong, V.T.; Kang, D.J.; An, J.W.; Kim, M.J.; Tran, T. Factors affecting the extraction of lithium from lepidolite. *Hydrometallurgy* 2013, 134, 54–61. [CrossRef]
4. Luong, V.T.; Kang, D.J.; An, J.W.; Dao, D.A.; Kim, M.J.; Tran, T. Iron sulphate roasting for extraction of lithium from lepidolite. *Hydrometallurgy* 2014, 141, 8–16. [CrossRef]