Preparation of lithium using vacuum carbothermal reduction of LiAlO$_2$

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Abstract

In this study, we investigated the preparation process of lithium metal using a novel carbothermal reduction process. Herein, thermodynamic calculations and experimental research methods were used to investigate the novel carbothermal reduction process of LiAlO$_2$ for preparing lithium metal in a vacuum. The results suggest that the temperature of the chemical reaction can be significantly reduced by reducing the pressure in the system. When the system pressure was 10 Pa, the reduction temperature, reduction time, molar ratio of C/LiAlO$_2$, and reduction rate were 1623 K, 120 min, 0.9, and 79.01%, respectively. Furthermore, the lithium content in the reduction residue was 2.1 wt%, suggesting the presence of the LiAl$_5$O$_8$ phase. Under these conditions, when 20% CaO was added, the reduction rate of lithium increased to 99.38%, and the lithium in the reduction residue takes the form of CaAl$_2$O$_4$. This shows that CaO, as an additive, can promote reduction, compromise the effect of LiAl$_5$O$_8$, and increase the reduction rate of lithium.

1. Introduction

As a novel energy and strategic resource, lithium has a wide range of applications such as in metallurgy, ceramics, and petrochemicals. In recent years, the demand for metallic lithium has increased owing to its application in high-precision technology fields such as aerospace, high-energy batteries, and lightweight and high-strength alloys required in railways and aerospace for lightweight structures [1–6]. Currently, electrolysis is generally used for preparing lithium metal [7, 8]; however, this process has several disadvantages, such as Cl$_2$ pollution, expensive electrolyte, and high content of K and Na impurities in the product. Consequently, several studies have investigated the process of preparing metallic lithium via vacuum thermal reduction [7, 9–20]. According to the different reducing agents, metal thermal reduction methods employ aluminum [18], silicon [9], iron [17], silicon–iron [18], and calcium carbide [16, 21, 22].

However, owing to the high cost of reducing agents, cost effective carbonaceous reducing agents have attracted attention. In 1937, for the first time, US Bureau of Mines [24] proposed the use of carbon as a reducing agent for producing lithium metal under normal pressure. The main chemical reaction that occurred was Li$_2$O + C = 2Li + CO. However, the temperature of this reaction was relatively high and the resulting lithium vapor easily reacted with CO, thereby forming carbides, carbonates, and oxides, upon cooling. Later, Kroll and Schlechten [15] proposed the use of CaC$_2$ and Li$_2$C$_2$ instead of carbon for reduction based on the following chemical equations: 3Li$_2$O + CaC$_2$ = CaO + 6Li + 2CO and Li$_2$O + Li$_2$C$_2$ = 6Li + 2CO. However, the proposed method could not be used due to the high temperature of the reduction reaction. Chen [7] and Eskar [22] used lithium carbonate as the raw material. First, to prepare Li$_2$O, Li$_2$CO$_3$ was thermally decomposed in vacuum. Then, reduction experiments were conducted with carbon powder and calcium carbide under vacuum.
conditions, and lithium metal with purity ranging between 54.34% and 58.28% was obtained. However, the carbon content in the lithium metal was between 24.8% and 41.11%. It is believed that lithium vapor react with CO inversely. Considering the current carbothermal reduction process that uses lithium carbonate as the raw material, the following limitations exist: First, the decomposition temperature of lithium carbonate in the decomposition process under vacuum conditions is higher than the melting point of lithium carbonate, which is prone to spraying and leads to losses. Second, the reactions between lithium vapor and CO are reverse reactions.

In this study, a novel carbothermic reduction process was developed to improve the recovery rate and purity of lithium. Herein, Li$_2$CO$_3$ and Al$_2$O$_3$ were used as raw materials, and LiAlO$_2$ was prepared under vacuum conditions by conducting carbothermic reduction. Lithium vapor was obtained via reduction reaction, aluminum liquid condensation was used to obtain the Al–Li master alloy, and vacuum distillation was conducted, if required; the entire process is shown in figure 1. To determine the optimal calcination conditions for the reduction reaction, cheap coking coal was used as the reducing agent for conducting carbothermic reduction of LiAlO$_2$ under vacuum for producing lithium metal, as shown in figure 1 (Part II). The effects of experimental parameters on the reduction reaction were systematically studied, including the reaction temperature, soaking time, molar ratio of C/LiAlO$_2$, and the amount of CaO added.

2. Experimental

2.1. Materials

Herein, LiAlO$_2$ raw material was prepared using Li$_2$CO$_3$ and Al$_2$O$_3$ under vacuum through a method reported in a previous study, as shown in figure 1 (Part I). The x-ray diffraction (XRD) analysis of LiAlO$_2$ is shown in figure 2.

The chemical composition of coking coal used herein was analyzed by chemical analysis, and the results are listed in table 1. Herein, CaO was used as the additive (analytically pure, Tianjin Feng Chuan Chemical Reagent Technologies Co. Ltd), and its composition is listed in table 2.
2.2. Methods

2.2.1. Procedure
During the experiment, LiAlO$_2$, coking coal, and CaO powders with a particle size of 149 $\mu$m were used as raw materials. Before the experiment, the target ratios of LiAlO$_2$, coking coal, and CaO powders were uniformly mixed and pressed into a block. In each experiment, approximately 20 g of the mixture was placed in a graphite crucible. By controlling the inflow of argon gas before increasing the temperature, the gas in the furnace was discharged, and then the pressure was maintained at the target pressure ($10$ Pa) via a vacuum pump. A vacuum gauge was used to measure the pressure in the vacuum furnace. Then, a precise temperature program was set to increase the temperature from 298 K to target temperature (1473–1623 K) at a rate of 10 K min$^{-1}$. The temperature was measured by a thermocouple, with an accuracy of 10 K in the range of 1473–1623 K. Under the system pressure of 10 Pa, the furnace temperature was also maintained at the target temperature for 30–150 min. When heating was completed, the sample was cooled naturally at an average rate of 20 K min$^{-1}$. The mass fraction of Li in the residues was analyzed by chemical analysis, whereas the crystalline structures of the residues were identified by XRD (D/Max-3B, Rigaku, Japan). The morphology and elemental composition of the particular regions were determined by Scanning Electron Microscopy (SEM, HITACHITM-3030 Plus) equipped with an Energy Dispersive x-ray Spectroscopy (EDS, INCA Oxford).

2.2.2. Apparatus
We used a vacuum lithium reduction furnace designed by the Kunming University of Science and Technology (figure 3).

2.2.3. Evaluation indexes
To determine the reduction rate of LiAlO$_2$ during vacuum carbothermal reaction, the Li content in the material before and after the reaction was obtained via chemical analysis. The reduction rate of the entire experiment can be calculated using the following equation:

![Figure 2. XRD pattern of LiAlO$_2$.](image-url)
where $\beta$, $M_1$, $M_2$, $\omega_1$, and $\omega_2$ represent the reduction rate of Li (wt%), mass of the raw material mixture before the reaction (g), mass of the residue after the reaction (g), mass fraction of Li before the reaction (wt%), and mass fraction of Li after the reaction (wt%), respectively.

3. Results and discussion

3.1. Results of thermodynamics calculation

Depending on the CaO addition and the product obtained, the possible chemical reactions for the reduction reaction between LiAlO$_2$ and coking coal under vacuum conditions are shown in reactions (1)–(3):

1. $5\text{LiAlO}_2(s) + 2\text{C}(s) = 4\text{Li}(g) + \text{LiAl}_2\text{O}_4(s) + 2\text{CO}(g)$ (1)
2. $4\text{LiAlO}_2(s) + 2\text{C}(s) + \text{CaO}(s) = 4\text{Li}(g) + \text{CaAl}_2\text{O}_4(s) + 2\text{CO}(g)$ (2)
3. $2\text{LiAlO}_2(s) + \text{C}(s) + \text{CaO}(s) = 2\text{Li}(g) + \text{CaAl}_2\text{O}_4(s) + \text{CO}(g)$ (3)

First, HSC Chemistry 6.0 software was adopted to calculate the standard state Gibbs free energy ($\Delta G_f^\circ$) of reactions under the atmospheric pressure (101 325 Pa). Then, van’t Hoff isothermal equation was adopted to calculate the Gibbs free energy in non-standard state ($\Delta G_f$) defined as follows:

$$\Delta G_f = \Delta G_f^\circ + RT \ln Q_p,$$

where $Q_p$ is the pressure quotient.

According to reactions (1)–(3), the total pressure of the system ($P_{\text{Total}}$) is the sum of the partial pressures of CO and Li. Therefore, the definition of $Q_p$ is as follows:

$$Q_p = \left( \frac{P_{\text{CO}}}{P^{\text{RT}}} \right)^m \cdot \left( \frac{P_{\text{Li}}}{P^{\text{RT}}} \right)^n,$$

where $m$ and $n$ are the reaction coefficients of CO(g) and Li(g) in reactions (1)–(3), respectively. $P_{\text{CO}}$ and $P_{\text{Li}}$ can be expressed as follows:

$$P_{\text{CO}} = \frac{m}{m + n} P_{\text{Total}},$$

$$P_{\text{Li}} = \frac{n}{m + n} P_{\text{Total}}.$$

When $P_{\text{Total}}$ are 101 325 and 10 Pa, the relationship between the Gibbs free energy and temperature of reactions (1)–(3) is plotted in figure 4.

It can be observed from figure 4 that reactions (1)–(3), wherein gas is generated in the reaction product, are significantly affected by the system pressure. In figure 4(a), when the system pressure is 101 325 Pa, the Gibbs free energy of reactions (1)–(3) is always greater than zero below 2100 K, indicating that reactions (1)–(3) do not take place. When the system pressure is 10 Pa, the initial reaction temperatures of reactions (1)–(3) are 1443.5,
1328.9, and 1305.9 K, respectively. This shows that reducing the system pressure can promote the vacuum carbothermal reduction reaction of LiAlO₂. In addition, with the introduction of CaO, it can be observed from figure 4(b) that the initial reaction temperatures of reactions (2) and (3) are lower than that of reaction (1), suggesting that the addition of CaO can reduce the initial reaction temperature of the LiAlO₂ vacuum carbothermal reduction reaction, and sustain the continuity of the chemical reaction.

3.2. Results of experiments
3.2.1. Effect of temperature on reaction rate
Reaction (1) suggests that without CaO, the starting reaction temperature of the carbothermal reduction reaction of LiAlO₂ under 10 Pa is 1443.5 K. Therefore, we kept the C/LiAlO₂ and soaking time constant at 0.9 and 150 min, respectively. We also studied the effects of different reaction temperatures (1473, 1523, 1573, and 1623 K) on the content of Li in the reduction residue and reduction rate.

As shown in figure 5, as the reaction temperature increased from 1473 to 1623 K, the reduction rate increased from 37.71% to 79.21%, whereas the Li content in the reduction residue decreased from 6.22 to 2.13 wt%. This is because an increase in the reaction temperature increases the heat transfer between the materials, thereby promoting the reaction, which is consistent with the trend of thermodynamic calculations. The reduction rate and content of Li varied significantly between 1473 and 1573 K, but these variations were slower between 1573 and 1623 K. Therefore, the optimal reaction temperature of the carbothermic reduction reaction of LiAlO₂ at 10 Pa is 1623 K.

3.2.2. Effect of soaking time on reaction rate
Based on the temperature of experimental results, the temperature was set to 1623 K. To further clarify the effect of soaking time on the vacuum carbothermal reduction reaction of LiAlO₂, the experimental conditions of the
system pressure and C/LiAlO₂ were set at 10 Pa and 0.9, respectively. Figure 6 shows the content of Li in the reduction residue and the reduction rate of Li under different soaking times (30–150 min).

During the vacuum carbothermal reduction reaction of LiAlO₂, both the reduction rate of Li and Li content in the residue changed with the extension of the soaking time, but eventually, it became stable (figure 6). When the soaking time was increased from 30 to 60 min, the increase in reduction rate and decrease in Li content were the most obvious. This is because as the soaking time increased, the heat absorption inside the reducing material increased, which promoted the occurrence of the reaction. It is worth mentioning that the reduction rate and Li content stabilized at 79% and 2.1 wt%, respectively, from 120 to 150 min. This indicates that the reduction reaction generally reacted completely when the soaking time was 120 min. Therefore, the optimum soaking time was 120 min. under a C/LiAlO₂ ratio of 0.9 at 1623 K.

3.2.3. Effect of C/LiAlO₂ on the reaction rate

Owing to the loss of coking coal during the actual reduction reaction, excessive addition of coking coal is required. Therefore, the effect of molar ratio of C/LiAlO₂ on the reduction rate and Li content was evaluated when CaO was not added, and when the system pressure, reduction temperature, and reduction time were 10 Pa, 1623 K, and 120 min, respectively. According to reactions (1)–(3), when CaO was not added, the C/LiAlO₂ molar ratio of LiAlO₂ vacuum carbothermal reduction reaction was 0.4, whereas when CaO was present, it was 0.5; the investigation range for setting the molar ratio of C/LiAlO₂ was 0.5–1.0. The results are shown in figure 7.

As shown in figure 7, the reduction rate of LiAlO₂ vacuum carbothermal reduction gradually increased with an increase in the C/LiAlO₂ molar ratio before it eventually stabilized. Simultaneously, the Li content in the residue gradually decreased. When C/LiAlO₂ was 0.5, the reduction rate and Li content were 31.57% and
7.16 wt%, respectively. When \( \text{C/LiAlO}_2 \) was 0.9, the reduction rate increased rapidly from 31.57% to 79.0%, and Li content decreased to 2.12 wt%. \( \text{C/LiAlO}_2 \) has a greater influence on the reduction reaction in the range of 0.5–0.9. When the \( \text{C/LiAlO}_2 \) was 1.0, the reduction rate and Li content were 79.37% and 2.07 wt%, respectively. Compared with the case when \( \text{C/LiAlO}_2 \) was 0.9, the change was not obvious. It indicated that when \( \text{C/LiAlO}_2 \) exceeded 0.9, the reduction rate and Li content did not increase significantly; however, it stabilized at approximately 79.0% and 2.1 wt%. This is because as the \( \text{C/LiAlO}_2 \) ratio increased, the amount of C added gradually increased, which increased the contact surface between C and LiAlO2 and promoted the progress of the reaction. Therefore, to save resources, the value of \( \text{C/LiAlO}_2 \) was chosen as 0.9 for all the subsequent experiments.

### 3.2.4. Effect of CaO addition on reaction rate

At a reducing temperature of 1623 K, the soaking time was 120 min and \( \text{C/LiAlO}_2 \) molar ratio was 0.9. The mass of the CaO added ranged from 0% to 20% of the raw material mass. The effect of CaO addition on the rate of LiAlO2 vacuum carbothermal reduction and Li content in the residue is shown in figure 8.

Figure 8 suggests as the amount of CaO added increased, the reduction rate exhibited an upward trend, while that of the Li content in the residue was in the opposite direction. When the amount of CaO added increased from 0% to 20%, the reduction rate increased from 79.0% to 99.38%, exhibiting an increase of 20.38%. Simultaneously, the Li content in the reduction residue decreased from 2.12 to 0.05 wt%. This shows that the addition of CaO can promote the carbothermal reduction reaction of LiAlO2 under a pressure of 10 Pa, and the 20% amount of CaO added resulted in a reduction rate of 99.38%.

When analyzing the carbothermic reduction reaction of LiAlO2 under 10 Pa, we discovered different phenomena after the experiment. When the amount of CaO added was increased from 0% to 20%, the color of the reduction residue gradually became dark and its hardness increased, as shown in figure 9. When the amount of CaO added was 20%, it was difficult to break the reduction residue, and the phenomenon of melting appeared, thus indicating that new substances were formed in the reduction residue.

SEM image suggests that gray–white and black areas appeared in the reduction residue. The EDS analysis shows that when the amount of CaO added was 0%, the black area was mainly C with a small amount of O and Al, and the gray–white area was mainly O and Al with a small amount of C. A part of Li may exist, but due to the limitation of the detection principle, the Li element cannot be detected effectively. When the amount of CaO added was 5%–20%, the black area was also mainly C, and the gray–white was mainly O, Al, and Ca, a certain amount of Li may also be present.

To further observe the distribution of the elements in the reduction residue, the EDS surface scan was performed on the reduction residue with CaO additions of 0% and 5%, as shown in figure 10.

The black area in figure 10(a) was mainly the distribution area of C, whereas the gray–white part is mainly Al and O. The distribution area of Al and O overlaps well, indicating that when no CaO was added, and Al, O, and undetected Li in the reduction residue existed in the form of \( \text{Li}_x\text{Al}_y\text{O}_z \). As shown in figure 10(b), the black part was also the distribution area of C, while the gray–white part was the area of Al, O, and Ca with good overlap. It shows that when CaO was added, Ca combined with the remaining Al and O to form xCaO·yAl2O3, and Li also existed in the form of \( \text{Li}_x\text{Al}_y\text{O}_z \). The specific phases present in the reduction residue can be obtained by XRD analysis.
The reduction reaction residues at different CaO additions were measured using a Japan Science D/max-3B x-ray diffractometer with a scanning voltage and current of 50 kV and 40 mA, respectively. The diffraction angle (2θ) was scanned from 10° to 90° with a scanning step of 2°/min. The results are presented in figure 11.

As shown in figure 11, when CaO was not added, a small amount of LiAlO₂ and large amount of LiAl₅O₈ phases were present in the remainder of the reduction reaction. Owing to the presence of LiAl₅O₈ phase, a considerable amount of Li was present in the reduction residue. Consequently, the reduction rate was only 79.0% and Li content in the reduction residue was 2.12 wt%, as shown in figure 8. When the addition of CaO was 5%, a small amount of CaAl₄O₇ and CaAl₂O₄ phases appeared in the reduction residue. Simultaneously, the peak intensity of the LiAl₅O₈ phases decreased or disappeared. When the amount of CaO added was 10%, the
peak intensity of the CaAl2O4 phase gradually increased, accompanied by the weakening of peak intensity of the LiAl5O8 phase. When CaO was 15%, CaAl2O4 was present in large amounts, whereas the LiAl5O8 phase disappeared almost completely. When the amount of CaO reached 20%, the LiAl5O8 and CaAl4O7 phases disappeared, and a large amount of CaAl2O4 phases was formed. In general, the phase transitions of LiAl5O8, CaAl4O7, and CaAl2O4 were affected by the addition of CaO. With a gradual increase in the amount of CaO, the LiAl5O8 phase gradually disappeared and the CaAl4O7 and CaAl2O4 phases were formed gradually, suggesting that the addition of CaO can effectively compromise the structure of LiAl5O8, release metallic lithium, and simultaneously generate CaAl4O7 and CaAl2O4, thereby promoting the LiAlO2 vacuum carbothermic reduction process. This phenomenon is consistent with the results obtained by experimental research.

4. Conclusions

The lithium reduction rate, lithium content in the reduction residue, and phase composition were studied in the LiAlO2 vacuum carbothermic reduction process. The most valuable and noteworthy conclusions are summarized as follows:

1. From thermodynamic calculations, it can be inferred that the reduction of system pressure can significantly reduce the reduction temperature. At 10 Pa, the addition of CaO influenced the occurrence of reduction reaction and reduced the reaction temperature to approximately 120 K.

2. Under optimal reaction conditions (reduction temperature, soaking time, and C/LiAlO2 molar ratio of 1623 K, 120 min, and 0.9, respectively), when no CaO was added, the reduction rate of the carbothermic reduction reaction of LiAlO2 at 10 Pa reached a maximum value of 79.01%, while the lithium content in the reduction residue was 2.1wt%. When CaO was added, the reduction rate increased as the amount of CaO added increased. The reduction rate of Li was 99.38%, while the Li content in the reduction residue was only 0.05 wt% when CaO was 20%.

3. The XRD patterns of the reduction residue showed that the added CaO changed the phase composition of the reduction residue and sustained the reaction. When CaO was not added, a large amount of LiAl5O8 phase was found in the reduction residue, which is consistent with the low lithium reduction rate phenomenon in the experimental results. With an increase in the amount of CaO added, new CaAl4O7 and CaAl2O4 phases were gradually discovered in the reduction residue with a gradual decrease in the LiAl5O8 phase. This shows that the addition of CaO compromises the structure of LiAl5O8 and reduces the residual Li in the reduction residue, thereby altering the carbothermic reduction reaction process of LiAlO2.

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